Evolution of nanoplate morphology, structure and chemistry during synthesis of pyrite by a hot injection method

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Pyrite (FeS₂) has a high light absorption coefficient and a suitable bandgap for photovoltaic applications but its poor performance in experimental cells has precluded its use until now. This is attributed to impurity phases and defects. It is important to understand the actual reasons to overcome these fundamental problems. Here we investigate the synthesis of pyrite nanoparticles by a hot injection method to understand the effects of synthesis parameters on the initial monomer concentration, nanoparticle size, morphology and the structure. Nanoparticle shapes such as cubes, plates and spheres were obtained and a mechanism for their formation is proposed. Experimental evidence is obtained to substantiate the model. Detailed study of the nanoplate evolution shows that it involves a nucleation stage followed by a self-assembly process to form the plate framework. The nanoparticles also appear to nucleate as FeS first and then transform to FeS₂.

Introduction

Solar energy harvesting ability of a material depends strongly on its absorption coefficient and bandgap. Pyrite (FeS₂) has a high absorption coefficient (~5 x 10² cm⁻¹) and a narrow bandgap of approximately 0.95 eV, which makes it a potential candidate for photovoltaic applications. Pyrite based solar cells would require very little active material because of its high absorption coefficient and would have reduced carrier recombination due to its natural internal electric field. Further, pyrite is abundant and nontoxic which makes it suitable for low-cost, high-volume photovoltaic applications. Despite these positive factors, pyrite is not a serious contender for such applications because its poor performance in experimental solar cells has precluded its use until now. This is attributed to impurity phases and defects. It is important to understand the actual reasons to overcome these fundamental problems.

In a previous study in the literature, where pyrite was used as the photon absorber layer in a photoelectrochemical cell, the open circuit voltage obtained was a low 200 mV. This was attributed again to the possibility of surface defects, such as S vacancies, contributing to electronic states within the bandgap. Recently, some computational scientists have contradicted this explanation but others have differing views. Such contradictions need to be resolved to understand the fundamental causes and improve the performance to acceptable levels for commercial application in a photovoltaic system.

Many synthesis routes are possible for pyrite thin films and particles. Pyrite thin films can be obtained by sulfurization of Fe and Fe oxide thin films, chemical vapor transport (CVT) and metal organic chemical vapor deposition (MOCVD) and chemical bath deposition (CBD). Pyrite particles have been synthesized using inverse micelle, solvothermal and hot injection methods. Both the inverse micelle and the solvothermal methods resulted in large, micron sized particles. In contrast, hot injection produced nanoparticles, nanowires and nanocubes. Such nanoparticles have large surface areas that could be advantageous for efficient charge transfer to adjacent transport layers in applications such as counter electrodes in dye sensitized solar cells (DSSCs). Of these shapes, the nanoplate form is interesting because of its two dimensional morphology where the electrical and catalytic properties of the facets could dominate the properties of the whole particle. Although, the synthesis of pyrite nanoparticles is not new, the mechanisms that promote the evolution of the plate morphology is still unclear. There is a very strong possibility that the particles produced in the early stage of synthesis may not be of the pyrite phase as the Fe–S alloy system is very complex. A previous report hypothesized that pyrite particles are indeed formed, even at the early stages of nucleation, and that they evolve into the plate morphology by aggregation. However, the reported experimental results are not convincing to establish the chemistry of the particle, particularly at the early stages. It is possible that the chemistry of the particle
evolves during synthesis, along with its shape and size. This aspect of synthesis has not been investigated previously.

Besides its good optical absorption properties, pyrite has adequate electrical conductivity and chemical stability in corrosive environments that makes it suitable as a counter electrode material in DSSC. Pyrite nanoparticles (NPs) with a diameter of about 10 nm deposited on fluorene doped tin oxide (FTO) has been tried as a counter electrode in DSSC and a good power conversion efficiency (PCE) of about 7.31% was obtained which is comparable to the efficiency of 7.52% shown in a similar cell with platinum (Pt)/FTO electrode. A high surface area is beneficial for a counter electrode to increase the catalytic activity. For this reason, NPs are superior to thin films. Faceted pyrite shapes, such as nanocubes or nanoplates have not been investigated in these applications. Specific crystallographic planes could be more catalytic due to their atomic arrangements, surface energies and defect densities implying that the use of specific faceted shapes could be advantageous. Pyrite nanocubes and nanoplates contain {100} facets which is more conductive as they are terminated by S vacancies resulting in locally reduced bandgap.

