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Surface thermal stability of iron pyrite nanocrystals: Role of capping ligands

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ABSTRACT

Iron pyrite (FeS₂) is a promising photovoltaic absorber material with a high natural abundance and low cost, but surface defects and low photoresponse inhibit sunlight energy conversion. The surface stability of pyrite FeS₂ nanocrystals synthesized in oleylamine (OLA) with trioctylphosphine oxide (TOPO) as an additional capping ligand was investigated using Fourier transform infrared spectroscopy, Raman spectroscopy and X-ray diffraction. Tunable laser exposure during Raman spectroscopy measurement was developed for convenient and systematic evaluation of the stability of FeS₂ nanocrystals. The surface stability of 100–200 nm diameter cubic nanocrystals with long-chain (OLA, TOPO) or small-molecule (pyridine) capping ligands was evaluated after high-intensity laser exposure as well as after thermal annealing in air and N₂. While increasing surface coverage with OLA and TOPO capping ligands provided additional protection against oxidation, FeS₂ nanocrystals capped with pyridine showed good stability at temperatures up to 200 °C in air and 400 °C in N₂. These results provide greater understanding of the processing of nanocrystal-based iron pyrite thin films for photovoltaic applications.

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1. Introduction

Due to its high natural abundance, nontoxicity, low cost and the high absorption coefficient of $1\text{--}5 \times 10^5 \text{ cm}^{-1}$ [1,2], an attractive application of iron pyrite (FeS₂) is as a photovoltaic (PV) absorber material. The estimated highest attainable efficiency of pyrite PV energy conversion is as high as that of single crystal silicon solar cells [3]. This prospectus is further promoted with the recent development of highly crystalline, phase-pure iron pyrite nanocrystal (NC) inks that enable large throughput and low cost fabrication of solar panels using established solution-based techniques [4–11]. Despite the huge promise iron pyrite holds, this material has not yet been developed into efficient PV devices. The highest pyrite PV device efficiency has been obtained in a photoelectrochemical cell with a reported short circuit current (I_{sc}) of 42 mA/cm², open circuit voltage (V_{oc}) of 187 mV, and fill factor (FF) of 50%, yielding an efficiency of 2.8% [2,12]. The limiting factor for high efficiency is the high dark current that leads to the very small V_{oc} , less than 20% of its bandgap (0.95 eV) [2,12–16].

Natural bulk pyrite and synthetic thin films generally have common traits of high carrier concentrations in excess of 10^{19} cm^{-3} and strong sub-bandgap absorption [17–19]. Photoresponse (e.g., photoconductivity) of these grown films has barely been observed at room temperature [20,21]. There are two types of possible factors that lead to the high dark carrier concentrations in iron pyrite: impurity phases and surface

defects. Previously it was believed that impurity phases such as marcasite and hexagonal troilite have much smaller bandgaps (0.34 eV for marcasite and 0.04 eV for troilite) [22]. More recently Law et al. declared that marcasite had band gap comparable to pyrite [23]. They also suggested that the high conductivity and low mobility of pyrite films might be caused by nanoscale amorphous impurities and surface effect and excluded the intrinsic bulk defects [23]. The surfaces of iron pyrite are terminated with S dimmers, that tend to segregate to the surface and cause the vanishing of the hybridized band at the top of the Fe layer, making the surface effectively similar to 1S terminated troilite or FeS_{2-x}. This results in large density-of-defect states in the middle of pyrite bandgap that reduced the bandgap energy at the surface to nearly zero [5,24]. Pyrite films may be heavily hole doped due to a hole-rich layer formed at the surface resulted from a large concentration of surface states located near the valence band edge and even in pyrite single crystals there might exist an n-type bulk layer and a p-type surface layer according to recent experimental work [23]. Although not conclusive, more and more evidence shows that the surface defects dominate the generation of large density of background charge density. It is suggested by theoretical calculations that FeS₂ is actually a stoichiometric compound because of the high energy required to generate S vacancies in bulk FeS₂, and thus, bulk defects are unlikely to cause the large carrier concentrations [19]. Instead of bulk S vacancies, the presence of high-density S vacancies at the surface has been calculated to be favorable in CoS₂ which has the same structure with FeS₂ [25,26]. Recent high resolution transmission electron microscopy studies of sulfurized pyrite films clearly revealed a S-deficient amorphous surface

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despite annealing in a very S-rich environment [19]. The pyrite crystal surfaces suffer incomplete coordination of iron by S due to the loss of S from the surface [27].

