Solution-Processable Pyrite FeS₂ Nanocrystals for the Fabrication of Heterojunction Photodiodes with Visible to NIR Photodetection

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In the last decade, solution-processed thin films consisting of semiconductor nanocrystals have demonstrated excellent optoelectronic performance with unique advantages of tunable absorption characteristics by the quantum confinement effect1–2 and enabling large-area low-cost fabrications.3–8 Among them, cadmium and lead chalcogenide (CdX and PbX) nanocrystals exhibited excellent optoelectronic performance in the harvesting of photons ranging from visible to infrared wavelengths.3,9–11 However, the replacement of the toxic precursor, such as Cd and Pb, with more environmentally friendly materials has received considerable attention.12 Pyrite iron disulfide (FeS₂) NCs has recently become a promising candidate in this field because it has a large optical absorption coefficient (>10⁵ cm⁻¹) and a narrow band gap of 0.95 eV and, most importantly, the advantages of earth-abundance and non-toxicity.13–15 Colloidal pyrite nanocrystals (NCs) were recently synthesized,16 providing excellent potential for developing low-cost fabrications of photovoltaic devices by solution-processable pyrite NC ink. Previously, we have demonstrated the polymer (P3HT)/FeS₂ NC hybrid device with an extended red light harvesting of up to 900 nm resulting from the pyrite NCs in the organic/inorganic hybrid system, compared to a typical absorption edge 650 nm of a pristine P3HT.17 Recently, several efforts have been made in the syntheses and characterizations of FeS₂ NC thin film.18,19 However, the observation of optimal diode behavior with high rectification of the device based on the pristine FeS₂ NC thin film is limited because of a large leakage current,19 which substantially limits its potential optoelectronic applications. This study demonstrates a pyrite NCs based heterojunction photodiode with a device structure of ITO/ZnO/FeS₂ NC/MoO₃/Au. The formation of FeS₂ NC heterojunction structure with satisfied band alignment by the insertion of metal oxide layers effectively suppresses the leakage current and reduces the serial resistance of the device, providing the photodiode with a high on/off ratio of up to 8000 at −1 V under AM1.5 illumination (100 mW/cm²), and promising near infrared (NIR) photoresponse of up to 1150 nm. The result of using the earth-abundant and non-toxic nanocrystal pyrite (FeS₂)/metal oxides heterojunction photodiode device indicates its potential applications in infrared photodetectors and has provided a crucial step toward the success in producing colloidal pyrite NC thin films for low-cost and large-area photovoltaics.

The FeS₂ NCs were prepared by wet solution-phased chemical syntheses with a number of modifications.21 Figure 1(a) shows the transmission electron microscopy (TEM) image of well-dispersed FeS₂ NCs with an average diameter of 15 ± 3 nm. The high resolution TEM (HRTEM) image in Figure 1(b) shows the clear lattice fringes of the FeS₂ NCs with a lattice spacing of 0.27 nm, matching the (200) plane of pyrite. The X-ray diffraction (XRD) pattern of the FeS₂ NCs is also shown in Figure 1(c), and the 2θ peaks can be indexed to the (111), (200), (211), (220), and (311) planes of FeS₂, which are consistent with those of a standard FeS₂ pyrite (JCPDS no. 42-1340), indicating that the NCs have a single-phased pyrite structure. Figure 1(d) demonstrates the UV–Vis–NIR absorption spectrum of FeS₂ NC solution in chloroform and the absorption spectrum of FeS₂ NCs is tailored to near IR wavelengths ranging from 400 nm to 1300 nm. The inset of Figure 1(d) shows the photograph image of the FeS₂ NC solution, which was utilized to fabricate FeS₂ NC films and devices by spin-casting, as discussed in the following sections.