In this work, a hot-injection method was used to synthesize pyrite nanostructures as it is better suited for control of nanometer sized particles with mono-dispersed size distribution. The effect of the initial monomer concentrations on the shape and size of the product was studied. It was found that increasing the monomer concentration, changed the particle morphology from nanocubes to nanoplates, and then to spherical NPs. Effects of other synthesis conditions such as the precursor concentration, reaction temperature and S solvent were also be examined. This paper attempts to characterize the evolution of crystal structure, chemistry and morphology of the product, with special emphasis on understanding the coarsening mechanisms at the early stage of the synthesis.

Experimental procedures

The starting materials for the synthesis were 98% iron(II) chloride (FeCl₂), 70% oleylamine (OLA), S powder and 99% diphenyl ether (DE), all from Sigma-Aldrich. The synthesis followed a general hot-injection approach for metal sulfides (PbS, ZnS, CdS, and MnS). A typical experimental procedure was to mix 0.5 mmol (63.5 mg) of FeCl₂ with 5 mL OLA in a tri-neck flask and degas the mixture for 30 minutes, and then hold at 110 °C for 1 hour to let the Fe–OLA complex to form. Thereafter, the temperature was raised to 180 °C and 3 mmol (96 mg) of S mixed in 5 mL DE was injected into the flask while maintaining the temperature at 180 °C. Samples were extracted at time intervals of 5, 15, 30 minutes, and 1, 2 and 6 hours after S injection. In specific cases 24 hours samples were also taken. They were air cooled to room temperature; a large amount of methanol was added to precipitate the FeS₂ followed by centrifugation and dispersion in toluene.

To investigate the effects of precursor concentration, reaction temperature and the sulfur solvent, some comparison experiments (CE) were carried out, during which one of the parameters described in the typical experiment was changed.

- Comparison Experiment 1 (CE1): to study the effect of precursor concentration, the concentration of the reactants was doubled to 1 mmol FeCl₂ and 6 mmol S at the same OLA and DE volumes respectively. Synthesis under this “high” concentration was compared with the typical experiment which is at a “low” concentration.

- Comparison Experiment 2 (CE2): to evaluate the effect of reaction temperature, the temperature of the Fe–OLA mixture was raised to 220 °C. This was compared with the typical experiment.

- Comparison experiment 3 (CE3): to assess the effect of S solvent, 5 mL OLA was used to dissolve S instead of DE, as in the typical experiment. As the total OLA : DE ratio in CE3 would be different to the typical experiment, two sub experiments were conducted to isolate any effects of the solvent ratio. They are CE3-1, where 0.5 mmol FeCl₂ + 2.5 mL OLA and 2.5 mL DE, 3 mmol S + 5 mL OLA; and CE3-2, where 0.5 mmol FeCl₂ + 7.5 mL OLA, 3 mmol S + 2.5 mL DE. Note that in these sub experiments the OLA : DE ratios were the same but the S solvents were OLA and DE respectively.

Characterization

The crystal structure of the synthesized products was investigated by an X-ray diffractometer Shimadzu 6000 using Cu Kα incident rays (λ = 1.54178 Å) and JEOL transmission electron microscopes (TEM 2010 and 2100F). Samples from 3 different batches synthesized under the same conditions were examined in TEM. The size of the nanoparticles reported is the average of, at least, 50 particles. Phase purity was examined by Raman Spectroscopy Renishaw System 2000 with laser excitation wavelength 514 nm. The particle morphology was examined by JEOL field emission scanning electron microscope (FESEM 7600F). Samples for Raman were drop-cast on Si substrate, while X-ray diffraction (XRD) samples were drop-cast on glass. Light absorption spectra were characterized by a Cary 5000 UV-Vis-NIR Spectrometer.

Results

We first present the evolution of FeS₂ nanoplates with reaction time in the typical experiment. Then, we present the effects of the three synthesis parameters namely, precursor concentration, reaction temperature and sulfur solvent.

