On the Chemical Synthesis and Physical Properties of Iron Pyrite, Especially the (100) Surface

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On the Chemical Synthesis and Physical Properties of Iron Pyrite, Especially the (100) Surface Thesis directed by Prof. Conrad R. Stoldt

Given that iron pyrite (cubic FeS₂, fool's gold) is a semiconductor with a ~ 1 eV band gap, it has long been investigated for use in technological applications, especially photovoltaics. Unfortunately, numerous measurements indicate that it's properties, as currently synthesized at least, do not allow for effective devices. Photovoltages far below theoretical expectation are found as well as below band gap optical absorption. From a scientific standpoint, our understanding of the cause of these observations, the form of the density of states for instance, remains mired in uncertainty.

In this work we have attempted to gain insight into this problem by creating ensembles of pyrite nanocrystals that can then be treated and measured with well-developed wet-chemical nanocrystal techniques. Specifically, we interpret the existing literature to advocate that the surface states of this material dominate its observed electrical properties. In an effort to better understand the most prevalent surface, the (100) face, we developed a synthesis that nucleates small (< 20 nm) pyrite nanoparticles and then changes chemical conditions to grow all other faces besides {100} to extinction, creating ~ 37 nm nanocubes.

The optical properties of these nanocubes are measured and the phenomenon of resonance light scattering (RLS) is observed. This phenomenon, along with the poor colloidal dispersibility of these nanocubes is then used to promote the idea that an unusual dynamic electronic phenomenon exists on these surfaces. This phenomenon is found to be passivated by introducing charged ligands to the surfaces of these particles. Additionally, after this surface treatment, two very sharp absorption features are observed at 0.73 and 0.88 eV. In connection with recent theoretical work, these transitions are taken as evidence that the (100) surface of pyrite is spin-polarized with each absorption peak being the signal of band edge absorption across a spin-selected direct band gap.

A theoretical framework is proposed as a plausible explanation of the observed behavior. To

wit, highly localized and energetically disordered Fe d-orbital states fill in the band gap of the (100) pyrite surface that is not perfectly terminated (or nearly so). Frustration between energetic disorder and Coulomb repulsion then results in the formation of metastable states that obscure the observation of these surface transitions and cause the dynamical behavior observed. It is further reasoned that one of these transitions, the one at 0.88 eV, has been observed before in cryogenic absorption and photoconductivity studies, and argued that a plausible reinterpretation of the data from these studies is possible. This reinterpretation can be rationalized within the context of the physical model posited here whereby cryogenic temperatures increase the importance of Coulombic interactions, which results in a decrease in the metastable DOS at the Fermi level and an electronic arrangement closer to that predicted theoretically, despite existing disorder. Finally, it is argued that the frustrated movement of electrons in metastable states can qualitatively explain the apparent conundrum in which surface sensitive probes are unable to measure the effect of isolated defects, despite the highly localized nature of the pyrite (100) surface. Given the range of phenomena this model explains, it may constitute a significant advance in our understanding of the electronic properties of pyrite.

Additionally, given that electrochemical conversion of pyrite is a four electron process resulting in a high theoretical discharge capacity of 894 mAh g⁻¹, we have synthesized micron-sized pyrite nanocubes for use in lithium-ion battery research. Previously the use of pyrite in such batteries has only been possible in non-rechargeable architectures. However, work described here shows that a solid state electrolyte can be used to contain the dissolution of these micron sized particles, allowing for battery cycling. This synthesis, especially the effect of pH on morphology, is described within the context of targeted requirements for a battery cathode material.

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The study of pyrite has become a passion of mine over the years spent on this work. It's duality, being both approachable (*most prevalent sulfide on Earth's crust!*) and mysterious (*where's the semiconductor?*), is compelling. My advisor, Prof. Conrad Stoldt, recognized this as well as I and made this study possible with his support, technical guidance, and patience. I have since come to realize that in the academic world, longer-term indulgence in an intransigent problem is risky and therefore rare. I am so grateful for being granted the exception.

To my family, I acknowledge the lessons of childhood. A certain fortitude in the face of uncertainty and repetitive frustration is more necessary than intelligence, even, for success in research. If I have succeeded it was from a sanguine approach adopted by observation of you.

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Chapter 1

Introduction

Iron pyrite (cubic FeS₂, fool's gold) is a fascinating material. It has geological prevalence, technological potential, and interesting physical properties from a basic science perspective. All these aspects of this material will be discussed in this dissertation. In this current chapter I aim to succinctly summarize much of our state of knowledge of this material from a viewpoint divorced from application; mainly its physical properties: electrical, optical, and thermodynamic. In addition, a brief overview of its potential contribution to photovoltaic, electrochemical, and spintronic technologies is given. Lastly, the experimental work in this dissertation has used the principles of inorganic nanochemistry. These methods are described here in a general context.

1.1 Structure

Given the ubiquitous nature of pyrite it was one of the first minerals analyzed by x-ray diffraction during that method's inception (by the Bragg family) [1]. A cubic lattice of iron atoms in a face-centered cubic (fcc) arrangement was inferred. Additionally, it was further reasoned that the sulfur atoms must reside along diagonals of this cubic crystal system. Since that first study, refinements of the structure have reiterated that it belongs to the cubic crystal system and further is a member of the Pa $\bar{3}$ space group. In further identifying the symmetry of this structure it is advantageous to pick an iron atom to remain stationary so that we can discuss the resulting point group symmetry. In this view pyrite has T_h^6 point group symmetry in Schöenflies notation and $2/m\bar{3}$ or m $\bar{3}$ in international or Hermann-Mauguin notation (the two nomenclatures being

the full symbol and short symbol, respectively). T_h^6 indicates that the unit cell has tetrahedral symmetry (denoted by the "T") with an inversion center (denoted by the "h" subscript). This space group is known to be non-symmorphic, which is to say there is no choice of origin where all the symmetries can be decomposed into a product of translation and point group symmetry (i.e. there must be a screw axis or a glide plane). Structural refinements have shown the unit cell dimension to be a=5.416 Å [2, 3]. While the iron atoms sit at fcc sites, the sulfur atoms form dimers $(S_2 \text{ units})$ which exist at the midpoints of the cube edges and the cube center as shown in Figure 1.1. The position of these sulfurs can be given by a Wyckoff parameter (u). The positions are $\pm(u, u, u)$, $\pm(\frac{1}{2} + u, u, \frac{1}{2} - u)$, $\pm(u, \frac{1}{2} - u, \frac{1}{2} + u)$, $\pm(\frac{1}{2} - u, \frac{1}{2} + u, u)$ with u = 0.385 Å [4]. By trigonometry from these coordinates the S-S bond length is 2.160 Å and, as Bragg first reasoned, is found along the <111> direction. The unit cell therefore contains four formula units (as opposed to the primitive unit cell which, of course, contains one). Seen in an alternative way, this structure is the same as for a simple cubic structure such as NaCl where the iron atoms occupy one fcc sublattice and the centers of the disulfide units occupy the other [5]. A simulated x-ray diffraction pattern in given in Figure 1.2 (with Cu K α radiation) showing the expected reflections along with their associated Miller indices.

In this arrangement it is seen that iron atoms are in a trigonally distorted octahedron of sulfur atoms whereas sulfur atoms are in a distorted tetrahedron formed by three neighboring iron atoms and their dimer sulfur partner [7]. In order to rationalize this structure with the low-spin properties found by magnetic measurements it is well accepted that the iron atoms have a +2 oxidation state and the sulfur atoms have a somewhat unusual -1 oxidation state. Therefore, the disulfide unit is often represented as S_2^{2-} . Given these oxidation states a designation of "iron persulfide" in analogy with peroxides according to IUPAC naming systematics is probably more correct than iron disulfide, however this convention has not been widely adopted as yet.

Given the distortion of the octahedron of sulfur atoms surrounding the irons, the local symmetry is reduced from octahedral to trigonally distorted octahedral $(O_h \rightarrow C_{3i})$ [5, 8]. This distortion is a small perturbation on the octahedral geometry so many researchers, myself included, ofter

Figure 1.1: Structure of a unit cell of iron pyrite. Brown balls represent iron atoms and yellow balls represent sulfur atoms. Sulfur dimer bonds are shown. Rendered with Vesta [6].



Figure 1.2: Iron pyrite simulated powder x-ray diffraction structure. Cu K α radiation is assumed and Miller indices have been assigned. Simulated with Rietan software implemented in Vesta [6].



still refer to symmetry elements (especially Fe-d orbital ligand fields) using octahedral terminology. Usually this seems to be a relatively harmless simplification, however, the apparent contradiction must be noted here.

The Bravais lattice is simple cubic. Therefore the Brillouin zone (i.e. reciprocal lattice) is also simple cubic with an edge length of $\frac{2\pi}{a} \approx 1.16$ Å⁻¹ [9].

1.1.1 Symmetry and Vibrational Structure

As described above there are four formula units in the unit cell, so 12 atoms. Applying symmetry operations $(3 \times 3 \text{ matricies})$ to these results in a $36 \times 36 \text{ matrix [10]}$. The irreducible representation of this matrix (found by block diagonalization) is well known:

$$\Gamma = A_q + E_q + 3T_q + 2A_u + 2E_u + 6T_u \tag{1.1}$$

where A, E, T modes correspond to degeneracies of 1, 2, and 3, respectively and u and g represent ungerade and gerade transformations [11, 12, 13, 14, 15]. Gerade transformations are symmetric with respect to inversion, and ungerade transformations are antisymmetric. From character tables it is seen that the A_g , E_g , and T_g modes change the polarizability tensor are should therefore be Raman active. Likewise, character tables show that the T_u modes change the dipole moment of the atomic coordinates and should therefore be infrared active (actually only five modes rather than six, the sixth being indicative of pure translation). These infrared and Raman modes have been observed experimentally (Raman active vibrations given later in this study in Figures 2.3 and 3.5, infrared vibrational modes are found in the literature) [16, 17]. For completeness, it should be mentioned that the remaining modes A_u and E_u are often termed the "silent" modes.

1.2 Electronic Properties

In spherical symmetry the d orbitals of the iron atoms are five fold degenerate. In pyrite the sulfur atoms act as a classical crystal field and split the degeneracy of these iron d orbitals. The octahedral field, which I use to first approximation (described above), splits them into two bands:

 t_{2g} and e_g (named after their symmetry elements with the nomenclature similar to that described above). This distorted octahedral ligand field is shown in Figure 1.3. From magnetic measurements it has been seen that pyrite is diamagnetic [18, 19, 20, 21] so it is inferred that the d⁶ electronic configuration fills the t_{2g} manifold leaving the e_g states empty.

From photoelectron spectroscopy (mainly) it is argued that the t_{2g} manifold of states comprises the valence band of pyrite with only minor overlap with S 3p states. The conduction band is somewhat more complicated in that more hybridization is present between iron and sulfur states. Optical absorption measurements, and non-Ohmic behaviors of point contacts, have long been used to argue that there is a band gap between these states. Of the large quantity of existing absorption data a value of 0.95 eV has become *the* accepted and cited band gap. This value originates in the 1976 study by Schlegel and Wachter [12]. However, I believe the precision of this value is misleading. Many values in the general range around 1 eV seem to be based on equally accurate experimental evidence. Recent modeling suggests that the band gap is indirect and around 1 eV [22, 23]. Ultraviolet photoelectron spectroscopy (UPS) has been used to ascertain the density of filled states [24], thus data corresponds closely to expectations from density functional theory and tight binding approximations using the atomic iron orbitals and molecular disulfide orbitals as the basis set [25].

1.2.1 Macroscopic Electronic Properties

In addition to these atomistic considerations of pyrite's electronic properties, temperature dependent resistivities have often been measured. Much of Chapter 3 is focused on explaining the discrepancy in measured electronic properties of single crystals and thin-films. However, at this point I would like to note that single crystals and thin films display qualitatively different resistivity curves as shown in Figure 1.4. These data have been approximated from plots in Tomm et al. [26] and Birkholz et al. [27]. Quite generally it is seen that the carrier concentration can be frozen for single crystals as expected for a semiconductor but not for thin films.

Considering this electronic structure further, a few additional properties are immediately of

Figure 1.3: Vesta rendering of pyrite structure highlighting the crystal ligand field. Iron atoms are brown and sulfur atoms are in yellow.



Figure 1.4: Representative thin film and single crystal resistivities as a function of temperature. From Tomm et al. and Brikholz et al. [26, 27]. Data has been drawn from the figures in their respective papers.



note. For instance, holes occur in the nonbonding t_{2g} band. In conventional semiconductors holes correspond to a broken s-p bond, but not in this case. This has often been theorized, and shown experimentally, to have consequences on pyrite electrochemistry, specifically its susceptibility to corrosion [28].

1.2.2 Hall Measurements: Mobility and Carriers

For thin films, Hall coefficients have usually been too small to measure. Therefore, generally speaking, it is seen that mobility must be low and carrier concentration high. For single crystals, in contrast, Hall coefficients are measurable. This is taken (Chapter 3) as additional evidence that surface states have a very strong influence on the measured properties of this material.

More specifically, single crystals display a room temperature mobility in the 50-300 cm²/(Vs) range [29, 30, 31, 32, 33, 26, 34]. For thin film mobilities Willeke et al. reported 5 cm²/(Vs) [35] and Berry et al. [36] and Lichtenberger et al. [37] both reported values below their detection level $(< 1 \text{ cm}^2/(\text{Vs}))$. In addition, it has been established that electron mobility is about 100 times larger than hole mobility, [35] which fits nicely with theoretical expectations as well (i.e. from band dispersion arguments) [38].

Carrier concentration for single crystals has generally been in the range of $10^{16} - 10^{17}$ cm⁻³ [34, 26, 39, 31, 40]. Accurate measurements of carrier concentrations for thin films is significantly hampered by the small Hall coefficients measured. However, very large values (10^{18} cm⁻³) are observed when such measurements have been found possible [35]. To compliment these Hall transport measurements, low Seebeck coefficients have been observed. For single crystals negative Seebeck coefficients argue for n-type material [31, 32], while for thin films these coefficients have been found to be positive and of the range ~ 50 $\mu V/K$ [41, 42].

1.3 Optical Properties

Given the electronic structure described above, optical transitions occur mainly between d-d orbitals. However, a pure d-d transition is Laporte forbidden. Excitation by a photon is an electric dipole transition which has ungrade symmetry. So a triple product from a d-d transition would have $g \times u \times g = u$ symmetry. By symmetry considerations we know that this transition moment integral vanishes $(\langle \psi_n | \hat{\mathbf{r}} | \psi_m \rangle = 0)$ so such a transition is electric dipole (or Laporte) forbidden to first order. So it is seen that the excited electron must change (up or down) by one $(\Delta l = \pm 1)$. In the case of pyrite, however, there is enough S orbital mixing in the conduction band states to satisfy this requirement [29]. Specifically, the valence band is exclusively Fe d orbitals (l=2) whereas the conduction band is made up of a combination of Fe e_g orbitals and S $pp\sigma^*$ (using the notation in Hu et al. [7]). The S $pp\sigma^*$ have l = 1 so $\Delta l = -1$ in the absorption of a photon, satisfying this selection rule.

1.3.1 Pyrite's very intense optical absorption

One of the main advantages of pyrite as a photovoltaic absorber is that it has an impressive optical absorption $\alpha > 10^5$ cm⁻¹ when irradiated with visible light, as strong as many organic dyes [43]. Such a hugh optical absorption coefficient can be rationalized within the current discussion. Intense absorption in pyrite is due to the very close overlap of states in real space (so that we can call them d-d transitions) mixed with enough S states to make the selection rules allowed ($\Delta l = -1$). So these transitions are very efficient both in terms of eigenstates and momentum matrix elements.

As a case in point, the M point in band diagrams shows a direct band gap between the valence and conduction bands. Furthermore, both bands are nearly horizontal at this point. At such a point dE/dk is approximately equal to zero. Then, by:

$$g(E) = \frac{2g(k)}{dE/dk} \tag{1.2}$$

where g(E) and g(k) are the density of states as functions of energy and momentum, respectively, it is seen that the density of states diverges. Such a situation is known as a critical point. In reality the density of states does not become infinite but just very large, and are known as Van Hove singularities. Thus the largest contribution to the visible absorption spectrum of pyrite is thought to originate from this features [29].

