Phase-pure iron pyrite nanocrystals for low-cost photodetectors

Shenting Liu¹, Jiang Wu¹, Peng Yu¹, Qinghua Ding¹, Zhihua Zhou¹, Handong Li¹, Chih-chung Lai², Yu-Lun Chueh² and Zhiming M Wang¹*

Abstract

Earth-abundant iron pyrite (FeS₂) shows great potential as a light absorber for solar cells and photodetectors due to their high absorption coefficient (>10⁵ cm⁻¹). In this paper, high-quality phase-pure and single crystalline pyrite nanocrystals were synthesized via facile, low-cost, and environment friendly hydrothermal method. The molar ratio of sulphur to iron and the reaction time play a crucial role in determining the quality and morphology of FeS₂ nanocrystals. X-ray diffraction and high-resolution transmission electron microscopy confirm that phase-pure and single crystalline pyrite nanocrystals can be synthesized with high sulphur to iron molar ratio and sufficient reaction time. For the first time, a crystalline nanogap pyrite photodetector with promising photocurrent and UV-visible photoresponse has been fabricated. This work further demonstrates a facile route to synthesize high-quality FeS₂ nanomaterials and their potential in optoelectronic applications.

Keywords: Iron pyrite; Photodetector; Hydrothermal; Nanocrystal

Background

Iron pyrite (cubic β-FeS₂), commonly known as a non-toxic and earth-abundant compound, has been regarded as one of the most promising semiconductor materials to meet the urgent demand for cost-effective energy solutions [1,2]. FeS₂ has a band gap of 0.95 eV, which matches the solar spectrum, high absorption coefficient (approximately 10⁵ cm⁻¹ for hν > 1.3 eV) [3,4], excellent electric properties with carrier mobility about 360 cm² V⁻¹ s⁻¹, and long minority carrier diffusion length (approximately 0.1 to 1.0 μm) [1,2]. It provides a new alternative way for high-performance photovoltaic cells as well as optoelectronic devices.

Despite these attractive properties, the promises of FeS₂ have not been fulfilled. For example, the conversion efficiency of FeS₂ solar cells has been limited to only 3% and further improvement remains challenging [5]. The main issues to synthesize high-performance FeS₂ devices are phase impurities and surface defects, which could greatly undermine the superior properties of FeS₂ [6]. Although high quantum efficiency (>90%) and photocurrent (>42 mA cm⁻²) have been reported for FeS₂ solar cells [7-10], the poor crystal quality of bulk FeS₂ has led to very low open circuit voltages (<0.2 V) [5].

The recently realized high-quality FeS₂ nanostructures have triggered the new interest for their applications in various types of devices, such as solar cells, photoelectrochemical cells, photodetectors, and battery cathodes [11-14]. To date, various ways to synthesize FeS₂ nanostructures have been reported, including metal-organic chemical vapor deposition [15], thermal sulphidation [16], magnetron sputtering [17], hydrothermal synthesis [18], and hot injection method [1]. Among these methods, hydrothermal method has been favored due to its low temperature process, which can greatly reduce the phase impurities and surface defects [18].

In this work, we demonstrate a polymer-assisted hydrothermal method without using any expensive precursors or poisonous reagents to synthesize nanostructured FeS₂, including FeS₂ polygonal nanoparticles, nanocubes, and hierarchical nanostructures. In addition, a nanogap (with a gap as small as 200 nm) FeS₂ photodetector has been fabricated. Using such a simple nanogap photoconductor, promising photocurrents and UV-visible (UV-vis) spectral photoresponse have been observed. This facile method to synthesize high-quality FeS₂ nanomaterials and their potential applications in...
high-performance optoelectronics devices demonstrates the growing potential of this earth-abundant material towards low-cost optoelectronic applications.

Methods

To obtain high-quality FeS2, the synthesis was carried out using different reaction recipes. All reagents used in our work are of analytical grade from J & K Scientific (Edwardsville, Nova Scotia Canada). Firstly, gelatin of 0.54 g was dissolved in 30 mL hot deionized (DI) water. The gelatin here can be easily adsorbed onto Fe(OH)2, thus providing an encapsulation for FeS2 nanocrystal during the reaction. In this way, it can prevent the diffusion of S2– ions, S and H2S to the surface of Fe(OH)2, and the aggregation of nanoparticles into large microparticles [19]. Therefore, gelatin plays a key role in the size uniformity and stabilization of FeS2 nanocrystals. Secondly, 1.5 mmol FeCl2 · 4H2O was dissolved in 5 mL DI water and then added to the gelatin solution drop by drop at room temperature. The final concentration of gelatin was about 1.5% v/v. The prepared mixture was sealed in a stainless system with Ni-filtered graphite-monochromatized Cu-Kα radiation (λ = 1.54056 Å). Scanning electron microscopy (SEM) images were taken using JEOL JSM 5800LV field emission SEM system (JEOL Ltd., Tokyo, Japan). High-resolution transmission electron microscopy (HRTEM) scans were carried out using JEOL JEM 2010 transmission electron microscopy (TEM) with accelerating voltage of 200 kV. Selected area electron diffraction (SAED) was also carried out in the same JEOL JEM 2010 TEM. The morphologies of samples 1 to 6 were characterized by SEM after dip coating on silicon substrates.

