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Preparation and Characterization of β-$FeOOH/FeS_2$ Core/Shell Structure Nanocomposites†

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The β-FeOOH/FeS_2 core/shell structure nanocomposites were synthesized *via* a sulfuration method. The β-FeOOH nanorods were firstly functionalized as sacrificial templates then converted into β-FeOOH/FeS_2 core/shell nanocomposites using thioacetamide as a sulfur source. Morphologies of the materials were assessed by X-ray diffraction and scanning electron microscopy, while the thermal stability and magnetism properties were characterized by thermogravimetric analysis and vibrating sample magnetometer. It was found that β-FeOOH/FeS_2 core/shell nanocomposites could be obtained at the molar ratio of β-FeOOH to thioacetamide as 1:5-1:7. A possible conversion mechanism was proposed based on the experimental results.

Key Words: β-FeOOH, FeS_2, Core/shell structure, Sulfuration, Nanorods.

INTRODUCTION

The FeS_2 (pyrite) has shown promising material as a photovoltaic material for preparing thin film solar cell less than 200 nm thick, since it has an appropriate band gap (0.95 eV) and high optical absorption coefficient ($\alpha > 105$ cm^{-1} when $\lambda < 1$ μm)[1]. In the past decades, extensive investigations have been carried out to develop FeS_2-based solar cell materials[2-6]. For example, Liu *et al.*[7] studied FeS_2 thin films prepared by the sulfuration of Fe and Fe_3O_4. However, these studies focused on the preparation and properties of FeS_2 nanofilms and nanoparticles. To the best of our knowledge, few studies on β-FeOOH/FeS_2 core/shell structure nanocomposites have been reported as far.

In this paper, β-FeOOH/FeS_2 core/shell nanocomposites were synthesized by the sulfuration of β-FeOOH nanorods. The morphologies, thermal properties and magnetic behaviours of the nanocompostes were investigated.

EXPERIMENTAL

Analytically pure iron(III) chloride ($FeCl_3 \cdot 6H_2O$), thioacetamide (TAA), ammonia and HCl were all purchased from Shanghai Chemical Reagent Co., Ltd. All the chemicals were used as received.

Preparation: A brief summary of the β-FeOOH nanorods is given here. 2.7029 g $FeCl_3 \cdot 6H_2O$ was dissolved in 100 mL distilled water and adjusted to the pH = 2. The solution was then stirred at 80 ºC for 2 h. The brown-yellow precipitate was washed using distilled water and absolute ethanol and vacuum dried at 60 ºC for 6 h.

To obtain β-FeOOH/FeS_2 core/shell nanocomposites, the desired amount of β-FeOOH nanorods and thioacetamide (the molar ratio was 1:2, 1:5, 1:7 and 1:10) were put into small weighing bottles and Teflon-lined stainless steel autoclave of 100 mL capacity separately and kept at 140 ºC for 8 h. The resulting product was washed using distilled water and absolute ethanol and vacuum dried at 60 ºC for 4 h.

Characterization: The X-ray diffraction (XRD) data was obtained using a D/max-RA X-ray powder diffractometer equipped with a Cu-Ka source (λ = 0.154060 nm). Morphology observation of samples was performed by a S-4800 scanning electron microscope (SEM) at 20 kV. Thermogravimetric analyses (TGA) were conducted with a PE Pyris-I thermoanalyzer instrument. The vibrating sample magnetometer (VSM) was performed on a BHV-55 vibrating sample magnetometer.

RESULTS AND DISCUSSION

Fig. 1 shows the TG-DTG and DSC curves of β-FeOOH. It can be seen that the β-FeOOH undergoes a dehydration process and the phase transition in the temperature range 160-330 ºC.

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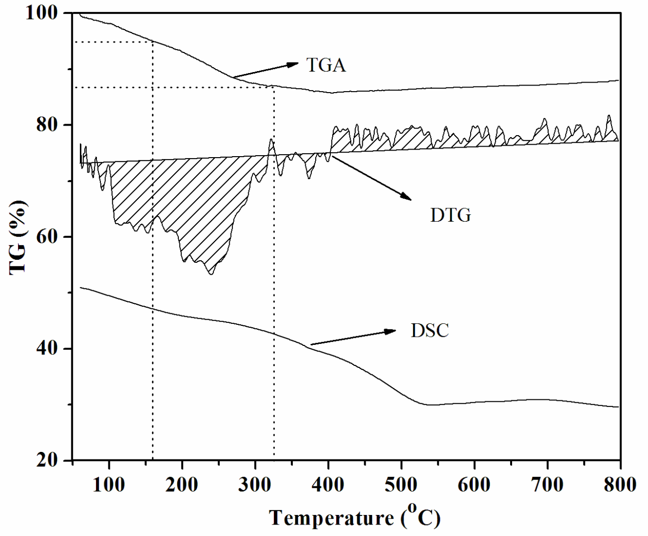