1.4 Stoichiometry and Phase Stability

Pyrite's range of thermodynamic stability has been a point of ongoing research [43, 44, 45, 46]. In particular there has been contentious discussion about the homogeneity range of pyrite. How close does a crystal need to be to the perfect FeS_2 stoichiometry for the phase to maintain its thermodynamic stability? In the past it has been argued that the homogeneity range could be relatively wide and that many sulfur vacancies could be thermodynamically stable [47]. This issue is discussed in Chapter 2; however, to complete this introductory chapter on the properties of pyrite it should be noted here that theoretical evidence and a survey of existing experimental evidence both propose that the homogeneity range of pyrite is rather small and that, by implication, it is a basically stoichiometric compound [48, 49, 50].

Additionally, it should be noted that pyrite decomposes incongruously at 743°C (FeS₂ \rightarrow Fe_{1-x}S+liquid) [44]. Therefore, the zone refining schemes that have been so instrumental in allowing for high-purity large single crystals of other materials (most notably silicon) are not of use here [51]. In addition to this it has been argued that an FeS always forms prior to FeS₂ given that such phases are more kinetically accessible [52].

Finally, there is another polymorph of FeS_2 ; it has an orthorhombic crystal structure and is known as marcasite. It has been argued before that the existence of marcasite could potentially cause degradation of ostensibly phase pure pyrite solar cells [53]. However, recent work has argued that it is also a semiconductor with a band gap of similar magnitude to pyrite [54]. Interestingly, we have converted pyrite to marcasite electrochemically as described in Chapter 4.

1.5 Possible Technological Applications

1.5.1 Electrochemical Application

Pyrite has been commercialized as a cathode in lithium ion nonrechargable batteries [55]. Chapter 4 gives our work in trying to create a battery architecture that allows for pyrite's use in a rechargeable battery. Either way, interest in this material as an electrochemical cathode stems from the fact that it is an oxidized structure in an electrochemical sense. It can take four electrons during it's conversion to elemental iron and Li_2S :

$$\operatorname{FeS}_2 + 2\operatorname{Li}^+ + 2e^- \leftrightarrow \operatorname{Li}_2\operatorname{FeS}_2$$
 (1.3)

$$\text{Li}_2\text{FeS}_2 + 2\text{Li}^+ + 2e^- \leftrightarrow 2\text{Li}_2\text{S} + \text{Fe}^0$$
 (1.4)

as described in [56] (for context the standard cathode material now in use, $\text{Li}_{1/2}\text{CoO}_2$, is a half electron reaction). This allows for a very large discharge capacity of ~894 mAh/g [57].

1.5.2 Photovoltaic Application

In order to understand pyrite's potential as a photovoltaic semiconductor it is necessary to understand the current "bottlenecks" to wide scale photovoltaic deployment. Electric energy converted from sunlight is, of course, an enticing avenue to help fulfill society's energy needs. This is so mainly because of the vast sum total of power (162 petawatts!) [58] coming from solar irradiation. However, while the aggregate amount of power is overwhelming, solar is afflicted by the common misfortune of renewable energies: the energy is so dispersed as to make collection and conversion of even a small fraction very challenging. Specifically, while the underlying physical principles are known, the economic feasibility of large-scale deployment continues to be the barrier to widespread adoption. The study of iron pyrite (FeS₂) as the active material in photovoltaic junctions is well positioned to directly address this predominant challenge, not because of it's potential efficiencies but because of its potential cheapness [59]. How could pyrite address the shortcomings of the current commercialized technology? Silicon or so-called 1st generation technology suffers from the a large cell thicknesses (>200 μ m) and an expensive energy input necessary to refine the material to its elemental state. Pyrite, by contrast would use very little material and iron and sulfur have inexpensive costs of extraction and are easier to refine. 2nd generation technology (thin films) have also been developed to address the shortcomings of silicon but so far have included toxic elements such as cadmium or rare ones such as indium. Pyrite addresses these shortcomings with its environmental abundances and compatibilities. In this way, pyrite, if it can be made to work as a semiconductor, could perhaps be termed as "Green 2nd Generation".

1.5.3 Spintronic Application

Very recently it has been argued that the (100) surface of pyrite is spin polarized [60, 61]. The development and experimental verification of these ideas is what most of Chapter 3 describes. Here I would like to note that such a spin polarized situation may allow for this material to display both semiconducting and spin polarized properties which may make it very interesting from both a theoretical science perspective and for technological application that involves manipulating the spin of the charge carriers in the material.

1.6 Semiconductor Nanocrystal Synthetic Techniques

1.6.1 Apparatus

The experimental methodology used in this dissertation is built on about three decades of accumulated knowledge concerning nanoparticle synthesis and measurement. Seminal works from this body of knowledge have been used heavily in understanding pyrite's unusual properties and how they can be manipulated and understood [62, 63]. In particular a conventional experimental apparatus has been used. A three neck flask has been attached to a Schlenk line through a condenser and heated with PID controlled heating mantle. The temperature is measured by a thermocouple that is immersed in the solution. A teflon coated stir-bar is put at the bottom of this system and it is set on a magnetic stir plate. In this way the an inert atmosphere can be easily established and the temperature easily manipulated while stirring action keeps the reaction homogeneous.

1.6.2 Synthetic philosophy

The synthesis of semiconductor nanoparticles is an extremely active topic in science currently. This is so mostly because once the size of a nanoparticle is near its exciton Bohr radius, it has size dependent electronic properties [64, 65]. Experimental protocols have been devised to grow monodisperse ensembles of these nanoparticles that then absorb and emit light as a function of their size [66, 67]. Pyrite has never been reliably created in a size near its Bohr radius so no effects of quantum confinement are confidently known. Instead the philosophy of the work given here is dramatically different. We wanted to gain information about the surface states existing on the surfaces of this material. Normally it is thought that to do such work a researcher must work with surface sensitive probes such as LEED, STM, S-XPS, etc. In the work presented here, I believe it is strongly shown that such states can also be accessed with common nanoparticle protocols and measurement techniques. Furthermore, the preparation of a well prepared specimen for use with the aforementioned techniques is usually quite involved. The use of nanocrystals with alkyl ligand shells has allowed for the work here to be relatively efficient in terms of experimental throughput and environmental sensitivity. In treating these surface states we have taken much inspiration from those trying to adapt semiconductor quantum dots for solar cells [68, 69]. In this case they are trying to increase the voltage of their cells and therefore have a vested interest in passivating surface states, just as for pyrite.

Chapter 2

Iron Pyrite Nanocubes: Size and Shape Considerations for Photovoltaic Application

2.1 Abstract

Multiple lines of recent research indicate that iron pyrite (FeS₂) requires a {100} terminated crystal morphology in order to maintain semiconducting properties. Additionally, the large absorption coefficient of pyrite allows for the near complete absorption of above band-gap radiation in <50 nm layers. However, to our knowledge <50 nm pyrite nanocubes have yet to be isolated. Herein, we demonstrate the synthesis of ~37 nm phase pure pyrite nanocubes by manipulating the sulfur chemical potential and ligand environment of the system. Ultraviolet-visible (UV-vis) absorption spectroscopy gives a signal of resonant light scattering (RLS) indicating strong electronic coupling between nanocubes, which may allow for nanocube films with superior electron mobility. The absorption spectroscopies of cubic and irregular nanocrystals are contrasted and compared with recent theoretical work in order to investigate the effect of shape on electronic properties. Specifically, nanocubes have been found to have absorption characteristics closer to theory as compared to irregular nanocrystals, especially for UV radiation: 250-350 nm. Pyrite nanocubes display an indirect band gap at ~1.1 eV in addition to two direct transitions at ~1.9 eV and ~3.0 eV, correlating well to theoretical values.¹

¹ Adapted with permission from: Macpherson, H.A., and Stoldt, C.R., ACS Nano **2012**, 6(10), 8940-8949. Copyright 2012 American Chemical Society.

2.2 Introduction

Iron pyrite (FeS₂, hereafter termed pyrite for simplicity) is a technologically important indirect band-gap semiconductor ($E_g \approx 0.95$ eV). It has been commercialized as a high-capacity electrode material in lithium-ion primary batteries [55], and recent developments indicate its viability in rechargeable batteries as well [56]. Understanding the surface chemistry of pyrite is an especially important issue for multiple applications. Recent work has identified the surface of pyrite as interesting for dilute magnetic semiconductor research with spintronic application [61]. Oxidative decomposition at pyrites surface has become vital in understanding the processes leading to the acidification of runoff coming from coal mining, a phenomenon known as acid mine drainage [70]. However, the most active pyrite research effort is directed towards its potential application as the photoactive material in thin-film solar cells, an additional application that, as described below, necessitates a better understanding of its surface properties.

Concerning photovoltaics, pyrites unique properties include an exceptionally large optical absorption coefficient in the visible region ($\alpha > 10^5 \text{cm}^{-1}$ at $\hbar \omega > 1.5 \text{eV}$) [71] coupled with large elemental abundances, nontoxicity, and low material refinement costs [59]. Its single junction thermodynamic limit (Shockley-Queisser Limit) is ~ 31%, slightly less than the 33.7% limit for an ideal band-gap of 1.34 eV [59]. Therefore pyrite as the active material in photovoltaic junctions is well positioned to directly address the predominant challenge in solar harvesting, the economic difficulty of widespread deployment.

Furthermore, such high optical absorption in pyrite allows for absorption of 90% of incident light in only ~ 40 nm thick layers (neglecting light scattering) [46]. If such ultra-thin films can be formed, it could potentially enable more efficient carrier extraction and the creation of novel heterojunction device architectures such as extremely thin absorber (ETA) cells, which can be considered "semiconductor-sensitized" in analogy to dye-sensitized cells [72].

In the 1980s work was undertaken to develop the technology, predominately by the Tributsch Group in Germany who succeeded in creating electrochemical cells with mostly favorable characteristics. However, photovoltage remained around 200 mV in these cells, far below theoretical estimates and thereby limiting efficiencies to below 3% [46]. This anomalously low open-circuit voltage has remained a persistent problem. With renewed interest, prompted mostly by the materials availability study of Wadia et al. [59], theoretical studies have begun to bring the source of the problem into clearer focus.

Historically, the most common explanation for the anomalously low open-circuit voltage has been sulfur deficiencies in the bulk material [51]. However, recent theoretical work [43, 48, 22] and a survey of experimental studies [50] now suggest that pyrite is essentially a stoichiometric compound $(O(10^6)/cm^3)$ with a sizable (~2.4 eV) sulfur defect formation energy. These same considerations have been used to argue against the presence of Fermi level pinning in the material [43].

Another possible explanation for the low open-circuit voltage is that trace impurities of the orthorhombic polymorph (marcasite) or iron monosulfide (FeS) phases may exist and limit voltage. Concerning marcasite, recent modeling has shown that it may itself be a semiconductor and that while one or two layers may grow on pyrite surfaces, no mid-gap states are created [38].

Considering surface structure, pyrite is commonly cleaved on either {100}, {111}, {210} faces [73]. Work by Alfonso argues that both of the low energy {111} and {210} faces create conductive surfaces [74]. The stoichiometric {100}-S faces (hereafter termed the {100} faces for simplicity), however, leave the surface basically unreconstructed and do not break bonds in the persulfide unit [75]. Therefore, surface iron atoms no longer have a distorted octahedral crystal field but are reduced to square pyramidal symmetry. The band gap of pyrite at the (100) surface has been evaluated theoretically with most studies showing only a slight decrease (0-0.3 eV) from the bulk value [60, 76, 38, 43].

As argued above, bulk considerations and the electronic state of the perfect $\{100\}$ face have not been able to explain the observed low photovoltage. However photoelectron spectroscopy [75], scanning tunneling microscopy [77], and modeling [76] have firmly established that there is a low energy route to defect states on the (100) surface. At the level of single sulfur defects Yu et al. [43] and Zhang et al. [60] both find that sulfur vacancies have low formation energies (~0.4 eV) on these faces, but differ regarding the relative impact on electronic properties. As the concentration of defect sites increases there can be a large percentage of iron monosulfide defects with a surface charge rearrangement that oxidizes iron to Fe^{3+} and reduces sulfur to S^{2-} [78]. Effectively, an iron monosulfide shell may be created, and such defects could cause the observed conductive behavior indicated by low open-circuit voltage measurements.

With such a high optical absorption coefficient in pyrite (penetration depth: $\delta \sim 15$ nm in the visible) [71] most excitons are created in the near surface of the material, magnifying the importance of surface considerations. Therefore, it is probably unsurprising that the best device results with pyrite have come from surface treatments prior to the creation of electrochemical interfaces. Specifically the Tributsch Group found that HF/CH₃COOH/HNO₃ [30] and KCl [79] treatments markedly improved the electrochemical performance of their photoelectrodes. In addition many high vacuum studies have found it necessary to wash their samples in acid prior to analysis to obtain a high-quality surface [80].

Given the size constraint, recent studies have created pyrite by nanocrystal synthetic routes [81, 53, 82, 83]. However, these studies either have not isolated {100} faces, or have done so at sizes 150 nm or larger [83]. Photovoltaic devices with this particle size (>150 nm) will have a mismatch between penetration depth and device thickness, necessitating longer diffusion lengths and negating the inherent strengths of pyrite as an absorbing material.

Additionally, UV-vis absorption spectroscopy in these studies, while generally indicating an indirect transition around 1 eV, have been significantly different so as to obscure a consistent determination of the electronic properties of the material. Such ambiguity in characterization of the optical band gap seems to preclude the possibility that the electronic band gap, including interfaces, will be appropriate for optoelectronic applications.

In the work described here, we have attempted to address pyrite's synthetic challenges by nanocrystal synthesis in order to grow < 50 nm particles with {100} faces. We use alkylamines of different lengths to constrain size, and leverage theoretical data indicating that {100} faces are favored when the chemical potential of sulfur is low to manipulate shape [74]. The resulting cubic

product reported here is amenable to various surface treatments that may help elucidate the surface processes active on the $\{100\}$ facets; such work will be vital for photovoltaic application as well as surface magnetism and oxidative decomposition studies, as described above.

It should be noted that this type of study is somewhat unique in the field of semiconductor nanocrystals in that no attempt at quantum confinement is made. This has distinctly altered the common requirements for a successful synthesis. Monodispersity and size requirements (normally for emission purity) are considerably relaxed whereas, as described above, shape and surface constraints are of primary importance.

2.3 Results and Discussion

2.3.1 Synthetic Scheme

The general synthetic scheme described in this work uses the chemical potential of sulfur along with alkylamines of different lengths and temperature to control the size and shape of the product. Specifically, Figure 2.1 shows the transition from irregular particles after the nucleation step to euhedral nanocubes after one growth step and further towards shape perfection after the second growth step. This figure also gives the solvent environments, molar sulfur/iron ratios, and temperatures employed to induce the indicated results. Here, and throughout this study, we use the term nucleation to mean the initial product of our synthesis rather than molecular seed crystals.

Figures 2.2A-B give additional TEM and HRTEM images of the final product of this synthesis indicating the cubic morphology of the particles and the size distribution. 500 nanocubes were measured from TEM images to give the size distribution histogram displayed in Figure 2C. The final product is measured to have an average edge length of 37 nm with a standard deviation of 11 nm. The measured lattice parameters estimated from HRTEM correspond well to accepted values [3].



Figure 2.1: TEM images and chemical conditions indicating the synthetic scheme employed.

Figure 2.2: (A) A TEM image of the synthesized FeS_2 nanocubes showing the sample morphology and size distribution, and (B) a HRTEM image showing lattice fringes with a measured d-spacing corresponding to the FeS₂ {100} lattice planes. In (C) the particle size distribution (number distribution) is determined from TEM measurements.



