Low-Temperature Hydrothermal Synthesis of Transition Metal Dichalcogenides

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A new aqueous solution based approach has been proposed to prepare transition metal dichalcogenides by hydrothermal reaction between aqueous transition metal salts and $Na_2S_2O_3$ or Na_2SeSO_3 at the low temperature of 130−140 °C. Pyrite NiS_2, CoS_2, FeS_2, and $NiSe_2$ and layered MoS_2 and $MoSe_2$ have been prepared this way. Transmission electron microscopy images show that these products consist of nanoscaled crystallites. The effect of different reaction conditions on the nature of products is discussed. The surface areas for the samples have been measured.

Introduction

Transition metal dichalcogenides have drawn considerable attention because of their technological importance as photoactive materials,[1] dehydrosulfurization catalysts,[2] solid-state lubricants,[3] cathode materials for high-energy density battery,[4] and so forth. The early transition metal dichalcogenides such as MoS_2, $MoSe_2$, TaS_2, and TiS_2 have a sandwich-layered structure and are used as an intercalation host to derive novel materials with modified physical properties.[5−7] The post transition metal dichalcogenides such as FeS_2, CoS_2, NiS_2, and $NiSe_2$ usually adopt the cubic pyrite structure and show interesting electronic, magnetic, and photovoltaic properties.[8−10]

Crystalline transition metal dichalcogenides have traditionally been prepared by direct stoichiometric combination of elemental metal and chalcogen in evacuated silica tubes at high temperature.[11] Recently, great efforts have been made to explore low-temperature routes to metal dichalcogenides to control the size and microstructure of crystallites and to approach new metastable phases.[12] Schleich et al. proposed metathesis reactions between transition metal halides and alkali-metal sulfides or covalence sulfiding agents to obtain amorphous transition metal disulfides in nonaqueous solvents.[13,14] Passaretti et al. reported the reaction between hexachlorometalates (IV) and hydrogen sulfides and between anhydrous transition metal chlorides and ammonium hydrogen sulfides in polar organic solvents.[15,16] Pyrolysis of dithiolato or dithioxamide complexes of Ni, Co, Fe, and Mo at an elevated temperature yield their sulfides.[17,18] Some thin films of VI and VIII group transition metal disulfides can be prepared by reacting transition metal carbonyls with various sulfur sources in nonaqueous media while an aqueous medium results in the formation of their oxides.[19] Kaner et al. reported the rapid solid-state synthesis of NiS_2 and MoS_2,[20,21] but the precursor of high-valence metal halides are not easy to prepare and are very sensitive to the air environment. Recently, a solvothermal process from anhydrous transition metal salt or oxides was reported to prepare NiS_2,[22] CoS_2,[23] and MoS_2.[24] It is well-known that precipitation of

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aqueous transition metal cations with H_2S or S^{2-} produce amorphous metal monosufides such as NiS and CoS, but so far to our knowledge, no aqueous solution based approaches are applicable for the synthesis of transition metal dichalcogenides. In many above-mentioned methods, even moisture in air could significantly influence the nature of final products. Herein, we report a direct hydrothermal synthesis of transition metal dichalcogenides with aqueous $Na_2S_2O_3$ or Na_2SeSO_3 at a low temperature of ≈140 °C. This hydrothermal process has many advantages in comparison with previous methods: (1) it is not necessary to prepare a toxic precursor and all starting materials are easy to obtain and are stable in ambient conditions; (2) water, a convenient and environment-benign medium, is preferred to other toxic organic solvents in industrial applications. Our experimental procedure is presented as follows.

Experimental Section

All starting materials are of analytical pure grade and are purchased from commercial sources. X-ray powder diffraction (XRD) analysis was conducted on a Rigaku Dmax X-ray diffractometer with 2θ ranging from 5° to 65°, using graphic monochoromatic Cu Kα radiation ($\lambda = 1.5406$ Å). A transmission electron microscope (TEM) at 200 kV was employed to characterize the morphology of products. The compositions of the samples were determined by chemical analysis according to the previous methods,[25] combined with X-ray photoelectron spectroscopy (XPS). The surface gas absorption was studied using N_2. The specific surface areas and pore diameters were calculated with the BET equation. The samples were pre-dispersed by an ultrasonic wave. The hydrothermal reaction to obtain the samples of dichalcogenides is described as follows.

