Designing materials for inorganic and living photocatalytic systems for air, water, and CO₂ reduction from sunlight

by

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Designing materials for inorganic and living photocatalytic systems for air, water, and CO_2 reduction from sunlight

Thesis directed by Assistant Professor Prashant Nagpal

Several strategies are currently being investigated for conversion of incident sunlight into chemical fuels, with readily available chemical feedstocks like air, water, and carbon-dioxide. This thesis focuses on research approach on designing high-efficiency and high-selective photocatalytic materials, ranging from inexpensive and stable inorganic photocatalysts to living nano-biohybrid organisms to achieve solar energy conversion.

This thesis is divided into multiple sections based on the materials and concepts in designing high-efficient and high-selective solar fuel generator. After a brief introduction of photocatalysis in Chapter 1, we describe a novel electrochemical anodization technique for making a wide-variety of doped metal-oxide nanotubes. Using optoelectronic and electrochemical characterizations, we systematically studied dopant (anionic and cationic) effects in photocatalytic water splitting from the aspect of light absorption, charge transport, and charge transfer (Chapter 2 to 4).

In the second part (Chapter 5), we describe a novel low-temperature amine-based synthesis and cation exchange method for synthesizing ultrathin two-dimensional metal chalcogenide nanostructures. We reported their extraordinary optoelectronic characteristics and potential applications in third-generation solar energy conversion devices. In the third section (Chapter 6), we describe formation of living quantum dot -synthetic bacteria nano-biohybrids, with desired metabolic pathways for selective formation of fuel, designed QD energy states for efficient light-sensitization, suitable alignment, and charge injection to bacterial enzymes for photocatalytic reduction, using cellular uptake, cell viability, and designed site-specific attachment of quantum dots from growth solutions to bacterial enzymes. These engineered nano-biohybrids affect efficient light-driven hydrogen and ammonia production from water and air-water reduction and shows no loss of enzyme function between purified nitrogen and air.

Finally, we demonstrate color tuning of upconversion photoluminescence by modulating the photophysics using surface plasmon polaritons (Chapter 7). Furthermore, by using ultrathin 2D semiconductor nanosheets, we demonstrate the efficacy of color tuning by transforming upconverted light into photocurrent. This can pave the way for designed metal nanostructures for highly-efficient utilization of low-intensity sub-bandgap infrared radiation in optoelectronic devices.

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Photocatalytic solar fuel generation: A brief introduction

- 1.1 Overview of photocatalysis for solar fuel production
- 1.2 Principles of photocatalytic water splitting
- 1.3 Design of high efficient photocatalysts for water splitting
- 1.4 Photocatalytic solar fuel generation beyond hydrogen
- 1.5 Efficiency definition and calculation
- 1.6 Characterization of photocatalytic systems

1.1 Overview of photocatalysis for solar fuel production

Photocatalysis refers to the alternation of the rate of a chemical reaction by light or other electromagnetic radiation, which can be classified into homogeneous and heterogeneous photocatalysis and have applications in environmental mediation (decomposition of toxic organic compound in wastewater, water disinfection) and renewable energy (converting solar energy to chemical fuels like hydrogen and hydrocarbons).^{1–3} It is now an extremely active and constantly growing research area.

The excessive reliance on traditional fossil fuels like coals and petroleum brings depletion of energy and environmental problems including air pollution and global warming. Solar energy as a clean, renewable energy has become one of the most important alternatives in the future. The sun delivers 120,000 TW of power to the earth surface, which far exceeds (over 10,000 times) the current worldwide demand.^{4,5} The solar energy can be converted to thermal energy,⁶ electric energy,⁷ and chemical energy^{3,8} through solar thermal panels, photovoltaics, and photocatalysis, respectively. Compared to other forms of energy, chemical energy has the advantages including easy combustibility, highly efficient and easy storage.^{3,5}

Among the chemical fuels, hydrogen is acknowledged as the most promising form of energy storage in the future, due to its high specific energy and no release of carbon dioxide under combustion.^{9,10} Currently, more than 90% hydrogen is produced industrially through steam reforming of fossil fuels, which is energetically costly and generate CO_2 as a by-product. About 4% of the hydrogen is produced from water electrolysis with the consumption of electricity.¹¹ Solar energy to hydrogen could be realized through two techniques, using solar cell-powered water electrolysis and direct photocatalytic water

splitting. The latter choice is usually favored since it avoids complex configurations and is energetically more efficient. Photocatalytic hydrogen production was first demonstrated by Honda and Fujishima¹² in 1972, where illuminated TiO₂ electrode oxides water to oxygen, with simultaneous generation of hydrogen on the platinum counter electrode. Photocatalytic water splitting can be realized with either wired (photoelectrochemical (PEC) cells) or wireless (standalone powder) configuration,^{13,14} and this process is the most promising and renewable choice for hydrogen production, which has recently employed in industrial effluent treatment.

1.2 Principles of photocatalytic water splitting^{3,8,10,13}

Thermodynamically, split water into hydrogen and oxygen is an uphill (non-spontaneous) reaction which requires energy input (237 kJ/mol). And from the electrochemistry aspect, reduction of proton and oxidation of water (in standard condition, pH = 0) requires an electron and hole redox potential more negative than 0.0 V and more positive than 1.23 V. In a (standalone) photocatalytic system (**Figure 1.1**), these electrons and holes are generated (~fs) upon excitation of light with photon energy equal or higher than the bandgap of the semiconductor. Hot electrons and holes quickly thermalized (~ps) to their corresponding vibronic ground states with phonon emission. The electron-hole pairs are then separated and transport (drift or diffuse) to the interface, with simultaneous recombination (bulk and surface recombination) through the radiative and non-radiative pathway, where loss of energy is released as photon and phonon, respectively. The electrons and holes on the semiconductor surface are then injected to the adsorbed water molecules to realize hydrogen and oxygen

production, respectively.



Figure 1.1 The principle of (standalone) photocatalytic water splitting. (i) electron-hole pair generation under light irradiation (red: excitation with photon energy lower than the bandgap, which is not sufficient to generate electron-hole pairs; green: bandedge excitation; blue: excitation with photon energy higher than the bandgap, which produces hot carriers) (ii) carrier relaxation (iii) charge transport to the surface (iv) charge transfer (injection) to water proton or water molecules (v) charge recombination. Solid circles and hollow circles represent electrons and holes, respectively.

The photophysical and photochemical processes in the wired (PEC cell) system are more complex and require description using semiconductor electrochemistry.^{15–17} The PEC cells can have different configurations (**Figure 1.2**) including a photoelectrode (photoanode or photocathode) with a counter electrode, and a photoanode with a photocathode (Z-scheme, similar to the natural photosynthesis process). Photoanode and photocathode are usually made from n- and p-type semiconductors, due to the alignment of their Fermi levels with the redox potential of water. For a PEC cell constructed with TiO₂ photoanode and platinum

counter electrode (**Figure 1.2a**), electron flow from TiO_2 surface to water upon contact due to its higher Fermi energy level compared to water redox potential and lead to upward band bending once equilibrium is reached. Band bending creates an internal electric field, which assists transport of light-induced holes and electrons to the TiO_2 surface and the bulk TiO_2 (then to the platinum counter electrode), and followed by water oxidation and reduction on separate electrodes. Compared to the standalone photocatalytic system, the more complex PEC cell has less restriction on the selection of photocatalytic materials. For semiconductor with no suitable conduction or valence band position, electric bias can be applied to allow overall water splitting.



Figure 1.2 The principle of the photoelectrochemical cell with different configurations. (a) A photoanode with a counter cathode (b) A photocathode with a counter anode (c) A photoanode with a photocathode. Solid circles and hollow circles represent electrons and holes, respectively.

- 1.3 Design of high efficient photocatalysts for water splitting
- 1.3.1 Requirements for materials used in photocatalytic water splitting

Based on the principle of photocatalytic water splitting described above, several

requirements should be met when choosing the materials:^{3,13,14,18}



Figure 1.3 Conduction and valence bandedge for some common semiconductors (potential vs. NHE at pH = 7). The reduction potential of H^+/H_2 (-0.41), O_2/H_2O (0.82) for water splitting, and reduction potential of (from top to bottom) CO₂/HCOOH (-0.61), CO₂/CO (-0.53), CO₂/HCHO (-0.48), CO₂/CH₃OH (-0.38), and CO₂/CH₄ (-0.24) for photocatalytic CO₂ reduction are also labeled.

The **bandgap** of the semiconductor has to meet the theoretical water splitting thermodynamic requirement (1.23 V). But practically, a bandgap of at least 2.0 eV is preferred with consideration of a series of energy loss pathways including the recombinations and water splitting overpotential. On the other hand, to maximally the utilization of solar energy, visible light-sensitive materials with smaller bandgap ($E_g < 3.0 \text{ eV}$) are usually considered.

The semiconductor **bandedge** must straddle between the redox potentials of water (0.0 and 1.23 V at pH = 0, or -0.41 and 0.82 V at pH = 7). However, this requirement is more stringent due to slow water reduction and oxidation kinetics. In practice, overpotential of 0.4 V and 0.6 V is considered for hydrogen and oxygen evolution. The bandedge requirement is relaxed in the case of PEC cells when electric or chemical bias is used.

To facilitate **charge transport** to the semiconductor surface and avoid electron-hole pair recombination, materials with higher charge mobility, conductivity fewer defect states should be considered. Carrier lifetime or diffusion length is also used to evaluate the goodness of charge transport.

Also, charge carrier must react fast enough with surface adsorbed substrates (H_2O) to prevent photocorrosion and loss of charge carriers due to surface recombination. This requires a catalytic surface for easy **charge transfer**.

Other issues including the **stability**, **availability**, **cost**, and **toxicity** of the photocatalytic materials are also important. **Figure 1.3** lists several semiconductors with their bandgap and bandedge positions. The blue parts are only UV-sensitive due to their large bandgaps. The green parts are visible light-sensitive but have instability issues (photocorrosion). The red parts do not have suitable bandedge and can be used only for photocatalytic water oxidation or reduction.

1.3.2 Photocatalytic materials for hydrogen production: Pros and Cons

Since the discovery of TiO_2 , many other semiconductor materials were tested for photocatalytic water splitting, including metal oxides, metal chalcogenides, elemental semiconductors, III-V semiconductor, etc. The following is a brief summary of these materials, with their advantages and disadvantages.

Metal oxides

Binary (TiO₂, ZnO, WO₃, Fe₂O₃ etc.) and ternary (BiVO₄ etc.) oxide semiconductors are the most studies materials due to their stability in photocatalytic reactions.

Titanium dioxide (TiO₂) was the first demonstrated material used in photocatalytic water splitting.^{8,12,19–23} TiO₂ is abundant, non-toxic, and can be used in an environment with a large

pH range (0~14). Since the conduction band of TiO₂ is slightly negative (-0.6 V vs. NHE at pH = 7) than water reduction potential, TiO₂ can be used as a standalone photocatalyst in hydrogen production. It can be produced in bulk by simple "soft" chemistry. However, due to its large bandgap ($E_g = 3.2$ or 3.0 for anatase and rutile phase, respectively),²⁴ less than 5% of the solar spectrum⁴ (ultraviolet part) can be utilized. Furthermore, TiO₂ also shows high electron-hole pair recombination due to surface states or defects, and large overpotential for H₂ and O₂ evolution. Theoretical maximum photocurrent for TiO₂ is 1 mA/cm², corresponding to an efficiency of about 2%.²⁵ A series of strategies have been used to improve the optoelectronic and electrochemical properties of TiO₂, including doping, sensitizing, morphology tuning, surface modification etc. The effect of doping on TiO₂ nanotubes will be discussed in Chapter 2 to 4.

Zinc oxide (ZnO) is another commonly used material in PEC hydrogen generation.^{26,27} It has similar bandgap ($E_g = 3.2 \text{ eV}$) but more positive conduction bandedge (-0.2 V vs. NHE at pH = 7) compared to TiO₂.²⁴ Due to the unsuitable conduction band position, ZnO is not able to realize overall water splitting. ZnO with different nanostructured morphology can be obtained using simple "soft" chemistry, including sol-gel and hydrothermal synthesis.²⁸ Apart from the same disadvantage of TiO₂ like large bandgap and hydrogen evolution overpotential, ZnO is prone to photocorrosion by holes under bandgap irradiation.¹⁸

Tungsten oxide (WO₃) with a bandgap of 2.7 eV²⁴ can utilize part of the visible light (>459 nm). It has a theoretical maximum photocurrent of 3.6 mA/cm² (about 6% efficiency).²⁵ WO₃ has a much higher hole diffusion length $(150~500 \text{ nm})^{29}$ compared to TiO₂ (~10 nm),³⁰ which facilitate fast hole transport to the surface to prevent recombination with

electrons. However, the conduction band $(0.36 \text{ V vs. NHE at } \text{pH} = 7)^{24}$ of WO₃ is more positive than water reduction potential, making it not able to produce hydrogen in a standalone photocatalytic or unbias PEC system. Also, WO₃ is not stable in neutral or basic solution and will slowly convert to WO₆^{2-.31}

Iron oxide (Fe₂O₃) with 2.2 eV²⁴ bandgap could use a large fraction of the visible solar spectrum (>564 nm), and a maximum theoretical efficiency of 15% can be achieved.²⁵ But similar to WO₃, it cannot act as standalone water splitting photocatalyst due to its unsuitable conduction bandedge (0.38 vs. NHE).²⁴ In addition, Fe₂O₃ suffers from severe low charge transport efficiency due to its non-conductive property and small hole diffusion length (2~4 nm).^{32,33} Strategies including doping and nanostructuring have been proposed to solve this problem.^{32,34,35}

Ternary metal oxide materials are also used in either ultraviolet or visible photocatalytic water splitting. Titanate^{36,37} (SrTiO₃, BaTiO₃, etc.), niobate^{38,39} (LiNbO₃, Ca₂Nb₃O₁₀, etc), and tantalate⁴⁰⁻⁴² (NaTaO₃, AgTaO₃, etc) have large bandgap (usually $E_g > 3$ eV) can only work under UV light excitation. Bismuth vanadate (BiVO₄) with 2.4 eV bandgap is one of the most studied visible-light sensitive ternary photocatalytic materials.⁴³⁻⁴⁶ Theoretical maximum efficiency of 9% can be achieved.²⁴ Like most oxide semiconductors, it has the problem of poor charge transport characteristics.

Metal Chalcogenides

Metal chalcogenides^{47–51} (sulfide, selenide, and telluride) are an important part of the visible-active photocatalysts (e.g. E_g for bulk CdS, CdSe and CdTe are 2.4, 1.7, and 1.5 eV, respectively).²⁴ Furthermore, they usually have higher (more negative) conduction bandedge

compared to metal oxides, which makes them suitable for standalone photocatalytic water splitting. However, these materials usually suffer severely photocorrosion due to oxidation of chalcogens.⁵² Sacrificial agent⁵³ (hole quencher) or resistive coating⁵⁴ can be used to deal with this issue.

Other materials like elemental semiconductor^{55–57} (silicon, etc.), III-V semiconductors^{58–60} (GaP, InP etc.) have also been studied by other groups, but none of them could satisfy all the requirements for good photocatalysts.

1.3.3 Strategies for improving photocatalytic efficiency

As mentioned previously, no one single material can fulfill all the requirements for photocatalyst, including the bandgap, bandedge, charge transport, charge transfer, stability requirements, etc. And nowadays, most of these photocatalytic materials show efficiencies less than 1%, which is far lower than the goal of 10% proposed by the department of energy (DOE).^{3,18,25} Though there is some report on III-V multi-junction PEC cells with an efficiency of 16.2%,⁶¹ the high cost of material and fabrication impede their practical use. Improving the photocatalytic efficiency of cheap, earth-abundant, easy-obtained semiconductor materials provides an economically attractive way to producing hydrogen from solar energy.^{3,25}

According to the principle of photocatalytic water splitting, three main factors control the efficiency: light absorption, charge transport, and charge transfer.^{62,63} Light absorption regards with the theoretical maximum energy that can be obtained from solar energy. In a traditional bulk semiconductor material (e.g., silicon), the most efficient light absorption is through bandedge excitation. Lower energy photons (hv < E_g) are transmitted and higher

energy photons ($hv > E_g$) suffer from energy loss (as heat) due to fast hot carrier relaxation. Charge transport regards with electron-hole pair separation, free charge carriers transport to the surface through drift or diffusion. Competitive charge recombination through radiative or non-radiative pathway could significantly reduce the charge transport efficiency and this is particularly severe in materials with a high amount of impurity or defect states. Charge transfer regards with the injection of surface-accumulated charge to adsorbed water molecules for hydrogen or oxygen generation. This efficiency is closely related to water reduction and oxidation reaction kinetics, in which is pretty low on most non-catalytic semiconductor surfaces. The following is the main strategies reported to tune these three factors to achieve higher solar hydrogen production efficiency.

Doping

Doping is a process of intentional introduction of an impurity into the (nominal) intrinsic semiconductor.⁶⁴ Introduction of dopant could create internal states within the bandgap of the semiconductor, which could significantly modify the optoelectronic properties of the original semiconductor. In the photocatalytic study, doping is commonly used to make an UV-absorption material (TiO₂, ZnO, SrTiO₃ etc) visible light sensitive due to bandgap shrinking. Furthermore, dopant could tune the electronic properties of the semiconductor, including the type of conductivity (p or n), carrier mobility, the density of states etc, which are important for tuning the charge transport efficiency in the photocatalytic process.^{65,66} In the case of TiO₂, different dopants (metal, non-metal, or both) incorporation was tested, with either increase or decrease of photocatalytic water splitting efficiency.^{8,19–21,62,67} The change of hydrogen yield has been explained by both experimental characterization and

computational simulation. Our group systematically studied the dopant (anion and cation) effects in electrochemical anodized TiO_2 nanostructures^{68–70} using a combination of optoelectronic and electrochemical (voltammetry and impedance) characterizations and showed the dopant-dependent effects in affecting the efficiency of light absorption, charge transport, and transfer. The details are discussed in Chapter 3 and 4.

Doping can be realized with either dry or wet process to make both powder and thin film photocatalysts.²⁰ Here, we use titanium dioxide as a model semiconductor and show a series of approaches to synthesize doped TiO_2 photocatalysts.

Doped TiO₂ powder can be obtained by gas phase treatment with TiO₂ powder. For example, nitrogen and carbon-doped TiO₂ can be synthesized by high-temperature treatment of TiO₂ powder in the NH_3^{71} and CO^{72} (or CH₄) flowing system, respectively. In a reverse way, they can also be synthesized by incomplete oxidation (high-temperature oxygen treatment) of titanium nitride⁷³ (TiN) and titanium carbide⁷⁴ (TiC). Plasma treatment,⁷⁵ mechanochemical method⁷⁶ (ball mining, with dopant precursor) was also applied to synthesize doped TiO₂. In the wet chemistry approach, dopant precursors (metal salts, ammonium salts, organic compounds etc) are incorporated in the sol-gel^{77–79} or hydrothermal^{80,81} TiO₂ synthesis system to make doped TiO₂.

Doped TiO₂ thin film can be fabricated with various reactive sputtering techniques^{20,82} (DC, RF, ion-beam, etc.) and deposition methods^{83,84} (physical or chemical vapor deposition), with the incorporation of correspondent dopants.

Our group has developed a novel doped metal oxide nanotube fabrication method. It is based on the principle of electrophoresis and has realized simultaneous (one-pot) nanotube growth and elemental doping.⁶⁸ This method has shown successful cation- (Cu, Nb, Fe, etc), anion- (N, C, etc), and co-doping of TiO_2 nanotubes with controllable dopant amount, and can be applied to make other tubular nanostructures including WO₃ and Fe₂O₃. The details are discussed in Chapter 2.

Nanostructuring

Nanomaterials refer to materials with at least one dimension in nanoscale (usually 1~100 nm).^{85,86} Compared to the bulk materials, nanomaterials show unique optical, electronic, and chemical properties, which have some advantages in photocatalytic efficiency enhancement, including shortened carrier collection pathway, improved light distribution, quantum size confinement, potential determining ions (interfacial energetics control), surface-area enhanced charge transfer, and multiexciton generation.^{3,63,87}

Based on the dimensionality, nanomaterials can be briefly classified as zero-dimensional (nanoparticles or quantum dots), one-dimensional (nanowires, nanorods, nanotubes) and two-dimensional (nanosheets or quantum well) nanostructures, which has confinement of free electron gas in three, two, and one directions, respectively.⁸⁸ This confinement leads to significant change of the material electronic properties, including the density of states, bandgap, and the carrier mobility.

Nanoparticles (0D) are attractive candidates as catalysts due to their larger surface area, which features more catalytic reaction sites.^{3,14,18,88} Also, nanoparticle catalysts are easier recycled than their bulk counterpart. In photocatalytic water splitting, quantum confined nanoparticles (quantum dots) with larger bandgap can have more negative conduction bandedge²⁵ and boost electron transfer to produce hydrogen. Furthermore, phonon bottleneck

effects^{89–91} in quantum dots could generate hot electrons and prevent energy loss. However, compared to bulk materials, small nanoparticles are not able to create internal electric field (due to complete depletion) and the only approach for charge transport is through diffusion, showing lower charge transport efficiency.^{17,25}

In photocatalytic water splitting, one-dimensional (1D) nanomaterials have one unique character of orthogonalization of light absorption and charge transport.^{22,23,26} The long axial size facilitates high enough light capture (especially for indirect semiconductor which has low extinction coefficient) and the short radial size ensures fast transport of charge carrier to the material surface. This property is rather important in most oxide materials, where hole diffusion length is very small (2~4 nm for Fe₂O₃ and ~10 nm for TiO₂).^{30,32,33} Unlike the hopping mechanism of charge transport between nanoparticles, the carrier could flow through the axial direction of the 1D nanostructure with much ease (higher mobility). Ordered 1D nanostructure array (ZnO, TiO₂, etc) synthesized directly on conductive glass or metal sheet through hydrothermal reaction^{19,28} or electrochemical anodization^{8,22,23,28,68} (Chapter 3 and 4) can be used to fabricate high-efficient PEC cells.

Two-dimensional materials (2D), including the graphene, MoS₂, are among the most important materials for device fabrication due to their extremely high carrier mobility.^{92–95} In catalysis, a 2D material with larger surface area can provide more reaction sites. Graphene is a zero-bandgap material,⁹² which is not able to produce electron-hole pairs under light excitation. But due to its superior electron transport character, coupling a semiconductor photocatalyst with graphene (nanocomposite or heterostructure) could significantly enhance charge separation and improve the photocatalytic activity of the semiconductor.^{96–98} Partial oxidation of graphene opens the bandgap and the resulting graphene oxide has demonstrated as a visible light sensitive photocatalyst.^{96,98–100} Monolayer MoS₂ with high carrier mobility and extraordinary optical absorption could serve the same function as graphene or graphene oxide in photocatalytic water splitting.^{101–105} Apart from the most studied 2D materials, we developed a universal approach of synthesizing metal chalcogenides¹⁰⁶ MX or M₂X (M = Cd, Cu, Ag, and Pb, X = S, Se) using a low-temperature amine-based synthesis^{107,108} and cation exchange.¹⁰⁹ We showed the high carrier mobility, low exciton-phonon coupling, and multi-excitonic characters of these nanosheets. These properties are important in designing novel, third-generation solar energy converters,^{110,111} including the solar cells and photocatalysts. The details are discussed in Chapter 5.

Co-catalysts

Thermodynamically, water splitting requires a theoretical minimum bias of 1.23 V. But in practical water electrolysis, a higher voltage is used to attain a certain current density and the difference between the practical voltage and theoretical voltage is termed as overpotential, which reflects an energy loss in water splitting.^{25,63,112–114} The overpotential is related to the kinetics of water splitting and a value of 0.4 and 0.6 V is commonly used for water reduction (hydrogen evolution) and water oxidation (oxygen evolution).^{63,112} One goal of water electrolysis industry is to find anodes and cathodes with sufficiently low overpotential. Several materials with electrocatalytic properties have been commercially been used, including platinum and Fe-Ni electrodes.^{115,116}

Similar to the case of water electrolysis, photocatalytic water splitting also faces the same problem. As most of the photocatalytic semiconductor surface has large overpotential

for hydrogen and oxygen generation, catalysts for hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) should be incorporated.^{117–119} As seen in Chapter 3, TiO₂ nanotubes without platinum nanoparticles as HER co-catalyst show almost no hydrogen generation, but with extremely high hydrogen yield with only 1% platinum nanoparticle coating.⁶⁹

For hydrogen production, platinum is most frequently considered catalyst due to its almost zero overpotential (0.07 V).^{113,114} Coating the semiconductor with platinum nanoparticles can be realized using chemical reduction or photocatalytic reduction of chloroplatinic acid, which almost stoichiometric conversion.^{28,55,120} Earth-abundant HER catalysts, including graphene, MoS₂, Fe-Ni dual layer etc. is also developed.¹¹⁷

Compared to hydrogen generation, overpotential for oxygen generation is even higher, due to the multielectron process (4e⁻) character of oxygen generation.^{25,113} Sometimes, the difficulty of water oxidation to oxygen can be relieved by using easier oxidation species (sacrificial hole quencher) like H_2O_2 and alcohols. But for full water splitting, oxygen generation from water is required. Several OER co-catalysts have been developed and commonly used in photocatalytic water splitting, including Co-based Co₃O₄ and Co-Pi, RuO₂, IrO_2 etc.¹¹⁹

Natural photosynthetic systems (PS I and PS II) are able to produce O_2 and carbohydrates from water and CO_2 with high efficiency and selectivity.^{121–123} This is mainly attributed to the highly specific and effective enzymatic systems, including the oxygen evolution center (OEC) and enzymes related to CO_2 assimilation. Inspired by this, people have tried to couple the inorganic semiconductor system to some specific enzyme,^{124–130}

including TiO₂-OEC, CdS-hydrogenase, Si-formate dehydrogenase to realize highly efficient and selective O_2 , H_2 , formic acid generation. This idea has been also used in living cell (in-vivo) solar fuel generation. For example, Yang et. al. demonstrated that by coupling the CdS with the nonphotosynthetic bacteria, *Moorella Thermoacetica*, this biohybrid system is able to convert CO_2 to acetic acid with a peak quantum efficiency of 2.44%.¹³¹ Other configuration, such as photoelectrochemical reduction of CO_2 or water to target chemical fuels using semiconductor nanowire-bacteria system is also reported.^{132,133} The enzymes or bacteria have the same function of the inorganic co-catalysts in solar fuel generation (including hydrogen).

Inspired by the recent discovery of solar-assisted nitrogen fixation using CdS-MoFe nitrogenase biohybrid system,¹³⁴ we proposed an alternate system composed of CdS@ZnS core-shell nanoparticles and histidine-tagged MoFe nitrogenase which can be formed in-situ through zinc-histidine affinity and showed high efficient solar hydrogen and ammonia production. Furthermore, the in-vivo test showed the possibility of using the aerobic nitrogen-fixing bacteria, Azotobacter Vinelandii DJ995,¹³⁵ with CdS@ZnS to realize photocatalytic living cell hydrogen and ammonia production in the air. Details can be found in Chapter 6.

Other approaches

Apart from the above three main strategies used in the publications, several other methods are also demonstrated.

Plasmonic water splitting¹³⁶ using gold nanorods or nanodisks on Nb-doped TiO₂ was reported^{137,138} to have a peak incident photon-to-current efficiency (IPCE) of $5\sim10\%$. This is

due to the addition of metal nanostructures (gold in this case) that support localized surface plasmon resonance (LSPR), which leads to additional absorption beyond the substrate materials. Furthermore, it can also help charge separation and generate hot electrons to enhance photocatalytic efficiency. Other Au-TiO₂ plasmonic water splitting systems were also studied.^{139,140} Instead of using expensive noble metal, silver and copper nanoparticles can be alternatives. For example, copper nanoparticles protected with conformal TiO₂ ALD coating¹⁴¹ can be a potential plasmonic water splitting catalyst.

Multiple exciton generation (MEG) refers to generation of several excitons by one photon with higher energy (hv > $2E_g$, $3E_g$, etc.).^{142–144} This phenomenon was initially discovered in PbS/PbSe nanoparticles and have been used in solar cells with efficiency surpass the Schockley-Queisser limit.^{145–147} MEG can also be utilized in photocatalytic water splitting, as reported by Turner et. al. recently using a PbS-TiO₂ PEC device.¹⁴⁸ An internal quantum efficiency of about 200% was realized with incident photon energy 2.7 times higher than the PbS bandgap ($E_g = 0.96 \text{ eV}$).

Unlike hot electrons and MEG that allow the utilization of higher energy photons from solar spectrum, the capture of lower energy photons (infrared irradiation) can be realized through a upconverting process, where two (or more) lower energy photons were absorbed with the emission of a higher energy photon.¹⁴⁹ This principle has been applied to third generation photovoltaics and also solar-assisted water splitting. For example, by incorporating rare-earth upconversion nanomaterials (NaYF₄:Yb,Er) into hematite photoelectrode, photocurrent at 980 nm laser irradiation is observed, though with a low incident light-to-current efficiency (1.24×10^{-4} %) due to the low efficiency of upconversion.

In Chapter 7, we describe the coupling of upconversion nanoparticles to two-dimensional nanosheets (MoS_2 and CdSe) and demonstrate the efficacy of color tuning by transforming upconverted light into photocurrent. These composite nanostructures are promising in photovoltaic and photocatalytic applications.

Tandem structures can be used to realize full solar spectrum absorption by tuning the bandgap of each absorber layers. This idea was first realized in tandem solar cells, where the top subcell absorbs higher energy photons and the transmitted lower energy photons are captured by the bottom subcell. A theoretical efficiency of 45.6% can be achieved in an optimized configuration (with 1.6 and 0.95 eV bandgap for top and bottom subcells, respectively).^{63,110} Tandem structures are also used for photocatalytic hydrogen production and have achieved a record of 16.2 % solar-to-hydrogen (STH) efficiency using multi-junction III-V semiconductors.⁶¹

In the natural photosynthetic system, electrons in photosystem (PS) II and holes in PS I recombine through a series of electron donor and acceptor and leave higher energy holes and electrons in PS II and I, respectively.¹²¹ Though the maximum quantum efficiency is lowered by half since two photons are required to produce one electron-hole pair, the separation of electron and holes in two different systems can prevent electron-hole recombination and also backreaction, which significantly improve the charge transport efficiency with a small cost of light capture efficiency. In a Z-scheme photoelectrochemical system,^{150,151} the photoanode and photocathode are wired and light-induced electrons in photoanode and holes in a tandem configuration to allow fully solar spectrum utilization. In a standalone photocatalytic

system,^{150,152} electrons and holes in the two semiconductors are recombined through a redox pair (e.g. iodide/iodate, Fe^{3+}/Fe^{2+}). Another advantage of using Z-scheme is to overcome the insufficient electron or hole energy (less negative electron potential or less positive hole potential) in photocatalytic water reduction or oxidation with a single material and realize overall water splitting.

Using Ferroelectric material-semiconductor heterojunction to enhance photocatalytic or photoelectrochemical water splitting efficiency is based on easier charge separation by internal polarization.^{153,154} For example, 5 nm BiTiO₃ (BTO) coated TiO₂ nanowires show 67% photocurrent enhancement compared to the pristine TiO₂ nanowires in photoelectrochemical hydrogen production and this is the result of increased charge separation induced by the ferroelectric polarization in the BTO shell.³⁷ Similar effects have also seen in BiFeO₃-TiO₂,¹⁵⁵ BiFeO₃-Au¹⁵⁶ systems.

1.4 Photocatalytic solar fuel generation beyond hydrogen

Photocatalytic reduction of CO₂ to carbonaceous feedstock such as hydrocarbons and alcohols, aldehydes is a promising strategy in both storing energy in chemical forms and mitigating the ever growing CO₂ level in the atmosphere. Compared to hydrogen, liquid fuels show advantage of easier and safer storage.^{157–162} However, theoretically and technically, the photocatalytic CO₂ reduction is facing more challenge from the aspect of energetics and selectivity. Energetically, CO₂ is one of the most stable molecules ($\Delta G_f^0 = -394.4$ kJ/mol) and high energy is required to activate the CO₂ (C=O bond energy: 794 kJ/mol).¹⁶³ This leads to a redox potential of -1.9 V¹⁵⁹ (vs. NHE at pH = 7) for CO₂ activation, which is far more
negative than most of the semiconductor conduction bandedge position. Proton-assisted photocatalytic CO_2 reduction provides an energetically favorable pathway for CO_2 conversion, through a multiple electron transfer process. As shown below, redox potential (vs NHE at pH 7) of CO_2 to CO, carboxylic acid, aldehyde, alcohols, and alkanes are significant higher (less negative) though proton-assisted reaction:^{160,162}

$$CO_{2} + 2H^{+} + 2e^{-} \rightarrow HCOOH (-0.61 V)$$

$$CO_{2} + 2H^{+} + 2e^{-} \rightarrow CO + H_{2}O (-0.53 V)$$

$$CO_{2} + 4H^{+} + 4e^{-} \rightarrow HCHO (-0.48 V)$$

$$CO_{2} + 6H^{+} + 6e^{-} \rightarrow CH_{3}OH + H_{2}O (-0.38 V)$$

$$CO_{2} + 8H^{+} + 8e^{-} \rightarrow CH_{4} + 2H_{2}O (-0.24 V).$$

However, the multielectron process brings the problem of slow reaction kinetics and co-catalysts are usually required to achieve the detectable CO_2 reduction. Another challenge of photocatalytic CO_2 reduction using inorganic semiconductor material is the low solar fuel selectivity.^{159,164} Unlike the natural photosynthetic process which selectively converts CO_2 to a specific hydrocarbon, photocatalytic CO_2 reduction using inorganic semiconductor usually results in mixtures of organic compounds that needs post-separation.

The semiconductor-based photocatalytic CO_2 reduction is first studied by Inoue et. al in 1979.¹⁶⁵ They examined the semiconductor powder, including TiO₂, WO₃, ZnO, CdS, and SiC, suspended in CO₂ saturated water, in CO₂ conversion under xenon lamp irradiation. A small amount of formic acid, formaldehyde, methanol, and methane were produced. Nowadays, standalone photocatalytic and photoelectrochemical CO₂ reduction have been realized in many different systems, including single semiconductor materials^{159–161} (Group IV,

III-V, chalcogenides, and oxides), multi-semiconductor systems^{159,160} (heterojunction, Z-scheme, and solid solutions), and semiconductor-enzyme biohybrid systems.¹⁶⁶ The efficiency is still much lower than photocatalytic hydrogen production using the same semiconductor material. The major reduction products reported are formate (formic acid) and carbon monoxide, and the selectivity and efficiency highly depend on the use of co-catalysts.¹⁵⁹

Photocatalytic dinitrogen reduction uses dinitrogen and water as substrates and produces ammonia, which is used as fertilizer rather than fuels. Due to the triple bond character, dinitrogen is extremely difficult to activate. Industrial ammonia production (Haber-Bosch method) is a highly energy-intensive process, which requires high temperature (>400 °C) and high pressure (>150 atm).^{167,168} Photocatalytic ammonia production could provide an alternate cheap way of nitrogen fixation using renewable solar energy. Though first demonstrated in 1977 with iron oxide-modified titania powder, no much following work was reported. Several inorganic semiconductor and biohybrid materials has shown relatively high efficient photocatalytic dinitrogen reduction to ammonia, including BiOBr nanosheets,^{169,170} hydrogenated Bi₂WO₄ nanoframe,¹⁷¹ BiO quantum dots,¹⁷² hydrogen-terminated diamond,¹⁷³ CdS nanorod-nitrogense biohybrids.¹³⁴

1.5 Efficiency definition and calculation

Several different measurements of efficiency exist for both wired (PEC cell) and wireless (slurry) photocatalytic systems, and the misuse of these efficiencies in references often causes confusion. Here we list a series of frequently used efficiencies and give their definitions and calculations. It is defined for hydrogen production but can be easily modified for other systems.^{15,25,63,112}

Solar-to-hydrogen (STH) efficiency

STH efficiency is the benchmark efficiency used to describe the overall efficiency of a whole PEC system. It is measured using a zero-biased (electric and chemical bias) two-electrode (2E) configuration in an electrolyte with no sacrificial agents (electron or hole quencher), under broadband solar irradiation (AM 1.5G). Either production of H_2/O_2 or the short-circuit photocurrent can be used to calculate STH (under 1 SUN condition):

$$STH = \left[\frac{(mmolH_2/s) \times (237,000J/mol)}{P(mW/cm^2) \times Area(cm^2)}\right], \text{ or}$$
$$STH = \left[\frac{|j_{SC}|(mA/cm^2) \times 1.23V \times \eta_F}{P(mW/cm^2)}\right],$$

where P, j_{SC} , and η_F refer to the irradiation intensity, short-circuit current density and Faradaic efficiency of water splitting.

Applied bias photon-to-current efficiency (ABPE)

ABPE is similar to STH efficiency, with the exception of applying a bias and it is not the true overall efficiency of the PEC cell. It is usually used as a diagnostic efficiency when STH is not available (or overall water splitting is not achievable). It can be calculated as follows:

ABPE =
$$\left[\frac{|j_{SC}| (mA/cm^2) \times (1.23 - |V_b|) V \times \eta_F}{P (mW/cm^2)}\right],$$

where V_b is the applied bias to the working electrode.

Incident photon-to-current efficiency (IPCE)

IPCE describes the photocurrent collected per incident photon flux as a function of illumination wavelength and it is one of the most important diagnostic efficiency used in evaluating a PEC cell. It is also termed as external quantum efficiency (EQE) and can be

calculated as:

$$IPCE(\lambda) = EQE(\lambda) = \frac{|j_{ph}| (mA/cm^2) \times 1239.8 (V \times nm)}{P_{mono}(mW/cm^2) \times \lambda (nm)},$$

where j_{ph} refers to the photocurrent density, P_{mono} and λ refer to the intensity and wavelength of the incident irradiation.

In the case of a standalone photocatalytic system, IPCE can be calculated by dividing the number of electrons/holes generated by the numbers of the incident photon.

IPCE can be conducted in both three-electrode and two-electrode configurations, both with or without bias. IPCE conducted in unbiased two-electrode configuration can be integrated with solar spectrum to obtain the correspondent short-circuit photocurrent density, which can be used to obtain the maximum STH efficiency:

$$j_{SC} = \frac{1}{1239.8} \int \lambda \times IPCE(\lambda) \times E(\lambda) \ d\lambda,$$

where $E(\lambda)$ is the solar spectrum irradiance at specific wavelength.

IPCE can be further decoupled into three separate efficiencies:

$$IPCE = \eta_{abs} \eta_{transport} \eta_{transfer},$$

where η_{abs} refers to the efficiency of generating electron-hole pairs via light excitation, $\eta_{transport}$ refers to the efficiency of charge transportation from the site it generated to the material surface, $\eta_{transfer}$ refers to the efficiency of charge transfer from material surface to the substrates (H₂O in water splitting and CO₂ in carbon dioxide reduction). The evaluation of the three efficiencies will be the topic of Chapter 3 and 4, by using a series of optoelectronic and electrochemical techniques.