Fig. 1. TGA, DTG and DSC curves of β-FeOOH

Fig. 2 shows the XRD traces of β-FeOOH precursors and β-FeOOH/FeS_2 core/shell structure nanocomposites with various molar ratios of β-FeOOH to thioacetamide. Fig. 2(a) shows a typical XRD pattern of β-FeOOH. All the diffraction peaks are in good agreement with the standard PDF data of tetragonal β-FeOOH (JCPDS file 75-1594). The XRD patterns of β-FeOOH/FeS_2 core/shell nanocomposites with different molar ratios (1:2, 1:5 and 1:7) of β-FeOOH to thioacetamide are shown in Fig. 2(b, c and d). Besides the β-FeOOH peaks, the characteristic diffraction peaks corresponding to cubic FeS_2 (JCPDS file 71-2219) can be observed, which indicate the formation of β-FeOOH/FeS_2 nanocomposites after the sulfidation treatment of β-FeOOH precursors. With the increasing molar ratio of β-FeOOH/TAA to 1:10, a typical XRD pattern of FeS_2 has been observed in Fig. 2(e), which suggests that β-FeOOH has completely transformed to FeS_2.

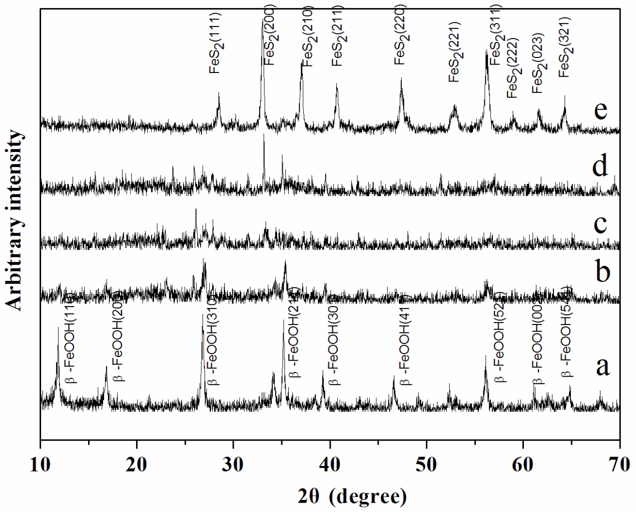
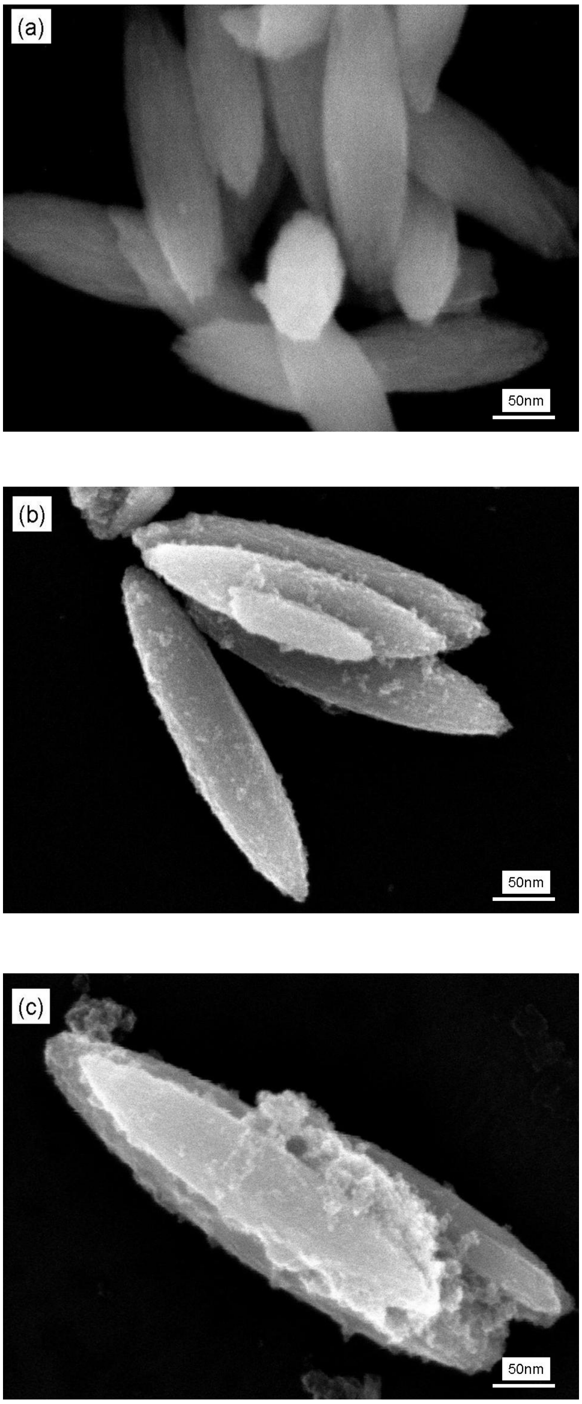


