

**DEVELOPMENT OF SOLID SOLUTION MATERIALS FOR SOLAR ENERGY
CONVERSION**

by

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Development of Solid Solution Materials for Solar Energy Conversion

Thesis directed by Assistant Professor Gordana Dukovic

Of the many efforts to develop new sustainable and renewable energy resources, hydrogen production from solar driven water splitting has been intensely explored. For this application, it is essential to find and develop semiconductor materials that are able to generate visible light-induced charge carriers at energies suitable for water splitting, which is the ultimate goal of the projects in this dissertation.

A bulk scale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, solid solution of GaN and ZnO, is a promising photocatalyst for overall water splitting under visible illumination. Even though it exhibits composition-dependent visible absorption, the value of x (ZnO content) that can be obtained for the bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is limited in the conventional synthetic route. Thus, it was desirable to develop a new synthetic route for $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with a wide range of x values in order to investigate the potential of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ in solar energy absorption. In addition, nanoscale semiconductors generally show better photocatalytic properties than their bulk counterparts in many aspects. The work described in Chapter 2 and 3 details the synthesis, reaction mechanism, and structural and optical characterizations of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with a wide range of compositions. We examined how the band gap depends on composition and observed a minimum of 2.25 eV at $x = 0.87$. Finally, we find that $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals exhibit photoelectrochemical water oxidation activity that is higher than that of bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with the same composition.

Cobalt mixed-metal spinel oxides, $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, have been predicted to exhibit favorable properties as photocatalysts for solar energy conversion. Chapter 4 focuses on the synthesis and structural and optical characterizations of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ with a range of $0 \leq x \leq 1$. UV-vis absorbance data revealed that the absorption onset energies decreased monotonically with increasing x . Finally, the photocatalytic activities were evaluated via photodegradation of methyl orange. Remarkably, low energy (<2.5 eV) ligand-field transitions contributed between 46–72% of the photoactivity of $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$.

This thesis is dedicated to my parents.

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Table of Contents

List of Tables	xi
List of figures	xii
List of schemes	xviii
Chapter 1. Introduction	1
1.1 Motivation	1
1.2 Background	2
1.2.1 Visible light driven overall water splitting	3
1.2.2 Photocatalytic and photoelectrochemical water splitting.....	4
1.2.3 Common deficiencies of single semiconductors.....	8
1.2.4 Solid solution and Vegard's law.	10
1.2.5 Solid solution of GaN and ZnO, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$	12
1.2.6 Cobalt based mixed metal spinel oxide, CoM_2O_4	14
1.3 Summary and Outline of Dissertation	16
1.4 References	17
Chapter 2. $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ Nanocrystals: Visible Absorbers with Tunable Composition and Absorption Spectra.....	25
2.1 Introduction	25
2.2 Results and Discussion	28
2.2.1 Synthesis of nanocrystalline starting precursors and $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$	28
2.2.2 Role of nitridation temperature.	29

2.2.3 Control of oxy(nitride) composition.	31
2.2.4 Particle crystallinity.	35
2.2.5 Optical spectra as a function of composition.	36
2.3 Conclusion	38
2.4 Experimental.....	39
2.4.1 Chemicals.....	39
2.4.2 Synthesis of ZnGa_2O_4 nanocrystals.....	39
2.4.3 Synthesis of ZnO nanocrystals.....	39
2.4.4 Ligand exchange procedure for ZnGa_2O_4 nanocrystals.	40
2.4.5 Synthesis of nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$	40
2.4.6 Characterization.	41
2.5 References	42
Chapter 3. Synthesis and Characterization of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ Nanocrystals with a Wide Range of Compositions	46
3.1 Introduction	46
3.2 Results and Discussion	49
3.2.1 Formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals	49
3.2.2 $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with a broad range of compositions.....	58
3.2.3 PEC activity of bulk and nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$	66
3.3 Conclusions	70
3.4 Experimental.....	71
3.4.1 $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystal synthesis.	71
3.4.2 Characterization.	71

3.4.3 Fabrication of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)/\text{FTO}$ Electrodes.	72
3.4.4 Measurement of Visible Light Induced PEC Current from $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)/\text{FTO}$ Electrodes.....	72
3.5 References	73
Chapter 4. Synthesis, Optical, and Photocatalytic Properties of Cobalt Mixed-Metal Spinel Oxides $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$	
4.1 Introduction	80
4.2 Results and Discussion	83
4.2.1 Single-source (ss) route to bulk spinel oxides, ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($x=0, 0.5$, and 1)	83
4.2.2 Multi-source (ms) route to nano and bulk spinel oxides, ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($x=0, 0.25, 0.50, 0.75$, and 1)	88
4.2.3 Optical properties of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ materials.....	92
4.2.4 Photocatalytic degradation of methyl orange (MO).	94
4.3 Conclusions	99
4.4 Experimental.....	100
4.4.1 Chemicals.....	100
4.4.2 Preparation of $[\text{Ga}(\text{O}^t\text{Bu})_3]_2$	101
4.4.3 Synthesis of single-source (ss) molecular precursors, $[\text{Co}\{\text{M}(\text{O}^t\text{Bu})_4\}_2]$ (M= Al or Ga):	101
4.4.4 Single-source (ss) route to bulk ss- CoM_2O_4 (M= Al or Ga)	101
4.4.5 Multi-source route (ms) to nanoscale ms- CoM_2O_4 (M= Al or Ga) and ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($x=0.25, 0.5$, and 0.75) nanocrystals	102

4.4.6 Photocatalytic activity test	102
4.4.7 Recyclability and stability test of the photocatalysts	103
4.4.8 Photodegradation of phenol	103
4.4.9 Characterization	104
4.5 References	105
Chapter 5. Conclusion.....	108
Bibliography	111

List of Tables

Table 1.1 Lattice parameters (a and c) of GaN and ZnO.....	12
Table 2.1 Elemental analysis for 650 °C nitridation with varying x . Reprinted with permission from Lee et al. <i>Nano Lett.</i> 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.....	32
Table 4.1 Elemental analysis results collected by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Reproduced from Lee et al., <i>J. Mater. Chem. A</i> , 2015 , 3, 8115 – 8122 with permission from The Royal Society of Chemistry.	87
Table 4.2 Surface area of both ss- and ms-Co(Al _{0.5} Ga _{0.5}) ₂ O ₄ , the amount of methyl orange (MO) adsorbed to each photocatalysts during dark adsorption, and the number of MO molecules adsorbed per 1 nm ² during the dark adsorption. Reproduced from Lee et al., <i>J. Mater. Chem. A</i> , 2015 , 3, 8115 – 8122 with permission from The Royal Society of Chemistry.....	91
Table 4.3 Apparent quantum efficiency values measured for ms-Co(Al _{0.5} Ga _{0.5}) ₂ O ₄ under full spectrum illumination and with a 495 nm longpass filter before illumination (0 h) and after illumination for 1 hour (1 h). Reproduced from Lee et al., <i>J. Mater. Chem. A</i> , 2015 , 3, 8115 – 8122 with permission from The Royal Society of Chemistry.	98

List of figures

Figure 1.1 A plot of AM 1.5 Global spectral irradiance. Further details on the spectrum are available at http://rredc.nrel.gov/solar/spectra/am1.5/	2
Figure 1.2 Schematic illustration and energy diagram of the heterogeneous photocatalytic water splitting in the presence of a particulate semiconductor.....	4
Figure 1.3 Schematic energy diagrams for a PEC cell system. The process of hydrogen and oxygen production for (a) n-type and (b) p-type semiconductors are shown.....	5
Figure 1.4 Positions of the valence band edge and conduction band edge for (a) general metal oxide semiconductors, (b) visible absorbing metal oxide semiconductors, and (c) non-oxide semiconductors.	8
Figure 1.5 Schematic energy diagram of water splitting based on two-step photoexcitation (Z-scheme).	9
Figure 1.6 (a) Ideal behavior of Vegard's law. (b) Positive and (c) Negative departure from the ideal behavior.....	11
Figure 1.7 Proposed band structures of CoAl_2O_4 , $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, and CoGa_2O_4	15
Figure 2.1 Nanocrystalline starting materials for $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesis. (a) Low resolution TEM image of ZnGa_2O_4 nanocrystals. (b) Low resolution TEM image of ZnO nanocrystals. (c) Powder XRD pattern of ZnGa_2O_4 nanocrystals. (d) Powder XRD pattern for ZnO nanocrystals.....	28

Figure 2.2 Powder X-ray diffraction (XRD) patterns of the products of nitridation of a mixture of ZnGa_2O_4 and ZnO nanocrystals at varying reaction temperatures.	30
Figure 2.3 TEM images and size analysis of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with varying composition: (a) $x=0.54$; (b) $x=0.66$; (c) $x=0.76$; and (d) $x=0.87$	32
Figure 2.4 Powder XRD patterns of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with varying values of x , synthesized at 650 °C. (Inset) Lattice parameters a and c , determined from positions of (100) and (002) peaks respectively.	33
Figure 2.5 Aberration-corrected HRTEM images of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals, with fast Fourier transforms of each particle (insets).	35
Figure 2.6 Absorption spectra of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with varying x , normalized at 380 nm. The absorption shifts continuously to longer wavelengths with increasing x ; (Inset) Values of absorption onset as a function of x	36
Figure 2.7 Photograph of nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ samples with varying.	37
 Figure 3.1 Powder XRD patterns of the products obtained from nitridation of ZnGa_2O_4 nanocrystals for 10 hours at varying reaction temperatures.	50
Figure 3.2 (a) Powder XRD patterns of the products from nitridation of a starting mixture with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$ for 0–16 hours at 650 °C. (b) Area ratio of (400) spinel peak to (100) wurtzite peak (blue) and position of (100) peak of wurtzite (red). (c) Values of $\text{Zn}/(\text{Zn}+\text{Ga})$. (d) Values of $\text{O}/(\text{O}+\text{N})$. (e) ADF-STEM image of the product after 10 hours of nitridation.	51
Figure 3.3 Fitting of XRD patterns of the nitrided products for 0–16 hours at 650 °C from a starting material mixture with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$	53

Figure 3.4 Low-magnification TEM images of the nitrided products for 0–16 hours at 650 °C from a starting material mixture with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$	54
Figure 3.5 Diffuse reflectance spectra (normalized at 250 nm) of the products of nitridation for 0–16 hours at 650 °C with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$. Inset shows the absorption onsets of the products as a function of the nitridation time along with that of the starting mixture (SM, dashed line).	55
Figure 3.6 (a) Powder XRD patterns, (b) (100) peak position, (c) Elemental analysis from ICP-OES, and (d) Diffuse reflectance spectra (normalized at 350 nm) of the products from nitridation of a starting mixture ($\text{Zn}/(\text{Zn}+\text{Ga})=0.78$).	56
Figure 3.7 Powder XRD patterns of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with $0.06 \leq x \leq 0.98$. The inset represents the variation of lattice parameters compared with the linear behavior expected from an ideal solid solution.	58
Figure 3.8 Low magnification TEM images of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, ($x=0.06, 0.24, 0.91$, and 0.98).	59
Figure 3.9 XPS spectra of the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with $x=0.40, 0.52, 0.76$, and 0.93 for (a) $\text{Zn}2p_{3/2}$, (b) $\text{O}1s$, (c) $\text{Ga}2p_{3/2}$, and (d) $\text{N}1s$. (e) Binding energy of lattice oxygen (red) and nitrogen in nitride (N^{3-}) versus the x value.	61
Figure 3.10 Diffuse reflectance spectra of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with varying composition with (a) $x=0.06$ – 0.66 and (b) $x=0.76$ – 0.98 , along with that of ZnO . Spectra are normalized at 350 nm. (c) Band gap energies of the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ products as a function of ZnO fraction (x).	63
Figure 3.11 Band gap determination of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ from (a) fitting the below-band gap absorption features for $x=0.42$ sample. (b–j) Tauc plots of $(\alpha h\nu)^2$ against $h\nu$. (k) Band gap	

energy determined from the direct band gap absorption (Tauc plot), absorption onset, and below-band gap absorption (free carrier + Urbach tail).	64
Figure 3.12 Current-voltage curves for films of bulk and nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40$ for bulk; $x=0.40, 0.52$, and 0.87 for nanocrystals) obtained from (a) Water oxidation in pH 4.5 $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution and (b) Sulfite oxidation in pH 7 phosphate buffer solution with $0.5 \text{ M Na}_2\text{SO}_3$	67
Figure 3.13 Incident photon-to-current efficiency (IPCE) spectra of nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40, 0.52$, and 0.87) obtained from sulfite oxidation. Diffuse reflectance (DR) spectra are also shown.....	69
Figure 4.1 (a) UV-vis absorbance spectra (benzene solvent) of molecular precursors. (b) DRIFTS spectra of molecular precursors in the Co–O, Al–O, and Ga–O region.	84
Figure 4.2 Powder X-ray diffraction patterns of the products obtained from annealing the amorphous (a) CoAl_2O_x and (b) CoGa_2O_x at varying temperature ($500 - 1000 \text{ }^\circ\text{C}$).	85
Figure 4.3 (a) Powder X-ray diffraction patterns of ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ annealed at $1000 \text{ }^\circ\text{C}$. (b) lattice parameter plotted against the fraction of Ga (x). Scanning electron micrographs of ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, $x=0$ (c), $x=0.5$ (d), and $x=1$ (e).....	86
Figure 4.4 Powder X-ray diffraction patterns of (a) ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanocrystals and (b) annealed ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ at $1000 \text{ }^\circ\text{C}$ for 1 hour. (c) Lattice parameters, a , determined by the (311) reflection against Ga content (x). (d) Domain size of ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanocrystals, annealed ($1000 \text{ }^\circ\text{C}$, 1h) ss- and ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ calculated using Debye-Scherrer equation.	89

Figure 4.5 Transmission electron micrographs of the ms-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$ nanoparticles, $x=0$ (a), $x=0.5$ (b), and $x=1$ (c). Scanning electron micrographs of the annealed ms-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$, $x=0$ (d), $x=0.5$ (e), and $x=1$ (f).....	90
Figure 4.6 Diffuse reflectance spectra of annealed (1000 °C, 1 h): (a) ss-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$; (b) ms-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$ with varying x ; (c) absorption onsets as a function of x ; (d) suggested band structure of Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$	92
Figure 4.7 (a) UV-vis absorbance spectra of ms-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$ nanocrystals with varying x . (b) Absorption onsets as a function of Ga content x	93
Figure 4.8 (a) Photodegradations of MO with annealed ms- or ss-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ at pH 3 over 6 h illumination. (b) pH effect on photodegradation of MO with (red) and without (blue) annealed ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ under 4 h of illumination. (c) Photodegradation of MO with annealed ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ at pH 3 under full spectrum solar simulated illumination (red, w/ AM1.5G filter) and visible light irradiation (blue) using a AM1.5G filter and a 495 nm long pass filter. (d) Recycling experiment showing the photodegradation rate of MO at pH 3 under visible illumination is retained when using the same annealed ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ sample for 3 fresh MO solutions.....	94
Figure 4.9 UV-vis absorbance spectra of methyl orange (MO) solutions after various times at pH 3 under AM1.5G illumination in the presence of (a) ss-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ (b) ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$	95
Figure 4.10 UV-vis absorbance spectra of methyl orange (MO) in the presence of ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ at (a) pH 3 (b) pH 5 (c) pH 7, and (d) pH 9 under AM1.5G illumination.....	96
Figure 4.11 Spectral profiles employed in the MO degradation studies using a Xe lamp with (black) AM1.5G filter or (red) AM1.5G and 495 nm longpass filter.....	97

Figure 4.12 Powder X-ray diffraction patterns of ms-Co(Al_{0.5}Ga_{0.5})₂O₄ before (black) and after (green) three cycles of MO degradation at pH 3 under visible illumination for 6 h each cycle..... 98

List of schemes

Scheme 4.1 Single-source route to bulk ss-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$. Reproduced from Lee et al., <i>J. Mater. Chem. A</i> , 2015 , 3, 8115 – 8122 with permission from The Royal Society of Chemistry.....	83
Scheme 4.2 Multi-source (ms) route to nano ss- Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$ and bulk annealed ss-Co($\text{Al}_{1-x}\text{Ga}_x$) $_2\text{O}_4$. Reproduced from Lee et al., <i>J. Mater. Chem. A</i> , 2015 , 3, 8115 – 8122 with permission from The Royal Society of Chemistry.	88

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Chapter 1. Introduction

1.1 Motivation

Nowadays our global energy consumption is increasing sharply due to the fast expansion of industry and growth of the world population.^{1,2} However, it is expected that the current energy resources depending on fossil fuels will be depleted in the near future, although there are disagreements on the exact time.³ In addition, the use of fossil fuels produces green house gas (CO_2) and noxious gases such as NO_x and SO_x , contributing to global warming and air pollution, respectively.^{4,6} It is imperative to find clean, sustainable and renewable energy resources such as solar, wind, and geothermal energy, etc.⁷ Among the alternatives, solar energy has drawn a lot of interest due to its enormous power on the earth.⁸ The annual amount of human energy consumption can be delivered by the sunlight in one hour.^{1,7} Thus, a lot of efforts have been devoted to converting solar energy into useful forms.^{7,9}

Producing hydrogen from water splitting is an intriguing class of solar technology, as hydrogen is a clean and highly energy dense fuel.¹⁰ In this process, the solar energy is stored into chemical bonds similar to photosynthesis, which converts carbon dioxide to sugar. This is in contrast with the photovoltaic system which requires a separate energy-storing technology to overcome a temporal variation of solar energy. Water splitting is a non-spontaneous reaction, but can be driven by solar energy with suitable semiconductor materials that can utilize sunlight. In 1972 Fujishima and Honda first demonstrated the transformation of solar energy into hydrogen fuel from photoelectrochemical (PEC) water splitting over a single crystal of rutile TiO_2 under ultraviolet (UV) irradiation.¹¹ After this pioneering work many semiconductors have been studied

for water splitting while considering the conversion efficiency, low cost, and stability.¹² However, most of them have suffered from their inherent deficiencies. For instance, TiO_2 meets the fundamental criteria of suitable electronic properties to transfer solar energy into water molecules to break its chemical bonds. However, it has a wide band gap of 3.2 eV, which allows it to absorb a small fraction of the solar spectrum in the UV region, leading to low conversion efficiency (See Figure 1.1). Thus, scientists have been attempting to find or design new semiconductors to improve the efficiency of solar energy conversion.

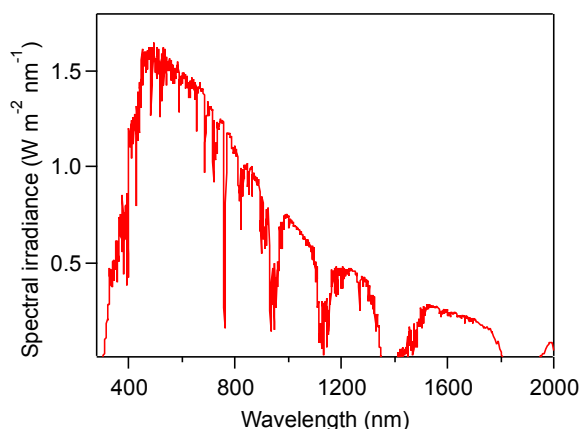


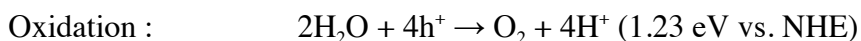
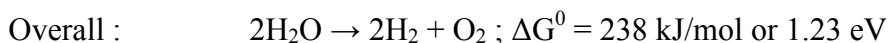
Figure 1.1 A plot of AM 1.5 Global spectral irradiance. Further details on the spectrum are available at <http://rredc.nrel.gov/solar/spectra/am1.5/>.

1.2 Background

This dissertation mainly focuses on the synthesis of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ and $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ and on studying structural and absorption properties of these two solid solution materials that have been expected or predicted to exhibit potentially promising properties as photocatalysts in water splitting. In this section, some background knowledge on water splitting, a solid solution, and the synthesized materials in this dissertation are briefly reviewed.

1.2.1 Visible light driven overall water splitting

Overall water splitting is the sum of two half reactions – hydrogen and oxygen evolution. The overall reaction of water splitting into hydrogen and oxygen and each half reaction in acidic media are described below:



The change in Gibbs free energy of the overall water splitting is positive, so it is thermodynamically uphill and requires external driving energy ($> 1.23 \text{ eV}$) for the reaction to occur. If the reaction could be driven by solar energy, it could address the demands for clean, renewable, and sustainable energy resources. The key idea in solar driven water splitting is employing semiconductor materials that can utilize sun light to drive the two half reactions.

Semiconductors can be characterized by their band gap (1–3.5 eV), which is the energy spacing between the valence band (the highest energy band filled with electrons) and the conduction band (the lowest energy empty band). The electrons in the valence band can cross the band gap to the conduction band when the semiconductor absorbs light with energy higher than the band gap. This results in photo-generated charge carriers – electrons in conduction band and holes in valence band. As indicated in the half reactions above, the protons can be reduced with the electrons having a more negative potential than 1.23 eV (vs. NHE). The holes can oxidize water molecules when their potential is more positive than 0 eV (vs. NHE). Therefore, the band gap of the semiconductor and the positions of each band edge have to satisfy the following requirements in order to generate charge carriers under visible illumination and have them thermodynamically favorable for the two half reactions:

- The band gap must exceed 1.23 eV to compensate for the required external driving energy for water splitting. At the same time, the band gap has to be small enough to absorb visible range of solar irradiation.
- The energy level of the conduction band edge must be higher than the reduction potential of the protons in order for the electron-transfer from the conduction band to the protons to take place.
- The energy level of the valence band edge must be lower than the oxidation potential of water for the hole transfer from the valence band to water molecules to take place.

1.2.2 Photocatalytic and photoelectrochemical water splitting

There are two main experimental approaches that have been investigated to achieve solar driven water splitting using semiconductor materials; photocatalytic and photoelectrochemical (PEC) water splitting.

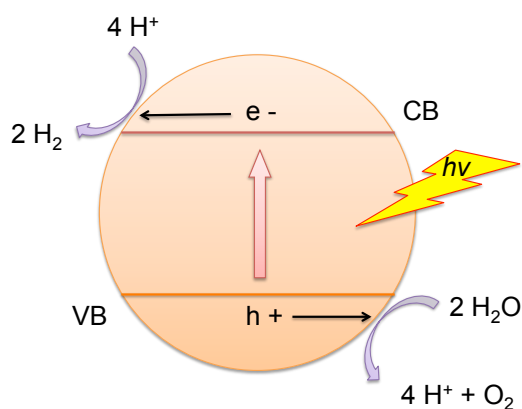


Figure 1.2 Schematic illustration and energy diagram of the heterogeneous photocatalytic water splitting in the presence of a particulate semiconductor.

Figure 1.2 describes the reaction process of photocatalytic water splitting. In this system the semiconductor (photocatalyst) is a fine powder that is suspended in aqueous solution.¹³ After

light absorption upon the principles discussed above, the photo generated electrons and holes migrate to the particle surface on which they drive the hydrogen evolution and water oxidation, respectively. The electrons and holes may also recombine in a very short period of time before reaching the surface, which releases energy in the form of heat or photons and causes a loss in conversion efficiency. Having a smaller particle size of photocatalyst could benefit efficiency by decreasing the distance of the migration of carriers and reducing the probability of charge recombination. Since impurities and defects in the semiconductor can provide a recombination site, pure and highly crystalline photocatalysts are desired to avoid recombination. Photocatalytic water splitting is based on the particulate semiconductor materials dispersed in aqueous solution, whereas PEC water splitting requires the use of a conductive substrate and wire connections. From the viewpoint of large-scale hydrogen production, the photocatalytic system has advantages with its simplicity and low cost over the PEC system.¹⁴ In addition, powdered photocatalysts are encouraging when pursuing new materials since there are many synthetic strategies reported to control the particle properties such as size and morphology.

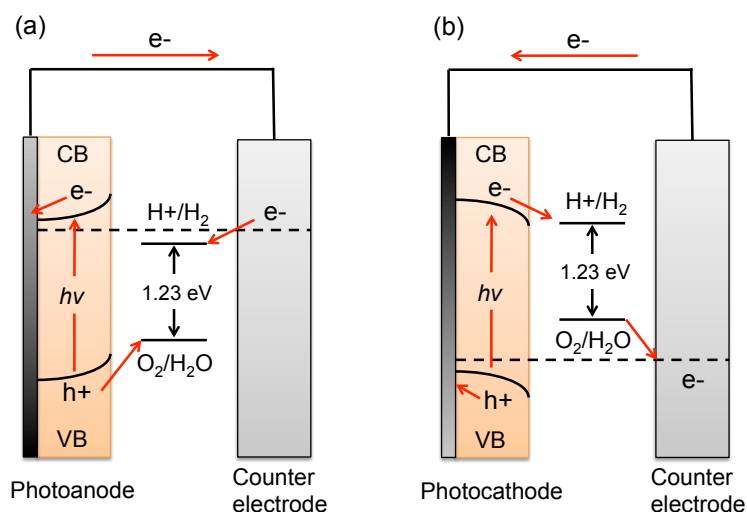


Figure 1.3 Schematic energy diagrams for a PEC cell system. The process of hydrogen and oxygen production for (a) n-type and (b) p-type semiconductors are shown.

Figure 1.3a and b depict the schematic diagram of PEC water splitting cells based on single-component semiconductors, n-type and p-type semiconductors, respectively. The PEC cell typically consists of a working electrode (photoanode for n-type semiconductor and photocathode for p-type semiconductor), counter electrode (e.g. Pt metal), and an external circuit between the two electrodes. A reference electrode can also be employed to determine the potential values with respect to the reference electrode. The working electrode is typically a semiconductor deposited on a conductive and transparent substrate such as indium tin oxide (ITO) or fluorine doped tin oxide (FTO). When the working electrode is immersed in an electrolyte solution, charge transfer occurs at the interface between the semiconductor and the electrolyte so that the Fermi level of the semiconductor reaches an equilibrium with the redox potential of the electrolyte.¹⁵ The charge transfer produces an electric field at the interface between the semiconductor and the electrolyte, which is the key feature for effective photo generated charge separation. In the PEC cell with an n-type semiconductor electrode, the semiconductor donates electrons to the electrolyte because the Fermi level is typically more negative than the reduction potential of the electrolyte, leading to a positively charged region within the semiconductor (space charge region) and an upward band bending as shown in Figure 1.3a. Upon illumination with higher energy than the band gap, photogenerated holes move to the surface to oxidize water while the electrons are transferred to a counter electrode through an external circuit to drive the hydrogen production. On the other hand, for the PEC cell with p-type semiconductor, the Fermi level is generally lower than the redox potential and hence the semiconductor accepts electrons from the electrolyte to attain equilibrium. This generates negative charges in the space charge region and downward band bending as shown in Figure 1.3b. As opposed to the case of the n-type semiconductor, the photogenerated electrons reduce

protons on the surface of the semiconductor while water is oxidized by holes on the counter electrode. The single-component PEC cells (n-type or p-type) allow one to characterize fundamental properties of materials. For example, the potential of the band positions can be determined using the PEC system. Understanding the materials can provide directions for further improvement.

