Surfactant-assisted Hydrothermal Synthesis of Single Phase Pyrite FeS2 Nanocrystals

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Iron pyrite (FeS2) has long been a material of interest for photovoltaic devices.1 With an indirect energy transition at 0.95 eV, a direct transition at 1.03 eV,2 and an integrated absorption coefficient of $3.3 \times 10^5$ cm$^{-1}$ for the energy spectrum of wavelength values ($\lambda$) between 300 nm and 750 nm, it is ideally suited for photovoltaic applications. This coupled with low procurement costs and vast abundance gives pyrite the potential to be a disruptive photovoltaic material when compared to many other candidates.3 Numerous iron sulfides exist in nature, each with unique magnetic and electrical properties that are strongly related to the stoichiometric ratio between Fe and S as well as crystalline structure. Pyrite has previously been prepared using several high temperature approaches including: MOCVD, sulfurization of iron films, sulfurization of iron oxide films, reactive sputtering and spray pyrolysis.4,5 Yet at elevated temperatures, segregation of iron and sulfur species is unavoidable, which could change the stoichiometry and material phase of the deposited film. In fact, the best demonstrated pyrite photovoltaic device by these techniques shows a modest 2.8% power conversion efficiency.6 This low performance was partially explained by a high density of surface defects, but the unusually low open circuit voltage of 200 mV suggests that phase purity may also play a role.7,8 Orthorhombic marcasite FeS$_2$ and hexagonal troilite FeS$_2$ are both common iron sulfur phases but because they have much smaller band gaps (0.34 eV for marcasite and 0.04 eV for troilite), even trace amounts would explain the low open circuit voltage observed in this previous work.

Semiconductor nanocrystals have been used as building blocks to assemble a range of electronic and photonic structures, including light emitting diodes, lasers, and photovoltaics.9 Critical to the functionality of these types of devices are the purity, crystallinity, stoichiometry, size of the nanocrystal building blocks. While some low temperature solution phase colloidal nanocrystal synthesis approaches to pyrite have been explored,10 these efforts are early and unlike their thin film predecessors, there are no reports on photovoltaics made from these synthetic materials.

Single source molecular precursors with precisely defined composition can provide a high degree of control of nanocrystal synthesis, as demonstrated with the growth of CdS, ZnS, CdSe, ZnSe, Sb$_2$Te$_3$, In$_2$S$_3$ nanocrystals6 as well as


as the growth of CdS and ZnS nanowires. Herein, we report the use of single-source molecular precursors for the growth of single phase FeS$_2$ pyrite nanocrystals through a hydrothermal reaction. Surfactant selection and control of solution pH have been found to play key roles in the preparation of single phase iron pyrite.

Our synthetic approach starts with the formation of the single source molecular precursor iron (III) diethyl dithiophosphate ([[(C$_2$H$_5$O)$_2$P(S)S]$]_3$Fe) in aqueous solution through the reaction between iron (III) chloride (FeCl$_3$) and diethyl dithiophosphate ammonium salt ((C$_2$H$_5$O)$_2$P(S)SNH$_4$) (formation of this product was confirmed through mass spectrometry studies and is detailed in the supplemental information). Then, the single source precursor with the addition of hexadecyltrimethylammonium bromide (CTAB) acting as a surfactant undergoes thermal decomposition by a hydrothermal reaction in a 125ml teflon lined stainless steel acid digestion bomb at 200 °C. We also demonstrate an alternative approach where the molecular precursor may be formed in-situ and is detailed in the supplemental information.

XRD studies (Fig. 1a) show the materials prepared in this way are cubic pyrite FeS$_2$ (JCPDS 03-065-1211, Fig. 1a red lines) without any noticeable impurity peaks from orthorhombic marcasite FeS$_2$ or hexagonal troilite FeS. Transmission electron microscopy (TEM) studies (inset, Fig. 1a) show large quasi-cubic nanocrystal agglomerations with an average size over 100 nm. The pyrite nanocrystals were further investigated through X-ray photoelectron spectroscopy (XPS) (Fig. 1b). Iron peaks in the XPS spectrum are associated with FeS$_2$. The Fe 2p$_{3/2}$ binding energy of 707 eV (Fig. 1b, left panel) is characteristic of pyrite (with no observable impurities from troilite). The S 2p$_{3/2}$ and S 2p$_{1/2}$ peaks at 162.28 eV and 163.47 eV respectively (Fig. 1b, right panel), are also consistent with the sulfur binding energy in bulk pyrite.

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To elucidate their electronic structure, the FeS$_2$ nanocrystals have been studied by X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES). XAS probes the local unoccupied electronic structure (conduction band); XES probes the occupied electronic structure (valence band); and the addition of resonant inelastic X-ray scattering (Raman spectroscopy with X-rays) can provide significant insight into the energy levels that reflect the chemical and physical properties of semiconductors. The experiment was performed on BL7 at the Advanced Light Source, Lawrence Berkeley National Laboratory.

Laboratory. The resolution was set to 0.1 eV for XAS and 0.2 eV for XES.

The X-ray absorption and emission spectra of nanostructured iron pyrite were recorded at the S L-edge and Fe L-edge. The S 2p XAS spectrum (Fig. 2, inset) reflects the density of states of the conduction band. The spin orbit splitting of about 1.2 eV is also reflected in the XAS spectrum, indicated as A1 and A2. The non-resonant excited S L-edge XES spectrum (Fig. 2) shows the density of states of the valence band. The intensive band around 145-150 eV arises predominantly from levels with 3s character, while the upper valence band (UVB) being mostly of 3p character shows a much weaker intensity due to the dipole selection rule of the XES process. The small band close to the Fermi level at around 161 eV is attributed to S 3d states that are hybridized with Fe 3d states. Its asymmetric shape indicates the two components due to the valence states projected on L shell vacancies with spin orbital splitting of 1.2 eV for 2p3/2 and 2p1/2. When resonantly exciting A1 and A2 in the XAS spectrum, one can see the resonant enhancement for each corresponding component S1 and S2.

In conclusion, we have demonstrated a single-source molecular precursor that can be used for the synthesis of single phase pyrite FeS2 nanocrystals. Characterization confirms an indirect transition and a bandgap of 0.95 eV. The reaction temperature, pH value, precursor, and surfactant have been found to play important roles in the control of material purity. These single phase pyrite FeS2 nanocrystals represent a good candidate material for studies of nanoscale photovoltaic solar cells based on non-toxic and earth abundant materials.

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Supporting Information Available: Detailed procedures about experiments, molecular structure and mass spectrum of the molecular precursor, XPS spectrum of the pyrite FeS2 nanocrystals and TEM images of nanocrystals containing marcasite impurities synthesized using CTAB and oleylamine mixture. This material is available free of charge via the Internet at http://pubs.acs.org.

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