

# Single-Source Approach to Cubic FeS<sub>2</sub> Crystallites and Their Optical and Electrochemical Properties

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Cubic FeS<sub>2</sub> crystallites have been synthesized via a single-source approach using iron diethyldithiocarbamate as precursor under hydrothermal conditions. The sample is characterized by XRD, IR, TEM, and FESEM. The optical properties of the as-prepared FeS<sub>2</sub> reveal that there exists a red shift compared with that of bulk materials. Meanwhile, the electrochemical properties of FeS<sub>2</sub> demonstrate that it delivers a large discharge capacity, which might find possible application as an electrode material in lithium cells. It is also found that the reaction temperature is of importance to the formation of cubic FeS<sub>2</sub> crystallites.

## Introduction

During the past decades, much attention has been focused on the fabricating nanoscale inorganic materials, which have exhibited fascinating chemical and physical properties and potential applications in the future devices.<sup>1–3</sup> Furthermore, transition metal sulfides are of great interest for industrial applications such as catalysis, lubrications, refractories, pigments, battery fabrication, and optical and magnetic devices, because of their wide range of semiconducting properties and unique structural characteristics.<sup>4–6</sup>

FeS<sub>2</sub> crystallizes in the pyrite structure with the space group of *Pa3*, in which the Fe atoms are octahedrally coordinated by six S atoms, while the S atoms are tetrahedrally coordinated to three Fe atoms and one S atom. It has received growing attention in recent years owing to its potential as a useful material for solar-energy applications,<sup>7,8</sup>

as the cathode for high-energy-density batteries,<sup>9,10</sup> and as depolarizer anode for hydrogen production.<sup>11</sup> Considerable progress has been made since Wöhler<sup>12</sup> first prepared artificial pyrite by reaction of Fe<sub>2</sub>O<sub>3</sub> with liquid sulfur and NH<sub>4</sub>Cl in an open system. Many different methods were put forward to prepare FeS<sub>2</sub> crystals such as the toluene–thermal process,<sup>13</sup> in situ formation of boron sulfides and their subsequent reactions with metal-source oxides (Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>) at 550 °C,<sup>14</sup> the plasma-sprayed approach,<sup>15</sup> and the thermal spray method.<sup>16</sup>

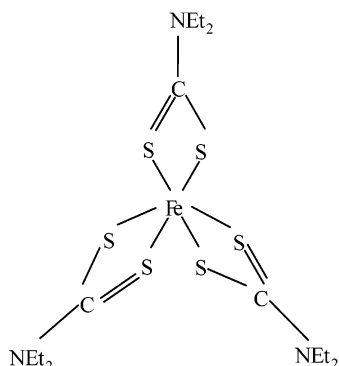
To search for more green or environmentally benign processes, it is necessary to reduce the amounts of organic solvents and hazardous substances.<sup>17</sup> From the viewpoint of green chemistry, the hydrothermal approach is a good candidate since the reaction can proceed at a mild temperature in H<sub>2</sub>O under a sealed environment.

Herein, we present a single-source approach to fabricate cubic FeS<sub>2</sub> crystallites by the thermal decomposition of an iron diethyldithiocarbamate complex obtained by mixing sodium diethyldithiocarbamate (NaS<sub>2</sub>CNET<sub>2</sub> or NaDDTC) and FeCl<sub>3</sub> in absolute ethanol. It was reported that NaDDTC

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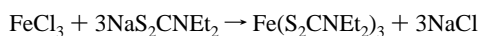
**Figure 1.** Possible framework of the metal complex structure.

could be used as complex reagent to form  $\text{Sb}_2\text{S}_3$  and  $\text{Bi}_2\text{S}_3$  nanorods,<sup>18,19</sup> but there is no report on the preparation of  $\text{FeS}_2$  formed with the aid of NaDDTC. The optical properties of the as-prepared cubic  $\text{FeS}_2$  crystallites reveal that there exists a red shift compared with that of bulk materials. Furthermore, the electrochemical properties of  $\text{FeS}_2$  demonstrate that it delivers a large discharge capacity, which might find possible application as an electrode material in lithium cells. The single-source approach may open the opportunity to fabricate other transition metal sulfides or polysulfides simply using NaDDTC as complex reagent and sulfur source.

## Experimental Section

All the analytical reagents were purchased from Shanghai Chemical Reagents Company and used without further purification.