Results and discussion

Table 1 The experimental parameters used for the hydrothermal synthesis of FeS2 nanoparticles

| Sample number | [S]/[Fe] | Reaction time (hour) | PH  | Phase and impurities                      | Morphology                  |
|---------------|---------|----------------------|-----|------------------------------------------|-----------------------------|
| 1             | 1/1.5   | 24                   | 11.5| FeS2 + FeO1−x + S                       | Polygonal nanoparticles     |
| 2             | 1/0.75  | 24                   | 11.5| FeS2 + FeO1−x + S                       | Polygonal nanoparticles     |
| 3             | 2/1     | 48                   | 12.3| FeS2 + FeO1−x                           | Nanorods                    |
| 4             | 2.5/1   | 48                   | 12.3| FeS2 + FeO1−x                           | Nanocubes and polygonal nanoparticles |
| 5             | 3/1     | 48                   | 12.3| FeS2 + FeO1−x                           | Nanocubes and hierarchical particles |
| 6             | 3.75/1  | 48                   | 12.3| FeS2                                    | Hierarchical particles      |

[S]/[Fe] represents the molar ratio between sulphur and iron elements. The reaction temperature is maintained at 200°C.
Sulphur-rich condition. The nanoparticles evolve to more complicated structures, which include both nanocubes and hierarchical nanostructures as shown in Figure 1d,e, when \([S]/[Fe]\) is further increased. The excess sulphur maintains high chemical potential for crystal growth in other directions than \([100]\) and \([111]\). As the result, the high \([S]/[Fe]\) produces rod-shaped and other hierarchical nanocrystals [21]. When \([S]/[Fe]\) is so high that the different facets has sufficient supply of \(S^2-\), nanocubes cannot be synthesized, as shown in Figure 1f. The crystal structures of the samples are further examined by XRD and the patterns are shown in Figure 2a. For all samples, the diffraction peaks associated with pyrite \(FeS_2\) are observed and can be indexed as a pure cubic phase of \(FeS_2\) (space group \(P1(1)\) with a lattice constant of 5.417 Å, which is consistent with the value given in the standard card (JCPDS no. 65-1211). However, diffraction peaks related to impurities, such as \(Fe_3O_4\) and \(S\), also present in the XRD patterns of samples 1 and 2. For...
those two samples, the reaction time is only 24 h. The appearance of impurities is an indication of inadequate reaction time in this case. The average crystallite size of samples 1 and 2, calculated using size strain plots method, is 24.7 and 26.6 nm, respectively, which is in agreement with the high-magnification SEM images in Figure 2b,c. With the increase of sulphur concentration and reaction time, pyrite FeS$_2$ becomes the dominating materials while the intensity of iron oxide peaks drops dramatically. By increasing the reaction time to 48 h, sulphur impurity cannot be observed anymore. The high-magnification images in Figure 2b,c,d,e,f,g show that as [S]/[Fe] increases, the average size of the nanoparticles increases in addition to the morphology evolution. As sulphur is much less reactive than Fe$^{2+}$, excess sulphur is needed to drive the reaction processes towards formation of S$_2^{2-}$. Therefore, a larger [S]/[Fe] facilitates the reaction and thus formation of larger nanoparticles. In addition, with the increase of sulphur, XRD patterns clearly show that impurities are significantly reduced and nearly disappear for sample 6.

