Production of Iron Disulfide Nanoparticles by Hydrothermal Process

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Abstract:
In this research, a single-stage low-temperature hydrothermal synthesis route was successfully developed for preparation of Iron Disulfide. The prepared powder was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). These analyses showed that nanoparticles were well crystallized, pyrite was the main product and the shape of crystals was nanorod. Also, the influences of reaction temperature and iron source on the formation of the target compound were investigated.
Keywords: *Iron Disulfide, nanoparticles, hydrothermal process, Pyrite*

1. INTRODUCTION

Iron Disulfide (FeS_2) is a semiconductor with a suitable energy band gap (Eg≈0.95 eV) and a very high optical absorption coefficient ($\alpha \approx 5\times10^5$ cm^{-1} for $\lambda<750$ nm) which is two orders of magnitude higher than that of crystalline silicon [1, 2]. Therefore, Iron Disulfide has been receiving growing attention because of its promising potential for application as an optoelectronic or photovoltaic material. Furthermore, FeS_2 as an appealing cathode material for thermal batteries, demonstrates plenty of unique features, such as very high capacity, low environmental impact (nontoxic elements with respect to Fe and S), and affordable cost (abundant and cheap).

Several methods have been applied for preparation of Iron Disulfide, such as: thermal sulfuration [3–7]; mechanical milling [8–12], wet chemical route [13] and solvothermal process [14–18]. In the last few years, attention has been shifted towards the synthesis of one-dimensional nanostructure materials because of their fundamental importance as well as wide range of potential applications in nanodevices. Therefore, it is necessary to design a low-temperature synthesis route for solving these problems. Recently, the hydrothermal process by attractive traits, for instance, simple operation and low temperature has opened a fruitful route for synthesis of advanced inorganic materials such as Iron Disulfide.

In previous studies, reaction system was a small impeller-free reservoir. While in this research, a reactor equipped with impeller was used. Also, this paper discusses the effects of reaction temperature and iron source on formation of FeS_2 powder.

2. EXPERIMENTAL

All reagents were of analytical grade and were used without further purification. In a typical process, $Na_2S_2O_3$ (13.16 g), either $FeSO_4.7H_2O$ (23.15 g) or $Fe(NO_3)_3.9H_2O$ (33.63 g) were used as the starting materials. Iron and sulfur sources were separately