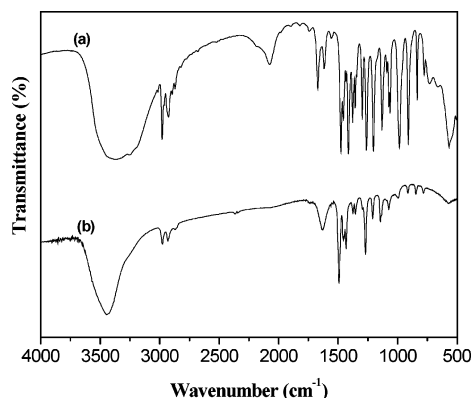
**Synthesis of Iron Diethyldithiocarbamate Complex.** The iron diethyldithiocarbamate complex was prepared from stoichiometric amounts of 1 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 3 mmol of NaDDTC in 50 mL of absolute ethanol. The obtained black precipitate was filtered off, washed with distilled water and absolute ethanol several times, and dried at room temperature. The reaction for the preparation of iron diethyldithiocarbamate complex can be formulated as follows:



On the basis of previous reports,<sup>19,20</sup> a possible framework for the metal complex structure is demonstrated in Figure 1.

**Synthesis of Cubic  $\text{FeS}_2$  Crystallites.** In a typical procedure, 0.4 g of  $\text{Fe}(\text{S}_2\text{CNET}_2)_3$  and 40 mL of distilled water were added to a Teflon-lined stainless steel autoclave with a capacity of 50 mL. The autoclave was sealed, maintained at 180 °C for 12 h, and cooled to room temperature naturally. The precipitate was filtered off, washed with distilled water and absolute ethanol several times, and dried in a vacuum at 50 °C for 6 h.

**Instruments and Characterization.** X-ray powder diffraction (XRD) patterns were determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromatized  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.541874 \text{ \AA}$ ). Fourier transform infrared (FTIR) spectra of the as-prepared products were recorded at room temperature with a KBr pellet on a VECTOR-22 (Bruker) spectrometer ranging from 400 to 4000  $\text{cm}^{-1}$ . Transmission electron



**Figure 2.** IR spectra of the as-prepared Fe-DDTC complex (b) and pure NaDDTC (a).

microscopy (TEM) images were characterized by Hitachi H-800 transmission electron microscope with a tungsten filament and an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FESEM) images were taken with a JEOL JSM6700F scanning electron microscope.

Optical absorption spectra of the sample at ambient temperature were recorded at optical wavelength between 1200 and 1500 nm with a Shimadzu UV-365 spectrophotometer. The electrochemical performances were examined with metallic lithium as the anode at room temperature. The positive electrodes were fabricated by pasting slurries of the as-prepared  $\text{FeS}_2$  crystallites (85 wt %), carbon black (Super P, 10 wt %), and polyvinylidene (PVDF, 5 wt %) dissolved in *N*-methylpyrrolidinone (NMP) on Al foil strips by the doctor blade technique. Then the strips were dried at 160 °C for 24 h in an air oven, pressed under 20 MPa pressure, and kept at 120 °C for 12 h in a vacuum. The electrolyte was 1 M  $\text{LiPF}_6$  in a 1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DEC); the separator was Celgard 2500. The cells were assembled in the glovebox filled with highly pure argon gas. The cells were galvanostatically cycled in the 2.5–1.0 V range at a current density of 0.2  $\text{mA} \cdot \text{cm}^{-2}$ .

## Results and Discussion

IR spectra of the as-prepared Fe-DDTC complex (b) and pure NaDDTC (a) are given in Figure 2. In Figure 2b, the characteristic absorption peaks at 1490 and 987  $\text{cm}^{-1}$  can be assigned to the stretching vibrations of C–N and C–S, respectively,<sup>21</sup> and the frequency of the C–N stretching vibration of the complex shifted from 1477  $\text{cm}^{-1}$  in the pure NaDDTC (Figure 2a) to 1490  $\text{cm}^{-1}$ . The shift of the C–N stretching vibration implies that the sulfur in the diethyldithiocarbamate coordinates with the metal ion in the complex.<sup>22</sup> On the basis of the IR spectra, it is believed that the  $\text{Fe}(\text{DDTC})_3$  complex is successfully synthesized via the reaction of NaDDTC and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in absolute ethanol.

