Synthesis of NiS Nanowhiskers *via* Surfactant-aid Hydrothermal Reaction

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Uniform NiS nanowhiskers have been prepared *via* a hydrothermal reaction between $NiCl_2 \cdot 6H_2O$ and $Na_2S_2O_3$ in the presence of surfactant of $C_{17}H_{33}COOK$ (potassium oleate). The images characterized through XRD and TEM indicates the morphology of hexagonal NiS is uniform nanowhiskers with an average diameter of 80 nm and length in micrometer scale. The formation mechanism and surfactant effect were discussed in details.

Recently, the effects of surfactants on the growth of nanocrystal have been investigated by many scientists. The basic reason for using surfactants is that crystal sizes and corresponding size distributions may be controlled under certain reaction conditions and the selection of surfactants. Many inorganic materials, such as $BaCrO_4$, $CaSO_4$, and TiO_2[1,2] can grow into a complex structure with uniform size. More recently, Alivisatos and co-workers developed an effective method in the synthesis of CdSe and Co nanorods under a hot solvent condition with the presence of surfactants.[3,4] Controlled manipulation for the synthesis of low-dimensional nano-materials is always an important area of current research.[5,6] The amazing properties accompanying with one-dimensional nanomaterials have sparked increasing interest in the future generation nanoelectronic and biomedical devices. So far, considerable progresses have been made in the development of new methods for preparing one dimensional nanomaterials,[7–9] However, due to their extremely small size and their anisotropy, the control of nucleation and growth of one dimensional nanostructure materials is still a big challenge.

Nickel monosulfide (NiS) has been the subject of considerable interest due to its properties as metal-insulator, paramagnetic-antiferromagnetic phase-changing material,[10,11] and its usage in hydrosulfurization catalyst and solar storage.[12] NiS exists in two forms: high-temperature form with NiAs structure and low-temperature form with hexagonal structure.[13] In the past decades, the traditional methods for the preparation of hexagonal NiS usually required high processing temperature, long reaction time, and toxic reagents, and such experimental methods have led almost invariably to thermodynamically stable phases with simple lattice structure of high density and high symmetry. Moreover, their products have had high crystallinity and low surface area,[14,15] which preclude the further application of this material.[15] Most recently, nanoparticles of NiS have been studied extensively because they can be easily fabricated using established methods.[16] However, synthesis of one-dimensional NiS has seldom been reported. In this communication, we present a simple strategy for synthesizing NiS nanowhiskers *via* hydrothermal reaction with the presence of surfactant $C_{17}H_{33}COOK$.

$NiCl_2 \cdot 6H_2O$, $Na_2S_2O_3$, and $C_{17}H_{33}COOK$ were of analytic grade purity and used without further purification. Three reagents were dissolved in distilled water to prepare aqueous solutions with a concentration of 0.01 M, respectively. In a typical procedure, 15 ml of the $NiCl_2 \cdot 2H_2O$ solution and 15 ml of the $Na_2S_2O_3$ solution were put into a Teflon-lined stainless steel autoclave, then 20 ml surfactant solution was added to fill the autoclave up to 90% of the total volume. The sealed autoclave was maintained at 140 °C for 24 h, then cooled to room temperature naturally. A black precipitate was collected by vacuum filtration and washed several times with distilled water and absolute ethanol, then vacuum dried at 60 °C for 6 h. The obtained samples were characterized by X-ray powder diffraction (XRD) using Japan Rigaku Dmax γ-A X-ray diffractometer with graphite monochromatized CuKα radiation ($\lambda = 0.15406$ nm). The microstructure and morphologies of the sample were analyzed with transmission electronic microscopy performed at 200 KV using Hitachi 800 (TEM).

The XRD pattern of as-obtained sample showed in Figure 1 could be indexed to the hexagonal phase of NiS and no obvious impurity phase could be found. After refinement, the calculated cell constant a $= 9.618$ Å is consistent with the literature datum (JCPDS 12-41). The shape of the diffraction peaks suggested that the powder be well crystallized.