Evolution of FeS₂ nanoplates with reaction time in the typical experiment

The particles obtained at increasing times are sequentially shown in the TEM micrographs of Fig. 1 and their corresponding XRD data is shown in Fig. 2(a). Fig. 1(a) shows the first few particles precipitated in 5 minutes, almost immediately after S injection. Since, lattice planes could be imaged in this high-resolution micrograph, the particles are crystalline. However, their size and quantity might be too small in the sample for detection by XRD as evident in Fig. 2(a). The nuclei formed at this stage appear relatively spherical. Further, the particles are not aggregated and their average size is...
The product obtained after 15 minutes, shows plate morphology as evident in Fig. 1(b). A closer examination shows that it is not a single crystal but, an aggregate of smaller, single crystal particles. The contrast within the plate varies indicating that the aggregate is still porous and that the surface is also not planar. The plate side length is about 40 nm. FFT shown in the inset of Fig. 1(b) indicates two pairs of brackets, instead of rings, which is characteristic of a fine polycrystalline structure where the individual crystals are converging towards a single crystal structure. The plate shape is evident but atomic rearrangement within the plate for shape perfection is still in progress. The two pairs of brackets are near the (200) and (020) poles of FeS2 indicating that these two planes are the preferred facets.

Fig. 1(c) and (d) show the particles after 30 minutes and 1 hour respectively. It is clear that the particles have self-assembled to plate morphology. They are now clearly polycrystalline with grain boundaries. After 2 hours, Fig. 1(e) shows a nanoplate of about 20 nm in side length, and Fig. 1(f) shows a nanoplate after 6 hours where the rectangular plate morphology is clear.

Fig. 2(a) shows the powder XRD data. The 5 and 15 minutes samples did not show any crystalline products possibly because product quantities in the samples are too low. Diffraction peaks became detectable after 30 minutes and they became increasingly sharper with increasing time supporting the TEM observations and signifying improved crystallinity and growing grains. The XRD peaks obtained in 30 minutes closely match the FeS2 pyrite structure (ICSD file 10422) which is cubic, space group $P6_3/mmc$ with $a = 5.4179$ Å.

Since FFT structure identification is not conclusive, especially when the sample is out of the zone axis, and also since XRD could not detect crystalline products in 5 and 15 minutes, Raman spectroscopy was used as a complimentary technique to clarify the phases present. Fig. 2(b) shows the Raman spectroscopy of the series of samples. Peak shifts are clear at 290 cm$^{-1}$ and 357 cm$^{-1}$ in 5 and 15 minutes but for longer times they occur at 338 cm$^{-1}$ and 374 cm$^{-1}$. The peak shifts of 5 and 15 minutes correspond to FeS while the others correspond to FeS$_2$. Hence, FeS is the transient first phase to nucleate which is subsequently sulfurized to FeS$_2$ in 30 minutes. This phenomenon of a transient phase formation was never reported previously in the synthesis of pyrite by the hot injection method and will be discussed further in Discussion.

Optical absorption characteristics of the synthesized particles also support the notion of coarsening made previously. Fig. 2(c) shows the optical absorption spectra for the sample series. It is clear that at 5 minutes, the sample shows three sharp peaks at 432 nm, 533 nm and 660 nm. This was reported previously in the literature as the absorption spectrum of pyrite quantum dots. However, as shown above, the phase formed in 5 minutes is FeS. Hence, we attribute the absorption peaks seen in the 5 minutes sample to FeS quantum dots, and not to pyrite. The spectra for 15 minutes and 30 minutes show an absorption shoulder, different to the 5 minutes sample which could be due to the larger particle size. After 1 hour, the absorption spectra changes to a broad peak at about 600 nm first, and then shifts to 850 nm and 1000 nm for 2 hours and 6 hours respectively. This change in the peak position for larger times could be attributed to increasing grain size which was confirmed by TEM previously. The behavior of the two intermediate time samples at 15 and 30 minutes could be interpreted as a transition from the quantum dot characteristics of sharp absorption peaks to a polycrystalline characteristic of broad peak of diffused absorption. Since TEM showed that the larger particles are aggregates of fine particles, they could be showing dual optical absorption characteristics of the quantum-dot-like behavior of fine isolated particles, and of the larger plates. This agrees with the mechanism of coarsening by aggregation observed by TEM. Besides, the individual particles are also transforming from FeS to FeS$_2$ within the first 30 minutes.
Comparison experiments

Three different shapes of particles were obtained when the conditions were changed. These are near-spherical, nanoplate and nanocube shapes. Electron micrographs of particles synthesized in all comparison experiments are shown in Fig. 3. Their XRD data and UV absorption spectra are shown in Fig. 4.

