Synthesis, characterization and magnetic property of 3D flower-like nickel sulphide nanocrystals through decomposing bis(thiourea) nickel(II) chloride crystals

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Abstract. Three-dimensional (3D) flower-like cubic Ni_3S_4 nanoplates with single crystalline nature were successfully prepared through decomposing bis(thiourea) nickel(II) chloride crystals (BTNC). The samples were characterized by X-ray diffraction, scanning electron microscope, transmission electron microscope, selected area electron diffraction and Raman spectroscopy. Results show that the as-prepared products are pure cubic Ni_3S_4 and stable in range of 180–220°C with single crystal nature providing high surface areas, and higher reaction temperature leads to lower surface areas. Typical Raman peaks of the as-synthesized 3D flower-like cubic Ni_3S_4 at 200°C are located at 239, 286, 337, 379, 423, 478 and 630 cm^{-1} . Magnetization measurement indicates that single crystalline Ni_3S_4 nanoplates prepared at 200°C displays antiferromagnetic behaviour.

Keywords. Nanocrystal; thermal decomposition; BTNC; nickel sulphide; characterization; magnetic property.

1. Introduction

As one of the transition metal chalcogenides, nickel sulphides such as $\text{Ni}_{3+x}\text{S}_2$, Ni_3S_2 , $\text{Ni}_4\text{S}_{3+x}$, Ni_6S_5 , Ni_7S_6 , Ni_9S_8 , NiS , Ni_3S_4 and NiS_2 have attracted considerable attention owing to their promising properties and potential applications in high-performance cathodes for lithium ion batteries and as an electroactive material for high-performance supercapacitors,^{1–3} and as catalyst for unprecedented hydrodesulphurization activities and co-catalyst for photocatalytic hydrogen evolution.^{4–6} Nickel sulphides also have its unique electromagnetic and conductivity properties combined with bulk and toughening effect.^{7–9}

Ni_3S_4 (polydymite) with the cubic spinel structure has not been extensively investigated, because it is difficult to obtain pure phase Ni_3S_4 in the laboratory owing to the instability of Ni_3S_4 at higher temperatures. Traditionally, Ni_3S_4 crystallites synthesized were always accompanied by NiS and NiS_2 impurities.^{10,11} Recently, many methods such as pH controlled homogeneous precipitation,¹² two-step reduction sulphidation,¹³ colloidal chemical process,¹⁴ ambient temperature reaction^{15,16} and hydrothermal process¹⁷ have been introduced to synthesize Ni_3S_4 nanocrystallites. A variety of morphologies of Ni_3S_4 (polydymite) were thus obtained. These include irregular prismatic shapes¹³ two-dimensional nanoplates,¹⁴ hollow structure¹⁸ and nanoparticles.¹⁹ Up to

now, there was no report about the pure 3D-like Ni_3S_4 microcrystallites.

In this research, a single-source approach was adopted to obtain pure flower-like 3D Ni_3S_4 microcrystallites consisting of single nanocrystal plates with the thickness of about 25 and 100 nm at different temperatures, using bis(thiourea) nickel(II) chloride crystals (BTNC) complex as precursor in a Teflon-lined autoclave under thermal decomposition conditions. It is worth noting that the as-prepared 3D flower-like cubic Ni_3S_4 single crystal nanostructures providing high surface areas may exhibit some novel properties, which can lead to new and important applications in hydrogenation and hydrodesulphurization catalysts, electrode materials and magnetic devices.

2. Experimental

All the analytical chemicals were purchased from Shanghai Chemical Reagents Company and used without further purification. The precursor–BTNC–was prepared according to the reported method²⁰ using nickel chloride and thiourea in a stoichiometric ratio 1:2.

In a typical experimental procedure for fabrication of Ni_3S_4 nanocrystallites, 2 g BTNC was transferred into a 30 ml Teflon-lined stainless steel autoclave, which was then filled with 0.1 ml distilled water. The autoclave was sealed and maintained at 200°C for 20 h. After cooling to room temperature naturally, the dark products were obtained,

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washed with distilled water and absolute ethanol for several times, and dried in air atmosphere at 50°C for 10 h. For comparison, precursors with different reaction temperatures were prepared while keeping other conditions unchanged.

X-ray powder diffraction (XRD) patterns were recorded on an XD-2 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54187 \text{ \AA}$) in 2θ range of 10–70°. SEM images were taken with a KYKY2800B scanning electron microscope. Transmission electron microscopy (TEM) images and selected

area electron diffraction (SAED) pattern were obtained on a Tecnai G2 20 transmission electron microscope with an accelerating voltage of 200 kV. The Raman spectrum was measured with a Renishaw Invia laser Raman spectrometer. The magnetic measurement was carried out in a vibrating sample magnetometer (VSM) (MPMS-XL-7) at room temperature.