Hydrothermal Reactions between Ni^{2+}, Co^{2+}, Fe^{2+}, and $Na_2S_2O_3$ or Na_2SeSO_3. The same general reaction scale and procedure were adopted for all the reactions exemplified here for nickel disulfide. $NiCl_2 \cdot 6H_2O$ (1.188 g, 0.005 mol) and $Na_2S_2O_3 \cdot 5H_2O$ (2.482 g, 0.010 mol) were put into a Teflon-lined autoclave with a capacity of 30 mL and dissolved with 25 mL of distilled water to form a clear green solution. This autoclave was maintained at 140−150 °C and autogenerated pressure for 12 h. As-prepared black precipitate was collected by filtering, was washed with carbon disulfide and distilled water, and then was dried at 65 °C for 2 h. As for the preparation of $NiSe_2$, the selenium source Na_2SeSO_3 solution was prepared by refluxing appropriate amounts of selenium powder and Na_2SO_3 in distilled water for 10 h.

Hydrazine-Assisted Hydrothermal Reaction between Aqueous Na_2MoO_4 and $Na_2S_2O_3$ or Na_2SeSO_3. Aqueous $Na_2S_2O_3$ (2.482 g, 0.010 mol) and Na_2MoO_4, prepared by dissolving MoO_3 (0.72 g, 0.005 mol) in 10 mL of 0.5 mol/L NaOH solution, were added to an autoclave with 15 mL of 50% aqueous hydrazine (N_2H_4) solution and stirred into a clear, colorless solution. This solution was transferred to an autoclave and maintained at 135 °C for 12 h. The resulting black solid, after being washed and dried, was crystallized at 350 °C for 9 h in a flowing high-pure N_2 atmosphere. The synthesis of $MoSe_2$ was carried out by a similar procedure as mentioned above using Na_2SeSO_3 as a selenium source.

Results and Discussion

All the samples obtained by hydrothermal reactions were structurally characterized by X-ray powder diffraction and their compositions were determined by traditional chemical analysis. The average sizes of crystallites are calculated by XRD data using the Scherrer's Equation.[22] The results and refined lattice parameters are presented in Table 1. The crystalline Ni, Co, and Fe disulfides and $NiSe_2$ can be prepared directly from hydrothermal reactions without post-treatment of heating as shown in Figure 1. As for the as-prepared FeS_2, its XRD pattern reveals the formation of pyrite FeS_2 and minor marcasite FeS_2. TEM images shown in Figure 2 indicate that the as-prepared NiS_2 comprises homogeneous cubic particles with an average size of ≈50 nm. The crystallites of CoS_2 also display the cubic shape. Unlike traditional hydrothermal processes that usually involve solid−liquid interactions, these hydrothermal reactions in this study start with a clear mixed solution of initial reagents. The atom-scale dispersion of starting materials may contribute to the regularity and homogeneity of final products. Crystalline $NiSe_2$ has been prepared successfully by a similar hydrothermal reaction. Its composition was determined by an XPS spectrum to be $NiSe_{1.90}$.

Table 1. Composition, Size, and Crystal Structure of the Samples of Transition Metal Dichalcogenides[a]

products	chemical analysis	average size[a]	crystal structure	lattice parameters
NiS_2	$NiS_{2.02}$	≈50 nm	cubic pyrite type	$a = 5.660$ Å
CoS_2	$CoS_{1.96}$	≈70 nm	cubic pyrite type	$a = 5.520$ Å
FeS_2	$FeS_{1.92}$	≈85 nm	pyrite (minor marcasite)	$a = 5.398$ Å
$NiSe_2$		>200 nm	cubic	$a = 5.958$ Å
MoS_2	$MoS_{1.92}$	≈4 nm	layered hexagonal	$a = 3.22$ Å $c = 13.11$ Å
$MoSe_2$		≈7 nm	layered hexagonal	$a = 3.22$ Å $c = 13.11$ Å

[a] The crystallite sizes are calculated using Scherrer's Equation from XRD data.

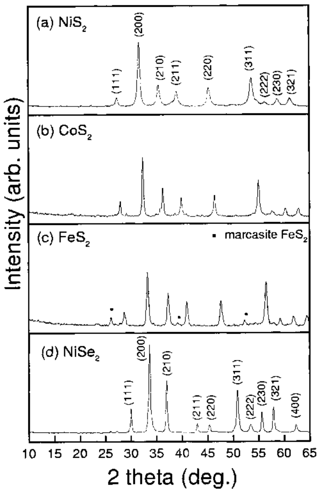

Figure 1. X-ray diffraction patterns for the samples of (a) NiS_2, (b) CoS_2, (c) FeS_2, and (d) $NiSe_2$.