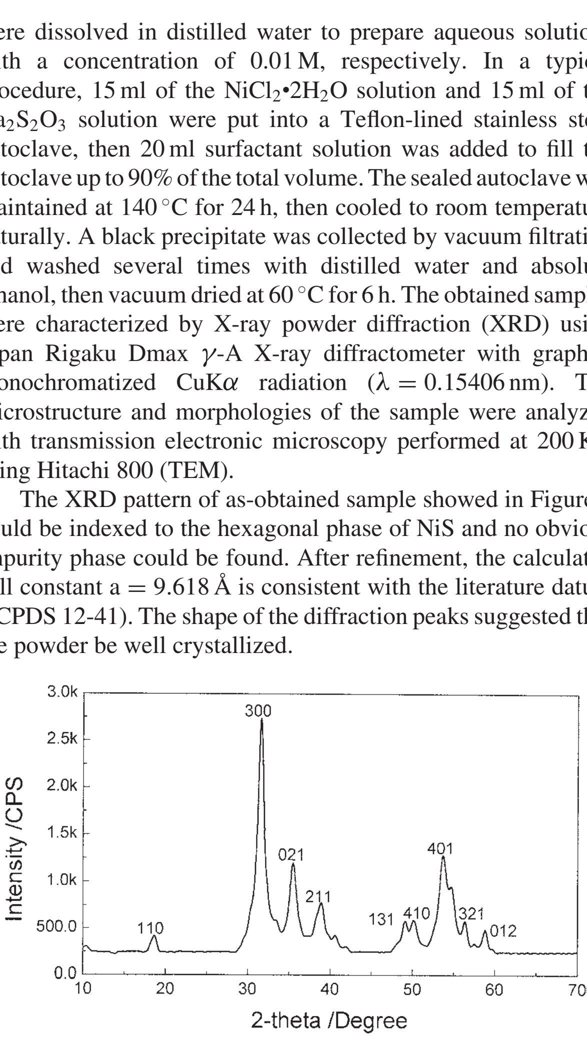


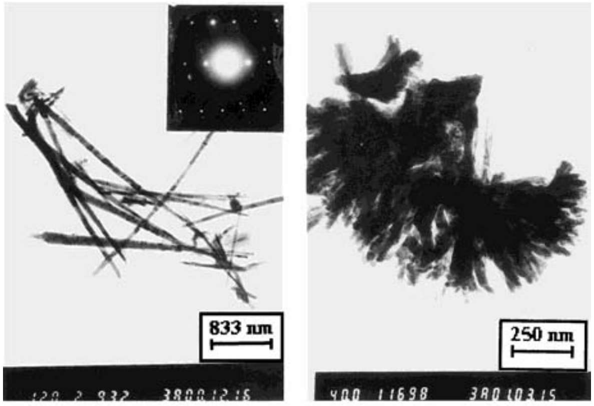
Figure 1. X-ray powder pattern diffraction of NiS nanowhiskers obtained via hydrothermal reaction with the presence of surfactant $C_{17}H_{33}COOK$ under 140 °C.

Figure 2a is the TEM images of the as-prepared product, which indicates the morphology of the NiS is uniform nanowhiskers with an average diameter of 80 nm, and the length of the whiskers is in micrometer scale. The electron diffraction pattern (inset in Fig. 2a) taken from the selected area of NiS nanowhisker shown in Fig. 2a, using a convergent lens also shows that the NiS powder was well crystallized.

In this experiment, the surfactant-aid hydrothermal reaction of NiS could be expressed as following:

$$2NiCl_2 + 3S_2O_3^{2-} + 3H_2O \longrightarrow 2NiS + 4SO_3^{2-} + 4HCl + 2H^+$$

The Ni^{2+} ions could be exchanged into the uniform micelles formed by surfactant $C_{17}H_{33}COOK$ in the solution, then the S^{2-}



(a) (b)

Figure 2. TEM images of (a) NiS nanowhiskers obtained under 140 °C. (b) the aggregation of NiS whiskers obtained under 180 °C.

anions from $S_2O_3{}^{2-}$ under hydrothermal condition were infused into the micelles to form NiS nucleation. And during this stage the growth of NiS crystals is limited in the micells. Once the nucleation occurred in the micells was completed, the growth of NiS nanowhisker could be confined by the micelles. When the growth proceeds, the michells are broken due to the decrease in surface tension. Through the charge transfer, the surface tension is lowered, which may result in the modification of crystal growth in certain direction and finally resulted in the growth of uniform-sized nanowhiskers. This growth pattern was also observed by Weller et al. for PbS needles in amphiphilic block copolymer micelles.[17]

It was found that the morphology of the NiS nanocrystal was affected by the Ni^{2+} and $S_2O_3{}^{2-}$ concentrations and the detailed preparation procedure. When the $NiCl_2{\bullet}2H_2O$ and $Na_2S_2O_3$ concentration were 0.02 M, keeping the other conditions constant, the grain size of NiS crystals was enlarged. Moreover, the increasing of hydrothermal temperature could result in the aggregation of the NiS nanowhiskers, which could be seen from Figure 2b.

The surfactant concentration was also expected to influence the size and shape of nanocrystals. Without the existence of surfactant, only nanoparticles can be obtained. This phenomenon has also been observed by other researchers.[15,16] Furthermore, in our experiment, when molar ratio of Ni(II)/surfactant ranged from 1 to 3, the size and the shape of NiS nanowhiskers kept unchanging. The formation and stabilization of surfactant micelle structures in a certain concentration range might explain this. Besides, when keeping the other condition constant, using the absolute ethanol as the solvent in stead of surfactant, we only obtained nanocrystalline NiS with the average size of 30 nm just as the literature reported.[18]

In summary, NiS nanowhiskers have been successfully prepared through a hydrothermal process in the presence of ionic surfactant $C_{17}H_{33}COOK$. The formation mechanism and surfactant effect were discussed in detail. Given the generality of this approach, we hope to extend our synthetic method to prepare other well-defined low-dimensional structure materials.

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