# Synthesis of Nickel Sulfide via Hydrothermal Microemulsion Process: Nanosheet to Nanoneedle

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Monolayer-dispersed two-dimensional (2-D) nickel sulfide nanosheets have been synthesized by a simple microemulsion-assisted hydrothermal process. It has been found that the 2-D nanosheets can roll into one-dimensional (1-D) nanoneedles. The mechanisms of the sulfuration reaction and the formation of low-dimensional (LD) nanostructures were discussed.

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Currently, shape control has raised significant concern in the fabrication of semiconductors, metal nanocrystals and other inorganic materials.[1–3] Hard template route, hydrothermal/solvothermal process, microwave technique, ultraviolet-irradiation and sonochemical methods have been successfully utilized to synthesize LD nanomaterials.[1] With the promise of a better control of size and shape, the w/o microemulsions for the preparation of nanomaterials have attracted extra attention.[2] The 1-D nanostructures have been widely studied in the last decade and a number of strategies can be used for reference. However, the reports on 2-D nanostructures, i.e. nanosheets,[3] are relatively sparse.

Nickel sulfide, as one of transition metal chalcogenides, has attracted considerable attention because of their unique properties and potential applications, i.e. unusual physical properties, toughening effect, solar storage, and catalyst for hydrodenitrogen and hydrodesulfurization.[4] Additionally, nickel sulfides are a complex system and contain multiple phases, so lots of unknown aspects need to be studied further.[5] Traditionally, nickel sulfides were prepared by high temperature solid-state reaction or vapor phase reaction.[6] Recently, some soft chemical methods have been used to synthesize nickel sulfides, such as rod-like and petal-like crystals, nanowhiskers and layer-rolled structures.[7] To the best of our knowledge, the 2-D nickel sulfide nanosheets have not been reported. In this study, we developed the w/o microemulsions of cetyltrimethyl ammonium bromide (CTAB)/*n*-pentanol/*n*-hexane/water as a novel technique to synthesize nickel sulfide nanosheets and nanoneedles under the hydrothermal condition.

All reagents were analytical grade and used with no further purification. The microemulsions were prepared using CTAB as surfactant and *n*-pentanol as cosurfactant. The 0.01–0.1 M of $Ni^{2+}$ solutions, obtained by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ in distilled water, were used as the water phase and *n*-hexane as oil phase. The reactant molar ratio of $Ni^{2+}$:$CS_2$:urea was kept 1:3:3. In a typical experimental procedure, a mixture of 2.73 g of CTAB, 0.07 g of urea, 7.0 mL of *n*-pentanol, 60 mL of *n*-hexane and 4.0 mL of $Ni(NO_3)_2$ aqueous solution ($[Ni^{2+}] = 0.1$ M) was filled into a wild-mouth bottle of 125 mL. The mixture was magnetically stirred, ultrasonicated and gently heated under 100 °C, and the optically transparent microemulsions were achieved. Then 0.07 mL of $CS_2$ was added into the microemulsions. The resultant microemulsions were poured into a Teflon-lined stainless steel autoclave with a volume of 100 mL and maintained at 130 °C for a desired time (5 or 15 h). The obtained black suspensions of nickel sulfide were decompressedly distilled at ca. 60 °C in a vacuum dryer to remove the volatile organic reagents. The collected precipitates were repeatedly washed with acetone and ethanol, and then centrifuged. The obtained precipitates were dried in a silicagel desiccator at room temperature for characterization. The samples treated in microemulsions for 5 and 15 h were denoted as NS-5 and NS-15, respectively.

The phases of the samples were identified by X-ray diffraction (XRD) with a D/max 2550V diffractometer (Cu K$\alpha$, $\lambda = 1.5406$ Å). The morphologies were observed by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE-SEM) using a JEM200CX transmission electron microscope and a JSM-6700F scanning electron microscope, respectively. The stability of the samples was examined by thermogravimetry (TG) and differential scanning calorimetry (DSC) performed on a NETZSCH STA 449C at a rate of 10 °C min$^{-1}$ in nitrogen flow.

The XRD patterns of NS-5 and NS-15 are shown in Figure 1. In Figure 1a, all the strong reflection peaks can be readily indexed to the hexagonal phase $NiS_{1.03}$ (space group: $P6_3/mmc$). The calculated lattice constants of $a = 3.423$ Å and $c = 5.313$ Å are consistent with the standard literature values of $a = 3.44$ Å and $c = 5.35$ Å (JCPDS 02-1273) within the error range. In Figure 1b, in addition to the peaks belonging to $NiS_{1.03}$, there obviously appears another set of peaks, which can be indexed to millerite-NiS (JCPDS 12-0041). The reflection peaks of millerite-NiS also occur in Figure 1a, but their intensities are much lower than those of the ones in Figure 1b. This indicates that the millerite-NiS content of NS-5 is much less than that of NS-15. In both samples, some weak peaks of $Ni_3S_4$ (JCPDS 08-0106) can be detected. The shape of the strong diffraction peaks indicates that the samples are fairly well crystallized.