Alternatively, in practice, both n-type and p-type semiconductors can be connected in series instead of using a Pt counter electrode. By constructing the tandem system, semiconductors having unfavorable band positions for overall water splitting and/or small band gaps (<1.23 eV) can be employed, which drives water splitting without external bias (described later) and provides an increase in visible light absorption.¹⁶⁻¹⁹

Although the external electric setup required in PEC water splitting costs more than the simple photocatalytic system, it has several advantages. Firstly, a power supply can be employed to apply an external voltage to the electrodes. Regardless of the type of semiconductor, the potential of electrons on the counter electrode is identical to the Fermi level of the semiconductor, and it can be moved by applying an external voltage.²⁰ Thus, when the electrons on the counter electrode are not energetic enough to drive the redox reactions, the external voltage can be applied to compensate for the potential deficiency. Another advantage is that hydrogen and oxygen can be produced separately from each electrode, which, unlike the photocatalytic method, does not require gas separation. Moreover, the separate gas production alleviates the safety concerns with producing the reactive gases in the same chamber.¹⁴ Also, the electrochemical method enables the determination of the efficiency of the materials accurately.¹⁴ Lastly, as mentioned above, the PEC system enables one to understand the electrode materials.

In Chapter 3, PEC experiments were conducted to study the nano scale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ in comparison with the bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$.

1.2.3 Common deficiencies of single semiconductors

Since the first demonstration of water splitting by Fujishima and Honda¹¹, various metal oxide semiconductors have been investigated for solar driven water splitting due to their photo-responsive properties and high resistivity against photocorrosion.²¹ However, most metal oxide semiconductors such as TiO_2 and ZnO can utilize only the UV range of solar irradiation due to their intrinsic wide band gap. In typical metal oxides, the upper valence bands, which consist predominantly of O 2p orbitals, are located at deeply positive potential (more positive than 3 eV vs. NHE at pH 0).²² This causes the inherent wide band gaps of metal oxides, and consequently they are responsive to only UV light. Since UV light accounts for only 5 % of solar irradiation while the visible light contributes 50%, the wide band gap leads to a low solar to hydrogen conversion efficiency (Figure 1.1 and 1.4a).

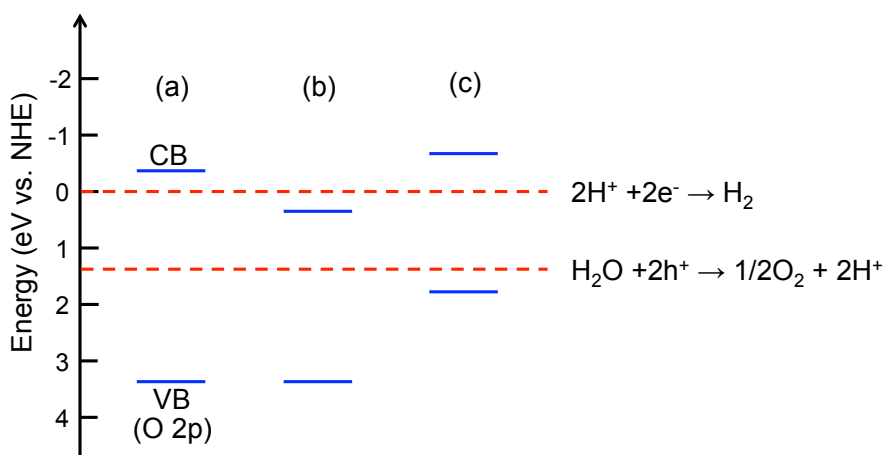


Figure 1.4 Positions of the valence band edge and conduction band edge for (a) general metal oxide semiconductors, (b) visible absorbing metal oxide semiconductors, and (c) non-oxide semiconductors. Redox potentials for the water splitting half reactions with respect to the normal hydrogen electrode (NHE) are also indicated.

Although a few metal oxides such as WO_3 have narrow band gaps matched with visible light, their valence band edges are still too low in energy and conduction band edges are located at a potential below the hydrogen reduction potential, which is inappropriate for hydrogen production (Figure 1.4b).²³ Some II/VI, III/V, and group IV materials have the appropriate band energy levels and appear to be suitable for overall water splitting under visible light (Figure 1.4c).²⁴ However, these materials generally have issues with photocorrosion.²⁵ For example, the chalcogen anions (S^{2-} and Se^{2-}) in metal chalcogenides (e.g., CdS and CdSe) are oxidized more easily than water, resulting in degradation of the photocatalysts themselves.^{26,27} Gerischer has studied the thermodynamics of reductive and oxidative decompositions of semiconductors, and reported the decomposition can be prevented when both decomposition potentials are located outside the bandgap.²⁵ In conclusion, it is challenging for single semiconductor materials to satisfy all the requirements: visible responsive band gap, stability, and appropriate band edge positions for overall water splitting due to their intrinsic deficiencies.

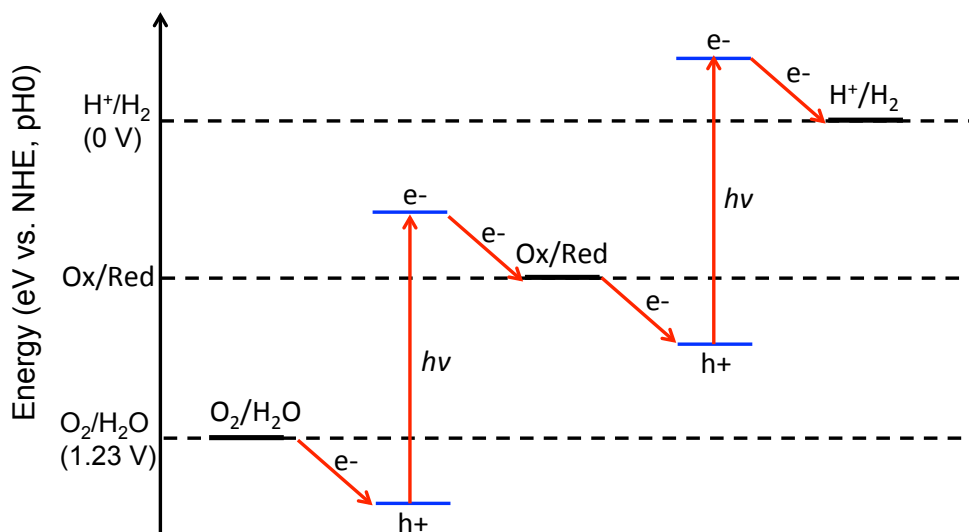


Figure 1.5 Schematic energy diagram of water splitting based on two-step photoexcitation (Z-scheme).

One of the promising approaches to overcome the problems of single semiconductors is Z-scheme where it is possible to employ semiconductors that are alone not suitable for overall water splitting.^{17-19,28-30} In the Z-scheme system, the water splitting reaction is separated into two stages, which are H_2 production and the O_2 evolution. The reactions separately occur on two semiconductors (referred as H_2 photocatalyst and O_2 photocatalyst), and these are connected with reversible redox pair (Ox/Red). Figure 1.5 depicts the Z-scheme water splitting using two different semiconductors. On the H_2 photocatalyst, the photoexcited electrons reduce protons to H_2 , and holes oxidize the reductant (Red) to yield the corresponding oxidant (Ox). On the other side (O_2 photocatalyst), the oxidant is reduced back to the reductant by the excited electrons, and water oxidation occurs with the holes. By breaking up the water splitting into the separate stages in the Z-scheme, semiconductors that have either H_2 or O_2 production potential can be employed on one side of the system. In other word, the semiconductors in Z-scheme do not have to satisfy the potential requirements for both half reactions, thus it enables to use various semiconductor materials. Z-scheme is also advantageous over single semiconductor system from the ability to produce H_2 and O_2 separately by employing a porous separator that permits only the redox pair to be transferred between the two semiconductors.

1.2.4 Solid solution and Vegard's law.

As discussed in the previous section, there are limitations to engineering the band structure of conventional single semiconductors due to the inherent nature. Formation of a solid solution is an interesting strategy to tune band gap energy since both band edge positions can be controlled with composition.²¹ For example, successful band gap tuning has been demonstrated

in the pseudobinary or ternary solid solution systems such as $(\text{GaP})_{1-x}(\text{ZnS})_x$,³¹ $(\text{ZnS})_{1-x}(\text{GaP})_x$,³² ZnCdSe ,³³ InGaN ³² etc. Here, a brief introduction of a solid solution is presented.

A solid solution is a crystalline solid that contains two or more chemical compounds, which forms a single solid phase with continuous variation in the composition.^{34,35} This system can be formed when the compounds have: (i) similar atomic size (less than 15 % difference), (ii) same crystal structure, (iii) similar electronegativities, and (iv) same valency.³⁶ All the phases of a solid solution with varying composition have the same crystal structure as their parent materials. Interestingly, however, certain properties of a solid solution can often be engineered by changing the composition. This is a desirable aspect of a solid solution for designing new materials having desired properties for specific applications.³⁷ The mixed phases of a solid solution are one of two types: (i) Substitutional solid solutions: The atoms of one parent compound replace those of the other parent material or (ii) Interstitial solid solutions: The introduced atoms occupy positions that are empty in the crystal structure.³⁴ In the formation of a solid solution, the unit cell expands/shrinks when atoms are replaced by larger/smaller ones, which leads to a shift in X-ray diffraction patterns from Bragg's law.

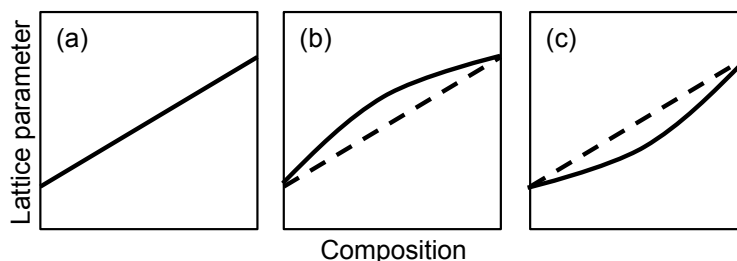


Figure 1.6 (a) Ideal behavior of Vegard's law. (b) Positive and (c) Negative departure from the ideal behavior.

According to Vegard's law³⁸, the unit cell parameters change linearly with composition assuming that the changes are ruled only by the size of the atoms in the solid solution. Therefore,

a plot of the lattice parameters obtained from a series of solid solution materials against their compositions will be linear as shown in Figure 1.6a. In practice, however, departure from the linear behavior has been experimentally observed in many solid solutions with no systematic correlation between the type of departure (i.e. positive or negative) and structural features or compositions of the solid solutions (Figure 1.6b,c).³⁷

1.2.5 Solid solution of GaN and ZnO, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$

The Domen group developed a synthetic method for a bulk scale solid solution of GaN and ZnO, $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, in 2005.³⁹ $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ has drawn interest due to its reduced band gap and photocatalytic activity in overall water splitting under visible light when it is modified with proper cocatalysts.⁴⁰⁻⁵⁰ It is not well understood how $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ possesses these unique properties, therefore many efforts have been made to examine the material.⁵¹⁻⁶⁰ In this section, some representative research on $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is reviewed.

	a (nm)	c (nm)
GaN	0.319	0.519
ZnO	0.325	0.521

Table 1.1 Lattice parameters (a and c) of GaN and ZnO.

GaN and ZnO are well known materials with wide band gap energies (3.4 eV for GaN and 3.2 eV for ZnO) and have been studied for overall water splitting under UV irradiation.^{61,62} Both materials have the same crystal structure (wurtzite) with similar lattice parameters as shown in Table 1.1, which enables them to form a solid solution.^{63,64} In the original synthesis of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ developed by Domen, the mixture of $\beta\text{-Ga}_2\text{O}_3$ and ZnO is heated under a flow of ammonia gas at 1123K.⁴⁹ The composition was controlled by varying nitridation time, since the Zn in the solid solution volatilizes at the high nitridation temperature. The formation of a solid

solution was confirmed with X-ray diffraction (XRD) patterns in which $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ shows a single wurtzite peaks located between those of GaN and ZnO. The continuous peak shifts with composition also indicate that the products are a solid solution of GaN and ZnO instead of a physical mixture.

In common solid solution materials, the potentials of both band edges lie between the ones of their parent materials, so the band gap energy is given by the intermediate value.⁶⁵ The most intriguing feature of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is that its band gap corresponds to visible light whereas GaN and ZnO have wide band gap energies in the UV range. In addition, it was found that the band gap of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ decreases with increasing Zn content. In early reports from the Domen group, the origin of the band gap reduction was suggested to be from the p-d repulsion between the Zn3d and N2p orbitals in the upper valence band of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. This results in an upward shift of the valence band edge without significant changes in the conduction band edge. In their later studies they proposed another model stating that the visible absorption occurs via electron transition from Zn-related acceptor levels to the conduction band or unfilled O donor levels.^{51,58} Many other studies have also focused on elucidating the origin of visible absorption experimentally or theoretically, but it is still under debate.^{52-55,57,59,60}

Chen et al. have closely monitored the formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ in the original synthetic route using time-resolved XRD.⁶⁵ It was found that the reaction forms an intermediate spinel ZnGa_2O_4 from which the final solid solution is evolved. Thus, the achievable Zn content in the solid solution is limited ($x \leq 0.3$) by the spinel intermediate. Since the band gap of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is known to change with composition, new synthetic routes have been investigated to produce $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with wide ranges of composition. Chen et al. reported the bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with x equal to and higher than 0.5 through an alternative synthetic route

where a mixture of ZnO and GaN was nitrided at high temperature under high pressure.⁶⁶ Mapa et al. also reported ZnO-rich $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ via a solution combustion method.⁶⁷ Wang et al. used layered double hydroxides containing Zn^{2+} and Ga^{3+} ions as a precursor for nitridation at 800 °C. The composition was controlled by varying the ratio of the metal ions in the precursors, resulting in the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with x values ranging from 0.46 to 0.81 and with band gaps ranging from 2.6 eV to 2.37 eV.⁶⁸

Several groups recently reported new synthetic methods for nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. Han et al. and Ward et al. prepared Ga-Zn-O nanoprecursors via a sol-gel method and nitrided them at relatively low temperature to produce $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals.^{69,70} Hahn et al. produced $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanotubes with compositions up to $x = 0.10$ through an epitaxial casting approach and experimentally demonstrated improved photocatalytic activities over the bulk products.⁷¹ As described in Chapter 2, we have developed a method for synthesizing nano scale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with a wide x range ($0.30 \leq x \leq 0.87$) and shown that higher x values correlate with lower band gap energies.⁷² Li et al. most recently reported hollow $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanospheres with a wide range of x ($0.18 \leq x \leq 0.95$), synthesized via a template method using carbon nanospheres.⁷³ Chapters 2 and 3 will detail the formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals and the studies on their fundamental properties.

1.2.6 Cobalt based mixed metal spinel oxide, CoM_2O_4

A lot of research exploring suitable materials for water splitting has focused on metal oxides due to their stability to photocorrosion.²¹ Recently, there have been efforts to develop new classes of multi-ternary oxide materials, which combine multiple cations based on their individual properties to engineer the material properties.⁷⁴ Similarly, ternary cobalt based spinel

oxide materials have recently been explored as an effort to search for metal oxide semiconductors with a band gap in the visible range. Woodhouse et al. have developed an alloy system of cobalt based spinel oxides ($\text{Co}_{3-x-y}\text{Al}_x\text{Fe}_y\text{O}_4$) with a tunable band gap (1.6 to 2.0 eV).^{75,76} Metal nitrate precursors were patterned on a conductive glass substrate using ink jet printing and subsequently pyrolyzed to yield an electrode with a combinatorial array of cobalt metal oxide. The electrode was tested for PEC activity with laser scanning, which generates cathodic photocurrent and identifies some promising compositions. Although the PEC response was weak mainly due to its poor electrical conductivity⁷⁷, it inspired further studies on the system of cobalt based metal oxides.

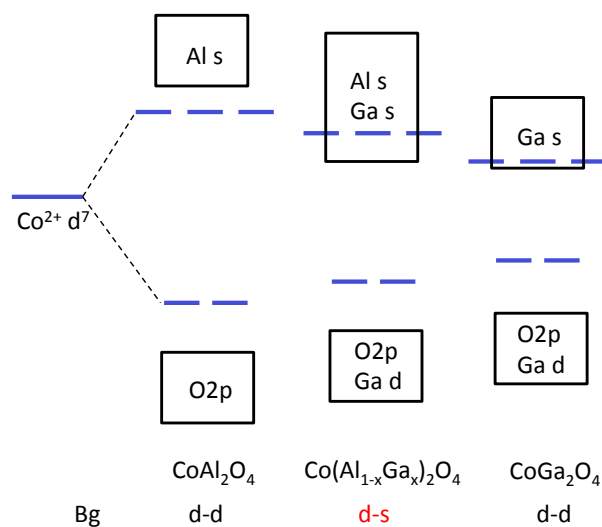


Figure 1.7 Proposed band structures of CoAl_2O_4 , $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, and CoGa_2O_4 .^{78,79}

Walsh et al. have reported combined theoretical and experimental studies on the electronic structure, optical properties, and PEC performance of cobalt metal spinel oxides, CoM_2O_4 (M= Al, Ga, and In).⁷⁸ CoAl_2O_4 has a high stability in aqueous solution, but exhibits inefficient PEC properties due to its large band gap and poor electrical conductivity. In the electronic structure of CoAl_2O_4 , Co(II) d orbitals split into Co e_d and t_{2d} under tetrahedral crystal field (see Figure 1.7). The valence band edge consists of Co e_d orbitals while the conduction

band edge is composed of Co t_{2d} . The Al 3s state is located at a higher energy than the Co t_{2d} , thus the band gap of CoAl_2O_4 is determined by the d-d transition, leading to localized photocarriers and poor conductivity. Replacement of Al with Ga or In was found to reduce the band gap and improve the conductivity. Al has no d electrons as a 2nd row element, while Ga and In have filled d orbitals lying in the upper valence band. Thus, the d orbitals couple with the O2p, which moves the valence band edge upward (p-d coupling). Also, the conduction band moves downward due to the lower s state of Ga and In compared to Al. The latter effect also leads to the enhanced electric conductivity through orbital mixing of the cation s state into the conduction band. In the following study, it was theoretically predicted that the electronic structure of the cobalt metal spinel oxides, CoX_2O_4 (X= Al, Ga, and In) could be further tuned by forming cobalt mixed metal spinel oxides, $\text{Co}(\text{AlGaIn})_2\text{O}_4$.⁷⁹ This study proposed some promising compositions of the materials to lower the band gap and enhance the conductivity by orbital mixing. For example, they calculated that the band gap of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ decreases with increasing Ga content (x) when x is smaller than 0.75. The band gap reduction is attributed to the decrease of the crystal field splitting of d orbitals. Thus, the material has poor carrier mobility in the range of x . On the other hand, when the Ga content is larger than 0.75, the Ga s state drops faster than Co d orbital, leading to d→s band gap transition and consequently improved conductivity (Figure 1.7). Chapter 4 in this dissertation will describe the experimental studies on the predicted cobalt mixed metal oxide materials.

1.3 Summary and Outline of Dissertation

Solar energy conversion to hydrogen from water splitting is seen to be one of the most interesting technologies that can address the current energy and environmental issues. In the

research field of water splitting from photocatalytic or PEC systems, it is essential to introduce appropriate semiconductor materials that can utilize solar energy to drive the process. While there has been a lot of research to find suitable materials over the past 40 years, thus far, the efficiency of the hydrogen production is low due to the inherent deficiencies of the semiconductors.

The work presented in this dissertation mainly focuses on the synthesis of solid solution materials that were expected to have promising properties. Chapter 2 is based on the publication in Nano Letters (2012) and describes the new synthetic method for nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ and its structural and optical characterizations. The work in Chapter 3 follows Chapter 2 and aims to understand the mechanism in the formation of the materials with a wide range of compositions. This chapter also presents the chemical state and PEC properties of the material. Chapter 4 is based on the publication in Journal of Materials Chemistry A (2015) and focuses on the development of cobalt mixed metal spinel oxides, $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$. This chapter outlines the synthesis, structural and optical characterization, and photocatalytic activities in the degradation of methyl orange.

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Chapter 2. $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ Nanocrystals: Visible Absorbers with Tunable Composition and Absorption Spectra^a

2.1 Introduction

In the bulk form, the oxy(nitride) $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ has recently emerged as a promising photocatalyst for water splitting at wavelengths >400 nm.¹⁻⁴ This material is a solid solution of ZnO and GaN and has the rare combination of visible absorption, appropriate band edges for the reduction and oxidation half-reactions required for water splitting, and resistance to photocorrosion. For the purposes of solar energy harvesting, it is necessary to decrease its band gap while maintaining sufficient driving force for water splitting. It is not well understood why $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ exhibits visible absorption given that GaN and ZnO have band gaps of 3.4 and 3.3 eV respectively.⁵⁻¹⁷ There is even disagreement between experimental reports of how bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ band gaps depend on composition.^{5,18} In materials prepared by mixing ZnO and GaN powders under high pressures and temperatures, the oxy(nitride) with $x=0.49$ had a lower band gap (~ 2.5 eV) than both GaN-rich ($x=0.22$) and ZnO-rich ($x=0.76$) materials.⁵ This behavior is known as band gap bowing. In contrast, in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesized by nitridation of layered double Zn^{2+} and Ga^{3+} hydroxides, the band gap decreased over the

^a This chapter is reproduced with permission from a publication. *Nano Lett.* **2012**, 12, 3268 – 3272.

0.46< x <0.81 range, to as low as 2.37 eV.¹⁸ This difference in behavior is not understood, and it has important implications for how much of the solar spectrum can be harvested by the oxy(nitrides).

In addition to control of composition and absorption spectra, it is desirable to reduce the sizes of oxy(nitride) particles from the submicrometer bulk regime to dimensions around 10 nm. In bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ functionalized with a H^+ reduction cocatalyst, the water-splitting quantum yield is governed by the competition between carrier migration, surface redox reactions, and carrier trapping and recombination.^{3,19} The highest reported quantum yield of water splitting under visible illumination is 6 %.²⁰ Nanocrystalline oxy(nitrides), with dimensions comparable or smaller than the mean free paths of electrons and holes in the material, may exhibit improved photochemical quantum yields. Because of high surface area-to-volume ratios and the lack of grain boundaries, the probability that a carrier would reach a catalytic surface site rather than decay via energy wasting relaxation pathways may be higher in nanocrystals than in the bulk form. Similar advantages of nanostructures over the bulk material have been demonstrated for Fe_2O_3 and $\text{KCa}_2\text{Nb}_3\text{O}_{10}$.^{21,22} However, synthetic methods for oxy(nitrides) with sub-100 nm dimensions are scarce.²³⁻²⁵ Notably, Han et al. have reported synthesis of nanoparticles with diameters as low as 10 nm and values of x up to 0.48.²³ Oxy(nitride) nanocrystals with a wide range of compositions have not been previously reported. In particular, because of the possibility of achieving lowest band gaps at high values of x ,¹⁸ ZnO-rich oxy(nitride) nanocrystals may be particularly suitable for solar water splitting.

In this chapter, we describe a synthetic method that produces nanocrystals of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with an unprecedented range of compositions (0.30< x <0.87). Our strategy was to use nanocrystalline ZnGa_2O_4 and ZnO as precursors in varying ratios and convert them to the

oxy(nitride) by exposure to NH_3 . The required nitridation temperatures were lower than those needed for the synthesis of the bulk material, which allowed the nanoscale morphology to remain intact while producing high-quality crystals. The resulting materials were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD), diffuse reflectance spectroscopy, and samples with $x=0.76$ were imaged by aberration-corrected high-resolution TEM. The dependence of lattice parameters on x was found to deviate from Vegard's law, in agreement with theoretical predictions.¹² The band gaps of these visible absorbers decreased continuously with increasing x , from 2.7 eV for $x=0.30$ to 2.2 eV for $x=0.87$. The fraction of solar photons that can be absorbed increases by 260% over this range, demonstrating the solar-energy harvesting potential of ZnO-rich oxy(nitride) nanocrystals. The contrast with previously reported band gap bowing in bulk oxy(nitrides) synthesized at high pressures can be attributed to the formation of lower-density structures during nitridation reactions at atmospheric pressure.⁵

2.2 Results and Discussion

2.2.1 Synthesis of nanocrystalline starting precursors and $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$.

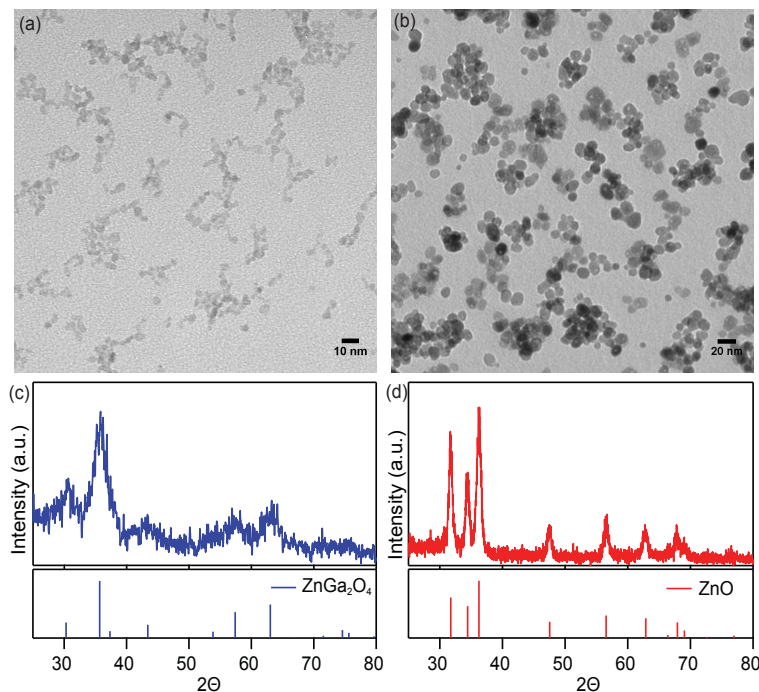


Figure 2.1 Nanocrystalline starting materials for $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesis. (a) Low resolution TEM image of ZnGa_2O_4 nanocrystals. Size measurements on 311 particles showed that the average diameter was 3.6 nm with a standard deviation of 1.0 nm; (b) Low resolution TEM image of ZnO nanocrystals, which had an average diameter of 10.6 nm with standard deviation of 2.1 nm (392 particles measured); (c) Powder XRD pattern of ZnGa_2O_4 nanocrystals, showing agreement with the literature pattern for cubic spinel ZnGa_2O_4 (JCPDS #38-1240). Peaks are broad due to the small particle size. (d) Powder XRD pattern for ZnO nanocrystals, showing agreement with the JCPDS #05-0664 pattern for wurtzite ZnO . Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

Synthesis and characterization of nanocrystalline ZnGa_2O_4 ,²⁶ ZnO ,²⁷ and $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ are described in detail in Experimental section (2.3). ZnGa_2O_4 nanocrystals had the diameters of 3.6 ± 1.0 nm (Figure 2.1a) and were soluble in organic solvents. The ZnO particles were larger ($d = 10.6 \pm 2.1$ nm) (Figure 2.1b) and were dispersible in ethanol. To ensure mixing of the two precursors, we adapted ligand-exchange procedures for CdS ²⁸ to ZnGa_2O_4 and obtained

water-soluble nanoparticles capped with 3-mercaptopropionic acid. Mixtures of these starting materials were treated with NH_3 in a quartz tube furnace for 10 h at temperatures above 500 °C to yield the oxy(nitride) product.

