



ELSEVIER

Contents lists available at SciVerse ScienceDirect

## Materials Letters

journal homepage: [www.elsevier.com/locate/matlet](http://www.elsevier.com/locate/matlet)

# Synthesis of iron pyrite nanocrystals utilizing trioctylphosphine oxide (TOPO) for photovoltaic devices

S.C. Mangham<sup>a,\*</sup>, M. Alam Khan<sup>a</sup>, M. Benamara<sup>b</sup>, M.O. Manasreh<sup>a</sup>

<sup>a</sup> Department of Electrical Engineering, University of Arkansas, Fayetteville, AR 72701, USA

<sup>b</sup> Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville, AR 72701, USA

## ARTICLE INFO

### Article history:

Received 7 December 2012

Accepted 23 January 2013

Available online 31 January 2013

### Keywords:

Iron pyrite

Characterization

Trioctylphosphine oxide (TOPO)

Photovoltaic

## ABSTRACT

Iron pyrite nanocrystals with trioctylphosphine oxide (TOPO) were synthesized and characterized bearing in mind their use for photovoltaic devices. The nanocrystals were characterized by using optical absorption, X-ray diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The optical absorbance spectra exhibit large absorption in the visible and near infrared spectral range. Utilizing the X-ray diffraction, the FeS<sub>2</sub> nanocrystals were found to have a face-centered cubic structure by comparing and matching the pattern to a data reference pattern. The SEM and TEM images indicate that the FeS<sub>2</sub> nanocrystals exhibit face-centered cubic crystallographic structure.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Iron pyrite (FeS<sub>2</sub>) more commonly known as fool's gold, is an abundant mineral of low cost with potential photovoltaic device characteristics. The abundance of FeS<sub>2</sub> as well as the low potential production cost that is easily scalable for either small or large scale production at an economical rate of around <0.000002 €/W of material extraction cost [1,2]. Another characteristic of FeS<sub>2</sub> is that this compound exhibits high optical absorption in the visible and near infrared light spectrum with a band gap of 0.95 eV [3–8].

To produce the desired properties for photovoltaic devices, highly pure face-centered cubic iron pyrites with superior optoelectronic and structural properties are needed. The combination of Fe and S produces compounds in the forms of FeS and Fe<sub>1-x</sub>S<sub>x</sub>. The different possible chemical compounds (poly-phase) can lead to a lack of uniformity of the adjust ratio, which leads to local defects within the material [1,9]. Due to the ease of FeS<sub>2</sub> being able to exist in several crystal forms, it can create different structures, ranging from a pyrite and marcasite to a pyrrhotite that changes to Fe<sub>1-x</sub>S<sub>x</sub>, and finally the ability to be a troilite with a formula of FeS [1,10]. The band gap of various FeS<sub>2</sub> phases ranges between 0.7 eV and 2.62 eV [11]. The band gap of 0.95 eV makes FeS<sub>2</sub> suitable for solar cell applications [4,12]. Combining the band gap and the photon absorption characteristic, FeS<sub>2</sub> could theoretically provide 3.5 TW of power, making FeS<sub>2</sub> a primary producer of electricity in the nation with less than 10% of the

waste FeS<sub>2</sub> produced by the United States of America [4]. The optical absorption of FeS<sub>2</sub> depends upon the annealing conditions and the thickness of the FeS<sub>2</sub> films. The annealing conditions also have an effect on the electrical resistivity [13], while a decrease in the temperature of the testing environment has an effect on the resistivity as well [14].

There have been a multitude of methodologies reported that are able to grow crystalline face-centered cubic FeS<sub>2</sub> nanocrystals, as confirmed by different testing methods, including X-ray diffraction (XRD) patterns [10,15–18]. One of these methods is the synthesis of FeS<sub>2</sub> nanocrystals by combining FeCl<sub>2</sub> with oleylamine in a heated environment. The sulfur, in a powder form, was added to FeCl<sub>2</sub> with oleylamine to create the nanocrystals [10]. Another method utilizes the solvent oleylamine and trioctylphosphine oxide (TOPO) at relatively low temperatures to form soluble iron precursor [18]. TOPO helps due to its reported properties of increasing the solubility of materials with chloroform [19,20]. Along with increasing the solubility of the material, TOPO is also considered a stabilizing agent that has been reported to increase the stability and viability of FeS<sub>2</sub> for photovoltaic devices [18].