When the hydrothermal time is 5 h and $[Ni^{2+}]$ equals 0.1 M, the unique morphology of 2-D nanosheets was observed as shown in Figure 2a. The sheets are of large areas and thin thicknesses, and some of them seem to overlap to form sheet-bundles. When the concentration of $Ni^{2+}$ decreased to 0.01 M and the other con-

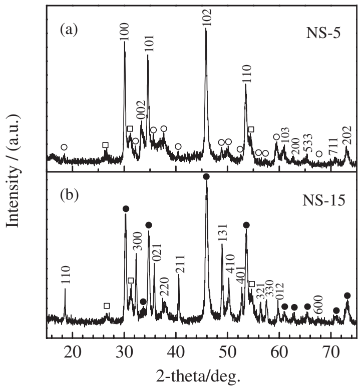

**Figure 1.** The XRD patterns of the obtained samples by hydrothermal treating for (a) 5 h (NS-5) and (b) 15 h (NS-15): (●) $NiS_{1.03}$, (○) millerite-NiS, (□) $Ni_3S_4$.

ditions were kept the same, almost monolayer-dispersed 2-D nickel sulfide nanosheets were achieved (shown in Figure 2b). The thickness of the nanosheets is estimated to be less than 5 nm by TEM image. The inserted SAED pattern shows that the nanosheet is single crystal. Consequently, a low concentration of reactants is entailed in order to obtain monolayer-dispersed nickel sulfide nanosheets. The monolayer-dispersed nickel sulfide nanosheets have larger specific area than bulk nickel sulfides, which may result in some excellent properties, particularly in catalytic property.

Figure 3a shows the FE-SEM image of NS-15. The predominant morphology is 1-D nickel sulfide nanostructures, which have a diameter of ca.80–150 nm and a length of above 1 μm. Figure 3b shows the TEM image of the same sample. The 1-D nanostructures with sharp ends, i.e. so-called nanoneedles, can be observed. The contrast of light-coloured center and fuscous sides (marked with arrow in Figure 3b) suggests that the nanoneedle is hollow, which reminds us that the nanoneedles may result from the rolled nanosheets.

The TG-DSC curves of NS-5 and NS-15 show that there are three endothermal peaks and corresponding mass losseses. The first endothermal peak at 98–106 °C with a distinct mass loss may be associated with the evaporation of the adsorbed water. The second endothermal peak at 360–379 °C can be attributed to the phase transition of nickel sulfides,[5,8] and the corresponding mass loss is most likely to be due to the loss of sulfur resulting in a sulfur-deficient $NiS_{1-X}$.[5] The third one at 490–600 °C and the corresponding mass loss is probably the result of the samples decomposing into sulfur-low compounds.[5]

In the experiments, the possible chemical reactions for the synthesis of nickel sulfides can be expressed as following:[9]

$$CS_2 + CO(NH_2)_2 \rightarrow COS + NH_4SCN \qquad (1)$$

$$COS + H_2O + Ni^{2+} \rightarrow NiS + CO_2 + 2H^+ \qquad (2)$$

The procedure for the synthesis of the 1-D nickel sulfide nanoneedles can be divided into two steps: one is the formation of 2-D nanosheets; the other is the rolling of the nanosheets. During the first step, we speculate that the w/o microemulsions play a crucial role for the formation of the 2-D nickel sulfide nanosheets. The polar $CO(NH_2)_2$ is dissolved in aqueous phase, while the nonpolar $CS_2$ is dissolved in organic phase.[10] So the reaction of Eq 1 must be confined in the interface of aqueous phase and organic phase.[10] The limited interfacial reaction slows down the provision rate of sulfur ions. The reduced release rate of $S^{2-}$ makes the crystal growth proceed in a quasi-equilibrium environment within the water pools of the microemulsions, which is favorable for the self-assembly and the orientated growth process.[10,11] Thus, the role of the microemulsions can be summed up in two aspects: One is the provision of incompatible two-phase environment which results in the slow release of $S^{2-}$; the other is the provision of soft template for the orientated crystal growth by coalescing water pools to form lamellar or limited 1-D space under a certain pressure and temperature.[12] The obtained nanosheets then roll into nanoneedles within the heated microemulsions. The driven force for the rolling behavior can be attributed to the decrease of the surface free energy. The single nanoneedles can bond parallel to be nanoneedle-bundles and do across to form cross-linked nanostructures. X. Jiang et al.[7] obtained NiS layer-rolled structures with large diameters of 0.5–1.0 μm in a $NH_3{\cdot}H_2O–CS_2$ system, while what we achieved were hollow nanoneedles with distinct transition state of 2-D nanosheets. The obvious difference of the results might be attributed to the roles of the w/o microemulsions.

