

Two-phase synthesis of olive-like NiS particles and chain-like Bi₂S₃ nanowires

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Highly dispersed olive-like NiS particles were synthesized in a liquid-liquid biphasic system at room temperature, where nickel xanthate in organic solvents (toluene and benzene) and sodium sulfide in water solution were used as nickel and sulfide sources, respectively. NiS particles were formed at the stabilized phase interface. The structures, chemical composition and optical characteristics of the products were investigated by transmission electron microscopy, scanning electron microscopy, X-ray photoelectron spectroscopy and ultraviolet-visible spectroscopy. The organic solvents obviously influenced the morphology of the NiS particles. The olive-like NiS with smooth surface and sharp ends was obtained at benzene/water interface, while spindle-like NiS particles with rough surface and circle ends were formed when using toluene as a solvent. Analogously, chain-like Bi₂S₃ nanowires were produced at chloroform/water interface. The effect of the experiment parameters including reaction time, solvent and concentration of reactants on the size and morphology of the products was discussed in detail and a possible formation mechanism was suggested.

Keywords: *two-phase method; crystal morphology; nanomaterials; semiconducting materials*

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1. Introduction

The controlled fabrication of semiconducting materials with well-defined shapes, such as nanodots, nanorods, sheets and spheres has attracted much attention in recent years because of their shape-dependent physical and chemical properties [1]. Above all, a number of strategies have been developed to prepare inorganic nanocrystals with naturally inspired shapes including flower-like, dendrite-like, sheaf-like, peanut-like (or dumbbell-like) structures. For instance, olive-like nanostructures have been synthesized via wet-chemical [2], solvothermal [3], sonochemical [4], and hydrothermal methods [5], etc. However, it still remains a great challenge to develop simple and template-free methods for preparing nanomaterials with non-thermodynamic equilibrium shape.

Nickel sulfide, as one of transition metal chalcogenides, has caused significant concern because of its unique properties and application as a metal-insulator, paramagnetic-antiferromagnetic

phase changing material, hydrogenation catalyst and solar storage [6]. Nickel sulfide nanocrystals have been prepared in diverse morphologies, such as nanorods, triangular nanoprisms [7], hollow spheres [8], nanotubes and nanoneedles [9, 10]. However, to the best of our knowledge, little work has been reported about the synthesis of olive-like NiS nanoparticles via a simple interfacial method.

Two-phase interface provides a common boundary, where ions are more prone to react with the surrounding species, driven by the reduction in the interfacial energy, which affects the growth dynamics of nanocrystals [11, 12]. Two-phase interface methods have successfully been utilized to synthesize metal (Ag, Cu and Au), chalcogenides (CdS, ZnS and CuS) and oxides (Fe₂O₃ and ZnO) nanocrystals with controlled shape and size at room temperature [13–18]. In our previous work, freestanding Sb₂S₃ films and nanorings were easily formed at the interface of toluene and water at room temperature using Sb xanthate and Na₂S as precursors [19]. Herein, olive-like NiS particles and chain-like Bi₂S₃ nanowires were synthesized

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at the interface of toluene or benzene/water, and chloroform/water, respectively. Unlike previous reports, in this work solvents played an important role in the morphologies and structures of the products.

2. Experimental

2.1. Sample preparation

All reagents used in this work were analytical grade and used as received without further purification. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and $\text{C}_2\text{H}_5\text{OCS}_2\text{K}$ were purchased from Sinopharm Chemical Reagent Co., Ltd. $(\text{C}_2\text{H}_5\text{OCS}_2)_2\text{Ni}$ and $(\text{C}_2\text{H}_5\text{OCS}_2)_3\text{Bi}$ were prepared according to our previous reports [20]. 3 g of Na_2S in 20 mL of distilled water were added dropwise into 40 mL of toluene containing 0.005 g of $(\text{C}_2\text{H}_5\text{OCS}_2)_2\text{Ni}$ (0.4 mmol/L). The reaction proceeded without disturbances for different times at room temperature. The product was formed at the interface and collected by filtration, washing with distilled water and absolute ethanol several times, and drying at room temperature. Bi_2S_3 particles were prepared in a similar way.

2.2. Characterization

Transmission electron microscopy and high-resolution transmission electron microscopy were carried out on a JEM-2100 (JEOL) transmission electron microscope (TEM). Scanning electron microscopy was performed using a JSM-5610LV scanning electron microscope (SEM). X-ray photoelectron spectra (XPS) were recorded on a PHI QUANTERA II X-ray photoelectron spectrometer, using Al $K\alpha$ radiation as the exciting source. The results obtained in the XPS analysis were corrected by referencing the C 1s line to 284.8 eV. Ultraviolet-visible spectra (UV-Vis) were recorded on a Shimadzu UV-240 spectrometer and the samples were dispersed in ethanol.