To further investigate the crystal quality of the synthesized nanoparticles, HRTEM measurements were performed on samples 1 and 6 (Figure 3). The SAED of sample 1 shows that the nanoparticles are mainly polycrystalline; single crystalline nanocrystals can also be observed from the HRTEM images (Figure 3a,b). The observed lattice plane spacing of the nanocrystals (2.7 and 5.4 Å) corresponds to the (100) and (200) lattice spacings of pyrite. The presence of an oxide layer may explain the formation of uniform polygonal FeS$_2$ nanoparticles, as the passivation layer suppresses the anisotropic growth of nanocrystals. In agreement with the XRD results, the existence of this iron oxide and FeS$_2$ can be attributed to the lack of S or insufficient reaction time. From the TEM image of sample 6 shown in Figure 3c, the hierarchical particles are mainly made of polygonal nanocrystals due to a sulphur-rich environment. Figure 3d displays the HRTEM image and the corresponding fast Fourier transform (FFT) pattern, which confirms that the FeS$_2$ has single crystalline pyrite structure (the measured lattice spacing is approximately 2.7 Å). The energy dispersive X-ray spectroscopy (EDS) spectrum measured from sample 6 in Figure 3d also confirms that the nanocrystals are made from Fe and S with only tiny amount of O being detected.

Nanogap photodetectors with high-quality FeS$_2$ nanocrystals, schematically shown in Figure 4a, were fabricated by standard photolithography on a p-type silicon substrate covered with a thick layer of thermal oxide (axial direction: <100>, silicon thickness: 500 ± 10 μm, oxidation thickness: 2,000 ± 20 nm, resistivity of silicon: 0.05 Ω cm). A bridge-like electrode was fabricated by depositing a 300-nm-thick Ni film, which is used to form inexpensive ohmic contact for FeS$_2$, using e-beam evaporation. The Ni metal wire that connects the two 500 × 500 μm$^2$ electrode pads was 200 μm

Figure 3 Low-resolution and HRTEM images of samples 1 and 6. The low-resolution (a) and HRTEM images (b) of sample 1. The inset in (a) is the SAED pattern of the nanocrystals. The low-resolution (c) and HRTEM images (d) of sample 6. The inset is the FFT pattern of HRTEM in (d). The EDS spectrum (e) from sample 6.
long and 10 μm wide. Focused ion beam (FIB) was employed to break the wire and create a narrow gap about 200 nm in width and 300 nm in depth. The method was used to ensure that the breaking of Ni wire as well as the insulation SiO₂ layer is not being damaged by FIB milling. FeS₂ nanocrystal ink was sonicated in an ultrasonic bath for over half hour in order to uniformly disperse the nanocrystals. The Ni electrode nanogap was then filled with nanocrystals which were further sulphurized in a furnace at 500°C for 2 h in order to minimize the amount of the unreacted iron oxide and thus the contact resistance between nanocrystals and Ni electrodes. The current-voltage (I-V) characterization of the nanogap device was carried out by an Agilent parameter analyzer (Agilent Technologies, Sta. Clara, CA, USA) under the illumination of an incandescent lamp. The spectral photoresponse was measured using a PV Measurements Inc. QEX 10 system (Boulder, CO, USA) at room temperature. The nanogap between two Ni metal electrodes is about 200 nm (Figure 4b). A layer of nanocrystals covers the nanogap by dip coating (Figure 4c).

Figure 5a shows the I-V characteristics in dark and under illumination. As shown in Figure 5a, despite the small illumination area, the photocurrent is rather high since the nanogap is only 5 μm long and approximately 200 nm wide. The photocurrent obtained by subtracting
In conclusion, single phase pyrite FeS$_2$ nanocrystals were successfully synthesized using a facile hydrothermal approach. The high-quality crystalline pyrite FeS$_2$ nanocrystals were further confirmed by HRTEM and XRD measurements. The sulphur-deficient phase in the inner crystals and the high density of the surface states can make the film more conductive but reduce the photocurrent [6, 25]. Thermodynamically unstable surfaces are generally terminated with sulphur dimers [26, 27]. The sulphur dimers separate the surface from the inner crystals, thus destroying the continuity of the hybridized band. This structure corresponds to a single sulphur layer, making the surface of nanocrystal to act as a layer of FeS. Therefore, a high density of the surface defect states can lead to high current leakage [10, 28]. Therefore, the performance of the detector can be further improved via passivation of the surface states. The photoresponse spectrum of the nanogap detector shows a broadband photoresponse in the UV-vis spectral region as shown in Figure 5b. It is difficult to accurately measure the band gap of the pyrite FeS$_2$ nanocrystals due to the light scattering and Urbach tail of defect states [1]. The spectral coverage can be further tuned to the infrared region through doping.