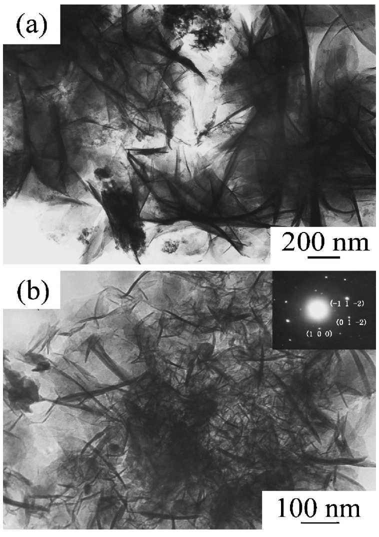

**Figure 2.** The TEM images of the 2-D nickel sulfide nanosheets by hydrothermal treating for 5 h: (a) $[Ni^{2+}] = 0.1$ M (NS-5) and (b) $[Ni^{2+}] = 0.01$ M (inserted SAED pattern recorded along the [021] zone axis).

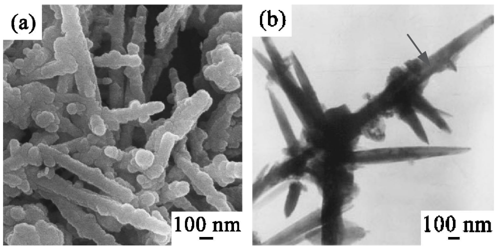

**Figure 3.** The (a) FE-SEM and (b) TEM images of the 1-D nickel sulfide nanoneedles synthesized by hydrothermal treating for 15 h (NS-15).

In summary, monolayer-dispersed 2-D nanosheets of nickel sulfides have been successfully synthesized via a simple microemulsion-assisted hydrothermal process. It has been found that the 2-D nanosheets can roll into 1-D nanoneedles by prolonging the hydrothermal time. The w/o microemulsions play a crucial role during the formation of 2-D nickel sulfide nanosheets. The nickel sulfide nanosheets reported here are likely to be useful for catalytic applications, and the technique can be an effective approach for the synthesis of other LD nanomaterials.

## References

1 J. Xiao, Y. Xie, R. Tang, and W. Luo, *J. Mater. Chem.*, **12**, 1148 (2002); S. I. Nikitenko, Y. Koltypin, Y. Mastai, M. Koltpin, and A. Gedanken, *J. Mater. Chem.*, **12**, 1450 (2002).
2 M. Chatterjee and A. Patra, *J. Am. Ceram. Soc.*, **84**, 1439 (2001).
3 J.-K. Lee, W. Lee, T.-J. Yoon, G.-S. Park, and J.-H. Choy, *J. Mater. Chem.*, **12**, 614 (2002); S.-H. Yu and M. Yoshimura, *Adv. Mater.*, **14**, 296 (2002).
4 J. Trahan, R. G. Goodrich, and S. F. Watkins, *Phys. Rev. B*, **2**, 2859 (1970); W. M. Kriven, *Mater. Sci. Eng., A*, **127**, 249 (1990); R. Cid, P. Atanasova, R. Lopez-Corderp, J. M. Palacios, and A. Lopez-Agudo, *J. Catal.*, **182**, 328 (1999).
5 D. W. Bishop, P. S. Thomas, and A. S. Ray, *J. Therm. Anal. Calorim.*, **56**, 429 (1999).
6 R. Coustal, *J. Chem. Phys.*, **38**, 277 (1958); A. Wold and K. Ddwight, *J. Solid State Chem.*, **96**, 888 (1992).
7 Z. Meng, Y. Peng, W. Yu, and Y. Qian, *Mater. Chem. Phys.*, **74**, 230 (2002); B. Xie, Y. Jiang, S. Yuan, Q. Li, Y. Wu, J. Wu, and Y. Qian, *Chem. Lett.*, **2002**, 254; X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He, and Y. Qian, *Adv. Mater.*, **13**, 1278 (2001).
8 G. Kullerud and R. A. Yund, *J. Petrol.*, **3**, 126 (1962).
9 G. Gattow and W. Behrendt, *Top. Sulfur Chem.*, **2** (1977).
10 P. Zhang and L. Gao, *Langmuir*, **19**, 208 (2003).
11 M. Remskar, A. Mrzel, R. Sanines, H. Cohen, and F. Levy, *Adv. Mater.*, **15**, 237 (2003).
12 Y. Li, J. Wan, and Z. Gu, *Mater. Sci. Eng., A*, **286**, 106 (2000).

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