Fig. 2. XRD patterns of (a) β-FeOOH nanorods and β-FeOOH/FeS_2 core/shell structure nanocomposites with different molar ratios of β-FeOOH to thioacetamide (b) 1:2, (c) 1:5, (d) 1:7 and (e) 1:10

SEM images of the products are shown in Fig. 3. Fig 3(a) shows the typical morphology of β-FeOOH nanorods, in which large quantities of nanorods with diameter in the range of 60 nm and length up to 220 nm are observed. The morphology of β-FeOOH/FeS_2 nanocomposites with different molar ratios of β-FeOOH to thioacetamide are shown in Fig. 3(b, c, d and e). Fig. 3b shows that a few FeS_2 particles were attached on the surface of β-FeOOH nanorods, whereas Fig. 3(c) shows that β-FeOOH nanorods were tightly coated by FeS_2 and their surface is much rougher than that shown in Fig. 3(a), which indicates the formation of β-FeOOH/FeS_2 core/shell structure. With increasing the molar ratios, it can be seen that more and more FeS_2 particles were formed and encapsulated on the β-FeOOH surface (Fig. 3d). However, at the molar ratio 1:10, only FeS_2 nanoparticles can be observed in Fig. 3(e).



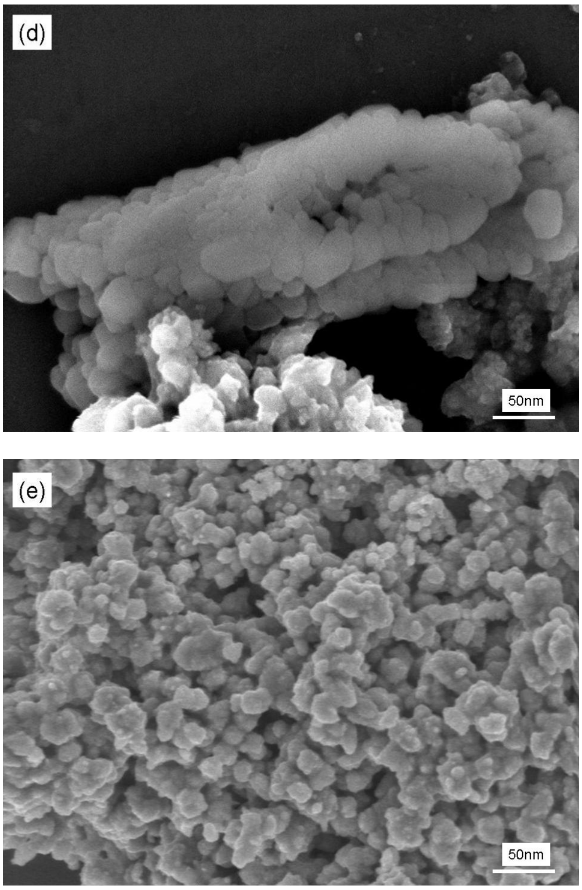


Fig. 3. SEM images of (a) β-FeOOH nanorods and β-FeOOH/FeS_2 core/shell structure nanocomposites with different molar ratios of β-FeOOH to thioacetamide (b) 1:2, (c) 1:5, (d) 1:7 and (e) 1:10

Fig. 4 shows the TGA curves of β-FeOOH/FeS_2 core/shell nanocomposites. FeS_2 nanoparticles (Fig. 4d) exhibit the highest thermal stability compared to β-FeOOH/FeS_2 core/shell nanocomposites. Clearly, with increasing amount of thioacetamide, the nanocomposites exhibit higher starting degradation temperature, which indicates that the presence of FeS_2 can impart β-FeOOH/FeS_2 core/shell nanocomposites with higher thermal stability.