Figure 3 shows the XRD patterns of  $\text{FeS}_2$  crystallites obtained at different reaction temperatures. When the reaction was carried out at 160 °C for 12 h, the products were of mixture of orthorhombic phase  $\text{FeS}_2$  (JCPDS Card No. 37-0475, marked with “■”) and cubic phase  $\text{FeS}_2$  (JCPDS Card

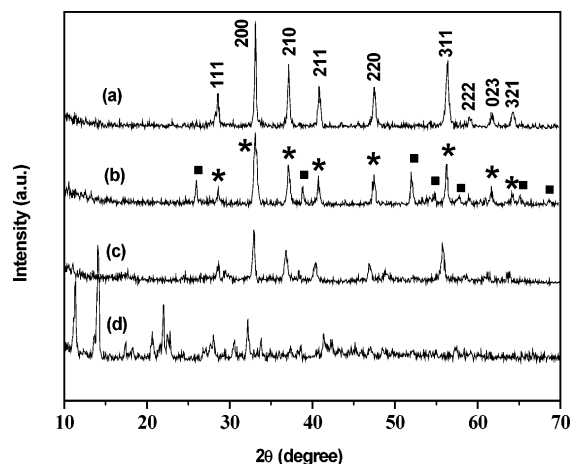
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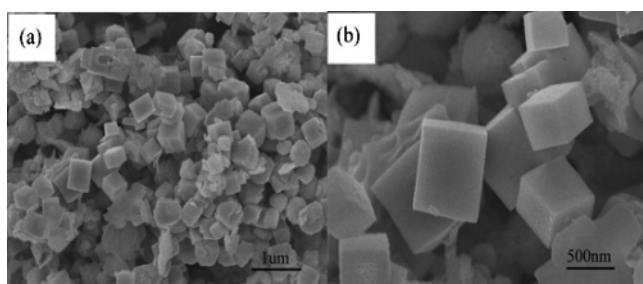
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**Figure 3.** XRD patterns of FeS<sub>2</sub> crystallites obtained at different reaction temperatures: (a) 180 °C; (b) 160 °C; (c) 140 °C; (d) 120 °C.

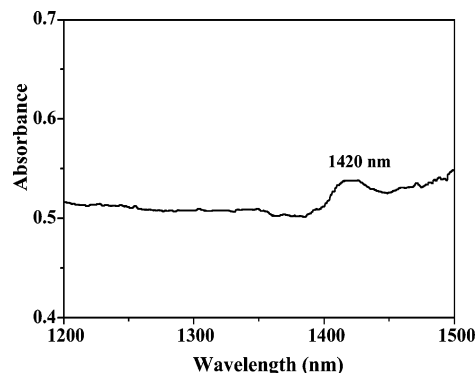


**Figure 4.** FESEM (a, b) and TEM (c) images of cubic FeS<sub>2</sub> crystallites obtained at 180 °C.

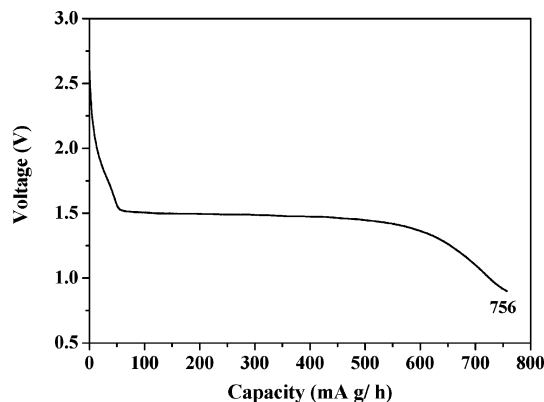
No. 71-2219, marked with “\*”). When the reaction temperature is increased to 180 °C, pure cubic phase FeS<sub>2</sub> with a lattice constant of  $a = 5.414 \text{ \AA}$  can be obtained, which is consistent with the reported value (JCPDS Card No. 71-2219,  $a = 5.417 \text{ \AA}$ ). Meanwhile, the XRD patterns in Figure 3c,d recorded at the reaction temperature of 140 or 120 °C are indiscernible.

Figure 4 a,b shows the FESEM images of cubic FeS<sub>2</sub> crystallites with different magnifications. It is seen that there exists a large number of cubic FeS<sub>2</sub> crystallites with the average diameter of 500 nm. The representative TEM image of the sample is shown in Figure 4c, consistent with those of a sample observed by FESEM.