2.2.2 Role of nitridation temperature.

The optimal temperature for the synthesis of nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ depends on the interplay of several competing factors. At relatively low nitridation temperatures, the chemical transformation of ZnGa_2O_4 and ZnO nanocrystals to the oxy(nitride) is slow because of a combination of insufficient energy to overcome the nitridation activation barrier and the slow diffusion of atoms both within and between nanocrystals. At relatively high temperatures, nanoparticles can fuse into the bulk form. Additionally, evaporation of Zn^0 at high temperatures (~ 900 °C) has plagued the commonly used bulk oxy(nitride) synthesis and limited the available x to <0.4 .^{1-3,29} The optimal temperature balances these factors, ideally allowing complete precursor transformation into the oxy(nitride) without loss of Zn, while maintaining nanoscale morphology.

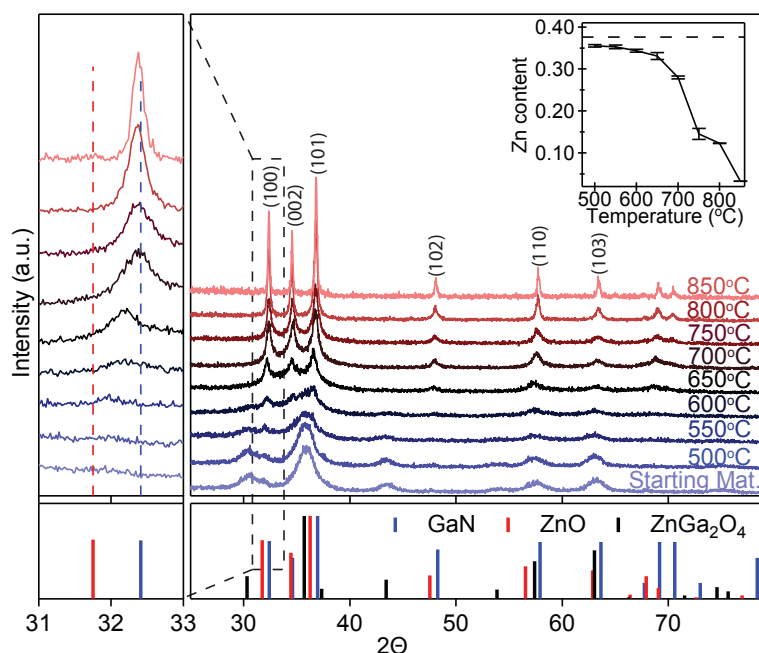


Figure 2.2 Powder X-ray diffraction (XRD) patterns of the products of nitridation of a mixture of ZnGa_2O_4 and ZnO nanocrystals at varying reaction temperatures. The Zn content ($\text{Zn}/(\text{Zn}+\text{Ga})$) in the starting material was 0.38. Reference patterns for cubic spinel ZnGa_2O_4 (JCPDS #38-1240), wurtzite ZnO (JCPDS #05-0664), and wurtzite GaN (JCPDS #2-1078) are shown as vertical lines. Assignments for the wurtzite peaks are also shown; (Inset) Values of x as a function of nitridation temperature. The x in the starting material is shown by the dashed line. Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

Powder X-ray diffraction (XRD) patterns of the nitridation product as a function of temperature are shown in Figure 2.2. Because longer reaction times can compensate for lower temperatures, all nitridations discussed here were carried out for 10 hours. The starting material was a mixture of cubic spinel ZnGa_2O_4 and wurtzite ZnO with Zn content ($\text{Zn}/(\text{Zn}+\text{Ga})$) of 0.38, as determined by elemental analysis of acid-digested samples using inductively coupled plasma optical emission spectroscopy (ICP-OES). At 500 °C, the product XRD pattern is very similar to that of the starting material. With increasing temperatures, increasing fractions of the wurtzite phases are observed, and cubic spinel phase is not detectable at temperatures ≥ 650 °C. This is most evident as the disappearance of the peak at $2\theta=43^\circ$. The enlarged view of the region around

$2\Theta=32^\circ$ shows the appearance of the wurtzite (100) peak with increasing temperature. At 650°C , there is a relatively broad peak centered between ZnO and GaN (100) positions, and it shifts towards GaN at higher temperatures. This peak also narrows with increasing temperature, indicating an increase in the crystallite size. The XRD data suggests that the conversion to $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is complete at 650°C , and higher temperatures lead to decreased Zn fraction. Elemental analysis of the nitridation products indeed shows a precipitous decline in Zn content at temperatures above 650°C (Figure 2.2 inset) due to the Zn^0 evaporation described previously.^{2,23,29} Temperatures required for synthesis of bulk oxy(nitrides) by nitridation are typically higher ($>800^\circ\text{C}$).^{1-4,18} The chemical transformation of nanocrystalline precursors is faster likely due to higher surface energies and to the relatively short atomic diffusion distances necessary to obtain oxy(nitride) nanocrystals.

2.2.3 Control of oxy(nitride) composition.

To obtain nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with a wide range of x , we combined nanocrystals of ZnGa_2O_4 and ZnO in varying ratios. The mixtures were then subject to nitridation at 650°C for 10 hours. Values of x in starting materials and products were determined by ICP-OES of acid-digested samples (Table 2.1). Comparison of x values in the starting materials and products indicates no appreciable loss of Zn. A comparison was also made between elemental analysis results obtained by ICP-OES and EDS techniques because many papers in the field report composition determined by EDS. The values of x obtained by the two techniques are similar. Standard deviations are from at least 3 measurements (ICP-OES) or at least 3 different spots on the SEM sample (EDS).

x in starting material	x in product (ICP-OES)	x in product (EDS)
0.30 ± 0.00	0.30 ± 0.00	0.31 ± 0.02
0.41 ± 0.00	0.42 ± 0.00	-
0.54 ± 0.00	0.54 ± 0.00	0.56 ± 0.01
0.65 ± 0.00	0.66 ± 0.00	0.73 ± 0.01
0.78 ± 0.00	0.76 ± 0.00	0.80 ± 0.00
0.89 ± 0.00	0.87 ± 0.00	0.90 ± 0.01

Table 2.1 Elemental analysis for 650 °C nitridation with varying x . Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

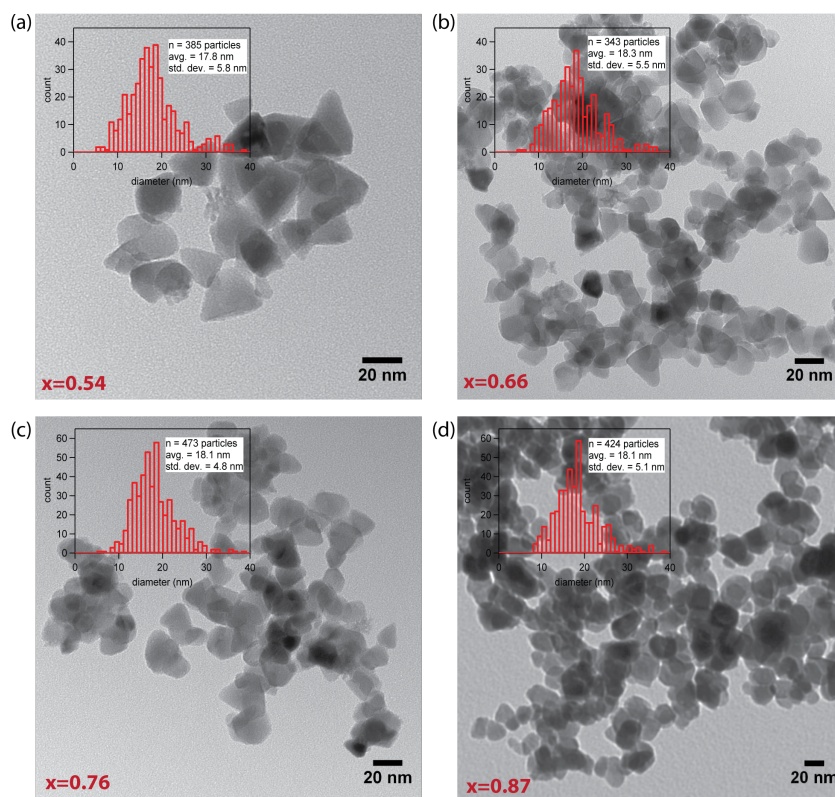


Figure 2.3 TEM images and size analysis of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with varying composition: (a) $x=0.54$; (b) $x=0.66$; (c) $x=0.76$; and (d) $x=0.87$. The average particle dimensions are ~ 18 nm in all four cases. Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

TEM images of oxy(nitrides) with $x=0.54, 0.66, 0.76$, and 0.87 and the corresponding size analysis are shown in Figure 2.3. The particles appear faceted and reminiscent of hexagonal-cone shaped ZnO nanocrystals.³⁰ Particle sizes remained constant over the composition range, with dimensions around 18 nm and standard deviations ~ 5 nm. In this size regime, we do not expect to observe effects of quantum confinement because the exciton Bohr radii in ZnO and GaN are <5 nm.

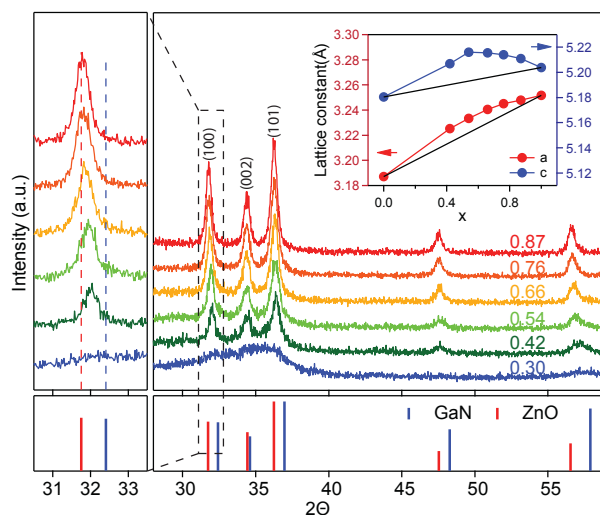


Figure 2.4 Powder XRD patterns of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with varying values of x , synthesized at 650 °C. Enlarged view of the wurtzite (100) peak shows a peak shift away from GaN and toward ZnO with increasing x ; (Inset) Lattice parameters a and c , determined from positions of (100) and (002) peaks respectively, showing deviations from ideal solid solution behavior represented by the black lines. Lattice parameters could not be determined for the $x=0.30$ sample due to poor crystallinity. Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

XRD patterns of nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with x ranging from 0.30 to 0.87 are shown in Figure 2.4. The product with $x=0.30$ exhibits poor crystallinity for reasons that we do not yet understand. It was also observed in bulk oxy(nitrides) that addition of ZnO to the starting material improved product crystallinity and photocatalytic activity, even though the remaining Zn fraction was <0.3 , but the reason for this improvement is not known.³¹ Oxy(nitrides) with x

values of 0.42, 0.54, 0.66, 0.76, and 0.87 exhibit well-defined single wurtzite peaks in the XRD, indicating the presence of one product. An enlarged view of the (100) peak shows its position shifting away from GaN and toward ZnO with increasing x .

The variation of lattice constants a and c , determined from positions of (100) and (002) XRD peaks respectively, is shown in the inset of Figure 2.4. Both lattice constants deviate from the linear ideal solid solution behavior described by Vegard's law. Similar deviations were predicted theoretically for bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, and were attributed to bond distortions that arise because of the nonisovalent nature of the solid solution.¹² The deviations in Figure 2.4 are also similar, though somewhat higher in magnitude, to those seen in bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ made by mixing of ZnO and GaN under high pressures (up to 6.2 GPa) and high temperatures ($>700^\circ\text{C}$).⁵ One major difference is the lattice constant c for materials with approximately equal amounts of ZnO and GaN: in the bulk, the $x=0.49$ was closer to the value for the ideal solid solution than the GaN- and ZnO-rich samples,⁵ while in Figure 2.4 $x=0.54$ is the furthest from the ideal value. This contrast implies that the chemical bonds in the c direction in $x\sim 0.5$ samples are relatively long in our materials and relatively short in those obtained by high-pressure mixing of ZnO and GaN powders, suggesting structural differences and possibly even different phases of the material in the two experiments. The atomic level structure of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, including the nature of the local chemical bonding, the spatial distribution of the constituent elements, and the balance between the enthalpic cost of mixed valence and the entropic benefit of mixing, is not yet understood.^{5,6,10,12-14,32,33} Nevertheless, differences in the reaction pressures can account for the longer bonds observed here: high-pressure conditions generally favor higher-density phases, while the atmospheric-pressure nitridation described here produces a more expanded lattice,

especially in the $x \sim 0.5$ case. There may be additional differences in pressure response due to the nanoscale size regime,³⁴ but they are outside the scope of this study.

2.2.4 Particle crystallinity.

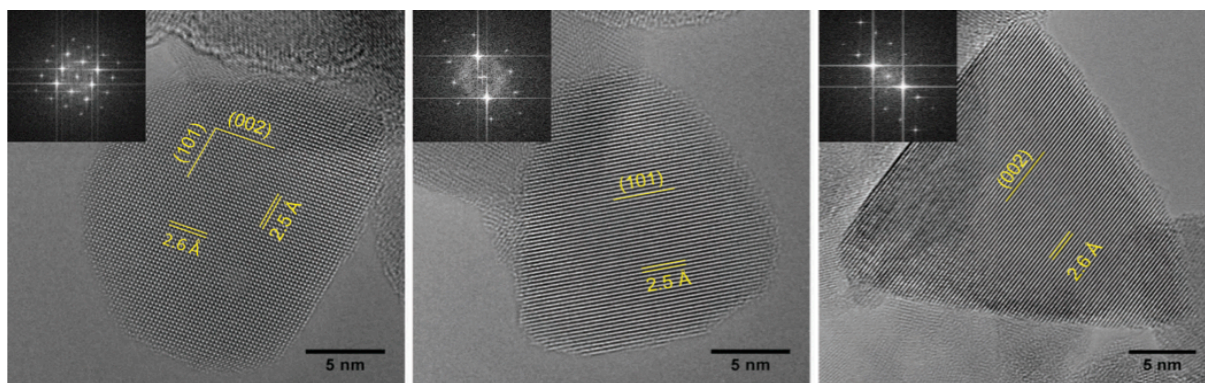


Figure 2.5 Aberration-corrected HRTEM images of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals, with fast Fourier transforms of each particle (insets). Particles are single-crystalline and lattice spacings can be indexed to the wurtzite d-spacings consistent with XRD patterns. Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

To illustrate the crystalline quality of the materials described here, we focus on samples with $x=0.76$. Aberration-corrected HRTEM images of three particles are shown in Figure 2.5. The particles are single-crystalline and their lattice spacings can be indexed to wurtzite, consistent with the XRD patterns (Figure 2.4). Crystallite size analysis by the Scherrer method³⁵ is consistent with the nanoparticle sizes measured from low-resolution TEM images (Figure 2.3c), suggesting that most of these $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanoparticles are single-crystalline. The high quality of the nanocrystals is promising for achieving improved water-splitting quantum yields because of the decreased probability of energy-wasting internal carrier trapping and recombination processes.

2.2.5 Optical spectra as a function of composition.

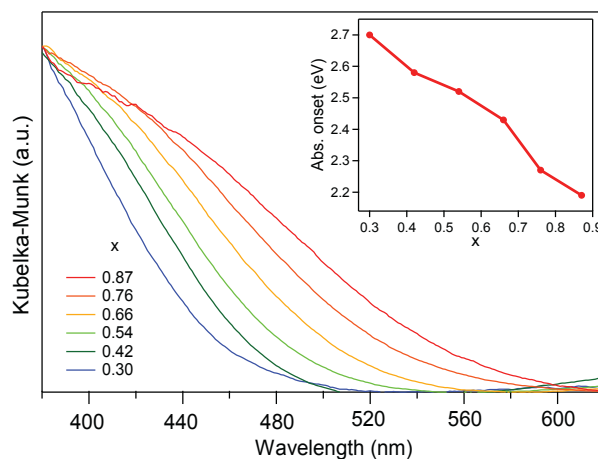


Figure 2.6 Absorption spectra of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with varying x , normalized at 380 nm. The absorption shifts continuously to longer wavelengths with increasing x ; (Inset) Values of absorption onset as a function of x . Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

The ability to control x in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals allowed us to also tune their absorption spectra, as shown in Figure 2.6. The spectra were obtained by conversion of diffuse reflectance to absorbance using the Kubelka-Munk function. A photograph of the samples (Figure 2.7) shows the gradual change of color from yellow to orange with increasing x .⁵⁻¹⁷ The origin of the visible absorption in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is not well understood. Furthermore, both band-gap bowing and the improved band-gap lowering in ZnO-rich oxy(nitrides) have been predicted by theoretical studies.^{7,9,10,12} We made no assumptions about the direct or indirect nature of the visible absorption, and simply reported the absorption onset values, determined by linear extrapolation of the absorption edge to zero absorbance (Figure 2.6 inset).³⁶ The absorption onset shifts to the red almost linearly from 460 nm (2.7 eV) for $x=0.30$ to 565 nm (2.2 eV) for $x=0.87$. This observation is in contrast to the case of bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesized by mixing of ZnO and GaN powders under high pressure and temperature, which exhibited band gap bowing with the minimum gap at $x=0.49$ (2.5 eV).⁵ Instead, our results agree with the observation for

bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesized by nitridation of layered double hydroxides, which had red-shifting absorption onsets over the range $0.46 < x < 0.81$, to values as low as 2.37 eV.¹⁸ We attribute this qualitatively different behavior to the structural differences between the high-pressure oxy(nitrides) and those obtained under atmospheric pressure, described above. The results reported here demonstrate that achieving ZnO-rich compositions of nanoscale oxy(nitrides) is an attractive strategy for band gap lowering. We do not yet know the value of x at which the band-gap starts approaching that of pure ZnO.

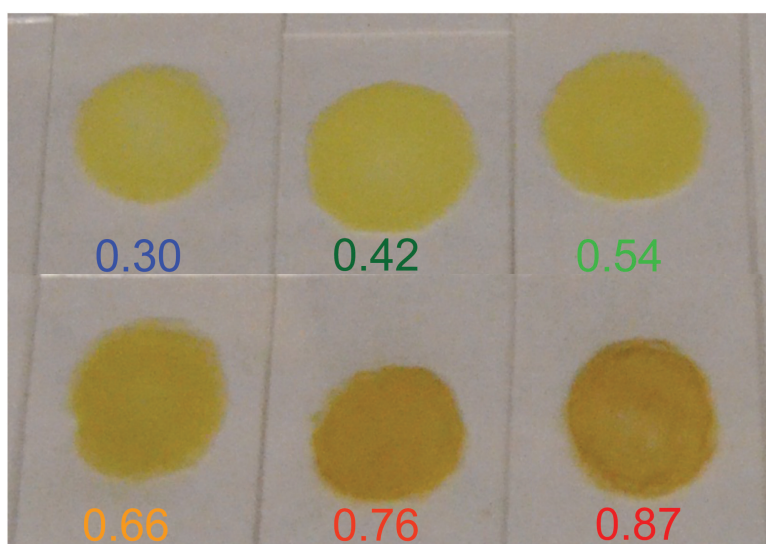


Figure 2.7 Photograph of nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ samples with varying x showing a color change from yellow to orange with increasing x . Reprinted with permission from Lee et al. *Nano Lett.* 2012, 12, 3268 – 3272. Copyright © 2012, American Chemical Society.

The ability to synthesize oxy(nitride) nanocrystals with high ZnO content and lower band gaps has important practical implications. Because the solar photon flux rises sharply across the 300-550 nm range, relatively small differences in absorption onsets in this region can significantly impact the solar-harvesting capacity of a material. A semiconductor with a band gap of 2.7 eV can absorb 5.8% of terrestrial solar photons, while one with a band gap of 2.2 eV can absorb 15.3%.³⁷ Thus, a shift in the absorption onset between our $x=0.30$ and $x=0.87$ samples

increases the fraction of solar photons that can be absorbed by a factor of 2.6. If the quantum yields of water splitting were otherwise equal (i.e., if the shifted band edges still had proper overpotentials for water splitting), this shift translates to 260% more H_2 that could be produced by the same amount of material under identical solar irradiation. One potential caveat is the effect of increased ZnO concentration in the solid solution on particle stability. ZnO is known to be susceptible to anodic photo-corrosion.³⁸ Because of the limited range of compositions available, literature examples of the use of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ for photocatalytic water splitting focus on GaN-rich materials.^{1,2} In these cases, the photocatalysts were stable for more than 15 hours during water splitting in acidic media.^{1,2,39} Mixing GaN and ZnO into a solid solution provides resistance to photo-corrosion and it remains to be seen whether this phenomenon extends to ZnO-rich oxy(nitrides).

2.3 Conclusion

We have reported the synthesis and characterization of high-quality $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ nanocrystals over a broad range of compositions, $0.30 < x < 0.87$. Control of x was achieved by nitridation of nanocrystalline $ZnGa_2O_4$ and ZnO precursors in varying ratios. Use of nanoscale precursors and relatively low nitridation temperatures prevented both the formation of bulk oxy(nitride) and the evaporation of Zn, and this strategy produced high-quality nanocrystals. Over the range of compositions studied, the absorption onset decreased monotonically from 2.7 to 2.2 eV with increasing x , which corresponds to a 260% improvement in solar photon absorption. We expect that the nanocrystalline morphology as well as the tunable composition and band gap will prove beneficial for the use of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ in solar photochemistry.

2.4 Experimental

2.4.1 Chemicals.

All chemicals were purchased from Sigma-Aldrich and used without further purification. All reactions were carried under atmospheric pressure, which is ~620 torr in Boulder, CO.

2.4.2 Synthesis of ZnGa_2O_4 nanocrystals.

Synthetic procedure was adapted from a previous report.²⁶ 1 mmol of $\text{Zn}(\text{acac})_2$ (99.995%), 2 mmol of $\text{Ga}(\text{acac})_3$ (99.99%), 5 mmol of 1,2-hexadecanediol (90%), 6 mmol each of oleic acid ($\geq 99.0\%$) and oleylamine (70%), and 10 ml of benzyl ether (98%) were placed in a three-necked round bottom flask and heated to 40 °C under Ar. After the mixture became optically clear, the temperature was increased to 100 °C under vacuum to remove O_2 and H_2O . The temperature was then raised to 200 °C under Ar for 30 min. It has been reported that this intermediate temperature step is critical for synthesis of uniformly sized spinel particles.⁴⁰ The reaction was further heated to 280 °C and maintained at this temperature for 2 h. Upon cooling to room temperature, the resulting ZnGa_2O_4 nanocrystals were collected by centrifugation and purified three times by precipitation from 5 ml of hexane and 45 ml of ethanol.

2.4.3 Synthesis of ZnO nanocrystals.

This synthesis was carried out following a previously reported procedure.²⁷ 40 mmol of ZnCl_2 ($\geq 98\%$) was dissolved in 200 mL of 1,2-ethanediol (99.8%) and heated to 150 °C under air. Upon reaching 150 °C, 16 mL of 5 M NaOH solution was added dropwise (~1 drop/second) to the above solution with stirring, while maintaining the reaction temperature at 150 °C. After all the base was added (approximately 10 minutes), the solution was allowed to cool to room temperature. The resulting white powder was collected by sedimentation and the supernatant solution was discarded. The sedimentation was repeated five times in water to remove NaCl

from the product. The ZnO nanoparticles were then collected by centrifugation and further purified three times by washing with water.

2.4.4 Ligand exchange procedure for ZnGa₂O₄ nanocrystals.

As-synthesized ZnGa₂O₄ nanocrystals were soluble in non-polar solvents, while the ZnO nanoparticles were hydrophilic. In order to produce uniform nanocrystal mixtures, ZnGa₂O₄ ligands were exchanged for 3-mercaptopropionic acid (3-MPA, ≥99.0%) by modification of a procedure reported by Amirav et al.²⁸ 0.5 g of 3-MPA was dissolved in 3 ml of methanol and tetramethyl ammonium hydroxide (≥97%) was added until pH reached 11. 60 mg of ZnGa₂O₄ were dispersed in 3 ml of hexane and 15 ml of ethanol was added, which resulted in precipitation of ZnGa₂O₄. Then the basic 3-MPA solution was added to the ZnGa₂O₄/hexane/ethanol mixture with stirring. After the mixture became optically clear, indicating ZnGa₂O₄ solubility in polar solvents, 25 ml of toluene was added and the ligand-exchanged ZnGa₂O₄ was collected by centrifugation. After drying, particles were collected under vacuum, dissolved in 5 ml of water again, washed with 20 ml of ethanol and 25 ml of toluene, and collected by centrifugation.

2.4.5 Synthesis of nanocrystalline (Ga_{1-x}Zn_x)(N_{1-x}O_x).

Mixtures of ZnO and MPA-capped ZnGa₂O₄ nanocrystals (~100 mg total) were dispersed in an approximately 1:1 water-ethanol mixture, deposited on a glass slide, and allowed to dry. Nitridation was carried out in a tube furnace (Lindberg Hevi-Duty) under an atmosphere of anhydrous NH₃ (99.99%, Airgas) for 10 hours, at temperatures ranging from 500 to 850°C. Furnace temperature was calibrated using a thermocouple device. The NH₃ flow rate was approximately 100 ml/min.

2.4.6 Characterization.

Powder X-ray diffraction (XRD) patterns were recorded with a Scintag X-2 X-ray diffractometer (Figure 2.1 and 2.2) and a Scintag Pad V diffractometer (Figure 2.4), both equipped with Cu K α radiation ($\lambda=0.1540562$ nm). Peak positions were determined by fitting with Lorentzian functions. Values of lattice constants a and c in wurtzite (Ga $_{1-x}$ Zn $_x$)(N $_{1-x}$ O $_x$) were calculated from d-spacings of (100) and (002) peaks respectively. Crystallite size analysis was carried out using the Scherrer method³⁵ using a microcrystalline quartz XRD pattern to subtract instrumental broadening. Low-resolution transmission electron microscopy (TEM) was carried out using a Philips CM 100 microscope equipped with a bottom mounted 4 mega-pixel AMT v600 digital camera. Samples were prepared by drop casting from an ethanol suspension on carbon film, 300 mesh Cu grids (Electron Microscopy Sciences). Particle size analysis was carried out using the ImageJ software. High-resolution TEM imaging was carried out on an aberration-corrected FEI Titan 80-300 FEG-TEM microscope at the CAMCOR facility at the University of Oregon. Samples were prepared by drop-casting on lacey formvar film (stabilized with carbon) 300 mesh Cu grids (Ted Pella, Inc.). Diffuse reflectance spectra were collected on a Shimadzu UV-3600 spectrophotometer equipped with an integrating sphere, using BaSO $_4$ as a reflectance reference. Diffuse reflectance was converted to absorbance using the Kubelka-Munk equation ($A=(1-R_s)^2/2R_s$), where $R_s=R_{\text{sample}}/R_{\text{reference}}$. Elemental analysis by ICP-OES was carried out using ARL 3410+ inductively coupled optical emission spectrometer. Samples were analyzed in triplicate. In (Ga $_{1-x}$ Zn $_x$)(N $_{1-x}$ O $_x$) literature, values of x are often determined by EDS, rather than ICP-OES. To compare the two methods, elemental analysis was also carried out by energy-dispersive X-ray spectroscopy (EDS), using a cold cathode field emission scanning electron microscope (JEOL JSM-7401F) (Table 2.1).