Using iron pyrite NCs to fabricate the photovoltaic films avoids the formation of impurity phases as proven by their excellent phase purity and crystallinity [4,5,22,28]. However, the significantly larger surface-to-volume ratio of NCs is expected to bring challenges in maintaining stable iron pyrite surfaces. To our surprise, NC-based FeS₂ films show better stability than those made by other methods as indicated by the observed room temperature photoresponse in iron pyrite films [5]. The surface capping ligands on these NCs are proposed to play the major role in stabilizing the NC surface. Introducing surfactant capping ligands to stabilize NC surfaces is a commonly employed strategy in NC synthesis. The situation is especially complex for FeS₂ NCs because in addition to size and shape, the crystallinity and phase purity [22], colloidal stability against aggregation [29,30], stability of NC films [5], and optoelectronic properties [5,31,32], all have showed strong dependence on the surfactants used during NC synthesis or post-treatment.

In this paper, the function of ligands in stabilizing FeS₂ NC surface was studied by monitoring the thermal stability of FeS₂ NCs in air and N₂ after removing long alkane ligands by solvent wash, or exchanging the long ligand with short ligands of pyridine. The role of ligands in the oxidization behavior of FeS₂ NCs capped with different length ligands upon high-intensity laser irradiation and thermal annealing was investigated systematically using Raman spectroscopy and X-ray diffraction (XRD). Efforts were focused on determining the importance of the nature of the capping ligands, how they protect the thin films, and how these issues impact future device fabrication and processing.

2. Experimental details

2.1. Synthesis of FeS₂ NCs

Anhydrous iron (II) chloride (99.9%), sulfur (98%), trioctylphosphine oxide (TOPO), oleylamine (OLA), chloroform and methanol were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. Cubic shaped FeS₂ NCs were synthesized by the hot injection method reported previously with minor modifications [5]. In brief, a mixture containing 0.5 mmol of FeCl₂, 0.3 mmol of TOPO and 10 ml of OLA was heated to 170 °C and kept at that temperature for 2 h under N₂ to form Fe-surfactant precursor species. A solution of 3 mmol sulfur in 5 ml OLA was injected quickly into the Fe precursor and then the system was immediately heated to 220 °C and kept at that temperature for 2 h to complete the growth of the iron pyrite NCs. The reaction was terminated by removing the heating mantle and cooled down to room temperature naturally.

The FeS₂ NCs were precipitated by adding excess methanol and isolated by centrifugation at 3000 rpm for 10 min. For selected experiments, these as-prepared NCs were washed with chloroform/methanol, sonicated, and isolated by centrifugation to remove the excess of OLA and TOPO. These NCs were denoted as FeS₂-OLA/TOPO. To prepare pyridine-capped FeS₂ NCs (denoted as FeS₂-pyridine), the FeS₂-OLA/TOPO NCs were dispersed in 10 ml of pyridine, sonicated for 10 min and isolated by centrifugation. This process was repeated one more time to ensure the maximum exchange of the long-chain OLA and TOPO ligands by pyridine. Pyridine was chosen for ligand exchange because pyridine capped NCs are still dispersible in organic solvents, which are superior to ethanedithiol that causes aggregation of NCs and can only be applied for post-treatment of NC films. Both FeS₂-OLA/TOPO and FeS₂-pyridine NC samples were dispersed in chloroform and kept in a N₂ filled glove box for storage prior to further characterization.

NC-based thin films were formed on 1 × 1 cm² silicon wafers by drop casting from FeS₂ NC/chloroform dispersions. These films were annealed on a hot plate in air or in N₂ at different temperatures for 20 min, respectively. All of these FeS₂ films were stored in a N₂ filled glove box before

XRD and Raman measurements to avoid the unintentional gradual oxidation or decomposition of the FeS₂ NCs in air.