3. Results and discussion

At the beginning, the organic phase was yellow due to the dissolution of nickel xanthate, and the

water phase was colorless (Fig. 1a). With the extension of reaction time, color of the organic layer became lighter and lighter, and water layer became yellow, showing that the reaction between nickel xanthate and Na_2S occurred at the interface and the product $\text{C}_2\text{H}_5\text{OCS}_2\text{Na}$ was transferred from organic to aqueous phase. About half an hour later, black interface layer was observed, organic phase became colorless and water phase changed to yellow, which indicated that the reaction was completed (Fig. 1b). The possible chemical reaction was shown in Fig. 2.

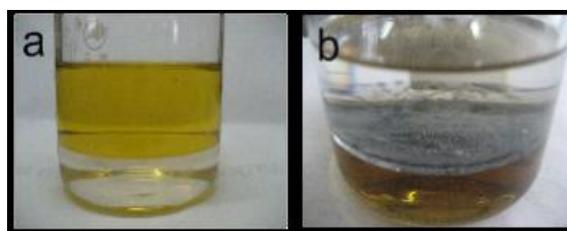


Fig. 1. Digital pictures of toluene/water interface at different reaction times of 0 h (a) and 60 h (b).

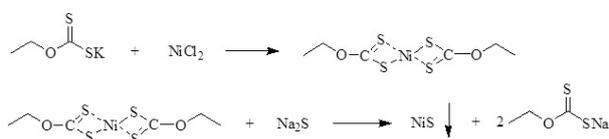


Fig. 2. Reactions for the formation of NiS.

The shape and structures of the as-prepared nickel sulfur were characterized by TEM. As shown in Fig. 3a, the products obtained at toluene/water interface after 60 h of ageing were olive-like, with an average length of 350 nm and a diameter in the range of 100 to 200 nm. A high-magnification TEM image shows that the olive-like particles with rough surface were assembled by smaller nanocrystals.

XPS spectra of olive-like NiS particles are shown in Fig. 4. The peak centered at 168.5 eV for S 2p indicates that oxidized sulfur species, such as sulfinate or sulfonate were formed after a few days of exposure to the atmosphere (Fig. 4a) [21]. Upon Ar^+ sputtering of the powders, the peak corresponding to oxidized sulfur species dramatically

decreased, showing that the oxidation must have occurred on the surface of the NiS particles. The binding energy at 855.5 and 861.9 eV could be attributed to Ni 2p 2/3 and Ni 2p 1/2, respectively (Fig. 4b). The ratio of integral area for Ni 2p to S 2p was about 1.1:1, which was close to stoichiometric ratio of NiS.

When the reaction was extended to 5 days, short rod-like structures with about 450 nm in length and 90 nm in width were observed (Fig. 3b). It may be suggested that the nanorods were obtained by the continuing growth of nanoparticles.

The concentration of nickel xanthate in toluene exerted a great influence on the morphology of NiS. When the concentration was increased to saturation (0.05 mol/L), NiS films were obtained (Fig. 3c). The SEM image shows that the sheets are of large area and thin thickness (Fig. 3d), and the selected-area electron diffraction (SAED) pattern indicates that the NiS films are poor-crystalline (inset in Fig. 3c). Therefore, extremely dilute concentration of Ni xanthate was important to form olive-like NiS structures because the nucleation was relatively slow for the growth in dilute solution, thus, the NiS nuclei grew in preferred direction, forming olive-like particles.

The solvents also affected morphology of the NiS particles. When using benzene as a solvent instead of toluene, olive-shaped NiS was also produced (Fig. 3e). However, it is noteworthy that two ends of the olive are sharp, with a size of 450 to 850 nm in length and 150 to 250 nm in diameter, and additionally the surface of the olives is smooth (Fig. 3f). The SAED pattern shows clear well-aligned diffraction spots, indicating that the olive-shaped particles are single crystalline in nature (inset in Fig. 3f). All these particles are different from those obtained in the toluene/water system. Less polarity of benzene than that of toluene might lead to stronger adsorption of xanthate ligands on the surfaces of NiS, thus, the particles grew orientedly, resulting in the formation of regular olives [22]. When using chloroform as an organic phase, a black thin layer was formed at the interface of water and air. The thin layer became white after ageing for several hours,