2.3.2 Structural and Elemental Characterization

Structural characterization of the resulting pyrite nanocubes is given in Figure 2.3. X-ray powder diffraction peaks in Figure 2.3A correlate well to pyrite with accepted lattice parameters (a=5.418 Å, u=0.385 Å) [3]. No peaks corresponding to marcasite (FeS₂) or pyrrhotite (FeS) are detected indicating phase purity for each growth step in the synthesis.

A Scherrer analysis of the final XRD pattern gives a crystallite size of 48 nm with a standard error of 5.2 nm; this being a volume-average size distribution is not directly comparable to the number-average size distribution given above from TEM measurements. Converting the TEM size data to a volume-averaged basis gives a value of 46 nm. Therefore, the XRD size and the TEM size agree to within the errors of the measurements, indicating that the resulting nanocubes are singlecrystal domains. However, stacking faults are quite prevalently observed as indicated in Figure 2.1. Details of the Scherrer analysis are given in the methodology section.

Raman spectroscopy has also been utilized for structural analysis, with the results reported in Figure 2.3B. All 5 Raman active modes for pyrite result from vibrations of the sulfur atoms with stationary iron, so this characterization method gives high-resolution information about the chemical environment of the S₂ units [84]. In this analysis we have used $\lambda = 532$ nm for excitation; at this wavelength pyrite is highly absorbing with an absorption coefficient ~ 4 × 10⁵ cm⁻¹ [71, 85], This excitation wavelength gives a penetration depth typical for metals, not semiconductors, and as a consequence, much of the Raman scattering reaching the detector results from the near surface of the material.

This Raman analysis gives 3 peaks which have previously been indexed to different stretching and librational modes of the persulfide units and show close correspondence [17]. Also, the $T_g(3)$ mode is a mixture of stretching and librational motion of 4 adjacent S₂ units and the relative strength of this mode has been argued as indicating good long range order in the crystal [15]. Additionally, there is a small shoulder on the E_g mode at ~ 350 cm⁻¹. This shoulder has been ascribed to the $T_g(1)$ mode which to our knowledge has only been observed by using polarized light (to block out the overlapping E_g mode [86]) or a liquid-nitrogen cooled CCD [84]. Peaks sharp enough for the observation of this mode are taken to indicate a chemically homogeneous nature of the product.

Energy dispersive X-ray spectroscopy was utilized to analyze the elemental composition of the product through each of the growth cycles. The ratio of sulfur to iron remained stoichiometric within the experimental accuracy of the method for all three synthetic stages.

2.3.3 Optical and Electronic Properties

The use of UV-vis absorption spectroscopy to analyze the electronic structure of the pyrite nanocubes gave unexpected results. The as-prepared nanocubes agglomerated quickly; we were unable to keep them rigorously dispersed during the cleaning process. Therefore, to obtain a stable dispersion for analysis, we sonicated the solution with excess oleylamine (following the procedure described by Li et al. [83]). During this procedure, it was observed that the agglomerated black solution would turn purple/red in color and the optical density would increase as the nanocubes became more dispersed. As is normally observed for agglomerated nanoparticles, nanocubes that were less dispersed (i.e. not sonicated as long or with less oleylamine) had a significant UV-vis scattering tail, that is, higher absorption at longer wavelengths compared with more dispersed samples, as shown in Figure 2.4A. Unexpectedly however, Figure 2.4A also shows that these solutions of small agglomerates of nanocubes have more distinct excitonic features at ~ 300 nm and ~ 500 nm, in addition to the scattering tail. This phenomenon can be understood as a signal resulting from resonant light scattering (RLS). RLS is greatly enhanced light scattering that occurs when agglomerated chromophores are irradiated by light with a wavelength in close proximity to an electronic transition of the chromophore [87]. Despite the seldom-used terminology in this discipline, pyrite could certainly be termed a chromophore given its high absorption coefficient. Further, TEM images have often shown the propensity for these nanocubes to agglomerate in a face-sharing orientation. To investigate this further, the common test for RLS was conducted which uses a fluorimeter in a 90° configuration with synchronously scanning excitation and emission monochromators [88].
Figure 2.3: (A) Powder XRD of FeS_2 product through the nucleation and growth stages with JCPDS card no. 06-0710 for reference. (B) Raman spectra of the final FeS₂ nanocubes with modes indexed. (C) Elemental analysis with energy dispersive x-ray spectroscopy through the nucleation and growth stages.



Figure 2.4B shows distinctly increased light scattering at the two electronic transitions in question, persuasively implicating RLS as the cause of the distinct excitonic peaks in the less dispersed UV-vis spectrum shown in Figure 2.4A. Although RLS has been observed for metal nanoparticles [89] (often involving surface plasmon resonance as well) and semiconductor structures grown by molecular beam epitaxy, [90] no previous work has been identified by us where a significant RLS signal has been shown to result between semiconductor nanocrystals.

Given that RLS is an unusual explanation for the observed optical properties, it is important to constrain the chemical processes at work as best as possible. To this end, we are cautioned by the fact that previous studies have demonstrated that storage of some types of nanoparticles (CuInSe₂, for example) in excess alkylamines results in etching of the particles over time [91]. To understand if this is happening in this case, we have imaged nanocubes by TEM on the day of synthesis and after 17 days in chloroform with excess oleylamine (Figure A.1, Supporting Information). No change in size or morphology is evident. We therefore believe that sonication with excess alkylamine results in dispersions without bulk chemical changes to the particles. However, detailed analysis of amine surface bonding dynamics, and the resulting affect on RLS, remains to be evaluated.

While RLS in solution does not give new information about the electronic structure of pyrite, it does indicate that electronic coupling between nanocubes is readily achieved, to the point of being nearly unavoidable. Given that so much effort has been undertaken recently to make conductive nanocrystal films, this phenomenon may point to the amenability of this material to produce films with high electron mobilities. Of note, theoretical work indicates that the coupling energy between nanocubes is a factor of 3 higher than for spheres, given increased wavefunction overlap [92].

Studies have proposed ways to deconvolute the extinction spectrum of an RLS affected sample into scattering and absorption signals [89]. However, in order to obtain a signal from only absorption, we have dispersed these nanocubes in octadecylamine, which we have shown can sterically hinder RLS to an insignificant level (Figure A.2, Supporting Information). In Figure 2.5A UV-vis absorption spectra are given for the nucleation and both growth steps, and are now labeled as absorbance rather than extinction as in Figure 2.4. These data indicate similar electronic behavior

Figure 2.4: (A) Absorption spectroscopy of identical nanocube solutions that differ only in how long they were sonicated prior to analysis. (B) The resulting RLS spectrum (green) produced by synchronously scanning excitation and emission monochromators on a fluorimeter, plotted along with the previously measured absorption spectrum (blue) of that nanocube sample.



of the as nucleated nanocrystals and rationally grown nanocubes. However, they also indicate that growing the nanocubes causes decreased absorption at high-energy wavelengths ($\sim 255-350$ nm) and, to a lesser extent, increased absorption in the visible and near infrared ($\sim 550-1000$ nm).

In order to further understand the differences in the three spectra given in Figure 2.5A, we have compared the experimental results obtained here (after the final growth step) with the theoretical data of Vadkhiya and Ahuja [85]. Specifically, we have converted the absorbance data to absorption coefficient (α) and, not knowing the exact path length for the incident radiation in our experiment, normalized it to their data in Figure 2.5B. These two data sets show remarkably close correspondence. Compared to the data shown in Figure 2.5B, absorption for the as nucleated and first growth steps are anomalously large at 255-350 nm (i.e. above ~3.5 eV). Conversely, the final nanocube product shows higher absorption in the 550-1000 nm range compared with the nucleation and first growth products. While a much smaller affect, this absorption character of the final nanocubes is again closer to the theoretical data than that of the nucleation or first growth products. Lastly, as the synthesis proceeds the absorption peaks at ~440 nm and ~310 nm becomes more pronounced. These absorption differences may therefore be important in indicating the relative shape and/or surface perfection of the product.

Figure 2.5C gives $(A\hbar\omega)^n$ for the final nanocube product as a function of the energy of incident radiation, with n=1/2 for indirect transitions and n=2 for direct ones. Linear behavior is observed indicating an indirect transition at ~1.1 eV. The two excitonic features can also be approximated as transitions occurring at ~1.9 eV and ~3.0 eV.

This 1.1 eV band gap is slightly higher than the accepted experimental value of 0.95 eV. Of note, recent theoretical calculations also give a slightly higher band gap (1.02 eV) [22, 38]. However, the analysis given here assumes the existence of parabolic bands which may be a poor assumption for modeling pyrites quite flat bands [71]. Therefore, the data approximated in this way agrees with both previous experimental and theoretical data within the errors of the approximation. The two direct transitions can be tentatively indexed to interband transitions as given by the imaginary part of the dielectric constant in the theoretical works of Vadkhiya and Ahuja [85] and Antonov et

Figure 2.5: (A) UV-vis absorption spectroscopy of pyrite plotted for the nucleation and both growth steps. (B) Absorption spectroscopic data for the final product normalized to density functional theory results from Vadkhiya and Ahuja [85]. (C) Band-edge absorption of the final product assuming indirect (n=1/2) and direct (n=2) absorption character.



al. [93]. The 1.9 eV transition reported here is quite close to their calculations of 2 eV and 2.1 eV, respectively. However, the 3.0 eV second direct transition is $\sim 15\%$ less than their assignments of 3.6 eV and 3.5 eV, respectively. This difference may arise from the ambiguity of the proper level of absorption in this energy region, as described above.

2.3.4 Reaction Mechanism and Kinetics

As compared to other binary transition metal chalcogenides, the synthesis of dichalcogenides with the pyrite structure has proven problematic. This difficulty stems from the notion that no common precursor molecule decomposes to give the S_2^{2-} unit (or singly charged sulfide radicals). This may be because the S-S bond at ~265 kJ/mol is weak in comparison with common organosulfur bonds [94]. Fortunately, a large body of information on pyrite nucleation and growth comes from the earth science community. Given the lack of S_2^{2-} precursor ions, pyrite does not form directly from monomer in solution but goes through an FeS intermediate [52], a feature common to synthetic reactions as well [81]. Rapid nucleation of iron monosulfides seems to prevent a sufficiently high supersaturation for an adequate FeS₂ nucleation, often causing large sizes as a result [95]. Conversely, the slow dissolution of iron monosulfides creates reaction-controlled growth conditions which can cause the euhedral facets of pyrite often observed [81, 83, 96].

In addition to involving a precipitated reaction intermediate, we believe that pyrite precipitation can be considered an irreversible reaction. This has been shown by others who have indicated that hot-injection produces many nuclei that grow by agglomeration [82] and that higher concentrations lead to smaller particles [83], indicating a kinetically controlled reaction (see Shevchenko et al., [97] for example, for the attendant theory). To add to this body of evidence, even though we have grown these nanocubes over a period of many hours, Ostwald Ripening has not been observed.

In this study alkylamines have been used which are thought to be relatively weak ligands to semiconductor particles [98]. It is our conjecture that a relatively weak ligand is necessary in order that the FeS reaction intermediate is not isolated. Further, even if a ligand is not strong enough to isolate FeS, the slow dissolution of well-ligated FeS will create >100 nm sizes of FeS₂ [81], larger

than is the goal of this synthesis. Therefore, concerning the size of the nucleation product, we are constrained by wanting small particles but lacking the ability to vary the bond strength of the ligand to the final precipitated phase. However, monomer kinetics can still be altered significantly by varying the concentration and/or chain-length of the ligands [99]. Lowering the reactivity of the monomer by ligand concentration and chain-length is caused by steric factors, which will favor nucleation over growth, given that growth involves longer-range transport of monomer through the synthesis. Thus size control can be mediated by interligand interactions, which is the theoretical basis for the following analysis.

Given the foregoing constraints and the motivation for small (<50 nm) particles described above, we have chosen to nucleate in pure hexadecylamine (C16), which has strong interligand interactions given the long length of the alkane tail, to force the creation of small particles despite the slow dissolution of FeS. This has resulted in a mixture of cubic and completely irregular particles as shown in the left side of Figure 2.1. Such a kinetically constrained nucleation necessarily prevents an optimal shape and surface causing us to add oleylamine (C18), which has been shown to act like octylamine (C8) given its cis configuration [100], for the rational growth steps of the synthetic process. If no additional oleylamine is added and the existing hexadecylamine is used as the solvent for the growth steps, the product will be more irregular in shape (Figure A.3, Supporting Information). We believe this indicates conditions in which the limiting step to particle growth is monomer reaching the surface of the particle. Given that this reaction is considered irreversible, this leads to conditions in which particle shape does not evolve rationally. Conversely, the well-faceted nanocubes shown in Figures 2.1 and 2.2 indicate that the limiting step to nanocube growth with oleylamine added is the reaction of monomer with the crystal surface, giving the reaction-controlled conditions necessary to form euhedral facets.

Hexadecylamine has been used for nucleation instead of octadecylamine (C18) because, in the latter case, a more polydisperse product was observed with a large quantity of particles with irregular shape (Figure A.4, Supporting Information). It is possible that the ligand-ligand interaction of octadecylamine is so strong at 200° C (the growth temperature) that it becomes difficult for it to be in the "off" position often enough to allow for rational growth [98].

2.3.5 Controlling Shape by Sulfur Chemical Potential

As described above, ligand conditions were changed between the nucleation and growth stages to allow for reaction-controlled growth. However, reaction-controlled conditions are necessary, but not sufficient, to grow particles of a particular terminal face. For sufficiency it is also necessary to control the chemical potentials of the reacting constituents so as to affect their individual rates of adsorption onto specific crystal facets.

Theoretical work has elucidated the energetic differences between various common surface terminations as a function of sulfur chemical potential within the reaction conditions [101, 74]. These studies have found that $\{100\}$ faces attain the lowest energy at sulfur poor/iron rich conditions with $\{210\}$ and the $\{111\}$ faces becoming preferred as conditions become increasingly sulfur rich, successively. These results have been used as the handle with which to control the shape of the particles, using a lower concentration, and therefore chemical potential, of sulfur (relative to Fe chemical potential) during the growth of the preformed irregular nuclei. Specifically, [S]/[Fe]=6 for the nucleation stage was decreased to [S]/[Fe]=2.05 for the growth stages. In this way, the altered chemical potential of sulfur was used as a driving force to grow all other faces besides $\{100\}$ to extinction.

When grown at [S]/[Fe]=2, it was found that some pyrrhotite FeS was isolated (Figure A.5, Supporting Information). This can be explained by reference to the iron-sulfur binary phase diagram [44], where, if any H₂S evaporated (which is known to form in this reaction) [102] resulting in a loss of sulfur from the system, then thermodynamic considerations will predict a mixture of pyrite and pyrrhotite. Therefore, slightly excess sulfur has been used beyond what would seem to be ideal for promoting cubic faces. If the sulfur concentration is increased further ([S]/[Fe]=2.1, Figure A.6, Supporting Information), it is observed that the edges of the resulting particles become slightly more rounded than for [S]/[Fe]=2.05, indicating the sensitivity of this method to shape control.

It is interesting to note that despite pyrite being a cubic crystal system, and our attempts to create "nanocubes" as described in the preceding paragraph, many of the crystals actually have rectangular dimensions, as shown in Figure 2.1. This may be due, in part, to agglomeration during the nucleation stage. However, it seems to be a seldom-commented fact that the <100>crystallographic directions of pyrite are not interchangeable and only display 2-fold symmetry [52]. Therefore, it might also be due to different reaction rates on distinct $\{100\}$ faces. Which $\{100\}$ faces may be forming the larger and smaller area facets of these "nanocuboids" has not been evaluated in this study. Studies exploiting the chiral nature of this material may be interesting in the future.

