A Single-source Approach to Metastable Ni_3S_4 Crystallites and Their Optical Properties

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Metastable Ni_3S_4 with good crystallinity has been firstly synthesized via a single-source approach using nickel diethyldithiocarbamate as precursor under hydrothermal conditions. The optical properties of the as-prepared Ni_3S_4 are evaluated. It is found that the reaction temperature is of importance to the formation of Ni_3S_4 crystallites.

Among the family of metal sulfides, nickel sulfides have attracted much attention owing to their potential as a transformation-toughening agent for materials used in semiconductor applications,[1] catalysts,[2] and cathode materials for rechargeable lithium batteries.[3] Although a number of binary nickel sulfides such as $Ni_{3+x}S_2$, Ni_3S_2, Ni_4S_{3+x}, Ni_6S_5, Ni_7S_6, Ni_9S_8, NiS, Ni_3S_4, and NiS_2 have been reported,[4] only a few sulfides such as NiS and NiS_2 have been extensively investigated. For instance, NiS with different morphologies such as layer-rolled structures,[5] 3-D structures,[6] submicrometer hollow spheres,[7] nanorods, triangular nanoprisms,[8] and thin films[9,10] have been recently obtained.

Of the nickel sulfides, Ni_3S_4 with the cubic spinel structure was reported as a possible substitution of a small amount of Fe for Ni occuring in nature as a mineral, polydymite.[11] Because of the instability of Ni_3S_4 at higher temperatures, it is rather difficult to synthesize single-phase Ni_3S_4 in the laboratory. Traditionally, Ni_3S_4 crystallites accompanied with NiS and NiS_2 impuries were synthesized through solid-state reactions of Ni + S, NiS + S, or NiS + NiS_2 at 200–300 °C for 6–8 months.[12] Recently, Ni_3S_4[13] was fabricated by a pH-controlled homogeneous precipitation method at 70 °C with metal chlorides and thioacetamide in the ammonium chloride–ammonia buffer solutions adjusted to pH = 9.9. Manthiram et al.[14,15] synthesized Ni_3S_4 with poor crystallinity through an ambient temperature reaction between aqueous nickele chloride and sodium dithionite solutions.

Herein, we present a single-source approach to fabricate cubic Ni_3S_4 crystallites by the thermal decompostion of a nickel diethyldithiocarbamate complex obtained by mixing sodium diethyldithiocarbamate (NaS_2CNEt_2 or NaDDTC) and $NiCl_2$ in absolute ethanol. It was reported that NaDDTC could be used as complex reagent to form Sb_2S_3 and Bi_2S_3 nanorods,[16,17] but there was no report on the preparation of Ni_3S_4 formed with the aid of NaDDTC. The optical properties of the as-prepared Ni_3S_4 are evaluated, which might find possible applications as optical devices.

Synthesis of Nickel Diethyldithiocarbamate Complex: The nickel diethyldithiocarbamate complex was prepared from 1 mmol $NiCl_2 \cdot 6H_2O$ and 2 mmol NaDDTC in 50-mL absolute ethanol. The obtained white-green precipitate was filtered off, washed with distilled water and absolute ethanol several times and dried at room temperature. The reaction for the preparation of nickel diethyldithiocarbamate complex may be formulated as follows:

$$NiCl_2 + 2\ NaS_2CNEt_2 \rightarrow Ni(S_2CNEt_2)_2 + 2NaCl$$

Synthesis of Ni_3S_4 crystallites: In a typical procedure, 0.4 g $Ni(S_2CNEt_2)_2$ and 40-mL distilled water were added to a Teflon-lined stainless autoclave with a capacity of 50 mL. The autoclave was sealed, maintained at 180 °C for 12 h, and allowed to cool to room temperature. A black precipitate was filtered off, washed with distilled water and absolute ethanol several times and dried in a vacuum at 50 °C for 6 h.

X-ray powder diffraction (XRD) pattern was determined using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.541874 Å). Fourier transform infrared (FTIR) spectrum of the as-prepared products was recorded at room temperature with a KBr pellet on a VECTOR-22 (Bruker) spectrometer ranging from 400 to 4000 cm^{-1}. Scanning electron microscopic (SEM) images were obtained on a Hitachi (X-650) scanning electron microanalyzer. Ultraviolet and visible light (UV–vis) spectrum was recorded on a JGNA Specord 200 PC UV–vis spectrophotometer.

IR spectra of the as-prepared Ni–DDTC complex (b) and pure NaDDTC (a) are given in Figure 1. In Figure 1b, the characteristic absorption peaks at 1490 and 987 cm^{-1} can be assigned to the stretching vibrations of C–N and C–S, respectively.[18] The peaks at 2870 and 2931 cm^{-1} can be assigned to $\nu_{C\text{–}H}$. The deformation vibration C–H in $–CH_3$ and $–CH_2$ appears at 1355 and 1442 cm^{-1}.[19] And the frequency of the C–N stretching vibration of the complex shifted from 1477 cm^{-1} in the pure NaDDTC (Figure 1a) to 1490 cm^{-1}. The shift of the C–N stretching vibration implies that the sulfur in the diethylthiocarbamate coordinates with the metal ion in the complex.[17,20,21] On the basis of the IR spectra, it is believed that the $Ni(DDTC)_2$ complex is successfully synthesized via the reaction of NaDDTC and $NiCl_2$ in absolute ethanol.