Despite all the methods of synthesis of FeS<sub>2</sub> nanocrystals and the relatively reasonable characteristics for producing photovoltaic devices, there still remains the problem of low power conversion efficiency of FeS<sub>2</sub> nanocrystals based solar cells that is affected by the low open circuit voltage ( $V_{oc}$ ). This could in part be due to the presence of poly-phase defects in the FeS<sub>2</sub> nanocrystals [9]. These defects affect the chemical and physical properties [21]. The presence of poly-phase causes adverse effects on the properties of the iron pyrite including the energy band gap. This poly-phase problem is one of the major issues associated

\* Corresponding author. Tel.: +1 4795755444.

E-mail address: [mangham@uark.edu](mailto:mangham@uark.edu) (S.C. Mangham).

with the growth of iron pyrite. For example, the band gap of the hexagonal FeS troilite is 0.04 eV, while the  $\text{Fe}_{1-x}\text{S}_x$  pyrrhohtite phase has a band gap of 0.2 eV and  $\text{FeS}_2$  marcasite phase has a band gap of 0.34 eV [1,10].

This paper reports on the synthesis and characterization of low cost  $\text{FeS}_2$  absorber nanocrystals with an optimized amount of TOPO addition as a surfactant in octylamine as a coordinating solvent for phase-pure, comparatively high crystalline, optimum crystal size and stable nanocrystals for photovoltaic applications. Synthesis of the  $\text{FeS}_2$  nanocrystals was by the hot injection method with chloroform added to prevent coagulation. The methods used to characterize the nanocrystals include the UV–Vis optical spectrometer, XRD, and a scanning electron microscope (SEM). The UV–Vis optical absorbance spectra were measured in the spectral region of 300–2000 nm with a significant absorption band in the spectral region of 300–1200 nm. By comparing the measured XRD to a reference pattern of  $\text{FeS}_2$  nanocrystals with a face-centered cubic structure, the phase-pure crystalline face-centered cubic structure of the  $\text{FeS}_2$  nanocrystals is confirmed by matching the measured peaks to the reference peaks. The SEM is used to inspect and measure the individual average  $\text{FeS}_2$  nanocrystals size while a transmission electron microscope (TEM) is used to confirm the crystalline structure of the  $\text{FeS}_2$  nanocrystals.

## 2. Experimental

Iron pyrite face-centered cubic nanocrystals were prepared by a hot injection method using octylamine as coordinating ligands at suitable synthetic conditions. In a typical synthesis, 10 mL of octylamine (Aldrich) is injected into a Schlenk flask. Then 2.5 mmol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (Alfa Aesar) was mixed into the Schlenk flask in a  $\text{N}_2$  atmosphere, with mild stirring at 115 °C for 1.5 h to degas it. In another Schlenk flask, 500 mg of sulfur (Aldrich) was mixed in 15 mL of octylamine and degassed in a  $\text{N}_2$  atmosphere at 85 °C for 1 h. A 2.0 mmol of TOPO (Aldrich) is added into the Schlenk flask that contains the solution of 10 mL of octylamine and 2.5 mmol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ . This solution is stirred until the TOPO has been dissolved. The sulfur containing solution was injected in the first flask at temperature 230 °C and the reaction was carried out for 2 h with vigorous stirring. Afterwards, a few drops of chloroform (Aldrich) were added to prevent coagulation when the temperature reached 85 °C. Lastly, the solution was washed three times with methanol using a centrifuge (HERMLE Z300) at 5000 rpm for 10 min.

The optical absorption spectra of the nanomaterial were measured by using a Varian Cary 500 UV–Vis–NIR spectrophotometer in the spectral range of 300–2000 nm. Preparation of the material for the spectroscopy was made by diluting the  $\text{FeS}_2$  nanocrystals in chloroform followed by sonication for 30 min to produce a uniform diluted solution. A baseline correction utilizing chloroform was done before the measurement of the material in a chloroform solution. X-ray diffraction was performed using a Philips PW3040 X'Pert MRD High Resolution XRD. A FEI Nova Nanolab 200 Dual-Beam Focused Ion Beam with a FEG Scanning Electron Microscope was used to produce the SEM images. Iron pyrite was used as-prepared for both the XRD and SEM. A FEI Titan 80–300 Transmission Electron Microscope was also used to obtain a high resolution TEM images.