2.3.6 Additional Reaction Considerations

The focusing of the size distribution in this synthesis is unusual in the large size of the growth stages, specifically $[Fe]_{grow}/[Fe]_{nuc}=2$. More concentrated growth conditions have been shown to result in some smaller particles indicating a secondary nucleation (Figure A.7, Supporting Information). However, as can be seen in Figure 2.1, after the first growth step there are still some truncated cubes with either $\{210\}$ or $\{111\}$ faces. Therefore, a second growth phase has been employed, again at $[Fe]_{grow}/[Fe]_{nuc}=2$, to create more perfectly terminated nanocubes. Theoretically, the growth rate of a particle decreases linearly as the size of the particle increases if the experiment is reaction controlled, allowing the size-focusing shown in Figure 2.1 [103]. Additionally, there has been significant interest lately in using continuous monomer production to focus size distributions by keeping the amount of monomer above a level that allows Ostwald Ripening [104]. Although we think that the irreversible nature of this reaction prevents Ostwald Ripening, this study can be considered an extreme example of monomer production from the slow dissolution of FeS.

Despite the focus of this work in maintaining the semiconducting properties of pyrite, the procedure, being a noninjection synthesis, also makes it more amenable to scale-up and more reproducible than the hot-injection syntheses previously reported. Additionally, herein the metal chloride has not been dissolved in the alkylamine prior to the introduction of the sulfur as is standard with this type of synthesis, further streamlining the synthetic process. Also, because of

the large amounts of monomer added to the reaction, we have chosen to cool the reaction and allow it to freeze rather than injecting additional chemical species at the growth temperature. We believe that this approach makes the synthetic protocol significantly easier to undertake, less time sensitive, and more reproducible.

In addition to shape considerations, as described above, the control of the relative perfection of surfaces is important to the study of pyrite. Obviously the conditions for the best shape control might be quite different from those of optimal surface termination. There is a well-developed body of work in perfecting the surfaces of spherical nanocrystals so that their photoluminescent efficiency is maximized. The "bright point" of an ensemble of particles in a synthesis has been shown to occur when the surfaces of the particles are in diffusive equilibrium with the surrounding monomer, allowing time for optimal surface reconstruction [105, 106, 107]. As described above, we believe this reaction can be considered irreversible. Therefore, it is not possible to use the foregoing logic of diffusive equilibrium. Instead, the use of relatively low temperatures (200 °C) over long reaction times may allow for rational surface growth in addition to its effect on crystal shape. This conjecture is being actively tested in ongoing work in our laboratory.

2.4 Conclusions

We present a synthesis of iron pyrite (FeS₂) nanocubes in an attempt to address the fundamental problems inherent to the material. Specifically, by creating strong interligand interactions we have succeeded in decreasing growth kinetics and thereby nucleating small nanoparticles despite a necessarily small supersaturation (given the precipitation and slow dissolution of FeS). We have then decreased the interligand interactions to allow for more rational growth, now limited by the interaction of sulfur with the growing pyrite surface. Specifically, we have isolated $\{100\}$ faces by lowering the sulfur chemical potential of the reaction; this validates theoretical considerations that argue that $\{100\}$ faces become lowest in energy in sulfur poor/iron rich conditions. The resulting product has an average edge length of ~ 37 nm making it smaller than previous syntheses of nanoscale cubic pyrite. This may allow the design of pyrite thin-films with thicknesses more closely corresponding to the absorption coefficient of the material. The product has been shown to have unusual electronic properties including a strong resonant light scattering signal, indicating the ease with which electronic coupling occurs between particles. Shape engineered nanocubes are shown to have different electromagnetic absorption properties than irregular nanocrystals with the nanocube product demonstrating behavior closer to that produced by theoretical calculations. The resulting nanocube product may therefore be amenable to maintaining semiconducting behavior for applications.

2.5 Methods

The synthetic scheme employed heats anhydrous $FeCl_2$ and elemental sulfur in alkylamines. This chemical route has recently become somewhat standard in pyrite syntheses [81, 82, 83] and is an adaptation of the original method pioneered by Joo et al. [108] A 0.5 mmol (63.4 mg) amount of anhydrous $FeCl_2$ beads, 10 g hexadecylamine, and 3 mmol (96.2 mg) S flakes were brought to 250° C for 3 hours in a 50 mL 3 neck flask under argon atmosphere with magnetic stirring at 240 RPM. Uncommonly, this is a so-called "heating up" synthesis and the Fe-Cl-Amine complex that is usually formed previous to reaction with sulfur was not formed here [81, 108].

After the nucleation reaction was completed, the flask was allowed to cool naturally and the raw solution allowed to freeze with the hexadecylamine. Once room temperature was obtained, 1 mmol (126.8 mg) FeCl₂, 2.05 mmol (65.7 mg) S, and 15 mL oleylamine were added through one of the necks of the flask with argon flowing over the frozen solution (warning: oleylamine can cause chemical burns). The flask was then resealed and brought to 200° C for 9 hours, stirring at 750 RPM. This growth process was performed a second time except without the addition of more oleylamine (i.e. only FeCl₂ and sulfur). Upon completion of the second growth step, ~10 mL of chloroform was added and the solution was lightly centrifuged (2000 RPM for 1 minute) followed by decanting of the supernatant. The precipitate was cleaned twice in chloroform by redispersion and centrifugation, and was subsequently stored in chloroform for analysis.

TEM images were acquired with a Philips CM100 with a 100 kV accelerating voltage and a

bottom mounted digital camera. Samples were prepared by immersing a carbon coated TEM grid into a nanocube solution in chloroform for about a second and then drying in air, this was done immediately prior to analysis to avoid oxidation ambiguity. HRTEM images were acquired under the same procedure with a Philips CM200 operated at 200 kV.

XRD analysis was conducted on a Scintag PAD5 XRD using a Cu K-alpha x-ray source $(\lambda=0.154056 \text{ nm})$ accelerated by a 40 kV voltage. For analysis a nanocube sample in solution was pipetted onto a glass slide and the chloroform was allowed to evaporate. The slide was rotated at 0.12 °/min relative to the detector in a reflection (i.e. Bragg-Brentano) geometry.

The Scherrer equation to measure pXRD peak broadening is:

$$D = \frac{K\lambda}{B\cos\theta} \tag{2.1}$$

It is well known that deciding on an appropriate Scherrer Constant (K) is a difficult task. Stokes and Wilson computed K values for various reflections for cubic shaped crystals with a cubic crystal system [109]. They used the integral breadth definition as the measure of the width of the diffraction peaks (i.e. the value of B). This measure is defined as the area under the peak in question divided by its peak intensity. To use their Scherrer Constants we have followed this definition (instead of full width at half max (FWHM)). To use their K values we have also defined D as the cube root of the nanocube volume, rather than the more standard definition where D is the crystallite size in the direction perpendicular to the lattice planes.

With these definitions, the size of the crystallite domains of the particles have been evaluated for the (111), (200), (210), (211), (220), and (311) reflections with the reported result being an average of the six. Standard error is given as the standard deviation of these six measurements. These data are given in Table A.2 (Supplemental Information). Instrumental peak broadening was estimated by analyzing a sample of microcrystalline quartz.

Raman spectra were collected on a Jasco NRS-3100 using a 532 nm laser for excitation. An OD2 filter was used allowing the sample to be irradiated by 0.7 mW. Raman scattering was dispersed by a 2400 lines/mm grating. The CCD was cooled by a peltier element which kept it at -58° C. For analysis a nanocube sample in solution was pipetted onto a glass slide and the chloroform was allowed to evaporate. The sample was analyzed under 100X magnification.

Fluorimeter measurements were conducted on a Horiba Fluorolog-3 fluorimeter. The analysis was performed in chloroform or trichloroethylene in a 1 cm quartz cuvette. As described above, the analysis involved simultaneously scanning the excitation and emission monochromators. The emission monochromator is at a 90° orientation to the excitation. It was found that 3 nm slits for both excitation and emission monochromators gave the best signal. The signal was obtained as the ratio of emission per lamp intensity (S/R). The signal was background corrected by running an identical experiment with just the solvent and cuvette system.

Ultraviolet-Visible (UV-Vis) measurements were conducted on a Varian Cary 500 spectrophotometer. Samples were analyzed in chloroform with a double beam configuration and 1 nm data collection interval.

Energy dispersive X-ray spectroscopy (EDX) was performed on a JEOL JSM-6480LV scanning electron microscope equipped with an INCA PentaFET x3 EDX spectrometer. Samples were mounted on an aluminum stub with carbon tape and irradiated with an electron source set at 15 kV. For each data point three to six large-area (>2 um^2) spectra were taken and the results averaged.

Chapter 3

Evidence for Direct Band Gap Surface States with Defect Passivation on Iron Pyrite {100} Nanocubes

3.1 Abstract

Despite iron pyrites technological potential and geological prevalence, basic questions concerning its electronic structure remain, in particular the effect of surface states. Additionally, resonance light scattering (RLS) is observed in pyrite nanocrystal colloids and is evidence of unintended interparticle electronic coupling. In this study, surface treatments with charged ligands are performed on {100} terminated pyrite nanocubes resulting in crystalline ligand self-assembly on these faces. After surface treatment these nanocubes are more easily dispersed in nonpolar solvents and have a smaller RLS signal, indicating diminishing electronic coupling. Additionally, after surface treatment, two very sharp absorption features are observed at 0.73 and 0.88 eV. In connection with recent theoretical work, these transitions are taken as evidence that the (100) surface of pyrite is spin-polarized with each absorption peak being the signal of band edge absorption across a spin-selected direct band gap. A theoretical framework is proposed as a plausible explanation of the observed behavior. In this model highly localized and energetically disordered Fe d-orbital states fill in the band gap of the (100) pyrite surface that is not perfectly terminated (or nearly so). Frustration between energetic disorder and Coulomb repulsion then results in the formation of metastable states that obscure the observation of these surface transitions and cause the dynamical behavior observed.

3.2 A Program Note

Much of this chapter has been submitted for review as a journal article at the time of publication of this thesis. The chapter given here is similar but slightly longer and more detailed than that manuscript. I have attempted to add more detail here than could reasonably be included in a concise journal article.

3.3 Introduction

Iron pyrite (cubic FeS₂, fools gold) is an important geologic and technological material. Geologically, it is the most prevalent sulfide on Earths crust, with an estimated annual production of 5 million tons in the oceans [52]. Technologically, it is commercialized as the cathode material in Li-ion non-rechargeable batteries, for instance [55]. As a semiconductor with a $\sim 1 \text{ eV}$ bulk bandgap, a very high optical absorption coefficient ($\alpha > 10^5 \text{cm}^{-1}$ at $\hbar \omega > 1.5 \text{ eV}$) [71], and low toxicity and constituent refinement costs, it is also extremely attractive for photovoltaics [59]. As such it has been studied intensively in the past three decades. Despite this, prototype devices have suffered from very low photovoltages ($V_{OC} \approx 30 \text{ mV}$, Schottky contact at room temp., 80 mW/cm² light intensity), with concomitant dark currents, even on single crystals [110]. More fundamentally, optical absorption measurements show a nearly constant level of absorption, of order $10^2 - 10^3$ cm⁻¹, below the bandgap [12, 14, 111, 112]. Remarkably, considering the amount of effort invested in pyrite development, the cause of these observations remains quite unclear. Attempts to assign a physical picture to the density of states (DOS) in the band gap are few, with strong upward surface band bending being the most prevalent [113, 114, 115, 36, 54]. Further attempts to propose a chemical defect structure that could create such a physical picture are equally sparse, with amorphous impurities, [43], ubiquitous oxygen substitution [48], and sulfur-rich surfaces [60] comprising the few models existing in the literature (helpful synopses contained in refs. [36, 54]).

Despite this situation, important progress has been made in constraining the problem. Perhaps most important is the recognition that electrical transport properties of thin film and single crystal pyrite vary dramatically. Specifically, while room temperature resistivities are roughly similar between these two types of samples, upon cooling below 100 K thin film resistivity increases minutely (remains of order $10^0 \Omega$ cm) [36, 116, 117, 118, 119], while that of single crystals is often seen to increase by five orders of magnitude to ~ $10^5 \Omega$ cm [40, 26, 39]. Quite generally, it must be concluded that the carrier concentration can be frozen in a single crystal as normally expected for a semiconductor, but not for thin films. Necessarily, this implicates a large concentration of surface states in the band gap. Paradoxically, however, modeling of pyrites surface electronic structure does not give a facile explanation of the observed experimental data. For the (100) surface, the lowest energy face under many conditions [74] and the predominant face created upon fracture [73], these studies are in general agreement on a still sizable bandgap (0.55-1 eV) for a defect free surface [60, 38, 43, 23].

Surface states are, of course, also accessible by scanning probes and surface sensitive spectroscopies. With scanning tunneling microscopy (STM), imageable biases of ± 20 mV on the (100) surface have been used to argue for a quasi-particle bandgap of ~0.04 eV [120]. Ultraviolet photoelectron spectroscopy (UPS) has been used to interrogate the nature of the valence band, and has invariably shown the Fermi level coincident with the valence band for (100) surfaces [113, 24, 121, 122]. While less work has been undertaken to measure the position of the conduction band by inverse photoemission spectroscopy (IPES), the existing work seems to argue that the conduction band is also coincident with the Fermi level, indicating a closed band gap surface [123, 124, 125, 126]. Therefore, the existing set of surface sensitive measurements are in qualitative agreement with the electrical transport and optical absorption measurements described above. This, is turn, indicates that all available experimental evidence of the electrical properties of the (100) surface of pyrite are in contrast to existing theoretical models.

A large concentration of surface defect states on the (100) pyrite surface may then be implicated in lowering the band gap from that theoretically expected to the nonexistent measured one. This is especially plausible given that photoelectron spectroscopy has shown a significant population of sulfur vacancies on this surface [127]. To date, however, there is a complete lack of correlation between defect existence and measured electronic properties. STM measurements show no appreciable electronic change in scanning over defective or non-defective areas [120], surface photovoltage measurements show that the pyrite (100) surface, including defects, is laterally electronically uniform (i.e. no conductive channels) [114], and scanning tunneling spectroscopy (STS) data are fit best by assuming a closed band gap even though states in the gap are not directly observed by tunneling [128]. In contrast, theoretical works indicate that areas of relative perfection, or with isolated defects, should still display a measurable band gap [60, 23, 43]. Thus, if defects are to be implicated in closing the surface band gap of (100) pyrite, they manifest in an unusual manner in which their effects are both more severe than expected and only observable in a delocalized sense.

In addition to these static electronic considerations, additional STM work demonstrates unusual electronic dynamics on the pyrite (100) surface. For instance, it was reported by Rosso et al. [120] that it becomes impossible to image a surface by STM after irradiating it with UV light, x-rays, or low energy electrons, where it was stated that a tunneling contact could be established but would become unstable and result in tip crashes. Further the low energy electron diffraction (LEED) pattern remained unchanged through this process indicating that the effect was purely electronic. This study, then, gives circumstantial evidence for long-lived and dynamic charging properties on the pyrite surface that remain unexplained.

Our work has focused on the synthesis of pyrite nanoparticles with {100} faces [129]. This shape control has been undertaken in an effort to create ensembles of nanocubes that, consequently, have a high proportion of {100} surface states. These states can then be easily manipulated and measured by nanoparticle processing techniques that have become well developed over the last few decades. In the research reported here, we have undertaken surface treatments to passivate defects on these pyrite {100} faces. The result is nanocubes with greater colloidal dispersibility than normally found for pyrite nanocrystals. Additionally, these treatments have produced extremely sharp electronic transitions in the near infrared (NIR). We have used these observations to propose a plausible interpretation of the surface physics of (100) iron pyrite.

3.4 Results and Discussion

In order to create samples of pyrite with a large contribution of $\{100\}$ faces, we have synthesized pyrite nanocubes with an average edge length of ~ 30 nm, using an adaptation of our previous described method [129]. Specifically, we have nucleated small, irregular-shaped pyrite particles in coordinating amine solvent (Figure 3.1a) and then added precursors to create sulfur poor/iron rich conditions that have been shown to favor the isolation of $\{100\}$ faces (Figure 3.1b, synthetic details in Supporting Information).