**Effect of precursor concentration – CE1.** In the typical experiment NPs of plate morphology, with side length of about 20 nm was obtained as shown in Fig. 1(f). In CE1 on the other hand, spherical NPs of approximate diameter 10 nm were obtained after 1 hour as shown in the micrograph of Fig. 3(a). They remained spherical even after 24 hours and did grow to about 20 nm in diameter. The XRD results in Fig. 4(a) indicate that the spherical NPs are the pyrite phase. UV absorption of the spherical pyrite NPs is shown in Fig. 4(b). Compared to the nanoplates which show a broad peak at 1000 nm, the spherical NPs show shoulders at 500 nm (1 hour) to 600 nm (24 hours). The different shape obtained in CE1 could be explained by a probable variation in the growth mechanism when the precursor concentration is changed. In CE1, the monomer concentration would have been high enough even after the nucleation stage for the nucleated particles to continue to grow isotropically resulting in a more spherical shape at long times after the injection. Ostwald ripening could continue even after the monomer is fully consumed. In the typical experiment however, the monomer concentration might have fallen below a critical limit for continued growth. Then, coarsening occurs by an alternative mechanism to reduce the surface energy of the system. This will be discussed in detail later in this report. Such change in growth mechanism with change in the concentration of reactants and monomers has been reported in the synthesis of other compounds such as CdSe, CdS where a similar change in particle morphology was observed under some conditions.25-27

**Effect of reaction temperatures – CE2.** The reaction temperature also showed a strong effect on the final morphology of the NPs. In CE2, spherical NPs were obtained 6 hours after S injection, as shown in Fig. 3(b). This is in contrast to the nanoplate morphology obtained in the typical experiment. Hence, the effect of the higher temperature appears to be similar to that of higher precursor concentration observed in CE1.

**Effect of sulfur solvent – CE3.** Choice of S solvent is important because different solvents have different binding forces with S which will affect the S release rate. This will change the initial monomer generation rate for reaction with Fe. The shape obtained in CE3 was nanocubes (NCs) of size about 100 nm, as shown in the micrograph of Fig. 3(c). Again the XRD pattern of Fig. 4(a) shows that the NCs are the pyrite phase. Fig. 4(b) shows that the NCs have a broad peak at about 1100 nm in UV absorption. The differences between the various NPs in UV absorption could be attributed to their size and shape, which will be discussed in a later part.

In CE3-1, nanoplates were obtained, as shown in the micrograph of Fig. 3(d), while in CE3-2, NCs formed, as shown in Fig. 3(e) and (f). As both solutions contained the same amount of OLA (7.5 mL) and DE (2.5 mL), this difference cannot be attributed to OLA : DE ratio. The type of S solvent used must have influenced the morphologies. Different S solvents give rise to different S release rates. These effects will be discussed later in this report.

![Figure 2](image-url)  
**Fig. 2** Characterization of the samples obtained after different reaction times in the typical experiment. (a) XRD data, (b) Raman spectroscopic data, (c) normalized UV-absorption spectrum.
Discussion

**FeS to FeS\(_2\) transformation**

Results obtained in the typical experiment indicate that FeS is nucleated first during the synthesis. The Fe : S ratio was kept at 1 : 6 and hence excess S was always available, even after nucleation, which must exist in the elemental form (S\(^0\)), polysulfide form (S\(_x^{2-}\)) and as hydrogen sulfide (H\(_2\)S). The reaction between FeS and S to form FeS\(_2\) could occur in the three possible ways listed in Fig. 5. Among these ways H\(_2\)S is thought to be the most direct source of sulfurization.\(^{28,29}\)

**Different sulfur release rates of different sulfur solvents**

Thomson et al.\(^{29}\) proposed a set of possible reaction pathways for S with long chain amines, such as OLA to generate H\(_2\)S. This is given in Fig. 6 as four possible reaction steps. They proposed that metal sulfides are formed by the metal precursor reacting with the H\(_2\)S generated in each step. In a controlled experiment, Thomson et al. used commercial thioacetamide, instead of S, to dissolve in OLA to avoid the reaction 1 and precipitate the reaction 2 directly. The reaction kinetics in this controlled experiment was very rapid compared to using S powder dissolved in OLA which requires reaction 1 to take place first.\(^{29}\) Hence, they concluded that reaction 1 is the rate limiting step in this method of synthesis. This conclusion could explain the observations in our experiments too where when OLA was used as the S solvent, the system is less reactive because of the rate limiting reaction 1. Consequently, lower monomer concentrations may have resulted immediately after S injection. This rate limiting reaction does not exist when DE is used as the S solvent leading to rapid nucleation of sulfide.

