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One-step synthesis of pure pyrite FeS$_2$ with different morphologies in water

Binxia Yuan$^{a*}$, Weiling Luan$^{a}$, Shan-tung Tu$^{b}$ and Jiang Wu$^{a}$

In the paper, the pyrite FeS$_2$ with novel nanostructures had been obtained via ethanolamine (ETA)/water binary system. This method provided a uniform and homogenous environment for the nucleation and growth of the FeS$_2$. When only pure water was used as the reaction solvent, the marcasite FeS$_2$ with hollow sphere structure was achieved, and then transformed into pyrite phase with rod-like structure piled up by nanoparticles with the increase of reaction time. Moreover, cubic, flake-like, and two kinds of tetrakaidecahedron structures were obtained via the adjustment of volume ratio of ETA and H$_2$O. The formation mechanism from flower-like amorphous to kinds of morphologies of pyrite FeS$_2$ crystals was analyzed through the time-dependent controlled experiments. The Raman spectra of samples with different morphologies were investigated, which were consistent with the XRD analysis. The studies of optical properties indicated that the morphologies had a great influence on the absorption properties. This paper provided a very simple and low cost method to control the morphologies of FeS$_2$ crystals, which would be of great potential for the synthesis of other metal chalcogenides and lay the foundation for the development of the solar cell.

Introduction

Over the past years, there has been considerable interest in the synthesis and characterization of transition-metal chalcogenides owing to their excellent optical properties and wide applications in optical cells and devices. In particular, iron pyrite (FeS$_2$) is significantly attractive in both cost and availability comparing with other compounds. Pyrite FeS$_2$ is applied as photovoltaic cell, lithium batteries as a cathode material, and hydrogen production as a depolarizer anode. Related reports has proved that pyrite FeS$_2$ has a high optical absorption coefficient ($>10^5$ cm$^{-1}$) and a suitable band gap energy ($E_g=0.95$ eV) indicating potential application on solar cell.

The optical properties of pyrite FeS$_2$ have a great relationship with their morphologies. For instance, the team of Alivisatos employed a novel single source molecular precursor to obtain pure pyrite FeS$_2$ nanocrystals, showing quasi-cubic morphologies with a size over 100 nm. The group of Law successfully prepared oblate and spheroid single crystals with diameters of 5-20 nm by a solvothermal process in diphenyl ether media, which estimated the band gap of the NCs as 0.88-0.91 eV. The Wang group first reported synthesis of pyrite FeS$_2$ with cubic and octahedral shapes via a simple surfactant-assisted ethylene glycol-mediated solvothermal method. Huang's colleagues reported pyrite NCs with cubic shape using a surfactant assisted hot-injection method that yielded pure phase, highly crystalline, and surface stable NCs, indicating the direct optical band gaps was 1.38 eV. The group of Kotov had obtained FeS$_2$ nanoparticles, nanowires, and nanosheets in polar solvent and aqueous dispersions. Our group had reported the synthesis pyrite FeS$_2$ with cubic shape (about 100 nm) through oleylamine-mediated solvothermal process, corresponding to a band gap of 1.05 eV. However, most of the synthetic route mainly depended on complex molecular precursor or process route. Here, we adopted the hydrothermal synthesis method in autoclave, which is comparably simple and low cost.

In the paper, we reported a hydrothermal process in an ethanolamine (ETA)/water binary solvent for the synthesis of FeS$_2$ crystals without expensive single-source precursors and complex craft. The reaction time and the volume ratio of ETA and H$_2$O played a critical role in the formation of pure pyrite.
FeS₂ crystals. In the condition of pure water, the pyrite FeS₂ products weren’t obtained. But, interestingly, the hollow sphere shape of marcasite FeS₂ was observed, and which then converted into the rod-like FeS₂ crystals piled up with nanoparticles with the elongation of reaction time. Moreover, the pyrite of four kinds of morphologies, such as, cubic, flake-like, two types of tetrakaidecahedron, also were got. The formation mechanism of these morphologies had also been studied. Accordingly, the Raman and optical properties were measured in order to study the relationship between morphologies and them.