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Chapter 3. Synthesis and Characterization of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ Nanocrystals with a Wide Range of Compositions

3.1 Introduction

The oxynitride $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, a solid solution of GaN and ZnO, has drawn considerable interest for solar water splitting since its discovery in 2005.¹ This material is intriguing because its band gap can be tuned down to the visible region by varying the composition (fraction of ZnO, x) even though the parent semiconductors have band gaps in the UV region (3.4 eV for GaN and 3.2 eV for ZnO). The origin of the band gap reduction upon mixing of ZnO and GaN is still under debate.²⁻¹² Moreover, it has been demonstrated that $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ can act as a stable visible light driven photocatalyst for overall water splitting into H_2 and O_2 when it is modified with proper co-catalysts.¹³⁻²³ The first reported synthesis of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ involves nitridation of a mixture of bulk Ga_2O_3 and bulk ZnO at temperatures of 850 °C and above.^{1,14} In this reaction, spinel ZnGa_2O_4 forms and serves as an intermediate that converts to $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ under NH_3 flow.²⁴ The fraction of ZnO (x) that can be achieved in this synthetic route is limited by the spinel intermediate and high volatility of zinc at the high nitridation temperature. To examine the correlation between band gap and composition, other synthetic methods to make bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ have been explored.²⁵⁻²⁷ Because nanoscale particles can have improved crystallinity and shorter diffusion distances for photoexcited carriers transported to the surface,^{28,29} efforts have also been undertaken to synthesize nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. The earliest reported methods included nanowires as well as ~10 nm nanoparticles with a range of x values from 0.08 to 0.48.^{30,31} We subsequently reported a method for

synthesizing $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with x values ranging from 0.30 to 0.87.³² Other methods for synthesis of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanowires, nanotubes, and hollow nanospheres have since been reported.³³⁻³⁶

As described in our previous report,³² single crystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanoparticles with diameters of ~18 nm and x ranging from 0.30 to 0.87 can be obtained by exposure of a mixture of ZnO and ZnGa_2O_4 nanocrystals to NH_3 at 650 °C. The x value here refers to the overall molar composition of the sample usually measured by elemental analysis of the metal content, i.e., $x=\text{Zn}/(\text{Zn}+\text{Ga})$. The use of nanoscale precursors allowed us to lower the nitridation temperature from that used in the bulk synthesis^{1,14} and thus avoid the loss of Zn. The x values in products were tunable simply by changing the ratios of ZnO and ZnGa_2O_4 in the starting material mixture. To understand how properties such as band gap and photoelectrochemical (PEC) activity of nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ depend on composition, it is desirable to obtain a broader range of compositions approaching pure GaN ($x=0$) and ZnO ($x=1$). We have shown that, for nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, the absorption onset decreases monotonically from $x=0.30$ to $x=0.87$. However, the minimum band gap necessarily exists at a certain value of x , and this minimum value and the associated composition have not been determined. The composition that corresponds to the smallest band gap is the most useful from the standpoint of sunlight absorption. To achieve this broader range of compositions, it is necessary to understand the mechanism of formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals in the synthesis. Specifically, it is not obvious how the two nanocrystalline oxide precursors, wurtzite ZnO and spinel ZnGa_2O_4 , combine under NH_3 flow to make wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ at this relatively low temperature. Finally, because $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ materials are of interest for applications in solar water

splitting, it is necessary to assess whether the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ in a nanocrystalline form is PEC active.

In this chapter, we describe the broadest range of composition of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ obtained with one synthetic method, encompassing x values from 0.06 to 0.98. By examining the temperature-dependence of nitridation of ZnGa_2O_4 under NH_3 , we found that, at the relatively low synthesis temperature of 650 °C, inclusion of ZnO in the starting material is necessary to obtain wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. Monitoring the conversion of spinel ZnGa_2O_4 to the wurtzite final product under NH_3 over time allowed us to propose a mechanism in which $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ forms at the interface of ZnO and ZnGa_2O_4 by nucleating topotactically on ZnO. With the insights from these experiments, we expanded the range of x values at each end ($x=0.06, 0.24, 0.91$, and 0.98). We found that the lowest band gap, 2.25 eV, occurs at $x=0.87$. Little compositional mixing is necessary to achieve visible absorption, which is observed at both ends of the composition range, in agreement with previous observations in bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$,^{14,25,27,30,36,37} although the appearance of the spectra is qualitatively different at the two ends of the range. Finally, we compared PEC oxidation using thick films of nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ under visible irradiation and found that this material is photoactive, exhibiting higher photocurrent density than its bulk counterpart, albeit still too low for practical applications. The dependence of PEC activity on composition does not scale simply with absorption of visible light, which indicates that the measured photocurrents depend on multiple parameters that remain to be determined. The insights into the mechanism of formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals, the expanded composition range, and the optical and PEC properties improve our understanding of this unusual material and provide information useful for future studies of composition-dependent PEC properties of nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$.

3.2 Results and Discussion

3.2.1 Formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals

In order to expand the range of compositions of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals beyond $0.30 \leq x \leq 0.87$, we first closely examined how these materials form by nitridation of a mixture of ZnO (d~10 nm) and ZnGa_2O_4 (d~5 nm) nanocrystals under NH_3 at 650 °C. In the original synthesis of bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, a mixture of Ga_2O_3 and ZnO is heated under NH_3 at 850 °C.^{1,13,14} It has been demonstrated that the spinel ZnGa_2O_4 forms from the starting material mixture at 850 °C under NH_3 and serves as an intermediate that directly converts to wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$.²⁴ This mechanism would lead to a maximum x value of ~0.3 without an additional Zn source, although the values achieved at such a high temperature are lower because of evaporation of Zn.^{22,24,26} By using nanocrystalline precursors, we were able to lower the reaction temperature by 200 °C and avoid the loss of Zn.³² We attributed this lowering of required temperature to the higher surface energy and smaller diffusion distances for the solid state conversion when nanoscale precursors are used. Interestingly, however, nitridation of pure ZnGa_2O_4 nanocrystals under these conditions (650 °C for 10 hrs) does not lead to a crystalline wurtzite product, but rather to a material with one very broad peak in the XRD pattern and a similar value of $\text{Zn}/(\text{Zn}+\text{Ga})$ as the starting material (Figure 3.1).

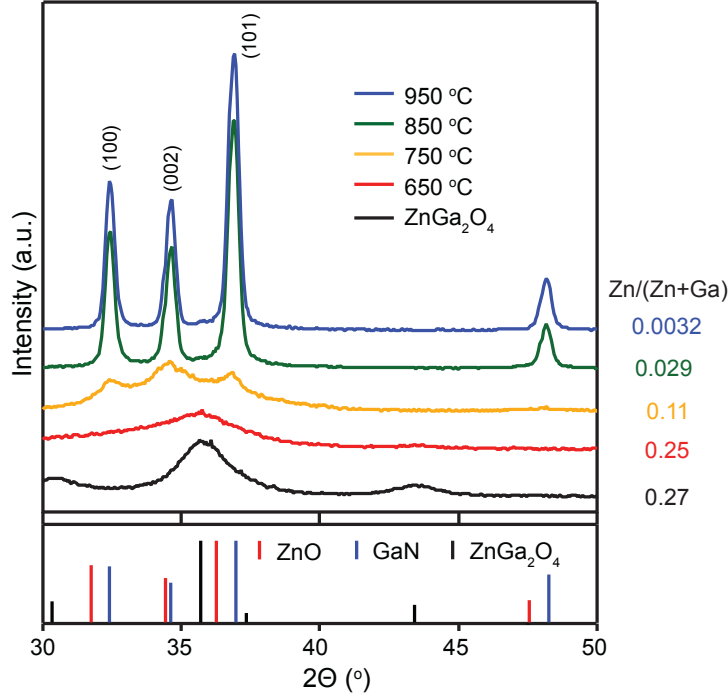


Figure 3.1 Powder XRD patterns of the products obtained from nitridation of ZnGa_2O_4 nanocrystals for 10 hours at varying reaction temperatures. The pattern of the ZnGa_2O_4 nanocrystals before nitridation is shown in black. The vertical lines represent the reference diffraction patterns of ZnGa_2O_4 (black, JCPDS #38-1240), ZnO (red, JCPDS #05-0664), and GaN (blue, JCPDS # 2-1078).

This could correspond to an amorphous material or one with very small spinel domains.^{38,39} By increasing the temperature to 750 °C, we see formation of wurtzite with broad peaks indicating a small crystalline domain size. Because of the increased temperature, we see a significant decrease in $\text{Zn}/(\text{Zn}+\text{Ga})$ due to loss of Zn. At 850 and 950 °C, this effect is even stronger, with well-defined wurtzite peaks but very small values of $\text{Zn}/(\text{Zn}+\text{Ga})$ (<0.03). From the data in Figure 3.1, we conclude that, under our experimental conditions, crystalline wurtzite ($\text{Ga}_{1-x}\text{Zn}_x$)(N_{1-x}O_x) nanocrystals cannot be prepared at 650 °C from ZnGa_2O_4 nanocrystals alone. To prepare crystalline wurtzite nanoscale ($\text{Ga}_{1-x}\text{Zn}_x$)(N_{1-x}O_x), addition of ZnO nanocrystals is required. Thus, in addition to serving as a source of Zn in the final product, ZnO plays a critical role in the product crystallinity. It has been shown in bulk ($\text{Ga}_{1-x}\text{Zn}_x$)(N_{1-x}O_x), with synthesis

temperatures of 850 °C and above, that the presence of ZnO in the starting material mixture improves the crystallinity of the final $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ product, as well as increasing the x value of the product.^{22,40}

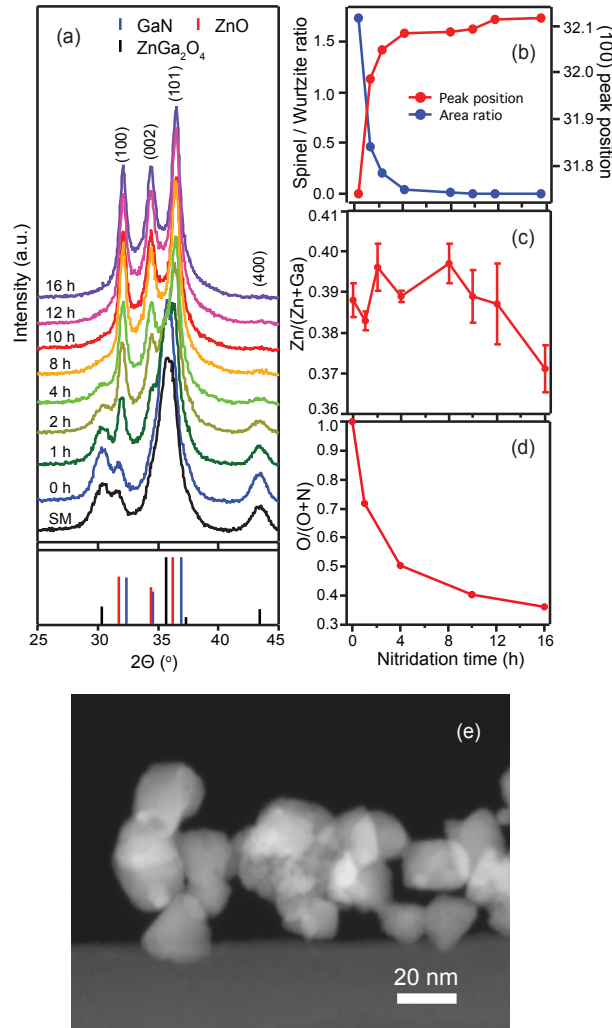


Figure 3.2 (a) Powder XRD patterns of the products from nitridation of a starting mixture with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$ for 0–16 hours at 650 °C. The vertical lines represent the reference diffraction patterns of ZnGa_2O_4 (black, JCPDS #38-1240), ZnO (red, JCPDS #05-0664), and GaN (blue, JCPDS # 2-1078). (b) Area ratio of (400) spinel peak to (100) wurtzite peak (blue) and position of (100) peak of wurtzite (red). (c) Values of $\text{Zn}/(\text{Zn}+\text{Ga})$. (d) Values of $\text{O}/(\text{O}+\text{N})$. (e) ADF-STEM image of the product after 10 hours of nitridation.

Next, we focus on how the spinel ZnGa_2O_4 in the starting material mixture with ZnO converts to wurtzite at 650 °C. We conducted a set of nitridations with a starting mixture with

$\text{Zn}/(\text{Zn}+\text{Ga})=0.39$. The starting mixture of ZnO and ZnGa_2O_4 nanocrystals was nitrided at 650 °C for 0, 1, 2, 4, 8, 10, 12 and 16 hours under flowing NH_3 . The XRD patterns of the nitrided products are shown in Figure 3.2a. The starting mixture (SM) displays both wurtzite and spinel peaks attributed to the presence of ZnO and ZnGa_2O_4 , respectively. The changes of ZnGa_2O_4 during the nitridation were examined via the well-resolved (400) spinel peak appearing at $2\Theta=43.4^\circ$ since the most intense (311) spinel peak at $2\Theta=35.7^\circ$ overlaps with the (101) peak of ZnO. The spinel (400) peak quickly decreases in intensity as the nitridation progresses and finally disappears between 8 and 10 hours of nitridation. The XRD patterns of the products from 0–8 hours of nitridation are fit well with a combination of spinel and wurtzite peaks, whereas the 10–16 hours products can be fit with wurtzite reference peaks alone (Figure 3.3). No intermediate phase was observed. Figure 3.2b shows the area ratio of the (400) spinel peak to the (100) wurtzite peak as well as the position of the wurtzite (100) peak. As the fraction of the spinel phase decreases, the wurtzite peak shifts from the ZnO value (31.7°) to the value of the nitrided products ($\sim 32.1^\circ$). Figure 3.2c shows that $\text{Zn}/(\text{Zn}+\text{Ga})$ does not change appreciably over this time course, indicating that the changes observed in the XRD patterns are not due to loss of Zn. The value of $\text{O}/(\text{O}+\text{N})$ in the nitrided products is shown in Figure 3.2d. It decreases from 1 to the $\text{O}/(\text{O}+\text{N})$ value in the final product as N is incorporated into the product. The product from 1 hour of nitridation had the same values of $\text{Zn}/(\text{Zn}+\text{Ga})$ and $\text{O}/(\text{O}+\text{N})$ (0.39 and 0.40, respectively), indicating the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesis is complete at the time. Figure 3.2e shows an ADF-STEM image of the product nanocrystals from the sample obtained after 10 hours of nitridation, demonstrating that the synthesis leads to a nanoscale product, as previously reported.³² The existence of particles with diameters in the 10-20 nm range is in agreement with the crystallite size determined from the XRD pattern in Figure 3.2a (~ 17 nm).

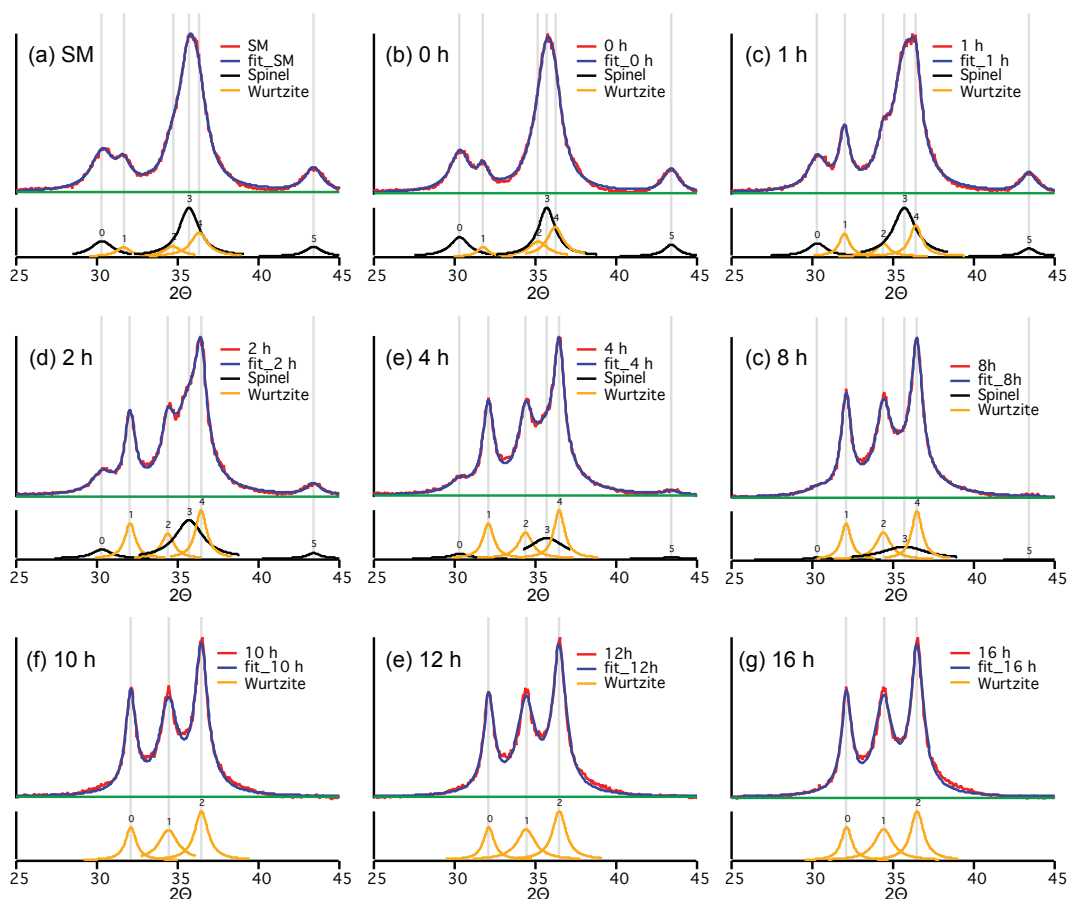


Figure 3.3 Fitting of XRD patterns of the nitrided products for 0–16 hours at 650 °C from a starting material mixture with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$.

The XRD and elemental analysis data in Figure 3.2 suggest that spinel disappearance, formation of wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, and N incorporation occur on a similar timescale with no crystalline intermediates. From Figure 3.1, we concluded that wurtzite ZnO is necessary for the formation of the wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ at 650 °C. From these observations, we propose that at 650 °C wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ forms by nucleation at the interface of ZnO and ZnGa_2O_4 , which is facilitated by the similar crystalline lattice of the underlying ZnO. Such topotactic nucleation is well known in solid state reactions, where the nucleation is promoted when there is structural similarity between the product and at least one of the reactants because the nucleus can form on the existing structure with less structural rearrangements.⁴¹ Upon

nucleation, the reaction can proceed by diffusion of the atoms of the elements that constitute the product and simultaneous chemical conversion to the oxynitride. Higher temperatures are needed to nucleate $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ from spinel ZnGa_2O_4 because the starting material is lacking wurtzite structure that aids in product nucleation. The formation of an interface between the ZnGa_2O_4 (~5nm) and ZnO (~10nm) particles can be seen in the TEM images at various time points in the reaction (Figure 3.4).

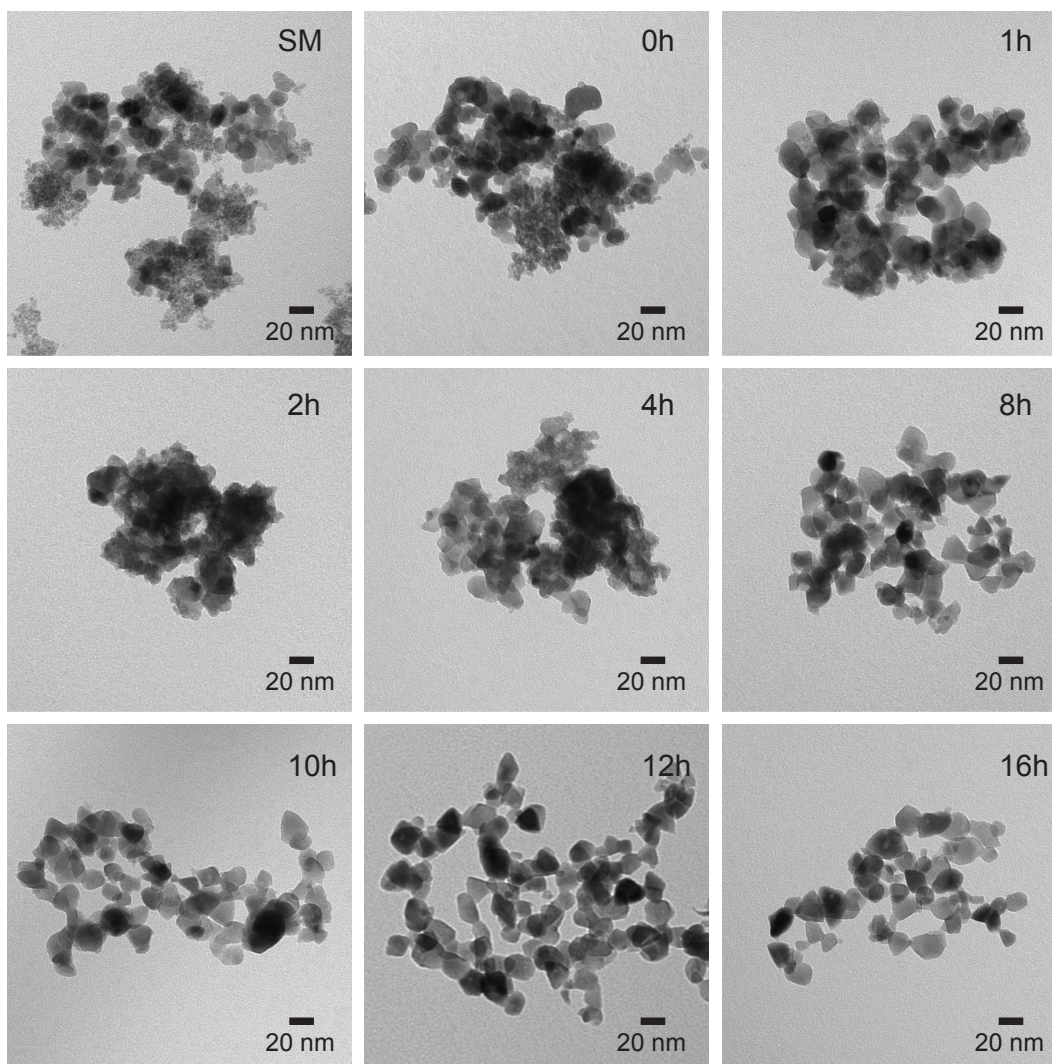


Figure 3.4 Low-magnification TEM images of the nitrided products for 0–16 hours at 650 °C from a starting material mixture with $\text{Zn}/(\text{Zn}+\text{Ga})=0.39$.

The two types of particles exist separately in the starting mixture, appear to fuse together over 0–2 hours of nitridation, and then the fused particles reach their final size from 4 hours of nitridation. This mechanism of the solid state reaction that forms the oxynitride product may result in heterogeneities due to the requirement for an interface between ZnO and ZnGa₂O₄ to nucleate the product. In the starting material mixture, there may be various interface arrangements. Some of this heterogeneity can be seen as differences in particle size and shape in the TEM images (e.g., Figures 3.2e and 3.4). An understanding of such heterogeneities is outside the scope of this manuscript. Thus, we emphasize that in this work, the value of x refers to the value measured by elemental analysis of the overall sample, and may vary from particle to particle.

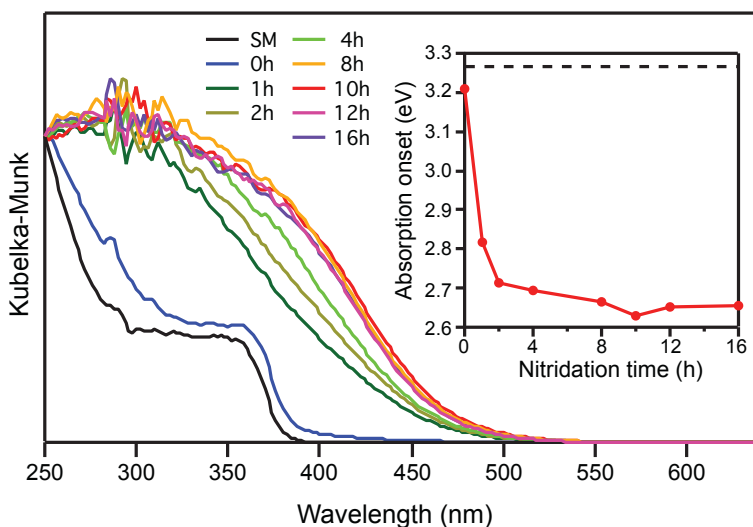


Figure 3.5 Diffuse reflectance spectra (normalized at 250 nm) of the products of nitridation for 0–16 hours at 650 °C with Zn/(Zn+Ga)=0.39. Inset shows the absorption onsets of the products as a function of the nitridation time along with that of the starting mixture (SM, dashed line).

Figure 3.5 shows the diffuse reflectance spectra of the nitrided products from Figure 3.2 along with that of the starting mixture, demonstrates how the visible absorption develops as the reaction progresses. In the absorption spectrum of the starting mixture, two absorption edges with onsets at 295 nm (4.2 eV) and at 390 nm (3.2 eV) are observed, which correspond to the

band gap absorption of ZnGa_2O_4 ⁴² and ZnO ,⁴³ respectively. These characteristic features disappear within the first hour of nitridation, and the absorption onsets of the nitrated products significantly shift to lower energy. This occurs at the same time as the changes observed in the XRD patterns and O/(O+N) analysis (Figure 3.2). After the most significant changes within the first hour of nitridation, the spectra continue to red shift with reaction time up to 10 hours with formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. The absorption spectra provide an indication for determining an optimized nitridation time for the reaction. The absorption onsets decrease until 10 hours of nitridation, and increase after then due to a small loss of Zn, consistent with the elemental analysis in Figure 3.2c. This suggests that 10 hours of nitridation is optimal. At that time, the values of $\text{Zn}/(\text{Zn}+\text{Ga})$ and $\text{O}/(\text{O}+\text{N})$ are equal (Figure 3.2c,d).