**Conclusions**

In conclusion, single phase pyrite FeS$_2$ nanocrystals were successfully synthesized using a facile hydrothermal approach. The high-quality crystalline pyrite FeS$_2$ nanocrystals were further confirmed by HRTEM and XRD measurements. The sulphur and iron molar ratio, [S]/[Fe], plays a critical role in nanocrystal quality and morphology. A nanogap pyrite FeS$_2$ nanocrystal photodetector was fabricated using standard photolithography and focused ion beam milling. The nanogap photodetector shows a very high photocurrent in the range of $10^{-2}$ to $1\ \mu$A. By normalizing the photocurrent to the nanogap area, the measured photocurrent is as high as $1$ to $100\ \text{A cm}^{-2}$ under the applied voltage from $0$ to $3\ \text{V}$. Such a high photocurrent implies good crystal quality of the pyrites. To confirm that the photocurrent is generated from the nanocrystals, the nanocrystals were washed away as shown in Figure 4d after the above measurements, and only very few nanoparticles remained in the gap. This time, the $I$-$V$ characteristics measured in dark and under illumination are almost identical and the current is reduced over two orders of magnitude compare to that measured before the removal of nanocrystals (Figure 5a). The resistance derived from the $I$-$V$ characteristics is comparable to that obtained from dip-coated films assembled from pyrite nanocrystals (approximately $10^{-6}\ \text{S cm}^{-1}$) [24]. The sulphur-deficient phase in the inner crystals and the high density of the surface states can make the film more conductive but reduce the photocurrent [6, 25]. Thermodynamically unstable surfaces are generally terminated with sulphur dimers [26, 27]. The sulphur dimers separate the surface from the inner crystals, thus destroying the continuity of the hybridized band. This structure corresponds to a single sulphur layer, making the surface of nanocrystal to act as a layer of FeS. Therefore, a high density of the surface defect states can lead to high current leakage [10, 28]. Therefore, the performance of the detector can be further improved via passivation of the surface states. The photoresponse spectrum of the nanogap detector shows a broadband photoresponse in the UV-vis spectral region as shown in Figure 5b. It is difficult to accurately measure the band gap of the pyrite FeS$_2$ nanocrystals due to the light scattering and Urbach tail of defect states [1]. The spectral coverage can be further tuned to the infrared region through doping.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

SL, JW, and ZMW conceived and designed the experiments. SL, QD, and ZZ synthesized the FeS$_2$ nanocrystals. SL and PY fabricated the devices. SL, JW, and PY performed $I$-$V$ characterization and photoresponse measurements. SL performed UV-vis absorption measurement. SL and HL performed XRD measurements. CL and YC performed TEM measurements. All authors discussed the results and contributed to the writing of the manuscript. All authors read and approved the final manuscript.

**Acknowledgements**

This work was supported in part by the National Basic Research Program (973) of China through Grants 2013CB933301 and the National Natural Science Foundation of China through Grants NSFC-51272038 and NSFC-61204060.

**Author details**

1. State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, People’s Republic of China. 2. Material Sciences and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan.