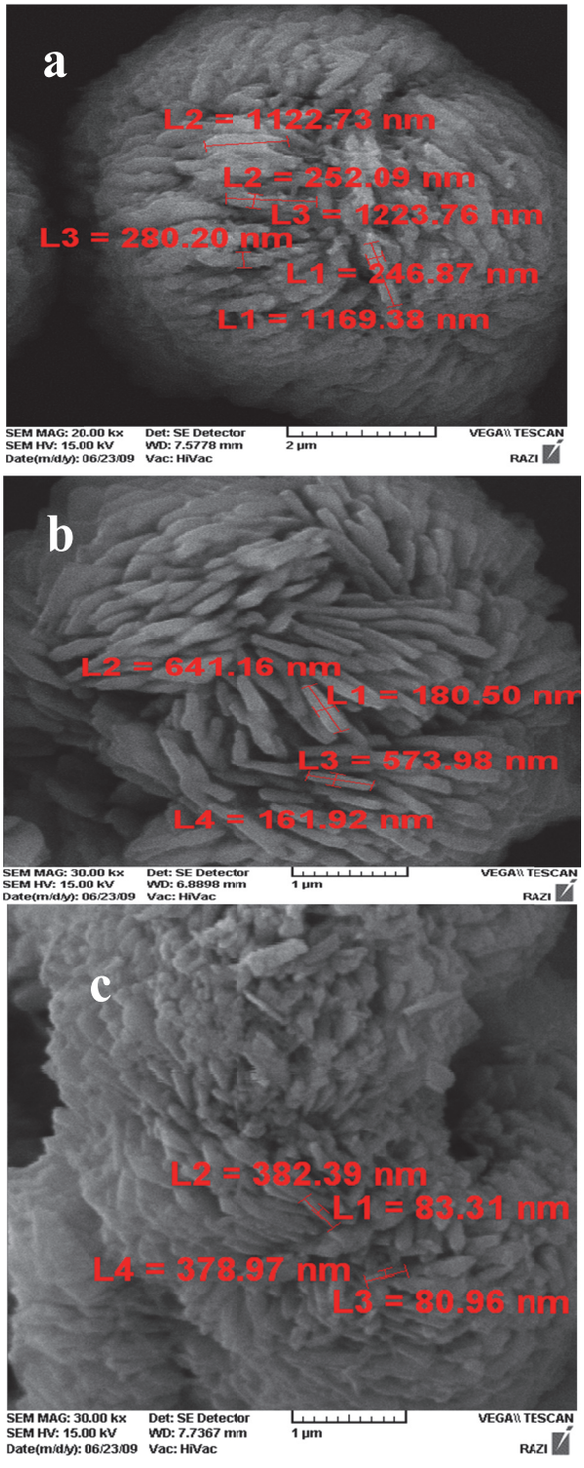

Figure 1: *SEM images of prepared FeS_2 at (a) 130˚C, (b) 150˚C and (c) 180˚C*

dissolved in deionized water and stirred with magnetic stirrer. After their complete dissolution, they were mixed and transferred into a stainless steel autoclave with 2 litter capacity and filled with distilled water up to 40% of the total volume. The autoclave was sealed and maintained at a temperature in the range of 130–180˚C for a period of 2 to 8 h. It was then cooled to room temperature naturally. The precipitates were filtered and washed with distilled water and then Carbon disulfide to remove the residual impurities. After being dried at 80˚C for 4 h, the black powders were collected for characterization.

The obtained samples were characterized by SEM and XRD to determine the structure and composition, respectively. SEM images were taken by a VEGA\\ TESCAN scanning electron microscope. The XRD analysis was carried out by an X-ray diffractometer.

3. RESULTS AND DISCUSSION

3.1. Effect of reaction temperature

In order to study effect of reaction temperature, the process was performed at various temperatures for 6 hr by using $FeSO_4.7H_2O$ and $Na_2S_2O_3$ as the initial materials. Figure 1 shows the SEM images of synthesized powder at different temperatures. It is observed that particles are in nanorod-like morphologies at all temperatures. Moreover, this figure indicates that increasing the reaction temperature will reduce the particles size.

FeS_2 can be crystallized not only as a cubic pyrite structure but also as an orthorhombic metastable marcasite structure which is detrimental to photovoltaic applications because of its low band gap (Eg = 0.34 eV). Therefore, it is better to perform the process at a temperature in which FeS_2 is produced without or with small amount of marcasite.

Figure 2 shows the XRD patterns of FeS_2 prepared by $Na_2S_2O_3$ (13.16 g) and $FeSO_4.7H_2O$ (23.15 g) at 150 and 180˚C after 6 hrs of reaction. The peaks of pyrite and marcasite are seen in XRD patterns. However, intensities of marcasite's peaks have decreased at higher temperature. In other words,