**Effects of morphology on UV-absorption**

Fig. 4(b) shows very different UV-absorption behaviors for the different pyrite NPs synthesized in this work. Spherical NPs after 24 hours (size 20 nm) show an absorption peak at 600 nm while those after 1 hour (size 10 nm) shows a shoulder at 500 nm. This difference could be attributed to the size effect. Comparing the spherical NPs after 24 hours with nanoplates (size 20 nm) it is clear that both the peak positions and the

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\begin{align*}
\text{FeS} + S^0 & \rightarrow \text{FeS}_2 \quad 1 \\
\text{FeS} + S_x^{2-} & \rightarrow \text{FeS}_2 + S_{(x-1)}^{2-} \quad 2 \\
\text{FeS} + H_2S & \rightarrow \text{FeS}_2 + H_2 \quad 3
\end{align*}
\]

**Fig. 5** Reactions of FeS with S\(^0\), S\(_x^{2-}\) and H\(_2\)S.
profiles are different. This could be attributed to shape difference as their typical sizes are similar. Besides, it has been proposed that facets may affect the UV absorption behavior. This could also have influenced the results since spherical NPs are unfaceted, while nanoplates are terminated by {100} facets. Nanoplates and NCs (size 100 nm) show similar peak profiles with slightly different peak positions although both these particles are terminated by {100} facets. Hence this difference could be due to the different particle sizes. A faint peak at about 1400 nm visible in some absorption spectra are due to the remnant OLA capping ligands. Hence our results show that size, shape and facets affect UV absorption behavior in the pyrite particles.

A particle coarsening model

Our results prove that the size and shape of the as-synthesized particles varies depending on the synthesis conditions such as precursor concentration, reaction temperature and S solvent. When any of these conditions are changed, the initial monomer concentration available at the very beginning of synthesis is affected. Increasing the precursor concentration increases the initial monomer concentration; increasing the reaction temperature accelerates the monomer generation rate and consequently increases the initial monomer concentration; changing the S solvent to OLA decelerates the S release rate and consequently slows down the initial monomer generation rate. Hence it appears as though the initial monomer concentration is a critical parameter that influences the super saturation level, and consequently the size and number of the stable nuclei formed in the early stages of synthesis. In the case of CdSe, it was experimentally shown that increasing the initial monomer concentration reduced the size of the early-stage particles produced which could be attributed to higher nucleation rate promoted by the higher super saturation level.

Thermodynamically, it could be argued that the equilibrium shape of any synthesized nanoparticle is controlled by the total surface free energy which depends on the surface energy per unit area of the exposed facets, the surface area fraction of each facet and the total surface area of the particle. In the case of pyrite, {100}, {110} and {111} planes are the three most favored facets, and their respective surface free energies are reported to be \( \gamma_{(100)} = 1.05 \text{ J m}^{-2} \), \( \gamma_{(111)} = 1.29 \text{ J m}^{-2} \) and \( \gamma_{(110)} = 1.60 \text{ J m}^{-2} \). A shape with lowest total surface free energy would be a truncated particle having these facets. Such a particle would have six {100}, eight {111} and twelve {110} facets. The area fraction of each facet would change with the overall size of the particle in order to minimize the total surface free energy. For example, Barnard et al. computed that for particles of sizes 3, 5, 10 and 20 nm, the fraction of {100} facets on the surface increases as 53%, 63%, 70% and 74% respectively. Thus, with increasing particle size, the {100} facets become dominating, which is expected because it has the lowest surface energy per unit area.

Gong et al. used this surface energy model of truncated nanoparticles to formulate a self-assembly model. He proposed that the smaller, truncated particles aggregate into larger particles by self-assembly on selected facets depending on the dominating facets in the initial particles. The different morphologies such as NCs and nanoplates arise from different self-assembling modes which, in turn, depend on the overall size of initial particles.