2.2. Characterization

The presence and exchange of capping ligands on FeS₂ NCs were identified by Fourier transform infrared spectra (FTIR) using a Nicolet Avatar spectrometer. A drop of the FeS₂ NC/chloroform dispersion was mixed with dry KBr powder (FT-IR grade, Alrich), and the solvent was allowed to evaporate. This mixture was ground and pressed into pellets for FTIR measurements. Morphology and size of the NCs were characterized by scanning electron microscopy (SEM) using a Quanta 200 FEG SEM at high vacuum mode with the operating voltage of 15 kV. The thermal stability of FeS₂ samples was investigated by Confocal Raman spectroscopy (RenishawinVia) with a 514 nm laser source. To investigate the effect of light intensity on the oxidation of the FeS₂ NCs, lasers with power of 1.5, 7.5 and 15 mW were focused on sample spots of approximately 25 μm² with the irradiation time of 10 s. These laser powers corresponded to power intensities of 6.0 × 10⁶, 3.0 × 10⁷ and 6.0 × 10⁷ mW/cm², respectively. The laser penetration depth is ~60 nm estimated by 1/α, where α is the absorption coefficient (~1.7 × 10⁵ cm⁻¹ at 514 nm) of the FeS₂ NCs [5,33]. Powder X-ray diffraction (XRD) patterns of the FeS₂ NC films were collected on a Rigaku D/Max-B diffractometer with Bragg–Brentano parafocusing geometry (Co Kα, λ = 1.7902 Å) with X-ray tube operating voltage of 40 kV and current of 30 mA.

3. Results and discussion

3.1. Ligand exchange studies

SEM images of the as-prepared pyrite FeS₂ NCs show that they had cubic shapes and diameters ranging between 100 and 200 nm (Fig. 1b). FTIR spectroscopy was used to identify the presence of OLA and TOPO capping ligands on the FeS₂ NCs (Fig. 1a). FTIR spectra of pure OLA and TOPO are also shown for comparison. The IR spectrum of OLA shows peaks at 2921 and 2852 cm⁻¹ that correspond to the asymmetric (ν₂(-CH₂-)) and symmetric (ν₃(-CH₂-)) stretching modes, respectively, of the oleyl groups. The peak at 3315 cm⁻¹ is due to the ν(N-H) stretching of the -NH₂ group. There is a small peak at approximately 1650 cm⁻¹ due to ν(C=C) stretching in OLA molecules [34]. The peaks in the region below 1650 cm⁻¹ correspond to complex combinations of the ν(C-C) stretching, CH₂ deformations and other motions [34]. All of these OLA peaks were seen in the FeS₂-OLA/TOPO NC spectrum (Fig. 1a, green curve) indicating the existence of this long-chain ligand on the NCs after washing.

For TOPO, there are also two peaks around 2900 cm⁻¹ assigned to the stretching mode of -CH₂ in the octyl group. Characteristic vibration bands of P=O and P-C groups in TOPO are observed at 1149 cm⁻¹ and 1411 cm⁻¹, respectively. The IR spectrum of the FeS₂-OLA/TOPO NCs clearly shows peaks that indicate the presence of OLA. While many of the TOPO P=O and P-C vibrational frequencies match those of OLA peaks, the presence of at least a small amount of TOPO is indicated in the 650–1250 cm⁻¹ region of the spectrum. This evidence indicates that OLA and TOPO capping ligands are present on the FeS₂ NCs after three washing cycles with chloroform/methanol. After ligand exchange with pyridine, the FeS₂-pyridine NC IR spectrum (blue curve in Fig. 1a) exhibits very little signal from OLA and TOPO, indicating the removal of most of the long-chain ligands.