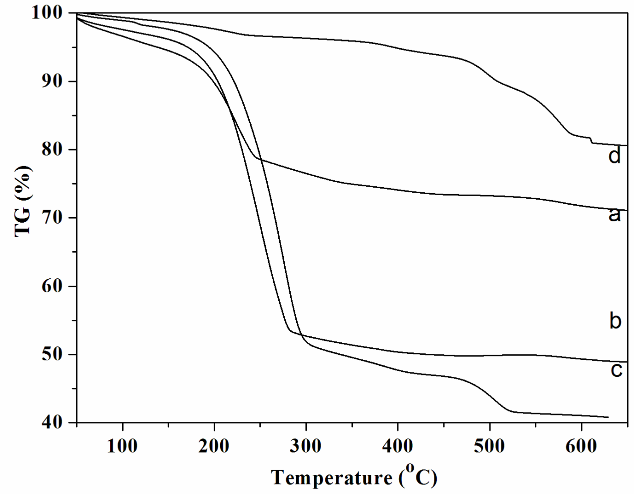
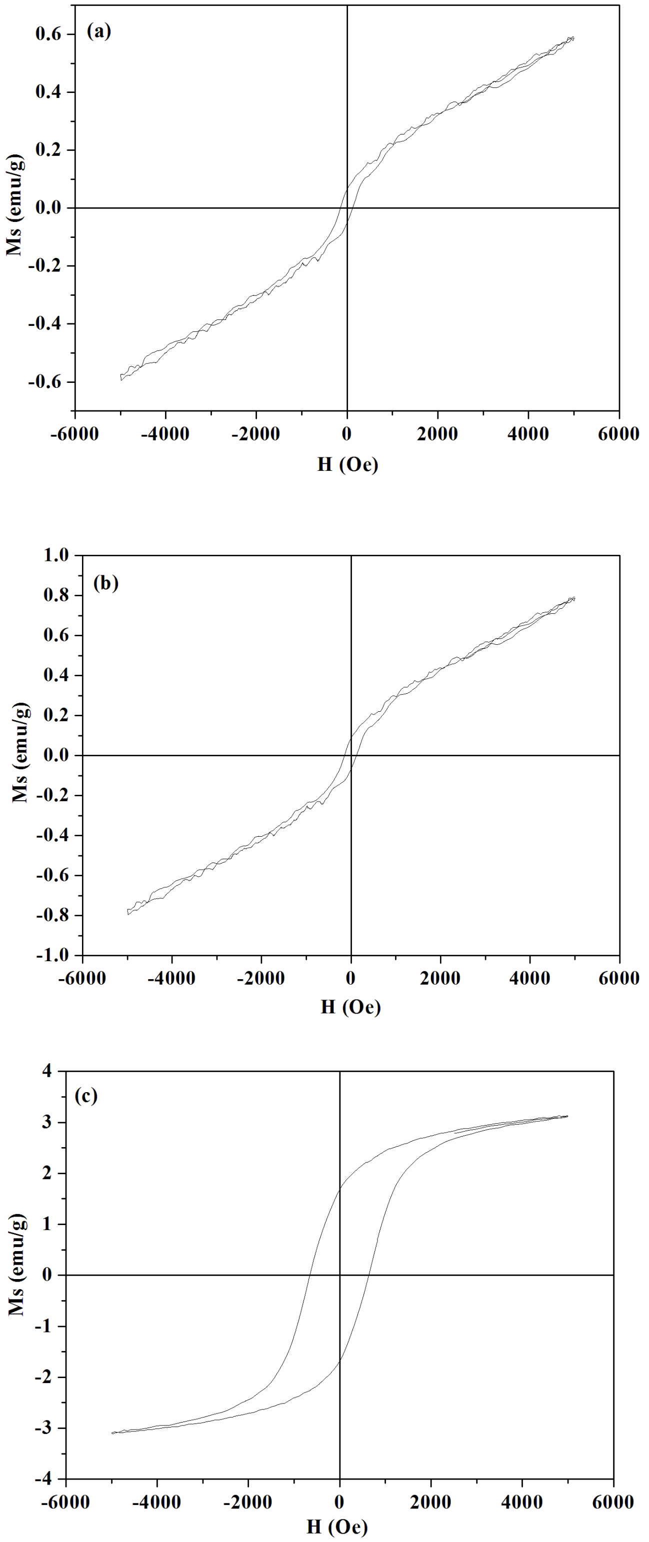


Fig. 4. TGA curves of β-FeOOH/FeS_2 core/shell structure nanocomposites with different molar ratios of β-FeOOH to thioacetamide (a) 1:2, (b) 1:5, (c) 1:7 and (d) 1:10

Fig. 5 shows the hysteresis loop-line of the products. Fig. 5(a) and (b) indicate that β-FeOOH and β-FeOOH/FeS_2 nanocomposites at β-FeOOH/FeS_2 molar ratio of 1:2 almost has no saturation magnetization. But from Fig. 5(c), (d) and (e), it can be seen that the magnetisms of the nanocomposites at the molar ratio of 1:5, 1:7 and 1:10 were 3.13, 6.33 and 6.57 emu/g, respectively. These data confirm that the magnetism of the nanocomposites enhances slightly with the increasing amount of FeS_2.