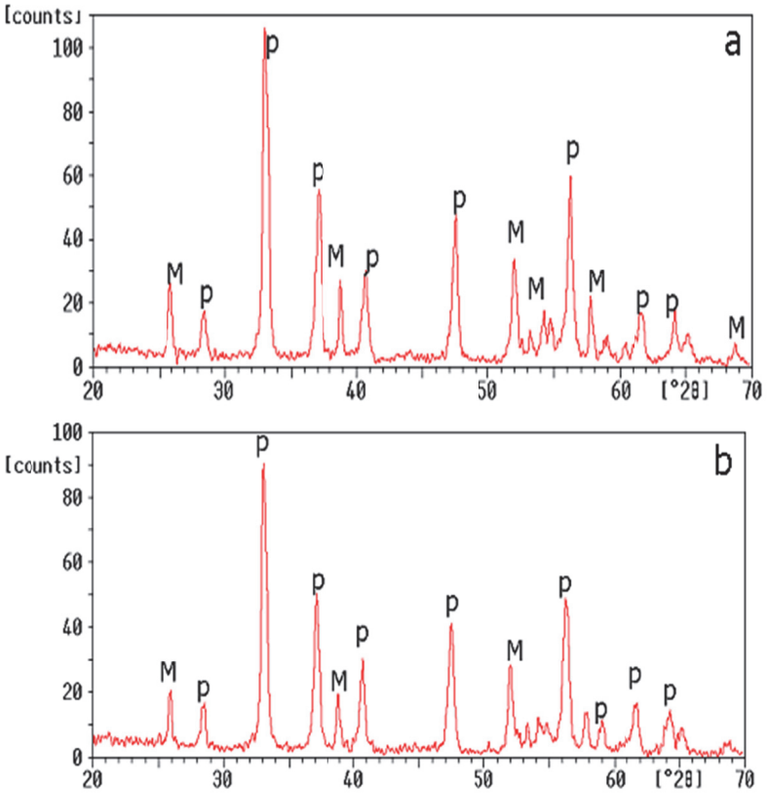

Figure 2: *XRD patterns of prepared FeS_2 at (a)150 ˚C and (b)180˚C for 6h (p:pyrite, m:marcasite)*

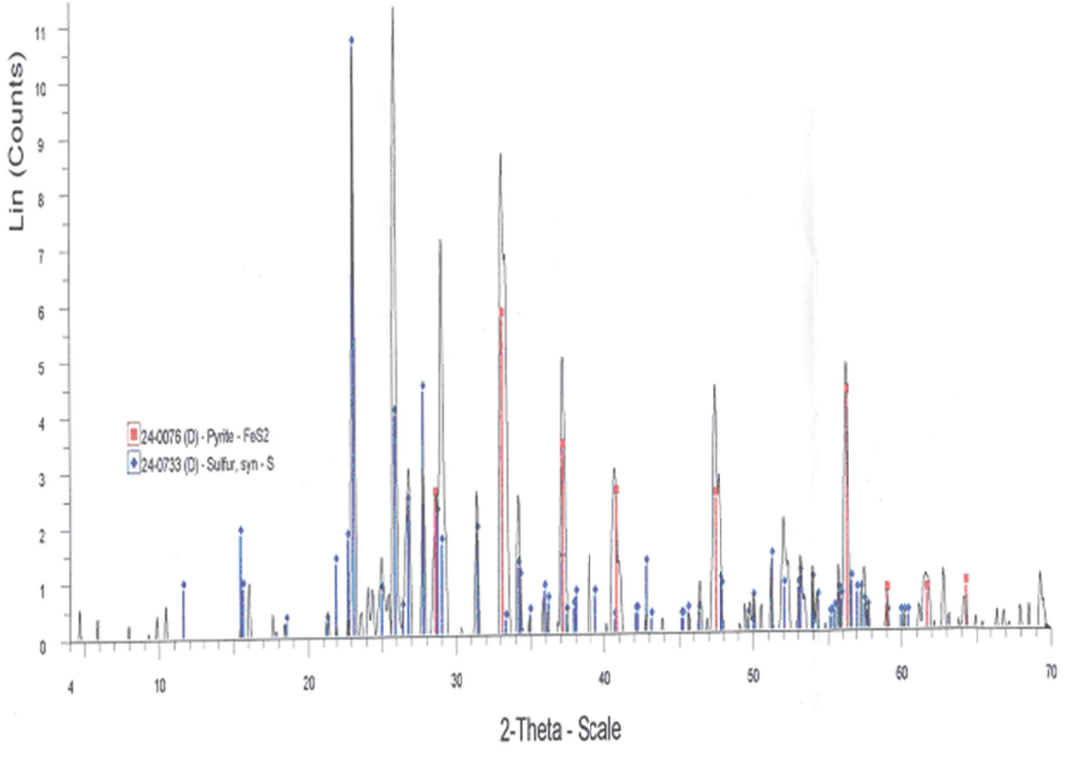

Figure 3: *XRD patterns of prepared FeS_2 by Fe $(NO_3)_3.9H_2O$ at 160˚C for 6h (p:pyrite,s:sulfur)*