As shown in Figure 3.1c, the as-formed nanocubes display optical absorption characteristic of pyrite, with slowly rising absorption in the NIR (\sim 900-1300 nm) indicative of an indirect transition, and a distinctive shoulder at \sim 500 nm. However, the resulting colloids also give indications of unusual physical behavior. First is the very poor colloidal dispersibility of the product, much worse than expected considering the particle size. Figure 3.1d shows that these particles will flocculate and fall out of solution in chloroform over the course of a few hours after synthesis (left and middle vials, respectively). True dispersion of the pyrite nanocubes is only possible through dilution and the addition of excess octadecylamine (Figure 3.1d, right side). The small absorption bands in the NIR region in Figure 3.1c, above 1200 nm, can be indexed as a signal of this excess ligand. This is clearly shown by the addition of a commensurate amount of ligand to a reference cuvette during an absorption measurement (Figure S1, Supporting Information). A second example of unusual physical behavior is the observation of resonance light scattering (RLS), demonstrated in Figures 1e-f, whereby aggregates of particles efficiently and selectively scatter light of wavelengths nearly coincident to strong electronic transitions in the material [129, 87]. Figure 3.1e indicates that without excess stabilizing ligand there is a larger RLS signal than when excess stabilizing ligands have been added, as in Figure 3.1f. This observed scattering is the cause of the larger and apparently red-shifted peak in the corresponding absorption spectrum at 500-900 nm. However, even in the case of the addition of excess octadecylamine, an RLS signal is still existent, but diminished in magnitude.

Figure 3.1: Properties of the pyrite nanocube synthesis before surface treatment. (a) TEM image of as-nucleated nanoparticles. (b) TEM image of as-formed nanocubes. (c) UV-vis absorption spectroscopy of the as-formed nanocubes dispersed with excess stabilizing ligand (octadecylamine). (d) Photographs of nanocubes directly after synthesis (left), after a few hours of storage in chloroform (middle), and dispersed with the aid of excess stabilizing ligand (octadecylamine, right). (e) Absorption spectroscopy (left axis) and light scattering (right axis) of a sample of nanocubes without excess stabilizing ligand. (f) Absorption spectroscopy (left axis) and light scattering (right axis) of nanocubes dispersed with excess stabilizing ligand (octadecylamine).



As described previously, there are physical properties of the pyrite (100) surface that remain poorly understood. Very poor colloidal dispersibility and RLS, being unexplained behavior related to the surfaces of these nanocubes, may therefore be symptomatic of such properties. RLS is a consequence of differences in the polarizability (i.e. dynamic charge distribution) between aggregates of particles and the surrounding solvent, with good electronic coupling between particles being necessary for its efficient occurrence [87]. Therefore, this phenomenon suggests that unusual electric field characteristics may exist on the pyrite surface, which may lead from aggregation to the ultimate loss of colloidal stability observed. With these considerations in mind, we have attempted to add charged (X-type) ligands to the pyrite (100) surface to investigate if such surface charge irregularities can be passivated.

Surface treatments were conducted by introducing various ligands to the pyrite nanocubes in oleylamine solvent and heating to 110° C for 12 hours (details in Methods). The ligands utilized are shown in Figure 3.2. Carboxylic acid and thiol ligands are representative of those commonly used in nanoparticle syntheses. The longer alkyl chain versions (stearic acid and octadecanethiol) were selected in an attempt to electronically isolate the particles in the colloid as much as practical. Cetyltrimethylammonium bromide (CTAB) was used as a representative cationic ligand given that pyrite has an acidic isoelectronic point [130], and that (100) surfaces are sulfur terminated [74]. Octadecanol was utilized in an attempt to find a ligand that could complex to a perfect (100) surface (i.e. without sulfur vacancies). It has been theorized that the oxygen atom of an OH group can complex to surface iron atoms that may be sterically hindered and inaccessible to bulkier ligands [131]. Given that all these ligands (except CTAB) are in their protonated form, and were dissolved in amine solvent, which can accept protons, it is thought that it is the deprotonated (X-type) forms that will interact with the pyrite surface.

It was found that, after this surface treatment process, the colloidal dispersibility of these treated nanocubes increased dramatically. Whereas excess octadecylamine was required for dispersal prior to surface treatment, these newly ligated nanocubes could be cleaned and dispersed directly into many solvents. However, as shown in Figure 3.3, with stearic acid capped nanocubes, these



Figure 3.2: The ligands utilized for surface treatments in this study.

treated particles are well dispersed by uncommonly polar solvents (dichloromethane, dichlorobenzene) and not dispersible at all in common nonpolar solvents like hexanes and toluene. Given that light scattering attributable to RLS occurs in the visible range of the electromagnetic spectrum, Figure 3.3 indicates not just colloidal dispersibility but also the extent of RLS in various solvents. Better dispersed samples appear more reddish than the black color created by the light scattering of longer visible wavelengths by the RLS mechanism.

Figure 3.3: Solutions of surface treated nanocubes with stearic acid. Solvent dielectric constant increases to the right. hexanes (hex), toluene (tol), trichloroethylene (TCE), chloroform (chloro), dichloromethane (DCM), dichlorobenzene (DCB), isopropanol (IPA), acetonitrile (ACN).



Absorption spectroscopy of these surface treated nanocubes yields unexpected features in the NIR, as shown in Figure 3.4. For all four ligand chemistries, sharp absorption bands developed at 1407 and 1693 nm (0.88 and 0.73 eV, respectively) among more minor features. In order to confidently report these features, solvents were chosen that do not absorb significantly in this region. Therefore, despite Figure 3.3, which indicates that solvents like chloroform and dichloromethane are preferable for ease of solubility, these treated nanocubes were dispersed in either trichloroethylene or tetrachloroethylene; and, despite the advantageous transparency of tetrachloroethylene in the NIR, we often found it difficult to use. It is quite nonpolar and many samples displayed large RLS signals,

obscuring the true absorption of the sample (Figure S2, Supporting Information). Additional electronic features also appear deeper in the infrared (Figure S3, Supporting Information), however, given strong absorption from ligands in this region, and lack of any theoretical assignment for these features, we have not investigated them further.

The spectra shown in Figure 3.4 suggest that the octadecanethiol treatment results in the largest NIR absorption bands (with the other three ligands being roughly similar) and also gives the least RLS (seen as the red-shifted peak in the spectra for the other ligand chemistries at ~500 nm; light scattering of octadecanethiol treated particles given in Figure S4, Supporting Information). Therefore, in the following structural and chemical analysis, we have focused on this thiol treatment to investigate its effect on the as-formed nanocubes.

The electron micrograph shown in Figure 3.5 indicates that during the ligand treatment process the cubic morphology remains although the edges of the nanocubes become slightly more rounded (in comparison to the TEM image displayed in Figure 3.1b). Also, Raman spectroscopy in Figure 3.5b gives no change in Raman scattering as a result of the thiol treatment. Therefore, this surface treatment affects the surfaces of these nanocubes without causing appreciable morphological or structural changes. Clear reflections from x-ray diffraction (XRD) analysis are hindered by the dense ligand layer formed by this process (described below), so XRD analysis is of limited value in this case.

Vibrational spectroscopies, both Fourier transform infra-red (FTIR) and Raman, have been used to gain information about the bonding configuration before and after the ligand treatment. Shown in Figure 6a, FTIR spectroscopy indicates that hydrocarbons, which presumably must be the amine ligands, are bonded on the surfaces of the as-formed nanocubes. However, we are unable to unambiguously identify the amine bonding configuration. After the thiol treatment, and multiple cleaning steps to remove excess ligands, the FTIR spectra changes dramatically, as shown in Figure 6a. Lack of an S-H stretching band in the 2550-2600 cm⁻¹ region indicates that the thiol molecules are incorporated into the nanocube surface structure, while C-H stretches in the 2800-3000 cm⁻¹ region become much sharper, indicating a larger quantity of ligand bonded to the nanocube surface.

Figure 3.4: Absorption spectroscopy of surface treated nanocubes with the ligands shown in Figure 2. Inset gives detail in the near infrared region.



Additionally, absorption bands at 1470 and 730 cm⁻¹ are indicative of CH_2 rocking and bending modes. Both of these modes are split into sharp doublets as shown more clearly in Figures 6bc. The splitting of these doublets is indicative of crystalline structure and, surprisingly, their sharpness is quite similar to that observed in high-density polyethylene (HDPE) [132]. Therefore, these results indicate that this surface treatment process, with octadecanethiol, creates a highly crystalline ordering of alkyl chains on the pyrite (100) surface, reminiscent of epitaxial growth.

These interesting FTIR results compelled us to investigate this crystalline ligand structure further with Raman spectroscopy. The scattering peaks in the fingerprint region in Figure 6d can all be indexed to crystalline polyethylene packing. The bands from 1500-1400 cm⁻¹ are attributed to CH2 rocking and bending modes [133]. Special attention has been given to the peak at 1415 cm⁻¹ as it has been shown to be very sensitive to changes in crystallinity [132]. The sharp peak at 1296 cm⁻¹ has been associated with CH₂ twisting of an all trans chain and the two peaks at 1130 and 1064 cm⁻¹ are assigned to C-C stretching of all trans chains [133]. The only peak in this spectrum that is not simply assigned to crystalline polyethylene is the band at 1100 cm⁻¹. The assignment of this band has recently has been identified as a signal of isolated gauche defects in the crystalline layer [134]. Upon reflection, gauche defects should be expected in the epitaxial packing of polyethylene on the pyrite (100) surface given the lattice mismatch between these two crystalline structures. Such a bonding situation is very similar to the large body of work on self-assembled alkyl thiol molecules on gold.

3.4.1 Localized and Disordered Surface States

Soon after the introduction of UPS, it was used by Li et al. to investigate the nature of pyrites valence band [135]. They reported a very narrow valence band peak, attributed it to the nonbonding t_{2g} manifold of iron 3d-states, and argued that the narrowness of the peak indicates its localized (as opposed to bandlike) nature. More recently, density functional theory has been used to model this band as very narrow (~1 eV), nearly dispersionless in k-space, and almost entirely of iron character, in excellent agreement with the earlier photoelectron data [38, 22]. By tight-binding

Figure 3.5: Characterization of the effect of thiol treatment on nanocubes. (a) TEM image of thiol treated nanocubes. (b) Raman spectra of product before (bottom) and after (top) thiol treatment with modes indexed.



Figure 3.6: Vibrational Spectroscopies (FTIR and Raman) of ligands on the pyrite surface. (a) FTIR spectroscopy of as-formed and thiol treated nanocubes. (b) Detail of a doublet feature at $\sim 1475 \text{ cm}^{-1}$ in the thiol treated FTIR spectrum. (c) Detail of doublet feature at $\sim 725 \text{ cm}^{-1}$ in the thiol treated FTIR spectrum. (d) Raman scattering of ligands on a thiol treated nanocube film.



approximation arguments, narrow bands that depend only weakly on k (the crystal momentum) have wavefunctions that overlap neighboring atoms only weakly [136]. Given weak overlap, states in such bands are more spatially localized than bands with more dispersion. The curvature of a band is inversely proportional to the effective mass of its charge carriers

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2},\tag{3.1}$$

so a band with very little curvature will have a very large effective mass and carrier movement will be restricted. In extending these arguments to the (100) surface of pyrite, recent modeling work indicates that the t_{2g} band may be sufficiently dispersionless that the exchange interaction between electrons outweighs their kinetic (or band) energy. In such a case, it becomes energetically favorable for the surface electronic bands to become exchange split and spin polarized, further decreasing the band-like nature of these states [60, 61].

Besides the intrinsic electronic features of pyrite, there is evidence for a large quantity of defects on the pyrite (100) surface, of which the most complete body of evidence concerns sulfur vacancies. Theoretically, a low surface sulfur vacancy formation energy ($\sim 0.4 \text{ eV}$) has been proposed [60, 43, 128]. This value is much less than the theorized bulk sulfur vacancy formation energy ($\sim 2.4 \text{ eV}$) [43, 22, 48, 23], so it is expected that vacancies will not migrate to the bulk and the surface sulfur defect concentration will remain far higher. Experimentally, synchrotron XPS shows a clear monosulfide doublet (S 2p core-level shift), representing broken sulfur dimers on this surface. Quantification of these peak areas indicates that only roughly 60% of surface sulfur vacancies has been studied theoretically. Either a decreased [60, 23] or closed [43] gap has been advocated. Experimentally however, and as mentioned previously, surface sensitive probes and spectroscopies have been unable to directly observe the electronic effect of individual defects [120, 114, 128], as would be anticipated for such highly localized states.

Besides the effect of isolated surface defects and their attendant electronic structure, we would like to emphasize the possible ensemble characteristics of a sizable distribution of such defects. A general phenomenon, known as Anderson localization, is that a randomly disordered potential can lead to wavefunction localization and the elimination of bandlike carrier transport [139]. This phenomenon is known to occur particularly easily in low dimensional systems [140]. Given that states become localized, transport in such cases occurs by the mechanism of variable range hopping, which is phonon assisted tunneling conduction between energetically disordered sites. For this mechanism, temperature dependent conductivity shows activated behavior except with a proximate $T^{-1/2}$ dependence [141]. In accord with this mechanism, thin-film pyrite conductivity measurements often show this temperature dependence [54, 116, 37, 117, 118, 119, 142].

To recapitulate: (1) the valence band of pyrite is expected by tight-binding theory to be intrinsically somewhat localized, (2) the (100) surface states may loose even more bandlike character by exchange splitting, (3) theory and spectroscopic evidence indicate that these surfaces contain significant disorder, mainly in the form of sulfur vacancies, (4) such vacancies are expected to lead to additional wavefunction localization by the Anderson localization mechanism, and (5) the hallmark experimental evidence for Anderson localization, variable range hopping, has often been observed. Therefore, it is very probable that highly localized and disordered electronic states exist in the band gap of the (100) pyrite surface.

Such considerations are also supported by recent XPS work. Bocquet et al. used XPS core level shift data to parameterize pyrite according to a configuration-interaction cluster model [143]. They report pyrite to be a borderline case between the charge-transfer and Mott-Hubbard insulator regimes. To further categorize pyrite, Nesbitt et al. conducted resonant XPS and found both charge transfer and direct emission contributions [144]. They argued that the direct emission contribution could originate from the surface layer. We take these studies as evidence that the surface electronic structure of pyrite can become so electronically isolated from the bulk that it acts like a surface Mott-Hubbard insulator. That is, an insulator of isolated transition metal coordination with low mobility. Therefore, in the bulk of pyrite there is some dispersion in the valence band because of sulfur-mediated interaction between iron t_{2g} states on different atoms. At the surface this isn't the case so the bands become basically dispersionless. So the surface is a Mott-Hubbard semiconductor along the lines of NiS_2 and MnS_2 [145].

Some possible implications of the preceding discussion may be of note. For instance, it is well accepted that, as electronic states become more localized, their decreasing mobility results in a large reduction in screening, which increases the importance of electron correlations [146]. Unfortunately however, a small electron-electron interaction is one of the attributes of materials that make a band description feasible at all (by allowing the description of an averaged field that an independent electron quasiparticle feels) [147]. Additional profound complications arise from the competition between disorder and these strong Coulombic effects. Disorder causes electrons to favor some sites compared to others, whereas Coulombic interactions favor an ordered and distributed electron arrangement (a Wigner crystal) [146]. When not all interactions can be simultaneously satisfied in a low energy state of a material, frustration is known to result, giving rise to metastable states of similar enegy [148]. Given that electrons in metastable states are locally stable, only collective rearrangements of the electron sallow the system to relax to a lower energy [149]. The low transition probability of collective electron rearrangements means that these metastable states are thought to exist for long time scales, far longer than the extremely fast movement usually associated with electrons.

Localization by disorder, as described above, is often termed Anderson localization, while localization by electrostatic interactions can be termed Mott localization. Since any method of localization leads to the diminishing efficacy of electronic transport, a material that is affected by both localization mechanisms is often termed a Mott-Anderson insulator. In the case of the pyrite (100) surface, such a designation may be applicable even if the band gap is closed by the defects mentioned above, since electrical transport cannot occur by diffusion but only by the hopping mechanism.