<u>Absorbed photon-to-current efficiency (APCE)</u>

APCE is similar to IPCE, but with the consideration of photon loss due to reflection or

transmission by the material. It is also termed as internal quantum efficiency (IQE) and can be calculated as:

$$APCE(\lambda) = IQE(\lambda) = \frac{IPCE(\lambda)}{\eta_{abs}} = \frac{|j_{ph}| (mA/cm^2) \times 1239.8 (V \times nm)}{P_{mono}(mW/cm^2) \times \lambda (nm) \times (1-10^{-A})}, A = -\log(\frac{I}{I_0}),$$

where A, I, and I_0 refer to the absorbance of light by the material, output light intensity, and input light intensity, respectively. Similar to IPCE, APCE can also be adapted to describe the standalone photocatalytic system.

Turnover frequency (TOF) and turnover number (TON)

TOF and TON¹⁷⁴ were originally used in enzymology and are now mainly used to describe homogeneous photocatalytic systems. They are defined as the number of turnovers per mol catalyst per unit of time (TOF), and the total number of turnovers per mol catalyst until it is no longer active (TON).

1.6 Characterization of photocatalytic systems

1.6.1 Material Characterization

Scanning electron microscopy (SEM)^{175–177}

SEM is one of the most versatile instruments available for the examination and analysis of the microstructure morphology and chemical composition characterizations. By scanning the material surface with a focused electron beam in a raster scan pattern, secondary electrons are emitted and collected by the detector, producing the surface topography images. Unlike in an optical system, resolution of SEM is not limited by the diffraction limit. It is limited by the volume of the specimen that interacts with the electron beam, leading to a resolution limit (~50 nm for conventional SEM and ~1 nm for field-emission SEM) not enough to image

individual atom.

SEM can also be used for elemental analysis or chemical characterization when combined with energy-dispersive X-ray spectroscopy (EDS). An atom within the sample is excited by the high energy electron beam, which ejects its electron from an inner shell and creates a hole where the original electron is. An electron from higher energy shell fills the hole and the energy difference is released as X-ray, which can be measured by the energy-disperse spectrometer for element identification.

In this thesis, SEM was mainly used in characterizing the morphology and crystallinity of the TiO_2 nanotubes, monitoring their change with doping. Also, EDS was used to detect the dopants and quantify the doping amount in these nanotubes (Chapter 2~4). In cation exchange of two-dimensional materials (Chapter 5), EDS was used to confirm complete replacement of cadmium with copper, silver, and lead.

Transmission electron microscopy (TEM)^{176–178}

Similar to the working principle of optical microscopy, TEM is a microscopy technique that forms an image from the interaction of high energy electron beam with the sample when it is transmitted through the specimen. Due to much shorter de Broglie wavelength $(\lambda = \frac{h}{\sqrt{2meV}} \times \frac{1}{\sqrt{1 + \frac{eV}{2mc^2}}})$, where h, m, e, V, and c are Planck's constant, electron mass, electron

charge, accelerating voltage and light speed in vacuum, respectively) of accelerated electrons (3.70, 2.51, and 1.96 pm for 100, 200, and 300 keV electron beam), much higher resolution (~0.1 nm) can be realized by TEM compared to optical microscopy. Compared to SEM, TEM can achieve atomic resolution, but has limitations to only ultra-thin samples due to its transmission characters.

In this thesis, TEM is mainly used to characterize two-dimensional nanostructures (Chapter 5) and upconversion nanoparticles (Chapter 8), including their shape and size.

Scanning tunneling microscopy (STM)^{179,180}

STM is a kind of surface probing technique used for imaging surface at the atomic levels, which can achieve 0.1 nm lateral and 0.01 nm depth resolution. It is based on the concept of quantum tunneling. The tunneling current is generated when an ultra-sharp conducting tip is brought very close to the material surface under an applied bias, which is a function of applied voltage, tip position, and local density of states (LDOS) of the specimen. Images are formed by monitoring the current as the tip scans through the surface. STM is initially developed in an ultra-high vacuum environment but is later adapted to air, water, and various liquid or gas conditions. Extremely clean and stable surface, ultra-sharp tips, vibration isolation system are essential for obtaining high-quality topographs. A conductive substrate (for example, highly-ordered pyrolytic graphite or ultra-smooth gold surface) is also required to perform STM measurements.

As an extension of STM, scanning tunneling spectroscopy (STS) can provide additional information including the LDOS and bandgap of the materials. It involves observation of changes in constant-current topographs with tip-sample bias, local measurement of the tunneling current vs. tip-sample bias (I-V) curve and measurement of the tunneling conductance.

In this thesis, STM and STS were used to obtain the material density of states (V vs. dI/dV), from where the material bandgap (Chapter 2~5), Fermi level (Chapter 2~4), dopant states (Chapter 2~4) can be determined.

Atomic force microscopy (AFM)^{180,181}

As an alternative scanning probe technique, AFM is based on the forces (mechanical forces, van der Waals forces, chemical bonding etc.) between the probe (a cantilever with a sharp tip) and the sample surface. When the probe approaches the sample surface, forces between the sample surface and the tip lead to a deflection of the cantilever according to Hooke's law. Such deflection can be detected using different mechanisms including optical, piezoelectric systems. AFM can be operated in both static (contact) and dynamic (non-contact or "Tapping") modes depending on the sample properties and can be performed in various environments including air, vacuum, and liquids. Contrast to STM, AFM is applicable for both conductors and insulators, but with a relatively lower resolution.

Microscopic electronic properties can also be measured by AFM. With the technique of current-sensing AFM (CSAFM) using a conductive substrate (e.g. ultra-smooth gold) and probes with gold-coated tip, electronic characters including conductivity, carrier concentration, and mobility can be measured.

In this thesis, AFM was used for characterizing two-dimensional material shape, lateral size, and thickness (Chapter 5, 8). CSAFM was used to obtain electronic parameters of two-dimensional materials (Chapter 5, 8) and doped TiO_2 nanotubes (Chapter 3, 4).

Ultraviolet-visible spectroscopy (UV-VIS)^{176,182}

UV-VIS refers to either absorption or reflectance spectroscopy in the ultraviolet and visible light (190~750 nm wavelength) range, which provides electronic transition information including the wavelength range and strength a material absorbs, and the material type. Small molecules with discrete energy levels undergo electron transitions at these

frequencies, whose peak absorption can be used to quantify the molecule concentration using Lambert-Beer's law. For bulk material with continuous energy levels, broad absorption is usually obtained. The bandgap and type of bandgap and be extracted from Tauc plot $((\alpha h\nu)^{1/n}$ vs. $h\nu$) based on the Tauc relation:

$$\alpha h \nu = A(h \nu - E_a)^n,$$

where α is the absorption coefficient, hv is is the photon energy, E_g is the material bandgap, and A is a material-specific constant. n with value of 0.5 and 2 indicates direct and indirect transition, respectively. For small nanostructures with quasi-discrete energy levels, UV-VIS can be used to determine the material size and study the quantum confinement effect.

In this thesis, UV-VIS is mainly used to determine the nanomaterial bandgap (Chapter $2\sim8$), study the quantum confinement in two-dimensional materials (Chapter 5), improvement of light absorption in doped TiO₂ nanotubes.

X-ray Powder Diffraction (XRPD)^{176,177,183}

XRPD is a technique to identify the atomic or molecular structures of crystalline material, including their phase, purity, and composition. XRPD is based on the elastic (Rayleigh) scattering of X-ray by the sample, with the angles between the coherent and incoherent scattering related by the Bragg's law:

$$n\lambda = 2d \sin\theta$$
,

where the integer n is the order of diffraction, λ is the incident X-ray wavelength, d is the atomic plane spacing, and θ is the angle between the atomic plane and the incident X-ray. Diffraction pattern (intensity vs. 2θ) can be obtained by varying both the X-ray and detector angle and it can be used to identify unknown compound by running through the database and

comparing with the standard pattern. Furthermore, average crystalline size can be determined by the Scherrer's equation:

$$\tau = \frac{\kappa\lambda}{\beta \cos\theta}$$

where τ is the mean size of the crystalline domains, K (~1, dimensionless) is a shape factor, λ is the incident X-ray wavelength, β is the line broadening at half maximum intensity (FWHM) and θ is the Bragg angle.

In this thesis, XRPD is used to determine the phase change of TiO_2 nanotubes upon elemental doping and to identify the dopant (Chapter 2~4). It is also used to determine the phase of cation-exchanged two-dimensional nanostructures (Chapter 5).

1.6.2 Photoelectrochemical (PEC) cell characterization^{15,112,113}

As described previously, while three-electrode (3E) measurements reveal the properties of a certain electrode, two-electrode (2E) measurement reflect the properties of the whole system. The following discussion will be focused on 3E characterization unless specifically indicated. In this thesis, the PEC cell characterization is covered in Chapter 3 and 4.

Linear sweep voltammetry (LSV)

LSV is a voltammetric technique, which measured the current of the working electrode with linearly varied (with time) voltage (between the working electrode and reference electrode) and is similar to the I-V curve measurement for semiconductor devices. In conventional electrochemistry, LSV can be used to identify unknown species (using half-wave potential) and its concentration (using limiting current). In PEC research, LSV technique is used to compare the I-V curve of a photoelectrode under dark and irradiation

condition, where onset photocurrent, saturated photocurrent, open circuit potential and flatband position can be determined. LSV is also commonly used in electrocatalysis study to determine the potential region (or overpotential) of a catalysts electrode for water reduction/oxidation or CO_2 reduction. High efficient electrocatalyst can then be integrated into photocatalytic or PEC system as co-catalyst.

Cyclic voltammetry (CV)

Similar to LSV, in a CV measurement, the working electrode potential is ramped linearly with time, but the scanning is reversed to its initial potential after a certain setpoint is reached. Multiple cycles can be recorded as needed. CV is usually used for studying analyte in solution, information such as reversibility and kinetic parameters (through Butler-Volmer equation) of an electrode reaction can be obtained. CV can also be used to determine the conduction band and valence band position of a semiconductor, either in the non-aqueous or aqueous electrolyte. In PEC research, CV is commonly used to study the mechanism of an electrocatalyst (co-catalyst), when combined with rotating disk or ring-disk electrode technique.

Chronoamperometry (CA)

CA is a technique to determine the response of a biased photoelectrode both in dark and illumination condition. Information obtained from CA is usually presented as current (or current density) vs. time plot with a fixed working electrode potential. The transition between dark and light can be used to study the charge carrier dynamics including the charge transport and surface-assisted recombination. CA is also used in assessing the stability of a photoelectrode by monitoring the photocurrent for long enough time. With monochromatic

light with a range of wavelength from 300 to 1000 nm, incident photon-to-current efficiency (IPCE) can be calculated. The result is presented as an IPCE vs photon energy (incident light wavelength) plot, which can provide information including the electrochemical bandgap and color-specific sensitivity of the photocatalytic material.

Electrochemical impedance spectroscopy (EIS)^{184,185}

EIS is a non-steady-state measuring technique which is extremely suitable for studying the electrode kinetics of a complex electrochemical system. In a typical EIS experiment, a small perturbation (for example, sinusoidal potential or current with a frequency range from mHz to MHz) is applied to the system and the response (current or potential) is measured. The impedance at each frequency can be calculated:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = Z'(\omega) + iZ''(\omega),$$

where V, I, and ω refers to measured/applied potential, current and the frequency of the sinusoidal perturbation. Z, Z', and Z'' refers to the impedance, real and imaginary part of the impedance. The modular $|Z| = \sqrt{Z'^2 + Z''^2}$ and phase $\varphi = \arctan(\frac{Z''}{Z'})$ can be presented using the Bode plot (|Z| or φ vs. frequency) and can give important charge lifetime information in photoelectrochemical process. A more useful representation is the Nyquist plot (Z'' vs. Z'), which is often used to fit to an equivalent circuit. An equivalent circuit is the simplification and symbolization of the complex microscopic charge processes (including resistive, capacitive and inductive) into lumped electronic components like resistor, capacitor etc. for easier description. A commonly used equivalent circuit to describe fast charge transfer reaction on the planar electrode ($O + ne^- \rightleftharpoons R$) is the Randles equivalent circuit, which includes components describing the double layer capacitance C_{dl}, charge transfer resistance

 R_{ct} , Warburg impedance W (used to describe the diffusion) and the solution resistance. In a photoelectrochemical cell, the phoanode (n-type semiconductor) can be modeled using the equivalent circuit described in Chapter 3 and 4. This equivalent circuit contains three parts including the solution, the photoanode-solution interface, and the bulk semiconductor, which can be used to fit the impedance data to obtain parameters describing charge transport and charge transfer.

Mott-Schottky (M-S) analysis

M-S is an EIS based technique which has been commonly used in metal oxide electrode research. It involves measurement of the space charge layer capacitance (C_{sc}) of the photoelectrode as a function of applied potential (E). The measured data is presented with Mott-Schottky plot using the relationship:

$$\frac{1}{C_{sc}^2} = \frac{2}{\epsilon_r \epsilon_0 A^2 e N} \left(E - E_{fb} - \frac{kT}{e} \right),$$

where ϵ_r , ϵ_0 , A, N, E_{fb} are material relative permittivity, permittivity of vacuum, electrode area, material carrier density, flatband potential, respectively. e and k are elemental charge and Boltzmann's constant, respectively. For an ideal system, flatband potential and charge carrier density can be determined from the x-intercept and slope of the M-S curve. With the information of material bandgap, conduction and valence bandedge position can also be obtained. Furthermore, conduction type of the material can also be indicated by the sign of the M-S curve slope, where a positive or negative slope refers to n or p-type semiconductor.

1.6.3 Photocatalytic characterization

Degradation of organic compounds^{186–189}

Photocatalytic degradation of organic compounds serves as an important tool to assess the photoactivity of the material. Organic dyes (for example, Alizarin S, Congo Red, Methylene Blue) are usually used due to their strong absorption in visible light range and their accurate stoichiometric reaction. In the photocatalytic reaction, the organic dyes are completely mineralized, with carbon converted to CO_2 , sulfur to sulfate and nitrogen remain as ammonium (-3 valency) or converted to N_2 (-N=N-). The experiment is usually performed in a quartz or glass container with the known amount of photocatalysts and dyes (slurry system), and the whole system is irradiated with stirring. The slurry was sampled at a certain time point and the photocatalysts are removed by centrifugation. The remaining clear solution containing the organic dye is measured with UV-VIS spectrometer. By monitoring the absorption peak change with time, kinetic behavior of the photocatalytic reaction and the quantum efficiency of the photocatalytic material can be determined.

Gas chromatography^{190,191}

Gas chromatography (GC) is a technique used for separation and analysis of volatile compounds, which can be used for gas, liquid, and even solid samples. Separation of each component is based on their partition between two phases: a stationary bed with a large surface area and a gas that percolates through the stationary bed. The sample is vaporized and carried by the carrier gas (mobile phase) through the column and their interaction (partition) with the stationary phase at a given temperature determines the elution time (intention time). For simple gas molecules (H₂, O₂, N₂, CO, CO₂, small hydrocarbons etc.), separation is based on their molecular weight, polarity or boiling point.

A basic gas chromatograph system includes a carrier gas, flow controller, injector,

column, detector, and data system. In photocatalysis study, the components to be analyzed include H₂, O₂, CO, small (C1, C2 etc.) hydrocarbons, alcohols, aldehyde, carboxylic acid. Except for formaldehyde and formic acid which have high detection limit or instability issues, successful quantify the other components depends on the effective instrumentation. Two detectors are usually used: thermal conductivity detector (TCD) based on the difference of thermal conductivity between the carrier gas and the vaporized components, and the flame-ionized detector (FID) based on detection of ions formed during combustion of organic compounds with oxy-hydrogen flame. TCD is a universal detector, but with a higher detection limit (~10 ppm). While FID is more sensitive (~50 ppb), it is limited to organic compounds (H₂, O₂, and CO have no signal). A trace amount of carbon monoxide (CO) can be measured with FID combined with a methanizer (Ni-catalyst), where CO was converted into methane by reaction with supplied H₂ and with much lower detection limit. Selection of column is crucial for separation of each component in the mixture, as correct quantification required non-overlap component peaks. Molecular sieves 5A, 13X are usually used for separation of simple molecules including H₂, O₂, and N₂. As CO₂ can block the molecular sieves pores and deteriorate the separation efficiency, Hayesep D, Porapak Q columns are usually used as replacements in photocatalytic CO₂-water reaction study. Selection of carrier gas is more related when TCD is used for detection. High sensitive detection relies on large thermal conductivity difference between the analyte and the carrier gas. For example, argon (or nitrogen) and helium are used as carrier gas for H_2 and O_2 detection, respectively. Gas sampling can be as simple as injection with an air-tight syringe, but gas sampling line with multi-way switching valve can be used to ensure contamination of air when trace O₂

detection is required.

Abbreviations	
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
2E	Two-electrode
3E	Three-electrode
ABPE	Applied bias photon-to-current efficiency
AFM	Atomic force microscopy
APCE	Absorbed photon-to-current efficiency
CA	Chronoamperometry
CSAFM	Current-sensing atomic force microscopy
CV	Cyclic voltammetry
DC	Direct current
DOE	Department of energy
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
EQE	External quantum efficiency
FID	Flame-ionized detector
GC	Gas chromatography
HER	Hydrogen evolution reaction
IPCE	Incident photon-to-current efficiency
IQE	Internal quantum efficiency
LDOS	Local density of states
LSPR	Localized surface plasmon resonance
LSV	Linear sweep voltammetry
MEG	Multiple exciton generation
M-S	Mott-Schottky
NHE	Normal hydrogen electrode
OEC	Oxygen evolution center
OER	Oxygen evolution reaction
PEC	Photoelectrochemical
PS	Photosystem
RF	Radiofrequency
SEM	Scanning electron microscopy
STH	Solar-to-hydrogen
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TOF	Turnover frequency

TON	Turnover number
UV-VIS	Ultraviolet-visible
XRPD	X-ray powder diffraction

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Chapter 2

Growth and doping of wide-bandgap titanium-dioxide nanotubes

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Titanium-dioxide (TiO₂) is a wide-bandgap semiconductor that is a key component of devices like solar cells, photocatalytic reactors, photoelectrochemical cells etc.¹⁻⁴ While doping (electronic, optical, and magnetic) allows careful tuning of desired properties, oxygen vacancies formed during synthesis are used as n-type dopants in these nominally "undoped" oxides. Since desired doping of these semiconductor nanostructures has proven challenging, most applications are focused on bulk semiconductor films.^{5–7} This can severely limit their applications and device architectures, like fabricating p-type oxide films or changing the doping level of n-type dopant for optimized configuration.^{1,3} Recent research in utilizing heavily-doped semiconductors for low-loss plasmonics^{8,9} has also generated interest in doping of these TiO₂ nanostructures, already used in thin film solar-cells, for enhanced light harvesting. Moreover, the addition of desired dopants, like shallow or deep donors, can also lead to the formation of heavily-doped transparent oxide nanostructures, or co-doped photocatalysts^{10,11} which can absorb infrared light. Other efforts to improve the performance of TiO₂ photocatalytic activity¹²⁻¹⁹ involve hybrid composites consisting of TiO₂ and carbonaceous materials (carbon nanotubes, activated carbons, and graphene) which cause red-shift in the absorption spectrum and increase electron mobility.²⁰⁻²³ Since doping can simultaneously tune the bandgap and increase charge conductivity, it can provide an important alternative. Therefore, desired doping of these wide-bandgap nanostructured films can provide important materials for a variety of applications in renewable energy, artificial displays, and other optoelectronic and magnetic processes.

Electrochemical anodized TiO2 nanotubes: a brief overview

One-dimensional (nanowire, nanotube, etc.) TiO_2 with high surface-to-volume ratios have shown useful and unique properties, with applications in sensing,^{24,25} photocatalysis,^{26– ³⁰ solar cells,^{31–33} energy storage,^{34,35} and drug delivery^{36,37} outperform colloidal TiO₂. Among them, highly ordered TiO₂ nanotube arrays are the most successful candidates. They can be produced by a number of methods, including the sol-gel process with organo-gelator,^{38,39} using nanoporous alumina template,^{40–43} hydrothermal synthesis,^{44,45} and seeded growth mechanisms.⁴⁶ However, none of the above approaches provide superior control over the TiO₂ nanotubes include the tube diameter, length, wall thickness etc.}

On the other hand, highly ordered TiO₂ nanotube arrays with precise control of their dimension and density can be realized by electrochemical oxidation $(anodization)^{26,47-50}$ in the fluoride-based electrolyte, which is based on local chemical dissolution using controlled, field-assisted oxidation and dissolution reactions. This simple synthesis provides a facile route towards large-scale fabrication of TiO₂ nanotubes, and it has gone through four generations since its discovery in 1999 using titanium alloy.⁵¹

A typical electrochemical anodization setup contains a titanium anode and a platinum (or platinum-coated, graphite) cathode immersed in an electrode with fluoride ion. A DC power is used to supply tunable constant voltage or current (potentio- or galvanostat) between the two electrodes. The growth of TiO₂ nanotube is initiated with the formation of oxide barrier layer by the reaction of oxygen ions with titanium metal.⁵² With the increase of barrier layer thickness, the current quickly decreases and the remaining small current is due to diffusion of O^{2-} and F⁻. A barrier layer with uniform thickness is finally obtained due to the difference of growth rate: thinner layer with smaller resistance grows faster and thicker layer with higher

resistance grows lower. The uniform barrier layer also ensures the uniform length of the final nanotubes. Meanwhile, electric field-assisted chemical dissolution by fluoride ion $(TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O)$ continues to form hollow structures. It is required that oxide barrier layer forms more rapidly than TiO₂ dissolution, and the final structure (porous or barrier layer) is highly dependent on the electrolyte composition.

Highly ordered TiO₂ nanotube array was first fabricated in 2001 using pure titanium sheet.⁵³ Later studies were focused on the control of nanotube morphology, length, pore size, and wall thickness.^{54–56} The first generation TiO₂ nanotubes were fabricated with aqueous electrolytes, using HF or HF with other acids (HNO₃, H₂SO₄, H₃PO₄, etc)^{53,57–59} with F concentration at about 0.5%. Lower voltage (usually < 20 V) was applied and a final nanotube length of about several hundred nanometers was obtained. This method is not able to fabricate long (micrometer range) nanotubes due to high TiO₂ dissolution rate in aqueous systems.

The second generation of TiO₂ nanotube fabrication was using buffered electrolyte,⁵⁵ which provides precise pH control. Fluoride salt (NaF or KF)-containing buffer solution with a variation of pH was used to tune the growing and dissolution rate, resulting in nanotubes with different length. Nanotubes with several micrometer lengths can be fabricated.

Even longer nanotubes (several hundreds of micrometers) can be fabricated using polar organic electrolyte (third generation), under higher applied voltage (up to several hundred volts). The electrolyte is composed of a small amount of water (1~6%), fluoride ion (NH₄F, 0.3~1%), and the polar organic electrolyte. Formamide (FA), N-methyl formamide (NMF), N, N-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), ethylene glycol (EG), diethylene glycol (DEG), glycerol are the commonly used electrolytes.^{47,60–63}

Non-fluoride based electrolytes (fourth generation) can also be used, including HCl, H_2O_2 , and HCl/H_2O_2 .^{64–66} But like the case of first-generation electrolytes, only short nanotubes can be obtained.

Doped TiO₂ nanotubes fabrication: A novel method developed in our lab

Since this synthesis provides a facile route towards the large-scale fabrication of TiO_2 nanotubes, simply incorporating desired dopants during growth can provide an important method for synthesis of doped wide-bandgap semiconductor nanostructures. However, the simple addition of desired concentration of precursors, especially cationic, does not lead to doping of nanotubes. Therefore, we designed a new electrochemical cell that enables doping and co-doping of TiO_2 nanotubes with desired cations and anions, and characterized their resulting optical, electronic and magnetic properties, to demonstrate the feasibility of this new method. Using detailed studies, we demonstrate that this method can provide an important route for the synthesis of doped wide bandgap TiO_2 semiconductor nanotubes.

In a regular setting of electrochemical cell, negative-biased platinum (Pt) electrode and positive-biased titanium (Ti) sheet are immersed in the electrolyte $2\sim3$ cm apart.^{26,47–50} In this configuration negative ions in the electrolyte move toward positive Ti sheet and positive ions move toward negative Pt sheet. Addition of desired dopant metal cations into the electrolyte results in the repulsion of the positively charged ions from the positively biased Ti sheet (away from the growing TiO₂ nanotubes). This prevents TiO₂ nanotubes from doping with metal cations.



Figure 2.1 Electrochemical cell design for doped-TiO₂ fabrication (a) A sketch showing the design of new electrochemical cell developed in this work, which is divided into two parts separated by a porous membrane to prevent from high currents and from cation deposition onto the platinum electrode. (b) Schematic illustration of a rectangular shape AC signal with parameters employed for doping nanotubes.

Replacing DC power supply with AC can provide a solution. During the "negative" cycle (switched polarities) of electrochemical growth, the desired cations are attracted by the titanium sheet, thus incorporating cationic dopants uniformly in the growing TiO₂ nanotubes (**Figure 1a**). However, the simple addition of cationic precursors in the growth solution leads to other problems. First, the added cations (especially in high doping concentrations) dramatically increase conductivity, making it impossible to apply high enough voltages (minimum of 5 V is required to initiate the growth^{26,47–50}) to enable TiO₂ nanotube growth. Second, during the nanotube growth phase (positive bias on titanium sheet and negative bias on Pt counter electrode), cation deposition on the Pt electrode (forming a reduced metal layer) will quickly degrade its performance.

To overcome these problems we modified the electrochemical cell. The electrochemical cell was divided into two sections, separated by a porous membrane (**Figure 1a**). One part of the cell contains Pt electrode and is filled with electrolyte free of dopant precursor. The

second part of the cell contains Ti sheet and is filled with an electrolyte that contains dopant precursor. The porous membrane provides a barrier for two different parts of the electrochemical cell to prevent from mixing, while still allowing the flow of electrolyte. The resulting currents in this configuration are comparable to the currents in regular electrochemical cells with DC power supply, ranging in 0.1~4.0 mA within voltage range 7~200 V. For the separating membrane, we used a hydrophilic polymer filter (with a pore size in 0.1~0.4 µm range). This membrane was attached in the middle of the container using epoxy. While the membrane provides a diffusion barrier, some cations move toward Pt electrode and over time the conductivity of the dopant-free electrolyte will increase. The electrolyte should be changed if the resistivity decreases by 50%.

Using an AC voltage source, rectangular shaped power pulses were used in this present study. The shape of AC voltage and its parameters are shown in **Figure 1b**. The period of AC voltage is characterized by positive part V₁, negative part V₂, frequency f, which is equal to $f = \frac{1}{t_1 + t_2}$, where t₁ and t₂ are durations for positive and negative parts of the cycle, which control the growth and doping times, respectively. From a series of detailed experiments, it was found that the dopant level, or dopant concentration n, mostly depended on the negative bias (V₂), frequency (f), t₁/t₂ ratio, and dopant precursor amount (c) in the electrolyte. Our studies showed that the dependence of n on f and t₁/t₂ at fixed V₂ and c is convoluted, depending on a number of factors. Therefore, we studied the dependence of doping (n) on each of these parameters separately, keeping the other parameters constant. The dependence of n on V₂ (when other parameters were fixed) was more predictable. However, a strong sublinear relationship between these two parameters was observed. The dependence between n and c in the electrolyte was nearly linear. Therefore, a variation of dopant concentration was used for systematically controlling the doping level in fabricated TiO_2 nanotubes.

The electrolyte used in electrochemical growth solution consisted of solvent (glycerol or ethylene glycol) with 1% ammonium fluoride (NH₄F), and 2% of water. As the starting material commercial Ti sheets of 99.99% purity were used. The growth rate of nanotubes in ethylene glycol was ~4 µm per hour. All as-grown samples were amorphous and annealed at 500°C for 1 hour in the air, to convert to anatase phase. Three main types of cationic dopants were used in this study: niobium (Nb), iron (Fe), and copper (Cu). Among the prominent anion dopants, we used nitrogen (N), while several combinations of co-doped anion and cation co-dopants were also prepared. Niobium (V) chloride, iron (III) chloride, and copper (II) sulfate precursors were used for Nb, Fe, and Cu doping, respectively. Nitrogen doping was performed by using hexamethylenetetramine in the electrolyte. The nitrogen doping level was controlled by changing the hexamethylenetetramine amount in the electrolyte. While this method can be applied to any cation, we focused on Nb, Fe, and Cu due to their importance for a variety of applications. For example, niobium was shown to be a shallow donor for TiO₂, and therefore, a good candidate for the growth transparent conducting oxide thin films.^{67–70} Fe is a good dopant for fabricating magnetic semiconductors.^{71–73} Cu and Nb co-doped TiO₂ thin films with N have been shown to increase photocatalytic activity of TiO₂.¹⁹



Figure 2.2 Representative scanning electron microscopy (SEM) images of electrochemical anodized TiO_2 nanotube arrays. (a) Top view of densely packed nanotubes. (b) Bottom view after removing nanotubes from the Ti metal, and the side view of the vertical, hollow, doped TiO_2 nanotubes. (c), (d) Side profile at different magnifications.



Figure 2.3 SEM images of the TiO_2 nanotubes grown at different anodization voltages, showing the variation of nanotube diameters. (a), (b) 18 nm diameter nanotubes grown at 7 V, (a) shows nanotubes at an early stage of the growth when nanotubes start forming. (c~g) Nanotubes with 43 nm (grown at 15 V), 86 nm (30 V), 170 nm (60 V), 322 nm (120 V), and 550 nm (200 V) diameter, respectively. Scanning electron microscopy (SEM) analysis showed that the morphology of TiO_2 nanotubes did not change after doping and the well-defined tubular structure was observed.


Figure 2.4 X-ray powder diffraction (XRPD) and energy-dispersive spectroscopy (EDS) analysis of TiO₂ nanotubes. (a) XRPD patterns for undoped, Nb, Cu, Fe, N- doped, Nb/N and Cu/N co-doped samples. (b) XRPD patterns for undoped and Nb-doped TiO₂ nanotube samples, with variations of doping levels. Only reflection peaks corresponding to anatase TiO₂ phase were detected in all samples indicating lack of secondary phases. (c) EDS for undoped, Fe, Cu, Nb, N-doped, Nb/N, and Cu/N co-doped TiO₂ nanotubes. (d) EDS for Nb-doped TiO₂ nanotubes with different concentrations of NbCl₅ precursor (a~d: 0.1%, 0.4%, 0.8%, and 1.2%, respectively). Well-pronounced characteristic X-ray emission peaks of dopants can be seen along with TiO₂ matrix (Ti and O peaks). This data prove the presence of desired dopants in TiO₂ nanotube films. (e) Niobium doping level in atomic percentage (blue) and the resistivity (red) of Nb-doped TiO₂ nanotubes, as a function of NbCl₅ weight percentage in the electrolyte. (f) A Linear fit of the EDS experimental data (also shown in (e) for Nb-doped TiO₂ nanotubes.

Figure 2.2 presents SEM images of doped TiO₂ nanotubes fabricated using our new electrochemical cell. The electron micrographs clearly show that the tubular structure of these TiO₂ nanotubes is well preserved after doping. **Figure 2.3** shows SEM images of different diameter nanotubes grown at different anodization voltages. XRPD patterns for all doped samples shown in **Figure 2.4a** presents X-ray diffraction peaks corresponding to anatase phase, with predominant peaks (101) and (200) at $2\theta = 25.3^{\circ}$ and at 47.95°, respectively.⁷⁴ The XRPD pattern of samples does not change even with heavy doping level up to 12%,

demonstrating uniform incorporation of dopants and absence of secondary phases. At such high doping levels (> 9%), they can also be regarded as solid solutions. As an illustration in Figure 2.4b, we show XRPD patterns for Nb-doped TiO₂ nanotubes with doping level up to 12%, which shows only reflection peaks corresponding to anatase TiO_2 without any detectable secondary phase. No shift of diffraction peaks was observed with the increase of niobium doping level up to 12%. This result could be explained by close ionic radii of Ti⁴⁺ and Nb⁵⁺, which are 0.605 Å and 0.64 Å, respectively.⁷⁵ For such similar lattice parameters, no significant distortion of crystal lattice was expected. Energy dispersive X-ray spectroscopy (EDS) confirmed the presence of element dopants in TiO_2 nanotubes as shown in Figure 2.4c. EDS analysis of undoped TiO₂ nanotubes showed no detectable emission peaks from impurities (only Ti and O emission peaks were seen). This indicates the impurity concentration was below the detection limit (<0.01%). The amount of incorporated dopants in TiO₂ nanotubes follows a linear relationship with the concentration of the precursor in the electrolyte. To demonstrate this, we show EDS spectra for Nb-doped samples fabricated with different NbCl₅ concentration (wt% in electrolyte) (Figure 2.4d), from which a nearly linear relationship between detected EDS niobium signal in TiO₂ nanotubes and wt% NbCl₅ precursor is clearly seen (Figure 2.4e), with an R^2 value of the linear fit (Figure 2.4f) calculated to be 0.995. Similar studies for other dopants (Nb, Fe, Cu, N) also showed a linear relationship between incorporated dopant and dopant concentration in the electrolyte. The conductivity of Nb-doped TiO₂ nanotubes increases (resistivity decreases) with wt% NbCl₅ precursor (Figure 2.4e), confirming incorporation of Nb into TiO₂ crystal. Nb is a well-known shallow donor in TiO₂ used for creation transparent conducting thin films.^{76,77}

EDS point scans taken from different points on individual doped TiO_2 nanotubes (or mapping the elemental distribution over a large area) for all doped nanotubes confirmed uniform doping instead of forming clusters or secondary phase oxides.

Due to a significant decrease of resistivity in high (>9%) Nb-doped TiO_2 nanotubes and their high transparency characters, Nb-doped TiO_2 nanotubes are promising in device applications as transparent conducting oxide materials. In the following section, such properties are discussed in detail.

Nb-doped TiO₂ nanotubes as transparent conducting oxide (TCO) materials

TCOs combine electrical conductivity and optical transparency that plays an important role in modern optoelectronic applications.^{78,79} Moreover, the high chemical stability of oxides, ability to functionalize the surface easily, large surface areas for hollow nanotubes, and optimal alignment of energy states for charge extraction, makes TCO nanotubes an excellent platform for nanostructured light absorption/emission and catalytic applications. Nb-doped TiO₂ nanotubes with high charge carrier concentrations, large conductivity, high transmittance and good field-emission properties can be used as a novel TCO material.



Figure 2.5 Scanning tunneling spectroscopy (STS) and current-sensing atomic force microscopy (CSAFM) of TiO₂ nanotubes. (a) STS for undoped (black) and Nb-doped (10.6%) TCO (red) nanotubes, with Fermi level (orange dash line) indicated. (b) Schematic of the CSAFM measurements, which allows electrical contact with single hollow nanotubes for characterizing individual nanotube electronic properties. (c), (d) Current-voltage (I~V) characteristics (red) and corresponding ln(I)~V plots (blue), for undoped and 10.6% Nb-doped TiO₂ nanotubes.

Shallow electron dopant niobium was used for anatase TiO_2 due to its low ionization energy (4~30 meV),^{67,76,77,80,81} high solubility,⁸⁰ and similar ionic radius (Nb⁵⁺ and Ti⁴⁺).⁷⁵ Niobium acts as a substitutional dopant for Ti and donates excess electron to the conduction band, forming strong hybridized 4d orbitals with the 3d orbitals of Ti.⁸² Density of states (DOS) measured by scanning tunneling spectroscopy (**Figure 2.5a**) revealed the formation of new uniform shallow DOS near the conduction bandedge upon niobium doping, and no additional states deep inside the bandgap show that niobium is likely a shallow donor. Electronic properties of single TCO nanotube were studied using current-sensing atomic force microscopy (CSAFM). As illustrated in **Figure 2.5b**, two-probe I~V characterization was conducted by using a sharp conductive (gold-coated) AFM tip and the open area of titanium sheets as two electrodes. The resistivity ($\rho = \frac{RS}{L} = \frac{S}{L} \times \frac{dV}{dt}$, where L is the length of nanotubes and S is the contact area of the tip) is calculated from the I~V curve (**Figure 2.5c**, **d**) and reveals a decrease of resistivity (**Figure 2.4e**, **red**) with increasing niobium amount, from $6 \times 10^{-1}\Omega \cdot cm$ (undoped) to $6.5 \times 10^{-4}\Omega \cdot cm$ (10.6% Nb-doped). This increase of conductivity is mainly due to the n-type doping character of niobium, which increases significantly the charge carrier (electron) density. To further characterize the carrier concentration, we used the ln(I)~V relationship in the intermediate bias regime, where reverse-biased Schottky barrier dominates the total current:⁸³

$$\ln(I) = \ln(S) + e\left(\frac{1}{kT} - \frac{1}{E_0}\right)V + \ln(J_S),$$

where J_s (a function of applied bias) is the current density through the Schottky barrier, S is the contact area associated with this barrier, E₀ is a carrier concentration (n)-dependent parameter and can be calculated as $E_0 = E_{00} \operatorname{coth}(E_{00}/kT)$ and $E_{00} = (\hbar e/2)(n/m^*\varepsilon)^{1/2}$. $\varepsilon = 31\varepsilon_0$ and $m^* = m_e$ are the dielectric constant and electron effective mass of TiO₂, respectively. e, k, and \hbar are the electron charge, Boltzmann's constant and the reduced Planck's constant, respectively. From the slope of ln(I)~V, the parameter E₀ and then the charge carrier density n can be obtained. As expected, significant increase of carrier concentration was observed in Nb-doped nanotubes, with a value of $3.4 \times 10^{21} \, cm^{-3}$ shown in 10.6% Nb-doped sample. Compared to the doping amount, this carrier density indicates an about 90% of the niobium is electronically active and contribute an additional charge carrier to the electronic states of TCO nanotubes.



Figure 2.6 Temperature-dependent I~V characteristics of 10.6% Nb-doped TCO nanotubes. (a) Richardson plot $(\ln(I/T^2)$ vs. 1/kT) obtained from temperature dependent current-voltage (I~V~T) characteristics. The inset shows the high-temperature region of the Richardson plot, where thermionic emission was dominant, from where an activation energy of 12 meV was obtained. (b) Conductance (I/V) vs. 1/kT for the same nanotubes. The slope gives an activation energy of 18 meV. (c) Activation energy (calculated from Richardson plot) vs. applied bias. Constant activation energy with voltage indicates no bias induced ionization or hopping was observed in these nanotubes.

Temperature-dependent I~V characteristics were used to understand the niobium ionization in the TCO nanotubes. An ionization energy of 12 meV (high energy region) for niobium was obtained from the Richardson plot $(\ln(I/T^2) \text{ vs. } 1/\text{kT}, \text{ Figure 2.6a})$. Similar activation energy (18 meV) was also obtained from the slope of $\ln(S) \sim 1/\text{kT}$ plot (conductance S=I/V, Figure 2.6b). This activation energy is very close to the reported values of niobium donors in TiO₂ (4~30 meV).^{67,77,80,81} The activation energy was also found to be constant with applied bias (from Richardson plot, Figure 2.6c), which rules out ionization due to the application of bias (or hopping of charges between niobium centers). Therefore, the low activation energy and clear evidence of uniform niobium incorporation (lack of phase segregation or secondary phases) can explain the high charge carrier density in these TCO nanotubes.