**Experimental**

**Chemicals**

All the reactions and operations were carried out in open-air. All chemicals were used directly without further purification. Iron nitrate (Fe(NO₃)₃·9H₂O, analytical reagent), and ethanolamine (ETA, analytical reagent, 99%) were purchased from Shanghai Chemical Reagent (SCR). Hexadecyl trimethyl ammonium bromide (CTAB, 99%), and L-cysteine (C₆H₇NO₂S, 99%) were purchased from Aldrich.

**Synthesis of the pyrite FeS₂**

In a typical procedure, 1 mmol Fe(NO₃)₃ and 5 mmol L-cysteine were added to a given amount of distilled water and were dispersed to form a white emulsion by vigorous stirring. Then, a certain amount of ETA was added into the above solution at room temperature and continually stirred for 15 min to form purple-blue solution. Finally, the resulting mixture was transferred into a Teflon-lined stainless autoclave (60 ml). The autoclave was sealed and maintained at 200 °C for 48 h, then cooled to room temperature naturally. After that the resulting black solid products were collected by centrifugation, washed with alcohol to remove the excess surfactants, and finally dried naturally as well as utilized for further characterization.

**Characterization**

X-ray diffraction (XRD) patterns were recorded with a Rigaku D/max 2250 V diffractometer operating with Cu Kα radiation. The operation voltage and current were set as 40 kV and 100 mA, respectively, and the samples were powder without further treatment. Field emission scanning electron microscope (FESEM) images were acquired using S-4800 operated at an acceleration voltage of 10 kV, and the samples were prepared by sonicating the products in absolute ethanol, then evaporating one drop of suspension on conductive adhesive. The Raman spectra were recorded on InVia-Reflexa Raman spectrometer operating with 512 nm laser. The absorption properties were acquired by Cary 500 UV-vis-NIR spectrophotometer, the samples were provided by sonicating the samples in ethylene tetrachloride (C₂Cl₄).

**Results and discussion**

**Structures and morphologies**

In our experimental, a homogenous reaction condition for the nucleation and growth of the product was provided. It was found that synthesis of FeS₂ particles with controlled morphologies could be obtained by adjusting the experimental conditions, such as reaction time or the volume ratio between ethanolamine and water. The obtained morphologies of FeS₂ particles were summarized in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>V&lt;sub&gt;ETA&lt;/sub&gt;: V&lt;sub&gt;H₂O&lt;/sub&gt;</th>
<th>Temperature/°C</th>
<th>Time/h</th>
<th>Morphology</th>
</tr>
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<tr>
<td>A</td>
<td>pyrite</td>
<td>8:1</td>
<td>200</td>
<td>48</td>
<td>cubic</td>
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<tr>
<td>B</td>
<td>pyrite</td>
<td>1:1</td>
<td>200</td>
<td>48</td>
<td>flake-like</td>
</tr>
<tr>
<td>C</td>
<td>pyrite</td>
<td>1:8</td>
<td>200</td>
<td>48</td>
<td>tetrakaidecahedron</td>
</tr>
<tr>
<td>D</td>
<td>marcasite</td>
<td>pure water</td>
<td>200</td>
<td>24</td>
<td>hollow sphere</td>
</tr>
<tr>
<td>E</td>
<td>pyrite and marcasite</td>
<td>pure water</td>
<td>200</td>
<td>48</td>
<td>rod-like</td>
</tr>
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</table>

The phases of the as-prepared samples were characterized by XRD, as shown in Fig. 1a. All diffraction peaks of samples A, B and C could be indexed as a pure cubic phase of FeS₂ (space group Pa3) with a lattice constant of 5.4287 Å, which is consistent with the value given in the standard card (JCPDS no. 42-1340). No impurities were detected, indicating the high purity of the as-synthesized samples. Moreover, the strong and sharp diffraction peaks implied their high crystalline structure. The crystal structure of pyrite FeS₂ is displayed Fig. 1b. The Fe²⁺ cations occupy the sites of a face-centered-cubic sublattice, and the (S₃)²⁻ dimers are centered at the midpoints of the cubic edges and body center, so that the phase-structure can be considered as NaCl-like. The axes of the (S₃)²⁻ dimers are oriented along the [111] directions; each Fe atom is coordinated by six sulfurs in a slightly distorted octahedron and each S atom...
is bonded to three Fe atoms and its dimer pair.