Combining the effects of initial monomer concentration on initial stable nuclei size, and effects of initial stable nuclei size on its self-assembly mode, a model is proposed here to relate the initial monomer concentration to the resulting final shape of the NPs. This model is schematically shown in Fig. 7. At very low monomer concentrations, bigger initial stable nuclei are formed whose truncated shape for optimum surface energy results in dominating {100} facets. Further growth of these particles does not occur as the super saturation level falls below a critical value. Yet, to reduce the total surface energy of the system, these small particles could self-assemble by surface interactions into larger particles as proposed by Gong et al. Since the dominating facets for such large truncated particles are {100} planes, they bind on these facets. As the truncated particles will have their {100} facets normal to all three \( \langle 100 \rangle \) directions, the self-assembly could take place along all the three \( \langle 100 \rangle \) directions equally, resulting in a cubic framework. The voids in the framework could get filled subsequently by atomic rearrangement and diffusion over a period of time to eventuate in a solid cube. Similarly, the surface could also reach a perfectly planar {100} facet to avoid exposing the high surface energy facets {110} and {111}. Hence, after adequate time, the cube framework could transform to a solid cubic particle with {100} facets. Fig. 3(f) shows a SEM micrograph of cubic pyrite particles obtained in this study. The size of the cube should be determined by the rate of OLA coupling on these facets. Bi et al. experimentally showed that OLA has a strong binding energy with {100} facets of pyrite. Coupling on any facet will prevent diffusion and bonding with Fe and S atoms in another pyrite particle. Such coupling will also prevent any growth
The coupling on the {100} facets of the plates, also at the edges. Similar to the case of the nanocubes, OLA coupling could drive the formation of {100} terminal facets since these planes have high surface energy, atomic rearrangement could prevent continued aggregation and growth of the particles. The initial particles formed may take a near-spherical morphology to minimize the overall surface area. Such unfaceted particles will not self-assemble and even OLA will not have any preferred coupling planes on the surface to arrest their growth. Hence, the spherical NPs will continue to grow isotropically until the super saturation level falls below the critical value for further growth. Subsequently, growth could take place by Ostwald ripening too at longer times.

This model could provide a useful guide to explain the development of particle morphologies during synthesis of pyrite by the hot injection method. Although, we classify the three possible product shapes as NCs, nanoplates and spherical NPs, the cube and plate forms are very similar. There may not be a clear boundary in monomer concentration demarcating the cube and the plate regions in Fig. 7. At low monomer concentrations, the nanocubes are expected to be large with approximately similar side lengths. With increasing monomer concentration, as the dominance of the {100} facets in the initial particle decreases, and self-assembly gets promoted on the largely exposed {110} facets with the consequence of two-dimensional growth but, the aggregation on {100} facets may not be completely prevented. Hence, the thickness of the final plates obtained could vary considerably with monomer concentration indicating that the transition from cube to plate morphology is gradual.

It is interesting that this model does not provide for one dimensional growth and formation of nanorods for any monomer concentrations. This is supported by that fact that no study in the literature reports pyrite nanorod synthesis by hot injection method. This journal is © The Royal Society of Chemistry 2014

**Conclusions**

In conclusion, we have demonstrated that the shape of pyrite nanoparticles obtained in the synthesis by a hot injection method can be manipulated by the initial monomer concentration. The initial monomer concentration could be controlled through the synthesis conditions precursor concentration, temperature and S solvent. It was experimentally shown that increasing the monomer concentration changes the shape of the final particle from nanocube, to nanoplate, and finally to unfaceted, spherical. The UV-absorption behaviors of various pyrite nanoparticles are strongly dependent on their size, shape and facets. A model elucidating the mechanisms involved is presented and discussed based on previous reports on this subject. Experimental evidence is presented to substantiate the
validity of this model, particularly for nanoplate formation by aggregation of fine initial particles. Besides, strong experimental evidence was obtained to show that the particles nucleated at the early stages of synthesis are not pyrite FeS$_2$, but could be classified as FeS, whose crystal structure is hexagonal. This FeS phase transforms to pyrite FeS$_2$ after 30 minutes. With increasing time, the plate-like aggregates of nanoparticles gradually undergo atomic rearrangement to become plates with {100} facets. The size of the nanoplates does not change significantly with increasing reaction time which could be attributed to the strong binding of OLA molecules to the {100} pyrite facets.

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