Figure 2.7 Temperature-dependent electron transport characteristics and optical transparency of Nb-doped nanotubes. Variation of (a) resistivity (black for 10.6% and red for 1.3% Nb-doped sample) and (b) carrier density (blue) and mobility (cyan) with temperature. (c) The transmittance of 10.6% Nb-doped TCO nanotubes, showing above 90% transmittance in the visible range.

Variation of ensemble TCO nanotubes resistivity with temperature (20~300 K) was used to understand their charge transport behavior. In low Nb-doped (1.3%) TCO nanotubes a monotonically decreasing of resistivity with temperature (Figure 2.7a) was observed, showing typical semiconductor transport behavior. On the other hand, in high Nb-doped (10.6%) TCO nanotubes, an opposite trend $(d\rho/dT > 0)$ showing "metal-like" behavior (or metallic conductivity) were seen. This switch from semiconductor to metallic conduction indicates that charge transport in heavily-doped samples is limited mainly by electron-phonon or electron-electron scattering, which decreases at low temperatures leading to a decrease in TCO resistivity.^{69,76} At high temperatures (100~300 K), the "metal-like" linear $\rho \sim T$ dependence ($\rho = \rho_0 (1 + \alpha \Delta T)$, where $\rho_0 \sim 1.76 \times 10^{-5} \Omega \cdot cm$ is the residual resistivity, $\alpha = 0.115 K^{-1}$ is the temperature coefficient, and ΔT is the temperature difference) is observed. The carrier concentration (n) only weakly depends on temperature (Figure 2.7b). Carrier mobility ($\mu = 1/(ne\rho)$) of highly doped samples (10.6%) increases by a factor 3.5 within the same temperature range (from 2.9 cm² V⁻¹s⁻¹ at 300 K to 10.3 cm² V⁻¹s⁻¹ at 20 K, Figure 2.7b). This behavior is typical of semiconductor transport, whereas lower conduction

electron scattering in heavily-doped TCO nanotubes causes the switch to metallic conductivity.

Besides their superior electrical properties, TCO materials are also desirable for their light transmission. Optical transparency of Nb-doped nanotubes was evaluated using reflectivity measurements and the transmittance η can be calculated as:

$$\eta = \left(1 - \frac{R_b - R_d}{R_s - R_d}\right) \times 100\%,$$

where R_b, R_s, and R_d refer to signals from blank Ti sheet, sample, and the background. As shown in **Figure 2.7c**, above 90% transparency with coverage of most of the visible wavelengths was seen, which is comparable to the commercially available ITO thin films. While nanotube films in this work were grown on non-transparent opaque titanium sheet, the grown nanotubes can be easily detached from Ti sheet and transferred onto transparent substrates as was shown in previous studies.^{84–86} In addition, using a titanium-coated (through sputtering, etc) transparent substrate (e.g. glass) as a replacement for nanotube growth, completely transparent samples can be obtained.^{87,88}



Figure 2.8 Field emission (IV) characteristics and corresponding Fowler–Nordheim plot (inset) of TCO nanotubes: undoped (green), 1.3% (blue) and 10.6% (red) Nb-doped nanotubes.

Field emission properties were evaluated due to high chemical stability and excellent charge transport of these TCO nanotubes. Measurements were performed in a high vacuum chamber (base pressure: 6.6×10^{-5} Pa) with a voltage range of 0~1000 V applied to a copper grid placed at a distance 150 μ m from the TCO nanotube surface.^{89,90} A significant increase of field emission current (**Figure 2.8**) was observed from undoped samples (green), to low (1.3%, blue) and high (10.6%, red) Nb-doped nanotubes. Corresponding Fowler–Nordheim plots (ln(I/E²) vs. 1/E) reveals almost linear behavior indicating predominant field emission current (22 mA)

observed in 10.6% Nb-doped nanotubes is due to decrease in field emission threshold and increase in electron carrier density and can be improved further by optimization of nanotube density (due to reduction of electric field screening effects).⁹⁰

Recently several groups have tried fabricating Nb-doped TiO₂ nanotubes using fluoroniobate anion⁹¹ during the anodization process, which simultaneously provides a niobium source for doping and fluoride anions required for nanotube formation. While the negatively charged fluoroniobate complex allows insertion of niobium in the TiO₂ nanotube structure (positive bias), this method requires synthesis of negatively charged complexes soluble in the electrolyte. This limits the flexibility of incorporating desired dopants due to the availability of soluble complex anions. Furthermore, since the metal to fluoride ratio is fixed, there is lack of simultaneous control of dopant precursor and fluoride, hence the lack of simultaneous the doping amount and the nanotube size. In contrast, our method works both with positively and negatively charged ions, and therefore is more easily applicable for formation of different TCO nanotubes. Moreover, anodizing metallic Ti-Nb allovs⁹² allows niobium doping up to 0.5%, which is far lower than the 10% doping for TCO applications. And the requirement of preparing metal-alloy sheets with different metal ratios to obtain TiO₂ nanotubes with variations of dopants is also another disadvantage compared to the facile incorporation of dopant metal precursor incorporation demonstrated here.

In conclusion, we presented a new method for nanotube doping during electrochemical anodization using alternating current that was enabled by a new electrochemical cell design. A variety of optical, electronic and magnetic dopants were successfully incorporated into the hollow nanotubes. Detailed investigations shown here prove that this versatile method is applicable for tailoring the dopant (cationic, anionic, mono and co-doping) and the doping level (from low doping to highly-doped semiconductors) over a wide range of materials and physical properties (semiconductor to metal-like transition). These results can have important implications for the development of new devices and device architectures for applications in the broad field of optoelectronics, catalysis, display technologies, and power electronics. As an example, we demonstrate the TCO nanotubes by doping TiO₂ nanotubes with shallow niobium donors. Nanotubes doped with 10.6% Nb shows metal-like behavior with significantly low resistivity ($6.5 \times 10^{-4} \Omega$ cm at T = 300 K) and light transmittance up to 90% within 400~1000 nm wavelength range. Niobium doping also improves the field emission properties of TCO nanotubes (reduction of field emission threshold and increase in emitter current). These results can have important consequences for fabrication of porous hollow TCO nanotubes membranes and have applications in nanostructured photovoltaics, photodetector, photoelectrochemical and photocatalytic devices.

Experimental

SEM, EDS and XRPD characterization of TiO₂ nanotubes

The morphology of grown TiO₂ nanotubes was examined in field-emission scanning electron microscope (FESEM) JEOL 7401F. Compositional analysis was performed by energy dispersive X-ray spectroscopy (EDS) embedded in FESEM JEOL 7401F instrument. The analysis was performed in different modes (2D mapping, point scan, etc.) to test for uniformity and possible secondary phases. The spatial resolution during EDS was limited by the focused spot size of the electron beam, which was ~10 nm. The crystal structure of doped

and undoped TiO_2 nanotube samples was analyzed by X-ray diffraction (XRPD) measurements, using a Scintag XDS 2000 X-ray diffractometer. The measurements were performed using Cu K α radiation at 45 kV and 40 mA.

Electrical characterization

I~V and I~V~T characterization were performed in two different ways: (1) single nanotube measurements using CSAFM; and (2) ensemble measurements using a Keithley source meter (Keithley 2612A, Tektronix Inc.). Temperature-dependent current-voltage characterization (I-V-T) was performed in a range of 20~300 K with 10 K steps, using our closed loop helium cryostat (ARS-202AE with ARS-2HW helium compressor, Advanced Research Systems Inc.). The voltage for these measurements varied from -20V to +20V. The sheet resistance of nanotubes R was calculated from I~V measurements using Ohm's law $I = \frac{V}{R}$, from where resistivity ρ was calculated ($R = \rho \frac{L}{A}$, where L is the nanotube length, and A is the total nanotube cross-section area estimated using the density of nanotubes, the thickness of nanotube wall, inner and outer diameters of nanotube measured from SEM images).

CSAFM measurements

CSAFM measurements were performed using modified Molecular Imaging PicoSPM II setup. The CSAFM tips used were coated in-house using thermal evaporator with 5nm of 99.99% Cr and 15 nm of 99.99% Au, both purchased from Kurt J. Lesker Company. The silicon tips for contact mode imaging and spectroscopy were obtained from NanoDevices Inc. Contact force was set to soft contact (deflection set point between -1 and -3 V). Multiple current scans were taken at different bias voltage ranging from -5 to +5 V with steps of 50 mV. The measurements were performed by contacting the top of vertically aligned TiO_2 nanotubes and the open area of Ti sheet as the second contact to form a complete circuit. **Figure 2.4b** illustrates the experimental configuration used for the CSAFM measurements. Alignment of the laser beam was done via the movement of the horizontal/vertical knobs to obtain the diffraction pattern from the gold-coated cantilever.

STM and STS measurements

Scanning Tunneling Microscope images were obtained using a customized Molecular Imaging PicoScan 2500 setup with PicoSPM II controller and an STM nosecone (N9533A series, Agilent Technologies). Chemically etched Pt-Ir tips (90:10) (Agilent Technologies) were used for imaging and taking spectroscopy at room temperature and atmospheric conditions. Images were taken with pre-amp sensitivity set to 1nA/v. Tunneling spectroscopy was obtained with varied bias range from -5 to 5 V applied to the tip with at a scan rate of 1V/s. For STM measurements, the pre-amp sensitivity set to 1nA/V. TiO₂ nanotubes were scratched from titanium substrate and dispersed in ethanol. A thin layer of TiO₂ nanotubes was formed on clean ITO coated glass (washed with acetone, ethanol, and water) by drop casting. The sample placed on a transparent ITO substrate was connected using a wire attached to the ITO glass using conductive silver paste.

Abbreviations	
AC	Alternate current
CSAFM	Current-sensing atomic force microscopy
DC	Direct current
DEG	Diethylene glycol
DMF	N, N-dimethyl formamide

DMSO	Dimethyl sulfoxide
DOS	Density of states
EDS	Energy-dispersive spectroscopy
EG	Ethylene glycol
FA	Formamide
FESEM	Field-emission scanning electron microscopy
ITO	Indium tin oxide
NMF	N-methyl formamide
SEM	Scanning electron microscopy
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
TCO	Transparent conducting oxide
XRPD	X-ray powder diffraction

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Chapter 3

Photocatalytic and Photoelectrochemical solar-to-fuel conversion with standalone anion- and co-doped titanium dioxide nanotubes

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Sun is the primary source of energy on earth, and generation of required chemical fuels from sunlight and abundantly available chemical feedstocks can provide a sustainable source of renewable energy. Several strategies are currently being investigated for generating fuels from the sun, including photocatalysis and photoelectrochemical reduction of water and carbon-dioxide. Nanostructured titanium dioxide (TiO₂) has generated a lot of interest for these solar-to-fuel conversion (STFC) applications due to their unique optical and electronic properties, chemical stability, and large surface area.^{1–13} Hollow nanotubes provide additional advantages over TiO₂ nanoparticles in STFC performance⁸⁻¹⁰ due to the realization of photon capture and charge transport in orthogonal directions, which simultaneously improve light absorption and charge separation. However, large bandgap (~3.2 eV), defects or surface states, poor water oxidation kinetics (high oxygen evolution overpotential) are important factors limiting the total STFC efficiency. Though efforts like morphology tuning, elemental doping, and surface modification have been proposed to improve their efficiency,^{9–13} lack of insight into detailed mechanism and kinetics of photogenerated charge carriers following light absorption, has impeded further progress. Here, we describe fabrication of undoped, anion-doped (nitrogen (N), carbon (C)) and co-doped (nitrogen/copper) standalone TiO₂ nanotubes membranes, and their detailed optical, electronic, voltammetry and impedance study to understand the effect of elemental doping on light absorption, charge transport, and charge transfer process. We also provide a detailed model to describe the photodynamics of charge carriers generated following light absorption and propose ways to better utilize these membranes for efficient STFC. Using both wireless (photocatalytic hydrogen evolution and methylene blue degradation measurements) and wired (photoelectrochemical cell) devices,

we evaluated the STFC efficiency of these nanotubes from different photochemical and photophysical effects. These results can help us understand the solar to fuel conversion process in these nanotubes and pave the way for designing optimal solar to fuel conversion devices.

Titanium dioxide nanotubes were fabricated using electrochemical anodization technique (Figure 3.1a, c).^{8,9,12,14} The applied voltage, solvent type, contents of water and etchant, growing time are crucial parameters controlling the diameter, length, wall thickness, density of these nanotubes. This method has also been used in making other nanotubular metal-oxide nanostructures.⁹ We recently reported a modified electrochemical cell for growing doped TiO₂ nanotubes by combining the electrochemical anodization with electrophoretic effect, which allows the dopant incorporation simultaneously with nanotube growth.¹² Doping precursors in the electrolyte are driven by the electric field and incorporated in the pores of the nanotubes, followed by heat treatment at high temperature to obtain elemental doping. Anion-doping is achieved by precursor addition, and cation-doping or co-doping utilizes a growing and doping method where polarity switching using alternate current is utilized to drive the positive-charged cations into the nanotubes. Doping levels are controlled by the precursor amount in the electrolyte, varying the alternating current waveform and a number of other modifications (Figure 3.1c, d, e). Dopants create states in the electronic bandgap of TiO₂ nanotubes, which help shift their absorption to higher wavelengths and improve absorption of incident sunlight.^{6,13,14} As shown in delaminated standalone TiO_2 nanotube thin films (Figure 3.1a), we were able to

incorporate different dopants (with controllable amount) to tune the thin film absorption from transparent (undoped) to translucent (N-doped) or opaque (Cu/N-doped and C-doped) membranes. In a typical electrochemical cell, titanium metal sheet and platinated metal mesh were used as anode and cathode. Ethylene glycol (EG) electrolyte with 1% wt. NH₄F (etchant) and 5% wt. water was used to relatively longer nanotube growth. То make doped nanotubes, ensure hexamethylenetetramine and L-ascorbic acid were added as nitrogen and carbon precursors, respectively. After 3 hours growing under applied 30 V DC voltage, these nanotubes were carefully washed and annealed to improve their crystallinity and decompose the precursors. TiO₂ nanotubes with $\sim 3 \mu m$ length, 80 nm diameter and 5 nm wall thickness (Figure 3.1c, 3.7) were grown using the described parameters. These nanotubes show anatase phases, verified using the X-ray diffraction peaks, and the morphology and phases are not changed with doping.^{12,14} Energy-dispersive X-Ray spectroscopy (EDS) reveals about 6% and 2% for nitrogen and carbon dopants (Figure 3.1d, e) in the two samples, each with 5% wt. precursors. The relatively low doping-level for carbon-doped sample is mainly due to the mismatch of atomic radius¹⁵ between carbon and oxygen (C: 77 pm, O: 73 pm) and partial oxidation of carbon to form CO₂ in ambient atmosphere. The similar atomic radius (N: 74 pm) between nitrogen and oxygen ensures a higher dopant corporation in nitrogen-doped nanotubes.



Figure 3.1 (a) Undoped/doped TiO₂ NTs thin films delaminated from the titanium metal substrates, showing transparent (undoped), translucent (N-doped) and opaque (Cu/N-codoped and C-doped) characters. (b) Photocatalytic water splitting schematics showing the water, solar energy in, fuels out configuration using TiO₂ nanotube stand-alone membrane. (c) Field-emission scanning electron microscopy (FESEM) image of undoped TiO₂ nanotubes, showing a diameter of 80 nm and a wall thickness of 5 nm. (d) Electron-dispersive spectroscopy (EDS) showing the atomic percentage of the carbon-doped TiO₂ nanotubes. (e) The Atomic percentage of elements detected by EDS for doped TiO₂ nanotubes. (f) Ultraviolet-visible (UV-VIS) spectrum of stand-alone undoped/doped TiO₂ nanotube thin films. (g) Current-sensing atomic force microscopy (CSAFM) measurements on undoped TiO₂ nanotubes, showing I~V and ln(I)~V behavior with calculated carrier density (n) and mobility (μ).

To facilitate rational design of high-performance photocatalysts for STFC and provide better insights in to the STFC process in these doped nanotube membranes, we decoupled the entire STFC process into three main events:^{6,16} photon absorption by the semiconductor photocatalysts, transport of light-induced charge carriers to the photocatalyst surface, and the injection of surface carriers to the molecules (semiconductor-electrolyte interfacial charge transfer).

$$\eta_{STFC} = \eta_{abs} \times \eta_{transport} \times \eta_{transfer}$$

Here, we focused on anion-doped nanotubes, since the incorporation of copper revealed a significant drop of STFC efficiency compared to undoped nanotubes (Figure 3.8), as seen in the significant decrease of photocurrent generation and the quantum yield of methylene blue degradation. We utilized a series of optical, electrical, and electrochemical characterization techniques to decouple the effects of doping on these three processes. Optical absorption determines the number or fraction of photons in the incident sunlight that can be absorbed and utilized for STFC by these nanotubes. The absorption efficiency is reflected in the bandgap and absorption coefficient of these materials. TiO₂ is a wide-bandgap semiconductor with a bandgap around 3.2 eV (anatase) or 3.0 eV (rutile),⁹ which limits its utilization of solar spectrum only in the ultra-violet range (~4%). Low absorption coefficient due to its indirect band character results in inefficient photon capture, which is mitigated by using longer nanotubes. Dopants create internal (donor or acceptor) states inside the band gap of TiO₂,^{7,13,17} resulting in the bandedge shrinking and enhanced light absorption in these doped nanotubes. As shown in the ultraviolet-visible (UV-VIS) spectra (Figure 3.1f), the bandgap of nanotubes changes from 3.10 eV to 2.93 and 2.49 eV for nitrogen and carbon-doped samples (Table 3.1, row 1), respectively. Electronic bandgap extracted from scanning tunneling spectroscopy (STS) also revealed (Figure 3.9) a decrease of energy bandgap for doped nanotubes (Table 3.1, row 2). A slightly higher electronic

bandgap value demonstrates the existence of exciton-like traps,¹⁸ likely arising from oxygen vacancies observed in these nanotubes,¹⁴ which might be the reason for relatively low carrier mobility in these nanotubes. Furthermore, bandedge tilting and interband peaks shown in the density of states (DOS) plot for doped nanotubes is another proof of the presence of dopant states inside the nominal TiO₂ bandgap. To evaluate the participation of these states in the STFC processes, we conducted further photoelectrochemical and photophysical studies.

Sample	Method	Undoped	N-doped	C-doped		
E _{op} (eV)	UV-VIS	3.10	2.93	2.49		
E _{el} (eV)	STS	3.23	3.04	2.79		
$n (cm^{-3})$	CSAFM	2.08×10^{18}	4.41×10^{18}	3.32×10^{18}		
$\mu (cm^2/V \cdot s)$		0.135	0.116	0.018		

Table 3.1 Parameters obtained from series of optical and electronic characterizations

The photon-induced electron-hole pairs need to be transported (though electric field-assisted drift or chemical potential-assisted diffusion) to the surface of the nanotubes and utilized for formation of chemical fuels. During this process, these free photogenerated charge carriers can be trapped by defect states, or even recombine. Charge carrier density and charge mobility are key parameters to evaluate the charge transport efficiency in these nanotubes. We used current sensing atomic force microscopy (CSAFM) (**Figure 3.1g, 3.10**) to study the transport of photogenerated and electrically injected charges, through single nanotubes.¹² This technique provided us insights into individual nanotube properties beyond the conventional two- or four-probe electronic characterization since it reveals potential variation in intrinsic

material characteristics, instead of ensemble device performance. Conductivity and carrier density derived from the slope of I~V and ln(I)~V relation in the intermediate-biased region were used to obtain carrier mobility of these nanotubes.¹⁹ The doped nanotubes showed improved conductivity due to increase in their carrier density (**Table 3.1, row 3**), which is contributed by the release of free carriers from the dopant levels. However, a small decrease of carrier mobility (**Table 3.1, row 4**) was observed in doped nanotubes, which can be caused by carrier trapping in the interband/surface states or smaller mobility of holes (compared with electrons) generated by the anion dopants.



Figure 3.2 Voltammetric characterization of TiO_2 nanotubes. (a) Linear sweep voltammetry (LSV) measurement on undoped/doped TiO_2 nanotubes in a three-electrode configuration, showing their current-voltage (J~V) behavior in dark (D)

and AM 1.5 (1 SUN) irradiation (L). (b) Three-electrode chronoamperometry (CA) with 0.5 V bias vs. Ag/AgCl reference, showing both the dark and light current-time (J~t) behavior of undoped/doped TiO₂ nanotubes. (c) Incident photon-to-current efficiency (IPCE) measurement in a three-electrode configuration, with 0.5 V bias vs Ag/AgCl.

Electrochemical measurements were used to evaluate the performance of these nanotube photoanodes (wired devices) in the dark and under irradiation.^{16,20,21} The combination of voltammetry and impedance technique is an effective tool to study the charge transport and transfer process in the nanotube and the nanotube-electrolyte interface, providing detailed information to access solar energy conversion efficiency using these photocatalysts. Linear sweep voltammetry (LSV) in a three-electrode (3-e) configuration (Figure 3.2a) was used to characterize the current-voltage behavior under both dark and 1 SUN (AM1.5) conditions. Polarization current (dark) was detected only with an applied potential of over 2.2 V. Light irradiation results in the onset of photocurrent with an applied voltage above the flatband, driving electrons to the counter electrode and holes to the TiO₂ nanotube surface, showing typical photoanode behavior. Photocurrent increases with applied voltage and saturates due to full extraction of available photocarriers. Stable photocurrent measured from chronoamperometry (CA) under same bias (0.5 V vs Ag/AgCl) (Figure 3.2b) indicates the relative intensity of photocurrent generation (Table 3.2, row 1) N-doped > C-doped > Undoped TiO₂ nanotubes, which directly reflects the total efficiency for their application as photoanodes for STFC. Constant Photocurrent indicates stability of these nanotube electrodes during the measurement.

	Method	Undoped	N-doped	C-doped
J_{ph} (mA/cm ²)	CA	0.045	0.166	0.069
E _{pec} (eV)	IPCE	3.05	2.92	2.70
k_{ct} (s ⁻¹)	OCP decay	1.23×10^{-3}	2.34×10^{-3}	1.74×10^{-3}
$ au_{eff}$ (ms)		4.08	0.622	0.879
$R_{ct} (k\Omega \cdot cm^2)$	PEIS	48.3	6.01	7.95
$C_{total} (\mu F/cm^2)$		14.7	33.3	142
$n (cm^{-3})$	Mott-Schottky	3.28×10^{18}	8.65×10^{18}	4.63×10^{18}

Table 3.2 Parameters obtained from series of electrochemical characterizations.

To study the photoresponse of these nanotubes with photon energy, we performed incident photon-to-current efficiency (IPCE) measurement¹⁶ under monochromatic light irradiation (**Figure 3.2c**). IPCE under same bias (0.5V vs Ag/AgCl) reflects the relative efficiency of these nanotube photoanodes. From the onset of IPCE, we clearly observed the bandedge shrinking in doped samples, especially for the carbon-doped sample. Optical bandgap and electrochemical bandgap (**Table 3.2, row 2**) match for undoped and nitrogen-doped nanotubes, with a 0.2 eV difference in carbon-doped photoanode. Interestingly, higher energy photons do not increase the IPCE significantly in carbon-doped nanotubes, as seen in undoped and nitrogen-doped nanotubes. Deep traps created by carbon dopants could explain both the mismatch of bandgap and the plateau IPCE character in carbon-doped samples.

To quantify the charge transfer efficiency, we compared the charge injection rate constant through open-circuit potential (OCP) decay measurement (**Figure 3.3a**).²²

Under ultraviolet (UV) radiation, the photon-induced holes transport to the nanotube surface and final equilibrium is achieved when the rate of charge accumulation equals the rate of surface recombination and charge injection. The negative shift of OCP (**Figure 3.11**) indicates typical n-type semiconductor character

upon irradiation. The irradiation is then blocked, leading to decay of surface charges, as shown in the exponential decay character of OCP:

$$V_{OCP} = V_{dark} + \Delta V_{OCP} = V_{dark} + V_{ph} = A - Bexp(-k_{ct}t)$$

where A, B are constants (V) and k_{ct} is the charge transfer rate constant (s⁻¹).

The magnitude of charge transfer rate constant (**Table 3.2, row 3**), reveals relative ease of charge transfer of surface accumulated holes to water molecules. A significant increase of charge transfer rate constant was observed with anion doping, especially in nitrogen-doped samples. This can be explained by the decrease of water oxidation activation energy due to the dopant on the surface.



Figure 3.3 Open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) of TiO₂ nanotubes. (a) The decay of OCP with the blocking of UV irradiation, with calculated charge transfer rate constant. (b) Bode plot of undoped/doped TiO₂ nanotubes, showing the frequency-dependent phase (Arg(Z)) of complex impedance in dark condition, with calculated charge transfer effective lifetime. (c) Equivalent circuit used to fit the experimental data taken from the n-type semiconductor-electrolyte system. (d) Nyquist plot with equivalent circuit fitting of undoped/doped TiO₂ nanotubes, showing the relation between the real and imaginary part of complex impedance in dark condition, with extracted charge transfer resistance and trap capacitance. (e) Mott-Schottky plot at 1 kHz.

Electrochemical impedance spectroscopy (EIS) is an important tool to study the behavior of charge carriers under AC perturbation,^{22–28} which allows us to understand the charge transport behavior in the bulk nanotubes and charge transfer process in the

nanotube-electrolyte interface. The simplification of complex electronic process to lumped circuit elements (resistors or capacitors) enables us to determine charge transport and transfer efficiency ($\eta_{transport}, \eta_{transfer}$) with an equivalent circuit fitting.^{29–31} Bode plot (phase plot) and Nyquist plot (relation between the real part and imaginary part of complex impedance) were used in our EIS investigations. The minimum of frequency-dependent phase (**Figure 3.3b**) was related with the ease of charge transfer process by:^{25,28}

$$\tau_{eff} = \frac{1}{k_{eff}} = \frac{1}{2\pi f_{min}}$$

where $\tau_{eff}(ms)$ was the effective time that the surface holes are quenched by the water. Significant decrease of the effective time (**Table 3.2, row 4**) in doped nanotubes demonstrated that dopants facilitate the injection of surface holes, corresponding to the charge transfer rate constant obtained from OCP decay test.

An equivalent circuit (**Figure 3.3c**) for a typical n-type semiconductor-electrolyte system was used to fit the impedance data²² (**Figure 3.3d**). This equivalent circuit contains the solution resistance (R_s), the capacitance of double layer (C_{dl}), charge transfer resistance (R_{ct}), space charge capacitance and resistance (C_{sc} and R_{sc}), and the capacitance and resistance ($C_1 \sim C_3$, $R_1 \sim R_3$) contributed from traps. Here, we focused on the charge transfer resistance (R_{ct}) and the trap capacitance ($C_{trap} = C_1 + C_2 + C_3$) to evaluate dopant effect²³ in surface charge transfer and trapping, respectively. A significant decrease of charge transfer resistance (**Table 3.2, row 5**) was observed with anion doping, especially for nitrogen-doped samples. These values (Undoped >>> C-doped > N-doped) follow the trend of increasing charge transfer rate constant in

effective OCP decreasing decay measurement time extracted from or frequency-dependent phase, showing effective promotion of hole injection in doped TiO₂ nanotubes. As for charge trapping, an only small increase of trap capacitance was observed for the nitrogen-doped sample (Table 3.2, row 6), indicating a slight deterioration of its charge transport performance. However, a notable increase of trapping effect was seen in carbon-doped nanotubes, which is due to the carbon as a deep dopant. Compared to nitrogen dopant, this poor charge transport property can significantly lower its STFC efficiency, though it has much larger photon capture ability (Figure 3.4). These results also correlate with the decrease of mobility in doped nanotubes, measured from CSAFM.



Figure 3.4 A three-dimensional plot (with projection) showing relative efficiency of undoped/doped TiO_2 nanotubes in photoelectrochemical solar energy conversion, in aspects of absorption, charge transport, and transfer, using the bandgap, charge

mobility and charge lifetime as parameters, respectively. Arrows point to the desired design of high efficiency.

Mott-Schottky curve (**Figure 3.3e**) exhibits the DC potential-dependent capacitance behavior of these nanotubes. Multiple linear regions with varied slopes indicate different internal levels inside the bandgap. Carrier density (N_d) and flat band potential (E_{fb}) can be obtained from the slope and x-intercept of Mott-Schottky curve, respectively, based on the Mott-Schottky equation for n-type semiconductors:^{16,20}

$$C_{sc}^{-2} = \frac{2}{\varepsilon q N_d} (E - E_{fb} - \frac{k_B T}{q})$$

where $\varepsilon = 31\varepsilon_0$ is the dielectric constant^{12,32} of TiO₂ nanotube. An increase of charge carrier density (**Table 3.2, row 7**), following the same trend of N-doped > C-doped > Undoped measured from CSAFM was observed in these doped nanotubes (**Figure 3.4**). These changes, however, were not significant compared to the initial high carrier density in undoped TiO₂ nanotubes, caused by high density of oxygen vacancies.¹⁴ This also explained a very small shift of the flatband position.



Figure 3.5 (a) A simple model used to describe the photophysical processes, including photogeneration, charge recombination, trapping, and injection, in TiO_2 nanotubes. (b) Intensity-dependent photocurrent density generation in nitrogen-doped and (c) carbon-doped TiO_2 nanotubes at different wavelength. (d) Log-log plot of light intensity-dependent photocurrent of undoped/doped TiO_2 nanotubes measured at bandedge excitation. (e) Log-log plot of light intensity-dependent photocurrent of light intensity-dependent photocurrent of N-doped TiO_2 nanotubes excited with different energy photons.

To characterize the interplay of all these photophysical processes, we used a model (**Figure 3.5a**) to describe the photogeneration, charge recombination, trapping effect, and charge injection in these TiO_2 nanotubes.⁷ The photogenerated electron-hole pairs can be quenched through conduction band-valence band

recombination, electron trap-assisted recombination, conduction band-dopant state recombination, or injection into water molecules. These charge carriers are generated directly from conduction band-valence band, and dopant state-conduction band excitation, or relax from the valence band to these dopant states for anion doping. In steady state, using the charge balance and charge neutrality relation, we can derive the following equations:

$$\frac{dp}{dt} = g_b - \alpha pn - \beta pn_t - r_d p - r \times p$$
$$\frac{dp_d}{dt} = g_d - \gamma p_d n - \delta p_d n_t + r_d p - r \times p_d$$
$$\frac{dn}{dt} = (g_b + g_d) - r_t n \left(1 - \frac{n_t}{N}\right) + r_{dt} n_t - \alpha pn - \gamma p_d n - R$$
$$n + n_t = p + p_d$$

$$R = r \times p + r_d \times p_d$$

where n is electron density in conduction band, p and p_d is the hole density in valence band and dopant states; n_t and N are trapped electrons and total number of trap states available; r_t and r_{dt} are trapping and detrapping rate between conduction band and electron trap states; α and γ are the rate constant for conduction band-valence band and conduction band-dopant state recombination; β and δ the rate constant for trap-assisted recombination for valence band and dopant state; g_b and g_d is the photogeneration rate for conduction band-valence band (UV excitation) and conduction band-dopant state (visible excitation); R is the photocatalysis rate, r and r' are corresponding rate constant for hole and electron injection. Observed photocurrent is linearly proportional to the rate of photocatalysis (R). For ultraviolet STFC process, $g = g_b$ and $g_d = 0$. Since $r_d p$ is smaller than the rest of processes, $p_d \approx 0$. For visible light photoexcitation, $g = g_d$ and p = 0.

From the above equations, we derived a relationship between the rate of photocatalysis and the rate of photogeneration. For visible light STFC, we derived:

$$g = \gamma p_d (p_d - n_t) + \delta p_d n_t + r \times p_d$$
$$r_t (p_d - n_t) \left(1 - \frac{n_t}{N}\right) = r_{dt} (p_d - n_t) + \delta p_d n_t$$

We identified two major regimes for doped TiO₂ STFC rates:

Unimolecular recombination (mainly for ultraviolet photoexcitation), where $\gamma, \alpha \ll \beta, \delta$ and $p_d, p \gg n_t$ resulting in $g \propto p, p_d$ linear slope $R \propto g$. Trapping-dominant recombination for visible light STFC, where N is large, therefore $n_t \propto p_d^{-x}$ (using second equation) and $g \propto p_d^{(1-x)}$, where x is between 0 and 1. This results in superlinear slope $R \propto g^{1/(1-x)}$, which depends on the trapping rate and recombination rate.

Bimolecular recombination, where $\gamma \gg \delta$ or $\alpha \gg \beta$; and $n, p, p_d \gg n_t$ can result in square root dependence between STFC rate with incident light intensity $R \propto g^{0.5}$. However, it is not observed in most STFC processes with TiO₂ due to the large recombination rate between trapped electrons and holes (β, δ), and strong density of electron traps (oxygen vacancies) present in these metal-oxide nanostructures.

To test the relationship between the photocurrent generation and the input photon flux, intensity-dependent photocurrent measurement was taken, using the same setup as for IPCE measurement. We observed an interesting trend in both nitrogen and carbon-doped TiO₂ nanotubes (**Figure 3.5b, c**). With the increase of photon energy, the intensity-dependent photocurrent showed a transition from superlinear to linear (**Figure 3.5d**), pointing to change in mechanism from the trap-dominant recombination, to unimolecular recombination between trapped electrons (large number of trapped electrons due to excitation to higher energy electron states and lower activation energy for electron trapping) and photogenerated holes in valence band. To compare the trapping effects in different nanotubes for bandedge excitation, we tested the STFC vs photon fluence relationship (**Figure 3.5e**) for these nanotubes. A slope of Undoped < N-doped < C-doped reflects the increasing trend of trapping effect in these samples, which matches well with the EIS and CSAFM measurements.

Apart from a photoelectrochemical assessment using undoped/doped TiO₂ nanotube photoanodes, photocatalytic methylene blue (MB) degradation technique^{33,34} was used to evaluate these nanotubes as stand-alone photocatalysts. This measurement was based on the oxidation of methylene blue by the photogenerated holes, which has been widely used for photodegradation of organic waste in water purification. From the absorption decrease (**Figure 3.12**), stoichiometry relation between MB and the holes, and the flux of photons, quantum yield of the photocatalysts was estimated. This process follows the first order reaction character (**Figure 3.6a**), and an increase of quantum yield was shown in doped nanotubes (**Figure 3.6b**), especially for the nitrogen-doped sample. Due to the fast charge transfer between the photogenerated holes and methylene blue molecules, we only observe a small increase of quantum
yield in the carbon-doped sample. With carbon doping, the benefit of higher photon capture ability is decreased by the poor charge transport and carrier trapping.



Figure 3.6 Photocatalytic methylene blue degradation and hydrogen generation with TiO_2 nanotubes. (a) First-order reaction plot (ln(Abs)~t) and (b) Calculated quantum yield of methylene blue (MB) degradation using TiO₂ nanotubes under UV irradiation. (c) Hydrogen generation amount with time under AM 1.5 (1 SUN) irradiation and (d) calculated hydrogen generation rate from photocatalytic hydrogen evolution measurements using stand-alone undoped/doped TiO₂ nanotubes powders, with 1% wt. photodeposited platinum nanoparticles and 50% (vol) methanol hole sacrificial agent to enhance the efficiency. Undoped TiO₂ nanotubes without platinum deposition and platinum-deposited commercial P25 TiO₂ nanoparticles were used as a comparison. The bar lines in (b) and (d) represent error bar for our measurements.

To test the STFC capability of these nanotubes, we used the photocatalytic hydrogen evolution reaction (HER) from these photocatalysts, using the hydrogen generation rate to evaluate their total solar energy to fuel conversion efficiency as standalone photocatalysts. Due to the large overpotential for hydrogen generation, HER co-catalysts (e.g. platinum) were normally deposited for hydrogen generation. Simultaneously, sacrificial agents (e.g. methanol) were used to facilitate the hole quenching. In these tests, platinum nanoparticles were deposited through a photochemical process.⁷ Commercial P25 TiO₂ nanoparticles with deposited platinum and undoped TiO₂ nanotube without platinum co-catalyst were used for comparison. A remarkable increase (more than 2 fold) of hydrogen generation rate (Figure 3.6c, d) was seen in doped nanotube photocatalysts and the trend N-doped > C-doped > Undoped matched well with the photoelectrochemical and methylene blue degradation measurements. The generation of hydrogen is stable for several hours during our measurements. After screening several anion- and co-doped TiO₂ membranes, we obtained the highest quantum yield for N-doped samples, along with stable generation of STFC product. Furthermore, a 30% higher efficiency than the commercial P25 TiO₂ nanoparticles demonstrates the advantage of using light absorption and charge carrier transport in orthogonal directions, in these one-dimensional nanotubes. In conclusion, we have synthesized and studied a series of undoped, anion doped (N, C) and co-doped TiO₂ nanotubes with a modified electrochemical anodization technique. We tested these nanotubes via a series of wired and standalone photoanode catalysts. Photoelectrochemical measurements, methylene blue degradation, and photocatalytic hydrogen evolution test consistently showed STFC trend N-doped > C-doped > Undoped TiO₂ nanotubes. To better understand dopant effects in light absorption, charge transport, and charge transfer, detailed optical, electric, electrochemical study were used. In general, dopants increase light absorption through the excitation of internal dopant states, the magnitude of which depends on the bandgap shrinkage. However, some dopants (especially deep dopants like carbon here), deteriorated the charge transport. While the lower bandgap and higher photon capture ability allowed them to significantly enhance the visible light to fuel conversion efficiency, irradiation with higher energy photons led to saturation of this efficiency and poor utilization of incident light energy for formation of solar fuels. On the other hand, dopants also increased the charge transfer rate, possibly through the decrease of activation energy required for water oxidation. Using several anion- and co-doped TiO₂ nanotube membranes, our results show highest quantum yield for photocatalytic and photoelectrochemical reactions with nitrogen-doped standalone TiO₂ membranes, and stable STFC using hydrogen evolution. Furthermore, we developed a detailed photophysical and photoelectrochemical model to explain the detailed kinetics of charge carriers formed using solar irradiation. We showed that while visible light STFC induces superlinear photoresponse in these doped TiO₂ standalone membranes and may benefit from higher light intensity or solar concentrators, ultraviolet light shows linear photoresponse using AM 1.5 irradiation and shows saturation of solar fuel production at higher photon flux due to charge trapping. The realization of optimal solar energy conversion requires optimization of each process, including using the dopants to help improve the light capture and charge transfer, with simultaneous improvement of charge transport. Therefore, this study can have important

implications for improving the efficiency of solar energy conversion by designing optimal STFC devices.

Experimental

Materials

Titanium foil (99.6%, 0.25 mm thickness), ammonium fluoride (>98%), L-ascorbic acid (99%), and hexamethylenetetramine (>99%) was purchased from Sigma-Aldrich, sodium sulfate anhydrous (>99%) was purchased from Fisher Scientific, the platinum-coated electrode was purchased from Technic Inc.