3.2. Stability study of the FeS₂ NCs by Raman spectroscopy

3.2.1. Thermal stability of FeS₂-OLA/TOPO NCs

Raman spectroscopy was employed to investigate the thermal stability and surface chemistry of the FeS₂ NC samples. Fig. 2 shows Raman spectra of FeS₂-OLA/TOPO NC samples after exposure to various

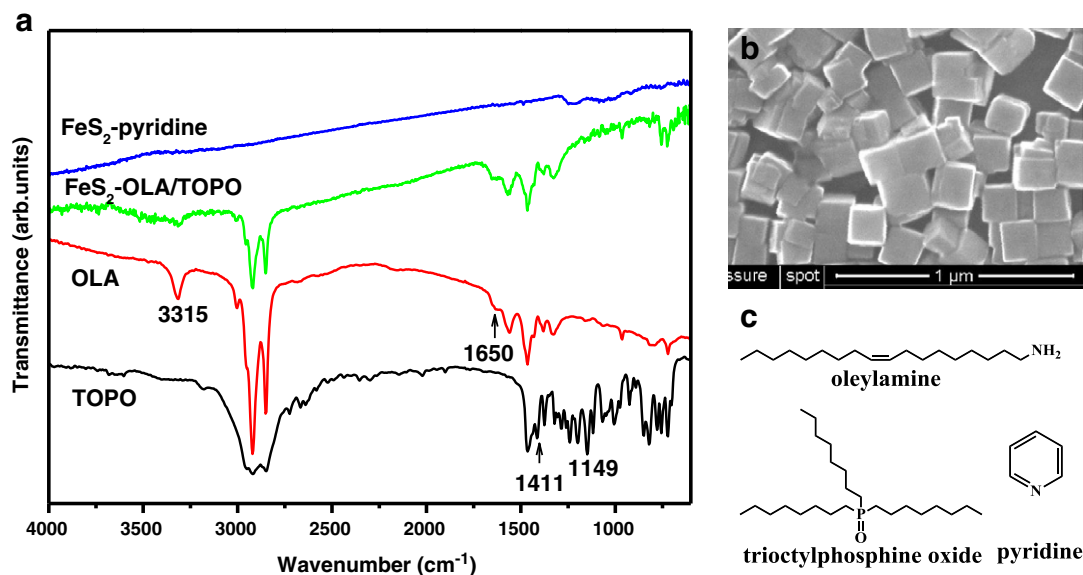


Fig. 1. (a) FTIR spectra of TOPO, OLA, as-prepared FeS₂-OLA/TOPO NCs, and FeS₂-pyridine NCs after ligand exchange. (b) SEM images of the cubic shaped FeS₂ NCs. (c) Chemical structures of the capping ligands used. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

laser power levels. After 1.5 mW laser exposure, the sample maintained the pure iron pyrite phase. The 338 and 371 cm⁻¹ peaks are assigned to the E_g and A_g modes, respectively, of pyrite-phase FeS₂. Following exposure to 5 times higher power laser (7.5 mW) gave stronger Raman signals while did not result in the formation of other noticeable phases (red curve in Fig. 2). Further increase in the laser power to 10 times higher (15 mW), two new peaks at 215 and 278 cm⁻¹ appeared and are assigned to a lattice mode and the symmetric stretching mode, respectively, of poorly crystallized or nanophase FeS [35–37]. This result indicates that the FeS₂ NCs were partially decomposed. We expect that the surface of the FeS₂ NCs under high power (15 mW) laser had undergone the following rapid decomposition reaction [5,24]:



The laser powers employed, 6.0×10^6 , 3.0×10^7 and 6.0×10^7 mW/cm², respectively, are far higher than that of AM1.5 simulated sunlight (100 mW/cm²). Exposure to this high intensity laser is expected to result

in a significant heat accumulation in the small measured area and subsequently accelerate the surface decomposition of the pyrite NCs. It is noted that laser annealing or high intensity flash light is broadly used to melt reformed NCs for polycrystalline solar cell fabrication, the understanding of stability of the NCs upon laser annealing is thus practically important.