Fig. 1. XRD patterns of FeS$_2$ crystals obtained under different conditions: (a) sample A, V$_{ETA}$: V$_{H2O}$=8:1; (b) sample B, V$_{ETA}$: V$_{H2O}$=1:1; (c) sample C, V$_{ETA}$: V$_{H2O}$=1:8, with reaction for 48 h at 200 °C, (b) the crystal structure of pyrite FeS$_2$.

To obtain the morphology and size information of as-prepared FeS$_2$ samples, the technique of SEM was employed. The SEM images (Fig. 2) depicted various crystals in different volume ratio of solvents at 200 °C for 48 h. When the volume ratio of ETA and H$_2$O (sample A in Table 1, Fig. 2a) was adjusted to 8:1, as shown in Fig. 2a, cubic-like FeS$_2$ particles with length of 400 nm were clearly observed. By simply decreasing the volume ratio of ETA and H$_2$O to 1:1 (sample B in Table 1, Fig. 2b), desultorily flake-like were obtained as presented in Fig. 2b. Interestingly, ployhedron shape was formed when the volume ratio of ETA and H$_2$O was reduced to 1:8 (sample C in Table 1, Fig. 2c). To further understand the morphology difference, it was worthwhile to investigate the change of relative intensity in each crystal lattice. Table 2 listed the crystals strength of different morphologies FeS$_2$ samples obtained under various reaction conditions. From the table, it could be found that the intensity values of sample A and theoretical sample in each lattice plane were essentially identical, which meant that sample A didn’t have orientated growth along specific crystal. With the increase of H$_2$O content (V$_{ETA}$: V$_{H2O}$=1:1), the strongest peak became (311) crystal plane. This proved that the (311) crystal face was dominant and had more chances to be diffracted, which indicated sample B grew up along (311) plane. This result was coincided with the SEM images with flake-like structure. When the volume ratio of ETA and H$_2$O was reduced to 1:8, the position of three strong peaks had no change and there were an increase in the relative intensities of (210), (220) and (023) crystal planes comparing with other planes. More investigation would be explained in detail later in this article.

Fig. 2. SEM images of FeS$_2$ crystals obtained under different conditions: (a) V$_{ETA}$: V$_{H2O}$=8:1; (b) V$_{ETA}$: V$_{H2O}$=1:1; (c) V$_{ETA}$: V$_{H2O}$=1:8, with reaction for 48 h at 200 °C.

<table>
<thead>
<tr>
<th>Crystal face</th>
<th>Sample A</th>
<th>Sample B</th>
<th>Sample C</th>
<th>Theoretical model</th>
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<tr>
<td>(111)</td>
<td>35.0</td>
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<td>31.0</td>
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<td>(200)</td>
<td>100.0</td>
<td>98.2</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>(210)</td>
<td>57.7</td>
<td>60.6</td>
<td>66.0</td>
<td>53.0</td>
</tr>
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<td>(211)</td>
<td>53.5</td>
<td>53.2</td>
<td>50.4</td>
<td>40.0</td>
</tr>
<tr>
<td>(220)</td>
<td>45.7</td>
<td>60.9</td>
<td>48.8</td>
<td>36.0</td>
</tr>
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<td>(311)</td>
<td>72.5</td>
<td>100.0</td>
<td>71.2</td>
<td>69.0</td>
</tr>
<tr>
<td>(222)</td>
<td>14.8</td>
<td>16.6</td>
<td>13.9</td>
<td>11.0</td>
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<td>(023)</td>
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<td>(321)</td>
<td>8.2</td>
<td>24.0</td>
<td>19.3</td>
<td>16.0</td>
</tr>
</tbody>
</table>
Under the reaction condition without ETA and the original molar ratio of iron and sulfur sources being 1:5, although CTAB phase catalyst (0.01-0.5mmol) was added and the reaction time was prolonged, the pure pyrite FeS₂ phase cannot be obtained. Generally, long reaction time leads to a preference for the formation of a thermodynamically stable phase. Therefore, marcasite FeS₂ was appeared first. With the extension of reaction time, marcasite would gradually transform into pyrite FeS₂. Fig.3 showed the evolution of XRD patterns from marcasite to pyrite FeS₂. When the reaction time was kept as 24 h, marcasite FeS₂ was the main product with a small amount of pyrite FeS₂. By Rietveld refinements from the XRD patterns, the weight of marcasite FeS₂ accounted for 71.4%, and the weight of pyrite FeS₂ was 28.6%. According to the XRD pattern, the characteristic peaks of pyrite FeS₂ (65.7% w.t.) accounted for the majority after 48 h, but marcasite FeS₂ (34.5% w.t.) could still be observed in the sample. Obviously, the transform process was quite slowly, the marcasite FeS₂ phase persisted after a long reaction time. Thus, it was difficult to obtain pure pyrite FeS₂ phase in the reaction system without ETA.