TiO₂ nanotubes (NTs) growth

Electrochemical anodization of titanium metal was used for TiO_2 nanotube growth.^{3,9,12,14} A typical two-electrode system with 99.6% titanium sheet (1" x 0.5") and platinum-coated electrodes were used as anode and cathode, respectively. Ethylene glycol (EG) containing 1% wt. NH₄F (etchant) and 5% wt. water was used as the electrolyte. The nanotubes were grown for 3 hours with applied 30 V DC voltage. Anion doping was done simultaneously with the nanotube growth by adding 5% wt. hexamethylenetetramine and 5% L-ascorbic acid into the electrolyte as nitrogen and carbon precursors, respectively. For cation doping, a polarity switching (titanium sheet as the cathode) was used to facilitate driving cation ions into nanotubes. 1% cation ion (Nb⁵⁺ and Cu²⁺) were used at a lower voltage (~15 V), and the doping was processed for 30 seconds with every 30 min nanotube growth. Co-doped (cation-anion) samples could also be made by combining cation and anion doping. All samples were annealed in air at 500 $^{\circ}$ C for 2 hours (with a ramping rate of 4 $^{\circ}$ C/min).

Stand-alone TiO₂ nanotube membrane

Annealed TiO_2 nanotubes were delaminated from the titanium foil using the same setup for nanotube growth, with +60 V DC bias applied to the nanotubes. Typically, the delamination takes 20 to 30 minutes. The delaminated thin film was carefully washed with ethanol to remove the remaining electrolyte.

Ultraviolet-Visible (UV-VIS) Spectroscopy

UV-VIS Spectrum was measured using VWR UV-1600PC spectrophotometer. The samples were sandwiched between two clean glass slides for measurements.

Scanning Electron Microscopy (SEM) Images

Field Emission SEM (JEOL JSM-7401F) was used to characterize the morphology and structure of the nanotubes. Nanotubes on Ti metal sheet were sputtered with gold before the imaging. A built-in Energy Dispersive X-ray Spectrometry (EDS) setup was used for elemental analysis (with Noran Software).

Electronic characterization

Microscopic single nanotube electronic characterization was performed with CSAFM and STM/STS, as described in Chapter 2.

Electrochemical Characterization

Electrochemical properties of these electrodes were measured using a Bio-logic SP-200 potentiostat/galvanostat. Potentiodynamic characteristics (dark and light linear sweep voltammetry, LSV) of Ti/TiO₂ NTs electrode was performed in 0.5 M (pH =

6.5) Na₂SO₄ solution with a scan rate of 10 mV/s. A three-electrode configuration with a platinum wire as a counter electrode and Ag/AgCl (filled with 1 M KCl solution) electrode as a reference electrode was used. The photodynamic evaluation was carried out under 1 SUN illumination using a 300 W xenon lamp (adjusted to 100 mW/cm² light intensity, with AM 1.5 filter). Chronoamperometry (CA) technique was used to evaluate the generation of photocurrent, under +0.5 V vs Ag/AgCl reference.

Electrochemical Impedance Spectroscopy (EIS) was used to evaluate the kinetic properties of these photocatalysts under AC polarization. Using the same conditions for LSV measurement, the experiments were conducted in a frequency range from 100 kHz to 100 mHz, with an amplitude of 10 mV AC polarization on a +0.2 V vs reference DC bias, with a 10 min delay to stabilize the systems. Bode plot and Nyquist plot were extracted from the measurements and fitted to the suggested equivalent circuit using the Z-fit function in EC-lab software (Bio-logic).

Mott-Schottky plot ($1/C^2 \sim E$) was extracted from the stair-potentio-electrochemical impedance spectroscopy (SPEIS). This experiment was done in the same three-electrode configuration cell setup as described above, under a constant frequency of 1 kHz and DC potential polarization.

Open-circuit potential (OCP) decay/relaxation was conducted using the same three-electrode setup to evaluate the charge transfer characters on the nanotube-electrolyte surface. The measurements were first taken in dark for at least 25 min (to stabilize the OCP), and then under UV irradiation, until the change of OCP was small (>35 min). The UV irradiation was then turned off and the relaxation measurements were taken for about 2 hours.

IPCE was measured using the same three-electrode configuration as mentioned above. Monochromatic light with less than 10 nm FWHM was obtained using a monochrometer (Princeton Instruments, Model: FA2448) with a 150 W halogen lamp. Light intensity was measured using a calibrated power meter (Newport, Model: 1918). Current density under dark and light was recorded with chronoamperometry technique under 0.5 V bias (vs. reference). IPCE was calculated using the following formula:

$$IPCE(\lambda) = \frac{|j_{ph}(mA \cdot cm^{-2}) \times 1239.8(V \times nm)}{P_{mono}(mW \cdot cm^{-2}) \times \lambda(nm)}$$

where j_{ph} is the photocurrent density, P_{mono} and λ are the intensity and the wavelength of the monochromatic light, respectively.

Photocatalytic Methylene Blue degradation test

Photocatalytic degradation of Methylene Blue (MB) was carried out in a capped quartz cuvette containing 3 ml 0.05 mM (150 nmol) methylene blue solution and wireless Ti/TiO₂ electrode, with an exposed surface area of about 1 cm². The whole system was irradiated with 365 nm monochromatic light (5.1 mW/cm²) using a 4 W UV lamp. The absorption of the solution was taken at 0, 10, 40, 80 and 120 min using a calibrated UV spectrometer, the decrease of absorption and the fading of a blue color indicates the degradation of methylene blue dye. The decrease of the absorption peak around 670 nm was used to calculate the kinetic constant of reaction and the quantum yield of photocarrier generation. The degradation exhibits clear first-order reaction character, the (apparent) reaction rate constant (k) was extracted from the slope of ln(Absorbance)~t plot.

The quantum yield (QE) can be calculated by the ratio of photon-induced charge carriers (here holes) to the number of incident photons, ³³

$$QE(\%) = \frac{flux(holes)}{flux(photons)} \times 100\%$$

 $flux(photons) = \frac{l\lambda}{hcN_A} \times S$ $= \frac{5.1(mW \cdot cm^{-2}) \times 365(nm)}{6.626 \times 10^{-31}(J \cdot s) \times 2.99 \times 10^8(m \cdot s^{-1}) \times 6.02 \times 10^{23}(mol^{-1})}$ $\times S(cm^2) = 5.60 \times 10^{-5}(mol \cdot h^{-1} \cdot cm^{-2}) \times S(cm^2)$ $flux(holes) = 22 \times \frac{moles \ of \ MB \ changed}{elasped \ time} = 22 \times \frac{\Delta Abs}{Abs(t=0)} \times \frac{moles(MB)}{t}$ $= 22 \times \left(1 - \frac{Abs(t=2h)}{Abs(t=0)}\right) \times \frac{1.5 \times 10^{-7}(mol)}{2(h)}$ $= 1.65 \times 10^{-6} \times \left(1 - \frac{Abs(t=2h)}{Abs(t=0)}\right) (mol \cdot h^{-1})$

where I is the illumination intensity of the UV light, S is the sample irradiation area, factor 22 is the stoichiometric number for the MB degradation reaction, where one MB dye molecule consumes 22 holes for complete degradation.

Photocatalytic hydrogen evolution test

Around 20 mg nanotubes were scratched from the as-grown sample. A photochemical approach was used to deposit platinum nanoparticles on TiO_2 nanotubes. The nanotube powder was dispersed in 5 ml ethanol under sonication and the system was flushed with nitrogen for 30 min. 0.2 ml chloroplatinic acid-ethanol

solution (with 1mg/ml platinum) was injected and irradiated with UV light using a 4 W UV lamp. After 2 hours, the products were centrifuged and washed with ethanol at least twice. Photocatalytic hydrogen evolution test was conducted in a septum-sealed reactor with 60 ml volume. The platinum-deposited nanotubes were dispersed in 10ml 1:1 (vol) methanol-water mixture and added to the reactor. The whole system was purged with argon gas for 15 min before irradiating with AM 1.5 solar light (1 SUN). The gas from the reactor was monitored with a calibrated gas chromatography (Agilent GB1530, TCD detector, argon carrier gas, molecular sieves 5A packed column) by using a syringe (0.1 ml) injection method.



Figure 3.7 Field emission scanning electron microscopy (FESEM) of doped TiO₂ nanotubes.



Figure 3.8 Linear sweep voltammetry of undoped and Cu-doped nanotubes showing the photocurrent density under AM 1.5 (1 SUN) irradiation. The inset is the light ON-OFF current density measurement taken at 500 mV bias vs. Ag/AgCl reference.



Figure 3.9 Scanning tunneling spectroscopy (STS) of undoped/doped TiO_2 nanotubes showing the density of states (DOS).



Figure 3.10 Current-sensing atomic force microscopy (CSAFM) measurement of (a) N-doped and (b) C-doped TiO₂ nanotubes, showing both the I~V and $\ln(I)$ ~V characters.



Figure 3.11 Change of Open-circuit potential with UV light on and off for N-doped TiO_2 nanotubes.



Figure 3.12 The decrease of absorption shows photocatalytic degradation of MB with N-doped TiO_2 nanotubes.

Abbreviations

AC	Alternate current
CA	Chronoamperometry
CSAFM	Current-sensing atomic force microscopy
DC	Direct current
DOS	Density of states
EDS	Energy-dispersive X-ray spectroscopy
EG	Ethylene glycol
EIS	Electrochemical impedance spectroscopy
FESEM	Field-emission scanning electron microscopy
HER	Hydrogen evolution reaction
IPCE	Incident photon-to-current efficiency
LSV	Linear sweep voltammetry
MB	Methylene blue
NT	Nanotube
OCP	Open-circuit potential
PEIS	Potentio-electrochemical impedance spectroscopy
QE	Quantum efficiency
SEM	Scanning electron microscopy
SPEIS	Stair potentio-electrochemical impedance spectroscopy
STFC	Solar-to-fuel conversion
STM	Scanning tunneling microscopy
STS	Scanning tunneling microscopy
TCD	Thermal conductivity detector

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Chapter 4

Deep and shallow dopant effect in cation-doped titanium dioxide nanotube membranes for solar energy conversion

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Titanium dioxide nanotubes have been used for several applications like water purification,^{1,2} solar energy conversion to electricity^{3–5} or fuels,^{6–11} gas detection sensors,^{12,13} hydrogen storage,^{14,15} and biomedical applications.^{16,17} For solar-to-fuel conversion (STFC) application, these nanotubular structures show better performance compared to the bulk or nanoparticulate TiO₂, due to their realization of the sunlight absorption and charge separation in orthogonal directions.^{6,7,10,18–22} Furthermore, progress on enhancing the STFC efficiency by using elemental doping, nanostructuring, surface engineering have to a certain extent overcome the intrinsic weakness of TiO₂ materials-large bandgap, defects or surface states, poor water oxidation kinetics.^{8,19,21,23–28} On the other hand, less study on the details of each process in STFC, namely photon absorption, charge separation and transport, and charge injection (chemical reaction), makes the STFC optimization difficult. For example, dopants in these nanotubes could not only help visible light utilization, but also affect charge separation and charge injection through space charge layer, creating defects or internal states, or catalyzing surface reactions.^{11,19} To better understand the metal dopant effects (deep and shallow dopants) towards designing higher efficiency STFC devices, we conducted a systematic study to fully understand their roles in each of these processes, provide a model for kinetics of photogenerated charged carriers in TiO₂, effect of photon fluence on photophysical and photochemical processes, and develop principles for better design of metal oxide nanotubes with higher STFC efficiency.

We recently reported a facile method of growing nanotubular structures with simultaneous elemental doping using a modified electrochemical anodization technique,²⁹ which can be used to synthesize various metal oxide nanotubes like TiO₂,

Fe₂O₃, and WO₃. Generally, anodization was realized using metal sheet anode and platinized metal mesh cathode in the fluoride (NH₄F) containing electrolyte (ethylene glycol). Nanotubes with varying length, diameter, wall thickness and density can be controlled by optimizing the etchant concentration, applied voltage, processing time. Cation dopants were incorporated by simply using a polarity-switching method or applying an alternating current with pre-set periodicity and bias. To improve the crystallinity and electrical conductivity of these nanotubes, high-temperature annealing was conducted. Here, TiO₂ nanotubes with about 3 μ m length, 80 nm diameter and 5 nm wall thickness were fabricated (Figure 4.1a, 4.7). The morphology of these nanotubes maintained even with high level cation doping, and no phase separation was observed even at high dopant concentrations, which is at about 10% and 2.5% for niobium and copper dopants (Figure 4.1b). X-ray powder diffraction (XRPD) of undoped samples showed the anatase structure of these anodization nanotubes, and also confirms absence of formation of any new phase in the XRPD spectra.²⁹ Similar XRPD spectra of cation-doped samples compared to undoped samples indicated no structural/phase change with addition of these dopants.



Figure 4.1 (a) Scanning electron microscopy (SEM) image of Cu-doped TiO_2 nanotubes. (b) Energy-dispersive X-ray spectroscopy (EDS) of Cu-doped nanotubes, with an atomic percentage for Ti, O, and Cu elements. (c) Ultraviolet-visible (UV-VIS) spectrum of delaminated TiO_2 nanotube thin films. (d) Scanning tunneling spectroscopy (STS) of TiO_2 nanotubes, showing the dI/dV~V relation (density of states, DOS), with labeled Fermi level, conduction and valence band (CB and VB) position. (d) I~V and ln(I)~V character of Cu-doped TiO_2 nanotubes from current-sensing atomic force microscopy (CSAFM) measurements, with calculated carrier density (n).

The photophysical and photochemical processes using light generated charge carriers in TiO_2 photoanode can be described as: when the TiO_2 surface is irradiated with a photon with energy higher than the bandgap of TiO_2 , electron-hole pairs will generate and they are separated through drift (assisted by electric field built inside the space charge region) or diffuse to the bulk and surface of TiO_2 , respectively. Some of the electrons and holes will recombine through either bandedge-bandedge or defect-assisted recombination. The holes on the TiO_2 surface will inject to water molecules for oxygen generation and the electrons will transport to the back (counter) electrode, followed by injection to water for hydrogen generation. To understand the

effects of the metal dopants in these photoanodes for solar energy conversion on different photophysical and photochemical processes,^{30–32}

$$\eta = \eta_{abs} \times \eta_{transport} \times \eta_{transfer}$$

the efficiency of the individual process, namely, photon absorption under light irradiation, charge carrier transportation from the bulk nanotube to its surface, and the carrier transfer from nanotube surface to the adsorbed water molecule for oxidation was evaluated separately. To assess the photon capture efficiency of these nanotubes, optical characterization using stand-alone TiO₂ thin film (delaminated from the titanium metal using a second anodization technique) in a transmission mode was performed. Ultraviolet-visible (UV-VIS) spectra (Figure 4.1c) reveal the increased absorption of doped TiO₂ nanotubes, as shown in the changes of bandedge absorption (E_{op}) from 3.0 eV to 2.5 and 1.9 eV for Nb-doped and Cu-doped samples, respectively (Table 4.1, row 1). The bandedge shrinking is also confirmed by the change of electronic bandgap (E_{el}, here defined as from dopant states to conduction or valence band) measured by scanning tunneling spectroscopy (STS) (Figure 4.1d, Table 4.1, row 2). The STS spectra of undoped and doped nanotubes also reveals the shallow donor states introduced by niobium dopant and the resulting n-type characteristics (close proximity of the Fermi-level to conduction band for both undoped and niobium-doped nanotubes, and the donor states in Nb-doped nanotube can be easily identified just below its conduction band), and the shifting of Fermi-level away towards the center and deep dopant states (presence of states well within nominal bandgap in measured electronic density of states (DOS) plot) introduced by copper doping. The difference between optical bandgap and electrical bandgap (about 200 meV) can be explained by exciton-like traps in these nanotubes,³³ which might be a contributing factor for low charge carrier mobility in these nanotubes. A significant difference between these two bandgaps in the Cu-doped sample can also be explained by the absorption from other internal states, which is not considered in the electronic bandgap. To discover the dopant effect in charge transport, we conducted single nanotube measurement using current sensing AFM (CSAFM) to better understand their current-voltage behavior and measure any potential differences in doping between individual nanotubes. These could give us intrinsic material characteristics instead of ensemble device behavior measured with a traditional four-probe test. The conductivity (**Table 4.1, row 4**) and the carrier density (**Table 4.1, row 3**) of these nanotubes obtained from I~V and ln(I)~V curves (**Figure 4.1e, 4.8**) taken in the intermediate-biased region give us the value of charge carrier mobility using the following equations,^{29,34}

$$ln|I| = \left\{ \frac{e}{kT} - 2\left[\hbar \sqrt{\frac{n}{m^*\varepsilon}} \coth\left(\frac{\hbar e}{2kT} \sqrt{\frac{n}{m^*\varepsilon}}\right)\right]^{-1} \right\} V + const$$
$$\sigma = \left[\frac{\pi D}{4} (R - R_{ITO})\right]^{-1}$$
$$\mu = \frac{\sigma}{ne}$$

where n is the carrier density, $m^*=m_0$ and $\varepsilon = 31\varepsilon_0$ are the effective mass of electron and dielectric constant for TiO₂ nanotubes, respectively.^{35,36} R and R_{ITO} are the measured resistance and the resistance of the ITO layer, respectively, with their difference giving the resistance of the nanotubes. D is the contact diameter of the probe. We observed significant increase (~15 fold) in conductivity with Nb-doped, and this metal-like high conductivity is beneficial for more efficient charge transport. However, conductivity is decreased by several magnitudes with copper doping, rendering almost insulating characteristics to the nanotubes. On the other hand, carrier mobility decreases (Table 4.1, row 5) in both doped nanotubes, and this could be mainly caused by more frequent impurity scattering or internal states trapping. Such decrease of mobility is much more prominent in the heavy-metal (copper, in this case) doped nanotubes. The different behaviour of niobium- and copper-doped nanotubes can be explained by the different characteristics of the dopants. Niobium acts as a shallow donor in TiO₂ nanotubes and increases the free charge carriers. Furthermore, shallow dopants also fill up surface states intrinsic to TiO₂ due to oxygen deficiency, leading to decrease of deep traps and showing upshift (negative shift) of flatband position and increase of open circuit potential (as shown later), which is beneficial for photocatalytic or photoelectrochemical applications. On the other hand, incorporating of copper (deep dopant) while improves light absorption, also significantly increases the deep traps in the nanotubes and these traps contribute to the recombination of electron and holes, and hence smaller values of conductivity and charge mobility.³⁷

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Sample	Undoped	Nb-doped	Cu-doped
E _{op} (eV)	3.03	2.53	1.93
E _{el} (eV)	3.23	2.91	2.82
$n (cm^{-3})$	2.32×10^{18}	5.56×10^{19}	3.64×10^{18}
σ (S/m)	4.62	71.7	0.00285
μ (cm ² /V•s)	0.124	0.0805	4.89×10^{-5}

 Table 4.1 Parameters obtained from optoelectronic measurements

To evaluate the performance of these nanotubes used as photoanodes, several electrochemical measurements were taken using the nanotubes on titanium substrates as the working electrode. Current-voltage characteristics were studied using linear sweep voltammetry (LSV) in a three-electrode configuration under both dark and 1 SUN (AM 1.5) solar irradiation, and the results were presented in reversible hydrogen electrode (RHE) scale. Polarization current (Figure 4.2a) detected in dark conditions appear only when a potential of over 2.2 V was applied. Under 1 SUN irradiation, photon-induced electron and holes are generated and an applied bias above the flat band results in the onset of photocurrent. The photocurrent increases with applied voltage and saturated once all available charge carriers are collected at the nanotube surface. Here, the Nb-doped nanotubes showed a decrease of onset potential (~200 meV) and higher photocurrent (Table 4.2, row 1) compared to undoped samples, indicating a better photoanode performance. This increase of open circuit potential shift upon irradiation proved the effect of niobium as a shallow dopant in helping to remove deep traps in undoped TiO₂ nanotubes as mentioned previously. As expected, the saturated photocurrent of the Cu-doped sample is much smaller than undoped samples, which is attributed to the sluggish charge transport character with copper doping. Chronoamperometry (CA) measurements with a fixed 500 mV bias vs Ag/AgCl reference (Figure 4.2b) indicates stable photocurrent generation with relative strength of Nb-doped > Undoped >> Cu-doped TiO_2 nanotubes (Table 4.2, row 2). An overshoot upon irradiation followed by exponential decay of photocurrent reveals the surface recombination of electron-hole pairs at the nanotube surface.³⁸ This recombination could compete with hole-driven water oxidation reaction and lower the STFC efficiency.



Figure 4.2 (a) Three-electrode Linear sweep voltammetry (LSV) showing the J~V character of TiO₂ nanotubes. (b) Three-electrode chronoamperometry (CA) showing dark and light J~t character of TiO₂ nanotubes, measured under 500mV vs. reference. (c) Incident photon-to-current efficiency (IPCE) of TiO₂ nanotubes, showing their photoresponse with varied energy photons. (d) Voltage-dependent Applied bias photon-to-current efficiency (ABPE) extracted from the LSV of two-electrode measurements for TiO₂ nanotubes.

Incident photon-to-current efficiency (IPCE) measurements^{10,30} were performed to study the photoresponse of these nanotubes under different energy photon irradiation (**Figure 4.2c, Table 4.2, row 5**). Here, the IPCE onset of undoped nanotube matches its optical bandgap, and the decrease of onset was seen in doped nanotubes. However, differences between this electrochemical bandgap and optical bandgap were observed in doped samples, especially in Cu-doped nanotubes. It seems that lower energy photons are unable to generate electron-hole pairs with sufficient redox potential for splitting water. The electron-hole pairs could be trapped in the dopant states, which required extra energy to become free charge carriers. The IPCE in the UV region correspond to the relative strength of photocurrent generation, with Nb-doped > Undoped >> Cu-doped nanotubes. To quantify the total efficiency of these nanotube photoanodes, applied bias photon-to-current efficiency (ABPE) was calculated using the current-voltage relation (**Figure 4.2d**) taken from two-electrode (2-e) measurements,³⁰

$$ABPE(\%) = \frac{J(mA \cdot cm^{-2}) \times (1.23 - V_{bias})(V)}{P(AM1.5)(mW \cdot cm^{-2})} \times 100\% = J \times (1.23 - V_{bias})\%$$

where J is the current intensity and P(AM1.5) is the power density of irradiation, which is 100 mW/cm² in the 1 SUN (AM1.5) condition. We found that a large bias (~1 V) is required to achieve their respective maximum efficiency. An interesting observation shows that though the Nb-doped nanotubes exhibit much higher efficiency at lower bias (~0.4 V), a higher operation voltage is required to realize its maximum efficiency (**Table 4.2, row 3, 4**). This can be explained from two aspects: a higher amount of generated charge carriers require larger carrier collection ability and the smaller carrier mobility requires a higher electric field to assist carrier transport.

Sample	Undoped	Nb-doped	Cu-doped
E _{onset} (V)	0.45	0.21	0.17
$J_{ph} (mA/cm^2)$	0.039	0.064	0.00060

 Table 4.2 Parameters extracted from voltammetric measurements

E _{optimal} (V)	0.85	0.94	0.86
ABPE _{max} (%)	0.0086	0.0089	6.7×10^{-4}
E _{ec} (eV)	3.05	2.92	2.73

To separately compare the charge transport and charge injection (transfer) efficiency in the bulk semiconductor and semiconductor-electrolyte interface, several potential and impedance-based techniques were used. The open-circuit potential (OCP) decay upon blocked irradiation (**Figure 4.3a**) could be used to determine the charge transfer rate (or carrier lifetime) for holes utilized for water oxidation,³⁸

$$V_{OCP} = V_{dark} + \Delta V_{OCP} = V_{dark} + V_{ph} = A - Bexp(-k_{ct}t)$$

where A, B are constants (V) and k_{ct} is the charge transfer rate constant (s⁻¹).

The exponential decay demonstrates a significant increase of charge transfer rate constant (or decrease in carrier lifetime) (**Table 4.3, row 1**) in Nb-doped samples compared to undoped or Cu-doped samples, which indicates improved charge injection on the surface of these Nb-doped nanotubes at potential catalytic sites for oxidizing water molecules.



Figure 4.3 (a) Open-circuit potential (vs. reference) decay of TiO_2 nanotubes after turn-off of ultraviolet irradiation. (b) Bode plot of the TiO_2 nanotube, showing the frequency-dependent phase (Arg(Z)) of complex impedance in AM 1.5 irradiation condition. (c) Equivalent circuit used to fit the experimental data. (d) Bode magnitude plot of TiO2 nanotubes in AM 1.5 irradiation condition, showing the variation of the module of complex impedance with frequency, with fit to the equivalent circuit proposed in (c).

Electrochemical impedance spectroscopy (EIS) is an important method used to study the behavior of charge carriers under AC perturbation.^{30,32,38–46} In a typical EIS study, both Bode plot (including frequency-dependent magnitude plot and phase plot) and Nyquist plot (relation between the real part and imaginary part of complex impedance) are commonly used. Here, the phase~frequency relationship is crucial to learn the carrier (hole) injection efficiency as the peak minimum position (f_{min}) corresponds to the charge injection lifetime (τ_{eff}),

$$\tau_{eff} = \frac{1}{k_{eff}} = \frac{1}{2\pi f_{min}}$$

Under light irradiation, the induced electron-hole pairs separated, with holes transport to the TiO₂ electrode surface and inject to water. Good photocatalytic performance requires fast charge injection, which corresponds to small charge injection lifetime and hence a peak minimum position at a higher frequency in Bode plot. Here, we saw a very close peak position for undoped and Cu-doped nanotubes, with an obvious shift of peak to a higher frequency in Nb-doped samples. Similar to the trend shown in OCP decay, we concluded that the charge lifetime (Table 4.3, row 2) is significantly lower in Nb-doped nanotubes, indicating more efficient hole injection to water molecules. Furthermore, we fitted the experimental impedance data with the equivalent circuit to extract quantitative values related to charge transport and charge transfer.³⁸ This kind of equivalent circuit (Figure 4.3c) was typically used for describing the impedance behavior of n-type semiconductor-electrolyte systems, which contains the solution resistance R_s, capacitance of double layer C_{dl}, charge transfer resistance R_{ct}, space charge capacitance and resistance, Csc and Rsc, and the capacitance and resistance $(C_1 \sim C_3, R_1 \sim R_3)$ contributed from trapping levels.⁴⁷ Here, we focused on the parameters (Table 4.7) that reflect the intrinsic behavior of electron transport and transfer processes in bulk nanotubes, and their interfaces. Charge transfer resistance (R_{ct}) was used to evaluate the ease of charge (hole) injection from nanotube surface to the water molecules. The relative value of charge transfer resistance (Table 4.3, row 3) indicates the charge transfer efficiency as Nb-doped > Undoped > Cu-doped. This follows the same trend in the phase~frequency relationship and OCP decay

measurement, as a large value of charge transfer resistance corresponds to a large carrier lifetime and a small charge transfer rate constant.

	1	1	
Sample	Undoped	Nb-doped	Cu-doped
k_{ct} (s ⁻¹)	1.21×10^{-3}	2.44×10^{-3}	1.00×10^{-3}
$ au_{eff}$ (s)	0.614	0.0949	0.810
$R_{ct} (k\Omega \cdot cm^2)$	4.96	3.73	6.07
$C_{total} (\mu F/cm^2)$	101	240	672

Table 4.3 Parameters extracted from potential and impedance-based measurements

Dopants also affect carrier transport to the depletion layer charge (characterized as C_{sc}) and can act as recombination centers for electron-hole pairs (characterized as $C_{trap} = C_1 + C_2 + C_3$). The total effects can be evaluated using the sum of the capacitance of the semiconductor part $C_t = C_{sc} + C_{trap}$. Due to the small value of space charge layer capacitance compared to relatively large trapping capacitance, the total capacitance reflects mainly the capacitance of trap levels. A larger value of C_t indicates stronger trapping of charge carriers in dopants, which largely decrease the available holes for surface reaction. Here, we saw the relatively small trapping effect in Nb-doped nanotubes compared to undoped samples (**Table 4.3, row 4**). However, a significant increase of total capacitance with copper dopants indicates a strong trapping effect in Cu-doped nanotubes. These traps act as effective recombination centers and result in very small carrier mobility measured from CSAFM. This kind of deep-level dopant behavior is common in heavy metal dopants, which dramatically decrease the STFC efficiency.



Figure 4.4 (a) Mott-Schottky plot of TiO_2 nanotubes under 1 kHz frequency and the (b) calculated space charge region width with applied bias. (c) Change of flatband potential (c) and charge carrier density (d) with frequency, obtained from Mott-Schottky curves.

To delve into the potential-capacitance behavior of these photoanodes, we conducted Mott-Schottky analysis using three-electrode configuration.^{30,32} The positive slope of Mott-Schottky curve (**Figure 4.4a**) indicates the n-type character of these nanotubes. With the increase of anodic bias above the flat band potential, the capacitance sharply decreased due to the generation of electron-hole pairs, until a plateau is reached. These curves contained two to three linear regions with different slopes, which were attributed to different numbers of internal levels inside the bandgap. And the nonlinear transition between these regions is caused by the contribution from multiple internal levels.^{38,47} Unlike the other samples, Nb-doped nanotubes showed

only two linear regions, which can be explained by its high carrier density (small slope of Mott-Schottky curve) character. These electrons fill all discrete donor states and make their single contribution indistinguishable. In contrast, the large numbers of trapping levels in Cu-doped nanotubes show clearly three distinct slopes in the Mott-Schottky curve. The carrier density (N_d) and flat band potential (E_{fb}) can be obtained from the slope and x-intercept of Mott-Schottky curve, based on the Mott-Schottky equation for n-type semiconductors,³⁰

$$C_{sc}^{-2} = \frac{2}{\varepsilon q N_d} (E - E_{fb} - \frac{k_B T}{q})$$
$$C_{sc} = -\frac{1}{2\pi f Im(Z)}$$

where $\varepsilon = 31\varepsilon_0$ is the dielectric constant of TiO₂ nanotube, $k_B = 1.38 \times 10^{-23}$ J/K and $q = 1.602 \times 10^{-19}$ C are Boltzmann constant and elemental charge, respectively,^{35,48} f is the frequency (Hz) used in the measurements, Im(Z) is the imaginary part of complex impedance (Ohm). The two parameters are strongly frequency-dependent due to the internal or trapping levels, and this frequency-dispersion phenomenon is commonly seen in metal oxide semiconductors. To study this frequency dependence, the same experiments were conducted under series of frequencies (**Figure 4.4c, d**). Carrier density with the general order Nb-doped > Cu-doped > Undoped follows exactly the same trend determined by the ln(I)~V characters (**Table 4.1**). An increase of carrier density with decreasing frequency reflects the trapping effect of internal states. At lower frequencies, the generated charge carriers were able to relax to these lower energy states and contribute to the depletion/space charge layer, showing higher

carrier concentration. This also contributed to the positive shift of flat band potential with decreasing frequency. The relative change of carrier density in lower and higher frequency was used to estimate the trapping ability of each dopant. As clearly seen in these nanotubes, Cu-doped samples show most significant change of carrier density with varied frequency, which indicates higher trapping (total) capacitance and stronger trapping effects. Similar trend was also shown in the change of flatband potential with frequency. The variation of flatband position with frequency is smallest in Nb-doped samples, showing lower trapping effect. Furthermore, at lower frequency, Nb-doped TiO₂ showed negative shift of flatband position compared to the other samples, indicating the shallow dopants help in removing/filling deep traps and increase open circuit potential. This result matches well with the change of "light-on" onset potential measured from linear sweep voltammetry.

In the nanotubes, the space charge region is formed by the depletion of charge carriers (electrons for n-type semiconductors) and will provide a built-in electric field for drifting charge carriers to the nanotube surface. The space charge region width can be calculated from the space charge capacitance (C_{sc}) obtained directly from SPEIS measurement using the equation,³²

$$d_{sc} = \sqrt{\frac{2\varepsilon}{qN_d}(E - E_{fb} - \frac{k_B T}{q})} = \frac{\varepsilon}{C_{sc}} = \frac{27.45}{C_{sc}(\mu F \cdot cm^{-2})}(nm)$$

The space charge layer width consistently increases with anodic bias (**Figure 4.4b**), reflecting the space charge capacitance character as seen in the Mott-Schottky plot. The space charge layer width of all three samples exceeds the wall thickness of

the nanotubes (~5 nm) under operation voltage (500 mV vs reference, or 1100 mV vs RHE). Therefore, the whole wall of TiO_2 nanotubes is constructed within the space charge layer, which facilitates charge transportation by its built-in electric field. This reflects the main advantage of separating light absorption and charge transport in one-dimensional materials. This kind of design is particularly beneficial for materials with low charge carrier diffusion length, like most oxide materials, especially for iron oxide.

To better understand all these related photophysical and photochemical processes, we developed a model to describe the charge carrier generation, transport, trapping, injection and recombination in these TiO_2 nanotube photoanodes. In this model, we considered the consumption of photon-induced charge carriers in the following path: conduction band-valence band recombination, electron trap-assisted recombination, valence band-dopant state recombination, or surface reaction. We have previously developed a model to describe the photophysics and photochemistry of anion (nitrogen and carbon) doped TiO_2 nanotube photoanodes. But, unlike those anions, which provide acceptor-like energy levels close to the valence band of TiO_2 , these cations provide donor-like energy levels close to the conduction band of titanium dioxide. Based on the charge balance and charge neutrality requirements in steady states, we derived the following equations:

$$\frac{dp}{dt} = (g_b + g_d) - \alpha pn - \beta pn_t - R$$
$$\frac{dn}{dt} = g_b - r_t n \left(1 - \frac{n_t}{N}\right) + r_{dt} n_t - \alpha pn - \gamma n_d p - R$$

$$n + n_t + n_d = p$$
$$R = r_n \times n + r_d \times n_d = r_p \times p$$

where n, n_d and n_t are number of electrons in conduction band, dopants, and trap states, N is the total number of traps, p is the number of holes in valence band; r_t and r_{dt} are trapping and detrapping rate between conduction band and electron trap states; α , β and γ are the rate constant for conduction band-valence band, trap states-valence band, and valence band-dopant state recombination, respectively; $g = g_b + g_d$ is the total photogeneration rate, which is the sum of photogeneration due to bandedge excitation and dopant excitation; R is the photocatalysis rate with r_n, r_d and r_p the corresponding rate constant.

We simplified this model based on two common situations for doped TiO₂ nanotube photoanodes, which can also be applied to other large band-gap semiconductors. One, on excitation with ultraviolet light, the photogenerated electrons and holes generated in bandedge TiO₂ states. In that case, we have $g = g_b$ and $n \approx p$. On the other hand, when irradiated with visible light, these lower energy photons are not sufficient to trigger bandedge excitation and the dopant excitation dominates, with $g = g_d$ and $n \approx 0$.

With the above assumptions, we could identify two major regions for doped TiO_2 samples:

1. When recombination occurs between doped electrons and photogenerated holes, where n_d , $n \gg n_t$ and $\gamma \gg \alpha$, β , we could obtain $g \propto n$, n_d , and the relation between the reaction rate and the photogeneration rate is linear ($R \propto g$). In this region, unimolecular recombination dominates.

2. If number of trapped electrons N is large, therefore $n_t \propto n_d^{-x}$ and $g \propto n_d^{(1-x)}$ with superlinear slope $R \propto g^{1/(1-x)}$, where x is between 0 and 1. In this region, trapping/dopant recombination is dominant.

Other cases, like bimolecular recombination (where the STFC rate is proportional to the square root of photogeneration rate), recombination occurs between photogenerated electrons and holes. However, due to a sufficient number of doped charge carriers in both shallow and deep dopants, and a sufficient number of oxygen vacancies in nominally undoped TiO_2 nanotubes,^{36,49} this regime was not seen in these semiconductor nanotubes.



Figure 4.5 (a) Photophysical/photochemical mechanism showing the carrier generation, transport, trapping, recombination, and injection processes. Log-log plot of the intensity-dependent photocurrent taken at varied wavelength monochromatic irradiation for (b) Nb-doped and (c) Cu-doped nanotubes, with slopes from the linear fit. (d) Variation of slopes with wavelength of incident irradiation in doped TiO_2

nanotubes. (e) Log-log plot of intensity-dependent photocurrent for undoped and doped TiO_2 nanotubes at bandedge excitation, with slope from the linear fit.

To verify the proposed model above, we carried out measurement of the photocurrent generation with varied light intensity (flux), using monochromatic light with different wavelength, covering from visible light to ultraviolet irradiation. These excitations correspond to sub-bandgap, bandedge, and hot carrier excitation. As can be clearly seen, these nanotubes show only negligible photocurrent with sub-bandgap excitation, and with the increase of photon energy, the generation of photocurrent is significant even with low-intensity light irradiation. To ease the description of photocurrent~light intensity relationship, we used log-log plot and showed the change of slope with varied photon energy. As shown in those log-log plots for photocurrent vs. photon fluence in these nanotubes, for shallow Nb-dopants, the slope is always superlinear, since these shallow dopants states follow similar photophysics as filled shallow electron traps or allow trapping of charges on nanotube surface (Figure **4.5b,d**). A completely different trend is seen in deep dopants, like Cu-doped samples, where the slope is 1 (unimolecular recombination between doped electrons and photogenerated holes) on ultraviolet excitation, whereas the slope increases with bandedge excitation, due to larger trapping of charges (Figure 4.5c, d). Comparing slopes and different photophysical regimes on the onset of photoexcitation between different nanotubes, we observed Undoped < Nb-doped < Cu-doped (Figure 4.5e), which reflects the increasing trend of trapping effect from undoped to niobium, to copper-doped nanotubes. These trends match well with our EIS measurements,

showing an increase of trapping capacitance from undoped to niobium and copper-doped samples.



Figure 4.6 (a) First-order reaction plot $(\ln(Abs)\sim t)$ of methylene blue (MB) degradation using TiO₂ nanotubes under ultraviolet irradiation. (b) Quantum yield (QE) calculated from the MB degradation test of TiO2 nanotubes. Hydrocarbon (CH₄) generation rate with time (c) and the average electron generation rate (d) calculated from photocatalytic carbon dioxide reduction measurements using TiO₂ nanotubes.

To further estimate the efficiency of these nanotubes for STFC, two wireless device measurements, photocatalytic methylene blue (MB) degradation and photocatalytic carbon dioxide reduction test were conducted.^{25,50} Similar to the principle of wastewater purification, the MB degradation by photon-induced holes (**Figure 4.9**) were used to assess the quantum efficiency of the photocatalysts. This process featured a typical first-order character (**Figure 4.6a**) and the half-time ($t_{1/2}$) and (external) quantum yield (QE) (**Figure 4.6b**) resemble the
same order of Nb-doped > Undoped > Cu-doped, as seen in photoanode measurements. Similar to water splitting, electron-hole pairs generated by the photocatalysts are also able to achieve simultaneous water oxidation (by holes) and CO_2 reduction (by electrons), a route similar to the natural photosynthesis for producing carbohydrates. The efficiency is estimated using a number of solar fuels (hydrocarbon molecules) or equivalently the electron production rates during this process. Using these nanotubes as either powder (removed from titanium substrates) or delaminated thin film (from titanium substrates), with pressurized CO_2 /water vapor and AM 1.5 irradiation, we detected stable methane (CH₄) generation (**Figure 4.6c**) from undoped and Nb-doped nanotubes within test time (90 min), with higher efficiency for Nb-doped samples (**Figure 4.6d**). However, we were not able to see detectable solar fuel production from Cu-doped nanotubes. This could be explained by the more stringent conditions for CO_2 reduction and deep trapping in Cu-doped nanotubes could not provide electrons with sufficient overpotential to process this multi-electron process.