First, we spin-coated the FeS₂ NC solution (80 mg/mL) onto glass substrates at 3000 rpm for 60 s to make the FeS₂ NC thin films. Because the as-synthesized FeS₂ NCs were usually passivated with ~2.5 nm long alkyl ligands (OA and OLA), which may prevent close nanocrystal packing of FeS₂ thin films and thus, impede charge transport.22 To remove the long chain ligands from NC surfaces and reduce interparticle spaces of NCs, the FeS₂ NC films were subsequently dipped in ethanol-diethanolamine (EDTA) (2 mM) in acetonitrile solution for 30 s, followed by a rinse with pure acetonitrile. Figure 2(a) shows FTIR spectra of FeS₂ NC thin films with and without EDT treatment. The FTIR result indicates that the FeS₂ NC thin film without EDT treatment has a strong N-H vibration peak at 3400 cm⁻¹, C-H stretching peaks at 2849 and 2918 cm⁻¹, and a -C=C stretching peak at 1640 cm⁻¹, which are typical characteristics of the amino group and long alkyl chain in the
capped ligands.\cite{23,24} When the FeS\textsubscript{2} NC thin film was treated with EDT, the IR signatures of capped ligands with long alkyl chains disappeared and were replaced by the EDT ligands with the C-S stretch peaks at 675, and 680 cm\textsuperscript{-1}.\cite{25} Therefore, we compared the conductivities of FeS\textsubscript{2} NC thin films with and without EDT treatment by depositing the inter-gold electrodes with a 50 \(\mu\)m separation distance on the FeS\textsubscript{2} NC thin films (Figure 2(b)). A nearly 20-fold increase in the conductivity \(5.4 \times 10^{-3}\) S cm\textsuperscript{-1} of the FeS\textsubscript{2} NC thin film with EDT treatment was obtained, as compared to \(2.6 \times 10^{-4}\) S cm\textsuperscript{-1} of the film without treatment. The increased conductivity caused by the removal of long alkyl ligands was not so high as compared to those in other NC systems using EDT treatment. The possible reason could be due to that the surface of FeS\textsubscript{2} nanocrystals may be not well-passivated by long-chain molecules. Figures 2(c) and (d) show the top and cross-sectional scanning electron microscopy (SEM) images of the densely packed FeS\textsubscript{2} NC thin film after EDT treatment by using Hall measurement. A p-type transport behavior of the FeS\textsubscript{2} NC thin film was obtained which differs from a typical n-type semiconductor of bulk pyrite.\cite{14} Subsequently, we performed a Riken Keiki AC-2 photoelectron emission and Tauc plot\cite{26} measurements to determine the valence band maximum (VBM) and conduction band minimum (CBM) of a FeS\textsubscript{2} NC thin film, as shown in Figure 3(a). The VBM of the FeS\textsubscript{2} NC thin film is \(-4.95 \pm 0.1\) eV below the vacuum level, and a small band gap of 1.0 \(\pm 0.1\) eV was obtained from the Tauc plot\cite{26} using the relation \(\alpha h \nu \propto (h \nu - E_g)^2\), where \(\alpha\) is the absorption coefficient, \(h \nu\) is the photon energy, and \(E_g\) is the optical gap. Based on the intrinsic characteristics of a p-type semiconductor with a lower bandgap of the FeS\textsubscript{2} NC thin film, we propose a device structure consisting of ITO/ZnO/FeS\textsubscript{2} NC/MoO\textsubscript{3}/Au, as shown in Figure 3(b), for the fabrication of a FeS\textsubscript{2} NC based photodiode. Figure 3(c) shows the relevant energetics of each component obtained from related literature\cite{27} in the ITO/ZnO/FeS\textsubscript{2} NC/MoO\textsubscript{3}/Au device. The ZnO thin film, which was prepared by using RF sputtering on ITO is an intrinsic n-type semiconductor,\cite{28} and the formation of ZnO/FeS\textsubscript{2} NC np heterojunctions with a satisfied energy-level alignment was expected to assist charge separation of photogenerated carriers. The FeS\textsubscript{2} NC active layer with an optimal thickness of 100 nm was deposited onto ITO/ZnO substrates by spin coating using the FeS\textsubscript{2} NCs solution (80 mg/mL) at 3000 rpm for 60 s. Before the deposition of the top Au electrode, a high work function molybdenum (MoO\textsubscript{3}) layer was inserted between the photoactive layer and anode metal for the function of hole-transporting or electron-blocking.\cite{29,30} Several thicknesses of ZnO and MoO\textsubscript{3} layers were used to optimize the device performance (see Supporting Information). The optimal thicknesses of ZnO and MoO\textsubscript{3} layers were 80 nm and 15 nm, respectively. The cross sectional TEM image of the device structure consisting of ITO/ZnO/FeS\textsubscript{2} NC/MoO\textsubscript{3}/Au is shown in Figure 3(d), in which five distinct layers of ITO bottom electrode, ZnO, FeS\textsubscript{2} NCs, MoO\textsubscript{3}, ITO, and ZnO.
and Au top electrode can be clearly distinguished. The TEM sample was prepared using the focused ion beam (FIB) technique. A layer of platinum deposited by a FIB instrument prior to the start of milling was also used to prevent top-surface damage.