## 3. Results and discussion

The XRD spectra for the as-synthesized  $\text{FeS}_2$  nanocrystals both without and with TOPO are plotted in Fig. 1. The measured XRD

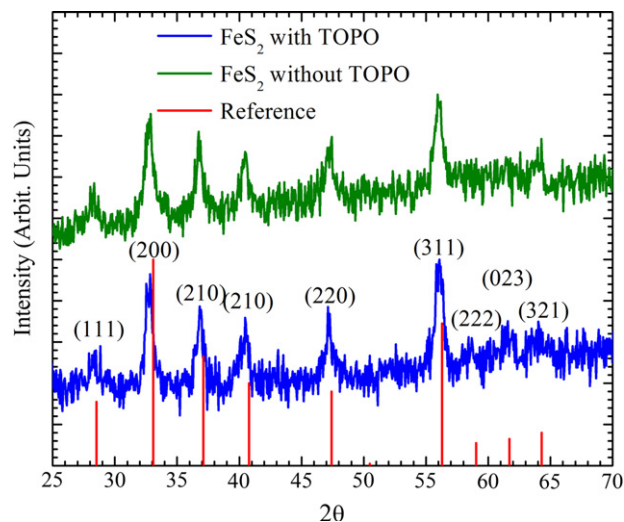


Fig. 1. X-ray diffraction patterns for as-synthesized  $\text{FeS}_2$  nanocrystals with the bottom spectrum representing  $\text{FeS}_2$  nanocrystals with TOPO and the top spectrum shows  $\text{FeS}_2$  without TOPO. The  $\text{FeS}_2$  spectra are compared to the reference pattern, represented by the vertical lines.

spectra are compared with the reference pattern (ICDD number 00–042–1340) of phase-pure face-centered cubic  $\text{FeS}_2$  nanocrystals that is necessary for potential photovoltaic devices. There is a slight shift in the peaks due to the influence of synthetic condition on the size of the  $\text{FeS}_2$  nanocrystals. The dominant peak position shown in Fig. 1 can be indexed as pure face-centered cubic crystal phase at 28.2°, 33.8°, 36.9°, 40.5°, 47.3°, 56.28°, 59.02°, 61.70°, and 64.28° corresponding to crystal phases (111), (200), (210), (211), (220), (311), (222), (023), and (321) respectively. The peaks in Fig. 1 are highly consistent between the two samples of  $\text{FeS}_2$  nanocrystals. However, the peaks at 59.02°, 61.70°, and 64.28° are slightly more apparent with the  $\text{FeS}_2$  nanocrystals with TOPO when compared to  $\text{FeS}_2$  nanocrystals without TOPO. The XRD spectra shown in Fig. 1 of the as-synthesized  $\text{FeS}_2$  nanocrystals are in line with the standard data for a face-centered cubic structure of  $\text{FeS}_2$  nanocrystals. These results indicate the phase-pure nature of the  $\text{FeS}_2$  nanocrystals without detectable impurity structures, such as marcasite, pyrrhotite, or griegyte. By matching the reference  $\text{FeS}_2$  XRD peaks, particularly the major peaks at 33.08° and 56.28° in Fig. 1 high crystallinity of phase-pure face-centered cubic structure of  $\text{FeS}_2$  nanocrystals with TOPO can be seen. Since TOPO is a stronger base than octylamine and binds well with Fe, however, the phosphorous in TOPO may bind and coordinate well with sulfur, owing to its obvious attractive affinity making nanoparticle surface passivated, robust, and stable.

The SEM image in Fig. 2(a) shows the as-synthesized  $\text{FeS}_2$  nanocrystals without TOPO where the individual nanocrystals sizes are about 70 nm. Fig. 2(b) displays the SEM image of the as-synthesized  $\text{FeS}_2$  nanocrystals with TOPO where the size of the nanocrystals ranges from 70 to 250 nm. This size was calculated using the Scherrer formula at 33.8° in the XRD spectrum (in Fig. 1) shows a grain size of 13.4 nm [22]. The HRTEM image in Fig. 2(d) further confirmed this result by showing a grain size of 17.3 nm. Since grains are agglomerated together in particles to increase the difficulty of analyzing the individual grains precisely, hence the discrepancy arises in the Scherrer formula calculated and measured HRTEM grain size. The high resolution TEM image in Fig. 2(c) and confirming by the usage of Bragg's law at 33.8° in the XRD spectrum in Fig. 1 for the  $\text{FeS}_2$  nanocrystals with TOPO has a lattice spacing of 0.27 nm; this lattice spacing is in accordance with Wang et al. [17].

Download English Version:

<https://daneshyari.com/en/article/1645880>

Download Persian Version:

<https://daneshyari.com/article/1645880>

[Daneshyari.com](https://daneshyari.com)