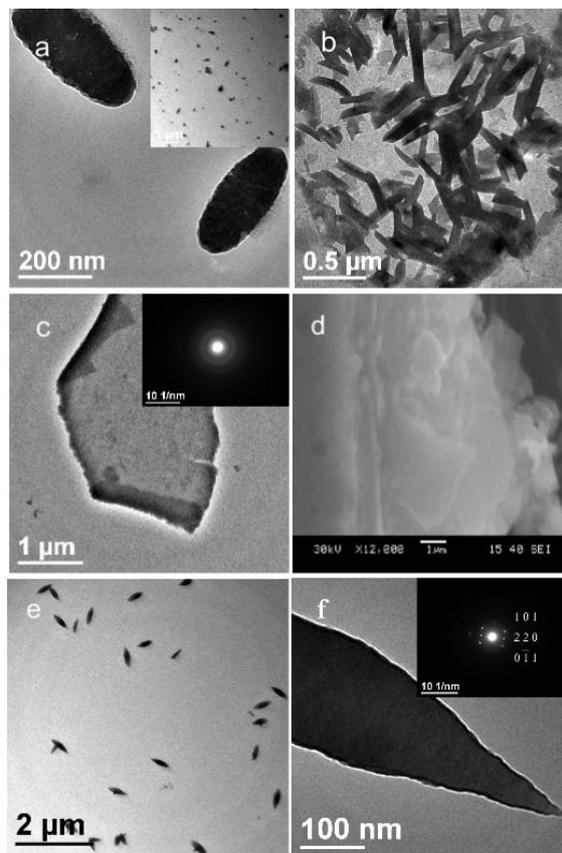


Fig. 3. (a) and (b) TEM images of NiS obtained at toluene/water interface after different ageing times for $[\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2] = 0.4 \text{ mmol/L}$: (a) 60 hours and (b) 5 days; (c) and (d) TEM and SEM images of NiS films obtained at toluene/water interface for $[\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2] = 0.05 \text{ mol/L}$, and the inset in (c) showing its SAED pattern; (e) and (f) TEM images of NiS obtained at benzene/water interface after 60 h of ageing for $[\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2] = 0.4 \text{ mmol/L}$, and the inset in (f) showing its SAED pattern.

showing that NiS in nanoscale was easily oxidized in the atmosphere.

The UV-Vis absorption spectra of olive-like NiS particles and NiS films prepared in toluene are shown in Fig. 5. The spectra of both NiS particles (Fig. 5a) and films (Fig. 5b) show one peak centered at about 260 nm (ca. 4.35 eV) and 215 nm (ca. 4.50 eV), respectively. As compared with bulk NiS (ca. 2.10 eV), the absorption spectra are shifted to higher energy because of the quantum confinement effect [23].

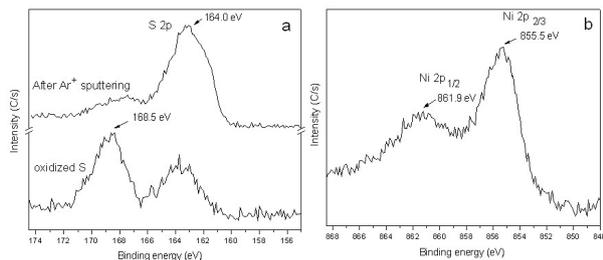


Fig. 4. XPS spectra of olive-like NiS particles: (a) S core and (b) Ni core.

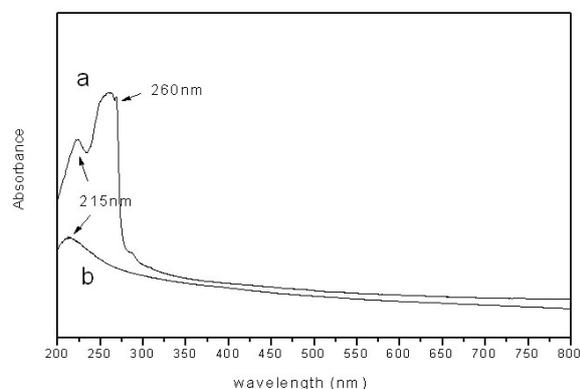


Fig. 5. UV-Vis spectra of (a) olive-like NiS particles and (b) NiS films obtained at toluene/water interface.

Similarly, Bi_2S_3 nanoparticles were synthesized at chloroform/water interface using Bi xanthate and Na_2S as precursors. TEM image (Fig. 6a) indicates that the products obtained within two days of ageing are chain-like nanowires composed of tiny particles. The SAED pattern (inset of Fig. 6a) shows that these particles are poor-crystalline. When using toluene or benzene instead of chloroform, Bi_2S_3 spheres aggregated by nanoparticles are observed (Fig. 6b). The polarity of the solvents should play an important role in the nucleation and growth of Bi_2S_3 nanoparticles. The effect of solvents is still unclear, and further investigation is underway.