In conclusion, we have synthesized a series of undoped and doped (Nb, Cu) TiO_2 nanotubes with deep and shallow metal dopants, and used them as photoanode to measure their total efficiency in solar energy conversion. Our results show a relative efficiency of Nb-doped > Undoped >> Cu-doped TiO₂ nanotubes to carry out STFC conversion in wired and wireless devices, indicating potential issues with using deep dopants states. To understand in depth the effects of elemental doping in the processes of light absorption, charge transport, and charge transfer, detailed optical, electric, voltammetry and impedance study were taken. Generally, we observed an improvement of light absorption and charge injection using doped nanotubes. Our results on charge transport showed variations where we

observed reduced charge transport in copper doped nanotubes, whereas even with a small decrease in carrier mobility due to increased scattering, higher charge carrier concentration lead to improved conductivity in Nb-doped nanotubes. Total STFC efficiency using wireless device measurements including photocatalytic methylene blue degradation and carbon dioxide photoreduction also showed improved STFC efficiency in shallow Nb-doped nanotubes, but a reduced solar fuel conversion with deep copper-dopants, when compared with undoped TiO₂ nanotubes. These results and the developed model can have important implications for improving the efficiency of solar energy conversion by designing optimal solar energy conversion devices.

Experimental

TNTs growth, optoelectronic, electrochemical characterizations, photocatalytic methylene blue degradation test were similar to the study of anion- and co-doped TNTs, as described in detail in Chapter 3.

Gas-phase reduction of CO₂ and H₂O

20 mg of the nanotube scratched from metal sheet was deposited in a rounded glass vial cut in half with a 0.64 cm² cross-sectional area. The vial was then enclosed in a 48-mL reactor and purged for 45 minutes with CO_2 (75 cm³ min⁻¹) humidified in a bubbler filled with D.I. water. After purging, the reactor was closed and irradiated with 1 SUN (100 mW cm⁻²) through a glass window using a solar simulator (ABET Technologies). One-milliliter samples were extracted from the reactor and injected into a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID)

for measuring concentrations. Separation of the hydrocarbons was done with a Hayesep D column. Reported data of photocatalytic rate and quantum yield were calculated based on the electron flux (μ mol cm⁻² h⁻¹) used to form CH₄.



Figure 4.7 Field Emission Scanning Electron Microscopy (FESEM) of undoped and Nb-doped TiO₂ nanotubes.



Figure 4.8 Current-sensing atomic force microscopy (CSAFM) measurement of (a) undoped and (b) Nb-doped TiO₂ nanotubes, showing both the $I \sim V$ and $ln(I) \sim V$ characters.



Figure 4.9 (a) The UV-VIS spectrum of methylene blue, showing the decrease of absorption with time under photocatalytic degradation of Nb-doped TiO₂ nanotubes. (b) The change of 670 nm peak absorbance with time under photocatalytic degradation of undoped and doped TiO₂ nanotubes.

	Undoped	Nb-doped	Cu-doped
$R_s (k\Omega \cdot cm^2)$	0.0170 ± 0.0008	0.0175 <u>+</u> 0.0007	0.0174 <u>+</u> 0.0009
$R_{ct} (k\Omega \cdot cm^2)$	4.96 <u>+</u> 0.20	3.73 <u>+</u> 0.18	6.07 <u>±</u> 0.29
$C_{dl} (\mu F/cm^2)$	424 <u>+</u> 22	328 <u>+</u> 16	317 <u>+</u> 14
$R_{sc} (k\Omega \cdot cm^2)$	0.593 <u>+</u> 0.029	3.84 <u>+</u> 0.19	6.44 <u>±</u> 0.30
C_{sc} ($\mu F/cm^2$)	1.75 <u>+</u> 0.070	8.99 <u>+</u> 0.36	12.3 <u>+</u> 0.55
$R_1 (k\Omega \cdot cm^2)$	0.720 <u>+</u> 0.036	0.400 ± 0.020	4.26 <u>±</u> 0.16
$C_1 (\mu F/cm^2)$	69.2 <u>+</u> 3.5	68.8 <u>+</u> 2.1	82.4 <u>+</u> 3.9
$R_2 (k\Omega \cdot cm^2)$	0.375 <u>+</u> 0.022	0.005 <u>+</u> 0.0003	12.4 <u>+</u> 0.50
$C_2 (\mu F/cm^2)$	2.31±0.14	49.8 <u>+</u> 2.5	431 <u>±</u> 20
$R_3 (k\Omega \cdot cm^2)$	0.212±0.009	0.027 ± 0.001	0.759 <u>+</u> 0.039
$C_3 (\mu F/cm^2)$	27.3 <u>+</u> 1.4	112 <u>+</u> 4.72	146 <u>+</u> 6.30

Table 4.4 Parameters extracted from the equivalent circuit fit

Abbreviations	
ABPE	Applied bias photon-to-current efficiency
AC	Alternate current
CA	Chronoamperometry
CB	Conduction band
CSAFM	Current sensing atomic force microscopy
DC	Direct current
DOS	Density of states
EDS	Energy-dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
FESEM	Field-emission scanning electron microscopy
FID	Flame-ionized detector

IPCE	Incident photon-to-current efficiency
LSV	Linear sweep voltammetry
MB	Methylene blue
OCP	Open-circuit potential
QE	Quantum efficiency
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscopy
SPEIS	Stair potentio-electrochemical impedance spectroscopy
STFC	Solar-to-fuel conversion
STS	Scanning tunneling spectroscopy
TCD	Thermal conductivity detector
UV-VIS	Ultraviolet-visible
VB	Valence band
XRPD	X-ray powder diffraction

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Chapter 5

Two-dimensional chalcogenides nanostructures with low exciton-phonon coupling, high charge carrier mobilities, and multiexciton properties for potential high efficient photocatalysts

Reproduced in part with permission from <u>Y. Ding</u>, V. Singh, S. M. Goodman, P. Nagpal. Low Exciton-Phonon Coupling, High Charge Carrier Mobilities, and Multiexciton Properties in Two-Dimensional Lead, Silver, Cadmium, and Copper Chalcogenide Nanostructures. *J. Phys. Chem. Lett.* **2014**, *5*, 4291-4297. Copyright 2014, American Chemical Society.

Ultrathin two-dimensional (2D) sheet of carbon atoms, graphene, has shown remarkable physical properties which are not observed in other low-dimensional carbon nanomaterials,¹ such as extremely high charge carrier mobility (limited by phonon-scattering), tunable interaction between phonons and charge carriers by dielectric screening,^{2,3} and a tunable bandgap by application of perpendicular electric fields, which has prompted similar investigations of other 2D nanomaterials. Atomically thin 2D nanostructures made from transition metal dichalcogenides, like MoS₂, have shown extraordinary optical absorption,^{4,5} very high carrier mobilities,⁶ a thickness dependent transition from an indirect to direct bandgap,⁷ large exciton-binding energies,⁸ and strong light emission from atomically thin 2D nanostructures.⁹ While weak bonding between atomic layers of graphite and some transition metal dichalcogenides makes them easier to exfoliate (mechanically and chemically) and measure the optoelectronic properties of their 2D nanostructures,^{10,11} lack of similar investigations for other materials has prevented further progress in making efficient 2D nanostructured semiconductor devices. Here, we report investigations of fundamental charge carrier-phonon interactions, along with optical and electronic properties of 2D nanomaterials made from colloidal syntheses of lead, cadmium, copper and silver chalcogenides (S, Se). Our findings reveal new interesting properties like low exciton-phonon coupling (both longitudinal optical phonons and acoustic phonons) in these 2D nanomaterials, two- to six-fold smaller than other bulk and low-dimensional semiconductors, which can enable improved light-emission and guide the design of other functional devices. Using dimensionality to reduce charge carrier-phonon coupling and improve conductivity in heavy-metal chalcogenide semiconductors (lead and cadmium chalcogenides here) can also

have important implications for the design of ultrathin thermoelectrics. Furthermore, high charge carrier mobilities in few-layer thick 2D nanomaterials (0.2-1.2 cm²V⁻¹s⁻¹ reported here, higher values expected with dielectric screening^{2,3,6}), observation of infrared surface plasmons in these ultrathin semiconductors due to partial oxidation, fundamental investigations of their electronic density of states (DOS) using scanning tunneling spectroscopy (STS), comparison of phonon-exciton interaction energies (bandgap shrinkage with temperature) for different crystal structures and multi-excitons, and optoelectronic measurements of single 2D nanosheets using current-sensing atomic force microscopy (CSAFM) measurements, also provide insights for development of functional 2D nanostructured devices.

To study the fundamental charge carrier interactions and optoelectronic properties in these 2D semiconductors, we utilized a low-temperature colloidal synthesis method with facet-specific binding of amine ligands (bottom-up synthesis).^{12–15} The low-temperature growth facilitates the formation of small clusters (which ultimately combine to form 2D nanostructures), and facet-specific binding of amine ligands in cadmium chalcogenides controls formation of a few-layers thick 2D nanostructures, as demonstrated by the transmission electron micrographs (TEM, **Figure 5.5**) and the atomic force micrographs (AFM, **Figure 5.1a**, **b**, **5.6**). Time-dependent optical absorption spectra reveal the formation of 2D nanostructures from clusters (**Figure 5.1g**, **h**). While the thickness of two-layer 2D semiconductor platelets remains the same during growth (confirmed by AFM characterization during different growth times), increase in lateral size results in an increase in optical absorption (**Figure 5.1g**, **h**). Furthermore, careful characterization of charge carrier mobility

during growth of these hexagonal crystal-structured 2D nanosheets/nanoplatelets also reveals slow removal of defects or vacancies in these ultrathin semiconductors, leading to improvement and gradual saturation in carrier mobility (constant charge carrier concentration but the increase in mobility, **Figure 5.1k**). To study other chalcogenide semiconductors, we used colloidal synthesis and cation exchange^{16–19} to form hexagonally-structured PbX, Cu₂X, and Ag₂X (X = S, Se) 2D nanostructured sheets/platelets (AFM and TEM in **Figure 5.1c-f**, **5.5**, XRPD and EDS data in **Figure 5.7**, **5.8**). Optical measurements of these two-layer ultrathin nanostructures were used to measure their strong quantum-confined energy bandgap at room temperature (**Figure 5.1g-j, 5.6**).





Figure 5.1 (a-f) AFM morphological characterization of 2D nanosheets made from (a) CdS; (b) CdSe; (c) Cu₂S; (d) Cu₂Se; (e) PbS; and (f) PbSe. The insets show respective line profiles, with corresponding thicknesses. (g-j) Optical absorption spectroscopy for 2D nanostructures. (g,h) Time evolution of ultraviolet-visible (UV-VIS) spectra for (g) CdS; and (h) CdSe 2D nanosheets. UV-VIS (black) and Fourier-transform infrared (FTIR) spectra (red) of (i) PbS; and (j) Cu₂Se 2D nanostructures. (k) Carrier density and mobility measured with varying synthesis times for CdS and CdSe 2D nanosheets.

Optical spectra for cadmium chalcogenide 2D nanoplatelets reveals a clear split in bandedge absorption peaks for cadmium chalcogenides (**Figure 5.1g, h**). These two peaks correspond to the electronic transition from the electron-heavy hole (1S_e-hh) and electron-light hole (1S_e-lh) quantized states and indicate the energetic splitting of strongly confined heavy/light hole states.^{20,21} The energy split from ensemble optical absorption measurements of CdSe 2D nanosheets, which exhibit two absorption peaks at 2.75 and 2.92 eV (**Figure 5.1h**), was correlated with the theoretically expected difference between light and heavy hole energies. Using this energy split $\Delta E_{lh,hh}$, $\Delta E_{lh,hh} = E_{g,bulk} + \frac{\hbar^2 \pi^2}{2L^2} \left(\frac{1}{m_e} + \frac{1}{m_{lh,hh}}\right)$

 $(E_{g,bulk}$ is the bulk bandgap, m_e mass of the electron, m_{lh} mass of light-hole, and m_{hh} mass of

heavy-hole), we calculated a sheet thickness $L = 1.7 \text{ nm.}^{20,21}$ This matches with the thickness of ~1.6 nm estimated from AFM scans (**Figure 5.1a-f**). Comparatively, the energetic splitting of CdS 2D nanostructures was harder to resolve, with about 0.1 eV difference corresponding to an estimated thickness around 1.5 nm (**Figure 5.1g**). Therefore, these two-layer thick 2D semiconductor nanostructures were used to study the fundamental interactions of charge carriers and investigate novel physical properties in these lead, copper, silver and cadmium chalcogenides.

Tunable exciton-phonon interactions in 2D nanomaterials and the possibility of obtaining phonon-scattering limited ultrahigh mobility using dimensionality in ultrathin semiconductors has generated a lot of interest. To measure the exciton-phonon coupling for bandedge and higher energy excitons in 2D CdSe and CdS nanosheets, we measured the temperature-dependent absorbance from 295 to 20 K. **Figure 5.2a**, **d** shows the blue-shift in the absorbance of 2D CdSe and CdS nanosheets with a decrease in temperature. The excitonic peak of these 2D nanomaterials is broadened by inhomogeneous broadening and interactions of the excitons with longitudinal and acoustic phonons. Using the full-width at half-maximum (FWHM) for different bandedge and higher energy excitons, we decoupled these effects by using temperature-dependent data and the relationship:^{22,23}

$$\Gamma(T) = \Gamma_0 + \gamma_{ph}T + \Gamma_{L0} \frac{1}{(e^{E_{L0}/k_BT} - 1)}$$

where Γ_0 represents the contribution from inhomogeneous broadening, γ_{ph} the exciton-acoustic phonon coupling and Γ_{LO} the exciton-optical phonon coupling (phonon energy $E_{LO} = \hbar \omega_{LO}$). The coupling coefficients were found to be different for CdSe

heavy-hole exciton-phonon ($\Gamma_0 = 25 \text{ meV}$, $\gamma_{ph} = 12 \mu eV/K$ and $\Gamma_{LO} = 11 \text{ meV}$, Figure 5.2b), and the light-hole exciton-phonon ($\Gamma_0 = 40$ meV, $\gamma_{ph} = 36 \ \mu eV/K$ and $\Gamma_{LO} = 50$ meV with energy $\hbar\omega_{LO} = 26.1$ meV, Figure 5.2b). The much lower coupling of phonons with heavy-hole exciton compared to higher energy excitons, and an increase in coupling coefficients with increasing layer thickness (and decrease in the energy difference between states) indicates the phonon-bottleneck arising from the difference in phonon energies compared to the energy spacing of the quantum-confined states. This reduced phonon coupling has also been observed in other 2D CdSe nanosheets ($\Gamma_{LO} = 11.6 \text{ meV}$ (4 ML) and $\Gamma_{LO} = 13.6 \text{ meV} (5 \text{ ML})$.²² The magnitude of light-hole exciton coupling with optical phonons ($\Gamma_{LO} = 50$ meV) suggests that Fröhlich interaction is dominant, especially when comparing with other reported magnitude of $\Gamma_{LO} = 49.4$ meV for CdSe films grown on bulk GaAs substrate²⁴ and $\Gamma_{LO} = 49.02$ meV for atomically thin CdSe nanosheets.²⁵ This is also supported by the increase in the light-hole FWHM for T > 100 K, where the LO phonon contribution is larger (Figure 5.2a). A similar dominant contribution from LO phonons towards higher temperatures has also been observed in CdSe/ZnSe quantum dots for T > 50K.²⁶ To understand the effect of 2D crystal structure on these fundamental properties, we compared the phonon interaction energies from our hexagonal crystal structured 2D CdSe nanosheets to other studies on zinc-blende CdSe 2D nanostructures. The phonon interaction energy and bandgap shrinkage was extracted from the peak shift with temperature using the expression (**Figure 5.2c**): $E_{exc}(T) = E_{exc}(0) - \frac{2a_{ep}}{(e^{\theta/T} - 1)}$ where $E_{exc}(0)$ is the exciton energy

at T = 0 K, a_{ep} is the exciton-phonon interaction, and θ is the phonon temperature. The phonon interaction constants for light-hole exciton ($E_{exc}(0) = 3.05 \text{ eV}$, $a_{ep} = 24.5 \text{ meV}$ and $\theta =$

140 K) and heavy-hole exciton ($E_{exc}(0) = 2.86 \text{ eV}$, $a_{ep} = 36.9 \text{ meV}$ and $\theta = 180 \text{ K}$) are similar to those reported for hexagonal CdSe ($a_{ep} = 36 \text{ meV}$ and $\theta = 179 \text{ K}$ for the bandedge exciton),²⁷ but much higher than the reported values for zinc-blende CdSe 2D nanosheets ($E_{exc}(0) = 2.709 \text{ eV}$, $a_{ep} = 6.6 \text{ meV}$ and $\theta = 87 \text{ K}$).²² However, the coupling coefficients between excitons and LO and acoustic phonons measured in our study are similar to those reported for zinc-blende CdSe 2D nanosheets,²² further indicating that this lower coupling likely arises due to dimensionality.



Figure 5.2 Measurements of exciton-phonon coupling for 2D nanostructures. (a,d) The temperature-dependent absorbance of 2D (a) CdSe; and (d) CdS nanosheets, showing a blue-shift with decreasing temperature. (b,e) Temperature-dependent FWHM for 1Se-lh and 1Se-hh excitons for (b) CdSe; and (d) CdS. The fitted parameters are contributions of inhomogeneous linewidth broadening (Γ_0), coupling coefficients of an exciton-acoustic and exciton-optical phonons (Γ_{LO}) energy phonon $(\gamma_{\rm ph}),$ with (E_{LO}) . (c,f)Temperature-dependent peak positions with the fitted parameters for exciton energy at T = 0K (E_{exc}(0)), phonon interaction energies (a_{ep}) and phonon temperature (θ), for (c) CdSe; and (f) CdS 2D nanostructures.

Our results for coupling between multiexcitons and phonons in CdS nanosheets are

much larger compared with CdSe (Figure 5.2d, e, f). This is also evident by the broad absorbance peak in CdS nanosheets (almost merged bandedge and higher energy exciton), compared with the clear split in two exciton peaks observed in CdSe nanosheets. Our measurements revealed $\gamma_{ph} = 234 \ \mu eV/K$, $\Gamma_{LO} = 134 \ meV$ with $\hbar\omega_{LO} = 37.3 \ meV$ (Figure 5.2e). Comparing these values with other reports on similar bandgap semiconductors, coupling coefficients of ZnO epitaxial layers with $\gamma_{ph} = 11.3 \ \mu eV/K$, $\Gamma_{LO} = 867.1 \ meV$ for banedge excitons, and $\gamma_{ph} = 26.5 \ \mu eV/K$, $\Gamma_{LO} = 783.3 \ meV$ for higher energy excitons, with a larger contribution of LO-phonons above T ≈ 100 K.²⁸ Other reports on GaN ultrathin films have shown lower energy peak with $\gamma_{ph} = 21 \ \mu eV/K$, $\Gamma_{LO} = 525 \ meV$ and higher energy excitons with $\gamma_{ph} = 22 \ \mu eV/K$, $\Gamma_{LO} = 495 \ meV.^{29}$ Our results on CdS nanosheets indicates lower coupling with LO phonons, which is significant for light-emission devices operating above 100 K, but a higher contribution from acoustic phonons compared to other thin epitaxial films. By contrast, bulk ZnSe and ZnSe (QW/MQW) have reported measured coefficients of $\gamma_{ph} = 11 \ \mu eV/K$, $\Gamma_{LO} = 81 \ meV$.³⁰ Our phonon interaction energies (Figure **5.2f**), obtained from the absorbance peak position ($E_{exc}(0) = 3.41 \text{ eV}$, $a_{ep} = 102 \text{ meV}$ and $\theta =$ 320 K) also match well with other reported values for GaN epitaxial layers ($a_{ep} = 121 \text{ meV}$ and $\theta = 316 \text{ K}$).³¹



Figure 5.3 Measurement of electronic DOS (using STS) for 2D nanostructures made from (a) CdS and CdSe ; (b) Cu_2S and Cu_2Se ; (c) Ag_2S and Ag_2Se ; (d) PbS and PbSe. The blue curves show the tunneling current, and the black curves represent the measured electronic DOS for the respective 2D nanomaterials. Some optically allowed transitions are marked with red and green arrows.

To further probe the novel optoelectronic properties of 2D semiconductors, we measured the electronic density of states (DOS) of these 2D nanostructures using scanning tunneling spectroscopy (STS) of single nanoparticles.³² Measurements of CdSe 2D nanosheets clearly reveals the positions of their respective Fermi-levels (0 V in **Figure 5.3**), positions of their conduction band (CB), valence band (VB), and higher energy quantum-confined states in 2D semiconductors (relative to tip ionization energy, 0 eV here), and the energy bandgaps. Using

the measurements of CdSe two-layer nanosheets CdSe (Figure 5.3a), accurate positions of heavy- and light-hole, and the two distinct transitions with the conduction bandedge were measured to be 2.64 and 2.95 eV. These energies correlate well with ensemble optical absorption measurements of CdSe 2D nanosheets (ensemble absorption peaks at 2.75 and 2.92 eV, Figure 5.1h). Similarly, quantum-confined bandedge absorption (Figure 5.1g-j, 5.6) for CdS (Abs: 3.32 eV, STS: 3.31 eV), PbS (Abs: 1.34 eV, STS: 1.41 eV), Cu₂Se (Abs: 2.73 eV, STS: 2.79 eV), Cu₂S (Abs: 2.80 eV, STS: 2.81 eV), Ag₂S (Abs: 1.31 eV, STS: 1.31 eV), Ag₂Se (Abs: 1.00 eV, STS: 0.93 eV), PbSe (Abs: 1.30 eV, STS: 1.21 eV) two-layer 2D nanosheets matches well with the separation of their measured electronic conduction and valence band states (Figure 5.3). Small differences between our STS and optical spectra can be attributed to the formation of a thin double-junction tunnel barrier due to ligands. While Cu₂Se and Cu₂S 2D nanostructures were synthesized with monovalent copper cations (Cu⁺), large surface areas accessible in these ultrathin semiconductors allow it's oxidation to Cu²⁺ ions with time, and results in excess charge carriers which are likely responsible for the broad infrared plasmon absorption seen in these 2D nanosheets (Figure 5.1j, 5.6a).^{33,34} Similar infrared plasmon absorption was also observed for PbS 2D nanosheets, as shown in Figure 5.1i. Therefore, these measurements reveal important information about the optical and electronic DOS in these new 2D nanomaterials and indicate the potential for developing ultrathin 2D plasmonic absorbers from these semiconductor nanosheets.



Figure 5.4 CSAFM measurement of 2D nanostructures. (a) Schematic of the experimental configuration. (b) I-V curves (red) and ln(I)-V curves (green) of Ag₂S 2D nanosheets, with the calculated carrier density and mobility. (c) Measured mobility (green circles, left scale) and carrier densities (red squares, right scale) for PbS, PbSe, Ag₂S, Ag₂Se, Cu₂S, Cu₂Se, CdS and CdSe 2D nanosheets.(d) CSAFM measurements of optoelectronic properties of single 2D nanosheets of CdSe.

To study the electronic properties of PbX, Cu₂X, CdX and Ag₂X 2D nanostructures, we measured charge carrier concentration and carrier mobilities for these 2D nanosheets. While colloidal semiconductor nanostructures allow fabrication of solution-processed thin films, differences in film processing and chemical treatments used for electronically coupling nanostructures can dominate charge transport properties.^{35–37} Therefore, we used CSAFM measurements of single 2D nanosheets to directly measure their electronic properties (schematically shown in **Figure 5.4a**). Using current-voltage (I-V) characteristics of single

2D nanostructures, we measured their conductivity $\sigma (R = \frac{\Delta V}{\Delta I} = \frac{L}{\sigma S})$, where R is resistance, L is contact length, S is contact area of the tip), charge carrier concentration (*n*) and carrier mobility (μ). We used the intermediate bias regime, where the reverse-biased Schottky barrier dominates the total current:^{32,38,39}

$$\ln(I) = \ln(S) + e(\frac{1}{kT} - \frac{1}{E_0})V + \ln J_s$$

where I/S is the current density through the Schottky barrier, E_0 is a parameter depending on carrier concentration n, e is the electron charge, k is Boltzmann constant, and J_s is a function of applied bias. The slope of ln(I) vs. V equals $e(\frac{1}{kT} - \frac{1}{E_0})$, and the carrier concentration was obtained (Figure 5.4b) from the following relationship: $E_0 = E_{00} \operatorname{coth}(E_{00} / kT)$, and $E_{00} = (\hbar e/2)(n/m^*\varepsilon)^{1/2}$ (h: Planck's constant, ε_0 : vacuum permittivity, ε : dielectric constant, and m^* is the electron effective mass). Measured charge carrier concentration $n \sim 10^{17} - 10^{18}$ cm⁻³ for different 2D chalcogenides nanosheets is shown in Figure 5.4c and Table 5.1. Copper chalcogenide 2D nanosheets show the highest charge carrier concentrations (measured immediately after synthesis) likely due to partial oxidation to Cu²⁺. Using carrier concentration and conductivity, we obtained the carrier mobility in different 2D nanostructures ($\sigma = ne\mu$, Figure 5.4c). While these two-layer thin 2D nanosheets are expected to demonstrate very high carrier mobilities limited only by phonon scattering,^{2,3} modest carrier mobilities were measured here $(0.2-1.2 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1})$. Higher mobilities can be expected on using dielectric screening, e.g. using a hafnium-oxide dielectric layer in FETs, as observed for MoS₂ and graphene 2D nanosheets.^{2,3,6} While surface defects, charge trapping etc. can potentially reduce the carrier mobilities achievable in these nanostructures, reduction

of these defects with colloidal 2D nanosheets growth (Figure 5.1k) offer opportunities for making high-efficiency, solution-processed 2D semiconductor films for optoelectronic applications.

Table 5.1 Electron effective mass, relative dielectric constant of the chalcogenides,^{40–44} calculated carrier density, and mobility of two-dimensional nanostructures.

Sample	m*/m ₀	ε _r	Carrier density (10 ¹⁷ cm ⁻³)	Mobility (cm ² V ⁻¹ s ⁻¹)
CdS (48h)	0.19(e), 0.96(hh), 0.23(lh)	9.65	16.4±1.38	0.376±0.056
CdSe (18h)	0.13(e), 0.9(hh), 0.19 (lh)	10.1	10.1±0.16	0.763±0.13
Cu ₂ S	0.3	12.5	18.9 ± 1.38	0.37 ± 0.027
Cu ₂ Se	0.5*	10.3	32.1±5.99	0.143 ± 0.049
Ag ₂ S	0.23	6	8.18±2.37	0.789 ± 0.18
Ag ₂ Se	0.32	11	8.75±1.51	0.4 ± 0.10
PbS	0.105	169	80.9±8.43	0.0669 ± 0.002
PbSe	0.047	210	54.2±1.9	0.214 ± 0.029

To test the optoelectronic properties of these 2D nanostructures, we illuminated single nanosheets with monochromatic light and measured their I-V photoresponse (using CSAFM), under dark and illumination. When normalized to the intensity of incident monochromatic radiation, the excitonic peak positions in the normalized photocurrent spectra ((I_{light} - I_{dark})/P_{light}, **Figure 5.4d**, **5.9**) matches well with the absorption peaks of these nanostructures (**Figure 5.1g, h**). However, the relative intensities of the bandedge ($1S_e$ -hh) and higher energy peaks ($1S_e$ -lh) are reversed from their optical absorption. Using clear splitting of these peaks in CdSe 2D nanosheets (peaks at 2.77 eV and 2.93 eV, **Figure 5.4d**), the light-hole exciton photocurrent at 2.93 eV exceeds the charge carriers collected from heavy-hole

excitons by ~20%. Considering the reversed trend in absorption (~10% higher absorption of light at 2.75 eV vs 2.94 eV, **Figure 5.1h**), the unequal absorbed photon-to-charge collection efficiency (1S_e-lh/1S_e-hh ~ 1/1.32) can be explained by the difference in the exciton-phonon interaction energies for the two peaks ($\Gamma_{LO} = 11 \text{ meV}$ for 1S_e-lh and 54 meV for 1S_e-hh, **Figure 5.2b**) required to dissociate the exciton and create charge carriers following photoexcitation. While stronger light-matter interactions^{4,5} and enhanced light-emission⁹ from 2D semiconductors can enable the design of practical devices, possible differences in exciton-phonon interaction energies for bandedge and higher energy excitons in these novel 2D nanomaterials can also lead to exploration of other interesting multi-excitonic^{45,46} phenomena in these 2D nanosheets now.

In conclusion, we have demonstrated measurements of fundamental charge carrier interactions, optical and electronic properties, and different multiexciton optoelectronic properties for lead, copper, cadmium and silver chalcogenide (S, Se) 2D nanostructures, using colloidal syntheses. Our findings indicate novel physical properties like two- to six-fold smaller exciton-phonon coupling in these 2D nanomaterials, compared with bulk and other low-dimensional semiconductors, for both longitudinal optical phonons and acoustic phonons. Furthermore, high charge carrier mobility in few-layer thick 2D nanomaterials (0.2-1.2 cm²V⁻¹sec⁻¹ without dielectric screening), measurements of their electronic density of states (DOS), infrared plasmon absorption due to oxidation and charge-asymmetry in Cu₂S, Cu₂Se and PbS 2D nanosheets, and optoelectronic measurements of single 2D nanomaterials using current-sensing atomic force microscopy (CSAFM) measurements. These studies provide insights for the development of solution-processable semiconductor nano-architectures,

which utilize dimensionality to modify the charge carrier-phonon coupling and improve conductivity.

Experimental

Materials

Cadmium chloride (99.999%), sulfur (99.5~100.5%), selenium powder (99.99%), trioctylphosphine (TOP, 97%), silver nitrate (99.9999%), lead (II) acetate trihydrate (>99%) and tetrakis (acetonitrile) copper (I) hexafluorophosphate (97%) were purchased from Sigma-Aldrich. 1-dodecylamine (DDA, 98%) and oleylamine (OLA, 80~90%) were purchased from Acros Organics.

Cadmium Sulfide Nanosheet Synthesis

Cadmium sulfide nanosheets were synthesized following the method reported by Son and co-workers¹² with the ligand octylamine (8C-amine) replaced by dodecylamine (12C-Amine). The cadmium-amine precursor was formed with DDA (10 g, 54.0 mmol) and CdCl₂ (275 mg, 1.5 mmol) under 120 °C and aging at the same temperature for 2 hours. The sulfur-amine complex was formed by dissolving elemental sulfur (144 mg, 4.5 mmol) in 5 g (27.0 mmol) DDA with gentle heating. The resulting reddish-brown solution containing the sulfur complex was injected into the cadmium-amine precursor at 50 °C. The final mixture became optically transparent, with a slight light yellow coloration. This solution was slowly heated at 2 °C/min and aged for 96 h at 70 °C. As the nanosheets were formed, the solution became turbid. The 0, 1, 4, 20, 28, 48, 72-hour samples were extracted with a long-needle syringe. The nanosheets were precipitated by centrifuging and washed with ethanol and were stored in chloroform with 3% DDA to ensure stability.

Cadmium Selenide Nanosheet Synthesis

Cadmium selenide nanosheets were synthesized by modifying the reported literature.¹²⁻¹⁵ The cadmium-amine precursor was prepared by heating CdCl₂ (0.15 mmol, 0.275 g), DDA (5 g) and OLA (5 mL) at 120 °C for 2 hours, then decreasing the temperature to 50 °C to avoid solidification. The selenium powder solution was made by dispersing selenium powder (4.5 mmol, 0.355 g) in DDA (5 g) and OLA (5 mL) under vigorous stirring and gentle heating. Rapid injection of Se solution into the cadmium precursor, followed with a 2 °C/min temperature ramp was carried out. The reaction was left at 100 °C for 18 hours. The solution was observed to change from dark-red to turbid yellow. Samples were extracted at 0, 0.5, 2, and 4 hours with a long-needle syringe. The nanosheets were precipitated by centrifuging, washed with excess ethanol (containing 3% TOP), and were re-dispersed in chloroform for further use.

Cation Exchange

Metal Chalcogenides M₂X (M=Cu, Ag and X=S, Se) were synthesized by cation exchange from CdS (98 h sample) and CdSe (18 h sample) nanosheets, using similar method for nanoparticles and nanorods reported by Son and co-workers.^{16–19} Based on the solubility products of different chalcogenides, cation exchange can be easily completed by reactions between cadmium chalcogenides and (excess) metal ion solutions. Lead sulfide and lead selenide were synthesized from the as-made Cu₂S and Cu₂Se. About 10 fold or more (than stoichiometric amount) of metal ions were used to ensure complete transformation.

Metal ion solutions were prepared by dissolving the correspondent metal salts in methanol

with sonication. Tetrakis (acetonitrile) copper (I) hexafluorophosphate, silver nitrate, and lead acetate were used as Cu(I), Ag(I) and Pb(II) sources. Concentrated solutions (About 42, 33, 73 mg/mL for Cu(I), Ag(I) and Pb(II), respectively) ensure complete cation exchange (at least 10 fold excess).

1 mL CdS solution (with estimated concentration less than 10mg/mL) was initially dispersed in 1mL toluene. Under vigorous stirring and at room temperature, 4 mL Cu(I) ion solution was added dropwise, with the solution gradually changes from yellow to brown. After 1 hour of reaction, excess ethanol was added and the precipitate was centrifuged at 5000 rpm and washed with ethanol before being dispersed in 2mL toluene. With this method, Cu₂S, Cu₂Se, Ag₂S, Ag₂Se (with brown, dark brown, black, and black color, respectively) were made.

1 mL Pb(II) solution was added drop by drop into 1 mL Cu₂S solution under vigorous stirring, 0.3 mL TOP was injected to help remove the exchanged copper(I) ions. After the solution color changes from brown to black, excess ethanol was added and the precipitate was centrifuged at 5000 rpm and washed with ethanol before being dispersed in 2 mL toluene. The same procedure starting with Cu₂Se yields PbSe 2D nanostructures.

Transmission Electron Microscopy (TEM)

TEM images were obtained with a Philips CM100 Transmission Electron Microscope at 80 kV. Samples were prepared on FCF-200-Cu (Formvar/Carbon Film on 200 mesh Copper grid) with very dilute nanostructure-toluene solutions.



Figure 5.5 TEM micrographs of (a) CdS, (b) Cu₂S, (c) Ag₂S, (d) PbS, (e) CdSe, (f) Cu₂Se, (g) Ag₂Se, and (h) PbSe 2D nanostructures.

Atomic Force Microscopy (AFM)

AFM measurements were done using a modified Molecular Imaging PicoSPM II setup. Silicon nitride AFM probes (Model DNP-10) for soft contact mode imaging were purchased from Brucker. The force was set to a soft contact. Samples were prepared using a spin coating of diluted nanostructure suspensions in toluene, on a cleaned silicon wafer.

Ultraviolet-Visible (UV-VIS) Spectroscopy

UV-VIS Spectrum was measured using VWR UV-1600PC spectrophotometer (with the wavelength ranging from 190 nm to 1100 nm), in nanostructures dispersed in toluene.



Figure 5.6 UV-VIS spectra (black) and Fourier transformation infrared (FTIR) spectra (red) of (a) Cu₂S, (b) Ag₂S, (c) Ag₂Se, and (d) PbSe 2D nanostructures.

X-Ray Powder Diffraction (XRPD)

The crystal structure of different 2D nanostructures was analyzed by X-ray powder diffraction (XRPD) measurements, using a Scintag XDS 2000 X-ray diffractometer. The measurements were performed using Cu K α radiation at 45 kV and 40 mA.



Figure 5.7 XRD data for (a) CdS, (b) CdSe, (c) Ag_2S , and (d) PbS 2D nanostructures. The data confirms the hexagonal phase observed in these 2D nanostructures and complete cation exchange of CdS 2D nanosheets to silver and lead sulfide nanostructures.

Energy Dispersive X-Ray Spectroscopy (EDS)

Compositional analysis was performed by energy dispersive X-ray spectroscopy (EDS) embedded in FE-SEM JEOL 7401F instrument. The analysis was performed in different modes (2D mapping, point scan, etc.) to test for uniformity and complete cation exchange.



Figure 5.8 EDS spectra showing complete cation exchange of CdS nanostructures to form PbS Ag₂S, and Cu₂S 2D nanostructures. The data presence of only Ag, Pb, Cu and S elemental peaks, with some small signal corresponding to the substrate (silicon) or from the capping ligands (carbon, oxygen). No Cd elemental peaks were detected ensuring complete cation exchange^{16–19} of CdS 2D nanosheets, by use of 10 fold or higher cation solutions.

Low-Temperature optical measurements

Low temperature (295-20K) was done using a closed-loop helium cryostat (cold head Model DE-202A) with a compressor (Model ARS-2HW) made from Advanced Research Systems Inc. Nanostructured thin films were prepared by suspending them in polystyrene and drop-casting them on a cleaned glass slide. UV-VIS measurements were done using VWR UV-1600PC spectrophotometer.

Electronic Measurements

Two techniques, the scanning tunneling spectroscopy (STS) and current sensing atomic force microscopy (CSAFM) were used to obtain the density of states and charge transport characteristics of these two-dimensional nanomaterials. The STS and CSAFM settings and parameters are similar to our previous measurement on TiO₂ nanotubes (described in Chapter 2 to 4). Samples were prepared by drop-casting diluted nanostructure-toluene suspension on indium-tin-oxide (ITO) coated glass substrates.

Photoresponse-CSAFM Measurement

Spectrally-resolved photocurrent was measured using CSAFM by illuminating the sample with different wavelengths of monochromatic light, through the bottom ITO substrate. The current at each wavelength was normalized, using the following equation at a constant applied bias:

Normalized Photocurrent=
$$\frac{I(\lambda) - I_{dark}}{Intensity}$$
,

where $I(\lambda)$ is the current under monochromatic light (wavelength: λ) illumination and I_{dark} is the current measured in dark.

The intensity of light was measured by a Newport power meter (Model 1918-R), with an 818-UV detector. Monochromatic light was provided by using a monochromator (Model sp2150i, Princeton Instruments), together with a Thorlabs 50.8 nm SQ 315-710 nm bandpass color filter.



Figure 5.9 CSAFM measurements of optoelectronic properties of single 2D CdS nanosheets.