3.4.2 Results Interpretation with the Foregoing Considerations

The foregoing arguments are supported by the existing body of pyrite research and, importantly for this study, give a theoretical framework that we use to interpret the results described here. For instance, we show that as-formed pyrite nanocubes, with alkylamines on the surface, have very poor colloidal dispersibility (Figure 3.1). Similar problems maintaining colloidal stability have been reported by others as well [83, 150]. Surface treatments have improved the dispersibility of these nanocubes. However, even so, it is observed that these treated nanocubes, which have been grown and treated in coordinating solvents, of both L-type and X-type ligands, with long alkyl chains, *still* cannot be dispersed in many common nonpolar media. A plausible explanation for this remarkable behavior must include the development of an attractive potential between particles. which currently does not exist in the literature to our knowledge. With the foregoing physical arguments, it is reasonable to ascribe this to the Coulombic interactions of localized electrons on the pyrite surface. According to this model, the hopping of such carriers between metastable states alters the electric field on the particle surface and mediates electronic interactions between particles. A solvent with a substantial dielectric constant can suppress these interparticle interactions and allow for better dispersibility. Therefore, the appropriate solvent for pyrite nanocubes becomes one that has a significant enough dielectric-screening factor to suppress Coulomb interactions while still maintaining an energetically favorable van der Waals interaction with the alkane ligands on the particle surface (as shown in Figure 3.3).

Additional evidence for the polar nature of the pyrite surface is given by our observation of RLS (ref. [129] and Figures 3.1e-f). This phenomenon involves anomalously large light scattering in close energetic proximity to electronic transitions from agglomerates of chromophores. To understand this phenomenon, we consider the scattering cross section (C_{SCA}) of the nanocube sample under the approximation of an ideal induced dipole. In this case, C_{SCA} is simply related to the complex polarizability of the aggregates (α) by:

$$C_{SCA} = \frac{k_m}{6\pi} |\alpha|^2 \tag{3.2}$$

where k_m is the wave vector of light in the medium [87]. Therefore it is seen that increased absorption, which is linearly related to the imaginary part of α to first order, will also induce increased scattering. However, besides the necessity of being a chromophore, this phenomenon is only observable if the chromophore ensemble has good electronic coupling [88]. Without the preceding theoretical framework we were unable to explain the existence of this phenomenon, which, to our knowledge, is unique among semiconductor nanoparticles. Taking into consideration the foregoing discussion a plausible explanation is to attribute the necessary electronic coupling to the hopping movement of localized electrons in metastable states at the (100) surfaces of solvated pyrite nanocubes.

We believe that this interpretation of the pyrite surface may also be able to shed light on some interesting and unexplained results existing in the literature. For instance, as described above, the behavior reported by Rosso et al. [120] in which STM tunneling instability occurs from irradiation of pyrite by UV or x-ray radiation or low energy electrons. This phenomenon can be tentatively explained by the existence of electron movement between metastable states induced by the perturbing beam. If the STM tip is introduced before this electron movement is relaxed, to a certain threshold, then the tip will be trying to make a tunneling contact with dynamic electronic states and tunneling instability can be speculated to result.

3.4.3 Interpretation of the Emergence of NIR Transitions

It was stated previously that recent theoretical work has shown that the (100) surface of pyrite may become so electronically localized as to make spin polarization energetically favorable. In addition to this, Zhang et al. theorized that each of these spin subbands has a direct bandgap transition about the Γ point, with a 0.72 eV gap for the majority spin channel and a 0.87 eV gap for the minority spin channel [60]. In this work, as shown in Figure 3.4, two transitions are observed to appear upon surface treatment, and are found at 1693 nm (0.73 eV) and 1407 nm (0.88 eV). The very close energetic proximity between that studys expectations and our findings, and the circumstance that these transitions are detected while trying to heal defects on {100} surfaces, gives evidence that these transitions are signals of band edge absorption for each of these two transitions.

In reviewing the pyrite literature, a sharp peak in the 0.9 eV region has been observed many times before. Kou and Seehra [111] and Yang et al. [112] both observed the development of a sharp peak at 0.87 eV during photoabsorption measurements when a single crystal sample was cooled below ~ 100 K. Additionally, Chen et al. [151], Tsay et al. [152], and Ennaoui and Tributsch [153], all measured photoconductivity on single crystalline pyrite and observed a very sharp increase in photoconductivity around this wavelength (0.87, 0.9, 1 eV, respectively), again only when the sample was cooled below ~ 100 K. These studies either reported this feature without interpretation, or attributed it to an exciton peak [111] or ionization of chromium impurities.[112, 151, 152] While either explanation is plausible, neither has been conclusively proven. Given that the shape and energetic position of the feature reported in these studies is nearly identical to the one reported here, it is reasonably concluded that all may be measurements of the same physical feature. In this case, we believe an additional interpretation of the emergence of this peak, as a surface state transition, is possible. This is so given that: (1) Such a peak, from a direct surface transition, has now been independently theorized to occur [60]. (2) In our current work this peak is observed upon surface treatment that neither adds new transition metal impurities to the system nor is thought to change the bulk exciton binding energy. And (3), all of these studies report using the (100)surface. Low temperature absorption and photoconductivity studies that do not show this feature either report using [29], or appear to have used [40], a (111) face.

While the aforementioned studies have all observed the transition at 0.88 eV, the transition at 0.73 eV has not been observed (except, possibly once [153]). This can be rationalized by noting that, in this study, the 0.73 eV transition is by far the smaller of the two. Besides the relative intensities of these two features, the remarkable sharpness of these absorption peaks (8 meV fwhm, room temperature) gives additional support to the notion that these states are so localized as to be disconnected from the bulk electronic structure, and therefore are not hybridized with it. Also, for a spin polarized state there is no degeneracy to be broken by spin-orbit coupling, further maintaining the narrow linewidth. Additionally, it is perhaps important to note that transitions between these spin-polarized states are expected to be spin forbidden.

To further verify that these features are associated with the (100) surface of pyrite, in Figure 3.7 pyrite nanoparticles, created in the first stage of the synthesis reported here (i.e. before they are

Figure 3.7: Surface treatment of irregularly shaped pyrite nanoparticles (TEM image in inset). Absorption spectroscopy is shown here for stearic acid capped particles. Blow-up gives detail of the NIR with the two spin polarized band-gaps shown.



grown into the cubic morphology, shown in Figure 3.1a and inset in Figure 3.7), are surface treated. It is seen that these spin polarized band gaps are still observable, but are greatly diminished in comparison to the nanocube morphology. It is thought that the observed signal is derived from the small proportion of (100) faces existing on these particles.

Absorption spectroscopy of pyrite nanocubes has been shown many times, including in this study with amine-terminated surfaces, without showing these features. In the case of adding charged ligands, their emergence can be explained by assuming that the head groups of the ligands used in this study can complex with the (100) surface and passivate defects more fully than on asgrown surfaces. Additionally, we believe that the conceptual model given above can also plausibly interpret the emergence of these peaks (or at least the larger one at 0.88 eV) by cryogenic cooling. Materials frustrated by the competing influences of disorder and Coulomb interactions have sensitive temperature dependent electrical properties. In fact the DOS itself is temperature dependent, with the energy of a specific localized site being dependent on the thermal occupation of all adjacent sites [154]. It has been shown that the DOS will increase at the Fermi level as temperature increases, washing out the band gap at some finite temperature [155]. Conversely, if the temperature is decreased to a point where thermal fluctuations are reduced, then screening becomes less effective and long-range electron interactions manifest [148]. Therefore, the electrons spread out or "Wigner crystallize". These long-range interactions are thought to also occur with the emergence of a Coulomb gap, that is, a gap in the density of states caused by Coulomb interactions [141].

According to this mechanism, passivating defects with charged ligands may act in a similar manner to cryogenic cooling: both processes decrease electronic frustration in the material. The charged ligands decrease disorder by healing defects and therefore increase the relative importance of Coulombic interactions, whereas cryogenic cooling increases the importance of Coulombic interactions while leaving the amount of disorder unchanged. Either way, increasing the importance of Coulombic interactions decreases screening and allows long-range electron interactions to manifest. The surface electrons then can become much closer to the ground state energy configuration modeled by Zhang et al. [60], so the expectations of that work become more readily observable.

3.4.4 A Plausible Physical Interpretation

Here we summarize the foregoing considerations into a plausible conceptual model of the electronic structure of the pyrite (100) surface, as shown schematically in Figure 3.8. Figure 3.8a represents the spin-polarized bands of a perfectly terminated surface as modeled in ref. [60]. In this situation, two significant band gaps exist between atomic-like d-orbitals, with magnitudes corresponding to the absorption transitions observed in Figure 3.4. With the addition of defects from either sulfur or iron vacancies or adatoms, the energetic positions of these atomic-like orbitals shift significantly [60, 23, 43]. A possible scenario is sketched in Figure 3.8b. Some areas of surface perfection remain, so some DOS corresponding to a perfect surface is still found (only the four band edge states are shown, for clarity). However, DOS from disordered d-orbital states are also shown (in green). Given the complication of this scenario, no attempt to differentiate spin-polarized behavior is possible. At the lowest temperatures, electrons in such states interact strongly given their reduced mobility, and thus screening. Therefore, by the arguments of Efros and Shklovskii, a small Coulomb gap at the Fermi level is formed (Figure 3.8b) [141]. Subsequently, as the temperature is raised, occupation of various states above the small Coulomb gap becomes possible. When such occupation occurs, the strongly interacting nature of these electrons changes the DOS. As first modeled by Davies et al. [154] this creates states at the Fermi level, washing out the small Coulomb gap at some finite temperature (as sketched in Figure 3.8c). These states are frustrated by the competing influences of disorder and Coulombic interaction and are therefore metastable.

This conceptual model is presented in order to rationalize the emergence of the spin-polarized direct band gaps with defect passivation or cryogenic cooling, and to explain the polar nature of these nanoparticles as observed by colloidal stability and RLS. Additionally, it may provide a qualitative framework with which to understand some of the outstanding questions related to the pyrite (100) surface. For example, as described in the introduction, areas of appreciable band gap should exist on the pyrite (100) surface according to theoretical models, but surface sensitive probes
Figure 3.8: Density of states (DOS) schematics. (a) Schematic representation of the DOS for a perfect surface, generally following the work of Zhang et al. [60]. The right axis represents the majority spin channel (occupation of these states is in red). The left axis is the minority spin channel (occupation of these states is in blue). Occupied states without spin polarization are given in purple. The transitions corresponding to those observed in Figure 3.4 are indicated. (b) A schematic representation of the same surface at zero temperature with disorder present. In this case it is no longer possible to separate the effect of spin-polarization, so one DOS axis is used (states in green). However spin-polarized states corresponding to the perfect surface are still thought to exist and are demarcated by their color from (a). (c) Schematic representation of the same surface as in (b) except at finite temperature.



have not observed these. Thus defects are observed to close the band gap in a homogeneous manner, and so, by implication, their electronic effect must be delocalized. However, such logic seems to be inconsistent with the highly localized nature of the pyrite electronic structure. It can be made plausibly consistent, however, if we consider the interpretation given here. The frustrated hopping movement of electrons in defect states, as shown schematically in Figure 3.8c, is thought to occur at the Fermi level, closing the small Coulomb gap. Further, the nature of frustrated metastable states is to perturb those around them (by Coulombic interaction), therefore such interactions may cause a closed band gap even in areas of relative perfection. Conversely stated, with this model it would be expected that the isolated effect of individual defects would be unobservable, as is found experimentally.

Finally, in relation to this model, recent work by Zhang et al. has extended pyrite thin-film conductivity down to 5 K and reported a switch from hopping transport to activated transport, with activation energy $E_a \approx 5$ meV, at the lowest temperatures [118]. Further, they have shown that as the sample is warmed the signal deviates from activated behavior by roughly 20 K. While these measurements were taken on thin films with, presumably, many different surface terminations, these results are not inconsistent with a small Coulomb gap that is filled in at finite temperatures (Figure 3.8b,c).

3.4.5 Extent of Perfection

We did not observe any measurable radiative recombination by exciting a colloidal sample with a continuous wave 808 nm laser. This gives evidence that although the surface has been passivated so that these absorption bands have become observable, there are still efficient nonradiative pathways for de-excitation. In addition to this lack of luminescence, the absorption data in Figure 4 show a number of minor absorption features throughout the NIR. The sources of these features are unknown at present and could constitute pathways to nonradiative recombination. Such considerations could be especially important if we assume that some of these small transitions may not be fully allowed by selection rules and may therefore be indicative of a significant DOS. Within the context of the model given here it is thought that with perfect defect passivation the surface band gaps will open to theoretical expectation, forming significant band gaps. Residual disorder will "smear" the band edges leading to the "soft" Coulomb gap behavior shown in Figure 3.8b. We think that the current case, despite displaying evidence for spin-polarized direct band gaps, is still influenced by this disordered Coulomb gap type behavior. This is so given a lack of linear photoluminescence and because these nanocubes still are not dispersible in the most nonpolar of solvents (toluene or hexane), indicating that metastable charge hopping is still active (albeit diminished).

In conjunction with the foregoing evidence on the extent of surface perfection attained in this study, the crystalline packing of octadecanethiol on these pyrite (100) surfaces gives a bound on the possible effectiveness of this surface treatment in passivating sulfur vacancies. Crystallography of HDPE gives a Pnma structure with an orthorhombic unit cell with dimensions a = 7.48 Å and c = 4.97 Å. This gives an alkane chain density of ~5.4 chains/nm². In contrast, the (100) surface of pyrite has a cubic unit cell of edge length 5.416 Å. Sulfurs on this surface are in a dimer conformation with one sticking above the plane and the other below. If we assume that only the top sulfur is available for bonding a surface sulfur density of ~6.8 sulfurs/nm² results. As a result, the density of sulfurs at the (100) surface of pyrite that may be defective is about 21% higher than a HDPE assembled layer of octadecanethiol can possibly passivate. Equivalently, the crystalline packing of octadecanethiol is indirect evidence that at least 79% of the top surface sulfurs are most probably present in this system. Therefore, it is thought that, in the current synthesis, if two sulfur vacancies occur next to each other then this surface treatment will only have the ability to passivate one of them. The other will remain unpassivated and inaccessible to further surface treatment given it's position underneath the crystalline alkane layer.

3.4.6 Relationship to other Physical Models

The observation of stark electrical differences between single crystals and thin films [156], and of curved Arrhenius plots [37], have existed in the literature for some time. Others have noted that such behavior can be attributed to hopping between localized states or to band bending/thermionic emission [54, 37, 117, 142]. However, regardless of curved Arrhenius plots, the ubiquitous measurement of p-type conductivity in thin films is often taken as an indication that there is sufficient band bending at the pyrite surface to create an inversion layer of holes regardless of the bulk majority carrier type [54, 36, 115].

The evidence for strong band bending has been inferred from photoelectron spectroscopy and electronic measurements. Given the coincidence of the valence band and Fermi level (described above), Bronold et al. [113] attributed all of their room temperature activation energy (200 meV) to the gap between the Fermi level and the conduction band. With a 950 meV band gap this infers large band bending of 750 meV. With such large band bending it is reasonable to conclude that some conduction band electrons could be excited through the barrier caused by the highly bent surface band gap, causing thermionic emission, dark current, and p-type conductivity. However, we believe there are deficiencies in this model as currently understood. (1) Band bending of this magnitude would be caused by a very large concentration of surface states above the valence band; the origin of such a quantity of states, at only this position, remains unclear despite many modeling efforts. (2) As Bronold et al. [114] showed, such band bending could not explain the measured photovoltage in its entirety, the problem being more severe than what could be caused by band bending alone. (3) This analysis assigns the band gap as 950 meV. While there is abundant evidence for this value as the bulk band gap, the ultraviolet radiation used in their UPS measurements is very surface sensitive, and there is no persuasive evidence that this value is still meaningful in this situation. A smaller band gap would imply smaller band bending. (4) Band bending should be amenable to band flattening by the application of a surface photovoltage. Bronold et al. [114] attempted this and found negligible band bending by applying a photovoltage at room temperature (confusingly, band position had a much larger temperature dependence). And (5), recent STS modeling supports the notion that extrinsic surface states (i.e. defects) pin the surface Fermi level and hinder band bending [128]. Therefore, while some small amount of band bending may be operative on the pyrite (100) surface, it seems to have a relatively minor affect on electronic properties. With regard to ubiquitous p-type conductivity measurements, we follow Zhang et al. [118] in assuming that the interpretation of Hall effect measurements may be quite complicated when electron transport is mediated by a hopping mechanism.

