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Synthesis of Nickel Sulfide Particles by Solvothermal Process

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Abstract: Pyrite nickel disulfide and millerite nickel monosulfide have been successfully prepared by solvothermal method based on the reaction of $Ni(NO_3)_2{\cdot}6H_2O$ and $H_2NC(S)NH_2$ in benzene and ethylenediamine (EDA). The final products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM). The effects of the solvent, reaction temperature and time on the morphology and phase of the products have been discussed.

Keywords: Chalcogenides, solvothermal synthesis, X-ray diffraction analysis.

Sulfides of many transition metals show electronic and optical properties such as semiconductivity and photoconductivity [1,2]. For example, nickel sulfide is a potential transformation toughening agent for semiconductor materials [3], while nickel disulfide adopts the pyrite structure and exhibits semiconducting properties [4]. Thus, the synthesis of the 3d transition metal sulfides has attracted great interests for several decades. Normally, these sulfides are prepared through stoichiometric amount of the metal and sulfur heated in evacuated and sealed quartz ampoules at 500-1000°C [5]. However, the low melting point and volatilization of sulfur in some cases may make the control of composition difficult, and then several low temperature routes to group VIII transition-metal disulfides were recently reported [5-7]. For the preparation of sulfides of nickel, several techniques, such as solid-state reaction [8], chemical vapor transport [3,9,10], and liquid phase technique [3,5,9-12], have been developed. It is reported that well-crystallized nickel sulfides could be obtained through the solvothermal technique, but the Na^+ was easily adsorbed on the nanocrystallite to contaminate the product. In this work, pyrite nickel disulfide nanoparticles and millerite nickel monosulfide with micrometer size have been obtained through solvothermal process based on the reaction of $Ni(NO_3)_2{\cdot}6H_2O$ and $H_2NC(S)NH_2$. The novel pathway effectively prevents the product from the contaminating of the Na^+ ions.

Analytical grade solvents and reagents were applied as raw materials. In a typical reaction, stoichiometric $Ni(NO_3)_2{\cdot}6H_2O$ and thiourea were added into 11 mL benzene or EDA and then poured into a 15 mL Teflon-lined autoclave. Maintaining at 160-200°C for 12-30 h, the autoclave was cooled to room temperature. A black powder was

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collected by filtration, washed several times with absolute ethanol and distilled water and air-dried at ambient temperature. XRD patterns were recorded on a Rigaku D/MAX 2200PC diffractometer with Cu-Kα radiation (λ=0.15418 nm) and graphite monochromator. JEM-100 transmission electron microscopy and Hitachi S-520 scanning electron microscopy were used to observe the morphology and size of the particles.

Because the interaction between the different solvents and Ni^{2+} is different, various sulfides of nickel were obtained in different solvents. When benzene was selected as solvent, pure NiS_2 was obtained, while pure NiS formed in EDA.

Figure 1 a shows the XRD pattern of pure NiS_2 sample. All the peaks can be indexed as the pyrite nickel disulfide (JCPDS: 11-99). The crystalline size of the sample was about 29 nm from the full-width at half maximum (FWHM) of the strongest diffraction peaks. The reaction time and temperature have an important effect on the phase composition of products during the solvothermal synthesis of NiS_2 powders. The optimal condition is 180-200°C for 16-30 h. Lower temperature or shorter time leads to an incomplete reaction and other phases, such as tetrahedral NiS or polydymite Ni_3S_4 (**Figure 1b**), millerite NiS and nickel sulfide NiS at higher temperature (**Figure 1 c,d**). It is likely that Ni_3S_4 decomposes to millerite NiS and tetrahedral NiS at 200°C since Ni_3S_4 is metastable[4]. Prolonging the reaction time to 16 h at 180°C or 18 h at 200°C, only the pyrite NiS_2 particles formed indicated by XRD patterns. It can be seen from **Figure 3a** that the prepared NiS_2 are spherical particles with the size of *ca.* 20 nm. But the particles tend to aggregate.

The reaction was significantly influenced by the coordinating ability of the solvent. If the solvent is EDA at the same condition, pure phase of NiS was obtained as demonstrated in **Figure 2**. All the peaks are indexed to millerite nickel sulfide (JCPDS: 12-41). This is different from the results of reference 12, in which spherical and cubic shape NiS_2 were obtained using the same precursor ($NiSO_4 \cdot 6H_2O$ with Na_2S_3) in benzene or EDA at 130°C for 8-12 h. In their experiments EDA was supposed as template for inorganic ion self-assembling and growth, while benzene operated as the solvent. EDA, with strong N-chelation ability and basicity acts as a bidentate ligand to form a relatively stable Ni^{2+} complex cation just like $[Ni(EDA)_3]^{2+}$[13], which is a purple solution at room temperature. The complex cation formed usually acts as a template which possibly increases the reactivity of Ni (II), promoting the reactions[14]. Although there was thiourea in the solution, the coordination ability of thiourea is much smaller than that of EDA[15]. The preparation process of NiS may be proposed as a liquid reaction: Firstly, $H_2NC(S)NH_2$ is soluble in EDA at room temperature and decomposed to produce S^{2-} in the base environment[16]. Then $[Ni(EDA)_3]^{2+}$ and S^{2-} were reacted to produce NiS powder. The whole process may be expressed as follows:

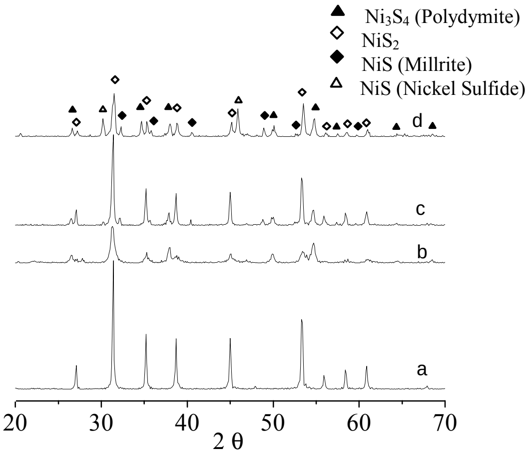
$$H_2NC(S)NH_2 \rightarrow S^{2-}$$

$$Ni^{2+} + 3EDA \rightarrow [Ni(EDA)_3]^{2+}$$

$$[Ni(EDA)_3]^{2+} + S^{2-} \rightarrow NiS\downarrow + 3EDA$$

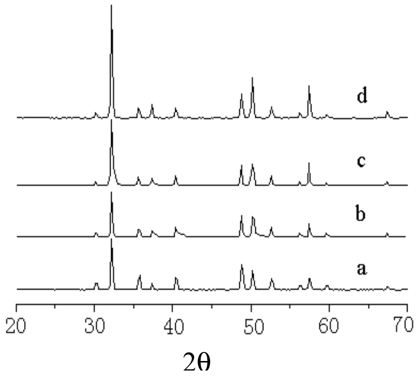
In our experiment, the optimal condition to prepare NiS was reacting at 200°C for more than 6 h. When the temperature was lower than 160°C, the reaction could not initiate even the heating time was 30 h. Heating time shorter than 6 h at 200°C led to

Figure 1 XRD patterns of obtained powders in benzene



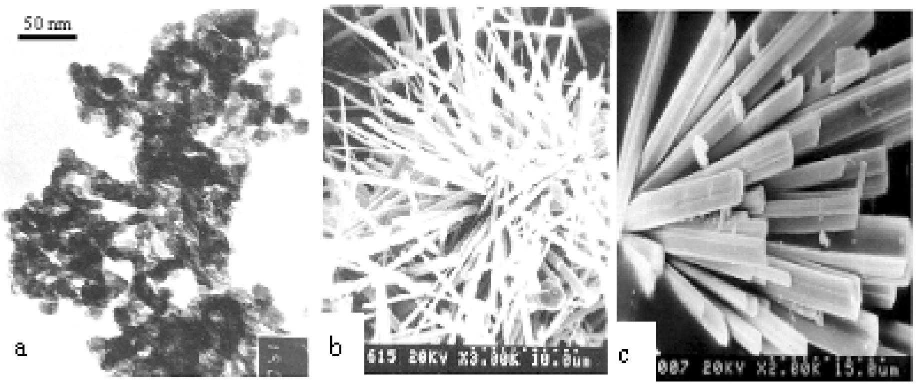
a. at 180℃ for 24 h; b. at 160℃ for 24 h;
c. at 180℃ for 12 h; d. at 200℃ for 12 h

Figure 2 XRD patterns of NiS powders obtained in EDA



at 200℃ for a. 6 h; b. 12 h; c. 18 h; d. 30 h

Figure 3 TEM and SEM graphs of the as-prepared products



(a) TEM graph of the prepared NiS_2 particles at 180°C for 24 h;
(b) SEM photograph of NiS particles at 200°C for 12 h;
(c) SEM photograph of NiS particles at 200°C for 30 h

incomplete reaction with decreased yield and a small amount of unknown impurity. Prolonging the time has no effect on the phase composition of the products. TEM photograph (**Figure 3b**) indicated that the NiS particles have a rod-like morphology with diameter of about 0.5-1.5 μm. The rod broadened with the time prolonging (**Figure 3c**) and the crystallinity increased from the intensity of the XRD peaks (**Figure 2**).

In conclusion, pyrite NiS_2 nanocrystallites and millerite NiS rod-like particles have been successfully prepared through a simple solvothermal route using different solvents. The difference of the formation mechanism of NiS_2 and NiS particles in benzene or EDA was owing to the different polarity and coordination ability to Ni^{2+} of these solvents.

The reaction temperature and time significantly affected the phase composition of NiS_2 powders, while that only affected the particle size of the NiS particles with the prolongation of the reaction time.

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