Received: 29 July 2014 Accepted: 25 September 2014

**References**

1. Pathusrej S, Seefeld S, Benny N, Gibbs M, Law M: Colloidal iron pyrite (Fe$_2$S$_3$) nanocrystal inks for thin-film photovoltaics. J Am Chem Soc 2011, 133:716–719.
2. Caban-Acevedo M, Faber MS, Tan Y, Hammers RJ, Jin S: Synthesis and properties of semiconducting iron pyrite (Fe$_3$S$_4$) nanowires. Nano Lett 2012, 12:1977–1982.
3. Ennaoui A, Fiechter S, Gosławsky H, Tributsch H: Photoactive synthetic polycrystalline pyrite (Fe$_2$S$_3$). J Electrochem Soc 1985, 132:1579–1582. 10.1149/1.2114168.
4. Daiz WC, Newman R: Intrinsic optical absorption in single-crystal germanium and silicon at 77 °K and 300 °K. Phys Rev 1955, 99:1151–1155.
5. Altamart P, Kiesewetter J, Ellmer K, Tributsch H: Specifying targets of future research in photovoltaic devices containing pyrite (FeS$_2$) by numerical modeling. Solar Energy Mater Solar Cells 2002, 71:181–195.
6. Macpherson HA, Stoldt CR: Iron pyrite nanocubes: size and shape considerations for photovoltaic application. ACS Nano 2012, 6:8940–8949.
7. Ennaoui A, Fiechter S, Jaegermann W, Tributsch H: Photooelectrochemistry of highly quantum efficient single-crystalline n-FeS$_2$ (pyrite). J Electrochem Soc 1986, 133:97–106.
8. Ennaoui A, Fiechter S, Tributsch H, Giersig M, Vogel R, Weller H: Photoelectrochemical energy-conversion obtained with ultrathin organometallic-chemical-vapor-deposition layer of FeS$_2$ (pyrite) on TiO$_2$. J Electrochem Soc 1992, 139:2514–2518.
9. Rezig B, Dahman H, Kenzari M: Iron pyrite FeS$_2$ for flexible solar cells. Renew Energy 1992, 2:125–128.
10. Ennaoui A, Fiechter S, Pettenkofer C, Alonsovante N, Buder K, Bronold M, Hopfen C, Tributsch H: Iron disulfide for solar-energy conversion. Solar Energy Mater Solar Cells 1993, 29:289–370.
11. Wang Y, Wang D, Jiang Y, Chen H, Chen C, Ho K, Chou H, Chen C: Fe$_3$S$_4$ nanocrystalline ink as a catalytic electrode for dye-sensitized solar cells. Angew Chem Int Ed 2013, 52:6694–6698.
12. Wu J, Liu L, Liu S, Yu P, Zheng Z, Shafa M, Zhou Z, Li H, Ji H, Wang ZM: High responsivity photocathodes based on iron pyrite nanowires using sulfurization of anodized iron oxide nanotubes. Nano Lett 2014. DOI: http://dx.doi.org/10.1021/nl503059s.
13. Jiao J, Chen L, Kuang D, Gao W, Feng H, Xia J: Synthesis of FeS$_2$ and Co-doped FeS$_2$ films with the aid of supercritical carbon dioxide and their photoelectrochemical properties. RSC Advances 2011, 1:255–261.
14. U.J.L Cabán-Acevedo M, Girard SN, Jin S: High-purity iron pyrite (Fe$_3$S$_4$) nanowires as high-capacity nanostructured cathodes for lithium-ion batteries. Nanoscale 2014, 6:2112–2118.
15. Meester B, Reijnen L, Goossens A, Schoonman J: Synthesis of pyrite (FeS$_2$) thin films by low-pressure MOCVD. Chemical Vapour Deposition 2000, 6:121–128.
16. Morrish R, Silverstein R, Wolden CA: Synthesis of stoichiometric FeS2 through plasma-assisted sulfurization of Fe2O3 nanorods. J Am Chem Soc 2012, 134:17854–17857.

17. Willeke G, Dasbach R, Sailer B, Bucher E: Thin pyrite (FeS2) films prepared by magnetron sputtering. Thin Sol Film 1992, 213:271–276.

18. Wadia C, Wu Y, Gu L, Volkman SK, Guo J, Alivisatos AP: Surfactant-assisted hydrothermal synthesis of single phase pyrite FeS2 nanocrystals. Chem Mater 2009, 21:2568–2570. 10.1021/cm901273v.

19. Golshiekh AM, Huang N, Lim H, Chia C, Harrison I, Muhamad M: One-pot hydrothermal synthesis and characterization of FeS2/pyrite/graphene nanocomposite. Chem Eng J 2013, 218:276–284.

20. Wang D, Wang Q, Wang T: Shape controlled growth of pyrite FeS2 crystallites via a polymer-assisted hydrothermal route. CrystEngComm 2010, 12:3797–3805.

21. Wang D, Wang Q, Wang T: Controlled growth of pyrite FeS2 crystallites by a facile surfactant-assisted solvothermal method. CrystEngComm 2010, 12:755–761.

22. Zhu L, Richardson B, Tartumihardja J, Yu Q: Controlling morphology and phase of pyrite FeS2 hierarchical particles via the combination of structure-direction and chelating agents. CrystEngComm 2012, 14:4188–4195.

23. Alfonso DR: Computational investigation of FeS2 surfaces and prediction of effects of sulfur environment on stabilities. J Phys Chem C 2010, 114:8971–8980.

24. Bi Y, Yuan Y, Extrom CL, Danveau SA, Huang J: Air stable, photosensitive, phase pure iron pyrite nanocrystal thin films for photovoltaic application. Nano Lett 2011, 11:4953–4957.

25. Hung A, Muscat J, Yarovsky I, Russo SP: Density-functional theory studies of pyrite FeS2(100) and (110) surfaces. Surf Sci 2002, 513:511–524.

26. Yan Y, Jones K, Jiang C, Wu X, Nouri R, Al-Jassim M: Understanding the defect physics in polycrystalline photovoltaic materials. Phys B Condens Matter 2007, 401:35–32.

27. Murphy R, Strongin DR: Surface reactivity of pyrite and related sulfides. Surf Sci Rep 2009, 64:1–45.

28. Birkholz M, Fiechter S, Hartmann A, Tributsch H: Sulfur deficiency in iron pyrite (FeS2) and its consequences for band-structure models. Phys Rev B 1991, 43:11926.