Fig. 3. Evolution of the XRD patterns with different reaction time (a) 24 h, (b) 48 h, reaction temperature is 200 °C

To further investigate the conversion process from marcasite to pyrite FeS₂ occurring at pure water, SEM analysis was conducted to characterize the samples at different conversion steps, as shown in Fig. 4. A hollow sphere of marcasite FeS₂ crystals was observed in Fig. 4a. The inserted panel in Fig. 4a was magnified single hollow sphere typically accumulation of many nanoparticles. When the reaction time was increased to 36 h, the morphologies of samples were still sphere structure (Fig. 4b), but a portion of hollow spheres became composed of rod-like by orderly particles. It implied that the marcasite phase was converting towards pyrite phase structure. Interestingly, when reaction time was further extended to 48 h, the sphere particles disappeared while rod-like ones appeared (Fig.4c and 4d). The rod-like particles were piled of many nanoparticles, with a length of about 500-600 nm and a diameter of about 100 nm.

Fig. 4. SEM images of FeS₂ crystals under the different reaction time: (a) 24 h; (b) 36 h; (c) and (d) 48 h, synthesis in pure water.

It was worthwhile to study the transformation process of from marcasite hollow sphere to pyrite rod-like. Based on diffusion and thermodynamic processes, the formation process of hollow spheres and phase transformation was discussed. On the thermodynamic, the stability of pyrite phase was higher than marcasite phase. According to free energy (G) vs. temperature (T) graph in allotropic transformation¹⁷, at a relatively low reaction temperature, marcasite and pyrite FeS₂ simultaneously grow in a competitive process. At the beginning of the reaction, the concentration of marcasite FeS₂ monomer (single FeS₂ molecule before its nucleation and growth) became increasingly higher, which lead to a high crystallization and growth rate. At the time when both Fe and S sources were consumed, the precipitation-solubility equilibrium of FeS₂ in solution became the main process. With extending of reaction time, thermodynamic control became the major factor and marcasite FeS₂ gradually converted to the thermodynamically stable phase of pyrite FeS₂.

As depicted in Fig. 5, at first the marcasite nuclei was acquired (step 1), these small particles agglomerated together to form larger hollow sphere clusters (steps 2 and 3), the allotropic
transformation of FeS\textsubscript{2} from marcasite to pyrite phase began to appear (steps 4 and 5), and rod-like pyrite was ultimately acquired via Ostwald ripening (step 6). Several reports\textsuperscript{18-21} had stated the relevant theoretical and experimental analysis of formation of hollow sphere. At the early stage, it was the surface diffusion along the early formed hollow walls. The diffusion was then thermodynamically driven by controlling the direction of the reaction. And the formation of hollow structures was thermodynamically instability in the long run. Compared with the hollow sphere structure, the rod-like structure had a higher stability. As a result, the hollow sphere finally reduced the empty space to minimize the interface energy. By controlling the atomic concentration and further collective ways of initial nuclei and diffusion properties of different ions, structural design for driving force could be acquired under a set of experiment parameters. Thus, studies of the synthetic mechanism of hollow sphere and phase conversion with the above investigations will be the great challenge in our future research.