The optical properties of FeS<sub>2</sub> crystallites dispersed in absolute ethanol by sonication were investigated with ambient temperature absorption spectroscopy (Figure 5). The product shows strong light absorption in the lower energy region. The FeS<sub>2</sub> crystallites possess a well-defined, broad optical absorption located at 1420 nm (0.87 eV). In contrast



**Figure 5.** Optical absorption spectrum of FeS<sub>2</sub> crystallites measured at ambient temperature.



**Figure 6.** Discharge curve of cubic FeS<sub>2</sub> crystallites recorded with a current density of 0.2 mA/cm<sup>2</sup>.

to the direct band gap (0.93 eV) of bulk FeS<sub>2</sub>,<sup>23,24</sup> there exists a red shift between them. It is probably caused by the cubic morphology of FeS<sub>2</sub> crystallites since Wei et al.<sup>24</sup> reported that the structure, crystallization, and stoichiometry remarkably influence the optical performance of the as-obtained pyrite. As for the light absorption at 1500 nm and probably below, it is generally assigned to the absorption of minor water in the absolute ethanol.

Electrochemical performance of the as-prepared cubic FeS<sub>2</sub> crystallites in the cell configuration of Li/FeS<sub>2</sub> was evaluated. Figure 6 shows the discharge curve of cubic FeS<sub>2</sub> crystallites on the first cycle with cutoff voltage of 1.0 V at a current density of 0.2 mA/cm<sup>2</sup>. The discharge capacity of cubic FeS<sub>2</sub> crystallites can reach about 756 mA h/g, which is approximately equivalent to that of natural FeS<sub>2</sub> cell (750 mA h/g) or synthetic FeS<sub>2</sub> cell (775 mA h/g) reported by Horn et al.<sup>25,26</sup> The high capacity of cubic FeS<sub>2</sub> crystallites makes it attractive as a possible cathode for rechargeable lithium cells in the future.

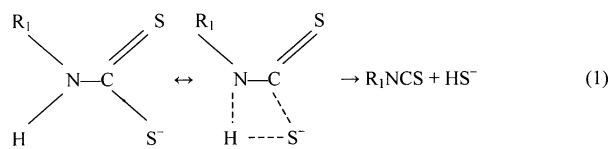
It was reported by Joris et al.<sup>27</sup> that a noncatalyzed decomposition of the DTC<sup>-</sup> ion could occur by means of a proton transfer from nitrogen to sulfur according to the following equations: However, there is no free proton for

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the hydrogen bond between nitrogen and sulfur in the Fe-DDTC precursors (shown in Figure 2), and the sulfur atoms in the dialkyldithiocarbamate are coordinated to the metal (Fe) ion. The formation process of the cubic FeS<sub>2</sub> crystallites perhaps proceeds as follows: A hydrogen bond probably forms between the nitrogen and sulfur with the aid of the proton from H<sub>2</sub>O suggested by Xie et al.,<sup>18</sup> and then the hydroxide anion will attack the electrophilic site of the ligand. Followed by the possible cleavage of Fe–S and C–S bonds under hydrothermal conditions, a simultaneous oxidation and reduction (Fe<sup>3+</sup> → Fe<sup>2+</sup>; S<sup>2-</sup> → S<sup>-</sup>) might occur in the autoclave, which further results in the formation of FeS<sub>2</sub> crystallites.

To investigate the influences of reaction conditions on the structure and morphology of the product, many experiments were conducted. When the reaction is carried out at 160 °C for 10 h, pure FeS<sub>2</sub> cannot be obtained by the characterization of XRD (shown in Figure 3b). When the reaction temperature is increased to 200 °C, pure FeS<sub>2</sub> can be obtained as that prepared at 180 °C. At the same time, the XRD patterns

recorded at the reaction temperature of 140 or 120 °C are also indiscernible, which are shown in Figure 3c,d. Therefore, it is believed that the reaction temperature is of importance to prepare pure cubic FeS<sub>2</sub> crystallites.

## Conclusions

In summary, we have synthesized cubic FeS<sub>2</sub> crystallites through a single-source approach using iron diethyldithiocarbamate as precursor under hydrothermal conditions. The as-prepared products are composed of a large number of cubic FeS<sub>2</sub> crystallites with the average diameter of 500 nm. The optical properties of the products show a red shift in contrast to that of bulk FeS<sub>2</sub>. The electrochemical properties of FeS<sub>2</sub> demonstrate that it delivers a large discharge capacity. The experimental results show that the reaction temperature is of importance to the formation of cubic FeS<sub>2</sub> crystallites. This single-source approach might open an opportunity to prepare other transition metal sulfides in the future.

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