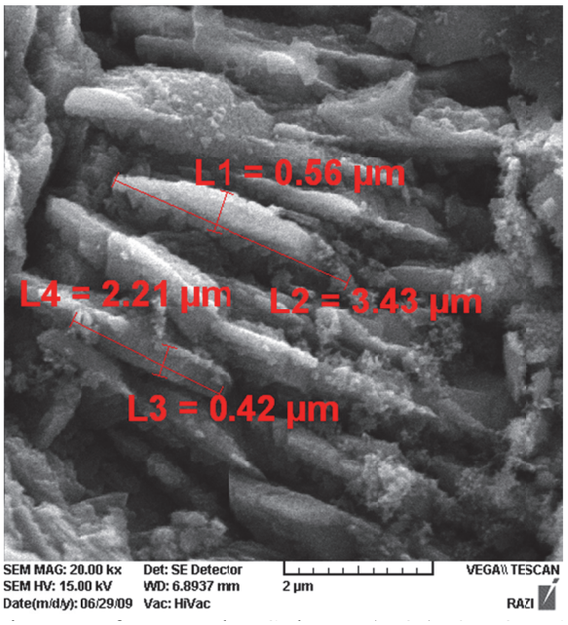

Figure 4: *SEM images of prepared FeS_2 by $Fe(NO_3)_3.9H_2O$ at 160˚C for 6h*

it seems that the amount of marcasite is lower at 180˚C (Figure 2b). It can be concluded that higher temperatures are more appropriate for producing pyrite.

It is also noticeable that averrage particle size was calculated around 30 nm at 180˚C and about 50 nm at 150˚C by using Debby-Sherrer equation.

3.2. Effect of iron source

$Fe(NO_3)_3.9H_2O$ was used instead of $FeSO_4.7H_2O$ to investigate the effect of iron source. Figure 3 shows XRD patterns of FeS_2 prepared by $Na_2S_2O_3$ (13.16 g) and Fe $(NO_3)_3.9H_2O$ (33.63 g) at 160˚C after 6 hrs of reaction. XRD patterns reveal that the prepared product contains pyrite and sulfur. This figure shows that sulfur is the major product. Furthermore, weight of product was much less than that of the previous case ($FeSO_4.7H_2O$ as iron source).

Figure 4 indicates SEM images of FeS_2 prepared by $Na_2S_2O_3$ (13.16 g) and Fe $(NO_3)_3.9H_2O$ (33.63 g) at 160˚C after 6 hrs of reaction. It demonstrates that obtained particles are microparticle with 2-3 µm in length and 400-500 nm in diameter. Therefore, it seems that $Fe(NO_3)_3.9H_2O$ isn't a suitable iron source.

5. CONCLUSIONS

Pyrite was successfully synthesized by hydrothermal method using $FeSO_4.7H_2O$ or $Fe(NO_3)_3.9H_2O$ and $Na_2S_2O_3$ as raw materials in temperature range of 130–180˚C. It was found that higher temperatures produce pyrite with better quality (smaller size and higher purity). Also, it was shown that $Fe(NO_3)_3.9H_2O$ shouldn't use as the iron source. Ultimately, results indicated that in optimum condition (temperature=180˚C, using $FeSO_4.7H_2O$ and $Na_2S_2O_3$) FeS_2 was obtained as nanorod with the lowest amount of marcasite.

6. REFERENCES

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