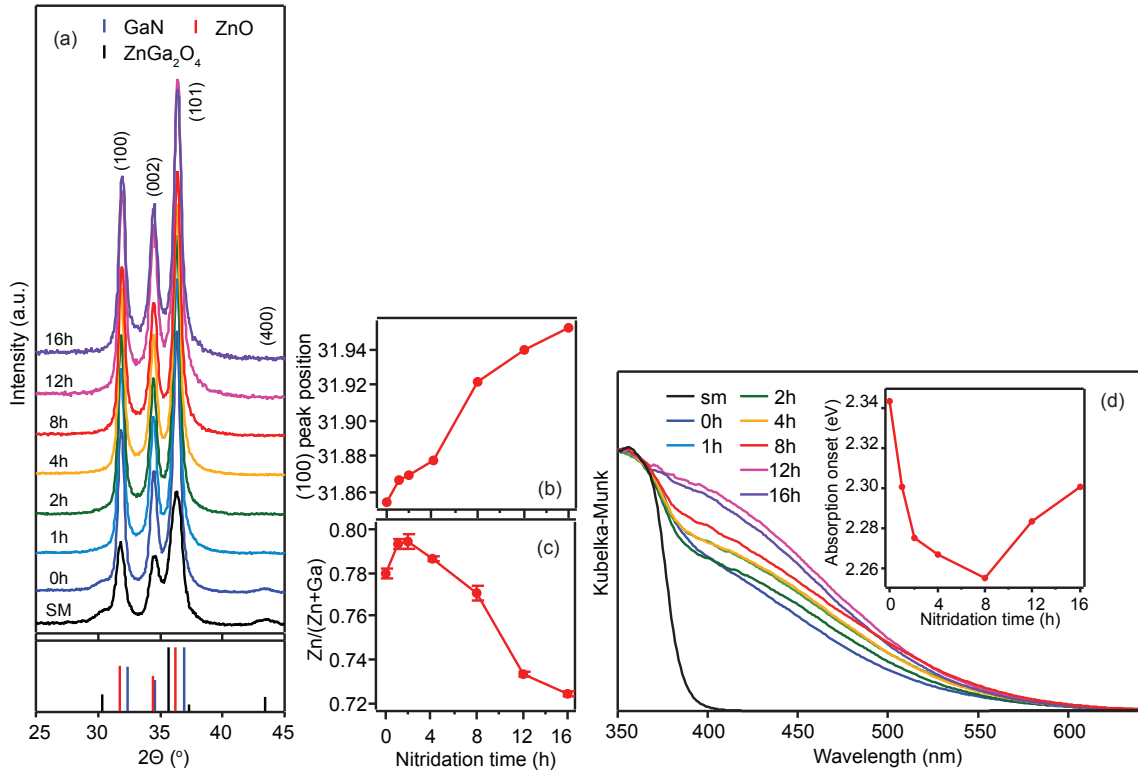


Figure 3.6 (a) Powder XRD patterns, (b) (100) peak position, (c) Elemental analysis from ICP-OES, and (d) Diffuse reflectance spectra (normalized at 350 nm) of the products from nitridation of a starting mixture ($\text{Zn}/(\text{Zn}+\text{Ga})=0.78$).

We conducted a similar set of nitridation-time dependent experiments for a ZnO-rich $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ synthesis ($x=0.78$). As shown in Figure 3.6, ZnO-rich starting mixture ($\text{Zn}/(\text{Zn}+\text{Ga})=0.78$) was nitrided for 0 - 16 hours. The XRD patterns of each nitrided product show that the spinel peaks of ZnGa_2O_4 in the starting mixture quickly disappear, and the (100) peak of ZnO shifts to higher angle in 2 hours of nitridation, resulting from the conversion of spinel ZnGa_2O_4 and wurtzite ZnO to wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, similar to what we observed from the $x=0.39$ sample set described above. The shift of the wurtzite (100) peak was not drastic in this ZnO-rich sample set since the starting mixture contains much smaller amount of ZnGa_2O_4 than that in the $x=0.39$ sample set. Zn loss appeared to be significant (on the order of 10%) after 2 hours of nitridation in the $x=0.78$ synthesis, which leads to the changes of the (100) peak position observed after 2 hours. The Zn loss is caused by reduction of ZnO to Zn under ammonia atmosphere, and subsequent volatilization of the Zn. This results in the peak shift towards GaN observed after 2 hours. In the diffuse reflectance spectra of the nitrided products, the absorption onsets rapidly shift to lower energy as the spinel ZnGa_2O_4 and wurtzite ZnO convert to wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ in the same time period. In conclusion, the observations from both ZnO-low and ZnO-rich sample sets reveal the consistent reaction mechanism where the conversion of spinel ZnGa_2O_4 to wurtzite occurs upon topotactic nucleation at a ZnO/ ZnGa_2O_4 interface, and this results in the red shift of absorption onsets.

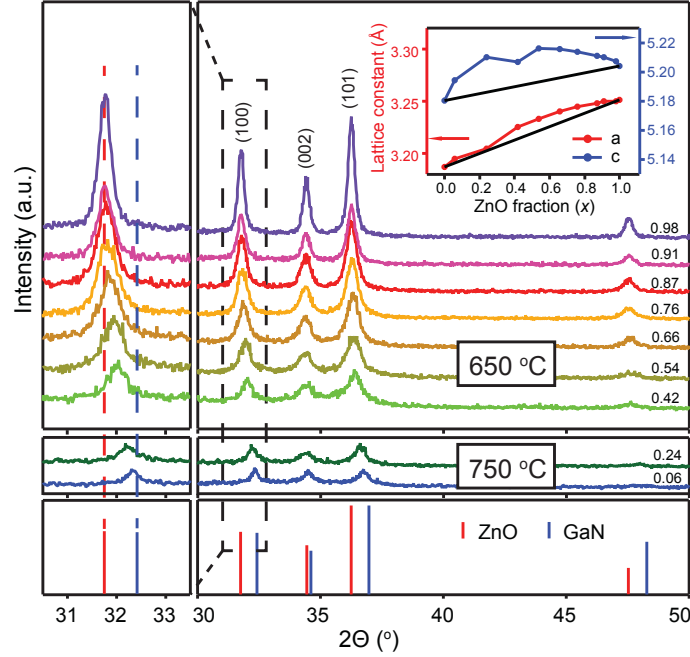


Figure 3.7 Powder XRD patterns of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with $0.06 \leq x \leq 0.98$. The inset represents the variation of lattice parameters compared with the linear behavior expected from an ideal solid solution. The vertical lines represent the reference patterns for ZnO (red, JCPDS #05-0664), and GaN (blue, JCPDS # 2-1078).

3.2.2 $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with a broad range of compositions

An improved understanding of the mechanism of formation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals allowed us to extend the range of x values from the previously reported $0.30 \leq x \leq 0.87$ to each end of the range. Broadening the sample composition range then allowed us to examine how the visible absorption behaves as the composition approaches pure GaN or ZnO, both of which are UV absorbers. Figure 3.7 shows XRD patterns and lattice constants for the wurtzite $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystal samples with x ranging from 0.06 to 0.98. For comparative purposes, this plot includes the XRD patterns of previously reported compositions ($0.30 \leq x \leq 0.87$).³² The preparation of the samples at the two ends of the range is described below.

The composition of the starting material ZnGa_2O_4 suggests that if it converts to $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, the resulting x value would be ~ 0.3 . This defines the lower limit on the x value

without loss of Zn. As shown in Figure 3.1, significant increases in temperature are necessary to obtain good crystallinity from nitridation of ZnGa_2O_4 alone, at the cost of significant Zn evaporation. To aid material crystallinity, and remedy some of the loss of Zn so that there is continuous control of composition, we add extra ZnO and elevate the temperature to 750 °C for 10 hours to obtain $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ samples with low x values. The starting mixtures having Zn/(Zn+Ga) values of ~0.3 and 0.4 were nitrided at 750 °C for 10 hours, leading to the products with x values of 0.06 and 0.24, respectively. The XRD patterns of the products show a wurtzite phase, and the XRD peak positions approach the values of GaN with decreasing ZnO fraction (x), as shown in Figure 3.7. The TEM images of the low- x products show that the product consists of particles that are more agglomerated than those made at 650 °C (Figure 3.8). It is possible that, with a low concentration of ZnO particles that aid in nucleation of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, direct conversion of spinel ZnGa_2O_4 to wurtzite is prevalent.

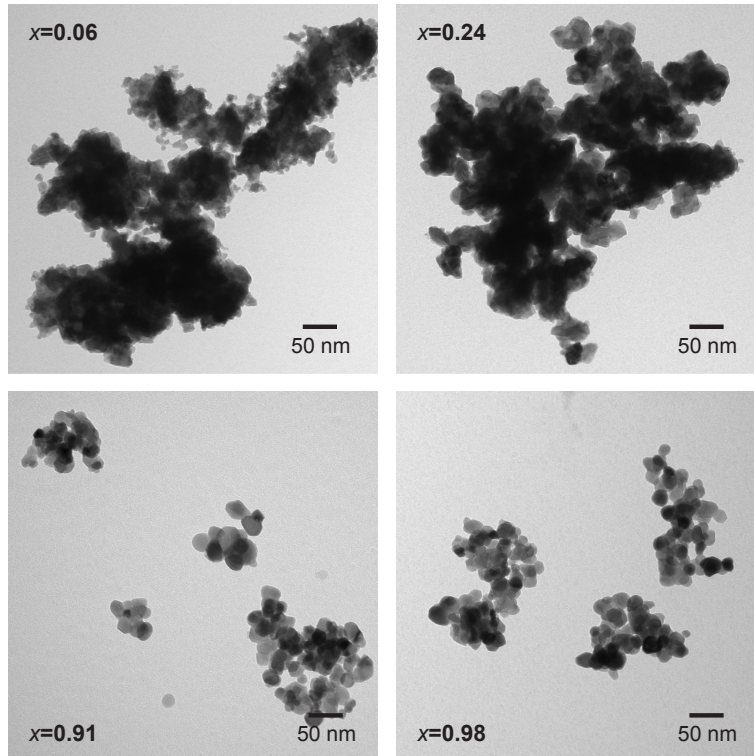


Figure 3.8 Low magnification TEM images of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, ($x=0.06, 0.24, 0.91$, and 0.98).

At the other end of the composition range, it is straightforward to synthesize ZnO-rich $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.91$ and 0.98) by adding more ZnO into the starting mixture. The starting mixture was nitrided at $650\text{ }^\circ\text{C}$ for 10 hours, as previously reported.³² The XRD patterns of these samples indicate that the ZnO-rich products have wurtzite structure with XRD peak positions that approach those of ZnO with increasing x (Figure 3.7). The low-magnification TEM images show particles with average diameters of 20 nm for $x=0.91$ and 29 nm for $x=0.98$ (Figure 3.8), consistent with the narrowing of the XRD peaks for these high- x samples.

The lattice constants c and a calculated from the XRD patterns for the full range of compositions are shown in the inset of Figure 3.7. The presence of single peaks that range in position from those of GaN to those of ZnO are consistent with previous reports and are indicative of a solid solution rather than isolated domains of GaN and ZnO.^{22,25-27,30,36,37} The linear behavior that would be expected for an ideal solid solution from Vegard's law is shown as the black line. Instead of the ideal behavior, we observe bowing that indicates that the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ wurtzite lattice is slightly expanded. This behavior may be due to the non-isovalent nature of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, and has been predicted and observed in bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$.^{10,26} The low- x samples prepared at $750\text{ }^\circ\text{C}$ appear to have the lattice constant a close to the value for an ideal solid solution, but this is not the case for the lattice constant c . The small bowing of the lattice parameter a has also been observed in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ hollow nanospheres.³⁶

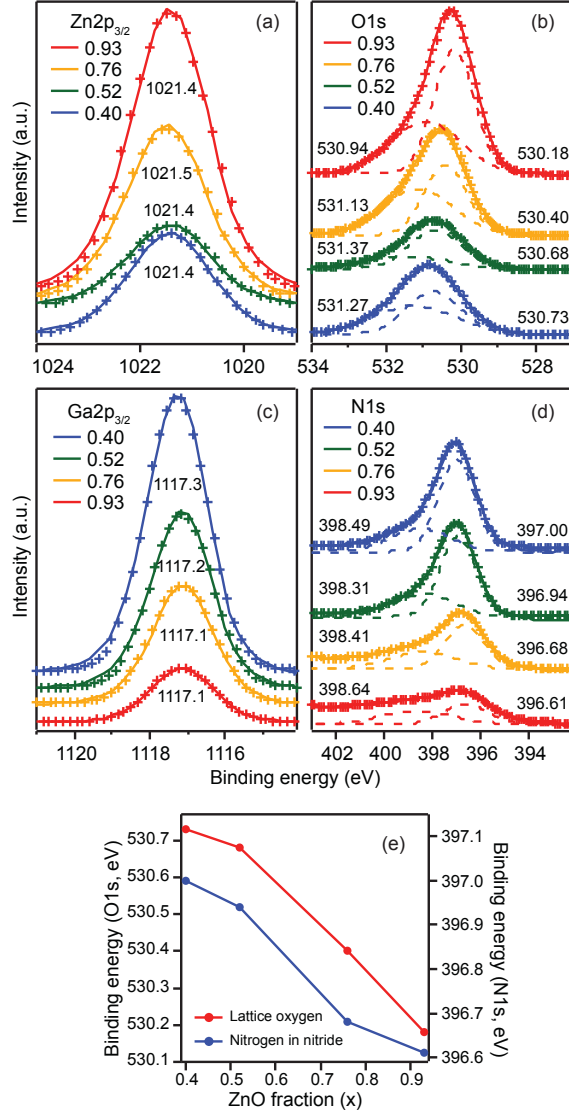


Figure 3.9 XPS spectra of the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with $x = 0.40, 0.52, 0.76$, and 0.93 for (a) Zn2p_{3/2}, (b) O1s, (c) Ga2p_{3/2}, and (d) N1s. (e) Binding energy of lattice oxygen (red) and nitrogen in nitride (N^{3-}) versus the x value.

Figure 3.9 shows the high-resolution XPS spectra for the O1s and N1s peaks of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with $x = 0.40, 0.52, 0.76$, and 0.93 . The Zn2p_{3/2} peaks of the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ appear at almost the same binding energy (1021.4–1021.5 eV) regardless of the composition, which is lower than the reference value of ZnO (1022.0 eV⁴⁴) as shown in Figure 3.9a. This indicates that Zn in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ has more electron density than in ZnO. The same behavior was observed in bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ and was attributed to the presence of Zn-N bonding and

lower electronegativity of N than O.¹³ The O1s peaks in Figure 3.9b were deconvoluted into two peaks that can be assigned to a crystal lattice oxygen (530.18–530.73 eV) and surface –OH group (531.13–531.37 eV).¹³ The peaks of the lattice oxygen appear at lower energies with increasing x , as shown in Figure 3.9e. The peak shift with composition suggests the existence of Ga-O bonds as well as Zn-O bonds in the lattice and the amount of each bonding changes with the composition. Higher x samples contain less Ga-O bonding and more Zn-O bonding, leading to the movement of more electron density towards O due to lower electronegativity of Zn than Ga (electronegativity: 1.65 for Ga; 1.81 for Zn based on Pauling scale).⁴⁵ For Ga2p_{3/2} peaks (Figure 3.9c), all the samples show similar peak position at 1117.1–1117.3 which are consistent with Ga2p_{3/2} in GaN (1117.1 eV⁴⁶). Because the reference peak of Ga2p_{3/2} in Ga₂O₃ (1117.5–1117.8⁴⁷) is very close to the one in GaN, the possible presence of the Ga-O bonding as well as the Ga-N bonding cannot be excluded. The N1s peak of all the samples consists of two components (Figure 3.9d).^{25,48-50} The peak of N1s at ~398.5 eV is similar to that of NH₃ and primary amines. The presence of the amine peak could be due to the NH₃ molecules adsorbed on the surface during the nitridation.⁴⁹ The other N1s peak appears at the lower binding energy (396.61–397.00 eV). We assign this peak to nitride (N³⁻) because the lattice nitrogen peaks of GaN and Zn₃N₂ appear at 397 and 395.7 eV, respectively.^{13,25,44,46,48-50} The nitride peaks continuously shift to lower binding energy with increasing x values (see Figure 3.9e). Similar to the case of oxygen, this shift can be also explained by the existence of Zn-N and Ga-N bonds in the lattice and lower electronegativity of Zn than Ga. With increasing Zn content, more electron density moves toward N lowering its binding energy. While XPS analysis of bulk (Ga_{1-x}Zn_x)(N_{1-x}O_x) has been described previously for a narrow range of compositions,^{13,25,27} composition-dependent XPS peak shifting over a broad range of compositions has not been reported before.

The XPS data in Figure 3.9 is consistent with formation of Ga-O and Zn-N bonds in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals, in agreement with XRD data in Figure 3.7.

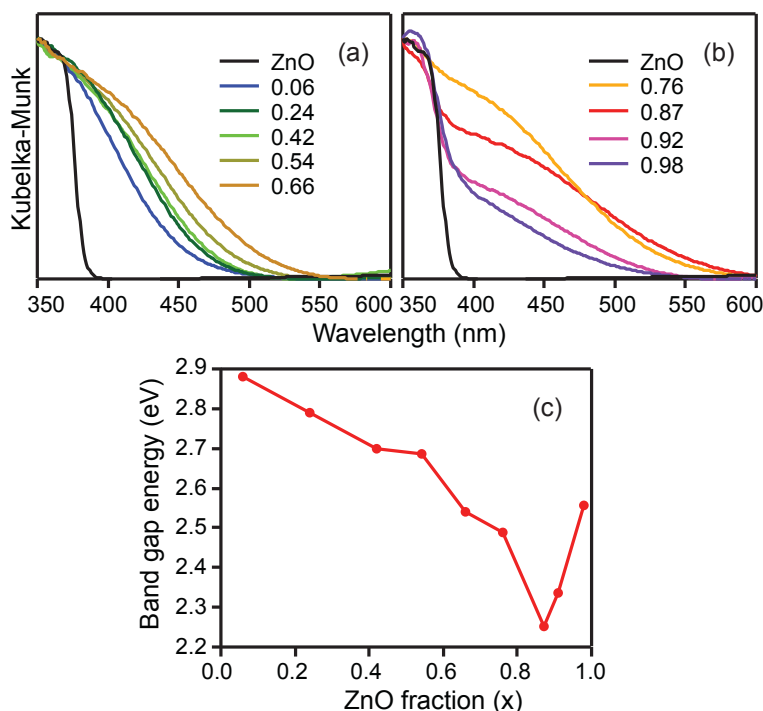


Figure 3.10 Diffuse reflectance spectra of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with varying composition with (a) $x=0.06$ – 0.66 and (b) $x=0.76$ – 0.98 , along with that of ZnO. Spectra are normalized at 350 nm. (c) Band gap energies of the $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ products as a function of ZnO fraction (x).

In Figure 3.10, the diffuse reflectance spectra of the newly synthesized samples ($x=0.06$, 0.24 , 0.92 , and 0.98) are plotted together with the previously reported compositions ($0.30 \leq x \leq 0.87$).³² For clarity, the spectra are separated according to composition with the range $0.06 \leq x \leq 0.66$ shown in Figure 3.10a and $0.76 \leq x \leq 0.98$ shown in Figure 3.10b. It is challenging to extract an accurate value for band gap energy (E_g) from the diffuse reflectance spectra of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ because below-band gap absorption features (free carrier absorption and Urbach tail) are present in addition to the direct band gap transitions.³⁷ The contributions of these features to the diffuse reflectance spectra of nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ are shown in Figure 3.11.

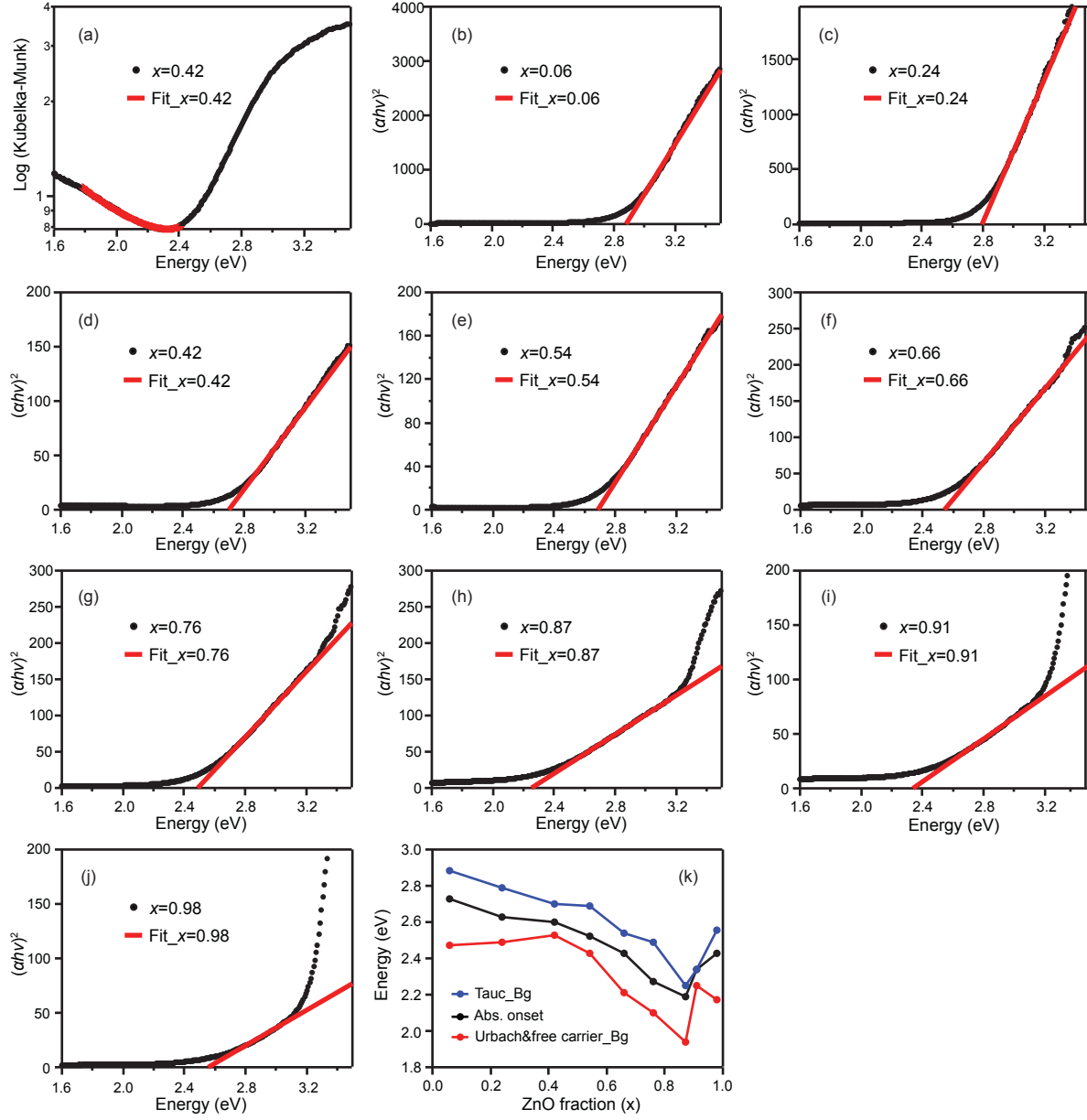


Figure 3.11 Band gap determination of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ from (a) fitting the below-band gap absorption features for $x=0.42$ sample as previously described.³⁷ The red line indicates a fit to $\alpha(E) = A \times e^{(E-E_g)/E_u} + B \times E^{-3} + C$, where A , B , and C are constants, E_g is band gap energy, and E_u is Urbach energy. The value of E_g determined by this method is highly dependent on the details of the fit, such as the energy limits. and (b-j) Tauc plots of $(\alpha h\nu)^2$ against $h\nu$. Tauc plot were fit with a straight line (red) below the energy of the absorption feature characteristic of ZnO (3.2 eV). The value of E_g is the x-intercept of the red fit line (k) Band gap energy determined from the direct band gap absorption (Tauc plot), absorption onset, and below-band gap absorption (free carrier + Urbach tail).

The value of E_g determined from the Urbach tail and free carrier contributions is consistently lower, by 0.1–0.4 eV, than that determined from a Tauc plot for direct band gap absorption, as shown in Figure 3.11k. However, the E_g value from the absorption below the band gap is very sensitive to the fitting range and difficult to determine uniquely. Because of this uncertainty, we use the values of E_g determined from Tauc plots to examine how they vary with composition (Figure 3.10c). Based on the analysis in Figure 3.11, these values are upper limits on the true band gap. We note that the composition-dependent behavior is independent of the band gap determination method (Figure 3.11k).

As shown in Figure 3.10c, the value of E_g for $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ shifts to lower energy range with increasing x value from $x=0.06$ to $x=0.87$. Interestingly, the minimum E_g is found at $x=0.87$ (2.25 eV), and a blue shift is observed above $x=0.87$. An E_g value of 2.25 eV is of interest for solar fuel generation because a semiconductor with this band gap has a maximum achievable solar-to- H_2 conversion efficiency of 12%.⁵¹ The products at each end (0.06 and 0.98) have E_g values of 2.9 and 2.6 eV, respectively. Considering the large band gap of GaN (3.4 eV) and ZnO (3.2 eV), very small compositional changes from the pure ZnO or GaN can cause a large band gap shift, as has been observed in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ materials synthesized by other methods.

14,25,27,30,36,37

At the low- x end of the composition range, the diffuse reflectance spectra have similar shapes, with the effect of the composition being simply the red shifting of the spectrum (Figure 3.10a). At the high- x end of the range, however, both the band gap and the spectral shape change with composition (Figure 3.10b). The absorption at wavelengths below 390 nm characteristic of ZnO begins to emerge in the spectra of the ZnO-rich samples starting with $x=0.76$. This ZnO-like absorption becomes stronger compared to visible absorption with increasing x . The ZnO-like

feature in the optical spectra of high- x $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ was also observed in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ samples prepared from a combustion method.²⁵ Remarkably, the visible absorption is still relatively strong even when $x=0.98$, i.e., almost pure ZnO (Figure 3.10b). It is possible that at such high x values, consist of only ZnO. However, we have recently reported evidence that such absorption can arise from $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals.¹² Transient absorption spectra of solubilized $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with $x=0.73$ exhibit both visible and UV ZnO-like bleaches, and their decay traces overlap, indicating that they share electronic character.¹² These experimental observations are consistent with a model for the visible absorption that involves interband transitions between a higher lying valence band made by intermixing of ZnO and GaN orbitals and a conduction band that originates mostly from Zn and O orbitals.^{5,8,12} We attributed the UV absorption to transitions from lower lying valence band levels to the same conduction band.¹² The spectra in Figure 3.10 are consistent with this picture, as a transition from a valence band that originates from compositional mixing to a conduction band that originates from ZnO would decrease in relative strength as the x value increases (i.e., GaN fraction decreases).