![Diagram](Image)

Fig. 5. Transformation mechanism of from hollow sphere to rod-like: formation process of marcasite nuclei (1), aggregation of nanocrystallites into single-hollow sphere (2 and 3), allotropic transformation (4 and 5), and creation of a rod-like via Ostwald ripening (6).

In the meantime, the FeS\textsubscript{2} phase couldn’t be obtained if Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O was replaced by FeSO\textsubscript{4}·7H\textsubscript{2}O or Fe\textsubscript{2}O\textsubscript{3} under other conditions kept unchanged. If using elemental sulfur as sulfur source, the acquired crystals were Fe\textsubscript{2}S\textsubscript{4} samples. The control experiments showed that the choices of iron sources, sulfur sources, and solvents were critical for the obtaining of different phases and morphologies FeS\textsubscript{2}.

**Time-dependent experimental.** In order to study the growth mechanism of FeS\textsubscript{2} crystals, a series of experiments were performed with different reaction time.

In the synthesis of cubic-shape pyrite FeS\textsubscript{2}, the ideal reaction temperature and volume ratio of ETA and water were adjusted to 200 °C and 8:1, respectively. Fig. 6 showed the SEM images of samples obtained at different time intervals. When the reaction time was kept as 1 h (Fig. 6a and 6b), a large number of uniform flower-like microspheres with a diameter about 500 nm were observed. XRD results proved the sample obtained at 1 h was amorphous. When increasing the reaction time to 12 h (Fig. 6c), the as-obtained sample was comprised of mixture of a large amount of stripe-like (length: 200-600 nm, width: 100 nm) with some small flake-like (about 100 nm). XRD analysis confirmed this result with “steamed bread” peak and three weak diffraction peaks of pyrite FeS\textsubscript{2}. When the reaction time was further extended to 24 h, the product was confirmed to be pyrite FeS\textsubscript{2} crystalline based on XRD with flake-like particles (Fig. 6d). When the reaction time was extended to 36 h (Fig. 6e), the flake-like started to become thick with a small quantity of cubic-shape FeS\textsubscript{2} appeared. While further prolonged the reaction time to 48 h (Fig. 6f), the flake-like samples almost transformed into cubic-shape structure with a side length about 400 nm.

![Images](Image)

Fig. 6. SEM images for the shape-evolution process of FeS\textsubscript{2} crystals under different reaction time in V\textsubscript{ETA}/V\textsubscript{H\textsubscript{2}O}=8:1: (a, b) 1 h; (c) 12 h; (d) 24 h; (e) 36 h; (f) 48 h

On the basis of the above investigation, the growth process
of the pyrite FeS$_2$ cubic-shape microparticles could be classified following two steps: an initial nucleating stage and a crystal growth stage, which involved a fast nucleation of amorphous primary particles followed by a slow aggregation and crystallization of primary particles. Firstly, because L-cysteine consists of $\text{–NH}_2$, $\text{–COOH}$, and $\text{–SH}$ functional groups, they have a tendency to coordinate with inorganic cations. Therefore, it was reasonable to conclude that L-cysteine reacted with free Fe$^{3+}$ to form relatively stable Fe-cysteine complex. With the extension of reaction time, system energy increased, flower-like microsphere Fe-cysteine complex became unstable, leading to flower-like microsphere decomposed and formation of pyrite FeS$_2$. When there is enough reaction time, the Fe-cysteine completely decomposed to form FeS$_2$ nuclei for later growth. It is generally regarded that with prolonged reaction time, the morphologies of sample would convert into the structure with small surface energy. For a cubic face-centered structure, the surface energy is considered to be in the order $\{111\} < \{100\} < \{110\}$, and the growth preferentially.