Abbreviations	
2D	Two-dimensional
AFM	Atomic force microscopy
CB	Conduction band
CSAFM	Current sensing atomic force microscopy

DDA	1-dodecylamine
DOS	Density of states
EDS	Energy-dispersive X-ray spectroscopy
FET	Field-effect transistor
FTIR	Fourier transform-infrared
FWHM	Full-width at half-maximum
ITO	Indium-tin-oxide
MQW	Multiple quantum wells
OLA	oleylamine
QW	Quantum well
STS	Scanning tunneling spectroscopy
TEM	Transmission electron microscopy
ТОР	Trioctylphosphine
UV-VIS	Ultraviolet-visible
VB	Valence band
XRPD	X-ray powder diffraction

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Chapter 6

Quantum dot-Azotobacter vinelandii living nano-biohybrid organisms cause light-driven air-water reduction: solar-powered living factories Many naturally occurring and synthetic bacteria can accomplish industrially important reactions, like conversion of nitrogen to ammonia in ambient conditions, using chemical energy to generate electrons and reduce readily available chemical feedstocks, and can be labeled as living factories.¹⁻⁶ However, they derive the chemical energy needed sometimes from valuable food stocks, thereby reducing their attraction for energy conversion to useful solar or biofuels. Inorganic photocatalysts directly derive energy from sunlight to generate photoelectrons for reduction of inexpensive and abundant chemical feedstocks like air, water, and carbon-dioxide, but their lack of selectivity, low efficiency, and sometimes use of conditions such as high-temperature and pressure limit their widespread application.⁷⁻¹⁸ Combining these desired functionalities of direct stimuli-activations via light, voltage, or magnetic field, with the versatility of designing desired synthetic metabolic networks in living cells can provide an unprecedented platform for designing and creating multifunctional living nano-biohybrid organisms (or nanorg's), and for specific applications as living solar-powered factories for direct energy conversion to solar fuels.¹⁹



Figure 6.1 (a) Band position of CdS and CdSe nanoparticles (black: CdS1 or CdSe1, red: CdS2 or CdSe2, blue: CdS3 or CdSe3) showing their bandgap, conduction band (CB) and valence band (VB) position (vs. NHE at pH = 7). Water redox potentials are also labeled. (b) Net light-induced hydrogen production from the quantum dot-MoFe nitrogenase biohybrids, in an argon atmosphere. (c) Net light-induced hydrogen production from the quantum dot-cell lysate mixture, in an argon atmosphere. (d) Net light-induced hydrogen and ammonia production from the quantum dot-cell lysate mixture, in dinitrogen atmosphere. 0ML~3ML refer to CdS@ZnS core-shell nanoparticles with 0~3 monolayer ZnS shells, respectively.

The first step towards development of such living organisms is chemical coupling, site-specific self-assembly²⁰⁻²⁴ from dispersion, and energetic coupling between QDs and synthetic bacteria by appropriately choosing QD size and material (core-shells, if different materials required for energetic alignment and chemical coupling/biocompatibility), QD surface charge and ligands, and desired site-specific attachment. To ensure good energetic alignment and efficient electron injection from the conduction band of photoexcited QDs to molybdenum-iron nitrogenase (MFN) enzyme in Azotobacter vinelandii²⁵ for multielectron
reduction of water to hydrogen, we conducted in-situ experiments with MFN from cell-lysate with different cadmium chalcogenide QDs. Since the choice of chalcogen virtually fixes the valence band state and any change in size and therefore quantum confinement tunes the conduction band position,²⁶ we identified different sizes of cadmium sulfide (CdS, **Figure 6.4a**) and cadmium selenide (CdSe, **Figure 6.4b**) QDs can energetically match the reduction potential for the MFN enzyme. Using detailed electrochemical measurements²⁷⁻²⁹ of these QDs, we identified that 3.6, 4.2, and 5.0 nm diameter CdS QDs had the desired electrochemical alignment (**Figure 6.1a, 6.6**), and while small CdSe QDs (2.3 nm) also had desired electrochemical potential, poor charge injection efficiency of photogenerated electron, strong electron-hole recombination, and smaller electron lifetime lead to lower number of photogenerated electrons from CdSe NPs to be utilized by MFN enzyme (**Figure 6.6, 6.7**). Consequently, using water reduction and generation of hydrogen in these in-situ measurements, we observed much lower photocatalytic activity from these nano-biohybrids (**Figure 6.1b, 6.13**).



Figure 6.2 (a) Cell growth inhibition in Burk media with nanoparticles at 200 nM, calculated from **Figure 6.16**. (b) The viability of cells treated with nanoparticle-containing ASC5 media (35 mM HEPES, 5 mM L-ascorbic acid, pH = 7.4), calculated from the resazurin assay result shown in **Figure 6.22**. (c) Colony forming unit and the calculated cell viability (no nanoparticle treatment as 100 %) of cells treated in ASC5 media with nanoparticles at 500 nM. The initial OD₆₀₀ is 10^{-4} . MPA (CZS-MPA), CYS (CZS-CYS), and CA (CZS-CA) refer to 3-mercaptopropionic acid, L-cysteine, and cysteamine-coated CdS@ZnS2ML nanoparticles. CdS-CYS refers to cysteine-coated CdS nanoparticles.

To identify suitable chemical coupling (and ensure biocompatibility, discussed later) and design site-specific attachment and self-assembly in chosen QDs, we tested large CdS and ZnS nanoparticles. These particles were suspended with cell lysate prepared from Azotobacter Vinelandii DJ995 bacteria followed by separation and the resulting protein-bound particles were analyzed using gel electrophoresis (SDS-PAGE) to identify the type of enzymes attached to the nanoparticle surface (**Figure 6.12**). While CdS nanoparticles showed non-specific attachment of different enzymes, ZnS nanoparticles selectively attached

MFN, thereby identifying the suitable choice of material for the QD surface-MFN interaction. We synthesized CdS QDs with different ZnS shell thickness (Figure 6.5) and conducted in-situ testing of biohybrid formed based on the coordination between zinc ion and histidine (Histidine-tagged MFN covalently binds to the ZnS surface of the CdS@ZnS core-shell nanoparticles) under 400 nm light irradiation. Using water reduction to hydrogen and dinitrogen-water reduction for hydrogen/ammonia production, different ZnS shell thickness demonstrated thickness-dependent photocatalytic performance. ZnS shell thickness affects the photogenerated electron transport characteristics and kinetics in CdS core. While increased shell thickness causes surface passivation to reduce surface states/defects, it also serves as a barrier for charge injection of photogenerated electron from the core. For the optimal design of biohybrid, CdS@ZnS core-shell QDs with nominal x monolayers (x=0~3) of ZnS shell and 3-mercaptopropionic acid (MPA) capping ligand were used to realize formation of MFN biohybrid in pH 7.4 media. Using our in-situ testing of hydrogen and ammonia generation under irradiation, with L-ascorbic acid or HEPES as sacrificial agent, significant enhancement of water and dinitrogen reduction (Figure 6.14a, 6.15) was observed in 1 and 2 monolayer thick ZnS shell, with maximum 615 nmol/ml cell lysate/h hydrogen generation rate in water reduction and 527/337 nmol/ml cell lysate/h hydrogen/ammonia generation rate in dinitrogen-water reduction for 2 monolayer thick CdS@ZnS QD-MFN biohybrid. As a comparison, QDs without ZnS shell MFN enzyme attachment show negligible yield. The selective binding of His-tagged MFN to zinc-rich nanoparticle surface is also confirmed by control experiments (Figure 6.14b, c), where addition of imidazole (coordinates with Zn^{2+}) or increasing media acidity (protonates histidine) inhibits such interactions and hence no hydrogen production by the biohybrid was observed (same as using only QD as control). Optimal design of 2 monolayers thick CdS@ZnS QD-MFN biohybrid was also evident by electrochemical impedance spectroscopy (**Figure 6.8**, small total capacitance and charge transport resistance), open-circuit potential decay (**Figure 6.9**, **Table 6.4**, reduced non-radiative charge recombination) and photoluminescence (**Figure 6.5**, removal of surface states), showing the importance of simultaneous optimization of surface tuning, photophysics, and charge tunneling (across QD-shell) in designing highly efficient QD-MFN biohybrids.

Another requirement for making living nano-biohybrid nanorg's was cell uptake^{30–33} and viability³⁴⁻³⁹ of designed QDs. An important aspect of this, besides biocompatibility of ZnS coating, is the ligand and charge on QD surface. Using three-different similar-sized QD ligands with different surface charge: mercaptopropionic acid (MPA, negative charge), cysteamine (CA, positive charge) and cysteine (CYS, zwitterion), we tested cell viability of CdS@ZnS QDs using three-different methods.⁴⁰⁻⁴² First, using cell growth (monitored using optical density) in the growing media (Burk media) with nanoparticles, we have observed high growth inhibition for MPA- and CA-coated nanoparticles (Figure 6.2a, 6.16), but no such inhibition for CYS-capped QDs even at high concentrations (similar to no treatment). Under light irradiation with non-growing nanorg cells in the photocatalytic media (Figure 6.18), cell viability is almost not affected with CYS-coated nanoparticles and low concentration MPA-coated nanoparticles. With higher concentration MPA-coated nanoparticles and even low (50 nM) concentration of CA-coated QDs, a significant decrease in cell viability was observed. Low cell viability renders the cell unable to remove the oxygen

in the air which causes deactivation of MFN enzyme reaction center leading to low ammonia yield (confirmed by conducting the same test in pure dinitrogen atmosphere and ammonia production was increased by almost one fold with CA-coated nanoparticles, **Figure 6.3a**, **b**). The second measure of cell viability used was resazurin dye assay, which also demonstrated high cell viability for zwitterion and negative-charged QDs (**Figure 6.2b**, **6.22**). A more detailed investigation with colony forming unit analysis (CFU) also showed same results (**Figure 6.2c**), with the highest viability for zwitterion and negatively charged QDs, followed by a strong reduction in the number of viable cells with CA-coating. While the cellular uptake with positively charged CA-coated QDs was much higher than negative or zwitterions ligands with similar sizes, strong non-specific attachment of QDs to negatively-charged cell organelles (like DNA, RNA, proteins) could be responsible for low cell viability, especially at high CA-coated QD concentrations.



Figure 6.3 (a, b) Photocatalytic ammonia turnover number (TON) in the air and pure dinitrogen atmosphere (at t = 1 h). The reaction phase contains (a) 200 nM or (b) 500 nM nanoparticles and $OD_{600}=1.0$ bacteria cells. MPA, CYS, and CA refer to CdS@ZnS2ML nanoparticles with 3-mercaptopropionic acid, L-cysteine, and cysteamine capping ligand. (c) Photocatalytic hydrogen and ammonia TON in ASC5, ASC10, ASC25 media (with L-ascorbic acid at 5, 10, 25 nM, respectively). The reaction phase contains 500 nM CYS-coated nanoparticles and $OD_{600}=1.0$ bacteria cells. (d) Photocatalytic hydrogen and ammonia TON of ASC5-CYS500 (CYS-coated nanoparticles at 500 nM, bacteria cell at $OD_{600}=1.0$ in ASC5 media).

Following design and self-assembly of appropriate living QD-Azotobacter vinelandii biohybrid nanorg's (CdS@ZnS with 2 monolayer shells, with cysteine ligand coating and site-specific attachment with histidine-tagged MFN enzyme), we tested their ability to fix light-energy into specific bonds using inexpensive chemical feedstocks like air and water. Optimized bacteria cell optical density (**Figure 6.23**, $OD_{600} = 1.0$), QD concentration (**Figure 6.24**), and irradiation intensity (**Figure 6.26**, 1.6 mW/cm²) were used for the following tests.

While different capping ligands with CdS@ZnS QDs lead to different optimal QD concentrations for improved ammonia production (Figure 6.25), due to different uptake and cell viability, the site-specific attachment of optimally designed CYS-coated CdS@ZnS (2 monolayer) QDs leads to moderate uptake compared to similar CA-capped QDs, but higher yield of ammonia generation with CYS-coated QDs (compared to MPA or CA ligands, Figure 6.25), due to dual effects of cell viability and uptake with different ligand capping and resulting QD surface charge. With cysteine-coated CdS@ZnS2ML nanoparticles at 500 nM with cell optical density (OD_{600}) at 1.0 and under 1.6 mW/cm² 400 nm light irradiation, hydrogen and ammonia production (using solar-driven air-water reduction) were also monitored in photocatalytic media with different L-ascorbic concentration (5, 10, 25 mM). The hydrogen generation (Figure 6.29) saturated at 1.5 hours, similar to the case of ammonia production. Comparison between photocatalytic reaction with QD only and nanorg's show an interesting L-ascorbic acid concentration-dependent yield. Hydrogen production is higher with the nano-biohybrid mixture at the low L-ascorbic acid level, but surpassed by pure nanoparticles at higher L-ascorbic acid concentration, due to faster quench of photogenerated holes and decrease in cell viability with higher L-ascorbic acid concentrations. Ammonia yield (Figure 6.27) is also higher in media with lower L-ascorbic acid concentration. Turnover frequency calculated in the first 1 hour (linear accumulated of ammonia and hydrogen with time) is $8.73 \times 10^3 \text{ s}^{-1}$ and $4.35 \times 10^3 \text{ s}^{-1}$ for ammonia and hydrogen generation (in ASC5 media), respectively (Figure 6.3d).

In conclusion, we have demonstrated the formation of a living QD-Azotobacter Vinelandii DJ995 nano-biohybrid nanorgs via the design of appropriate QDs and facile

mixing, self-assembly, and site-specific attachment of desired nanorg's. Based on the success of in-vitro testing, photocatalytic living cell ammonia and hydrogen production are realized in-vivo through air-water and water reduction using light irradiation in non-growing cells. We have shown the importance of optimal QD material and size design due to alignment and charge injection of a photogenerated electron to MFN-enzyme, the function of biocompatible ZnS shell in site-specific Histidine-tagged MFN enzyme binding, charge transport tuning, CdS cytotoxicity reduction. The cysteine-coated CdS@ZnS (2 monolayers thick) QDs showed sufficient cell uptake and cell viability of nano-biohybrids, to facilitate high-efficiency and high-selectivity in-vivo photocatalytic production of ammonia and hydrogen with an optimized turnover frequency (TOF) of 8.73 x 10^3 s⁻¹ and 4.35 x 10^3 s⁻¹, respectively. This could pave the way of designing highly efficient solar-powered living factories for solar fuel and solar fertilizer generator, using readily available chemical feedstocks. Furthermore, this idea could be extended as a platform technology to design, synthesize, and test other engineered living nano-biohybrid systems, with different combinations of semiconductor nanomaterials and synthetic microorganisms, to harness the power of desired biological processes with multifunctional properties of designer materials like external stimuli-activation with light, electrical pulses, or magnetic field, to wireless communication with living cells.

Experimental

CdS and CdSe nanoparticles (NPs) synthesis

CdS and CdSe nanoparticles were synthesized using a modified method developed by

Peng et al.⁴³ Their size can be controlled by varying the amount of oleic acid (OA) capping ligand. A total 12 g mixture containing 38.4 mg CdO, 316, 1904, or 5712 µl oleic acid (OA) and 1-octadecene (ODE) was vacuum-degassed at 80 °C and refilled with argon for three cycles, followed by heating to 300 °C and injection of sulfur precursor (4.8 mg sulfur powder dispersed in ODE). The resulting reaction phase was cooled down to 250 °C and the CdS nanoparticles were grown for 1 hour. The removal of unconsumed cadmium and oleic acid was performed by extraction with warm CH₃OH (50 °C) in a separation funnel. This process was repeated three times and the resulting ODE layer was obtained and the removal of residue CH₃OH was carried out under vacuum and 80 °C. To transfer the CdS nanoparticles to CHCl₃, the ODE layer was precipitated with CHCl₃ and acetone followed by washing for at least three times. The final CdS nanoparticles were re-dispersed in CHCl₃ and stored in dark. CdSe nanoparticles with different sizes were synthesized using the same method, with the replacement of sulfur precursor by selenium precursor (12 mg selenium powder dispersed in ODE with 41 µl tributylphosphine (TBP)). Ultraviolet-visible (UV-VIS) spectra (Figure 6.4) were measured using the UV1600PC UV-VIS spectrometer (VWR).



Figure 6.4 UV-VIS spectra of (a) CdS (3.6, 4.2, and 5.1 nm) and (b) CdSe (2.3, 2.6, 4.6 nm)

nanoparticles with different sizes.

ZnS shell growth on CdS nanoparticle cores

The growing of CdS@ZnS core-shell nanoparticles was adapted from the method reported by Peng et al.⁴⁴ The size and concentration of CdS core nanoparticles were determined using the following formula:

$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29$$
$$\epsilon = 5500 \times E \times D^{2.5}$$
$$c = A/\epsilon l$$

where λ , E, A are the wavelength, photon energy, and absorbance at first exciton peak, respectively. I is the optical path of the cuvette. D, ϵ , and c are the diameter, extinction coefficient and concentration of the CdS nanoparticles. The CdS stock solution (dispersed in ODE) was determined to have a concentration of 0.0377 mM.

Zinc precursor (0.1 M Zn^{2+}) were prepared by a heating degassed mixture containing 82 mg ZnO, 2.82 ml (2.51 g) OA and 7.2 ml ODE to 250 °C. The resulting clear solution was cooled down and stored in a septum sealed vial. The precursor was gently heated up to about 60 °C prior to use.

Sulfur precursor (0.1 M) was prepared by dispersing 32 mg sulfur powder in 10 ml ODE with sonication. The resulting clear solution was bubbled with argon for 30 min and stored in a septum sealed vial.

ZnS shells were grown using layer-by-layer deposition. A mixture containing 120 nmol CdS core nanoparticles (3.2 ml CdS stock solution) and 2 ml oleylamine (OLA) was vacuum

degassed and recharged with argon for three cycles under 120 °C. A certain amount of zinc and sulfur precursors was injected simultaneously and the reaction phase was kept at 120 °C for 5 min. The reaction was then raised up to 220 °C for the growth (20 min) of first ZnS layer. The reaction was then cooled down to 120 °C and the UV-VIS spectrum was taken to determine the extinction coefficient of the CdS@ZnS core-shell nanoparticles. The resulting solution could be either washed (similar to CdS core nanoparticles) or used for 2nd or 3rd ZnS layer growth. To grow 1~3 monolayer ZnS shell, 0.44, 0.60 and 0.77 ml (determined by simple geometrical calculation, as reported by Peng et. al.) zinc and sulfur precursors (each) were used, respectively. The real thickness of CdS shell and extinction coefficient of CdS@ZnS core-shell nanoparticles (summarized in **Table 6.1, 6.2**) were determined by UV-VIS spectrum (**Figure 6.5a**) and inductively coupled plasma mass spectrometry (ICP-MS), respectively.

The real thickness of the ZnS coating can be estimated from the cadmium and zinc ratio (determined by ICP-MS) by using simple geometrical calculations shown in **Scheme 6.1**. Take 1ML sample as an example:

The volume and moles of CdS core (diameter $D_1=3.55$ nm, density of CdS (CdS) = 4.82 g/cm³, MW~molecular weight):

$$V(CdS) = \frac{\pi}{6} \times D_1^3 = 2.34 \times 10^{-20} cm^3$$
$$n(CdS) = \frac{\rho(CdS) \times V(CdS)}{MW(CdS)} = 7.83 \times 10^{-22} mol$$

The total amount of Cd and Zn (in ppb) was determined by ICP-MS. Due to Zn impurity in Cd precursor used in the synthesis, the shell Zn was corrected by the amount of Zn in the CdS core (assume in a single nanoparticle, the Cd level is the same):

shell
$$Zn(1ML) = total Zn(1ML) - \frac{total Cd(1ML)}{total Cd (0ML)} \times total Zn(0ML) = 25390 ppb$$

The molar ratio of Zn to Cd (AW~atomic weight):

$$r(Zn:Cd) = \frac{shell Zn(1ML)/AW(Zn)}{total Cd(1ML)/AW(Cd)} = 0.462$$

The moles and volume of ZnS shell (density of ZnS $(ZnS) = 4.10 \text{ g/cm}^3$):

$$n(ZnS) = r(Zn:Cd) \times n(CdS) = 3.62 \times 10^{-22} mol$$

$$V(ZnS) = \frac{n(ZnS) \times MW(ZnS)}{\rho(ZnS)} = 0.860 \times 10^{-20} cm^3$$

The total volume and diameter of the CdS@ZnS nanoparticle:

$$V(CdS@ZnS) = V(CdS) + V(ZnS) = 3.20 \times 10^{-20} cm^{3}$$
$$D(CdS@ZnS) = (6 \times V(CdS@ZnS)/\pi)^{1/3} = 3.94 nm$$

The real thickness (in ML, ZnS monolayer thickness d(ZnS) = 0.312 nm):

$$Thickness(ZnS) = \frac{\left(D(CdS@ZnS) - D(CdS)\right)}{\left(2 \times d(ZnS)\right)} = 0.63 ML$$



Scheme 6.1 The CdS@ZnS core-shell nanoparticle, where D_1 (3.55 nm) and D_2 are the diameter of the CdS core and the whole CdS@ZnS nanoparticle, respectively.

CdS@ZnS	Total Cd (ppb)	Total Zn (ppb)	D _{total} (nm)	Real layer
0ML	469720	1427	-	-
1ML	94441	25677	3.94	0.6
2ML	38230	46066	4.91	2.2
3ML	243618	577668	5.74	3.5

Table 6.1 Total Cd and Zn (in ppb) determined from ICP-MS and determination of ZnS shell thickness (Real layer number)



Figure 6.5 (a) Ultraviolet-visible (UV-VIS) spectra and (b) photoluminescence of CdS@ZnS nanoparticles with different layers (nominal 0~3 ML), showing a redshift of absorption and light emission. With increasing numbers of ZnS layers, the first exciton peak in (a) is gradually flattened out. Figure (b) inset shows the change of emission colors from white to pure blue, due to the removal of surface states, as shown in the 0 ML and 1 ML photoluminescence (500~700 nm).

Table 6.2	First	exciton	peak	position,	extinction	coefficient	and real	thickness	of (CdS@	ZnS
nanopartic	les										

First Exciton Peak (nm)	Extinction Coefficient (µM ⁻¹ cm ⁻¹)
405	0.491
418	0.400
418	0.386
418	0.386
	First Exciton Peak (nm) 405 418 418 418

Differential Pulse Voltammetry (DPV) of CdX nanoparticles

DPV was used to determine the CdX nanoparticles conduction and valence band positions.^{27,29,45} This was done using a three-electrode configuration with a 2 mm platinum

plate electrode, platinum wire, and a silver wire as the working, counter, and (quasi-) reference electrode. Ferrocene was used as internal reference. CdX nanoparticles were suspended in CH_2Cl_2 with 100 mM n-Bu₄NPF₆ as the electrolyte. The whole system was purged with argon and the DPV was taken using Bio-logic SP200 potentiostat with the following parameters: 50 ms pulse width, 50 mV pulse height, 200 ms step width and 4 mV step height (which correspond to 20 mV/s scan rate). The results are presented in **Figure 6.6** and the conduction/valence band (CB/VB) positions are listed in **Table 6.3**.



Figure 6.6 Differential pulse voltammetry of (a, b) CdS and (c, d) CdSe nanoparticles colloidal suspension, showing the voltammogram for (a, c) backward and (b, d) forward scan. The arrows indicate the (a, c) conduction band (CB) and (b, d) valence band (VB) position (vs. NHE)

Table 6.3 Bandedge and bandgap information of CdS and CdSe nanoparticles (NPs) obtained

	$E_{CB}(V)$	$E_{VB}(V)$	$E_{g, ec} (eV)$	Eg, op (eV)	D (nm)
CdS1	-0.83	2.25	3.08	3.06	3.55
CdS2	-0.75	2.20	2.95	2.94	4.17
CdS3	-0.61	2.21	2.82	2.79	5.06
CdSe1	-0.72	1.89	2.61	2.50	2.30
CdSe2	-0.53	1.85	2.38	2.38	2.59
CdSe3	-0.31	1.88	2.19	2.07	4.58

from optical (UV-VIS) and electrochemical (DPV) measurement.

Note: E_{CB} , E_{VB} (vs. NHE) are conduction band and valence band position, respectively, from DPV measurements. $E_{g, ec}$ is the electrochemical bandgap determined from the conduction and valence band position ($E_{g, ec} = E_{VB}-E_{CB}$). $E_{g, op}$ is the optical bandgap from UV-VIS measurements ($E_{g, op}$ (eV) = 1239.8 / λ (nm), where λ is the wavelength of the first exciton peak). D is the diameter of the nanoparticles determined from the optical bandgap.

CdS, CdSe, CdS@ZnS nanoparticle thin film electrochemistry

The CdS, CdSe and CdS@ZnS nanoparticles (in ODE) were transferred into CHCl₃ by the above-mentioned method. 50 μ l of about 5 μ M suspension of nanoparticles were drop-casted on clean fluorinated-tin oxide (FTO) coated glass (about 0.5 cm²) and fully dried in a vacuum desiccator. Electrochemical measurements were taken using a three-electrode configuration, with nanoparticle coated FTO glass, platinum wire and Ag/AgCl electrode as working, counter, and reference electrodes. 0.5 M sodium sulfate (pH = 6.4) solution was used as electrolyte. The whole system was bubbled with argon for 20 min before the measurements.

Electrochemical impedance spectroscopy (EIS) was used to evaluate the charge trapping and charge transfer effect in these nanoparticles under light irradiation. Measurements were taken under 365 nm UV irradiation (~5 mW/cm²) at open circuit potential (OCP), with a frequency range from 100 kHz to 100 mHz. These spectra were presented using Nyquist plot (**Figure 6.7, 6.8**).



Figure 6.7 Electrochemical impedance spectroscopy (EIS) of (a, b) CdS and (c, d) CdSe nanoparticle electrodes, represented as Nyquist plots. (b, d) shows the high-frequency part (lower impedance) of the spectra in (a, c).



Figure 6.8 (a) Equivalent circuit used to fit the EIS spectra of CdS@ZnS nanoparticle electrode. This equivalent circuit contains three parts for electrolyte (R_s : solution resistance), interface (R_{ct} : charge transfer resistance, C_{dl} : double-layer capacitance) and semiconductor bulk (C_{sc} , R_{sc} : space charge layer capacitance and resistance; C_t , R_t : capacitance and resistance from defect states). Based on this equivalent circuit, charge trapping in the nanoparticles and charge tunneling through the ZnS shell could be evaluated from the C_{total} ($C_{sc} + C_t$) and R_{sc} , respectively. (b), (c) EIS spectra of CdS@ZnS nanoparticle electrode (**Figure 6.8c** is the same as **Figure 6.8b** with a smaller scale for better showing the spectra of 0~2 ML samples), presented as the Nyquist plot. (d) Evolution of C_{total} ($C_{sc} + C_t$) and R_{sc} with ZnS layer increase. Significant (by 1 magnitude) decrease of C_{total} was observed in samples with 2 and 3 ML ZnS shell compared to 0 or 1 ML samples, indicating notably reduced charge trapping and hence decreased charge recombination. R_{sc} slightly increases with the addition of ZnS shells but still remains small for 2 ML sample. A remarkable increase of R_{sc} was observed when the third ZnS shell was deposited, indicating a significant blocking effect for charge tunneling to the nanoparticle surface.

Open circuit potential (OCP) was measured with "turn-on" and "turn-off" irradiation. The OCP was first measured in dark, followed by irradiation of 365 nm UV light (~5 mW/cm²). The irradiation was continued until the OCP vs time curve levels off (**Figure 6.9**). The lifetime regarding the charge carrier dynamics was extracted from the OCP decay (irradiation "turn-off") curve and listed in Table 6.4. A bi-exponential function,^{27,46}

$$OCP(V) = A_1 e^{-t/t_1} + A_2 e^{-t/t_2}$$

was used to fit the OCP decay curve, where the two time constants (t_1 and t_2) indicate a fast decay for radiative or non-radiative charge recombination and a slow decay of charge injection to water. The coefficient (A_1 and A_2) indicates the relative fraction of these two pathways. In the case of 0 and 1 ML sample, almost all charges end up with recombination. On the other hand, charge injection cannot be ignored in 2 ML sample.



Figure 6.9 OCP change upon light "turn-on" (decrease of OCP, as shown in the vertical line) and "turn-off" (an exponential increase of OCP).

Table 6.4 charge carrier lifetime and coefficient extracted through a bi-exponential fit of the open circuit potential (OCP) decay curve

CdS@ZnS	$A_1(V)$	$t_{1}(s)$	$A_{2}(V)$	t ₂ (s)
0ML	-2.301	1482	-0.158	5680
1ML	-46.82	271.7	-0.0604	4734
2ML	-1.190	544.0	-0.204	3958
3ML	-	-	-	-

Ligand exchange of nanoparticles

Nanoparticles suspended in CHCl₃ were phase transferred into aqueous solution by ligand exchange with 3-mercaptopropionic acid (MPA), L-cysteine (CYS) or cysteamine (CA). In the case of ligand exchange with MPA, 0.1 ml MPA was added to 0.3 ml nanoparticle-CHCl₃ suspension (~10 mM) 0.3 ml EtOH was added and the mixture was vigorously stirred with gentle heating. After about 10 minutes 1 ml 1 M NaOH solution was added and the mixture was kept stirring for another 10 min. The upper part (aqueous phase) was collected centrifuged at 15,000 rpm. The precipitates were resuspended in pH 11 water. The concentration of the nanoparticle suspension was determined using the extinction coefficient obtained above. Ligand exchange with L-cysteine is similar to MPA ligand exchange. In the case of cysteamine, cysteamine hydrochloride was used with the replacement of 1 M NaOH solution by DI water and finally re-suspended in pH 4 water. The ligand-exchanged nanoparticle suspension was stored in the fridge (4 °C) and can be stable up to 1 week.

Azobacter Vinelandii DJ995 bacteria growth and cell lysate preparation

Azobacter Vinelandii DJ995 bacteria (wild type, which produces MoFe nitrogenase with 7x histidine tag on the C-terminal of the α -subunit) were kindly provided by Dennis's group (Virginia Tech).²⁵ The cells were grown in a nitrogen-free modified Burk media (500 ml for each batch, in a 2 L Erlenmeyer flask) with air bubbling (~ 1 LPM) and shaking (~300 rpm) for 24 hours. The resulting cells (dark brown color as shown in **Figure 6.10, left**) were precipitated at 6,000 rpm and washed twice with Tris buffer (25 mM Tris-HCl, 0.5 M NaCl,

pH = 7.9) and stored under -80 °C. The cell lysate was prepared using ultrasonication. The frozen cells were (~8 g) were anaerobically thawed and suspended in 16 ml fully degassed Tris buffer (with 0.2 mM PMSF and 2 mM sodium dithionite) and the resulting cell suspension was ruptured in a side-arm test tube using an ultrasonic probe at full power (Fisher Sonic Dismembrator Model D100). The cell suspension was cooled using an ice-water bath and the sonication was taken at 1 min sonication and 1 min rest cycle for 10 cycles. The ruptured cells were anaerobically transferred to an argon-flushed ultracentrifuge tube (Beckmann Coulter #355618) and centrifuged at 30,000 rpm (Beckmann Coulter L8-70M, with the Ti-45 rotor) for 30 min. The brown supernatant (**Figure 6.10, right**) was dropped into liquid nitrogen (LN2) using an air-tight syringe and stored as pellets in LN2 prior to use.



Figure 6.10 Photos of Azotobacter Vinelandii DJ995 cell pellets (left) and cell lysate (right)

Cell lysate activity determination

The cell lysate activity in proton reduction (hydrogen generation) and dinitrogen reduction was determined by a modified method reported by Dean et. al.⁴⁷

Proton reduction

The reaction was taken in a 25 ml septum sealed vial under argon atmosphere. 1 ml reaction volume containing 25 mM TES (pH 7.4), 2.5 mM ATP, 5.0 mM MgCl₂, 30 mM creatine phosphate and 0.125 mg creatine phosphokinase (CPK) were fully degassed and then added sodium dithionite (solid) to 20 mM. The headspace was charged with argon and the vial was kept in a 30 °C water bath. The reaction was started by injection of 50 ul freshly thawed cell lysate and terminated at 15 min by injecting 0.25 ml 2.5 M H₂SO₄. Headspace gas was analyzed by gas chromatography (SRI 8610C) with a molecular sieves 5A column and thermal conductivity detector (TCD) (sample volume: 0.1 ml). The coefficient between peak area and amount of H₂ (nmol) was determined by pure H₂.

N₂ reduction

 N_2 reduction was conducted similar to proton reduction, with the headspace charged with N_2 gas instead of argon. To avoid interference in the NH₃ assay, 35 mM HEPES (pH 7.4) was used instead of TES. And the termination of the reaction was done by injection of 0.25 ml 0.4 M EDTA at 15 min (pH 8.0). The determination of H₂ using gas chromatography is the same as mentioned above. The determination of NH₃ is done by using o-phthalaldehyde fluorescence method.⁴⁸ 25 µl sample was added into 0.5 ml reagent (pH 7.3) containing 20 mM o-phthalaldehyde, 0.2 M sodium phosphate, 5% ethanol and 3.4 mM mercaptoethanol and the mixture was maintained in dark for at least 30 min. The emission was measured at 472 nm with 410 nm excitation. Different concentration of NH₄Cl was used to obtain the calibration curve (**Figure 6.11**).



Figure 6.11 Calibration curve used in fluorescence ammonia assay.

 Table 6.5 Enzymatic cell lysate activity for proton and dinitrogen reduction

	Product	Cell Lysate Activity (nmol/ml CL/min)
Proton Reduction	H_2	260.4
Diviting and Deduction	H ₂	108.7
Dimtrogen Reduction	NH ₃	112.5

MoFe nitrogenase (MFN) purification

The MoFe nitrogenase produced from Azotobacter Vinelandii DJ995 bacteria have a 7x histidine tag on the C-terminal of its α-subunit, which can be purified using immobilized metal affinity chromatography (IMAC).²⁵ Zinc ion was selected as the binding metal due to the use of reducing agent sodium dithionite (DTT) in the buffer. The column (Hitrap IMAC FF 1 ml, purchased from GE Healthcare) was charged with zinc (using 0.1 M ZnSO₄) and equilibrated with fully degassed equivalent buffer (25 mM Tris-HCl, 0.5 M NaCl, 0.2 mM

PMSF, and 2 mM DTT, pH = 7.9) The cell lysate was loaded followed by washing with equivalent buffer, washing buffer (25 mM Tris-HCl, 0.5 M NaCl, 20 mM imidazole and 2 mM DTT, pH = 7.9) to wash away non-specific binding proteins. The His-tagged MFN was eluted using the elution buffer (25 mM Tris-HCl, 0.5 M NaCl, 250 mM imidazole and 2 mM DTT, pH = 7.9). The elution (dark brown color) was dropped into liquid nitrogen as small pellets and stored for future use. Protein purity and concentration were determined using sodium dodecyl sulfate-polyacrylamide gel electrophoresis (SDS-PAGE) and Bradford assay, respectively.

Selective protein binding to CdS or ZnS

CdS and ZnS particles were synthesized using reaction of 0.1 M Cd²⁺ (CdCl₂) or Zn²⁺ (ZnSO₄) with 0.1 M S²⁻ (Na₂S). The particles were washed with water (twice) and equivalent buffer (twice) and suspended in equivalent buffer. Around 10 mg CdS or ZnS were charged with 1 ml cell lysate and incubated at 4 °C for 1 hour. The mixture was then centrifuged and washed with equivalent buffer (2 x 0.3 ml) and wash buffer (0.3 ml) and resuspended in 0.1 ml equivalent buffer.

Determination of protein bound to CdS or ZnS

The proteins bound to CdS or ZnS were determined using SDS-PAGE. The CdS and ZnS particles bound with proteins were boiled with SDS sample buffer and centrifuged at 10,000 rpm to remove the particles. The samples were loaded on the 12% SDS-PAGE gel and the electrophoresis was run using constant voltage (200 V). The gel was stained with Coomassie G250 to show the protein bands (**Figure 6.12**). Cell lysate and purified MoFe nitrogenase were also tested as references.



Figure 6.12 SDS-PAGE of protein samples. Lane 1 and 6: protein molecular weight marker (From top to bottom: 116.0, 66.2, 45.0, 35.0, 25.0, 18.4, 14.4 kDa). Lane 2: cell-free extraction (cell lysate) from Azotobacter Vinelandii DJ995. Lane 3: purified MoFe nitrogenase (elution from Zn-IMAC column). Lane 4: protein bound to CdS. Lane 5: protein bound to ZnS.

Selective protein binding can be clearly seen with ZnS particles, as a single band was shown (**Figure 6.12, lane 5**). Compared to the purified MoFe nitrogenase (**Figure 6.12, lane 3**), its selectivity in MoFe nitrogenase is as good as the commercial IMAC column. However, CdS showed almost no selectivity in protein binding (**Figure 6.12, lane 4**). This test shows the importance of using ZnS-coated CdS nanoparticles for selective MoFe nitrogenase binding for photocatalytic H₂ or NH₃ production.

CdX:Nitrogenase biohybrid photocatalytic proton reduction

MPA-coated CdS or CdSe nanoparticles were anaerobically mixed with the purified nitrogenase. The mixture was incubated at room temperature for about 10 min and diluted

with fully degassed 100 mM L-ascorbic acid (pH ~ 7.4). The mixture (with 200 nM nanoparticles and 66 nM nitrogenase) was anaerobically transferred to several argon-purged 2 ml GC vials (with a small magnetic stirrer, 0.3 ml liquid volume). Photocatalytic proton reduction was taken by irradiating with a 400 nm LED panel at 1.6 mW/cm². Headspace gas was sampled at 30 min. The results are presented in **Figure 6.13**.



Figure 6.13. Light-induced hydrogen production using (a) CdS and (b) CdSe nanoparticles with or without coupling to MFN

Photocatalytic reaction for nanoparticle-cell lysate (NP-CL) biohybrid

Photocatalytic proton reduction reaction was taken in a 2 ml vial under stirring, with a total reaction volume of 0.3 ml. The reaction phase contained 200 nM nanoparticles, 100 mM ascorbic acid (pH 7.4) was vacuum-degassed and charged with argon (~1.7 ml headspace). Anaerobically thawed cell lysate (15 ul) was swiftly injected into the vial with an air-tight syringe. The mixture was incubated at 30 °C for about 5 min, followed by irradiating using a 400 nm LED panel (with about 1.6 mW/cm² at reaction site) for 30 min. The headspace gas was analyzed by gas chromatography (0.1 ml sampling) using the method mentioned above. Reaction media with the addition of 250 mM imidazole and with higher acidity (pH = 5.9)

were also used.

Photocatalytic N_2 reduction was taken in a similar condition, with the replacement of ascorbic acid by 300 mM HEPES and the headspace gas by UHP grade N_2 . H_2 and NH_3 were analyzed using the methods mentioned above.

The total amount of hydrogen produced from nanoparticle-cell lysate systems (xNP-CL) was compared with the nanoparticle-only (xNP) systems (x=0-3 indicating the number of ZnS shells. The ONP-CL shows (Figure 6.14a) only minor increase of hydrogen production compared to 0NP due to non-selective binding of nanoparticles to both active MoFe nitrogenase and non-active cell components through electrostatic interactions. These two different bindings will enhance and decrease hydrogen production due to catalytic effects and surface reaction site blocking, respectively, and hence no obvious improvement of H₂ generation. And due to the difficulty of electron tunneling through the thick ZnS barrier layer for electron injection to MoFe nitrogenase, 3NP-CL also shows low hydrogen yield. On the other hand, a significant increase of hydrogen production was observed in 1NP-CL (by 2.9 folds) and 2NP-CL (by 1.6 folds) compared to 1NP and 2NP, respectively. The highest H₂ generation rate reaches 3467 nmol/ml CL/h in 2NP-CL. Site-selective binding of His-tagged MoFe nitrogenase on the zinc-rich surface could be one explanation of this high yield. Control experiments with imidazole addition (at a high concentration of 250 mM, pH = 7.4) or using higher acidity (pH = 5.9) environment were performed. Imidazole could competitively bind to zinc and block the available sites for histidine attachment. In lower pH media, histidine is protonated and not able to coordinate with zinc. And as expected, in both cases no change of hydrogen production (Figure 6.14b, c) between xNP-CL and xNP was

observed.