Figures 4(a) and (b) show the current-voltage characteristics of the FeS$_2$ NC based heterojunction photodiodes with and without inserting the metal oxide layers, measured in the dark and under illumination, respectively. A linear current-voltage curve without any rectification was observed for the device without insertion of any metal oxide layer (ITO/FeS$_2$ NC/Au). The inset showed the photograph of real device. c) The energy level of ITO/FeS$_2$ NC/MoO$_3$/Au device. d) The cross sectional TEM image of the device structure consisting of ITO/ZnO/FeS$_2$ NC/MoO$_3$/Au.

and dark current of the ITO/ZnO/FeS$_2$ NC/MoO$_3$/Au device exceeded 8000 at −1 V, exhibiting a considerable enhancement in photosensitivity as compared to that of only 200 for the device with a ITO/ZnO/FeS$_2$ NC/Au structure. Figure 5 shows the external quantum efficiencies (EQEs) with a spectral range from 450 to 1150 nm for the photodiode based on the ITO/ZnO/FeS$_2$ NC/MoO$_3$/Au device under various bias conditions. The number of free carriers at the device can be further enhanced by applying a reverse bias to the junction, which may assist the separation of photogenerated electron-hole pairs. The absorptions of ZnO and MoO$_3$ are negligible at wavelengths longer than 450 nm, and all absorptions at these wavelengths are solely attributed to FeS$_2$ NCs. The EQE spectra of the ITO/ZnO/FeS$_2$ NC/MoO$_3$/Au device exhibited excellent consistence with the absorption spectrum of the FeS$_2$ NCs with spectral response ranging from visible to near IR wavelengths. The harvesting of extended near IR photogenerated carriers of the FeS$_2$ NC based device demonstrated excellent potential in the applications of infrared optoelectronics. Figure 6 presents the dependence of photocurrent and external quantum efficiency of the device operated at −1 V bias as a function of incident power under excitation with an 808 nm laser. The EQE at a low incident power of 12.5 mW is approximately 4.5%, and reduced to 1% at an incident power lower of 125 mW. The photocurrent of the device did not exhibit a linear increase with incident power because additional bimolecular recombination between free holes and electrons occurs when more photons are absorbed at higher powers,[35] which may be attributed to inefficient carrier transport and collection of the FeS$_2$ NC thin film because of trap states.[20,36]

To further understand carrier transport and collection of the FeS$_2$ NC heterojunction photodiode, we measured the transient photocurrent decay of the ITO/ZnO/FeS$_2$ NC/MoO$_3$/Au device under pulsed laser illumination (λ = 532 nm) measured at −1 V. The device demonstrated a slow photocurrent decay with a long lifetime of −550 μs, as shown in Figure 7, suggesting that photogenerated electrons or holes may be confined in the deeper trap states.[20,37] The slow photocurrent transient time in the current FeS$_2$ NC based device suggests that a large number of trap states existed in the middle of the band gap,[37] which may explain their lower leakage current and absence of an open circuit voltage.[20] The main limiting factor in the bulk pyrite solar cell is its high dark leakage current, which leads to a small open circuit voltage because of the iron pyrite phase impurities and large density of surface states[20] caused by a sulfur deficiency. This effect may be more crucial for devices based on FeS$_2$ NCs because of the higher surface to volume ratios with respect to the bulk counterpart. We analyzed the sulfur deficiency of FeS$_2$ NCs was by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The ratio of Fe to S in FeS$_2$ NC is 1:1.91 and the sulfur deficiency is approximately 4.5% higher than −1.92-1.94% for a
The further improvement of the crystallinity and surface qualities of FeS$_2$ NCs is crucial for improving the response time of a photodetector or making an efficient solar cell device possible.

In summary, we demonstrated a photodiode device based on pyrite FeS$_2$ NCs/metal oxide heterojunctions with an ITO/ZnO/FeS$_2$ NC/MoO$_3$/Au structure. This device exhibits an excellent photoresponse with a high photocurrent/dark current ratio, and has a spectral response ranging from visible to NIR wavelengths of up to 1150 nm. The promising optoelectronic properties of non-toxic, earth-abundant, and solution processable FeS$_2$ NCs offers considerable potential for the development of large-area and low cost photodetectors or solar cells.