3.4.7 Electron Glass Speculation

Coulombic interactions in electrically disordered systems have been shown to give rise to complicated and interesting materials physics. Specifically, such systems have been shown to form an electron glass at low temperatures. For such systems energetic relaxation to a global minimum is frustrated by the need for collective electron rearrangements, and if such rearrangements happen slowly enough, a kind of glass forms. This glass may then have physical properties that evolve very slowly and display aging (i.e. history dependent properties). The analysis given in this study argues that the pyrite (100) surface has properties analogous to those of an electron glass, but much work remains for such a categorization can be made.

3.4.8 Implications of Geological Importance

We believe that the model posited in this work can also give insight into the study of pyrite oxidation in geological environments. This is of particular importance given pyrites central role in the process known as acid mine drainage, whereby mined pyrite, exposed to surface conditions, decomposes to create sulfuric acid, poisoning the effected hydrological area. Additionally, for the burning coal it is necessary to separate the pyrite that is often intermixed (the burning of which would lead to acid rain). For both of these processes, it is necessary to separate the pyrite by some sort of surface selective chemical process (usually in conjunction with froth flotation). To this end, theoretical studies of pyrite oxidation and the absorption of various species have been undertaken. These studies model such processes by interactions of the electronic structure of nondefective pyrite or around discrete vacancies. However, the work from this study indicates that the charge dynamics of localized and metastable electron states must be taken into account for a comprehensive understanding of pyrite surface physics. Adding these considerations into theoretical oxidation models could lead to more rational advances in pyrite separation science.

3.5 Conclusions

We have treated the $\{100\}$ faces of iron pyrite nanocubes with various charged ligands in an attempt to passivate defects existing on these surfaces. This has led to the observation of increased colloidal stability (Figure 3.3) and the development of sharp electronic transitions in the NIR (Figure 3.4), along with a diminishing signal of RLS and the observation of crystalline ligand self-assembly (Figure 3.6). We have used these observations, in conjunction with our analysis of the existing knowledge concerning pyrite surfaces, to propose that the (100) surface of pyrite is significantly more electronically localized than has been stressed previously. Additionally, electronic disorder from a dense population of defects is argued to close the band gap. Frustration between energetic disorder and Coulomb repulsion may then cause the formation of a dense collection of metastable states in the band gap. The likely existence of these states is inferred from the unusual colloidal properties of these nanocubes (Figure 3.1). The disorder on these surfaces can be mitigated, to an extent, by treatments with charged ligands, with the most obvious result being the emergence of the two NIR transitions (Figure 3.4). Given the energies and linewidths of these two transitions, and given their emergence upon surface treatment, it is argued that they are very likely observations of the two spin-polarized direct band gaps recently postulated by Zhang et al. [60]. It is further reasoned that one of these transitions, the one at 0.88 eV, has been observed before in cryogenic absorption and photoconductivity studies, and argued that a plausible reinterpretation of the data from these studies is possible. This reinterpretation can be rationalized within the context of the physical model posited here whereby cryogenic temperatures increase the importance of Coulombic interactions, which results in a decrease in the metastable DOS at the Fermi level and an electronic arrangement closer to that predicted theoretically, despite existing disorder. Finally, it is argued that the frustrated movement of electrons in metastable states can qualitatively explain the apparent conundrum in which surface sensitive probes are unable to measure the effect of isolated defects, despite the highly localized nature of the pyrite (100) surface. We hope that this model can be used to aid future development of pyrite as an important geological and technological material with both semiconducting and spin polarized properties.

3.6 Methods

The synthetic scheme to create iron pyrite nanocubes is a very close adaptation of our previous work [129]. As opposed to that work a second growth step was not utilized in the present study, i.e. pyrite nanoparticles were nucleated and then grown into the cubic shape with only one addition of precursors. Detailed information for this synthesis is given again in the Supporting Information. After this synthesis was finished, these nanocubes were stored in 20 mL of chloroform.

For the surface treatments used in this study 300 mg of the desired ligand (the four utilized in this study are shown in Figure 2, either: stearic acid, cetrimonium bromide (CTAB), octadecanol, or octadecanethiol) was dissolved in 10 mL of oleylamine. Then 1 mL of the pyrite nanocube solution in chloroform was introduced. An argon atmosphere was established and this mixture was brought to 110° C for 12 hours with magnetic stirring. After the reaction was completed it was allowed to cool to room temperature naturally. Subsequently 20 mL methanol was added to the raw solution and this was centrifuged (4200 RPM/5 min) to collect the precipitate. This was then cleaned by redispersion in chloroform and destabilization with methanol. After a second centrifugation the product was dispersed in either chloroform, trichloroethylene, or tetrachloroethylene for further analysis.

Chapter 4

Solid State Enabled Reversible Four Electron Storage

4.1 Abstract

We report that a solid-state battery architecture enables the reversible, four electron storage of fully utilized solvothermally synthesized cubic-FeS₂ (pyrite). With a sulfide based glass electrolyte we successfully confine electroactive species and permit the safe use of a lithium metal anode. These FeS₂/Li solid-state cells deliver a theoretical specific capacity of 894 mAh g⁻¹ at 60° C. We find that nanoparticles of orthorhombic-FeS₂ (marcasite) are generated upon recharge at $30-60^{\circ}$ C which explains a coincident change in rate kinetics.¹

4.2 A Program Note

This paper was published in a collaboration between myself and my advisor (Dr. Conrad Stoldt) and Dr. Se-Hee Lee's group also in the Mechanical Engineering department along with collaborators of his from South Korea. I created a synthetic method that resulted in micron sized phase pure pyrite nanocubes and these were used in this study with the solid-state electrolyte being developed by Dr. Lee's group. In this dissertation I will report on the motivation for this work, the materials synthesis that I did to enable it, and phase changes that were observed upon lithiation and delithiation. I will not present battery testing data. Even though I find it fascinating, I had no part in that work. The eager reader is referred to the primary source [56].

¹ Adapted with permission from: Yersak, T.A., Macpherson, H.A., Kim, S.C., Le, V.D., Kang, C.S., Son, S.B., Kim, Y.H., Trevey, J.E., Oh, K.H., Stoldt, C.R., Lee, S.H., *Advanced Energy Materials* **2013**, 3(1), 120-127. Copyright 2013 John Wiley and Sons.

4.3 Introduction

The late 1980s and early 1990s saw research efforts focused on the development of molten salt FeS /Li-Al batteries for transportation applications. Given that these cells required an operating temperature around 400°C, thermal FeS₂ battery research was soon abandoned in favor of the emerging room temperature lithium-ion and lithium-polymer technologies [157]. Yet interest in FeS₂ remained as it is inexpensive, environmentally benign and energy-dense. The FeS₂ four electron conversion reaction exhibits a theoretical capacity of 894 mAh g⁻¹ with two discharge plateaus at roughly 2.1 and 1.5 V versus Li⁺/Li. Research continued to examine the utilization of FeS₂ as an active material at ambient to moderate temperatures. To this end, FeS₂ has been successfully commercialized in high energy density primary cells [55]. Unfortunately, the FeS₂ conversion chemistry is irreversible in cells with a variety of polymer or liquid electrolytes at temperatures <135°C [158, 159, 57, 160, 161, 162, 163, 164, 165]. In this paper, we take advantage of a sulfide based glass electrolyte to address the problems commonly associated with FeS₂'s rapid capacity fade at lower temperatures. Along the way, we identify orthorhombic-FeS₂ (marcasite) as a charge product and use this discovery to come to a better understanding of the FeS₂ conversion chemistry.

4.4 Materials Synthesis Part of this Research Effort

The morphology of synthetically prepared FeS₂ was characterized with field emission scanning electron microscopy (FESEM) and the crystalline configuration by x-ray diffraction (XRD). Cu-K α x-ray diffraction analysis of synthetically prepared FeS₂ exhibits diffraction peaks that match well with the cubic-FeS₂ phase (Figure 4.1a). FESEM images reveal cubic FeS₂ particles with ~2.5 μ m wide faces (Figure 4.1b). Raman spectroscopy also confirms the cubic-FeS₂ phase (Figure 4.2).

4.4.1 Synthetic Details

FeS₂ was synthesized solvothermally utilizing a reaction scheme adapted from Wang et al. [96]. Polyvinylpyrrolidone (PVP, $M_{w,avg} = 10,000$, Sigma), FeCl₂ · 4H₂O (>99%, Sigma), ethylene

Figure 4.1: (a) Indexed x-ray diffraction of synthetic cubic-FeS₂. (b) FESEM image of synthetic cubic-FeS₂ that confirms cubic structure with 2-3 μ m cubes.



Figure 4.2: Raman spectroscopy of micron sized pyrite cubes.



glycol (99%, Mallinckrodt Baker Inc.) and sulfur (Fischer Scientific) were used as starting materials. HPLC grade water, analytical grade NaOH, and absolute ethanol were used without further purification. Using a magnetic stir bar, ethylene glycol (17 mL), PVP (600 mg), FeCl₂ · 4H₂O (0.64 mmol, 127 mg), NaOH (1 M, 8 mL) and sulfur (180 mg) are mixed sequentially. For ease of access the synthetic protocol is given in Table 4.1. This solution is stirred for 20 minutes and then dielectrically heated in a microwave reactor (Discover SP, CEM Inc.) [166]. The sample is irradiated with 75 W of power until it reaches 190 °C and is then held at this temperature for 12 hours. After the reaction is finished it is cooled by compressed air. The resulting silver colored precipitate is separated by centrifugation and washed 3 times by sonication in ethanol. It is then stored in ethanol and vacuum dried overnight at 50°C for battery utilization. Synthetic FeS₂ was characterized by Cu-K α x-ray diffraction (XRD) measurement, field emission scanning electron microscopy (FESEM, JEOL JSM-7401F), and Raman spectroscopy (Jasco NRS-3100).

Table 4.1: Micron sized iron pyrite cube synthesis conducted in a research microwave.

	Chemical	Quantity
Solvent	Ethylene Glycol	$17 \mathrm{mL}$
Iron Precursor	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	127 mg
Sulfur Precursor	Elemental Sulfur	181 mg
Control Kinetics	Sodium Hydroxide, NaOH	$8~\mathrm{mL}$ 1 M aqueous
Surfactant	PVP (polyvinylpyrrolidone)	600 mg

4.4.2 Analysis of this Synthesis

I believe that it is generally true that there are two reaction mechanisms to create pyrite, as demarcated by Rickard and Luther [52]. Specifically, it is believed that FeS is always formed previous to FeS₂, by kinetic necessity rather than any intrinsic reason. Subsequently, there are two general routes with which to convert this iron monosulfide to the disulfide (pyrite) form. Generally these are a redox reaction involving H_2S and a lewis acid/base reaction involving polysulfides (Figure 37 in Rickard and Luther is quite helpful) [52]. In relation to the current synthesis, it has been found that the H_2S pathway is much faster (about two orders of magnitude) than that of polysulfides. The relative prevalence of these two pathways is mediated by the pH of the reaction with the H_2S pathway dominating in acidic conditions and the polysulfide pathway in basic reactions [52]. Therefore, it is seen that the amount of NaOH used in this synthesis works to bias the pathway used and therefore the rate of pyrite crystal growth. Additionally, in comparison with theoretical expectation it is seen in this work that euhedral crystal faces (the {100} faces in this case) are grown in higher pH, and therefore at slower growth rates. Slow growth seems to favor rational crystal growth of low energy facets whereas fast growth seems to become diffusion limited. That is to say, whether or not precursor reaches a low energy facet or not, it reacts with the crystal surface, growing irregular shaped particles. Similar results, with pH controlling reaction kinetics, have been observed by others [96, 167]. These results are shown especially clearly in Figure 4.3.

Figure 4.3: Effect of increasing the molarity of NaOH (and therefore the pH) on pyrite morphology.



[OH]=0.28 M

[OH]=0.32 M

Further corroboration the $FeS \rightarrow FeS_2$ transition is x-ray diffraction (XRD) data of pyrite microcube samples like that shown in Figure 4.4. Non-pyrite material is obviously existing in the synthesis. XRD unambiguously shows that this material is a phase of FeS, Pyrrhotite (see Figure 4.1 small impurity peaks).

However, by still running the synthesis for the same time (12 hours) but turning up the temperature from $180^{\circ}C \rightarrow 190^{\circ}C$ a phase pure product can be isolated as shown in Figure 4.5. Additional time in the microwave reactor at $180^{\circ}C$ is also found to create an acceptably phase-pure



Figure 4.4: SEM image of pyrite micron cubes showing FeS intermediate product as well.

product.

4.5 Electrochemical Implications

As described above, this architecture has allowed for reversible cycling of pyrite whereas liquid electrolytes would loose capacity irreversibly, through the four electron process. Interestingly, however, it is demonstrated that the orthorhombic polymorph of FeS_2 is the phase that is reformed upon delithiation as shown in Figure 4.6. Rate kinetics as shown in the cycling data are found to increase after the first cycle, therefore it is argued that marcasite, which is a less dense structure, allows for faster kinetics and therefore conversion reactions.

Electron micrographs with cycling data are presented in Figure 4.7.



Figure 4.5: Pyrite micron cubes synthesized at $190^{\circ}\mathrm{C}.$

Figure 4.6: High resolution TEM image showing nanoscale domains formed upon delithiation of the cell. Electron diffraction indicates that these domains are orthorhombic FeS_2 , marcasite.



Figure 4.7: Voltage as a function of lithiation, with electron micrographs indicating the cathode morphology as certain points.



Chapter 5

Preliminary Results and Future Work

5.1 Photoluminescence

In Chapter 3 we indicate that the process developed in that work results in particles that do not show linear photoluminescence. However, preliminary work does indicate that nanocube colloids from that study exhibit nonlinear and broadband photoluminescence when irradiated by a 809 nm femtosecond laser. Here we describe this unpublished work and show the data collected so far.

This experiment was performed with a Ti:Sapphire laser focused on a quartz cuvette of thiol treated by nanocubes. Near infrared emitted wavelengths were captured in a backscatter geometry and focused into an infrared spectrometer. The luminescent signal at 30 mW laser intensity is shown in Figure 5.2.

For the spectrometer used here detection becomes much less efficient at longer wavelengths than ~ 1650 nm, so those data are excluded. The broadband nature of this luminescent signal is obvious. As describes in the text, the observed signal is highly nonlinear, as is shown here in Figure 5.2 where a power-law fit is seen to approximate the data well. This gives a slope of ~ 7 .

This data is difficult to interpret at present. Of note, nonlinear broadband photoluminescence has been recently observed with graphene [168, 169]. Besides an interpretation of luminescence to describe this signal, it could also be explained by a nonlinear scattering phenomenon. For instance, the particles studied could be self-focusing the laser pulses which could lead to self-phase modulation and supercontinuum generation. However, such nonlinear electromagnetic processes are

Figure 5.1: Broadband photoluminescence signal of thiol treated pyrite nanocubes when excited by 30 mW, 809 nm femtosecond laser pulses.



Figure 5.2: Integrated photoluminescence as a function of laser fluence on a log-log scale. Power law fitting is shown (n=7).



not the favored explanation given here. Instead, we would like to tentatively attribute this signal to luminescence. It's broadband nature can perhaps be explained by the very strong Coulomb scattering signal that may be thought to be operative in this case. The nonlinearity of this signal is quite unusual (n=7). A good explanation of such behavior does not exist at present.