3.2.2. Improved surface stability of FeS₂ NCs by long-chain capping ligands

After knowing the effect of laser power on the surface decomposition of the FeS₂ NCs, we continued to use the highest power (15 mW) to investigate their stability after multiple cycles washing to remove capping ligands gradually. As shown in Fig. 3, the thermal stability of FeS₂ samples decreased as the long chain ligands TOPO and OLA were partially removed. FeS₂ NCs easily underwent decomposition after washing three times when the greatest portion of the FeS₂ NC surface was exposed to strong laser irradiation in air. The observed improved stability by these capping ligands demonstrates the important role of the TOPO and OLA ligands against decomposition of the FeS₂ NCs.

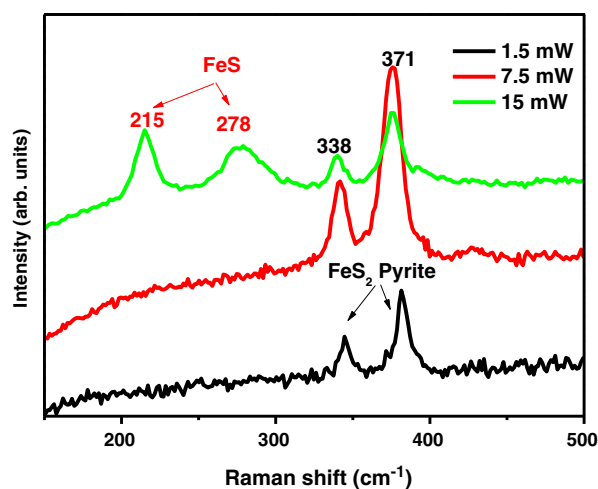


Fig. 2. Raman spectra of the as-prepared FeS₂-OLA/TOPO NCs after exposure to laser power of 1.5 (black), 7.5 (red) and 15 mW (green), approximately corresponding to power intensities of 6.0×10^6 , 3.0×10^7 and 6.0×10^7 mW/cm², respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

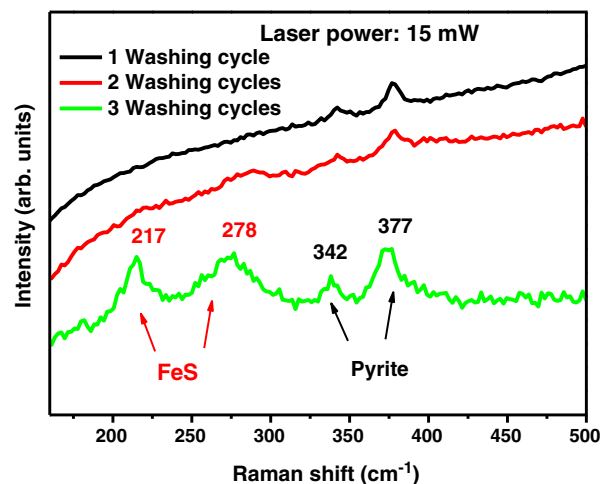


Fig. 3. Raman spectra of the as-prepared FeS₂ NCs capped with OLA and TOPO and different degrees of washing with chloroform/methanol after exposure to 15 mW laser.

3.2.3. Surface stability of FeS₂ NCs capped with a small-molecule ligand

Ligand exchange with small molecules, such as pyridine and ethanedithiol, to replace longer surfactant ligands such as OLA and TOPO is a commonly employed strategy in fabricating NC devices to enhance the electronic coupling between NCs [32]. The effect of short chain (pyridine) and long chain (OLA:TOPO) capping ligands on the stability was investigated by Raman spectroscopy as shown in Fig. 4. Both OLA:TOPO capped and pyridine capped FeS₂ NC films were found to be stable under the exposure to 1.5 mW laser power. However, under higher laser power of 7.5 mW, the emergence of the 216 and 276 cm⁻¹ Raman peaks of FeS indicates that the pyridine FeS₂ NCs were partially decomposed (blue curve), while the OLA:TOPO capped FeS₂ NC films did not show noticeable decomposition (green curve). The long chain ligands of OLA and TOPO can more effectively protect the FeS₂ NC surface by forming a closely coordinated shell on the NC surface. Nevertheless, pyridine-capped FeS₂ NCs showed good stability against oxidation upon exposure to 1.5 mW laser power. These NCs are still relatively stable in air under light illumination that is much higher than sunlight.