Figure 6. Dependence of photocurrent and external quantum efficiency of the FeS$_2$ NC based device operated at $-1$ V bias as a function of incident power under excitation with an 808 nm laser.
Experimental Section

Fabrication of iron pyrite FeS$_2$ NCs: In brief, FeCl$_3$ (189 mg), 1,2-hexadecanediol (384 mg), octadecene (30 mL), and oleic acid (OA) (12 mL) were mixed and subsequently reacted under N$_2$ gas at 100 °C for 1 h to form the Fe–oleic acid complex. Subsequently, oleylamine (OLA) (15 mL) solution of sulfur (576 mg) was quickly injected into the solution. The resulting solution was heated to 240 °C and maintained for 1 h. After the solution was cooled to room temperature, a large amount of methanol was added to precipitate as-grown FeS$_2$ NCs, followed by centrifugation. To obtain the FeS$_2$ NC solution with high solubility for film depositions, the as-grown Fe$_2$NCs were further purified by washing with ethanol, ethanol/chloroform (10/1 vol.), and methanol/chloroform (10/1 vol.). Subsequently, the larger NCs and any residual side products from the NCs suspension were removed by addition of chloroform, followed by centrifugation at 3500 rpm for 10 min. The resulting FeS$_2$ NC solution with high solubility and purification can be obtained.

Fabrications of FeS$_2$ NC heterojunction photodiode devices: First, the ZnO thin film was prepared by using RF sputtering on ITO to form an ITO/ZnO substrate. By controlling sputtering time, the ZnO thin films with thickness ∼40 nm and ∼80 nm were obtained. Before depositing FeS$_2$ NC thin films, the as-grown FeS$_2$ NCs were further purified by washing with ethanol, ethanol/chloroform (10/1 vol.) and methanol/chloroform (10/1 vol.), respectively. Subsequently, the larger NCs and any residual side products from the NCs suspension were removed by addition of chloroform followed by centrifugation at 3500 rpm for 10 min. The resulting FeS$_2$ NC solution with high solubility and purification can be obtained, which is required for deposition of the FeS$_2$ NC thin films with good quality. Next, we spin-coated the FeS$_2$ NC solution (80 mg/mL) onto ITO/ZnO substrates at 3000 rpm for 60 s to make the FeS$_2$ NC thin films. After deposition, the FeS$_2$ NC thin films were dipped in ethanedithiol (EDT) (2 mM) in acetonitrile solution for 30 s, followed by a rinse with pure acetone to remove the long chain ligands from NC surfaces. Finally, we deposited a high work function molybdenum disulfide (MoS$_2$) layer with various thicknesses (5, 15, 25 and 50 nm) and top Au electrode (100 nm) by using thermal evaporation process.

Characterization: High-resolution Transmission Electron Microscopy (TEM) (HR-TEM) images were obtained using a Philips Technai G2 (FEI-TEM) microscopy operating at 200 kV. X-ray diffraction (XRD) measurements were performed by Bruker D8 tools advance, operating with Cu Kα radiation (λ = 1.5406 Å) generated at 40 kV and 40 mA. Scans were done at 0.01° S−1 for 2θ value between 20° and 60°. UV/Vis/NIR absorption spectra were obtained using a Cary 500 UV/Vis/NIR spectrophotometer. FTIR spectra were obtained using a Perkin Elmer spectra 500. Samples were prepared on KBr substrates. Hall measurement was performed on the FeS$_2$ NC thin films by using an ECOPIA HMS-3000 Hall measurement system. Current-voltage measurements (Keithley 2410 source meter) were performed under 10−3 torr vacuum and measured under the simulated AM1.5 irradiation (100 mW/cm², Newport Inc.). The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to measure the atomic ratio of Fe:S NCs. The external quantum efficiencies (EQEs) were measured by using a Xe lamp in combination with a monochromator (Oriel Inc.). A UV filter was also used to avoid the overtones of the monochromator’s grating from illuminating the specimen. The near infrared (NIR) excitation was provided by an 808 nm continuous semiconductor laser, which only allowed the photoexcitation of FeS$_2$ NCs. Transient photocurrent measurements were performed by a frequency-doubled Nd:YAG pulsed laser (λ = 532 nm and pulse width ~5 ns) and the signals were recorded by a digital oscilloscope (Tetronix TDS5028B). The film thickness was measured by means of the Veeco M6 surface profiler.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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