4. Conclusions

In summary, unique olive-like NiS particles and chain-like Bi_2S_3 nanowires were obtained at the liquid-liquid interface at room temperature.

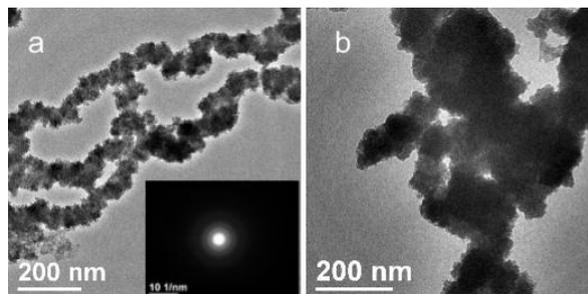


Fig. 6. (a) TEM images of chain-like Bi_2S_3 nanowires prepared at chloroform/water interface and the inset showing its SAED pattern; (b) spherical Bi_2S_3 particles prepared at toluene/water interface.

Encouraged by the success in producing the novel morphology of metal chalcogenides using xanthate as a precursor, we believe that this two-phase method can be applicable to synthesize a variety of other materials.

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References

- [1] GENG J., ZHU J.J., CHEN H.Y., *Cryst. Growth Des.*, 6 (2006), 321.
- [2] RAULA M., RASHID M.H., PAIRA T.K., DINDA E., MANDAL T.K., *Langmuir*, 26 (2010), 8769.
- [3] LU J., CHEN D., JIAO X., *J. Colloid Inter. Sci.*, 303 (2006), 437.
- [4] WANG H., ZHANG J.R., ZHAO X.N., XU S., ZHU J.J., *Mater. Lett.*, 55 (2002), 253.
- [5] WEI F., LI G., ZHANG Z., *Mater. Res. Bull.*, 40 (2005), 1402.
- [6] WELTERS W., VORBECK G., ZANDBERGEN H., DEHAAN J., DEBEER V., VANSANTEN R., *J. Catal.*, 150 (1994), 155.
- [7] GHEZELBASH A., SIGMAN JR M.B., KORGEL B.A., *Nano lett.*, 4 (2004), 537.
- [8] HU Y., CHEN J., CHEN W., LI X., *Adv. Funct. Mater.*, 14 (2004), 383.
- [9] CHEN D., GAO L., *J. Cryst. Growth*, 262 (2004), 554.
- [10] CHEN D., GAO L., ZHANG P., *Chem. Lett.*, 32 (2003), 996.
- [11] LIN Y., SKAFF H., EMRICK T., DINSMORE A., RUSSELL T., *Science*, 299 (2003), 226.
- [12] RAO C.N.R., KALYANIKUTTY K., *Accounts Chem. Res.*, 41 (2008), 489.

- [13] RAO C.N.R., KULKARNI G., THOMAS P.J., AGRAWAL V.V., SARAVANAN P., *J. Phys. Chem. B*, 107 (2003), 7391.
- [14] GAUTAM U.K., GHOSH M., RAO C.N.R., *Chem. Phys. Lett.*, 381 (2003), 1.
- [15] LUO K., SCHROEDER S.L.M., DRYFE R.A.W., *Chem. Mater.*, 21 (2009), 4172.
- [16] LIANG X., XING L., XIANG J., ZHANG F., JIAO J., CUI L., SONG B., CHEN S., ZHAO C., SAI H., *Cryst. Growth Des.*, 12 (2012), 1173.
- [17] TAKEDA S., WILTZIUS P., *Chem. Mater.*, 18 (2006), 5643.
- [18] FAN D., THOMAS P.J., O'BRIEN P., *Chem. Phys. Lett.*, 465 (2008), 110.
- [19] HAN Q., YUAN Y., LIU X., WU X., BEI F., WANG X., XU K., *Langmuir*, 28 (2012), 6726.
- [20] HAN Q., CHEN J., YANG X., LU L., WANG X., *J. Phys. Chem. C*, 111 (2007), 14072.
- [21] GROSVENOR A.P., BIESINGER M.C., SMART R.S.C., MCINTYRE N.S., *Surf. Sci.*, 600 (2006), 1771.
- [22] JIANG F., MUSCAT A.J., *Langmuir*, 28 (2012), 12931.
- [23] NAKAMURA M., FUJIMORI A., SACCHI M., FUGGLE J., MISU A., MAMORI T., TAMURA H., MATOBA M., ANZAI S., *Phys. Rev. B*, 48 (1993), 16942.

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