Teo et al. investigated the structural conversion of FeS and CoSe to pyrite phase FeS₂ and CoSe₂ induced by high energy laser during Raman measurement [33]. Their work demonstrated that controllable laser irradiation is an effective method for in situ investigation of phase change of metal chalcogenide thin films or powders and gives instructive information on how to avoid laser-induced structural changes and oxidation of metal chalcogenide materials (without surface ligand protection). The situation is more complex in FeS₂ NCs considering the small size and high surface-to-volume ratio, where surface protection of the NCs played a key role. In the present work, we used iron pyrite NCs capped with different kinds of ligands and investigated the roles of laser power, surface coverage of the NCs, and chain length of the capping ligands in the effective protection of the iron pyrite NCs. The maximum laser intensity in the present work (6.0 × 10⁷ mW/cm²) is coincidentally the same with that used in Teo's work [33]. The effect of ligand protection against decomposition is observed upon different laser intensities and the FeS₂ NCs show good stability with lower laser intensities even without long chain ligand protection.

3.2.4. Thermal stability of FeS₂ NCs in air and in N₂

In addition, we also used Raman spectroscopy to investigate the oxidation process of thermally annealed FeS₂ NCs in N₂ and air

atmospheres. A laser power of 1.5 mW was chosen to avoid additional reactions caused by laser heating during Raman measurements. As shown in Fig. 5, Raman spectra of the TOPO:OLA-capped FeS₂ NCs did not show any noticeable change after annealing in N₂ at 400 °C. Annealing in air at 200 °C for 20 min also did not result in noticeable oxidation. This lends promise to the idea of oxygen doping of pyrite that has been proposed to increase its bandgap for improved PV performance [38]. A controllable oxygen doping may be achieved by mild air annealing of NCs with proper ligand protection. The capping ligands could be removed after annealing. After heating at 400 °C in air for 20 min, the 224, 289 and 410 cm⁻¹ (Fig. 5, cyan curve) can be indexed to α-Fe₂O₃ [39] indicating that the FeS₂ NCs were completely oxidized with the disappearance of the pyrite peaks at 342 and 377 cm⁻¹. Given the boiling points of OLA (364 °C) and TOPO (411 °C), it is possible that the ligand can be evaporated from the NC surface or decomposed at such a high temperature, leaving exposed iron pyrite NC surfaces to react with air.

3.3. Phase change of the thermally treated FeS₂ NCs by XRD

In order to verify the oxidation process of the FeS₂ NCs in air at high temperature, we measured the XRD patterns of FeS₂ NCs with different ligands annealed in air and N₂ with increasing temperature, as shown in Fig. 6. The peaks of FeS₂ NCs without annealing can be indexed to iron pyrite (PDF# 42-130). No noticeable oxidation of the FeS₂ samples was detected by XRD after thermal treatment at 200 °C. In addition, there are several unassigned small peaks in Fig. 6 (denoted by circles) that are possibly due to the air exposure product of the capping ligands (oleylamine), which disappeared with further increase of annealing temperature. After thermal treatment of 20 min at 300 °C in air, both FeS₂-OLA/TOPO and FeS₂-pyridine NC films were partially oxidized. Both of the NC films were completely oxidized after thermal treatment at 400 °C in air for 20 min, and the diffraction peaks corresponding to FeS₂ almost disappeared (blue curves in Fig. 6a and b).

