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Convenient Solvothermal Synthesis and Phase Control of Nickel Selenides with Different Morphologies

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Owing to their special electronic properties and interesting chemical behaviors, the transition metal chalcogenides have gained much attention in the field of material science.[1,2] Merely for nickel selenides, the electronic structure, phase diagram, and X-ray spectra were studied.[3] The materials could be prepared by solid-state reactions at temperatures above 500 °C.[4] The reaction between bis(cyclooctadiene)nickel and triethylphosphine selenide gave Ni_3Se_2 at 270 °C,[5] which coexisted with elemental Ni. Parkin and co-workers synthesized amorphous $NiSe_2$ and NiSe from elemental reactions in liquid ammonia.[6] However, the powders were mixtures, which needed postheat treatment at 200 °C for crystallization. These nickel selenides usually exhibited no special morphologies.

Inorganic materials with different morphologies can exhibit different properties,[7,8] even if they are made up of the same elements. Therefore, the synthesis of these materials would be particularly interesting.

During recent years, the solvothermal method was emerging as an effective synthetic technique for chalcogenides.[1] In this study, a series of nickel selenides with different morphologies were synthesized via the solvothermal method under controlled conditions.

Experimental Section

Appropriate amounts of analytically pure $NiC_2O_4 \cdot 2H_2O$ and elemental Se were ground in an agate mortar. The mixture was put into a stainless steel 35-mL autoclave, which was filled with solvent up to 85% of its total volume. In the experiments, ethylenediamine (En), distilled water, pyridine, and tetrahydrofuran (THF) were selected as the reaction media. The autoclave was maintained at 170−230 °C for 8 h and then air-cooled to room temperature. The products were washed with ethanol and distilled water and dried in a vacuum at 60 °C for 1 h.

Table 1. Phase-Pure Nickel Selenides Synthesized from $NiC_2O_4 \cdot 2H_2O$ and Se under Various Conditions

solvent	temp (°C)	Ni/Se ratio (reactants)	product	Ni/Se ratio (measurement)	morphology
En	170	1:2.4	$NiSe_2$	1:2.11	octahedral
En	200	1:1	$Ni_{0.85}Se$	0.83:1	starfish-like
En	220	3:2	Ni_3Se_2	1:2.07	dendritic
water	180	1:1	$NiSe_2$	1:2.21	spherical
pyridine	180	1:2.2	$NiSe_2$	1:2.04	octahedral
THF	170	1:2.2	$NiSe_2$	1:2.03	octahedral