3.2.3 PEC activity of bulk and nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$

While visible absorption in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ is encouraging for applications in solar fuel generation, it is important to examine the photoactivity of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals. Bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ has been shown to exhibit PEC activity under visible illumination. $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ thin films prepared by sputtering exhibit n-type behavior and show a reduced band gap with an improved photoresponse compared to ZnO and N-doped ZnO films.^{52,53} Stoichiometric H_2 and O_2 generation was achieved from PEC water splitting using bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ on a FTO loaded with IrO_2 as a water oxidation co-catalyst.⁵⁴ ZnO-rich $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$

$_{x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ produced by solution combustion method generated visible driven photocurrent that was 30 times higher than for ZnO .⁵⁵ To assess the PEC behavior of our $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals, we compared them to bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ prepared by the originally reported synthesis method.¹⁴

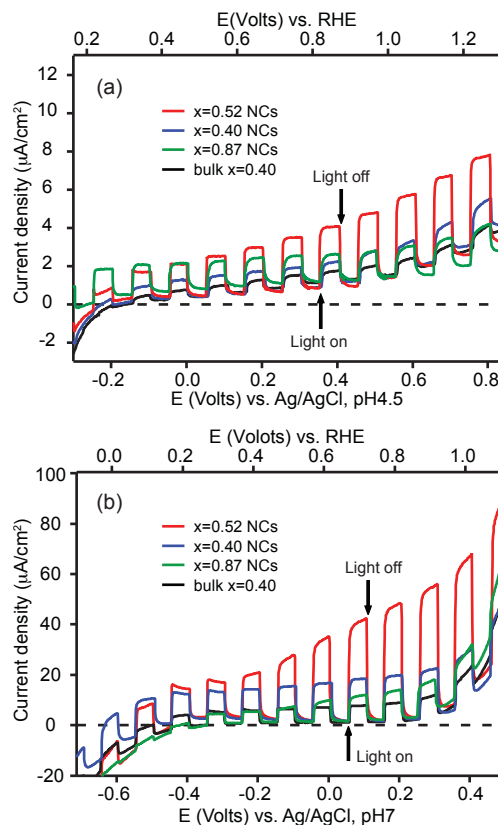


Figure 3.12 Current-voltage curves for films of bulk and nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40$ for bulk; $x=0.40$, 0.52 , and 0.87 for nanocrystals) obtained from (a) Water oxidation in pH 4.5 $0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution and (b) Sulfite oxidation in pH 7 phosphate buffer solution with $0.5 \text{ M Na}_2\text{SO}_3$. Both were measured under illumination with $\lambda > 435 \text{ nm}$.

The current-voltage curves measured for films of bulk ($x=0.40$) and nanoscale ($x=0.40$, 0.52 , and 0.87) $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ on FTO were measured in aqueous solution with $0.5 \text{ M Na}_2\text{SO}_4$ (Figure 3.12a). The experiments were carried out at pH 4.5 because the highest photocurrent for the bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ in PEC water oxidation was achieved at this pH.⁵⁴ The light source (300W Xe arc lamp) was passed through a 435 nm long pass filter to isolate the visible-light

driven photo-response. Both the bulk and the nanocrystalline samples exhibit n-type behavior (Figure 3.12a), which is necessary for PEC water oxidation. The bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40$) electrode produced photocurrents of $1\text{--}2\ \mu\text{A}/\text{cm}^2$ at $0.5\ \text{V}$, in agreement with previously reported results.^{54,56} Nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ showed higher photocurrents by a factor of two and four for $x=0.40$ and $x=0.52$, respectively. Similar improvement in overall visible-driven water splitting when nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ was used was reported in nanowires,³³ and, more recently, hollow nanospheres.³⁶

The photocurrents observed in Figure 3.12a are quite low compared to the amount of light absorbed. The origin of the photocurrent may be water oxidation, or it may be due to other processes, such as semiconductor decomposition or sulfate oxidation. The samples are thick films ($\sim 50\ \mu\text{m}$ in thickness), and carrier transport can limit the observed current.⁵⁷⁻⁵⁹ More work is needed to understand the factors that determine the PEC behavior of films of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals. Based on the strength of the visible absorption in solubilized $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals, we have recently shown that most of the incident visible light can be absorbed in a layer of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ that is $< 1\ \mu\text{m}$ thick.¹² Optimization of the device architecture may lead to higher photocurrent values.

Figure 3.12b shows that order of magnitude higher photocurrents can be detected for the similar electrodes as above when they are immersed in pH 7 phosphate buffer solution with $0.5\ \text{M}\ \text{Na}_2\text{SO}_3$. The increase in photocurrent can be attributed to sulfite oxidation, which is kinetically more favorable than water oxidation.^{59,60} This observation suggests that the photocurrents in Figure 3.12a are at least partially limited by slow oxidation kinetics and that functionalization with oxidation catalysts could enhance PEC activity.⁵⁹ Similar observation was made in the case of bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$, where electrode functionalization with a water

oxidation co-catalyst (IrO_2) led to an enhanced oxidation photocurrent and direct detection water splitting products.⁵⁴

Among the nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ samples in Figure 3.12, observed photocurrents do not directly correlate with absorption of visible light ($\lambda > 435$ nm). The $x=0.52$ sample absorbs 27% more of the visible photon flux than the $x=0.40$ sample, yet the observed photocurrents are more than a factor of two higher. Similarly, the $x=0.87$ sample, which exhibits the lowest band gap energy of all the samples, produces lower photocurrents than the $x=0.52$ sample, even though it absorbs 120% more of the $\lambda > 435$ nm photons. The values of photocurrent depend on multiple factors, including charge transport efficiency, as well as the band edge potentials, which change with composition.⁶¹⁻⁶⁷

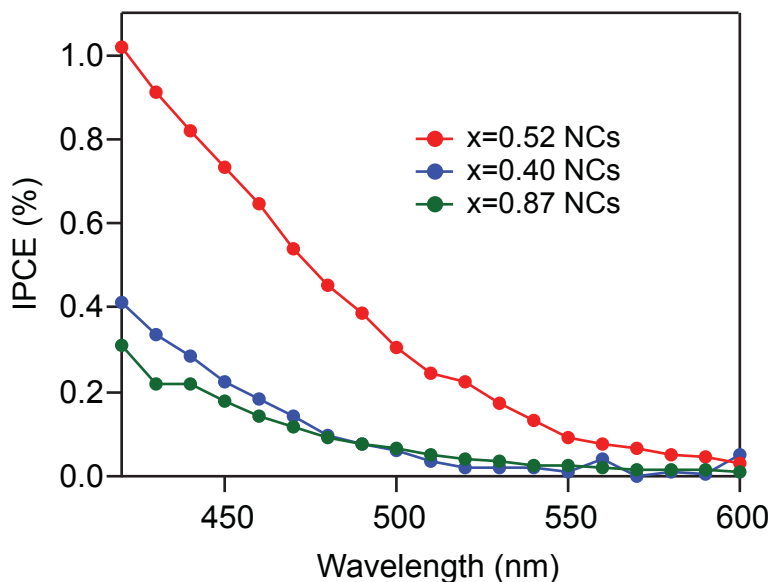


Figure 3.13 Incident photon-to-current efficiency (IPCE) spectra of nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40$, 0.52 , and 0.87) obtained from sulfite oxidation.

Incident-photon-to-current efficiencies (IPCE) for sulfite oxidation provide some insight into the discrepancy between the ability to absorb visible light and the photocurrent produced (Figure 3.13). The $x=0.52$ sample shows highest IPCE values across the spectrum. Interestingly,

the $x=0.87$ sample has an IPCE spectrum that resembles that of $x=0.40$ even though the diffuse reflectance spectra for the two samples are quite different in shape. Further work is necessary to understand how the oxidation photocurrent and light absorption are correlated in $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ and determine the composition that optimally balances absorption of sunlight with the other factors that govern photocurrent values.

3.3 Conclusions

We have characterized the properties of nanocrystalline $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with a broad range of compositions, with emphasis on aspects relevant for solar water splitting applications. Examination of the synthetic procedure for $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals suggests that $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nucleates topotactically at the interface of ZnO and ZnGa_2O_4 nanocrystals. Manipulating the synthetic parameters allows us to obtain a very broad range of sample compositions, $0.06 \leq x \leq 0.98$, and to examine how the optical spectra vary with composition. While visible absorption is achieved even in samples close to $x=0$ (GaN) and $x=1$ (ZnO), the minimum band gap of 2.25 eV occurs at $x=0.87$. Finally, we find that films of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals are photoactive for PEC oxidation, although with low photocurrents. The availability and optical characterization of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ nanocrystals with a broad composition range sets the stage for the investigation of these materials for visible-light driven water oxidation.

3.4 Experimental

3.4.1 (Ga_{1-x}Zn_x)(N_{1-x}O_x) nanocrystal synthesis.

All chemicals were purchased commercially and used without further purification. The starting materials (ZnGa₂O₄ and ZnO nanocrystals) were prepared and nitridations were carried out as described previously.³² Briefly, ZnO (d~10 nm) and 3-mercaptopropionic acid capped ZnGa₂O₄ nanocrystals (d~5 nm) were mixed and dispersed in a water/ethanol mixture and dropped onto a glass slide to evaporate the solvent over a hot plate. The starting mixture was then scraped out of the glass slide to gather the uniformly mixed starting mixture. Nitridations were carried out in a tube furnace (Across) with flowing NH₃ (~150 ml/min). The furnace was purged with argon for 1 hour and NH₃ gas for 30 min before increasing temperature with a ramp up speed of 20 °C/min. After nitridation, the furnace was allowed to cool down to room temperature with flowing NH₃ before removal of the nitrided products.

3.4.2 Characterization.

Powder X-ray diffraction (XRD) patterns were collected with Rigaku Ultima IV diffractometer equipped with Cu K α radiation ($\lambda=0.1540562$ nm). Elemental analysis of Zn and Ga was carried out using an ARL 3410+ inductively coupled plasma-optical emission spectrometer (ICP-OES). Oxygen and nitrogen content were measured using a LECO model TC 600 elemental analyzer. Diffuse reflectance spectra were collected on a Shimadzu UV-3600 spectrophotometer equipped with an integrating sphere. Diffuse reflectance was converted to absorbance using the Kubelka-Munk equation ($A=(1-R_{\infty})^2/2R_{\infty}$; $R_{\infty}=R_{\text{sample}}/R_{\text{reference}}$). The reflectance of reference ($R_{\text{reference}}$) was obtained using BaSO₄ as a reference material. Low-magnification transmission electron microscopy (TEM) images were recorded using a Philips CM100 microscope operated at 80 kV. Annular dark-field scanning transmission electron

microscopy (ADF-STEM) was performed on an FEI Titan microscope operated at 200kV. X-ray photoelectron spectra (XPS) for selected nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ samples ($x=0.40, 0.52, 0.76, 0.93$) were collected at Evans Analytical Group with a PHI 5802 Multitechnique XPS that is equipped with Al $K\alpha$ (1486.6 eV) or Mg $K\alpha$ (1253.6 eV) X-ray sources. Al $K\alpha$ X-ray source was used for the all XPS spectra except N1s. The XPS spectra for N1s were collected using a Mg $K\alpha$ X-ray source to avoid the peak interference of Ga Auger lines in the N 1s region. Binding energy was calibrated with C1s at 284.8 eV.

3.4.3 Fabrication of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ /FTO Electrodes.

Bulk $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40$) was synthesized using the originally reported synthetic method¹⁴ in order to compare with nanoscale $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$. Electrodes were prepared by doctor blading for both bulk and nano- $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ ($x=0.40$ for bulk; $x=0.40, 0.52$, and 0.87 for nano). 0.1 g of ethylcellulose and 10 mL of α -terpineol were mixed thoroughly. 10 mg of this mixture was added to 10 mg of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ and mixed by grinding to form a paste. The prepared paste was then applied onto the FTO, the edges of which were covered with tape. The paste on the FTO was flattened with a razor blade by scrapping out the excess paste over the tape. The film was dried at 100 °C for 10 minutes after removing the tape. The resulting films were annealed at 400 °C for 1 hour under air to burn out the organics.

3.4.4 Measurement of Visible Light Induced PEC Current from $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ /FTO Electrodes.

A three-electrode cell composed of $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ /FTO working electrode, Pt counter electrode, and Ag/AgCl reference electrode was utilized. A 300 Watt Xe-arc lamp (Newport 67005) was used as the light source. To approximate the intensity of 1 sun, the distance between the working electrode and the light source was adjusted using a $\text{GaP}_{0.98}\text{N}_{0.02}$ detector to determine

the electrode location. The lamp-electrode distance was chosen such that the $\text{GaP}_{0.98}\text{N}_{0.02}$ detector produced the same current as it does under AM1.5G illumination. Then, the light was passed through a 435 nm long pass filter. The photocurrents were collected from oxidation in pH 4.5 of 0.5 M Na_2SO_4 aqueous solution (pH adjusted using H_2SO_4) and sulfite oxidation in pH 7 phosphate buffer solution with 0.5 M Na_2SO_3 . Photocurrent was recorded while scanning the voltage from negative to positive with a rate of 10 mV/s. The light was chopped manually. Incident photon-to-current efficiency (IPCE) for sulfite oxidation was determined with the identical three-electrode cell setup described above in pH 7 phosphate buffer solution with 0.5 M Na_2SO_3 . Photocurrents were measured with illumination from 300 Watt Xe-arc lamp (Newport) passed through a monochromator at a potential of 0.5 V vs. RHE. A Si photodiode with known quantum efficiency was used to collect a reference spectrum in the same instrumentation. The IPCE was calculated as: $\text{IPCE (\%)} = \text{photocurrent} \times (\text{quantum efficiency/reference spectrum}) \times 100$.

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Chapter 4. Synthesis, Optical, and Photocatalytic Properties of Cobalt Mixed-Metal Spinel Oxides $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ^b

4.1 Introduction

The quest to diversify the world's energy resources from fossil fuels to those derived from renewable and sustainable energy has led to significant researches in both the fundamental and applied sciences.¹⁻³ Despite great progress, one of the major limitations to widespread adoption of renewable energy is its intermittency – neither the sun nor the wind provides a source of power that continuously matches demands. It is in this context that many researchers are motivated to explore generating fuels directly from sunlight, and in particular hydrogen from solar water splitting.⁴⁻¹⁰ The overall water splitting reaction into gaseous hydrogen and oxygen is thermodynamically uphill ($\Delta G^0 = 238 \text{ kJ/mol}$) and requires efficient catalysts to rapidly shuttle charges away from the photoelectrode surface toward productive proton-coupled electron transfer reactions.^{5,11} For this purpose, semiconductors that function as a monolithic system must be able to satisfy four main requirements: (1) Small band gap energy for absorbing visible light (1.7–2.2 eV), (2) Generation of electrons and holes at the proper potential for reducing protons and oxidizing water, (3) Chemical stability to reducing and oxidizing equivalents in the

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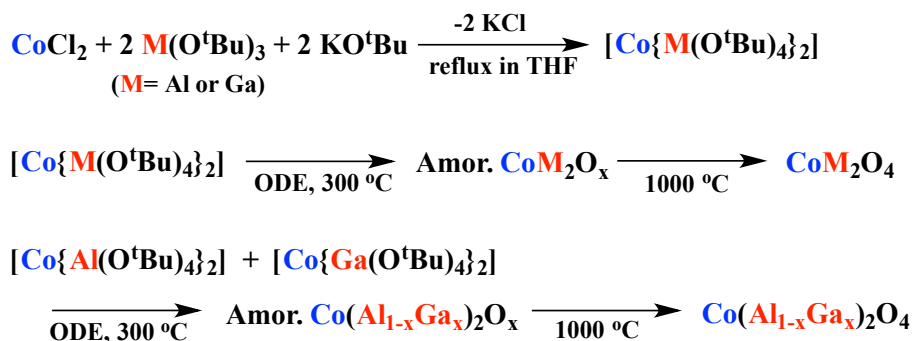
electrolyte, and (4) Fast transport of photogenerated charge carriers to the semiconductor/electrolyte interface. Metal oxides such as TiO_2 have attracted the attention as a possible candidate due to its photoactivity for water oxidation, low cost, and stability.^{4,5} However, the band gap energy of most metal oxide semiconductors is too large to absorb the visible portion of the solar spectrum, leading to inefficient solar conversion. Finding suitable semiconductors that satisfy all four requirements is a considerable challenge.⁵⁻¹⁰

One intriguing class of candidates that may be able to meet these challenges are cobalt spinel oxides, which have been shown to meet several of the requirements noted above. For example, Woodhouse et al. developed p-type $\text{Co}_{3-x-y}\text{Al}_x\text{Fe}_y\text{O}_4$ spinel oxides with tuneable band gaps (from 1.6 to 2.0 eV) by varying the Fe/Al ratio. These materials exhibited weak cathodic photocurrent under negative bias.^{12,13} The low PEC response was later attributed to poor electrical conductivity.¹⁴ Related cobalt spinel oxides, CoM_2O_4 ($\text{M} = \text{Al}, \text{Ga}, \text{and In}$), were examined both theoretically and experimentally to understand the optical properties, electronic structure, and PEC performance.¹⁵ This study found that the optical properties are dominated by $d \rightarrow d$ transitions resulting from Co(II) d orbitals split into Co e_d and t_{2d} states under the tetrahedral crystal field (A site in AB_2O_4 spinel structure).¹⁵ Substituting Ga and In for Al at the B site was found to decrease the band gap through both enhanced O 2p–Ga/In d coupling (driving the valence band edge upward) and increased influence of group 13 cation s states (moving the conduction band downward).¹⁵ In a subsequent study, it was calculated that the electronic structure of these cobalt metal spinel oxides could be further tuned by forming cobalt mixed-metal spinel oxides $\text{Co}(\text{Al}_x\text{Ga}_y\text{In}_{1-x-y})_2\text{O}_4$ to lower the band gap further and increase orbital mixing, which potentially could lead to enhanced charge carrier mobility.¹⁶

In this chapter, we detail efforts to prepare cobalt mixed-metal spinel oxides, $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, via both single-source and multi-source methods to evaluate the effect of pre-forming Co–O–M bonds on the spinel structural and optical properties. The single-source (ss) molecular precursor method has been explored for synthesizing solid-state materials through both chemical vapor deposition (CVD) and sol-gel techniques.¹⁷⁻²² This method offers the unique prospect of pre-forming chemical bonds, in this case Co–O–M (M = Al, Ga) in molecular precursors $[\text{Co}\{\text{M}(\text{O}^i\text{Bu})_4\}_2]$ (M = Al or Ga) that should be retained in the final material. In contrast, the multi-source (ms) method features individual Co- and M-containing precursors that are decomposed simultaneously and may not exhibit intimate Co and M mixing (which could more easily lead to phase segregation). Non-aqueous synthetic methods for metal spinel oxides nanocrystals (e.g., CoFe_2O_4 or ZnGa_2O_4) have been reported and were adopted for the multi-source route in the present study.²³⁻²⁵ The resulting products from each synthetic route were characterized both before and after annealing, and the experimentally obtained optical properties were discussed compared to the predicted ones.¹⁶ Lastly, photocatalytic activity of the materials was tested for the photodegradation of methyl orange.

4.2 Results and Discussion

4.2.1 Single-source (ss) route to bulk spinel oxides, ss-Co(Al_{1-x}Ga_x)₂O₄ (x= 0, 0.5, and 1)



Scheme 4.1 Single-source route to bulk ss-Co(Al_{1-x}Ga_x)₂O₄. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

Single-source molecular precursors [Co{M(O^tBu)₄}]₂ (M = Al or Ga) were synthesized by the reaction of CoCl₂ with M(O^tBu)₃ and KO^tBu. These complexes were then thermally decomposed to form bulk ss-Co(Al_{1-x}Ga_x)₂O₄ as shown in Scheme 4.1. A similar process was reported by Meyer et al. for nanoscale CoAl₂O₄ spinel oxides, but in that case the [Co{Al(O^tBu)₄}]₂ precursor decomposition was accomplished via hydrolysis within a micro-emulsion.¹⁷ Here, the single-source molecular precursors [Co{Al(O^tBu)₄}]₂ and [Co{Ga(O^tBu)₄}]₂ were thermally decomposed in anhydrous solvent (octadecene, ODE) at 300 °C, which should result in better retention of the Co–O–M structural motif (which can decompose under hydrolysis conditions) in the amorphous CoAl₂O_x and CoGa₂O_x products.

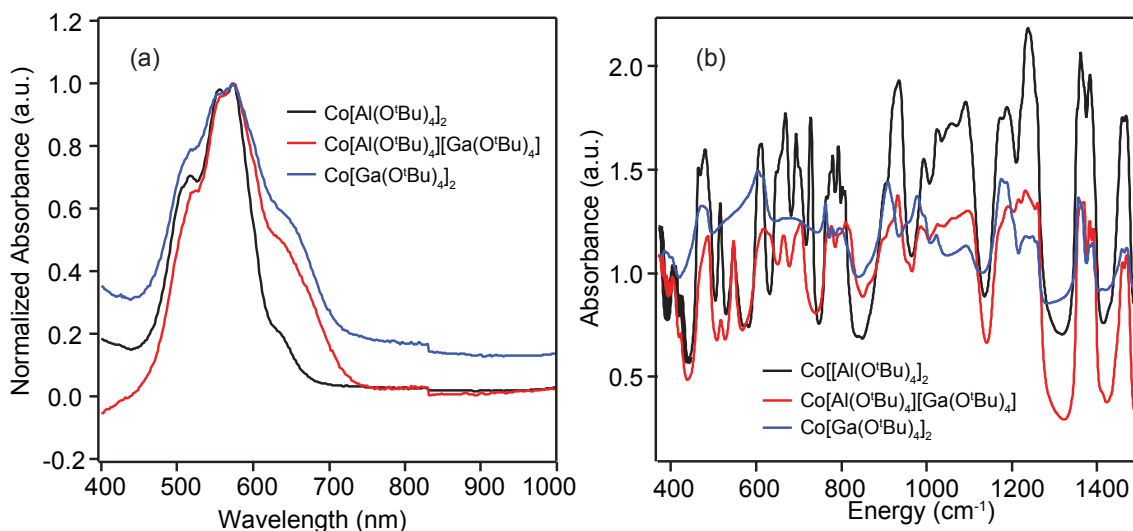


Figure 4.1 (a) UV-vis absorbance spectra (benzene solvent) of molecular precursors. Black: $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$; Red: product from reaction of $\text{CoCl}_2 + \text{Al}(\text{O}^i\text{Bu})_3 + \text{Ga}(\text{O}^i\text{Bu})_3 + 2\text{KO}^i\text{Bu}$; Blue: $[\text{Co}\{\text{Ga}(\text{O}^i\text{Bu})_4\}_2]$. (b) DRIFTS spectra of molecular precursors in the Co–O, Al–O, and Ga–O region (cast as films from toluene solutions onto Al-coated Si substrates). Black: $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$; Red: product from reaction of $\text{CoCl}_2 + \text{Al}(\text{O}^i\text{Bu})_3 + \text{Ga}(\text{O}^i\text{Bu})_3 + 2\text{KO}^i\text{Bu}$; Blue: $[\text{Co}\{\text{Ga}(\text{O}^i\text{Bu})_4\}_2]$. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

Several routes to the ss molecular precursor $[\text{Co}\{\text{Al}_{0.5}\text{Ga}_{0.5}(\text{O}^i\text{Bu})_4\}_2]$ were unsuccessful. For instance, reaction of 1:1:1 molar ratio CoCl_2 , $\text{Al}(\text{O}^i\text{Bu})_3$, and $\text{Ga}(\text{O}^i\text{Bu})_3$ conducted identically to that above provided a purple powder that contained a 1:1.17:0.86 ratio of Co/Al/Ga that is close to the expected values. Both FTIR and UV-vis absorbance data showed features resembling those of the di-substituted complexes $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$ and $[\text{Co}\{\text{Ga}(\text{O}^i\text{Bu})_4\}_2]$ that suggested the presence of Co–O, Al–O, and Ga–O structural units (Figure 4.1), but given the metal ratio did not appear to be tunable based on the initial stoichiometry (likely owing to different reactivity rates of the $\text{Al}(\text{O}^i\text{Bu})_3$ and $\text{Ga}(\text{O}^i\text{Bu})_3$ precursors), this strategy was not pursued further. Similarly, reaction of a 1:1 molar ratio of CoCl_2 and $\text{Al}(\text{O}^i\text{Bu})_3$ did not give the desired mono-substituted product $\text{ClCoAl}(\text{O}^i\text{Bu})_4$ but instead yielded the purple di-substituted $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$. Thus, the amorphous cobalt mixed metal oxide, $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_x$, was prepared by decomposition of a 1:1 molar ratio of $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$ and $[\text{Co}\{\text{Ga}(\text{O}^i\text{Bu})_4\}_2]$.

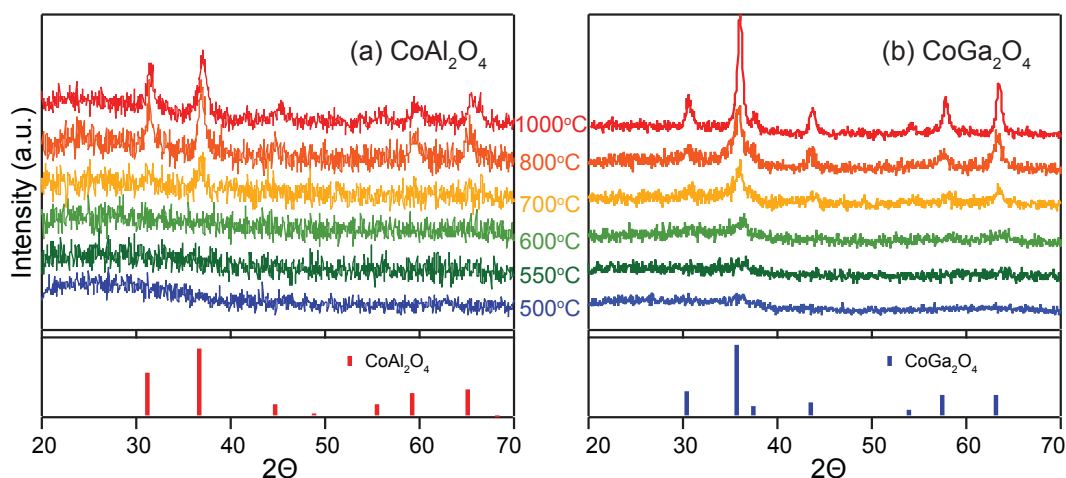


Figure 4.2 Powder X-ray diffraction patterns of the products obtained from annealing the amorphous (a) CoAl_2O_x and (b) CoGa_2O_x at varying temperature (500 – 1000 °C). The amorphous oxides (CoM_2O_x) were crystallized to spinel oxides (CoM_2O_4) with increasing annealing temperature. The vertical lines below the X-ray diffraction patterns represent the expected peak positions of spinel oxides (PDF#00-010-0458 for CoAl_2O_4 ; PDF#00-011-0698 for CoGa_2O_4). Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

As shown in Figure 4.2, as-prepared CoAl_2O_x and CoGa_2O_x exhibit X-ray diffraction patterns consistent with an amorphous structure. In-situ annealing experiments from 500 to 1000 °C showed that conversion from amorphous to the spinel structure began near 700 °C for CoAl_2O_4 and 550 °C for CoGa_2O_4 (as evidenced by a peak for the (311) reflection at 36.8° for CoAl_2O_4 and at 35.7° for CoGa_2O_4), but more highly crystalline material with sharper peaks required temperatures of 1000 °C. Interestingly, crystallization occurred at lower temperatures for CoAl_2O_x prepared from $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$ under anhydrous conditions than that from hydrolysis in micelles, which required 800 °C before the spinel phase was observed.¹⁷ This result suggests that decomposition of ss molecular precursors under anhydrous conditions preserves better the Co–O–Al structural unit that then leads to a lower barrier to crystallization.