Annealing in a N₂ atmosphere from 200 to 400 °C did not result in noticeable phase changes. This was consistent with the Raman spectroscopy studies. The thermal stability against decomposition in an inert atmosphere is similar to previously reported results of bulk FeS₂ that is stable up to 400 °C upon annealing without air [24]. According to the XRD spectra of completely oxidized FeS₂ samples (blue curves, 400 °C), the main oxidation product is a mixture of FeSO₄ (PDF# 73-1057) and α-Fe₂O₃ (PDF# 87-1165). We propose that FeS₂ NCs exposed

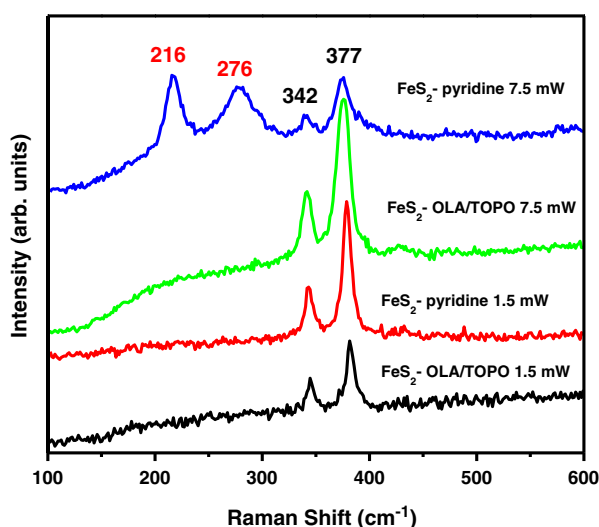


Fig. 4. Raman spectra of FeS₂-OLA/TOPO and FeS₂-pyridine NC films exposed to 1.5 mW and 7.5 mW laser power.

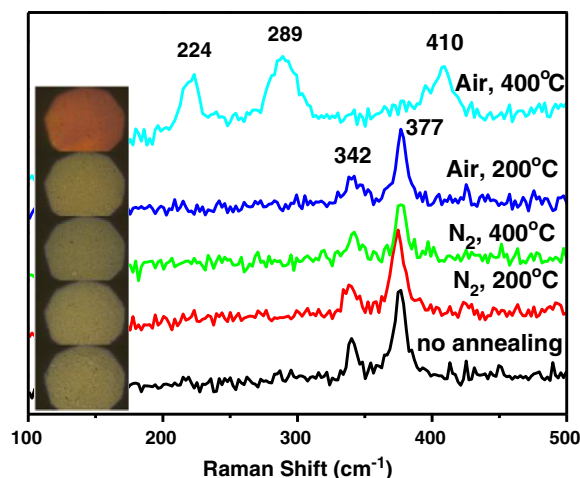


Fig. 5. Raman spectra of the FeS₂-OLA/TOPO NCs after thermal annealing for 20 min at 200 and 400 °C under N₂ and air atmospheres (laser power of 1.5 mW). The inset shows the color change of the annealed NCs under the confocal microscope before Raman measurement. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