5.2 Low Temperature Absorption Spectrscopy

Low temperature absorption spectroscopy has been shown to be a very interesting analysis method for pyrite. As argued in Chapter 3 this is because the surfaces of pyrite have a strong temperature dependent density of states. With that in mind we have attempted to study pyrite absorption spectroscopy at low temps (non-surface treated). This preliminary data is shown in Figure 5.3. The data shown here are astounding and as-yet quite difficult to interpret. Of note, the absorption from the cryogenic dewar has not been subtracted out of the spectrum in this case. Additionally, there was not a way to run a baseline during this experiment, so the discontinuous jump in the absorption data at 900 nm is a signal of the spectrometer changing between it's infrared detector and visible range detector, not any signal inherent to the material. By comparison with previous data taken with this dewar it is seen that the peak at ~1390 nm is a signal of the dewar and not the pyrite.

In interpreting this data it must be noted that the absorption of the pyrite film remains the same from the lowest liquid Nitrogen temperatures (77 K) until about 170 K. After this, anomalously high absorption in the ultraviolet region (\sim 300 nm) is observed. This absorption climbs until 205 K. Then the signal becomes much more broad and rises across the entire range of wavelengths observed. Subsequently it decreases homogeneously and returns to a spectrum that looks quite similar to what was observed at the lowest temperatures.

As a tentative explanation, we believe this data may be interpretable with the conceptual framework posited in Chapter 3. To wit, frustrated metastable states are allowed to unfreeze at around 170 K and then become dynamic, especially in the presence of ultraviolet light. Subsequently, after they are completely unfrozen their motion and absorption spectroscopy becomes



Figure 5.3: Absorption spectroscopy of a thin films of pyrite (from the synthesis described in Chapter 2) as a function of temperature.

incoherent so a strong absorption signature is no longer observed and the spectra again looks as it did for the lowest temperatures.

5.3 Future Work

I believe that there is much future work to be done with the pyrite research given here. The model given to explain the (100) surface of this material (in Chapter 3) must be considered tentative at this time. Therefore, obvious future work is directed towards testing this model. Low temperature photoconductivity or absorption experiments of (100) and another face ((111) for instance) should be completed. It is our contention that the surface states seen in Figure 3.4 will only be observed for the (100) face. In the same vein, any surface sensitive probe is postulated to see qualitatively different behavior as a defective surface is cooled to cryogenic temperatures. Magnetic measurements, as with a SQUID for instance should also indirectly detect this behavior. Some studies in the literature have shown magnetic behavior at low temperatures ([170], for instance) but much work remains.

Additionally, these surface states are spin polarized and therefore have a magnetic moment. Magnetic circular dichroism (MCD) is therefore a very appropriate analytical method [171]. Also of note, TEM images of pyrite always look unusual in that there seem to be changes in contrast across the surface that remain unexplained. Such contrast is conceivably a surface signal of an imperfect or frustrated physical situation. Fresnel fringe analysis or other methods may then become useful in quantifying the potential on the surface [172, 173, 174].

5.3.1 Core/Shell Strategies

As a surface engineering approach, future work should study the use of a monolayer of a dissimilar material to form a shell around our pyrite nanocubes. This shell layer will be chosen to maintain the ability to remove charge carriers from pyrite while giving the particle surface thermodynamic stability (disallow sulfur vacancies). This type of procedure is currently an intensely studied topic in various nanoparticle research fields even for materials that do not seem to need

the benefits of a shell to the extent that pyrite is perceived to [68].

5.3.1.1 Cadmium

For example, a cadmium shell has been shown to greatly improve the properties of both PbS and SnS nanoparticles [68, 175]. Cadmium (Cd) will therefore be used in this study. Previous work has shown that there is a strong affinity for Cd to the pyrite surface, so much so that gentle conditions will need to be employed to prevent phase separation [176].

The success of monolayer shelling will be studied by XPS and inductively couple plasma atomic emission spectroscopy (ICP-AES). XPS will show the chemical binding environment of the cation while ICP-AES will quantify the amount contained in the sample. If the shell structure can be successfully proven, UV-vis, PL, and thin film measurements will be undertaken in addition to testing the stability of this surface by the protocol described above.

5.3.1.2 Ruthenium Disulfide (RuS_2)

In addition to cadmium, ruthenium will be explored as a monolayer and few-layer shell. The ruthenium analog to the pyrite structure, RuS₂, has been shown to have many advantageous properties. RuS₂ is a semiconductor with a 1.4 eV band gap, slightly higher than iron pyrite. It has been reported to have good (100) cleavage (that of iron pyrite is usually described as poor) [177]. STM images of RuS₂ show that surfaces with long-range order, hundreds of nanometers across, are easily attained, in contrast to the broken terrace structure of iron pyrite [178]. Additionally, RuS₂ surfaces have been shown to be air stable for many months, in stark contrast to the effects measured for iron pyrite [179]. Therefore, a layer of RuS₂ presents a new and exciting route to circumventing the stability problem inherent to iron pyrite. While scanning tunneling spectroscopy (STS) of RuS₂ gives evidence of gap states, the problem seems to be much reduced as compared to iron pyrite (lowest imageable bias being ± 300 mV for RuS₂ verse ± 20 mV for FeS₂) [120, 179].

While it may be argued that using ruthenium negates the strengths of iron pyrite as an earth abundant material, we believe that the quantity needed for monolayer formation will be so little that the inherent advantages of pyrite will remain. Additionally, demonstrating a mechanism for the improvement of the photovoltage of pyrite would give an important proof-of-principle that could then be engineered in more inexpensive ways with alternative materials. Successful shelling of RuS₂ onto FeS₂ (as measured by XPS and ICP-AES) will be followed by conventional nanoparticle spectroscopy (UV-vis and PL), stability testing, and thin film measurements.

5.3.1.3 Chlorine

Lastly, we will also study a chlorine-passivated surface. Very recently, Pietryga and colleagues at Los Alamos discovered that their PbSe nanoparticles were better stabilized by chloroform than other nonpolar solvents, and they hypothesized that Cl^- containing contaminants were the reason for this. A subsequent study to cap their particles with Cl^- ions found superior stability and photoluminescent properties [180]. This may have direct implications for pyrite since in our own research, and in that of many other groups, pyrite is found to be exclusively dispersible in chloroform among nonpolar solvents. Like the previously described core/shell strategies, the presence of chlorine will be studied by XPS and ICP-AES and the resulting properties by UV-vis, PL, and thin-film measurements.

5.3.2 Increasing Surface Perfection

The work described here has focused on healing defects on the (100) surface by introducing charged alkyl ligands. However, much more work can be done in this effort; utilizing higher temperatures and excess sulfur, for instance, may allow us to create more perfect surfaces than can be made by low-temperature surface treatments alone. Such work, if properly designed, may be thought to thermodynamically drive surface perfection rather than just passivating as many defects as possible (as with our current protocol). Theoretical work indicates that only a small range of chemical potentials of sulfur will result in the perfect (100) surface being the low energy face [60]. Exciting future work should study this range experimentally by a series of experiments where the amount of sulfur precursor added to the system is carefully monitored along with the resulting effect on optical properties.

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Appendix A

Supporting Information to Chapter 2: Iron Pyrite Nanocubes: Size and Shape Considerations for Photovoltaic Application

A.1 Materials

FeCl₂ anhydrous beads (99.99%) and sulfur flakes (99.998%) were purchased from Sigma-Aldrich. Technical grade hexadecylamine (90%) and oleylamine (70%) were also purchased from Sigma. Chloroform (99.8%) was purchased from Fischer Scientific. Trichloroethylene (99.5+%) was purchased from Sigma-Aldrich. All chemicals were used as received. All reactions were conducted in a Schlenk type vacuum manifold.

A.2 Supporting Figures

Table A.1: Size of coherent x-ray scattering domains for the as grown nanocube product measured by the Scherrer equation. Scherrer constants for each particular reflection are also given.

Reflection	$\mathbf{K}^{\mathbf{a}}$	Measured Size (nm)		
(111)	1.1547	42.84		
(100)	1.0000	53.84		
(210)	1.0733	49.36	Average (nm)	Standard Deviation (nm)
(211)	1.1527	41.61	47.79	5.18
(110)	1.0607	42.34		
(311)	1.1359	50.76		

a: Stokes and Wilson [109]

Figure A.1: TEM images of the nanocube product after the first growth cycle. After 17 days of being stored in excess oleylamine particle size and shape has not changed demonstrably.



Figure A.2: Extinction of a well-dispersed sample with octadecylamine as the ligand and the corresponding RLS signal. Of note, it is now thought that this data shows too little scattering. See data in Chapter 3 for more recent analysis of light scattering when octadecylamine is used.





Figure A.3: Nanocrystal product with no oleylamine added for growth steps



Figure A.4: Nanocubes and irregular shapes found when using octade cylamine as the solvent.

Figure A.5: The product grown at [S]/[Fe]=2 showing predominantly pyrite but also a pyrrhotite impurity. The particular superstructure of pyrrhotite has not been rigorously studied but pyrrhotite 5C is displayed for reference.



Figure A.6: Synthetic product when [S]/[Fe]=2.1 showing more rounded edges than for more sulfur deficient conditions.



Figure A.7: Synthetic product when $[Fe]_{grow}/[Fe]_{nuc}=3$ showing smaller particles attributed to a secondary nucleation at such concentrated conditions.



Appendix B

Supporting Information: Chapter 3: Evidence for Direct Band Gap Surface States with Defect Passivation on Iron Pyrite {100} Nanocubes

B.1 Materials

FeCl₂ anhydrous beads (99.99%), sulfur flakes (99.998%), stearic acid (95%), cetyltrimethylammonium bromide (CTAB, 95%), octadecanol (99%), and 1-octadecanethiol (98%), octadecylamine (90%), 1,2-dichlorobenzene (99%), trichloroethylene (99.5+%), tetrachloroethylene (¿99%), and 2-propanol (99+%) were purchased from Sigma-Aldrich. Technical grade hexadecylamine (90%) and oleylamine (70%) were also purchased from Sigma. Chloroform (99.8%), toluene (99.9%), and hexanes (99.9%) were purchased from Fischer Scientific. Anhydrous methanol (ACS Reagent grade) and dichloromethane (99.5%) were purchased from Macron Chemicals. Acetonitrile was purchased from Mallinckrodt Chemicals. All chemicals were used as received. All reactions were conducted in a Schlenk type vacuum manifold.

B.2 Synthesis

The synthetic scheme employed here is a very close adaptation of our previous work [129]. A 0.5 mmol (63.4 mg) amount of anhydrous FeCl₂ beads, 10 g hexadecylamine, and 3 mmol (96.2 mg) S flakes were brought to 250° C for 3 hours in a 50 mL 3 neck flask under argon atmosphere with magnetic stirring at 240 RPM. This step was termed the nucleation step in our previous work as it resulted in small (~20 nm), irregularly shaped particles. After the nucleation step was completed the flask was allowed to cool naturally and the raw solution to freeze with the hexadecylamine.

Once room temperature was obtained, 1 mmol (126.8 mg) FeCl₂, 2.05 mmol (65.7 mg) S, and 15 mL oleylamine were added through one of the necks of the flask with argon flowing over the frozen solution. The flask was then resealed and brought to 200° C for 9 hours, stirring at 750 RPM. This step was termed the first growth step in our previous work. As opposed to our previous work a second growth step was not utilized in the present study. Upon its completion \sim 10 mL of chloroform and 5 mL methanol were added and the solution was lightly centrifuged (3000 RPM for 1 minute) followed by decanting of the supernatant. The precipitate was cleaned twice in chloroform/methanol mixtures by redispersion and centrifugation, and was subsequently stored in 20 mL chloroform for analysis and surface treatments.

B.3 Analytical Methods

TEM images were acquired with a Philips CM100 with a 100 kV accelerating voltage and a bottom mounted digital camera. Samples were prepared by immersing a carbon coated TEM grid into a nanocube solution in chloroform for about a second and then drying in air, this was done immediately prior to analysis to avoid oxidation ambiguity.

Raman spectra were collected on a Jasco NRS-3100 using a 532 nm laser for excitation at 0.7 mW intensity. For analysis a nanocube sample in solution was pipetted onto a glass slide and the chloroform was allowed to evaporate. The sample was analyzed under 100X magnification.

Fluorimeter measurements were conducted on a Horiba Fluorolog-3 fluorimeter. The analysis was performed in chloroform or trichloroethylene in a 1 cm quartz cuvette. The analysis involved simultaneously scanning the excitation and emission monochromators. The emission monochromator is at a 90 orientation to the excitation. It was found that 3 nm slits for both excitation and emission monochromators gave the best signal. The signal was obtained as the ratio of emission per lamp intensity (S/R). The signal was background corrected by running an identical experiment with just the solvent and cuvette system. The data was smoothed because of large changes in lamp intensity.

Ultraviolet-visible (UV-vis) measurements were conducted on a Varian Cary 500 spectropho-

tometer. Samples were analyzed in chloroform, trichloroethylene, and tetrachloroethylene in a 1 cm quartz cuvette with a double beam configuration and 1 nm data collection interval.

Fourier transform infra-red (FTIR) spectroscopy was conducted on a Nicolet Nexus 670 system. Samples were created by drop casting a drop of pyrite nanocube solution onto a KBr card. A resolution of 2 cm^{-1} was used.

The pyrite nanocube model in the table of contents graphic was rendered with Vesta version 3.0.7 [6].

B.4 Postscipt

B.4.1 t_{2g} states

In pyrite the iron atoms are in a trigonally distorted octahedral crystal field. Therefore, denoting these states as the t_{2g} band is not rigorously correct (as it would be for the case of a true octahedron). See Prince et al. for discussion [5]. However, as the trigonal distortion is a small perturbation, we follow many others in keeping this notation.

B.4.2 Sulfur vacancies of vacuum fractured pyrite

In the discussion make arguments about the relative perfection of the (100) pyrite surface based off of photoelectron spectroscopy from vacuum fractured samples. It can be argued that analyzing vacuum fractured samples will overemphasize the prevalence of sulfur vacancies compared to other preparations. Optimizing sputtering/annealing cycles [181] or introducing sulfur gases [75] may be interesting in preparing more stoichiometric surfaces; still, we believe that the sensitivity of the pyrite surface to sulfur loss has been firmly demonstrated. Indeed, it seems to be a significant challenge to find ions light enough (He⁺, rather than Ne⁺ or Ar⁺) and bias conditions low enough, not to significantly destroy surface sulfur dimers during pyrite sputtering (as measured by Auger Electron Spectroscopy [182] or XPS [137]).

B.5 Supporting Figures

Figure B.1: UV-vis spectroscopy of pyrite nanocubes (not ligand treated) dispersed with the aid of excess octadecylamine. For the blue curve a commensurate amount of octadecylamine was added to the reference cuvette. Therefore it is shown that the NIR absorption bands, before ligand treatment, are due to the excess ligand and not the pyrite electronic structure itself.



Figure B.2: UV-vis absorption spectroscopy of pyrite nanocubes, in this case treated with stearic acid and dispersed in either trichloroethylene (blue) or tetrachloroethylene (red). The RLS signal associated with dispersing the nanocubes in the less polar solvent is immediately evident. The absorption in the trichloroethylene data at ~ 1650 nm is sometimes observed and is due to trichloroethylenes absorption at that wavelength. Thus, this figure displays the trade-offs inherent in these two different solvents: either too nonpolar but transparent in the NIR (tetrachloroethylene) or polar enough but with absorption bands in the NIR (trichloroethylene). Also note that the minority spin channel band gap transition is red-shifted for trichloroethylene with respect to tetrachloroethylene. It has been observed as a general of this transition that it displays positive solvatochromism, although this has not been studied further in the current work.



Figure B.3: Sample of thiol treated pyrite nanocubes in trichloroethylene showing the entire region allowable by our system (limited by the quartz cuvette). The features deeper in the infrared have not been studied in the current work and their origin remains unknown.



Figure B.4: The RLS signal of thiol treated nanocubes. While light scattering is shown, it is at a far lower level than for pyrite nanocubes either without excess ligand (Figure 3.1e) or with excess octadecylamine added (Figure 3.1f). For comparison, the maximum light scattering for the previous two cases occurs at ~ 650 nm while it can be seen here that there is very little scattering in that region.