Figure 6.14 Photocatalytic proton reduction using CdS@ZnS nanoparticle-cell lysate biohybrids under 400 nm irradiation in (a) pH 7.4, 100 mM L-ascorbic acid, (b) pH 7.4, 100 mM L-ascorbic acid with 250 mM imidazole, and (c) pH 5.9, 100 mM L-ascorbic acid. NP and NP-CL refer to photocatalytic reaction with only CdS@ZnS nanoparticles and nanoparticle-cell lysate biohybrids, respectively. xML (x=0~3) refers to numbers of nominal ZnS coating.

In the case of dinitrogen reduction with MoFe nitrogenase, both H_2 and NH_3 were generated (**Figure 6.15**). Similar to proton reduction, a significant increase of H_2 and NH_3 yield was observed in 1NP-CL and 2NP-CL, with maximum hydrogen and ammonia production rate of 1587 and 693 nmol/ml CL/h in 2NP-CL. And no improvement of hydrogen yield was observed in 0NP-CL and 3NP-CL. Compared to the enzymatic dinitrogen reduction with MoFe nitrogenase, the deviation of H_2 to NH_3 ratio from 1:2 is probably due to direct

hydrogen generation from nanoparticles.



Figure 6.15 Photocatalytic dinitrogen reduction using CdS@ZnS nanoparticle-cell lysate biohybrids under 400 nm light irradiation, and the generation of hydrogen and ammonia were presented in (a) and (b), respectively. NP and NP-CL refer to photocatalytic reaction with only CdS@ZnS nanoparticles and nanoparticle-cell lysate biohybrids, respectively. xML (x=0~3) refers to numbers of nominal ZnS coating.

Cell growth curve measurement

For the following test using living cells, if not specified, the nanoparticles refer to CdS@ZnS nanoparticles with nominal two-monolayer ZnS shell (CZS). The photocatalytic media refers to 35 mM HEPES buffer (pH = 7.4) with 5, 10 or 25 mM L-ascorbic acid (ASC5, ASC10, and ASC25, respectively) as sacrificial hole quencher.

Cell growth measurement was performed in both Burk media (BM) and photocatalytic media (PCM), with a variation of nanoparticle concentration. Nitrogen-free Burk media Azotobacter Vinelandii culture was obtained at OD_{600} ~1.0 (mid-log phase) and washed twice and resuspended in Burk media or photocatalytic media. The cell growth was taken in the 96 well microplate (30 °C, vigorous shaking) and monitored using a microplate reader (TECAN GENios) controlled by Megellan 7.2 software. Optical density was measured at 590 nm at

different time points. Photocatalytic media charged with CdS-ZnS2ML nanoparticles with different capping ligands (MPA, CYS, CA) at various concentration (50, 100, 200, 500, 750, 1000 nM) were used for cell growth. Cells treated with photocatalytic media and nanoparticles followed by growing in nitrogen-free Burk media were also tested. The cells were first incubated in photocatalytic media (with nanoparticles) for two hours (under both dark and 1.6 mW/cm², 400 nm irradiation), followed by washing and resuspending in Burk media for the growth. For all cell growth measurement, the initial cell OD_{600} is 0.1.



Figure 6.16 Cell growth in nitrogen-free Burk media with different concentrations of nanoparticles. MPA, CYS, CA refer to nanoparticles with 3-mercaptopropionic acid, L-cysteine and cysteamine capping ligand, respectively. CZS and CdS refer to CdS@ZnS nanoparticles with 2ML and 0ML ZnS shell. Blank refers to cell growth in Burk media without nanoparticles. The numbers (50~1000) are the nanoparticle concentration.

The inhibition of cell growth indicates the cell toxicity of the nanoparticles. Here, ligand-dependent cell toxicity can be clearly seen (**Figure 6.16**). While a significant inhibition of cell growth is shown with MPA- or CA-coated CZS nanoparticles, no such inhibition was seen with CYS-coated CZS nanoparticles. Compared to the CZS nanoparticles with same ligand (CYS), some toxicity was observed in CdS nanoparticles. Toxicity in CdS nanoparticles can be due to the leak of Cd^{2+} ions, and the ZnS could prevent such leakage.



Figure 6.17 Cell growth in nitrogen-free Burk media after treating the cells with photocatalytic media ASC5 (5 mM L-ascorbic acid, 35 mM HEPES, pH = 7.4) or Burk media for 2 hours in dark. MPAx, CYSx, CAx (x = 50, 100, 200, 500, 750, 1000 indicating the concentration of nanoparticles in nM) refer to cell treatments in ASC5 media containing nanoparticles with 3-mercaptopropionic acid, L-cysteine and cysteamine capping ligand, respectively (the same below). ASC5C and BMC refer to cell treatments in ASC5 media and Burk media without nanoparticles (the same below).

From the bacteria cell growth, it is obvious that cell treatment in dark with ASC5 media

(no nanoparticles) slightly decrease the cell viability (compared to cell growth in Burk media without treatment) due to L-ascorbic acid inhibition effect. However, compared to cell treatment with or without nanoparticles in ASC5 media, we observed the ligand-dependent cell viability. While no remarkable change was seen in MPA or CYS-coated nanoparticles from low to high concentration (50~1000 nM), a decrease of cell viability starts to appear when cells are treated with 500 nM CA-coated nanoparticles and a complete cease of cell growth for higher concentration (750 and 1000 nM) nanoparticle treatment. This indicates that dark cytotoxicity is very low with CdS@ZnS nanoparticles with MPA and CYS surfactant, where the nanoparticle surface is negatively charged or has zwitterion characters, respectively. On the other hand, CA-coated nanoparticles with positive surface charge can easily penetrate through the cell membrane and non-selectively binds to all cell components (which are negatively charged), showing high toxicity for the cells.



Figure 6.18 Cell growth in nitrogen-free Burk media after treating the cells with photocatalytic media ASC5 or Burk media for 2 hours with 400 nm irradiation at 1.6 mW/cm^2 . The notations are the same as in Figure 6.17.

The photo-toxicity of these nanoparticles is similar to their dark toxicity. While CYS-coated nanoparticles still show no change of cell viability up to 1000 nM, inhibition of cell growth was observed with a high concentration (750 and 1000 nM) MPA-coated nanoparticle treatment. This indicates the non-toxic property of L-cysteine as capping ligands, which is crucial in in-vivo photocatalytic ammonia generation with nanoparticle-living cell systems.



Figure 6.19 Cell growth in ASC5 media in dark. ASC5C, ASC10C, and ASC25C refer to cell growth in photocatalytic media (5, 10, 25 mM L-ascorbic acid, 35 mM HEPES, pH 7.4) without nanoparticles. ASC5-CYS, ASC10-CYS, and ASC25-CYS refer to cell growth in photocatalytic media with cysteine-coated nanoparticles at 500 nM. ASC5N refers to nanoparticles in ASC5 media (without cells).

As shown in **Figure 6.19**, no cell growth was observed in the photocatalytic system. The cell will be dormant in the media (non-growing media) but may resume growth once they were re-suspended in Burk media, as seen in **Figure 6.17** and **6.18**.

Cell viability assay

Cell viability assay was performed in a 96 well microplate using resazurin dye as an indicator. The cells ($OD_{600}=1.0$) were incubated in photocatalytic media with different concentration nanoparticles for two hours (both dark and under 1.6 mW/cm², 400 nm irradiation), followed by washing (twice) and re-suspending them in the same amount of Burk media. Resazurin was added to a final concentration of 0.1 mg/ml and the fluorescence

(excited at 485 nm) was measured at 620 nm using the microplate reader.



Figure 6.20 Resazurin assay for testing cell viability after nanoparticle treatment in photocatalytic media or Burk media for 2 hours in dark. The notations are the same as in Figure 6.17 and 6.19. BM-CYS refers to cell treatment with 500 nM cysteine-coated nanoparticles in Burk media.



Figure 6.21 Cell viability (cell treatment in dark) calculated from the resazurin assay in **Figure 6.20**, by taking the slope of the rising part of the time-dependent fluorescence curve and compared to the control. (a) The ASC5C (mentioned above) is used as control (cell viability = 100%) and cell viability of MPAx, CYSx, CAx is presented. (b) Cell viability of cell treatment with 500 nM L-cysteine coated nanoparticles in different media, using each media (without nanoparticles) as a control. (c) Cell viability with cell treatment in different media (without nanoparticles), using cell treatment in Burk media as a control.

As shown in **Figure 6.20** and **6.21**, no dark toxicity was seen with nanoparticles coated with MPA or CYS up to 1000 nM. On the other hand, toxicity appears when 500 nM CA-coated nanoparticles were used in cell treatment, and with higher concentration (750 and 1000 nM), complete loss of cell viability was observed. Compared with cell treatment in different media charged with or without CYS-coated nanoparticles (500 nM), an only very small decrease of cell viability is shown. Furthermore, cell treatment (without nanoparticles) in different media shows no statistical loss of cell viability with ASC5 and ASC10 compared to cells without treatment (directly growth in Burk media). Only with L-ascorbic acid at

higher concentration (25 mM), a small inhibition effect was observed.



Figure 6.22 Resazurin assay for testing cell viability after treating the cells with photocatalytic media or Burk media with different concentrations for 2 hours with 1.6 $mW/cm^2 400 nm$ light irradiation. The notations are the same as in **Figure 6.20**.

Conclusions obtained from nanoparticle treatment under light irradiation are similar to the correspondent cell growth measurement, where CYS-coated nanoparticles show non-toxic characters and MPA-coated nanoparticles show some toxicity at high concentration (750 and 1000 nM). And compared to resazurin cell viability test with cell treatment in dark, significant decrease of cell viability starts even at low concentration CA-coated nanoparticles, while cell viability is not completely lost even at high nanoparticle concentration, as also seen in the cell growth measurement. Another interesting phenomenon is the cell treatment in different media with or without nanoparticles. While in dark condition, no different of cell
viability is seen with media variation, an increase of cell viability in light irradiation condition was observed with increase L-ascorbic acid concentration. This can be explained by L-ascorbic acid as a better sacrificial agent (quencher) for holes compared to sucrose in Burk media. Under 400 nm light irradiation, the photo-generated holes, which are highly cytotoxic, can be easily quenched by L-ascorbic acid and such effect is facilitated with increasing L-ascorbic concentration. Therefore, higher cell viability was observed in ASC25 media.

Colony Forming Unit (CFU) assay

CFU assay was taken as another evaluation for cell viability. Cell culture was collected at $OD_{600}=1.0$ from nitrogen-free Burk media and washed twice with ASC5 media. Mixture with $OD_{600}=1.0$ bacteria cell, 500 nM nanoparticles (MPA, CYS, CA coated) in ASC5 were incubated at 30 °C for 2 hours. The mixture was then centrifuged and washed twice and resuspended in the same amount of nitrogen-free Burk media. The suspension was diluted step-wise to have the cells with OD_{600} 1, 10^{-2} , 10^{-4} , 10^{-6} , 10^{-8} and 10 µl of each suspension was inoculated on the B-plate (nitrogen-free Burk media with agar, in a squared petri dish). The inoculated B-plates were incubated under 30 °C and the CFU was counted by naked eyes. CFU from $OD_{600}=10^{-4}$ suspension is presented in **Figure 6.2c**, with the calculated cell viability using cells treated with no nanoparticles in ASC5 media as 100%.

Similar to the cell growth and resazurin cell viability test mentioned above (**Figure 6.16-6.22**), with MPA and CYS-coated nanoparticles (500 nM) treatment, no decrease of CFU is seen compared to treatment in the same media (ASC5) without nanoparticles. And the highly toxic CA-coated nanoparticles render the CFU to a very low value, showing only

about 5% cell viability compared to no nanoparticle treatment.

In-vivo photocatalytic ammonia and hydrogen generation test

In vivo photocatalytic reactions were conducted in either 96 well microplates or small test tubes and tested either in the air or pure dinitrogen atmosphere. The mixtures basically contain Azotobacter Vinelandii DJ995 cells, nanoparticles, and photocatalytic media and were incubated at 30 °C for 30 min and 150 μ l mixture was added to the wells and a LED panel with 400 nm emission was used to irradiate the system through the cover, in a top-down mode. Ammonia production was determined using fluorescence assay described above, with the same mixture without irradiation (dark) as a baseline. To optimize the condition for ammonia yield, variations of cell optical density (OD₆₀₀), capping ligands of the nanoparticles, nanoparticle concentration, and irradiation intensity were used.

First, 200 nM MPA-coated nanoparticles were used in ASC5 (5 mM L-ascorbic acid, 35 mM HEPES, pH 7.4) and irradiated with 400 nm light at 1.6 mW/cm² for 1 hour. The Azotobacter Vinelandii DJ995 culture from the Burk media was centrifuged at 6000 rpm and washed twice with ASC5. The cells were added to the above suspension with final OD_{600} from 0.1 to 1.0. The net ammonia production is shown in **Figure 6.23**.



Figure 6.23 Ammonia generation with varying Azotobacter Vinelandii DJ995 cell optical density.

The ammonia production increases with cell optical density, but not linearly. As from Azotobacter Vinelandii DJ995, $OD_{600}=1.0$ is at the mid-log phase of its growth and cells will start lysing at higher density. Therefore, we will use $OD_{600}=1.0$ for our following optimization.

With fixed cell optical density ($OD_{600} = 1.0$), the nanoparticles with different capping ligands (MPA, CYS, CA) and concentrations were used. The ammonia generation is presented in **Figure 6.24**. For MPA and CA-coated nanoparticles, the ammonia yield increases with nanoparticle concentration and have a peak value when 200 nM nanoparticles were used. The yield then drops down with higher nanoparticle concentration. As for CYS-coated nanoparticles, ammonia production levels off at 500 nM nanoparticle

concentration, with no further increase or decrease at higher concentration. This concentration and capping ligand-dependent ammonia yield can be related to varieties of factors, including the cell viability and nanoparticle uptake. To ensure high-efficiency photoelectron transfer from nanoparticles to MoFe nitrogenase, higher nanoparticle uptake is required to have more nanoparticles specifically bind to the active enzyme. Meanwhile, the cells should also be at the living condition, where oxygen in the air is consumed without diffusing into the reactive center to deactivate the oxygen-sensitive nitrogenase. With the cell viability measurement (Figure 6.18, 6.21) with cells treated in photocatalytic media under irradiation, the decrease of ammonia yield at high concentration (MPA and CA-coated nanoparticles) is due to partial loss of cell viability. Though cells have very high uptake for positively charged (CA-coated) nanoparticles, high nanoparticle toxicity at an even low concentration (50 nM) is the main reason for low ammonia yield. Decent uptake and non-toxic character of CYS-coated nanoparticle ensure high ammonia yield. While at lower nanoparticle concentration (50~500 nM) where MPA and CYS-coated nanoparticles show minor loss of cell viability, higher ammonia yield with CYS-coated nanoparticles is mainly due to higher nanoparticle uptake. No further increase of ammonia yield starts beyond 500 nM with CYS-coated nanoparticles could be limited by the amount of bacteria cells.



Figure 6.24 Ammonia turnover number (TON, mol NH₃/mol cells) with fixed cell optical density ($OD_{600}=1.0$) and nanoparticles with varied capping ligands and concentration.

Control experiments with the removal of some components (cells or nanoparticles) from the mixture were also taken. As shown in **Figure 6.25**, no difference of ammonia production between dark and light. Therefore, we ruled out the possibility of ammonia generation from only the bacteria cells or nanoparticles.



Figure 6.25 Control experiments with the removal of nanoparticles (Cells) or cells (MPA500, CYS500, and CA500) from the complete mixture. MPA500, CYS500, and CA500 refer to nanoparticles with correspondent capping ligands at 500 nM.

Irradiation intensity-dependent ammonia yield is also measured, with 500 nM CYS-coated nanoparticles and $OD_{600} = 1.0$ bacteria cells. Light intensity at reaction site from 0.16 to 2.42 mW/cm² was used in this assay. With low irradiation intensity, the ammonia yield is low (**Figure 6.26**) due to the limit of photo-induced electrons produced from nanoparticles. However, at high-intensity irradiation, there is a small decrease of ammonia production and this could probably be related to decreasing of cell viability under strong near-UV light irradiation. In the other tests, optimal light intensity (1.6 mW/cm²) was used.



Figure 6.26 Ammonia TON with irradiation intensity.

With fixed bacteria, cell optical density ($OD_{600} = 1.0$) and nanoparticle concentration (200 and 500 nM), photocatalytic dinitrogen reduction was taken in the air or pure dinitrogen atmosphere. A small test tube with 150 l mixture was sealed with a septum and for replacing air with pure dinitrogen gas, the headspace air was vacuumed and recharged with UHP grade N₂ using a syringe needle connected to the Schlenk line. The vacuum degassing and N₂ recharging were repeated for three cycles to ensure low O₂ level in the reaction system. As shown in **Figure 6.3a**, **b**, no difference of ammonia production was observed between microplate assay and test tube assay in the air, showing no dependence on ammonia production with the experimental setup. No change of ammonia yield was seen in the air or pure dinitrogen when MPA and CYS-coated nanoparticles at 200 and 500 nM were used, which indicates that nitrogen source (dinitrogen in the air or pure dinitrogen) is not a limiting factor. However, with CA-coated nanoparticles, ammonia production increases by almost one fold. This could be explained by the protection of the oxygen-sensitive nitrogenase under an inert atmosphere. Low cell viability in media with CA-coated nanoparticles could render the nitrogenase vulnerable to oxygen toxification as described previously. N₂ protection could be the main reason in higher ammonia production and this also reflects the importance of cell viability in in-vivo light-driven air-water reduction.

With the above optimization, time-dependent ammonia production was measured using photocatalytic ASC5, ASC10, ASC25 (35 mM HEPES with 5, 10, 25 mM L-ascorbic acid, pH = 7.4) and Burk media. The reaction mixture was scaled up from 150 1 to 1 ml to allow multiple sampling. The photocatalytic test was taken in a small test tube covered with aluminum foil and magnetically stirred to ensure enough air supply. 25 μl reaction phase was sampled at certain time point for ammonia assay. As shown in Figure 6.27, net ammonia generation increases with time and levels off at about 1.5 hours for photocatalytic reaction in ASC5 and ASC10 media. Ammonia yield is lower with ASC25 media but doesn't show saturation up to 4 hours. Unlimited sacrificial agent (L-ascorbic acid) supply could be one explanation and lower cell viability in high concentration (25 mM) L-ascorbic acid can be the reason of lower ammonia production. Furthermore, total ammonia production in Burk media is only half compared to ASC5 or ASC10. As from the cell growth curve (Figure 6.16~6.19), cells keep growing in Burk media but stay dormant in photocatalytic media. The consumption of generated ammonia could be the main reason of lower ammonia production. This phenomenon was also reported by Harwood et. al., where methane production is much higher in photosynthetic bacteria R. palustris (light-driven CO_2 reduction by nitrogenase) with non-growing cells compared to growing cells.



Figure 6.27 Ammonia generation with time in photocatalytic and Burk media. The reaction phase (1 ml) contains 500 nM CYS-coated nanoparticles, OD_{600} =1.0 bacteria cells. ASC5, ASC10, ASC25, and BM refer to photocatalytic media (35 mM HEPES with 5, 10, 25 mM L-ascorbic acid at pH 7.4) and Burk media, respectively.

The saturation of ammonia production could be due to depletion of the reducing agent (L-ascorbic acid or sucrose in photocatalytic or Burk media) or an increase of ammonia (inhibitor for MoFe nitrogenase) level in the reaction phase. To prove this assumption, ammonia was removed by separation the cells with centrifugation and replace the reaction phase with new media with nanoparticles every 1.5 hours. As shown from **Figure 6.28a**, ammonia production (partially) resumed with new media, though with decreased yield, as

shown in the recovery (**Figure 6.28b**) of ammonia TON from 100% to ~75% and ~50% in the second and third cycle, respectively. The decrease of recovery could be caused by the loss of cells or cell viability during the long period photocatalytic reaction or with repeated centrifugation and washing.



Figure 6.28 Ammonia TON in ASC5 media with 500 nM CYS-coated nanoparticles and $OD_{600}=1.0$ bacteria cells. (a) The photocatalytic reaction was continued for 3 cycles, each with 1.5 hours. At the end of each cycle, the cells were centrifuged down and recharged with new media. (b) Net ammonia production is presented at 1.5 hour time point in each cycle, and the recovery (with the first cycle as 100%) of the cell in generating ammonia was calculated.



Figure 6.29 Photocatalytic hydrogen generation in ASC5, ASC10, ASC25 media. The reaction phase contains 500 nM CYS-coated nanoparticles and $OD_{600}=1.0$ bacteria cells.

Finally, we tested the cell-nanoparticle system in photocatalytic hydrogen production in

the air atmosphere. The photocatalytic reaction (1 ml total volume) was performed in a small test tube as described above, with a rubber septum to retain the gas phase used for hydrogen quantification with gas chromatography. Headspace gas (total volume: 7 ml) was sampled at the certain time point and 0.1 ml gas was injected for hydrogen detection. Reaction phase contains 500 nM CYS-coated nanoparticles and OD₆₀₀=1.0 bacteria cells in photocatalytic media (ASC5, ASC10, and ASC25). The result is presented in Figure 6.29. Saturation of hydrogen production (Figure 6.29a) is seen at 1.5 hours, similar to the case of ammonia production. Control experiments with complete mixture (cells with nanoparticles in ASC5 media) kept in dark and with the removal of nanoparticles do not show detectable H₂ production. And with nanoparticles only, the H₂ yield is low in ASC5 media. However, with increasing L-ascorbic acid in the media (Figure 6.29b), hydrogen production with only nanoparticles increases and surpasses the yield with nanoparticle-cell mixture. An increase of hydrogen production with only nanoparticles is due to higher quenching rate of photogenerated holes with higher concentration L-ascorbic acid. Due to low nanoparticle uptake, most of the nanoparticles will favor direct charge injection to water for hydrogen production and interaction between non-uptaken nanoparticles will, on the other hand, hamper the hydrogen generation, as shown in lower H₂ yield of nanoparticle-cell compared to the nanoparticle-only system in ASC25 media.

The turnover number of the ASC5-CYS500 system for ammonia and hydrogen production was calculated, taking the number of cells (4.5 x 10^8 /ml x 1 ml = 4.5 x 10^8 at $OD_{600} = 1.0$) into account. The result is presented in **Figure 6.3d**. Turnover frequency within 1 hour (linear accumulation of ammonia and hydrogen) was calculated to be 8.73 x 10^3 s⁻¹

and 4.35 x 10^3 s⁻¹ for ammonia and hydrogen generation, respectively.

Abbreviations	
ASC	L-ascorbic acid
ATP	Adenosine triphosphate
CA	Cysteamine
CB	Conduction band
CFU	Colony forming unit
CL	Cell lysate
СРК	Creatine phosphokinase
CYS	L-cysteine
CZS	CdS@ZnS
DPV	Differential pulse voltammetry
DTT	Sodium dithionite
EDTA	Ethylenediaminetetraacetic acid
EIS	Electrochemical impedance spectroscopy
HEPES	4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid
ICP-MS	Inductive coupled plasma-mass spectroscopy
IMAC	Immobilized metal affinity chromatography
LED	Light emitting diode
LN2	Liquid nitrogen
LPM	Liter per minute
MFN	MoFe nitrogenase
MPA	3-mercaptopropionic acid
MW	Molecular weight
NHE	Normal hydrogen electrode
NP	Nanoparticle
OA	Oleic acid
OCP	Open circuit potential
OD	Optical density
ODE	1-octadecene
QD	Quantum dot
SDS-PAGE	Sodium dodecyl sulfate-polyacrylamide gel electrophoresis
TBP	Tributylphosphine
TCD	Thermal conductivity detector
TOF	Turnover frequency
TON	Turnover number
Tris	Tris(hydroxymethyl)aminomethane
UHP	Ultra high purity
UV-VIS	Ultraviolet-visible
VB	Valence band

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Chapter 7

Photophysical color tuning and integration with ultrathin two-dimensional (2D) optoelectronics for photon upconverting nanoparticles

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Upconversion in solar energy conversion: a brief introduction

The concept of upconversion (UC) can be traced back to Bloembergen's idea in 1959, who proposed that infrared (IR) photons could be detected and counted through sequential absorption in these systems in a process called the quantum counter action.¹ The further detailed explanation was interpreted independently by Auzel, Ovsyankin, and Feofilov in 1966.^{2,3} In principle, the upconversion process describes the nonlinear optical process of combining two or more low-energy photons to generate a single high-energy photon. With the fast development of nanoscience and nanotechnology, nanoscale UC materials have generated significant interest and broadened the scope of UC research, together with the potential for broad applications in energy and biology. Due to their unique merits such as large anti-Stokes shifts,⁴ photostability,^{5,6} sharp emission lines,^{7,8} multicolored emissions,^{9,10} and biological compatibility,^{11,12} lanthanide-doped upconversion nanoparticles (UCNPs) have shown great potential as optical imaging and sensing probes and therapeutic materials for biomedical applications.^{5,6,11,12} Since a major problem limiting the conversion efficiency of solar cells is their insensitivity to a full solar spectrum, UC materials provide an opportunity to increase performance as UC materials are coupled with solar cell devices.^{13–15} The same idea can also be applied to solar fuel production.

Sunlight is the most important renewable energy source which includes infrared, visible, and ultraviolet lights. Incident sunlight filtered through the earth's atmosphere is energetically broad and poses a challenge for efficient conversion to electricity using a finite bandgap semiconductor photocell.¹⁶ Even with crystalline silicon (c-Si, bandgap ~1.1 eV) semiconductor, 31% of the incident sunlight (infrared light) is not absorbed and is simply

transmitted through. Considering a thermodynamic maximum efficiency limit of 31% for conversion of sunlight into electricity, this unused infrared sunlight provides an important opportunity for enhancing the efficiency of solar cell for renewable energy generation and other electronic devices. UCNPs have important implications for solar energy conversion because of the upconversion property of combining two or more infrared photons to generate a single visible or ultraviolet photon. To design appropriate energy upconversion nanocrystals, we can control the infrared radiation absorbed by respective lanthanide ions, and their counterpart upconverted radiation wavelengths to tune the efficiency and emission energy. Even though theoretical predictions claim a significant performance increase when a UC material is coupled to a solar cell, so far no obvious enhanced performance of a UC-coupled solar cell has been reported under normal solar irradiation as compared to a pristine solar cell.^{17,18} But the potential for enhancement of photovoltaic conversion of sunlight by incorporating UC materials has generated much interest, and significant progress has occurred in the area including studies in silicon, dye-sensitized, polymer, wide bandgap, and organic solar cells. Being one of the most important photovoltaic materials, crystalline silicon (c-Si) has been in-depth studied to enhance the photovoltaic efficiency beyond the theoretical thermodynamical Shockley-Queisser limit (~31 %). One of the potential routes is to harness sub-bandgap photons (longer than 1100 nm) using upconversion nanoparticles to enhance absorption in the 800~1100 nm range. In this regard, Er^{3+} -doped UC materials are promising since they absorb in the 1450~1580 nm range and emit strong luminescence at 980 nm, 540 nm, and 650 nm. These absorption bands can be used to generate hot excitons that can contribute to the enhancement of photocurrent. A ~2.5% increase in external quantum

efficiency (EQE) of was reported by coupling erbium-doped sodium yttrium fluoride $(NaYF_4:Er^{3+})$ upconversion microcrystals with c-Si solar cells.¹⁵ Later, Hern ández-Rodr guez et al. reported the application of an Er^{3+} -doped UC material for induced photocurrent in a silicon solar cell by coupling it with Er^{3+} -doped UC up-converter material.¹⁹ A detectable photoresponse is observed under 1480 nm (not able to directly generate photocurrent in silicon due to its 1.1 eV bandgap) laser irradiation, showing an efficiency enhancement of the solar cells with UC nanomaterials.

The same idea has also been used in photocatalytic solar fuel generation. In photoelectrochemical water splitting, Zhang et. al. first reported the coupling of NaYF₄:Yb/Er UCNPs with hematite photoanode and achieved a small incident photon-to-current efficiency 1.24×10^{-4} % by using two of the upconversion emissions (520 and 550 nm) generated from NaYF₄:Yb/Er under 980 nm NIR laser irradiation.²⁰ Later, high efficient H₂ (0.18 mmol/h) and O₂ (0.08 mmol/h) production under 980 nm NIR irradiation was reported by Liu's group, using an Au-NaYF₄:Yb/Er-CdTe-ZnO photoelectrode.²¹ In standalone photocatalytic water splitting, erbium-doped SrTiO₃ was demonstrated to yield high rate H₂ (46.23 µmol h⁻¹ g⁻¹) production.²²

Instead of using chemical doping, we detailed studied the photophysical color tuning of upconversion nanoparticles with surface plasmon polaritons. By using ultrathin two-dimensional (2D) semiconductor nanosheets, we demonstrate the efficacy of color tuning by transforming upconverted light into photocurrent, which can have important applications in solar energy conversion devices, including the solar fuel generators.

<u>Photophysical color tuning using surface plasmon polaritons (SPPs) and coupling</u> <u>UCNPs with 2D nanosheets for NIR-induced photocurrent generation</u>

Combining multiple lower-energy infrared photons to emit a single photon (photon upconversion) can enable important applications in photovoltaics and near-infrared biological imaging. However, efficient utilization of sub-bandgap infrared radiation in these optoelectronic devices requires high upconversion efficiency and precise tunability of emitted visible light. While several studies have utilized chemical doping to tune the color of upconverted light, low upconversion-efficiency can limit their applicability. Here, we demonstrate color tuning of upconversion photoluminescence (UPL) by modulating the photophysics using surface plasmon polaritons. Using absorption of near-infrared light in Yb³⁺ ions, the occupation of different energy states in doped lanthanide nanoparticles was tuned, along with the relative rates of energy transfer to two-different dopants (Er³⁺ and Tm³⁺ here), we show a complete shift in color emission using a chromaticity diagram. Furthermore, by using ultrathin 2D semiconductor nanosheets, we demonstrate the efficacy of color tuning by transforming upconverted light into photocurrent. Therefore, photophysical color tuning and integration of these precisely tuned upconverting nanoparticles with ultrathin semiconductors can pave the way for designed metal nanostructures for highly-efficient utilization of low-intensity sub-bandgap infrared radiation in optoelectronic devices.



Figure 7.1 Room temperature upconversion emission spectra and simplified energy diagram. (a) Representative transmission electron micrograph (TEM) image of two upconversion nanoparticles. The size distribution obtained from several TEM images. Note that, the host and donor are NaYF₄ and 20 % Yb³⁺, and the scale bar is 100 nm for both TEM images. (b) Upconversion emission spectra of six nanoparticles on glass substrates. (c) Energy-level diagram, upconversion excitation, and visible emission schemes for the Yb³⁺-sensitized Er³⁺ and Tm³⁺ system. Dashed, solid, and curly arrows indicate upconversion energy transfer, radiative, and multi-phonon, respectively. The high efficiency of UPL can be achieved by improving the absorption in Yb³⁺ dopants and enhancing the energy transfer between Er³⁺, Tm³⁺, and Yb³⁺ (dashed lines). Yb³⁺ mainly absorbs 980 nm photons.

Upconversion photoluminescence (UPL) has been well-investigated to convert near-infrared excitation into a visible emission through lanthanide doping.⁴ Through controlling the relative concentration of lanthanide dopants, the emission tuning of different colors was obtained by several research groups in recent years,^{8–10,23–26} which has broadened potential applications such as biological imaging, solar cell, photonics and therapeutics.^{7,11,15,27–32} Doped-lanthanide nanoparticles also provide an important alternative

as upconverting nanoparticles (UCNPs), and a model system to study important physical processes like energy transfer, quenching between dopant ions, and different decay mechanisms (radiative and phonon relaxation) between multiple photoexcited states.^{4,7,24,30} Here we show series of synthesized UCNPs (Figure 7.1a, 7.6) and photophysical color tuning using surface plasmon. While generation of surface plasmons on the ultrasmooth gold pyramid substrate resulted in simultaneous improvement of absorption of infrared radiation (in dominant Ytterbium ions, Yb³⁺) using weak electromagnetic or Purcell enhancement,^{33–35} enhanced energy transfer rates between minority Erbium (Er³⁺), Thulium (Tm³⁺) dopant and Yb^{3+} , quenching, and enhancement of non-radiative relaxation, relative completion of energy transfer between ions provides an important opportunity to tune the color of emitted light by modulating the photophysics in these lanthanide dopants. We utilized spectrally-resolved confocal (or depth-resolved) imaging, steady-state and time-resolved upconverted photoluminescence measurements, single nanosheet current sensing AFM (CSAFM), and our theoretical model to decouple different photophysical effects. We also investigated the conversion of upconverted light directly into electric current in single nanoparticle photodetection device using UCNP's coated MoS₂ and CdSe nanosheets, studied using CSAFM.

To understand the relative photon upconversion and photophysics in as-synthesized nanoparticles, different lanthanide doped UCNPs (**Figure 7.1b**) were photoexcited on a glass substrate, using a 980 nm infrared diode laser. We observed a set of upconverted emissions bands corresponding to ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ at 450 nm (blue), ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ at 480 nm (blue), ${}^{1}G_{4} \rightarrow {}^{3}F_{4}$ at 660 nm (red), and ${}^{3}F_{2} \rightarrow {}^{3}H_{6}$ at 690 nm (red) in excited Tm³⁺ dopant; and ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ at 520

nm (green), ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ at 540 nm (green), and ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ at 650 nm (red) in excited Er dopant, respectively.^{23,24,29} Based on the experimental results and reported literature, 23,24,29 we outlined the energy diagram for Er³⁺, Tm³⁺, and Yb³⁺ codoped system, as shown in **Figure 7.1c**. Two emission peaks of Tm below 750 nm were missing because of the optical filter used during these measurements.



Figure 7.2 Confocal images of for blue, red and green emissions of NaYF₄: 20% Yb, 4% Er, 1% Tm nanoparticles on the gold pyramid substrate. (a, d and g) 2D confocal images for blue, green, and red emissions of NaYF₄: 20% Yb, 4% Er, 1% Tm nanoparticles on the gold pyramid substrate. (b, e, and h) 3D confocal scan images of blue, green, and red emissions of UCNPs on the gold pyramid substrate. (c, f, and I) Spatially resolved line intensity for blue, green, and red emissions on the gold pyramid substrate, using the 3D image.

In order to understand the detailed photophysical processes, we performed the plasmon-enhanced UPL experiments on the gold pyramid substrate for different lanthanide doping UCNPs. The periodicity of the pattern was chosen by setting the surface plasmon polariton (SPP) resonance at ~980 nm (Figure 7.7) which can enhance the infrared absorption of the donor (Yb) and the rate of energy transfer to the acceptors (Er and Tm), using Coulomb coupling.³⁶ Since SPP waves produce large fluctuations of charges (and also the electric field), resonant with the incident light waves, they exert a strong Coulombic effect on the near-field electronic and photophysical phenomenon.^{36,37} Using resonant SPP waves on a gold pyramid substrate, with uniform plasmon-enhancement along the gold pyramid, we analyzed the spatially-resolved multispectral UPL data from UCNP coated on the substrate (Figure 7.8). Figure 7.2 showed the blue (Figure 7.2a-c), green (Figure 7.2d-f) and red (Figure 7.2g-i) UPL 2D, 3D mapping and spatially resolved line intensity of NaYF4: 20% Yb, 4% Er, 1% Tm nanoparticles on a gold pyramid substrate using 980 nm incident light, which indicated uniform enhancement along the gold pyramid substrate. We also extracted spatially resolved line intensity for other five samples (Figure 7.9, 7.5) to obtain the values of tip-to-bottom ratios (Figure 7.3b, c), which were used for the further analysis. The spectra of six typical UCNPs on the gold pyramid (Figure 7.3a) showed that the blue and green emission got quenched and the red emission got enhanced compared to Figure 7.1b. Further analysis of respective upconversion enhancements, for different emitted light frequencies (representing respective radiative emission rates from Er and Tm states), revealed that average enhancements observed in blue and green emission (Figure 7.3b, c) were higher than the red emission (Figure 7.3b, c) due to the combination of enhancement and quenching

effects. The lower blue tip-to-bottom ratio compared to the green one in **Figure 7.3b** indicates less quenching on the flat gold for Tm compared to Er because Er and Tm have the same enhancement, which was indicated by the similar red bottom-to-tip ratios of Er, Tm (1 %) codoped UCNPs (**Figure 7.3b**) compared to the one of Tm (1 %) doped UCNPs (**Figure 7.3c**) due to Percell enhancement. The lower blue tip-to-bottom ratio in **Figure 7.3c** compared to the blue one in **Figure 7.3b** can be understood by the combination of less quenching on the flat gold for Tm and more energy transfer from Tm to Er as shown in **Figure 7.4b**.

To decouple the respective photophysical rates using our spatially resolved multispectral UPL data, we developed a model (**Figure 7.11**) describing photoexcitation, energy transfer, radiative and non-radiative recombination and occupation of different Er energy levels. Since Tm and Er have the same energy enhancement based on the observation in **Figure 7.3b**, we can successfully separate each Er energy level from series of Er, Tm (1%) codoped UCNPs. We also conducted experimental measurements on 3% Er doped UCNPs (**Figure 7.12, 7.13**) to understand the relative importance of the photophysical processes. To understand the effect of generation of plasmon waves on energy transfer rates (from Yb to Er), we analyzed the experimental UPL results following the same analysis from the previous work.^{36,38} We obtained an underestimate of the rate of energy transfer enhancement at 980 nm (plasmon enhanced energy transfer) for series of Er, Tm (1%) codoped UCNPs as shown in **Figure 7.4a**. While the rate of energy transfer resonant with the surface plasmons at 980 nm was enhanced ~6 times, our analysis suggests that the other non-resonant energy transfer processes of Er likely remain unchanged (or counterbalanced by enhanced phonon cooling,

quenching). Therefore, this resonant energy transfer, from Yb to Er ions is enhanced at least 6 times, thereby decoupling different photophysical effects in this model UPL system. Our analysis also showed that both energy enhancement and quenching increased with increasing doping concentration (**Figure 7.4a**), which was consistent with the bottom-to-tip ratios as shown in **Figure 7.3b**. To understand the results, we estimated the fraction of energy transfer to Thulium using the spectra on glass and gold pyramid substrates (**Figure 7.1b**, **7.3a**, **7.14**, and **Table 7.1**, **7.2**), respectively. Here we roughly estimated the fraction energy transfer to Thulium using the total intensity of each ion. **Figure 7.4b** showed that both fractions of energy transfer to Tm on the glass and gold pyramid substrates decreased with increasing Er concentration. In other words, the energy transfer to Er became more efficient at the high concentration, which possibly increased the energy distribution in each level in Er itself resulted in the energy enhancement and quenching increase with increasing Er concentration.