![Figure 7. SEM images for the shape-evolution process of FeS$_2$ crystals under different reaction time in V$_{\text{ETA}}$/V$_{\text{H}_2\text{O}}$=1:1 (a) 24 h, (b) 36 h, (c) 48 h](image)

In the synthesis of flake-like pyrite FeS$_2$ crystals, the volume ratio of ETA and H$_2$O is 1:1. Fig. 7 showed the SEM images of the samples obtained at different time intervals. These samples were indexed as pyrite FeS$_2$ crystal by XRD analysis. When the reaction time was 24 h (Fig. 7a), a large number of irregular micro-particles were observed. When the reaction time was extended to 36 h (Fig. 7b), the morphologies of crystals were slice-like. A further increasing reaction time to 48 h, the final products exhibited thin plate morphologies of a broader size distribution.

When the volume ratio of ETA and H$_2$O was adjusted to 1:8, the change of morphologies was quite interestingly and worthy of investigation, as shown in Fig. 8. At 24 h (Fig. 8a and 8b), a large number of flocculent structure constructed from curved nano-flakes and a few bulk structures were observed. When the reaction time was increased to 30 h (Fig. 8c), the as-prepared sample was comprised of a large amount of cubic-shape with different sizes. When the reaction time was further increased to 36 h (Fig. 8d), the products consisted of lots of tetrakaidecahedron. While the reaction time was extended to 48 h (Fig. 8e), the tetrakaidecahedron structure was different and had a change.

![Figure 8. SEM images for the shape-evolution process of FeS$_2$ crystals under different reaction time in V$_{\text{ETA}}$/V$_{\text{H}_2\text{O}}$=1:8 (a, b) 24 h, (c) 30 h, (d) 36 h, (e) 48 h.](image)
further cubic-shape FeS₂ crystals were got owing to the effect of ethanolamine. Table 3 showed the relative intensities of FeS₂ crystals in different crystal plane. When the reaction time was shorter than 30 h, the relative intensities of FeS₂ crystals in different crystal panel were close to the theoretical value. Although the shapes of inorganic materials often conveyed their intrinsic crystal structure nature, crystals can display diversiform morphologies under the influence of extrinsic environmental factors. The behavior led to distinct surface energies, directly resulting in different growth rates of the crystal face. Herein, the morphology of FeS₂ sample was subtly predominated by the facet-selective adsorption characteristic of ETA, which serves as a structure-directing coordinate template. Moreover, ETA acts as a phase catalyst in this system. According to the SEM images (Fig. 8c, 8d, and 8e), the sizes of samples remained unchanged about 3 μm with the increase of reaction time. The results indicated that the particle didn’t grow large but with morphology transformation by prolonging reaction time. When the reaction time was 36 h, the relative intensity of (111) crystal plane was greater than the sample prepared at 24 h and 30 h. It was indicated that the (111) crystal face had more chance to be diffracted, which meant the phase structure or morphology had changed a little. At 48 h, the intensity of the same plane was decreased but those of (210) and (023) showed a certain degree of increase, indicating a dominant role with the increase of reaction time. In order to further understand the formation process, the possible schematic diagram was shown in Fig. 9.

Table 3. The relative intensities of the different crystal faces (VETA/VH₂O=1:8)

<table>
<thead>
<tr>
<th>Crystal indices</th>
<th>sample</th>
<th>Theoretical model</th>
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<tr>
<td></td>
<td>24h</td>
<td>30h</td>
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<tr>
<td>(111)</td>
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</tr>
<tr>
<td>(321)</td>
<td>18.0</td>
<td>19.1</td>
</tr>
</tbody>
</table>

Fig. 9. Schematic illustration of the proposed formation mechanism of FeS₂ crystals

**Raman and optical properties of FeS₂.** The Raman spectra of the FeS₂ samples obtained at different reaction conditions were showed in Fig. 10. Generally, high-purity, crystalline FeS₂ with pyrite structure usually exhibits three characteristic Raman peaks at 340-353 cm⁻¹ (E₉, T₉), 377-383 cm⁻¹ (A₂g, T₉), and 427-466 cm⁻¹ (T₉) ²²⁻²³. The peak at 340 cm⁻¹ was E₉ mode which the sulfur atoms are displaced perpendicularly to the dimmer axes, the peak at 377 cm⁻¹ was A₂g mode which corresponds to in-phase stretching vibration of the S-S dimmer of pyrite FeS₂. Moreover, no other peaks were observed. Thus, the Raman results further indicated samples A, B, and C were of pure pyrite structure without marcasite FeS₂ or other impurities. On the contrary, the Raman peaks of sample D were located at 323 cm⁻¹ and 385 cm⁻¹, indicated a marcasite phase instead of pyrite. While the Raman spectrum of sample E showed three peaks at 323 cm⁻¹, 340 cm⁻¹ and 377 cm⁻¹, revealing a mixture of pyrite and marcasite FeS₂. Based on the above analysis, the phase structures of as-prepared samples were further proved, in agreement with XRD analysis.