3. Results and discussion

Typically, as an example, the reaction process speculated for fabricating nickel sulphide single crystals can be expressed in detail as follows:

It is well known that ligands like thiourea and thiocyanate with S and N donors are capable of combining with metal to form stable complex compounds through coordinated bonds. Taking advantage of the charge delocalization of nickel metal in coordination with thiourea, BTNCs have been grown using slow evaporation technique at room temperature. Meanwhile, as the S–C bonds of BTNC were weaker than S–Ni bonds at relative higher temperature, and easy to be broken, Nickel sulphide crystal was produced.

Figure 1. XRD pattern of the as-prepared Ni_3S_4 crystals at 200°C for 20 h.

Figure 2. SEM images of the as-prepared Ni_3S_4 nanocrystals at different temperatures: (a) and (b) 180, (c) 200 and (d) 220°C.

Figure 1 displays the XRD pattern of the as-prepared Ni_3S_4 crystals at the temperature of 200°C , and all the peaks can be indexed as cubic structure of Ni_3S_4 (JCPDS no. 47-1739, $a = 9.457 \text{ \AA}$, calculated values: $a = 9.463 \text{ \AA}$). No impurities such as Ni, NiO_x or other nickel sulphides are detected in the XRD pattern. Highly pure phase Ni_3S_4 are obtained that may contribute to this particular synthesis method. The reaction is carried out in the BTNC crystal interior that isolates the reaction product from air, and the result is to prevent oxidation of nickel. During the experiment, it was found that BTNC did not decompose in Teflon-lined stainless steel autoclave until reaction temperature was increased to 180°C , when the S–C bonds of BTNC were broken and Ni_3S_4 crystal was produced. Ni_3S_4 is the only and first appearing phase when BTNC begin decomposing. The average crystallite size of as-prepared Ni_3S_4 crystals at 200°C for 20 h, calculated from the XRD analysis using Debye-Scherrer's equations is about 29 nm.

Figure 2 depicts SEM pictures of the as-prepared cubic Ni_3S_4 nanocrystals at different temperatures. Figure 2a and b show the presence of 3D flower-like Ni_3S_4 nanocrystals

with a few square-shaped layered structures when reaction temperature is maintained at 180°C . When temperature is increased to 200°C , 3D flower-like Ni_3S_4 nanocrystals are obtained (figure 2c). It was also observed that thickness of the 3D flower-like Ni_3S_4 nanoplates and the square-shaped nanolayers were similar. Figure 3d shows the SEM images of as-prepared Ni_3S_4 nanocrystals at 220°C . It can be seen that the thickness of product have a obviously change, and nanoplates become thicker as reaction temperature increases. So it can be concluded that the reaction temperature has considerable influence on the morphology of the product, and higher reaction temperature, thicker nanoplates.

TEM images of as-synthesized cubic Ni_3S_4 nanocrystals at different temperatures are shown in figure 3a–c. The images indicate that the as-prepared Ni_3S_4 nanocrystals consist of nanoplates and nanoparticles (figure 3a and b). The thickness of the nanoplates and diameters of the particles are about 25 and 80 nm, respectively, when reaction temperature is maintained at 180°C . Nanoplates with thickness of about 25 nm were obtained when the reaction temperature increased to 200°C (figure 3c). Figure 3d is the

Figure 3. TEM images of Ni_3S_4 nanocrystals synthesized at (a and b) 180°C , (c) 200°C for 20 h, respectively and (d) SAED pattern of Ni_3S_4 nanoplate.

corresponding SAED pattern taken from the Ni_3S_4 nanoplates synthesized at 200°C for 20 h, which demonstrates the single crystalline nature of the nanoplates. The estimated thickness value of the single crystal nanoplates deduced from the photographic exposure level. According to the images, take figure 3b as an example, particles exposure level are close to three layers of the nanoplates, so it could estimate the thickness of nanoplates is one-third of nanoparticles. On this basis, it was assessed that the thickness of as-prepared nanoplates at 180°C was below 25 nm and that of those at 200°C was above 25 nm.