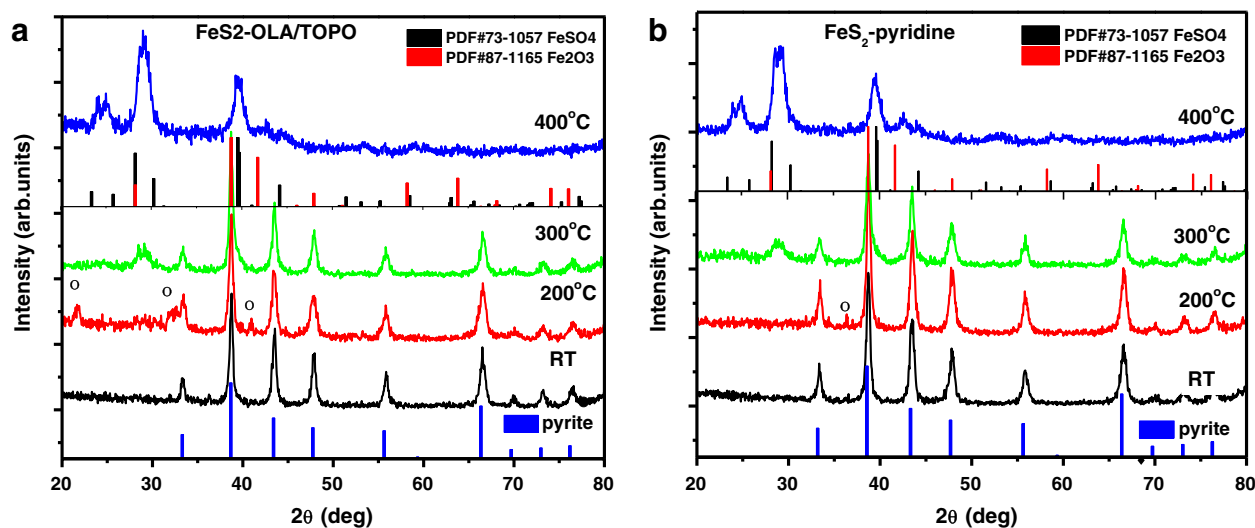


Fig. 6. XRD patterns of FeS₂-OLA/TOPO NCs (a) and FeS₂-pyridine NCs (b) after thermal treatment in air for 20 min from room temperature (RT, 20 °C) to 400 °C. The standard XRD patterns of iron pyrite, FeSO₄ and hematite α -Fe₂O₃ are given for comparison. Small peaks that are denoted by circles are possibly due to the air exposure product of the capping ligands. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

to air above 300 °C underwent the reactions shown in Eqs. (2) and (3) [24,40]:



Because of the high surface-to-volume ratio in NCs, surface defects are commonly observed, such as vacancies and dangling bonds [41]. The ligands used here, OLA and TOPO, can coordinate with the surface sulfur and iron atoms with dangling bonds [5], and also act as a barrier layer against oxygen exposure. In our previous work, it was shown that TOPO capping ligands can provide enhanced long term stability against the slow but spontaneous surface decomposition to FeS and sulfur [5]. In the present work, the stability of the FeS₂ NCs was studied systematically upon exposing to extreme conditions, such as high light intensity, high temperature and oxygen. The ligands with long alkyl chains have demonstrated their key role in protecting the NCs from decomposition and oxidation upon laser exposure and thermal treatment. The high thermal stability of NC surfaces was observed at annealing temperatures up to 400 °C under an inert atmosphere. This may be due to the high crystallinity of the cubic FeS₂ NCs. After thermal annealing in air at 200 °C, both the FeS₂-OLA/TOPO and FeS₂-pyridine NCs did not show noticeable oxidation. This demonstrates that even in the nanoscale with large surface-to-volume ratios, the thermodynamic stability of the pyrite phase is comparable to that of the bulk pyrite materials.

4. Conclusions and implications for pyrite FeS₂ research

The results reported here provide important guidance in designing proper pyrite FeS₂ NCs and the fabrication of NC films for photovoltaic applications. Of great importance is the minimization of the impact of large surface defect densities. Our results lend insight into ways to minimize the surface defects. Long-chain capping ligands such as OLA and TOPO improve long term stability against surface decomposition reactions [5] and increase thermal stability against oxidation under extreme conditions for photovoltaic applications. However these ligands are generally not preferred in PV devices due to their insulating nature. Encouragingly, small-molecule ligands such as pyridine can also preserve the surface integrity of the NCs as long as thermal annealing temperatures are below 200 °C. This high stability under medium thermal annealing temperatures provides more flexible processing options for

FeS₂ thin films and the practical possibility of controllable oxygen doping as a way to increase the bandgap [38].

The surface stability of iron pyrite is also a critical issue for its other versatile applications in renewable energy production and storage. As an earth abundant and nontoxic mineral, FeS₂ has been used as raw materials to produce sulfuric acid, catalysts in coal liquefaction [42], cathode materials for high energy density thermal batteries [43], and active layers in photoelectrochemical devices [2]. In addition, surface chemistry of iron sulfides has also played key roles in the global biogeochemical sulfur cycle and the evolution of the Earth [44,45]. Natural mines containing FeS₂ exposed to air and water can form acid mine drainage that has adverse environmental impacts and disrupt delicate equilibria in ecosystems [46]. Tremendous effort has been made to understand the surface physics and chemistry of iron pyrite that is in contact with air and water. This study of the pyrite surface reactivity should provide invaluable instructive information for reducing acid mine drainage, promoting mineral beneficiation, and understanding the prebiotic iron–sulfur world.

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