Direct hydrothermal reaction between Na_2MoO_4 and $Na_2S_2O_3$ with hydrazine (N_2H_4) yields a black precipitate of noncrystalline MoS_2. After annealing at 350 °C in a flowing inert gas atmosphere, it converts to crystalline products as shown in Figure 3. The TEM image shown in Figure 4a for the sample of annealed MoS_2

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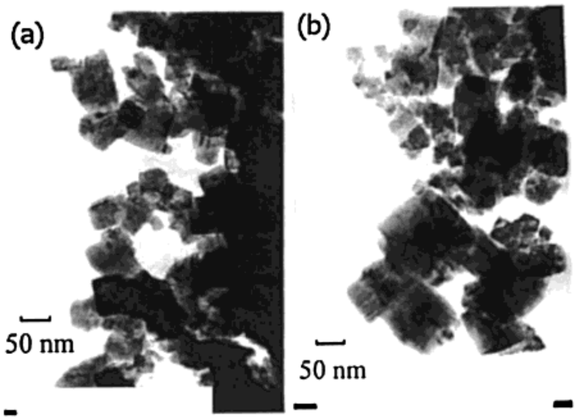

Figure 2. TEM images for the samples of monophasic (a) NiS_2 and (b) CoS_2.

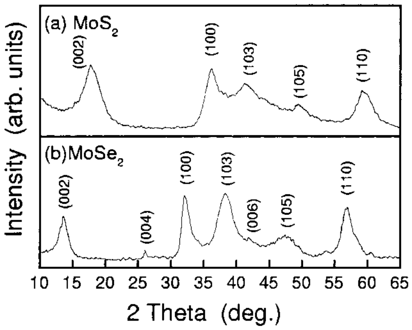

Figure 3. X-ray diffraction pattern for the samples of (a) MoS_2 and (b) $MoSe_2$ annealed at 350 °C for 9 h.

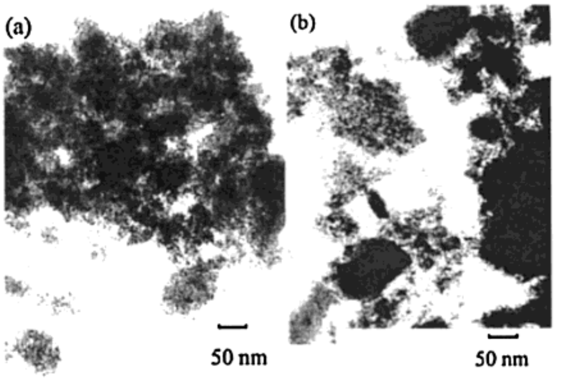

Figure 4. TEM images of the samples of (a) MoS_2 and (b) $MoSe_2$ annealed at 350 °C for 9 h.

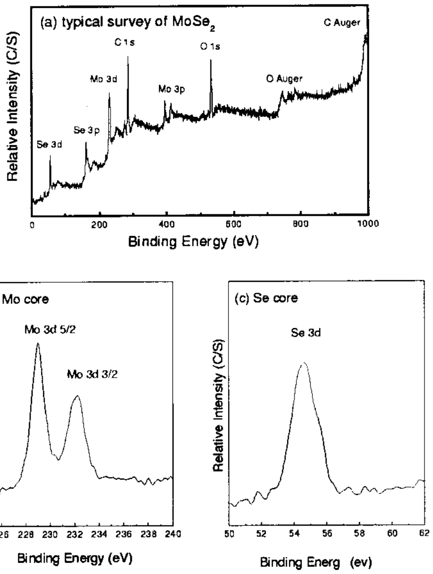

Figure 5. X-ray photoelectron spectra for the sample of $MoSe_2$: (a) typical survey, (b) close-up survey at Mo core, and (c) close-up survey at Se Core.