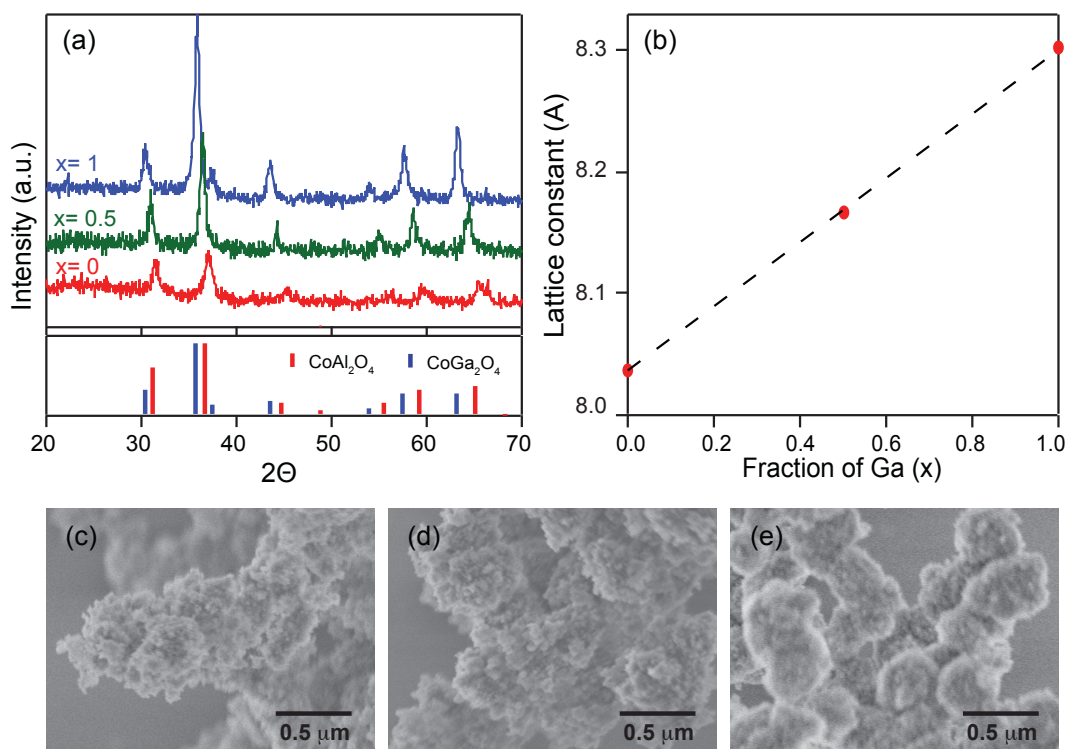


Figure 4.3 (a) Powder X-ray diffraction patterns of ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ annealed at 1000°C . The vertical lines below the X-ray diffraction patterns represent the expected peak positions of spinel oxides (PDF#00-010-0458 for CoAl_2O_4 ; PDF#00-011-0698 for CoGa_2O_4). (b) lattice parameter plotted against the fraction of Ga (x). Scanning electron micrographs of ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, $x=0$ (c), $x=0.5$ (d), and $x=1$ (e). Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

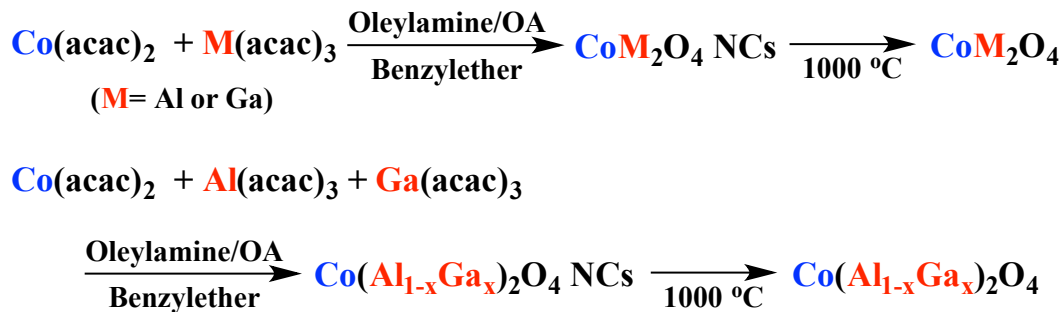
XRD patterns of ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($x=0, 0.5$, and 1) prepared by annealing the amorphous $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_x$ under air at 1000°C for 1 h are shown in Figure 4.3a. The diffraction peaks of CoGa_2O_4 appear at lower angles with respect to those of CoAl_2O_4 as the ionic radius of Ga is larger than Al. Interestingly, the diffraction peaks of $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ show single patterns of spinel structure and were located between the diffraction peaks of CoAl_2O_4 and CoGa_2O_4 . The lattice parameter, a , calculated from the (311) reflection, is plotted as a function of Ga fraction (x) in Figure 4.3b. Lattice parameter a increases linearly demonstrating ideal solid solution behavior according to Vegard's law.

	Formula	Al/Co	Ga/Co	Ga/(Al+Ga)
ss-Molecular Precursors	[Co{Al(O ^t Bu) ₄ } ₂]	2.07	-	-
	[Co{Ga(O ^t Bu) ₄ } ₂]	-	2.25	-
Amorphous oxides	CoAl ₂ O _x	2.19	-	-
	Co(Al _{0.5} Ga _{0.5}) ₂ O _x	1.19	1.16	0.49
	CoGa ₂ O _x	-	2.17	-
ss-CoM ₂ O ₄	CoAl ₂ O ₄	2.04	-	0
	Co(Al _{0.5} Ga _{0.5}) ₂ O ₄	1.07	1.10	0.51
	CoGa ₂ O ₄	-	2.13	1
ms-CoM ₂ O ₄ NCs	CoAl ₂ O ₄	1.89	-	0
	Co(Al _{0.75} Ga _{0.25}) ₂ O ₄	1.74	0.62	0.26
	Co(Al _{0.5} Ga _{0.5}) ₂ O ₄	1.13	1.18	0.51
	Co(Al _{0.25} Ga _{0.75}) ₂ O ₄	0.55	1.65	0.75
	CoGa ₂ O ₄	-	2.20	1

Table 4.1 Elemental analysis results collected by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

ICP-OES elemental analysis showed the ratios between the metals in the Co(Al_{0.5}Ga_{0.5})₂O₄ did not significantly change from the initial ratios of metal precursors (see Table 4.1). These observations from XRD and elemental analyses indicate that a solid solution of CoAl₂O₄ and CoGa₂O₄ was successfully synthesized through this synthetic route without phase segregation and also imply other product compositions could be synthesized by varying the molar ratio of [Co{Al(O^tBu)₄}₂] and [Co{Ga(O^tBu)₄}₂] precursors. Scanning electron micrographs of the ss-Co(Al_{1-x}Ga_x)₂O₄ samples annealed to 1000 °C display micron-sized agglomerates composed of irregular shaped nanoscale particles for all three compositions (Figure 4.3c-e). The nanoscale, polycrystalline nature of this material is consistent with the small domain size (~15 nm) calculated using the Scherrer equation applied to the XRD data (Figure 4.3a).

4.2.2 Multi-source (ms) route to nano and bulk spinel oxides, ms-Co(Al_{1-x}Ga_x)₂O₄ (x= 0, 0.25, 0.50, 0.75, and 1)



Scheme 4.2 Multi-source (ms) route to nano ss- Co(Al_{1-x}Ga_x)₂O₄ and bulk annealed ss-Co(Al_{1-x}Ga_x)₂O₄. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

Nonaqueous solution phase reactions have been shown to give nanocrystalline spinel oxide material without annealing and were adopted to prepare samples via the ms route in this study.²³⁻²⁵ Scheme 4.2 shows the preparation of ms-Co(Al_{1-x}Ga_x)₂O₄ (x= 0, 0.25, 0.50, 0.75, and 1) nanocrystals from cobalt and Al or Ga acac precursors. Briefly, Co(acac)₂ was combined with a stoichiometric amount of Al(acac)₃ and/or Ga(acac)₃ in the presence of oleylamine, oleic acid, and 1,2-hexadecanediol in benzylether, and this mixture was heated to high temperature (280 °C), leading to hexane-soluble Co(Al_{1-x}Ga_x)₂O₄ nanocrystals. The x values of the products were determined by ICP-OES elemental analysis (see Table 4.1). The ratios between the metals of the resulting nanocrystals were similar to the ratios of metal precursors that were used in the reaction, suggesting that the ms-Co(Al_{1-x}Ga_x)₂O₄ materials also exhibit homogeneous incorporation of both Al and Ga.

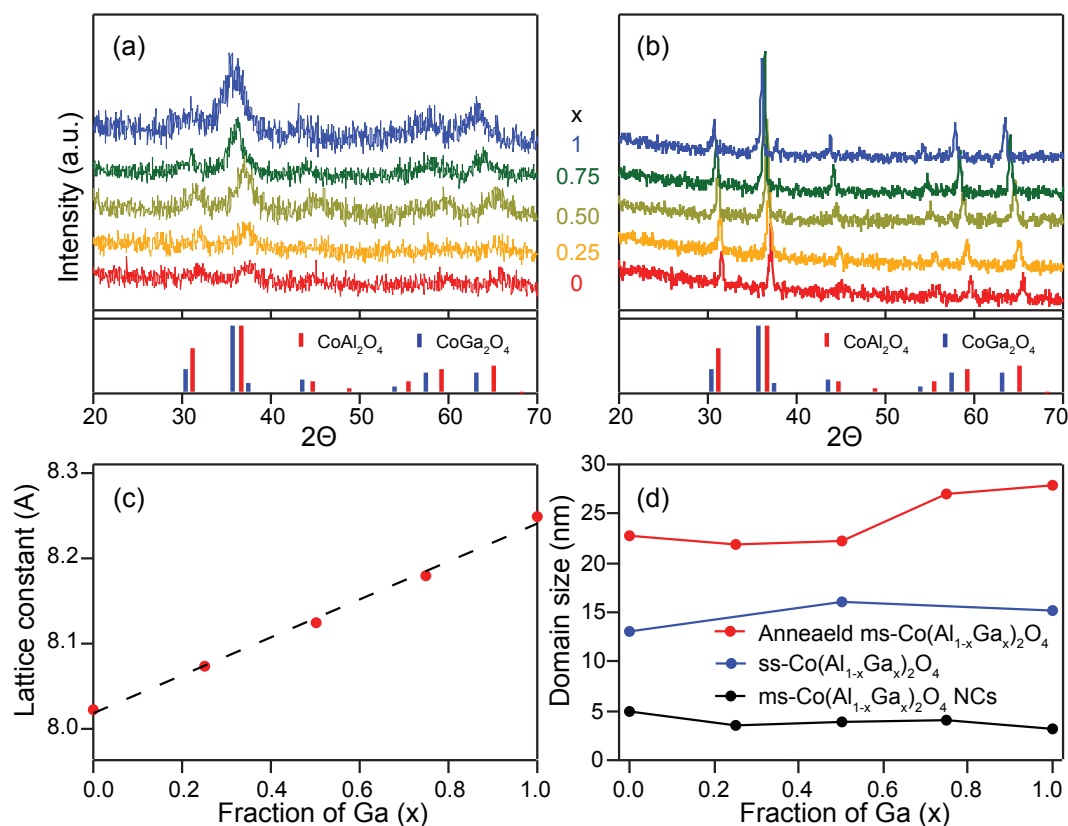


Figure 4.4 Powder X-ray diffraction patterns of (a) ms-Co(Al_{1-x}Ga_x)₂O₄ nanocrystals and (b) annealed ms-Co(Al_{1-x}Ga_x)₂O₄ at 1000 °C for 1 hour. The vertical lines below the X-ray diffraction patterns represent the expected peak positions of spinel oxides (PDF#00-010-0458 for CoAl₂O₄; PDF#00-011-0698 for CoGa₂O₄). (c) Lattice parameters, *a*, determined by the (311) reflection against Ga content (*x*). (d) Domain size of ms-Co(Al_{1-x}Ga_x)₂O₄ nanocrystals, annealed (1000 °C, 1h) ss- and ms- Co(Al_{1-x}Ga_x)₂O₄ calculated using Debye-Scherrer equation. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

In contrast to the amorphous oxides obtained from the decomposition of ss precursors, XRD patterns of as-prepared ms-Co(Al_{1-x}Ga_x)₂O₄ exhibit diffraction peaks that can be indexed to cubic spinel patterns without any post-synthesis annealing (Figure 4.4a). The average grain size of the nanocrystals calculated by a Debye-Scherrer equation is ~5 nm (Figure 4.4d). The nanocrystals were subsequently annealed at 1000 °C for 1 hour in order to increase the grain size and compare directly with the spinel products obtained from the single-source route. The XRD patterns of the annealed ms-Co(Al_{1-x}Ga_x)₂O₄ are shown in Figure 4.4b. Similar to the spinel

materials from the ss method, the peaks of ms- CoGa_2O_4 appear at lower diffraction angles than ms- CoAl_2O_4 . The solid solutions, ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, showed linear correlation between the lattice parameters and compositions (x), satisfying Vegard's law (Figure 4.4c). The domain size of the annealed nanoparticles is ~ 25 nm which is larger than that of the products from the ss route (cf. ~ 15 nm), indicating the ms route leads to larger grain size products under the same annealing conditions. This result could be rationalized that the initial ~ 5 nm crystallites from the ms route require less thermal energy for the larger grain growth than that required for the single-source route.

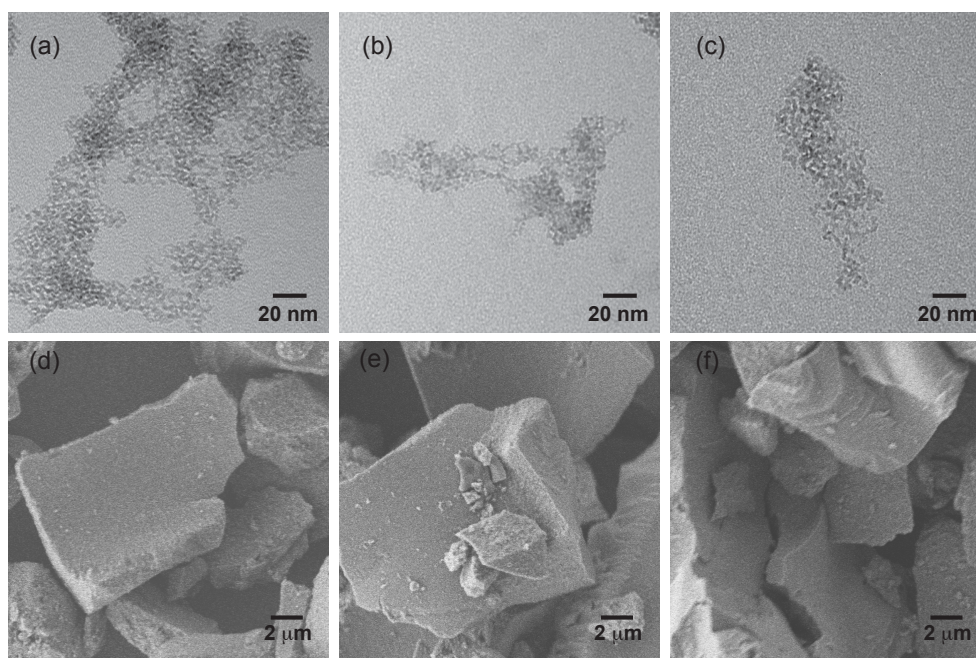


Figure 4.5 Transmission electron micrographs of the ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanoparticles, $x=0$ (a), $x=0.5$ (b), and $x=1$ (c). Scanning electron micrographs of the annealed ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, $x=0$ (d), $x=0.5$ (e), and $x=1$ (f). Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

The low resolution transmission electron micrographs of the as-prepared ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanocrystals show a mixture of shapes and no large agglomerates (Figure 4.5a–c) consistent with the ~ 5 nm crystallite size of the $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanocrystals calculated from the

XRD patterns. Scanning electron micrograph (SEM) images of annealed ms-Co(Al_{1-x}Ga_x)₂O₄ at 1000 °C are shown in Figure 4.5d–f, and all the compositions exhibit faceted particles on the micrometer scale. The nanocrystals appear to serve as seeds for grain growth to ~25 nm (from XRD analysis). Consistent with this observation, large, non-porous monoliths result from annealing nanocrystalline ms-Co(Al_{1-x}Ga_x)₂O₄ to high temperatures that contrasts the more porous structure resulting from annealing amorphous ss-Co(Al_{1-x}Ga_x)₂O_x (Figure 4.3c-e). BET surface area measurements also indicate the ss method gave a material with a slightly higher surface area (10.1 m²/g) than that from the ms method (8.1 m²/g; see Table 4.2). The larger grain size and monolithic structure of annealed ms-Co(Al_{1-x}Ga_x)₂O₄ may be more suitable for photoelectrochemical applications since it may lead to improved charge transport to the photocatalyst surface when compared to ss-Co(Al_{1-x}Ga_x)₂O₄ annealed at the same temperature.

	Surface area (m ² /g)	Dark adsorption (mol)	# MO molecules/nm ²
ss	10.1	1.43E-08	0.39
ms	8.1	1.27E-08	0.43

Table 4.2 Surface area of both ss- and ms-Co(Al_{0.5}Ga_{0.5})₂O₄, the amount of methyl orange (MO) adsorbed to each photocatalysts during dark adsorption, and the number of MO molecules adsorbed per 1 nm² during the dark adsorption. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

4.2.3 Optical properties of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ materials.

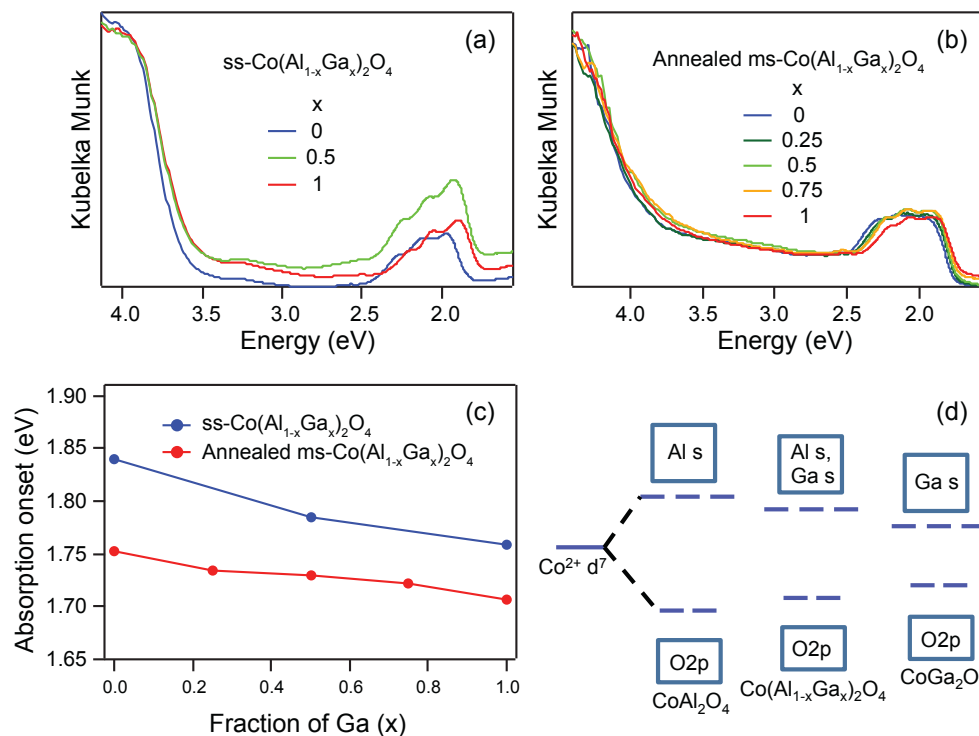


Figure 4.6 Diffuse reflectance spectra of annealed (1000 °C, 1 h): (a) $\text{ss-Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$; (b) $\text{ms-Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ with varying x ; (c) absorption onsets as a function of x ; (d) suggested band structure of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

Diffuse reflectance spectra were obtained from $\text{ss-Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ and $\text{ms-Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ bulk powders, shown in Figure 4.6a and b. The samples from both synthetic routes were annealed at 1000 °C for 1 h. Transmittance mode UV-vis absorbance spectra from hexane solutions of $\text{ms-Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanocrystals are shown in Figure 4.7a for comparison.

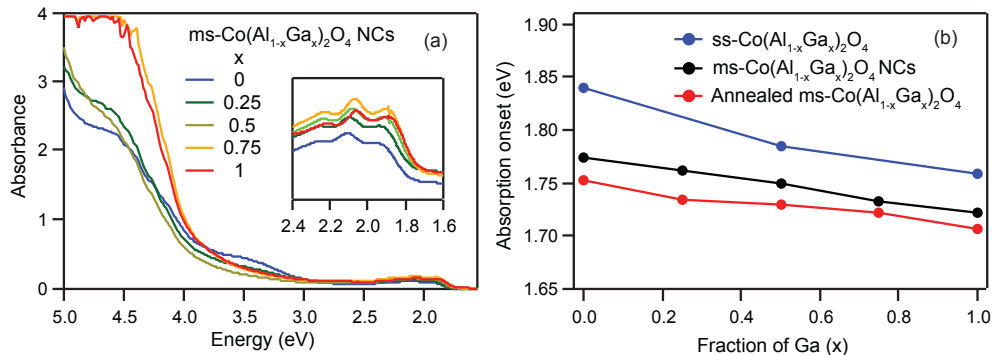


Figure 4.7 (a) UV-vis absorbance spectra of ms-Co(Al_{1-x}Ga_x)₂O₄ nanocrystals with varying x . (b) Absorption onsets as a function of Ga content x . Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

For all samples, low energy absorbance features from 1.7 to 2.4 eV result from tetrahedral $\text{Co}^{2+} {}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ ligand-field transitions,²⁶ which have been observed for both bulk²⁷ and nanoscale^{28,29} $\text{Co}^{2+}:\text{ZnO}$. These absorbance features confirm the presence of Co^{2+} in the tetrahedral spinel A site. The absorption onsets shift from 1.84 eV for $x=0$ to 1.76 eV for $x=1$ (for ss-Co(Al_{1-x}Ga_x)₂O₄) and from 1.75 for $x=0$ to 1.70 eV for $x=1$ (for ms-Co(Al_{1-x}Ga_x)₂O₄); Figure 4.6c). The shift to lower energy transitions with increasing Ga content for both ss- and ms-Co(Al_{1-x}Ga_x)₂O₄ is consistent with the prediction that the increasing lattice parameters owing to the larger Ga atom (cf. Al) reduces the crystal field splitting of Co^{2+} d states.¹⁶ However, it is found that these ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ ligand-field transitions also dominate the lower energy optical absorption even for complete Ga substitution ($x=1$). This contrasts the prediction that the Ga 4s states should become lower in energy than that of the Co d states (and lead to a Co d $\rightarrow$ Ga s transition) for Ga values of $x \geq 0.75$.¹⁶ This result suggests a possible band structure where the metal s states are located at higher energy state than Co d orbital (t_{2d}) for all values of x as shown in Figure 4.6d. Alternatively, lower energy absorption for Ga-rich compositions may have some contribution from other transitions such as defect-mediated field transitions resulting from these preparation methods.

4.2.4 Photocatalytic degradation of methyl orange (MO).

Photocatalytic degradation of methyl orange (MO) dye under simulated solar illumination was investigated to evaluate the possibility of performing productive redox chemistry with photogenerated charges from the cobalt mixed-metal oxide spinels. Though it was not studied in detail here, the MO degradation mechanism catalyzed by the metal oxides TiO_2 ³⁰ and ZnO ³¹ are known to proceed via both oxidative and reductive pathways.

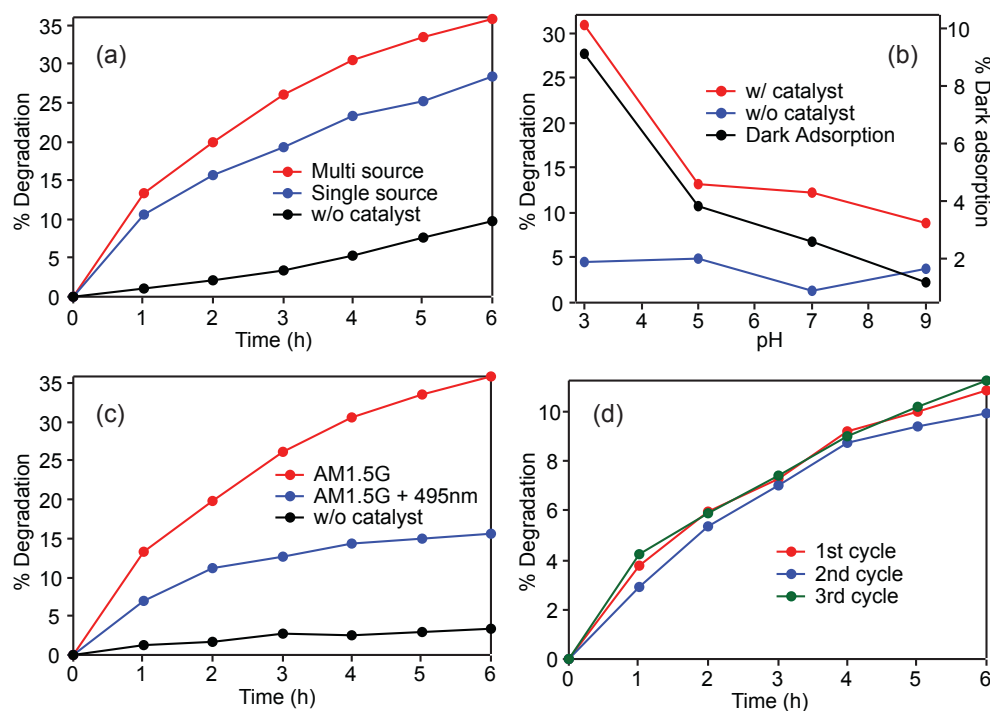


Figure 4.8 (a) Photodegradations of MO with annealed ms- or ss- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ at pH 3 over 6 h illumination. (b) pH effect on photodegradation of MO with (red) and without (blue) annealed ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ under 4 h of illumination. Black points correspond to the dark adsorption of MO molecules to the photocatalyst surface. (c) Photodegradation of MO with annealed ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ at pH 3 under full spectrum solar simulated illumination (red, w/ AM1.5G filter) and visible light irradiation (blue) using a AM1.5G filter and a 495 nm long pass filter. (d) Recycling experiment showing the photodegradation rate of MO at pH 3 under visible illumination is retained when using the same annealed ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ sample for 3 fresh MO solutions. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

The comparison of activities between ss- and ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ photocatalysts at pH 3 is shown in Figure 4.8a. After 6 hours of simulated solar illumination, MO degradation was

enhanced in the presence of annealed ss- or ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ relative to control experiments illuminating MO solutions with no oxide added. Despite the 25% higher surface area of ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$, the ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ had higher activity for MO degradation, which could be due to the larger grain size for the annealed ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ as noted above. Additionally, dark adsorption measurements at pH 3 showed that ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ adsorbed 10% more molecules of MO per unit area ($0.43 \text{ molecules/nm}^2$) than ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($0.39 \text{ molecules/nm}^2$) as shown in Figure 4.9 and Table 4.3, which could also account for the higher photocatalytic activity of ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$.