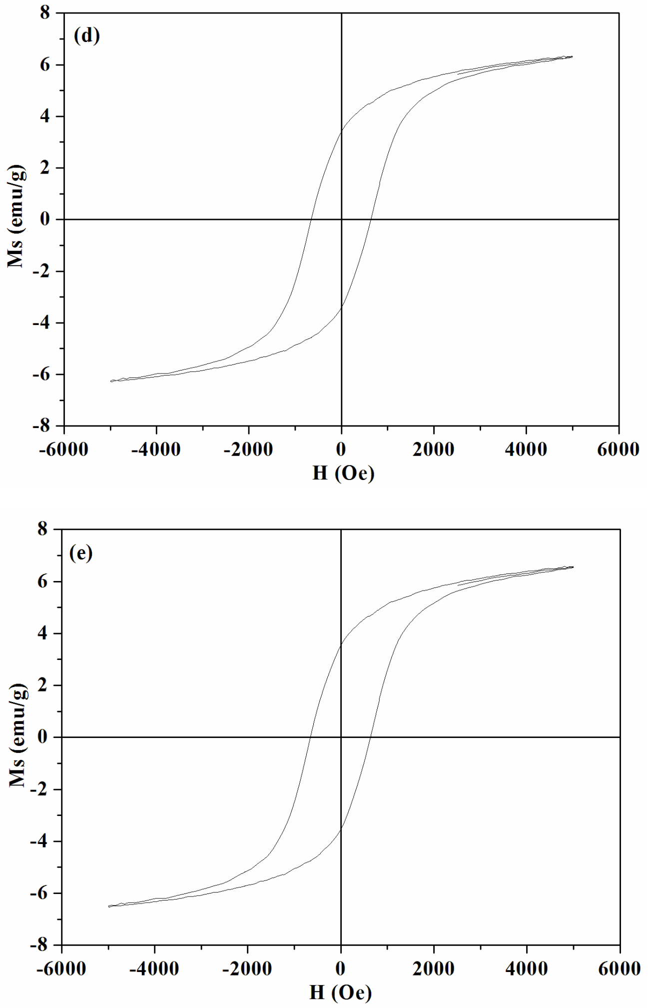


Fig. 5. VSM of (a) β-FeOOH nanorods and β-FeOOH/FeS_2 core/shell structure nanocomposites with different molar ratios of β-FeOOH to thioacetamide (b) 1:2, (c) 1:5, (d) 1:7 and (e) 1:10

The possible conversion mechanism has been proposed here according to the sulfuration of β-FeOOH. Several mechanisms have been reported to elucidate the process, including the well-known Ostwald ripening, classic and newly prevalent Kirkendall effect and inequivalent exchange of metallic atoms regarding the galvanic replacements reaction[8-11]. In this paper, the formation of β-FeOOH/FeS_2 core/shell nanocomposites can be explained by the diffusion and consumption process, which is schemed in Fig. 6. It is known that FeS_2 is more thermodynamically stable compared to β-FeOOH, therefore when thioacetamide is added, it will decompose to generate H_2S then reacts with β-FeOOH to generate FeS_2 microencapsulated on its surface. With increasing thioacetamide content, more and more β-FeOOH will convert into FeS_2 and finally when β-FeOOH reaches absolute sulfuration, amorphous FeS_2 nanoparticles were obtained.

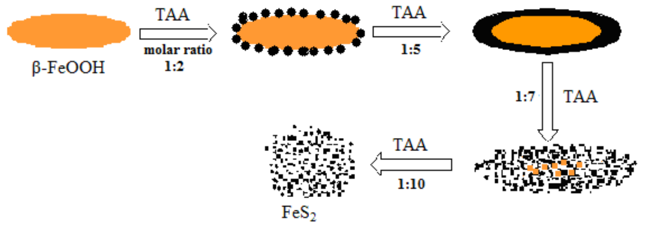


Fig. 6. Schematic illustration of the formation of β-FeOOH/FeS_2 core/shell structure nanocomposites

Conclusion

The preparation and characteristics of β-FeOOH/FeS_2 core/shell nanocomposites have been investigated. These materials can be obtained via a sulfidation process using β-FeOOH nanorods as sacrificial templates. This strategy may be extended to prepare other core/shell structured metal chalcogenides by using corresponding metal oxides with specific morphologies as precursors.

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