shows that it consists of homogeneous particles with an average diameter of 4 nm. The high Gibbs free energy forces these particles to agglomerate, and they are difficult to divide by an ultrasonic wave. Hydrothermal reaction of Na_2SeSO_3, Na_2MoO_4, and hydrazine yields an amorphous black powder of $MoSe_2$ which crystallizes at 350 °C in an inert atmosphere. Besides, a one-step hydrothermal reaction of appropriate amounts of Na_2MoO_4, Na_2SO_3, selenium powder, and hydrazine at 150 °C for 24 h also results in the formation of $MoSe_2$. Minor residue of Se powder can be removed readily due to its density being less than that of water. A typical XPS spectrum for the sample of $MoSe_2$ obtained by the one-step reaction is shown in Figure 5a, which indicates the presence of Mo, Se, and unavoided surface contamination of C and O from absorbed gaseous molecules. High-resolution spectra were taken in the regions of Mo and Se cores. The two strong peaks in Figure 5b correspond to Mo $3d_{5/2}$ and Mo $3d_{3/2}$ binding energy. Figure 5c shows the Se 3d binding energy. The ratio of Mo/Se calculated by measuring the areas of Mo and Se cores is close to its chemical stoichiometry.

These reactions, to obtain NiS_2, CoS_2, FeS_2, and $NiSe_2$, are of the self-redox type with partial $S_2O_3^{2-}$ or $SeSO_3^{2-}$ anions oxidized to SO_4^{2-} and partial reduced to ME_2 (M = Ni, Co, Fe; E = S or Se). SO_4^{2-} and H^+ can be detected in the residue solution after hydrothermal reactions. Various amounts of $Na_2S_2O_3$ were used to react with Ni^{2+}. However, only phase-pure NiS_2 forms with the initial ratios of $Na_2S_2O_3/Ni^{2+}$ in the range of 1.0−3.0. In the case of MoS_2, $Na_2S_2O_3$ is not enough to reduce Mo(VI) to Mo(IV), although self-redoxing of $Na_2S_2O_3$ also occurs to give S^{2-} for MoS_2 and generate SO_4^{2-}. Thus, hydrazine monohydride was added to the reaction medium to maintain a reducing atmosphere, which assists in the formation of the reduced MoS_2.

In our experiment, the influence of the pH value has also been considered. In the case of NiS_2, a basic medium with pH > 7.0 results in apple-green $Ni(OH)_2$ precipitate. If pH < 3.0, the mixture of NiS and Ni_3S_4 forms without NiS_2 being obtained. In the case of FeS, adding NaOH at the ratio of $NaOH/Fe^{2+} = 2:1$ yields the phase-pure nanocrystalline magnetite Fe_3O_4. The acidic medium gives a mixture of FeS and Fe_2S_3. Generally, as for the post transition metal, lowered pH values lead to a smaller amount of sulfur in the final products. In the case of MoS_2, the pH range from 7.0 to 14.0 has little effect on the nature of the products. But if the pH < 5.0, we can obtain reduced molybdenum keggin-type polyblue or bronzes. Therefore, by careful control of the pH value in the reaction media, other technologically important transition metal chalcogenides or reduced oxides could be prepared this way.

The surface properties were studied as a supplement to the bulk properties of the samples. XPS analyses indicate that the metal/chalcogen ratios are close to their bulk counterparts, although the unavoided absorbed O_2 molecules and C contamination were also detected. The specific surface area of the as-prepared MoS_2 calcuated by the BET method is $\approx$58 m^2/g, assuming the sphere-like shape of the average grain size of these particles is $\approx$24 nm. The BET average pore diameter was measured to be 1.3 nm. This indicates as-prepared MoS_2 nanoparticles are prone to agglomerate because of high Gibbs surface energy, as observed in the TEM image. The BET surface areas for the obtained NiS_2 and CoS_2 are $\approx$23 and $\approx$19 m^2/g, respectively. Assuming the cubic shape of the crystallites, the average grain sizes are 58 nm for NiS_2 and 73 nm for CoS_2, calculated from the BET specific surface areas. The results of surface analysis indicate that the samples obtained at low temperature show relatively large specific surface areas and are applicable for catalysis.

Conclusion

In summary, a convenient low-temperature hydrothermal synthesis of nanocrystalline transition metal disulfides has been proposed. The choices of the aqueous chalcogen sources of $Na_2S_2O_3$ and Na_2SeSO_3 are critical for preparing target products. Chemical control of synthesis by adjusting the variables in reaction media such as redox atmosphere, pH value, temperature, and different ligands may extend this hydrothermal method for preparation of other technologically important transition or main-group metal chalcogenides and novel oxides.

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