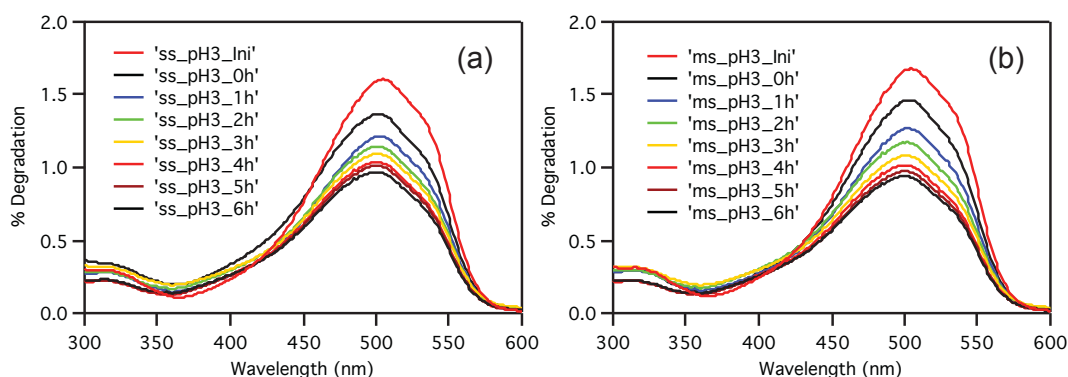


Figure 4.9 UV-vis absorbance spectra of methyl orange (MO) solutions after various times at pH 3 under AM1.5G illumination in the presence of (a) ss- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ (b) ms- $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

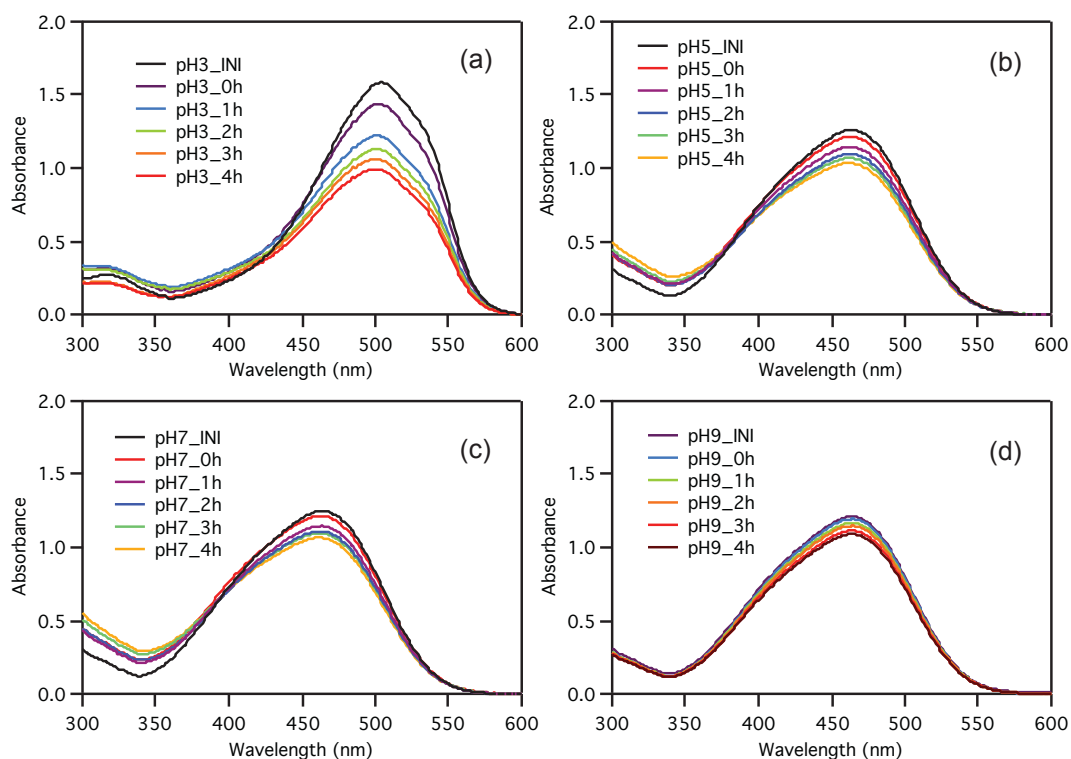


Figure 4.10 UV-vis absorbance spectra of methyl orange (MO) in the presence of ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ at (a) pH 3 (b) pH 5 (c) pH 7, and (d) pH 9 under AM1.5G illumination. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115–8122 with permission from The Royal Society of Chemistry.

The degree of MO adsorption is highly dependent on the pH, with MO adsorption decreasing by an order of magnitude upon increasing the pH from 3 to 9 for ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ (Figure 4.10 and summarized in Figure 4.8b). Unsurprisingly from this result, the degree of photocatalytic MO degradation was strongly pH dependent, with a 3-fold increase in MO degradation at pH 3 versus at pH 9 (Figure 4.8b). The pH dependence may be explained by surface charging of the catalyst given that the points of zero charge (PZC)^{30,32} for Al_2O_3 ³³, Ga_2O_3 ³⁴, and Co_2O_3 ³⁵ are all greater than pH 7. Under acidic conditions at pH values less than the PZC, we hypothesize that the surface of the spinel is protonated and more readily adsorbs the dye via the MO sulfate group, promoting degradation. Conversely, at higher pH values than the

PZC, the negatively charged spinel oxide surface repels the anionic MO sulfate group, reducing the dye adsorption and thus slowing degradation.

In Figure 4.8c, the MO degradation was probed using both AM1.5G filter and 495 nm longpass filter (blue), which only transmits light <2.5 eV that would be absorbed only by the $\text{Co}^{2+} {}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ ligand-field transitions (Figure 4.11). Remarkably, 46% of the total degradation relative to full spectrum light from the simulated solar illumination was observed (35% degradation after 6 h under full spectrum; cf. 16% under visible light). Moreover, this observation agrees with the apparent quantum efficiency,³⁶ which does not take into account light absorbed but only light impinging upon the sample. The apparent quantum efficiency was $2.4 \times 10^{-4}\%$ for initial MO degradation (0–1 h) under visible illumination, which is 72% of the $3.4 \times 10^{-4}\%$ apparent quantum efficiency observed for full spectrum illumination (Table 4.3). Importantly, these results demonstrate that the redox equivalents photogenerated by these lower energy transitions contribute significantly (between 46–72%) to catalytic MO degradation.

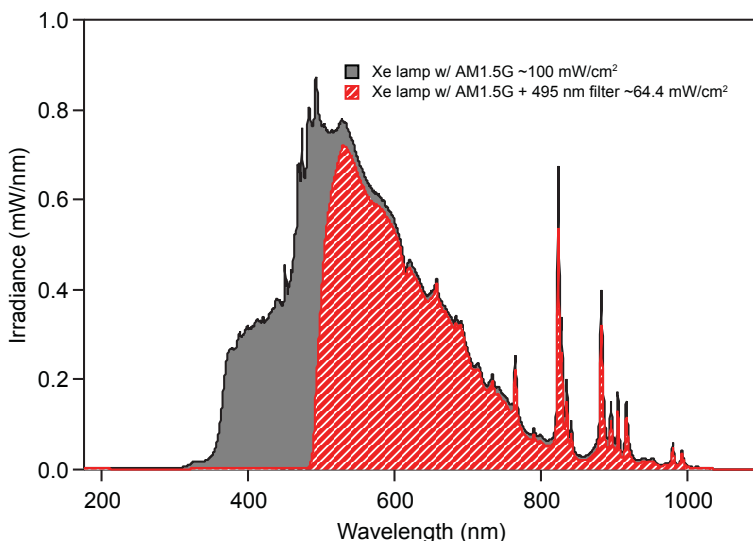


Figure 4.11 Spectral profiles employed in the MO degradation studies using a Xe lamp with (black) AM1.5G filter or (red) AM1.5G and 495 nm longpass filter. Reproduced from Lee et al., *J. Mater. Chem. A*, 2015, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

Apparent quantum efficiency (ϕ) was calculated according to the following equation:

$$\phi = \frac{d[x]/dt}{d[h\nu]/dt}$$

where $d[x]/dt$ is the rate of change of the concentration of the reactant and $d[h\nu]/dt$ is the total optical power impinging on the sample.

Illumination source	Time	[x] (mmol)	$d[x]/dt$ (mmol/s)	$d[h\nu]/dt$ (mmol/s)	Apparent quantum efficiency (%)
AM1.5G	0 h	8.74×10^{-5}	3.24×10^{-9}	9.60×10^{-4}	3.4×10^{-4}
	1 h	7.57×10^{-5}			
AM1.5G + 495 nm	0 h	8.43×10^{-5}	1.64×10^{-9}	6.72×10^{-4}	2.4×10^{-4}
	1 h	7.84×10^{-5}			

Table 4.3 Apparent quantum efficiency values measured for ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ under full spectrum illumination and with a 495 nm longpass filter before illumination (0 h) and after illumination for 1 hour (1 h). Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

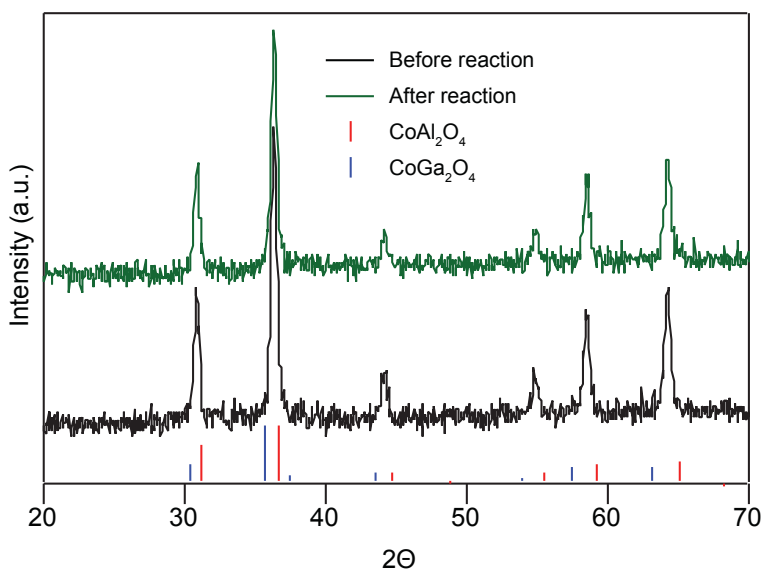


Figure 4.12 Powder X-ray diffraction patterns of ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$) $_2\text{O}_4$ before (black) and after (green) three cycles of MO degradation at pH 3 under visible illumination for 6 h each cycle. Reproduced from Lee et al., *J. Mater. Chem. A*, **2015**, 3, 8115 – 8122 with permission from The Royal Society of Chemistry.

To assess the stability of the photocatalyst, three successive MO degradation experiments were carried out by recycling the used annealed ms-Co(Al_{0.5}Ga_{0.5})₂O₄ and adding this to a fresh MO solution. As shown in Figure 4.8d, the photocatalytic activity was retained, and the photocatalyst did not change appreciably after the recycling as evidenced by XRD (Figure 4.12).

Finally, Bae et al. have demonstrated that a single photocatalytic activity test does not represent the general activity of a photocatalyst.³⁷ To explore the general photocatalytic activity of these cobalt spinel oxides, we conducted similar degradation tests using phenol as a substrate instead of MO. After illuminating a 200 ppm solution of phenol in ethanol for 6 h under full spectrum in the presence of annealed ms-Co(Al_{0.5}Ga_{0.5})₂O₄, no phenol degradation was observed by GC-MS. Though an exhaustive effort to explore a variety of reaction conditions and substrates was not conducted, these preliminary experiments suggest that the photocatalytic degradation provided by these cobalt spinel oxides is substrate-specific. However, although we do not have evidence of generalized photocatalytic activity, the observed visible response for MO degradation, with 46–72% of the degradation coming from the visible part of the solar spectrum, demonstrates that the transitions in the visible part of the spectrum of these spinel materials can be photoactive.

4.3 Conclusions

In summary, we have developed single-source and multi-source synthetic routes for Co(Al_{1-x}Ga_x)₂O₄. Whereas spinel oxide materials from single-source precursors required annealing to induce crystallization, the multi-source route produced nanoscale spinel products without annealing. Annealing amorphous materials from the single-source route to 1000 °C gave ~15 nm crystallites, and identical heat treatment on the nanocrystalline material from the multi-

source method grew the grain size from ~5 nm to ~25 nm. Both methods afforded ideal solid solutions of the mixed Al-Ga compounds. The optical properties of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ were found to be consistent with $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$ ligand-field transitions dominating the lower energy optical properties for all compositions. Finally, the photocatalytic activities of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ materials from both routes showed that, despite a higher surface area for materials from the single-source route, spinel oxides from the multi-source method adsorbed more methyl orange substrate per unit surface area. The degree of substrate adsorption was critical to the photocatalytic activity, which was found to be highly dependent on the substrate surface affinity. Remarkably, under appropriate substrate binding conditions, photogenerated redox equivalents from low energy (1.7–2.5 eV) ligand-field transitions contribute 46–72% to the photocatalytic activity of these cobalt spinel oxides.

4.4 Experimental

4.4.1 Chemicals

All the chemicals were purchased commercially from Sigma-Aldrich unless otherwise noted. Tetrahydrofuran (THF), hexane and tert-butanol ($^t\text{BuOH}$) were purified from sodium/benzophenone ketyl, alumina column, and sodium, respectively. $\text{Al}(\text{O}^t\text{Bu})_3$ (technical grade) was purified by dissolving the as-received grey powder (50 g) in hexane (500 mL) and filtering using a cannula filter before recrystallization at $-30\text{ }^\circ\text{C}$ to yield a colorless powder. The other chemicals employed in the synthesis were used without further purification. All handling and manipulation of air-sensitive compounds were carried out under nitrogen using an inert-atmosphere glove box and/or Schlenk line technique.

4.4.2 Preparation of [Ga(O^tBu)₃]₂

The dimer [Ga(O^tBu)₃]₂ was prepared by adding a solution of ^tBuOH (4.70 g, 63.4 mmol, 3.1 equiv) in hexanes (60 mL) to a suspension of [Ga(N(CH₃)₂)₃]₂ (4.13 g, 20.5 mmol; Strem, 98%) in hexanes (40 mL) and stirring this mixture at room temperature for 15 h. After removing liquid volatiles at room temperature in vacuo, the resulting colorless solid was heated to 50 °C for 1 h to remove the HN(CH₃)₂ adduct. This crude product was purified by sublimation at 140 °C (10 mTorr), giving a colorless solid [4.4 g, 75%; ¹H NMR (C₆D₆): δ 1.56 (s, 18 H, bridging -O^tBu), δ 1.48 (s, 36 H, terminal -O^tBu)]. This dimer will be referred to as the monomer Ga(O^tBu)₃ for simplicity in the Results and Discussion section.

4.4.3 Synthesis of single-source (ss) molecular precursors, [Co{M(O^tBu)₄}₂] (M= Al or Ga):

The single-source molecular precursors were prepared via modification of literature procedures.³⁸ CoCl₂ (130. mg, 1.00 mmol), Al(O^tBu)₃ (485 mg, 1.97 mmol) or [Ga(O^tBu)₃]₂ (570. mg, 0.985 mmol), and KO^tBu (≥98 %, 221 mg, 1.97 mmol) were loaded into a three neck flask with THF (20 mL) as a solvent. The reaction mixture was heated to reflux for 15 hours under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and the solvent was evaporated under vacuum. The resulting purple solid was extracted with hexanes and filtered via cannula (3 × 10 mL); residual hexanes were removed in vacuo to leave a purple solid (product yield: ~80%).

4.4.4 Single-source (ss) route to bulk ss-CoM₂O₄ (M= Al or Ga)

A small amount (typically, 150 mg) of the molecular precursor [Co{M(O^tBu)₄}₂] (M= Al or Ga), was dissolved in octadecene (ODE, 2 mL) and thermally decomposed under reflux without stirring at 300 °C for 4 h. The as-prepared amorphous oxide CoM₂O_x were collected via filtration (Büchner funnel, in air), and rinsed first with 3 × 5 mL of hexane and then with 3 × 5

mL of ethanol. Amorphous cobalt mixed-metal oxide, $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_x$, was also prepared through the same procedure using a 1:1 molar ratio of $[\text{Co}\{\text{Al}(\text{O}^i\text{Bu})_4\}_2]$ and $[\text{Co}\{\text{Ga}(\text{O}^i\text{Bu})_4\}_2]$. The resulting amorphous oxides were heated to 1000 °C with a ramp rate of 20 °C/min and annealed for 1 hour under air to effect crystallization into the spinel phase.

4.4.5 Multi-source route (ms) to nanoscale ms- CoM_2O_4 (M= Al or Ga) and ms- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($x= 0.25, 0.5$, and 0.75) nanocrystals

$\text{Co}(\text{acac})_2$ ($\geq 99\%$, 257.2 mg, 1 mmol), $\text{Al}(\text{acac})_3$ ($\geq 99\%$, 648 mg, 2.00 mmol) or $\text{Ga}(\text{acac})_3$ (99.99%, 734 mg, 2.00 mmol), 1,2-tetradecanediol (90%, 1150. mg, 5.00 mmol), oleylamine (70%, 2.82 mL, 6.00 mmol), oleic acid (90 %, 2.21 mL, 6.00 mmol), and benzylether (10 mL) were placed into a three-neck flask and heated to 40 °C under argon. Upon dissolution of all reagents, the mixture was heated to 100 °C and placed under vacuum (10 mTorr) for 30 min to remove residual O_2 and H_2O . The reaction was heated over 10 min to 200 °C and held for 30 min to nucleate particles, and then heated to refluxed at 280 °C (ramped over 15 min) for 2 h to promote nanocrystal growth; this procedure avoided a wide nanocrystal size distribution that has been reported from direct heating without the nucleation step.²³ The resulting nanocrystals were collected via centrifugation and purified three times by dissolving the products with 5 mL of hexane and by precipitation with a mixture of 2-propanol and ethanol (20 mL each). For the cobalt mixed-metal spinel oxide nanocrystals, $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ ($x= 0.25, 0.5$, and 0.75), $\text{Co}(\text{acac})_2$ (257 mg, 1.00 mmol), stoichiometric amounts of $\text{Al}(\text{acac})_3$ and $\text{Ga}(\text{acac})_3$ were used as metal precursors in the above preparation. All the resulting nanocrystals were annealed at 1000 °C for 1 h under air to compare with the bulk ss- $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$.

4.4.6 Photocatalytic activity test

The photocatalytic activity of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ was evaluated via the photodegradation of methyl orange (MO). $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ (0.02 mmol) materials were dispersed in MO aqueous

solution (2 mL, 5×10^{-5} M). The pH of these solutions was adjusted by adding HCl for acidic condition or NaOH for basic condition in a quartz cuvette. The reaction sample was sonicated for 2 min and then stirred for 30 min in dark. The sample was then illuminated by a Xe lamp (200 W, Oriel) passing through an AM 1.5G filter. The light intensity was adjusted to 100 mW/cm² using a power meter (Newport 407A). To investigate the photocatalytic activity from only visible transition, the AM1.5G light was passed through a 495 nm longpass filter and the light intensity decreased to 66.4 mW/cm² (Figure 4.11). At hourly intervals, the cuvette was centrifuged to precipitate the suspended particles and achieve an optically transparent MO-containing solution before taking UV-vis absorption spectra.

4.4.7 Recyclability and stability test of the photocatalysts

To confirm the recyclability and stability of the photocatalyst, recycling ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$)₂O₄ was performed by conducting MO degradation at pH 3 for 6 h, recovering the solid photocatalyst via centrifugation, and adding fresh MO solution. A total of 3 MO solutions were used. The reaction conditions were identical to the above the single experiments, but all quantities were scaled up by a factor of 10 so the recovered oxide catalyst could be examined by XRD before and after the degradation experiments.

4.4.8 Photodegradation of phenol

Another photodegradation was conducted using a different substrate, phenol, to test the general photocatalytic activity of the photocatalyst. 100 g of solution of phenol in ethanol (200 ppm) was prepared in a pyrex reactor having a quartz window. 100 mg of annealed ms-Co($\text{Al}_{0.5}\text{Ga}_{0.5}$)₂O₄ was dispersed in the solution via sonication for 2 min, followed by stirring for 30 min in the dark. A solar simulated illumination (AM1.5G, 100 mW) was used as a light source. 1.5 ml of aliquots were withdrawn from the reaction at hourly intervals during 6 hours of

the illumination and filtered by a 0.45 μm PTFE syringe filter (MicroLiter Analytical Supplies, Inc.). Phenol concentration of the aliquots was analyzed by GC-MS.

4.4.9 Characterization

Powder X-ray diffraction (XRD) patterns were collected using Rigaku Ultima IV equipped with Cu K_{α} radiation ($\lambda = 0.1540562$ nm). The crystal domain size was calculated using the Debye-Scherrer equation ($L = 0.9 \lambda / B \cos \theta$; L: domain size, λ : wavelength of X-ray source, B: full width half maximum). Scanning electron microscopy was carried out using a field emission scanning electron microscope (FESEM, JEOL JSM-7401F) operated at accelerating voltages/working distances of 2.0 kV/1.7 mm and 5.0 kV/9.3 mm for ss- and ms-products, respectively. Transmission electron microscopy (TEM) images were taken using a Philips CM100 microscope operated at accelerating voltage of 80 kV. The absorption spectra of $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ nanocrystals were recorded by UV–visible absorption spectrophotometer (Agilent 8453). Diffuse reflectance spectra for the bulk $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ powder samples were collected on a Shimadzu UV-3600 spectrophotometer equipped with an integrating sphere. BaSO_4 was used as a reference material. Diffuse reflectance was converted to absorbance using the Kubelka-Munk equation ($A = (1 - R_{\infty})^2 / 2R_{\infty}$; $R_{\infty} = R_{\text{sample}} / R_{\text{reference}}$). Elemental analysis was carried out with ARL 3410+ inductively coupled plasma-optical emission spectroscopy (ICP-OES) by the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado Boulder. Phenol concentration was determined using an Agilent Technologies 7890A GC system equipped with a flame-ionization detector (FID) and an Agilent Technologies 5975C inert XL mass selective detector (MSD). An Agilent 19091S-433 HP-5MS capillary GC column was used (30 m x 0.250 mm I.D. X0.25 mm film thickness 5% phenyl-95% methylsiloxane).

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Chapter 5. Conclusion

Water splitting to produce H_2 fuel in photocatalytic or PEC system is a sustainable and environmentally friendly method for solar energy conversion. In this thesis, we targeted two solid solution materials that were expected to be promising for the technology.

Chapter 2 described a new synthetic method for nano scale $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ with a wide range of compositions ($0.30 \leq x \leq 0.87$). A mixture of nano scale $ZnGa_2O_4$ and ZnO was used in the nitridation at a relatively low temperature ($650^\circ C$). The composition (x) in $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ was controlled using different molar ratios of zinc and gallium in the starting nanocrystals. As a result of introducing nano-sized starting materials, we were able to use temperatures lower than those needed in the conventional synthetic route. Consequently, the volatilization of zinc and fusion into bulk was avoided during the nitridation. The absorption onset continuously shifts from 460 nm for $x=0.30$ to 565 nm for $x=0.87$. This tunability of absorption onset could allow greater percentage of solar photons to be absorbed by the material, resulting in higher efficiencies of water splitting under identical solar irradiation.

In Chapter 3 we examined the reaction mechanism in forming $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ nanocrystals and found that nitridation of $ZnGa_2O_4$ and ZnO leads to a conversion of the spinel $ZnGa_2O_4$ to wurtzite product accompanied by fusion with ZnO and N incorporation. The observations from the mechanistic study allowed us to expand the range of compositions with the new composition samples lying on each end, ZnO-low ($x=0.06$ and 0.24) and ZnO-high ($x=0.91$ and 0.98). The band gaps of the products in the range of $0.06 \leq x \leq 0.98$ showed a minimum of 2.25 eV at $x=0.87$. XPS characterizations support the formation of solid solutions. Lastly, we

investigated the PEC water oxidation under visible illumination, where the highest photocurrent was found at $x = 0.52$.

Chapter 4 described the development of two synthetic routes to cobalt mixed metal spinel oxides, $\text{Co}(\text{Al}_{1-x}\text{Ga}_x)_2\text{O}_4$ with a range of $0 \leq x \leq 1$: Single-source and multi-source routes. Single-source metal precursors, $[\text{Co}\{\text{M}(\text{O}^i\text{Bu})_4\}_2]$ ($\text{M} = \text{Al}$ or Ga), were thermally decomposed to yield amorphous oxides. Multi-source precursors, stoichiometric mixtures of metal acetylacetonate (acac), produced nanocrystalline cobalt spinel oxide materials. Both were subsequently converted to bulk spinel products by annealing at 1000°C . The X-ray diffraction data of the materials showed an ideal solid solution behavior that followed Vegard's law for both routes, with the multi-source route giving more crystalline bulk material than the single-source route. Absorption data revealed that the absorption onset energies decreased monotonically with increasing x (from 1.84 eV for $x = 0$ to 1.76 eV for $x = 1$ from the single-source method; 1.75 eV for $x = 0$ to 1.70 eV for $x = 1$ from the multi-source method). The photocatalytic activities of the cobalt spinel oxides were evaluated via the photodegradation of methyl orange and phenol, which showed that the photoactivity of the materials was dependent on both pH and substrate. Remarkably, under appropriate substrate binding conditions (pH 3 with methyl orange), low energy (< 2.5 eV) ligand–field transitions contributed between 46 and 72% of the photoactivity of $\text{Co}(\text{Al}_{0.5}\text{Ga}_{0.5})_2\text{O}_4$ prepared from the multi-source route.

The major contribution of the work presented in this thesis is the synthesis of the new solid solution materials with a guidance of the predictions. The synthetic work can be extended to understand how to control the particle properties such as size, shape, surface, and crystallinity etc. Also, modification of the materials with co-catalyst or introducing other elements into the system could improve the properties for application to water splitting. Although we have also

focused on evaluating the composition-dependent optical properties of the materials, it is not clear what originates the visible absorption combining with the electronic structures. Further efforts with advanced characterizations such as dynamics of charge carriers will allow us to identify the processes and provide feedbacks to the synthesis for further improvements.

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