Figure 4 shows the XRD patterns of samples obtained at different temperatures. All reflection peaks in figure 4a and b can be indexed as pure phase of cubic Ni_3S_4 (JCPDS No. 47-1739), when reaction temperature is kept at 180 and 220°C for 20 h respectively. It suggests that the as-prepared cubic Ni_3S_4 is stable in the range of 180 – 220°C . Figure 4c can be indexed as a mixture of NiS_2 (JCPDS No. 11-0099) and Ni_3S_4 (JCPDS No. 47-1739), which indicates that phase transition occurs when reaction temperature is mounted to 250°C for 20 h. The crystallite size of as-prepared Ni_3S_4 crystals at 180 and 220°C for 20 h were also calculated using Debye-Scherrer's equations. Results showed that increase in temperature leads to the growth in crystal size (from 25 to 38 nm). As mentioned, reaction temperature growth leads to the reduction surface area of plates as shown in SEM images (figure 2), which could assume that may be caused by the growth of nanocrystal.

Raman spectroscopy is an effective technique for exploring the structures of nanosized crystals. For further confirmation and characterization, Raman spectrum for the 3D flower-like cubic Ni_3S_4 with single crystals nature was carried out at room temperature

Figure 4. XRD patterns of as-prepared nickel sulphide crystals at different temperatures for 20 h; (a) 180°C , (b) 220°C and (c) 250°C .

Figure 5a displays room temperature Raman spectra of pure 3D flower-like cubic Ni_3S_4 nanocrystals synthesized at 200°C for 2 h. The vibrational frequency peaks located at 239, 286, 337, 379, 423, 478 and 630 cm^{-1} respectively, which partly agree well with previously reported results.²¹ According to literature, there are five Raman active modes at the Γ point of Ni_3S_4 , which can be classified as $\Gamma_{\text{Raman}}(\text{Ni}_3\text{S}_4) = A_g + E_g + 3T_g$.²² As for the 3D flower-like cubic Ni_3S_4 nanometric single crystals, peak located at 239 cm^{-1} should correspond to a stretching vibration peak with E_g mode, peaks located at 286 and 337 cm^{-1} should be assigned to T_g modes, and peak appearing at 379 cm^{-1} should be classified as A_g mode. Peaks located at 423, 478, 630 cm^{-1} might correspond to $2E_g$ and $2T_g$ modes. However, $2A_g$ has not been observed in the spectroscopy. It suggests that A_g mode is weak and E_g and T_g modes are the main vibration mode in cubic Ni_3S_4 nanometric single crystals. Meanwhile, the sharp peak located at 478 cm^{-1} with $2T_g$ mode suggests good crystallinity of sample, and the appearance of overtones may be due to good crystallinity also.

Figure 5. (a) Raman spectra and (b) magnetic hysteresis loop at room temperature of the Ni_3S_4 nanocrystals synthesized at 200°C for 20 h.

The magnetic properties of nanomaterials are believed to be highly dependent on the structure and size of the grain and crystallinity. Figure 5b shows the magnetization vs. applied magnetic field ($M-H$) curve at room temperature for the as-synthesized nickel sulphides at 200°C for 20 h. It can be seen that the sample presents an antiferromagnetic behaviour, although bulk Ni_3S_4 shows ferromagnetic behaviour with a Curie temperature T_c about 20 K¹⁵ and Ni_3S_4 nanoparticles show a paramagnetic behaviour at 5 K.¹⁹ The paramagnetic behaviour of the nanoparticles might arise from the so-called finite-size effect and/or surface effect.²³ However, the as-prepared Ni_3S_4 nanocrystals display an antiferromagnetic behaviour (hysteresis loop curve of the Ni_3S_4 is linear). This suggests that long-range antiferromagnetic order is not destroyed. According to the SEM and TEM images, thickness of the nanoplates synthesized at 200°C for 20 h are about 25 nm, which is close to the long-range area. But, the width of the nanoplates are around 500 nm. This means that the long-range antiferromagnetic order is along the nanoplates. In other words, the whole or most of one nanoplate is a continuous crystal, which suggests the single crystal nature of the product.

4. Conclusion

In summary, cubic 3D flower-like Ni_3S_4 structures with single crystalline nature providing high surface areas and antiferromagnetic behaviour were successfully prepared through decomposing BTNC at 200°C. It is found that pure cubic Ni_3S_4 (JCPDS 47-1739) nanoplates were obtained in range of 180–220°C, and phase transition occurred when reaction temperature mounted to 250°C. TEM and SEM images showed that thickness of as-prepared 3D flower-like cubic Ni_3S_4 nanoplates and nanolayers was about 25 nm at 180°C, and higher temperature lead to thicker plates. Raman spectroscopy study indicated that typical peaks of the pure cubic 3D flower-like Ni_3S_4 were located at 239, 286, 337, 379, 423, 478 and 630 cm^{-1} . Magnetization measurement indicated that single crystalline Ni_3S_4 nanoplates as-prepared at 200°C showed antiferromagnetic behaviour.

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