Fig. 10. Raman spectra of products obtained in the different samples A, B, C, D, and E.

The optical properties of FeS₂ dispersed in ethylene
tetrachloride (C₂Cl₄) by sonication were studied at ambient
temperature absorption spectroscopy from 300 nm to 2500 nm,
as shown in Fig. 11. It was found that absorption properties are
quite different among the samples because of their diverse
morphologies. Although samples A, B, and C were all pyrite FeS₂
crystal, the absorption curves were different due to different
morphologies. Sample A exhibited a broad absorption peak at
1200 nm (1.03 eV) and a sharp optical absorption locating at
1724 nm (0.72 eV). In contrast to the direct band gap (0.96 eV)
of bulk FeS₂, the results showed that the absorption peaks had a
blue shift. Other reports showed that band gap of bulk FeS₂ is
much larger due to its size effect. Sample B didn’t show evident
absorption peaks and the absorption curve was decreased from
300 nm to 2000 nm. Comparing with sample B, the absorption
curve of sample C and sample A showed more similarity due to
their similar morphologies. Meantime, the absorption curves of
the samples D and E were also different due to different phases (pyrite
and marcasite) and morphologies (hollow sphere and rod-like). The
hollow sphere marcasite FeS₂ (Sample D) had a broad and weak
absorption peak at about 1700 nm (0.73 eV) and 1000 nm (1.24
eV), because of a small amount of pyrite FeS₂. In contrast to
sample D, sample E possessed a well-defined, broad optical
absorption spanning from 1200 nm to 1600 nm with a distinct
peak at 1380 nm (0.90 eV). Optical performance was mainly
influenced by its crystal structure, and morphologies, etc.

![Absorbance vs Wavelength](image)

Fig. 11. The UV-vis-NiR absorption spectra of products
obtained in the different samples A, B, C, D, and E.

Conclusion

In summary, through adjusting of reaction time and volume
ratio of ethanolamine and H₂O, pure pyrite FeS₂ crystals with
several kinds of morphologies were obtained via hydrothermal
process. The hollow sphere of marcasite FeS₂ was synthesis
with pure water, the morphology converted to rod-like along
with increase of pyrite FeS₂ phase as reaction time lengthened.
When V_{ethanol} : V_{H₂O} was kept at 8:1, the initial flower-like
amorphous crystal transformed into flake-like pyrite FeS₂ and
then cubic shape. While at 1:8, the flocculent morphologies
firstly form into cubic shape, and further transformed into
tetraokaidecaedron. At the initial stage of hydrothermal reaction,
free Fe³⁺ could coordinate with L-cysteine to form Fe-cysteine
precursor which then decomposed to FeS₂ nuclei. The
cubic-shape FeS₂ was obtained and then changed owing to the
effect of ethanolamine. The absorption properties showed a
Corresponding change with diverse morphologies, implying that
the optical performance was influenced by the structure and
morphologies.

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Notes and references

a Shanghai Engineering Research Center of Power Generation
Environment Protection, Shanghai University of Electric Power,
Shanghai 200090, P. R. China
b The State Key Laboratory of Safety Science of Pressurized System,
School of Mechanical and Power Engineering, East China University of
Science and Technology, Shanghai 200237, P. R. China
* E-mail of corresponding author: luan@ecust.edu.cn; Fax: +86 21
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Through adjusting of the volume ratio of ETA and H$_2$O, cubic, flake-like, tetrakaidecahedron, hollow sphere, and rod-like are observed.