Figure 7.3 Tip-to-bottom ratios using spatially resolved line intensity for blue, green, red emissions on the gold pyramid substrate (a) Upconversion emission spectra of six nanoparticles on gold pyramid substrates. (b) Blue, green, and red tip-to-bottom ratios as a function of Er^{3+} concentration for NaYF₄: Yb³⁺, Er^{3+} , Tm³⁺ nanoparticles on gold pyramid substrates. (c) Blue and red tip-to-bottom ratios as a function of Tm³⁺ concentration for NaYF₄: Yb³⁺, Tm³⁺ nanoparticles on gold pyramid substrates.



Figure 7.4 Photophysics and color tuning of upconversion nanoparticles (a) Energy transfer enhancement and quenching as a function of Er^{3+} concentration for NaYF₄: Yb³⁺, Er³⁺, Tm³⁺ nanoparticles on gold pyramid substrates. (b) The fraction of energy transfer to Tm³⁺ as a function of Er³⁺ concentration for NaYF₄: Yb³⁺, Er³⁺, Tm³⁺ nanoparticles on glass and gold pyramid substrates (c) Luminescent photos showing corresponding colloidal solutions. (d) CIE1976 chromaticity diagram of corresponding nanoparticles on glass substrates. Insets: the real color of 3% Er³⁺ and 3% Tm³⁺ nanoparticles. (e) CIE1976 chromaticity diagram of corresponding nanoparticles on gold pyramid substrates.

In order to understand this result, we introduced the theory for resonance energy transfer which has been derived from classical and quantum mechanical consideration. The rate of energy transfer (k_T) between donor (Yb) and acceptor (Er or Tm) is given by,³⁹

$$k_T(r) = \frac{Q_D \kappa^2}{\tau_D r^6} \frac{A}{Nn^4} \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda, \tag{1}$$

where r is the distance between donor and acceptor, Q_D is the quantum yield of donor in the donor in the absence of acceptor, κ^2 is a factor describing the relative orientation in space of the transition dipoles of donor and acceptor (note that, κ^2 is usually assumed to be equal 2/3.), τ_D is the lifetime of the donor in the absence of acceptor, A is a constant, N is Avogadro's number, n is the refractive index of the medium, $F_D(\lambda)$ is the corrected fluorescence intensity of the donor in the wavelength range λ to $\lambda + \Delta \lambda$. $\varepsilon_A(\lambda)$ is the extinction coefficient of the acceptor at the wavelength, λ . In **Equation 1**, only the distance and the overlap integral can affect the energy transfer rate, and other parameters should be constant for light doped NaYF₄. Because different Er doping UCNPs have similar size and narrow size distribution as shown in Figure 7.1a and 7.6, the higher Er concentration with the fixed Yb concentration (20%) in the ~38 nm UCNPs can reduce the distance (r) between the donor (Er) and the acceptor (Yb) according to the probability theory. Thus, the energy transfer rate should increase with the increase of Er concentration according to **Equation 1**, which is in good agreement with the results from our analysis as shown in Figure 7.4a. Since higher Er doping concentration with a higher energy transfer rate should absorb more energy from the donor (Yb), the decrease of the fraction of energy transfer to Tm with the increase of Er concentration on both glass and gold pyramid substrates in Figure 7.4b sounds reasonable.

Another interesting result in **Figure 7.4b** is that more energy transferred to Tm as samples on the gold pyramid substrate compared to the same NPs on the glass substrate, which can be understood by the increase of the overlap integral in **Equation 1** through the SPP coupling. As shown in **Figure 7.7b**, the gold pyramid substrate has a broad absorption at ~980 nm, which not only increases the SPP coupling for the donor (Yb) but also increases it

for the acceptors (Tm, Er). Since one photon process in Tm (${}^{3}H_{6} \rightarrow {}^{3}H_{5}$, **Figure 7.1c**) never interacts with 980 nm photons when the samples on the glass substrate, the SPP coupling should lead more energy transfer to Tm as the samples on the gold pyramid substrate, which is resulted of the high fraction of energy transfer to Tm in **Figure 7.4b**.

The other effect of lanthanide doping and SPP is the color tuning. **Figure 7.4c** directly showed the color change of difference UCNPs solution under a 980 diode laser. In order to understand the SPP color tuning, we estimated the color of UCNPs on the glass substrate using the spectra in **Figure 7.1b**. Transformations from spectra to colors are straightforward and given as, $X, Y, Z = k \int P(\lambda) \alpha_i(\lambda) d\lambda$.⁴⁰ Where, X, Y, Z are the standard CIE primaries, the corresponding functions, α_i (i = X, Y, Z), are color-matching functions, $P(\lambda)$ is the power distribution as a function of wavelength, λ , and k is a constant for self-luminous bodies. Using the relations, $u' = \frac{4X}{X+15Y+3Z}$ and $v' = \frac{9X}{X+15Y+3Z}$.⁴⁰ we calculated the emission color for each samples as shown in **Figure 7.4d**. The photographic and the simulated colors for each sample were almost identical because there were no extra effects for both solution and on the glass substrate. This gave us the confidence to estimate the color tuning by SPP enhancement as shown in **Figure 7.4e**. SPP tuned the color of all samples to the red region since SPP only enhanced red emissions and quenched the blue and green emissions as we discussed above.



Figure 7.5 CSAFM measurements of optoelectronic properties of MoS_2 and CdSe nanosheets, and their behaviors using UCNPs excited by the 980 nm laser. (a) Schematic design of optoelectronic characterization. (b) Photocurrent as a function of wavelength for MoS_2 nanosheets. Inset: Absorbance of MoS_2 nanosheet. (c) Photocurrent as a function of wavelength for CdSe nanosheets. Inset: Absorbance of MoS_2 nanosheet. (d) Photocurrent as a function of 980 nm laser power for corresponding nanoparticles on MoS_2 nanosheets. The slopes indicate two-photon or three-photon process. (e) Photocurrent as a function of 980 nm laser power for corresponding nanosheet. The slope indicates a three-photon process.

To test the upconversion enhanced photovoltaics, we first measured optoelectronic properties of two 3-layered nanosheets, MoS₂ and CdSe (Figure 7.15) using the setup as shown in Figure 7.5a. We illuminated individual nanosheets with monochromatic light and measured their current-voltage photoresponse using current sensing atomic force microscopy (CSAFM), under dark and illumination. When normalized to the intensity of monochromatic radiation, the photocurrents (Figure 7.5b, c) were expected to mimic the absorbance (insets of Figure 7.5b, c) of the nanosheets. Secondly, we measured enhanced photocurrents on two nanosheets with different UCNPs to test the idea on upconversion enhanced photovoltaics. As increased the laser diode power, we observed a continuous increase of photocurrents for all samples. Therefore, these results point to possible pathways to improve photovoltaic effect from these ultrathin 2D nanomaterials using UCNPs. Moreover, we found the slopes were 1.8 for 3% Er, 2.0 for 2% Er, 1% Tm, and 2.7 for 3% Tm doped UCNPs on MoS_2 nanosheets, and 2.9 for 3% Tm on CdSe nanosheets, demonstrating mostly the two-photon absorption for Er and the three-photon absorption for Tm in the excitation process, which were in good agreement with the energy diagram in Figure 7.1c and the result of Figure 7.13. It was interesting to estimate quantum yield (QY) given as, $QY = \frac{I_{UCNP}}{P_{laser} \sum c_j \cdot S_j}$, where I_{UCNP} is the photocurrent on nanosheets coated UCNPs by deducting the dark current, $P_{laser} =$ 164.9 mW is the highest power of the laser diode, c_i is the intensity fraction at j-th peak in Figure 7.1b, S_i is values in Figure 7.5b, c at j-th peak position. We estimated the QY (0.0095% for 3% Tm, 0.011% for 2% Er, 1% Tm, and 0.015% for 3% Er UCNPs on MoS₂ nanosheets, and 0.054% for 3% Tm on CdSe nanosheets) using photocurrent results (Figure

7.5b-e), which were in good agreement with the literature values.⁴¹ Considering SPP enhancement (100 X), we can easily obtain decent quantum yield of upconversion enhanced photovoltaics as the device coupled with SPP structure for future investigation.

In conclusion, we found that not only doping can tune the color of UPL, but also SPP can affect the color emission in lanthanide-doped UCNPs. Our spatially-resolved multi-photon confocal measurements, combined with steady-state UPL and our theoretical model shows that the enhancement occurs due to a combination of weak-Purcell enhancement and increased energy transfer rates. The energy transfer rate increased with increasing Erbium doping concentration because the fraction of energy transfer to Erbium increased combined with the increase of energy transfer rate of Er. These results pointed to the need for careful coupling of plasmon modes with the desired photophysical processes. The upconversion enhanced photovoltaics was tested on 2D nanosheets. These findings can benefit renewable energy applications of UPL and have important implications for other fluorescent and excitonic systems like organic and other excitonic solar cells.

Experimental

Materials

Yttrium oxide (Y₂O₃, 99.9 %), ytterbium oxide (Yb₂O₃, 99.9 %), erbium oxide (Er₂O₃, 99.9 %), thulium oxide (Tm₂O₃, 99.9 %) were purchased from Alfa Aesar. Sodium acetate (CH₃COONa, 99 %), sodium fluoride (NaF, 99 %), molybdenum (IV) sulfide microparticles (MoS₂, < 2 μ m, 99 %) oleic acid (OA, 90 %), 1-octadecene (ODE, 90 %) were purchased from Sigma Aldrich. Acetic acid (CH₃COOH, 99.7 %), potassium hydroxide (KOH, 85 %),

sodium dodecyl sulfate (SDS, 99 %) were purchased from Fisher Scientific. Silicon wafer ([100]-oriented, p-type) was purchased from University Wafer. Gold pellets (99.99 %) were purchased from Kurt Lesker.

Nanoparticle synthesis

The co-doped lanthanide upconversion nanoparticles were synthesized by a thermal decomposition method.⁴² In a typical synthesis (e.g. NaYF₄: 20 % Yb³⁺, 2 % Er³⁺, 1 % Tm³⁺), 87.1 mg Y₂O₃, 39.5mg Yb₂O₃, 3.8 mg Er₂O₃, and 2.1 mg Tm₂O₃ were dissolved in 2 mL CH₃COOH. The lanthanide solution was prepared by dissolving this mixture in 6 mL of oleic acid and heating it to 100 °C under vacuum for 60 min. The fluoride-containing solution was synthesized by dissolving 82.3 mg CH₃COONa and 84.2 mg NaF in 2mL of oleic acid and 10 mL of 1-octadecene at 100 °C under a vacuum for 30 min. The fluoride solution was then heated under nitrogen to 320 °C, and the lanthanide solution was injected within 1 min. The homogeneous, single-phase reaction mixture was maintained at 320 °C for 30 min under nitrogen, and then allowed to cool to room temperature. The nanoparticles were then precipitated by the addition of ~100 mL of acetone, and isolated by centrifugation at 5000 rpm. The samples were re-dispersed and then washed with acetone at least three times. The final products were suspended in toluene for transmission electron microscopy (TEM) characterization and further experiments. Figure 7.1a and 7.6 show TEM image of upconversion nanoparticles with different lanthanide doping concentration and their size distributions.



Figure 7.6 TEM images of co-doped lanthanide upconversion nanocrystals. (a) 1% Er, 1% Tm. (b) 3% Tm. (c) 1% Tm. (d) 0.2% Tm. Note that, the host and donor are NaYF₄ and 20% Yb³⁺, and the scale bar is 100 nm for all TEM images.

Gold pyramid fabrication

The plasmonic substrates were fabricated using the self-limiting anisotropic KOH etching for pyramids, on a silicon template. When the surface of a [100]-oriented silicon wafer is exposed to a solution of KOH, anisotropic etching can lead to gold pyramidal divets.⁴³ We formed such patterns by coating a wafer with gold, selectively removing these layers with photolithography, and immersing the substrate in KOH. The divets were coated with ~250 nm of the gold film by thermal evaporation, which was removed with epoxy to produce gold pyramid arrays. The gold pyramids were smooth, highly reproducible, and exhibited sharp tips with radii of curvature as small as 10 nm (**Figure 7.7a**). The evaporated

gold film has a rough surface after deposition, but the device uses the opposite interface, which is smooth.^{42,44} The gold patterned arrays were then coated with a uniform layer of UCNPs (**Figure 7.8**) and measured their steady state upconverted fluorescence at 980 nm (using an Ocean Optics USB4000 spectrometer).



Figure 7.7 (a) Scanning electron micrograph of a gold pyramid array, made by optical lithography and anisotropic KOH etching, with 2 μ m periodicity. The inset shows higher resolution image of the gold pyramid at a steep angle. (b) The optical absorbance spectrum of the gold pyramid substrate. There is a clear broad plasmon absorption peak at ~980 nm. The peak ~500nm is attributed to interband d-transitions in gold metal.



Figure 7.8 Atomic force microscopy image of the gold pyramid substrate coated with 3% Er UCNPs. White arrows point out a few nanoparticles on the gold pyramid substrate as examples.

2D nanosheets preparation
MoS_2 nanosheets can be prepared using ultrasonication-assisted liquid exfoliation method.⁴⁵ MoS₂ microparticles (2 g) was added to 200 mL of distilled water containing 0.12 g of SDS. The mixture was then ultrasonicated for 2 hours at a minimum power of 20 W. The final solution was dried during 2 days until all the water was removed. The nanostructures were then washed with a hexane/ethanol (50/50 by volume) mixture (3 x 50 ml) and precipitated by centrifuging at 5000 rpm for 5 minutes to remove some of the unbounded SDS. The nanosheets were finally stored in pure ethanol at a concentration about 75 mg/ml.

CdSe nanosheets were prepared using the low-temperature amine-based method,⁴⁶ as described in detail in Chapter 5.

Confocal PL characterization

To analyze the effect of plasmon-enhancement on upconversion photoluminescence, confocal (or depth-resolved imaging) was performed by excitation with a 980 nm femtosecond pulse from a tunable (680-1080 nm) Ti:Sapphire oscillator (140 fs, 80 MHz, Chameleon Ultra-II, Coherent), and by epi-detection with various interference filters used to separate the fluorescent light from the excitation laser beam.⁴⁷ The nonlinear optical process of two-photon absorption by UCNPs allows better spatial resolution with spectrally-resolved two-photon excitation fluorescence microscopy imaging, which was obtained for blue, green, and red emissions here by using filters. The spatial and multispectral resolution allows mapping of upconverted fluorescence with different plasmon enhancements along substrates and extracts spatially resolved line intensity for different color emissions as shown in **Figure 7.2, 7.9, 7.10**.



Figure 7.9 Spatially resolved line intensity for blue, green, and red emissions on the gold pyramid substrate. (a-c) NaYF₄: 20% Yb, 2% Er, 1% Tm nanoparticles. (d-f) NaYF₄: 20% Yb, 1% Er, 1% Tm nanoparticles.



Figure 7.10 Spatially resolved line intensity for blue and red emissions on the gold pyramid substrate. (a, b) NaYF₄: 20% Yb, 3% Tm nanoparticles. (c, d) NaYF₄: 20% Yb, 1% Tm nanoparticles. (e, f) NaYF₄: 20% Yb, 0.2% Tm nanoparticles.

Model of the upconversion processes for Er³⁺ in UCNP

To enable quantitative analysis, a set of equations were established based on the well-known upconversion $process^{4,48-50}$ as shown in **Figure 7.1c**, which summarized the

main upconversion, energy transfer, nonradiative, and radiative processes in the Yb³⁺/Er³⁺ codoped β -NaYF₄ system. To verify the theoretical description, we utilized the following equation to understand the energy transfers (ET) for radiative and nonradiative decay (red marked photophysical processes were observed to be more important in these experiments):^{48–50}

$$\frac{dN_{Er,1}}{dt} = W_{21}N_{Er,2} + C_{50}N_{Er,5}N_{Er,0} - \sigma_{14}IN_{Er,1} - k_2N_{Er,1}N_{Yb,1} - W_1N_{Er,1}$$
$$W_{21}N_{Er,2}: \text{ Non-radiative decay from level 2 to 1}$$

 $C_{50}N_{Er,5}N_{Er,0}$: "Reverse-Auger-like" cross-relaxation (lack of emission from level 3 and 1) $\sigma_{14}IN_{Er,1}$: Direct two-photon absorption in minority erbium (negligible especially for low absorption cross-section)

k₂N_{Er,1}N_{Yb,1}: ET excitation from level 1 to 4

W₁N_{Er,1}: Bandedge emission from level 1 (Not observed in experiments ~1300-1500 nm)

$$\frac{dN_{Er,2}}{dt} = W_{32}N_{Er,3} + \sigma_{02}IN_{Er,0} + k_1N_{Er,0}N_{Yb,1} - \sigma_{25}IN_{Er,2} - k_3N_{Er,2}N_{Yb,1} - W_2N_{Er,2} - W_{21}N_{Er,2}$$

W₃₂N_{Er,3}: Non-radiative decay from level 2 to 1

 $\sigma_{02}IN_{Er,0}$: Non-radiative decay from level 3 to 2 (N_{Er,3} is negligible)

 $k_1 N_{Er,0} N_{Yb,1}$: Direct absorption of 980 nm in minority erbium (negligible due to low Er ~3%) and low absorption cross-section

 $\sigma_{25}IN_{Er,2}$: ET excitation from Yb. This process is resonant with plasmons and is enhanced 6.3 times on tips)

 $k_3N_{\text{Er},2}N_{\text{Yb},1}$: Direct two-photon absorption in minority Erbium (negligible, especially for

low absorption cross-section)

W₂N_{Er,2}: ET excitation from Level 2 to 5

W21NEr,2: Direct emission from Level 1 (Not observed in experiments)

$$\frac{dN_{Er,3}}{dt} = W_{43}N_{Er,4} + C_{50}N_{Er,5}N_{Er,0} - W_{32}N_{Er,3} - W_3N_{Er,3}$$

 $W_{43}N_{Er,4}$: Non-radiative decay from level 3 to 2 (single exponential decay dynamics rule out strong NR decay)

 $C_{50}N_{Er,5}N_{Er,0}$: "Reverse-Auger-like" cross-relaxation (lack of emission from level 3 and 1) $W_{32}N_{Er,3}$: Non-radiative decay from level 3 to 2 ($N_{Er,3}$ is negligible) $W_{3}N_{Er,3}$: Direct emission from level 3 (not observed in experiments)

$$\frac{dN_{Er,4}}{dt} = \sigma_{14}IN_{Er,1} + k_2N_{Er,1}N_{Yb,1} + W_{54}N_{Er,5} - \sigma_{46}IN_{Er,4} - k_4N_{Er,4}N_{Yb,1} - W_{43}N_{Er,4} - W_4N_{Er,4}$$

 $\sigma_{14}IN_{Er,1}$: Direct two-photon absorption in minority erbium (negligible especially for low absorption cross-section)

k₂N_{Er,1}N_{Yb,1}: ET excitation from level 1 to 4

 $W_{54}N_{Er,5}$: Non-radiative decay from level 5 to 4 (single exponential decay dynamics rule out strong NR decay)

 $\sigma_{46}IN_{Er,4}$: Direct three-photon absorption in minority Erbium (negligible especially for low absorption cross-section)

 $k_4N_{Er,4}N_{Yb,1}$: ET excitation from level 4 to 6 (due to small blue emission observed, all analysis of level 6 was neglected here)

 $W_{43}N_{Er,4}$: Non-radiative decay from level 3 to2 (single exponential decay dynamics rule out strong NR decay)

W₄N_{Er,4}: Red UPL

$$\frac{dN_{Er,5}}{dt} = \sigma_{25}IN_{Er,2} + k_3N_{Er,2}N_{Yb,1} + W_{65}N_{Er,6} - C_{50}N_{Er,5}N_{Er,0} - W_{54}N_{Er,5} - W_5N_{Er,5}$$

$$\sigma_{25}IN_{Er,2}$$
: Direct two-photon absorption in minority erbium (negligible especially for low absorption cross-section)

k₃N_{Er,2}N_{Yb,1}: ET excitation from level 2 to 5

 $W_{65}N_{Er,6}$: Non-radiative decay from level 6 to 5 (single exponential decay dynamics rule out strong NR decay)

 $C_{50}N_{Er,5}N_{Er,0}$: "Reverse Auger-like" cross-relaxation (lack of emission from level 3 and 1) $W_{54}N_{Er,5}$: Non-radiative decay from level 5 to 4 (single exponential decay dynamics rule out strong NR decay)

W₅N_{Er,5}: Green UPL

$$\frac{dN_{Er,6}}{dt} = \sigma_{46}IN_{Er,4} + k_4N_{Er,4}N_{Yb,1} - W_6N_{Er,6} - W_{65}N_{Er,6}$$

 $\sigma_{46}IN_{Er,4}$: Direct three-photon absorption in minority erbium (negligible especially for low absorption cross-section)

 $k_4 N_{Er,4} N_{Yb,1}$: ET excitation from level 4 to 6

W₆N_{Er,6}: Blue UPL

 $W_{65}N_{Er,6}$: Non-radiative decay from level 6 to 5 (single exponential decay dynamics rule out strong NR decay)

Due to small blue emission observed, all analysis of level 6 was neglected here.

$$\begin{aligned} \frac{dN_{Yb,1}}{dt} &= I\sigma_{Yb}N_{Yb,0} - k_1N_{Er,0}N_{Yb,1} - k_2N_{Er,1}N_{Yb,1} - k_3N_{Er,2}N_{Yb,1} - k_4N_{Er,4}N_{Yb,1} \\ &- W_{Yb,1}N_{Yb,1} \\ N_{Yb} &= N_{Yb,0} + N_{Yb,1} \end{aligned}$$

$$N_{Er} = N_{Er,0} + N_{Er,1} + N_{Er,2}$$

where k is the energy transfer coefficient, $N_i\,$ is the electron population of level i of \mbox{Er}^{3+} or Yb^{3+} , W_{ij} indicates the nonradiative relaxation rate from level i to level j of Er^{3+} , W_i is the radiative decay rate of level i of Er^{3+} , C₅₀ is the rate of cross-relaxation for ${}^{2}\text{H}_{11/2}$ and ${}^{4}\text{S}_{3/2}$ + $^{4}H_{15/2} \rightarrow ^{2}I_{13/2} + \ ^{4}I_{9/2}. \ \sigma_{ij} \ \text{is the absorption cross-section between level i and } j \ \text{of } Er^{^{3+}} \ (\text{low}$ values for multiphoton 51), $\,\sigma_{Yb}\,$ is the absorption cross-section between level 0 and 1 of $Yb^{3+},$ and I is the pump flux. We conducted detailed experiments to refine the model. For example, we measured the absorbance of nanoparticles, and absence of direct absorption by the minority Er^{3+} dopants and low Er^{3+} doping level (with low absorption cross-section⁵¹) led us to neglect the direct single ($W_1N_{Er,1}$) and two- or three-photon absorption $(\sigma_{25}IN_{Er,2}, \sigma_{14}IN_{Er,1}, \sigma_{46}IN_{Er,4})$, especially at the low laser fluence used in these experiments. Moreover, direct measurements of UPL on glass substrate reveals that direct emission from level 3 $(W_3N_{Er,3}, Figure 7.1c)$ is not observed,^{36,38} and hence reverse Auger-like cross-relaxation process ($C_{50}N_{Er,5}N_{Er,0}$, shown with dotted arrows, Figure 7.1c) and also the occupation of this intermediate level is negligible at steady state. Further, the single exponential decay dynamics shown in time-resolved PL (Figure 7.12) for both red and green the non-radiative relaxation processes for levels 4 emission indicates and 5

 $(W_{54}N_{Er,5}, W_{43}N_{Er,4})$ can be neglected when compared to other energy transfer and radiative relaxation ($k_2N_{Er,1}N_{Yb,1}, W_4N_{Er,4}$ and $k_3N_{Er,2}N_{Yb,1}, W_5N_{Er,5}$). Therefore, the simplified steady-state model for each energy level of Erbium was given as,^{36,38}

$$0 = W_{21}N_{Er,2} - k_2N_{Er,1}N_{Yb,1},$$
(S1)

$$0 = k_1 N_{\text{Er},0} N_{\text{Yb},1} - k_3 N_{\text{Er},2} N_{\text{Yb},1} - W_{21} N_{\text{Er},2}, \qquad (S2)$$

$$0 = k_2 N_{Er,1} N_{Yb,1} - W_4 N_{Er,4},$$
(S3)

$$0 = k_3 N_{Er,2} N_{Yb,1} - W_5 N_{Er,5},$$
(S4)

$$0 = f I \sigma_{Yb} N_{Yb,0} - k_1 N_{Er,0} N_{Yb,1} - k_2 N_{Er,1} N_{Yb,1} - k_3 N_{Er,2} N_{Yb,1}.$$
 (S5)

where fI is the effective pump flux because the emission of Yb³⁺ is proportional to the absorption. This simplified model and experiments reveal several important insights into the photophysics of this coupled system.

Using the experimental data, along with estimates of enhancement of respective non-radiative decay as a function of plasmon-enhancement, we observed that blue and green UPL emissions were strongly quenched on flat gold (**Figure 7.2a-f**), whereas red emission was relatively unaffected (**Figure 7.2g-i**), leading to large apparent UPL enhancements and inverted ratios of green to red emission (**Figure 7.3a**). To account for this morphology dependent quenching on Erbium, we modified **Equation S4** to include quenching:

$$0 = k_3 N_{Er,2} N_{Yb,1} - W_5 N_{Er,5} - k_q N_{Er,5}.$$
(6)

where k_q is the quenching factor. This wavelength-dependence of quenching is not surprising, since the generation of propagating SPP waves can lead to strong quenching close to SPP wavelength (above SPP, additional momentum is required which is not present on ultrasmooth gold⁴³). Therefore, we can successfully decouple the effects of electromagnetic enhancement, quenching (k_q) , and increased phonon cooling rates due to the generation of plasmon waves (Figure 7.11).



Figure 7.11 Schematic of the energy transfer, upconversion, and quenching processes on the top and bottom of the gold pyramid substrate for 3% Er UCNPs. The ultrasmooth gold pyramid provides a good platform to study all of these photophysical processes in the doped-lanthanide nanoparticles.



Figure 7.12 Time-resolved spectroscopy of 3% Er UCNPs. (a) Red emission. (b) Green emission. Note that, the black lines indicate the fit with a single exponential.

Analysis of Purcell enhancement, quenching, and energy transfer enhancement

Figure 7.2d showed a 2D micro-photoluminescence confocal mapping with the green upconversion emission of NaYF₄: 20% Yb, 4% Er, 1% Tm. The large contrast of the top to the bottom of the pyramid indicated that the tips of the pyramids enhanced the photoluminescence. In order to obtain the ratio of the enhancement, we used the 3D map (**Figure 7.2e**) to exact the line spectra (one example was shown in **Figure 7.2f**). We got the average ratio of the top to the bottom was 130 for green emission and the average ratio of red emission was 5.9 which was obtained according to **Figure 7.2g-i**. These outstanding results provided an opportunity for deeply understanding the role of surface plasmon, especially on the energy transfer.

Figure 7.1b and 7.3a showed the upconversion emissions of NaYF₄: 20% Yb, 4% Er, 1% Tm nanoparticles under the excitation of a 980 nm laser diode. The changes in the upconversion emissions intensity ratio of ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ transitions of Er³⁺ on the glass and gold pyramid substrates were interesting. The energy gap between two thermal coupled levels is about 600 cm⁻¹ as estimated from the upconversion emission spectra.⁵² Because the characteristics depend on a thermalization process,^{48,53} the ratio should be related to the heating process by the pumped laser. According to a Boltzmann-type population distribution, the intensity ratio of green upconversion emissions can be presented as, $R = \frac{I_H}{I_S} = Bexp(\frac{-\Delta E}{k_BT})$, where $\Delta E = 600 \text{ cm}^{-1}$, k_B is Boltzmann constant, and B is a constant. By assuming the temperature of the sample on the glass substrate is 300 K, we can estimate the temperature of other two samples according to the ratios of two green emissions as shown in **Table 7.2**. The results were useful for our analysis.

Using Equations S1, S2 and S5, we can get $N_{Yb,1} = \frac{f(1-\alpha)I\sigma_{Yb}N_{Yb,0}}{2k_1N_{Er0}}$. We assume that $N_{Yb,0}$ and $N_{Er,0}$ can be approximated by the total density of Yb^{3+} and Er^{3+} ions in nanoparticles at a low pumping level considering the fact that long after the pulse has ceased.⁵⁰ Then $N_{Yb,1} = \frac{f(1-\alpha)I\sigma_{Yb}N_{Yb}}{2k_1N_{Fr}}$. According to **Equations S1, S3** and S4, we get $W_4 N_{Er,4} = W_{21} N_{Er,2}$ and $W_5 N_{Er,5} = k_3 N_{Er,2} N_{Yb,1}$. Then the green to red ratio is obtained as $R_{G/R} = \frac{W_5 N_{Er,5}}{W_4 N_{Er,4}} = \frac{k_3}{W_{21}} \frac{f(1-\alpha) I \sigma_{Yb} N_{Yb}}{2k_1 N_{Er}} = 2.05 \text{ for the glass substrate (Figure 7.4b). This linear$ pump power dependence agrees with the result reported by Li et al.⁴⁹ Where, we simply take $C = \frac{f(1-\alpha)I}{R_{G/R}} = \frac{16}{2.05} = 7.8 \text{ as a constant, thus } W_{21} = C \frac{k_3 \sigma_{Yb} N_{Yb}}{2k_1 N_{Er}}.$ The important term $W_{21} = \frac{k_3}{2.05} \frac{f(1-\alpha)I\sigma_{Yb}N_{Yb}}{2k_1N_{FT}}$ was obtained, which is the phonon relaxation constant strongly enhanced by the vibrational quanta by the surface hydroxyl group.49 According to $W_{21}(T) = W_{21}(0)(\frac{1}{\exp(\frac{\hbar\omega}{k_{\rm p}T})-1}+1)^{\rm p}$,⁵³ where, $k_{\rm B}$ is the Boltzmann constant, T is temperature, and p is the number of phonons that the ion transfers to the lattice depends on the energy difference between the lower and excited states, ΔE , as well as the dominant phonon energy of the lattice $\hbar\omega$ (p = $\frac{\Delta E}{\hbar\omega}$). Within the temperature range (**Table 7.2**), W₂₁ is a constant.

Using **Equation S2**, we get $N_{Er,2} = \frac{k_1 N_{Er,0} N_{Yb,1}}{W_{21} + k_3 N_{Yb,1}} = \frac{k_1 N_{Er} N_{Yb,1}}{W_{21} + k_3 N_{Yb,1}}$. Then the emission of level 4 is $W_4 N_{Er,4} = W_{21} N_{Er,2} = W_{21} \frac{k_1 N_{Er} N_{Yb,1}}{k_3 N_{Yb,1} + W_{21}}$. On the top of pyramids, only the very sharp tip attaches the nanoparticle, the distance between pyramid and nanoparticle becomes bigger as shown in **Figure 7.11**. Thus the enhancement is dominated on the top of pyramid, and the FDTD indicates the enhancement is about 5, I' = 5I = 5 * 16 = 80 mW. Because of the strong absorption of 980 nm light for gold pyramid (**Figure 7.7**), the energy transfer k_1 should be enhanced as $k'_1 = ak_1$, but the energy transfer between level 0 and level 5 should

be unchanged $(k'_3 = k_3)$ because the energy gap is far away from the absorption peak. But the bottom is different, and the quenching effect is dominated as the flat gold. Using the constant $W_{21} = \frac{k_3}{2.05} \frac{f(1-\alpha)I\sigma_{Yb}N_{Yb}}{2k_1N_{Er}}$, the top to bottom ratio was obtained as,

$$\begin{split} W_4 N_{\text{Er,4bottom}} &= W_{21} N_{\text{Er,2}} = \frac{k_1 N_{\text{Er}} \frac{f(1-\alpha) I \sigma_{\text{Yb}} N_{\text{Yb}}}{2k_1 N_{\text{Er}}}}{k_3 \frac{f(1-\alpha) I \sigma_{\text{Yb}} N_{\text{Yb}}}{2k_1 N_{\text{Er}}} + \frac{k_3}{2.05} \frac{f(1-\alpha) I \sigma_{\text{Yb}} N_{\text{Yb}}}{2k_1 N_{\text{Er}}}}{k_1 N_{\text{Er}}} \\ &= \frac{N_{\text{Er}} f(1-\alpha) I}{\frac{k_3}{k_1} f(1-\alpha) I + \frac{k_3}{2.05 k_1} f(1-\alpha) I} = \frac{N_{\text{Er}}}{\frac{k_1^2 N_{\text{Er}}}{k_1^2 + \frac{k_3}{2.05 k_1}}} = \frac{k_1 N_{\text{Er}}}{(1+\frac{1}{2.05}) k_3} \\ W'_4 N'_{\text{Er,4tip}} &= W_{21} N'_{\text{Er,2}} = \frac{k'_1 N_{\text{Er}} \frac{f(1-\alpha) I' \sigma_{\text{Yb}} N_{\text{Yb}}}{2k'_1 N_{\text{Er}}} + \frac{k_3}{2.05} \frac{f(1-\alpha) I \sigma_{\text{Yb}} N_{\text{Yb}}}{2k'_1 N_{\text{Er}}} \\ &= \frac{5N_{\text{Er}}}{\frac{5k'_3}{k_1'} + \frac{k_3}{2.05 k_1}} = \frac{5N_{\text{Er}}}{\frac{5k_3}{3k_1} + \frac{k_3}{2.05 k_1}} = \frac{5N_{\text{Er}} k_1}{(5/a + \frac{1}{2.05}) k_3} \\ \text{as the ratio} \ R_{\text{red}} &= \frac{\frac{5 + 1.488}{\frac{5}{7} + 0.488}}{\frac{5}{7} + 0.488} = 5.9, a = 6.5. \end{split}$$

Thus the ratio $R_{red} = \frac{5*1.488}{\frac{5}{a}+0.488} = 5.9$, a = 6.5. For the green emission, the top of the pyramid only has enhancement effect with factor 5,

and the bottom of the pyramid with quenching. The top to bottom ratio is given as,

$$W_{5}N_{Er,5bottom} = \frac{W_{5}k_{3}N_{Er,2}N_{Yb,1}}{W_{5} + k_{q}} = \frac{W_{5}k_{3}N_{Er,2}}{W_{5} + k_{q}} \frac{f(1 - \alpha)I\sigma_{Yb}N_{Yb}}{2k_{1}N_{Er}}$$
$$W'_{5}N'_{Er,5tip} = k'_{3}N'_{Er,2}N'_{Yb,1} = k'_{3}N'_{Er,2}\frac{5f(1 - \alpha)I\sigma_{Yb}N_{Yb}}{2k'_{1}N_{Er}} = k_{3}N'_{Er,2}\frac{5f(1 - \alpha)I\sigma_{Yb}N_{Yb}}{2ak_{1}N_{Er}}$$
The ratio, $R_{green} = \frac{5(W_{5} + k_{q})N'_{Er,2}}{aN_{Er,2}W_{5}} = 130$, gives $k_{q} = 27.6W_{5}$.



Figure 7.13 Pump power dependence of upconversion emission intensities of 3% Er UCNPs. The slope is ~2 which indicates a two-photon process.



Figure 7.14 The normal peak fit example for NaYF₄: 20%Yb³⁺, 2%Er³⁺, 1%Tm³⁺ nanocrystals on (a) Glass substrate. (b) Gold pyramid substrate.



Figure 7.15 AFM images of (a) MoS_2 (b) CdSe nanosheets. Topography curves of (c) MoS_2 (d) CdSe nanosheets. Note that, both nanosheets include two to three layers of the materials. CSAFM images of (e) MoS_2 (f) CdSe nanosheets. The scale bar is 200 nm for all images.

	Peak	Intensity (a.u.), Position (nm)						
		Er4%,	Er2%,	Er1%,	Tm3%	Tm1%	Tm0.2%	
		Tm1%	Tm1%	Tm1%				
Glass substrate	${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$	112, 655	70.6, 655	13.4, 652	-	-	-	
	${}^{1}G_{4} \rightarrow {}^{3}F_{4}$	54.5, 664	37.3, 664	7.48, 662	13.8, 664	11.6, 664	4.28, 663	
	${}^{3}F_{2} \rightarrow {}^{3}H_{6}$	10.7, 695	5.14, 696	3.01, 692	4.34, 694	3.03, 693	1.37, 694	
Gold pyramid substrate	${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$	335, 657	216, 659	164, 663				
	${}^{1}G_{4} \rightarrow {}^{3}F_{4}$	889, 677	602, 680	473, 680	454, 679	346, 679	209, 680	
	${}^{3}F_{2} \rightarrow {}^{3}H_{6}$	924, 697	567, 699	539, 698	438, 698	289, 698	194, 698	

 Table 7.1 Summary of peak intensity and position of red emission using the normal peak fit.

 Intensity (a w)

 Desition (aw)

Table 7.2 Summary of peak intensity and position of blue and green emission in **Figure 7.1** and **7.3**.

Intensity (a.u.), Position (nm)

	Peak	Er4%,	Er2%,	Er1%,	Tm3%	Tm1%	Tm0.2%
		Tm1%	Tm1%	Tm1%			
	$^{1}D_{2}\rightarrow ^{3}F_{4}$	19.3,	16.8, 453	14.9,	15.5,	10.8,	5.62, 475
Glass		452		452	453	451	
substrate	$^{1}G_{4} \rightarrow {}^{3}H_{6}$	45.0,	67.5, 477	48.2,	55.3,	43.1,	7.76, 483
		476		476	477	476	
	$^{2}\text{H}_{11/2} \rightarrow ^{4}\text{I}_{15/2}$	56.8,	44.5, 525	8.70,	-	-	-
		524		523			
	${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$	230, 542	173, 542	28.5,	-	-	-
				543			
Gold	$^{1}D_{2}\rightarrow ^{3}F_{4}$	42.5,	15.9, 454	11.5,	24.7,	17.6,	-
pyramid		451		449	452	451	
substrate	$^{1}G_{4}\rightarrow ^{3}H_{6}$	49.0,	49.3, 477	30.5,	89.4,	59.1,	-
		477		477	476	476	
	$^{2}\text{H}_{11/2} \rightarrow ^{4}\text{I}_{15/2}$	85.0,	38.9, 526	27.0,	-	-	-
		525		525			
	${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$	303, 541	149, 542	78.3,	-	-	-
				542			
Temperature (K)		316	302	313	-	-	-
R _{G/R} of Erbium		2.05	2.45	2.13			

Abbreviations

2D	Two-dimensional
AFM	Atomic force microscopy
CSAFM	Current sensing atomic force microscopy
c-Si	Crystalline silicon
ET	Electron transfer
FDTD	Finite-difference time-domain
IR	Infrared
NIR	Near-infrared
NR	Non-radiative
OA	Oleic acid
ODE	1-octadecene
QE	Quantum efficiency
SDS	Sodium dodecyl sulfate
SPP	Surface plasmon polariton
TEM	Transmission electron microscopy
UC	Upconversion
UCNP	Upconversion nanoparticle
UPL	TT

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