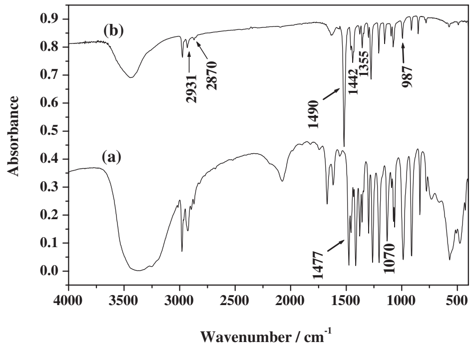

Figure 1. IR spectra of the as-prepared Ni–DDTC complex (b) and pure NaDDTC (a).

Figure 2 shows the typical XRD pattern of the sample obtained at 180 °C for 12 h. All the peaks in Figure 2 can be indexed as cubic Ni_3S_4 crystallites with cell parameter of $a = 9.474$ Å, which is in agreement with the reported value (JCPDS Card No. 47-1739, $a = 9.476$ Å). No obvious impurity can be detected. The XRD pattern obtained in this study has much better crystallinity than that of reported by Manthiram et al.[14,15] through an ambient-temperature reaction between aqueous nickele chloride and sodium dithionite solutions.

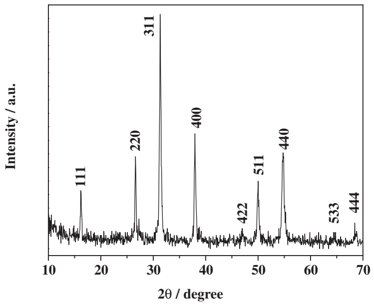

Figure 2. XRD pattern of the as-prepared Ni_3S_4 crystallites.

Representative scanning electron microscopic (SEM) images with different magnification are shown in Figure 3. It is seen that the as-prepared cubic Ni_3S_4 crystallites are composed of a large number of irregular microspheres with the average diameter of 2 µm. Further observation in Figure 3b reveals that the microspheres are constructed with nanoscaled Ni_3S_4 crystallites.

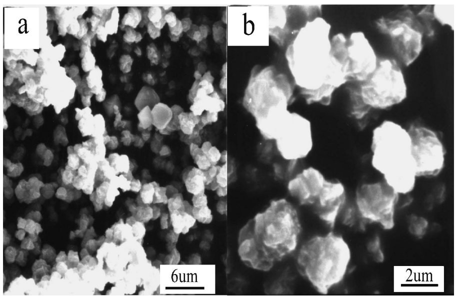

Figure 3. SEM images of the as-prepared Ni_3S_4 crystallites.

The optical property of Ni_3S_4 crystallites was investigated with ambient-temperature UV–vis absorption spectroscopy (Figure 4). The Ni_3S_4 crystallites possess well-defined, broad optical absorption located at 270 nm, silimar to that of NiS hollow spheres reported by Chen et al.[22] However, there are no reports about the band gap of the bulk Ni_3S_4 crystallites. Therefore, it is difficult to determine the shift of the as-prepared Ni_3S_4 crystallites in contrast to that of bulk materials.

In order to investigate the influences of reaction conditions on the structure and morphology of the product, many contrastive experiments were conducted. When the reaction was carried out at 160 °C for 10 h, pure Ni_3S_4 crystallites could not be obtained by the characterization of XRD. When the reaction temperature was increased to 200 °C, pure Ni_3S_4 crystallites could be obtained as that of prepared at 180 °C. Therefore, it is believed that the reaction temperature is of importance to prepare pure Ni_3S_4 crystallites.

In summary, it is the first time that metastable Ni_3S_4 crystallites have been synthesized through a single-source approach using nickel diethyldithiocarbamate as precursor under hydrothermal conditions. The optical properties of the as-prepared Ni_3S_4 are evaluated, which might find possible applications as optical devices. It is revealed that the reaction temperature is important to the formation of Ni_3S_4 crystallites. The present single-source approach might open an opportunity to prepare other inorganic materials in the future.

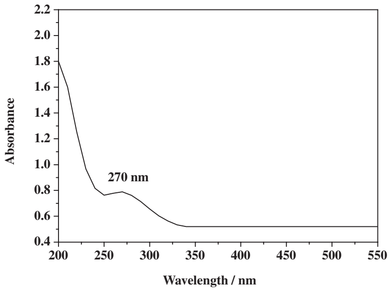

Figure 4. UV–vis absorption spectrum of Ni_3S_4 crystallites measured at ambient temperature.

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