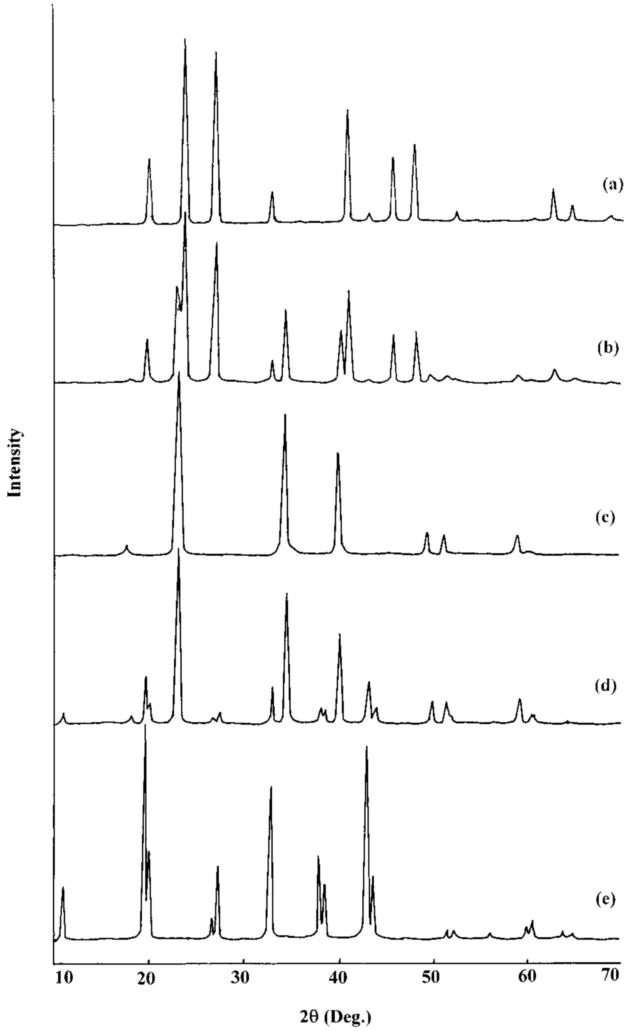

Figure 1. XRD patterns of typical samples synthesized in En: (a) $NiSe_2$ powders obtained at 170 °C; (b) coexistence of $NiSe_2$ and $Ni_{0.85}Se$ at 180 °C; (c) $Ni_{0.85}Se$ powders obtained at 200 °C; (d) coexistence of $Ni_{0.85}Se$ and Ni_3Se_2 at 220 °C; (e) Ni_3Se_2 powders obtained at 220 °C.

X-ray powder diffraction (XRD) was conducted on a Rigaku D/Max-γA X-ray diffractometer. Elemental analysis was carried out on a Perkin-Elmer 3100 atom absorption spectrometer. X-ray photoelectron spectra (XPS) were recorded on a VG ESCALAB MKII X-ray photoelectron spectrometer, using Mg Kα X-rays as the excitation source. Scanning electron microscopy (SEM)

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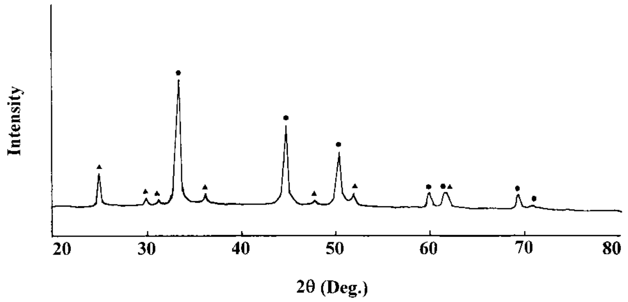

Figure 2. XRD pattern of the mixture of $Ni_{0.85}Se$ (marked with ●) and $Ni_{0.75}Se$ (marked with ▲) obtained in THF at 230 °C.

was performed on an X-650 scanning electron microanalyzer.

Results and Discussion

Table 1 lists the single compounds synthesized under controlled conditions. The molar ratios of reactants (Ni/Se) and temperature were found to play important roles in determining the phase distribution. Through the adjustment of the two factors in En, single phases such as cubic $NiSe_2$, hexagonal $Ni_{0.85}Se$, and triclinic Ni_3Se_2 were obtained under the conditions Ni/Se = 1:2.4 at 170 °C, Ni/Se = 1:1 at 200 °C, and Ni/Se = 3:2 at 220 °C, respectively. Their XRD patterns are shown in Figure 1a, c, and e. It was found that starting materials with stoichiometric ratios tend to give stoichiometric products in En. However, if the Ni/Se ratios deviated from stoichiometric ratios too much, mixtures would be produced. These facts can be confirmed by the XRD patterns given in Figure 1b and d.

The other selected solvents also afforded the cubic $NiSe_2$ single phases under 180 °C, as long as the Ni/Se ratios were appropriately kept (see Table 1). Increasing the Ni/Se ratio and temperature would lead to something else. When water served as the solvent, $Ni_{0.85}Se$ and $Ni_{0.75}Se$ were introduced above 180 °C when the Ni/Se ratio was larger than 1:1. In pyridine, $Ni_{0.85}Se$ and Ni_3Se_2 were generated at 180 °C if the Ni/Se ratio was larger than 1:2, while, in THF, the same ratio would give hexagonal $Ni_{0.85}Se$ and cubic $Ni_{0.75}Se$ at 230 °C, as shown in Figure 2.

It was found that adequate $NiC_2O_4{\cdot}2H_2O$ and higher temperature favor the formation of compounds with higher nickel contents. Excess selenium is essential to $NiSe_2$ and $Ni_{0.85}Se$ in pyridine, THF, and En, while, in water, sufficient nickel is necessary for $NiSe_2$. This may be attributed to the different solubilities of reactants

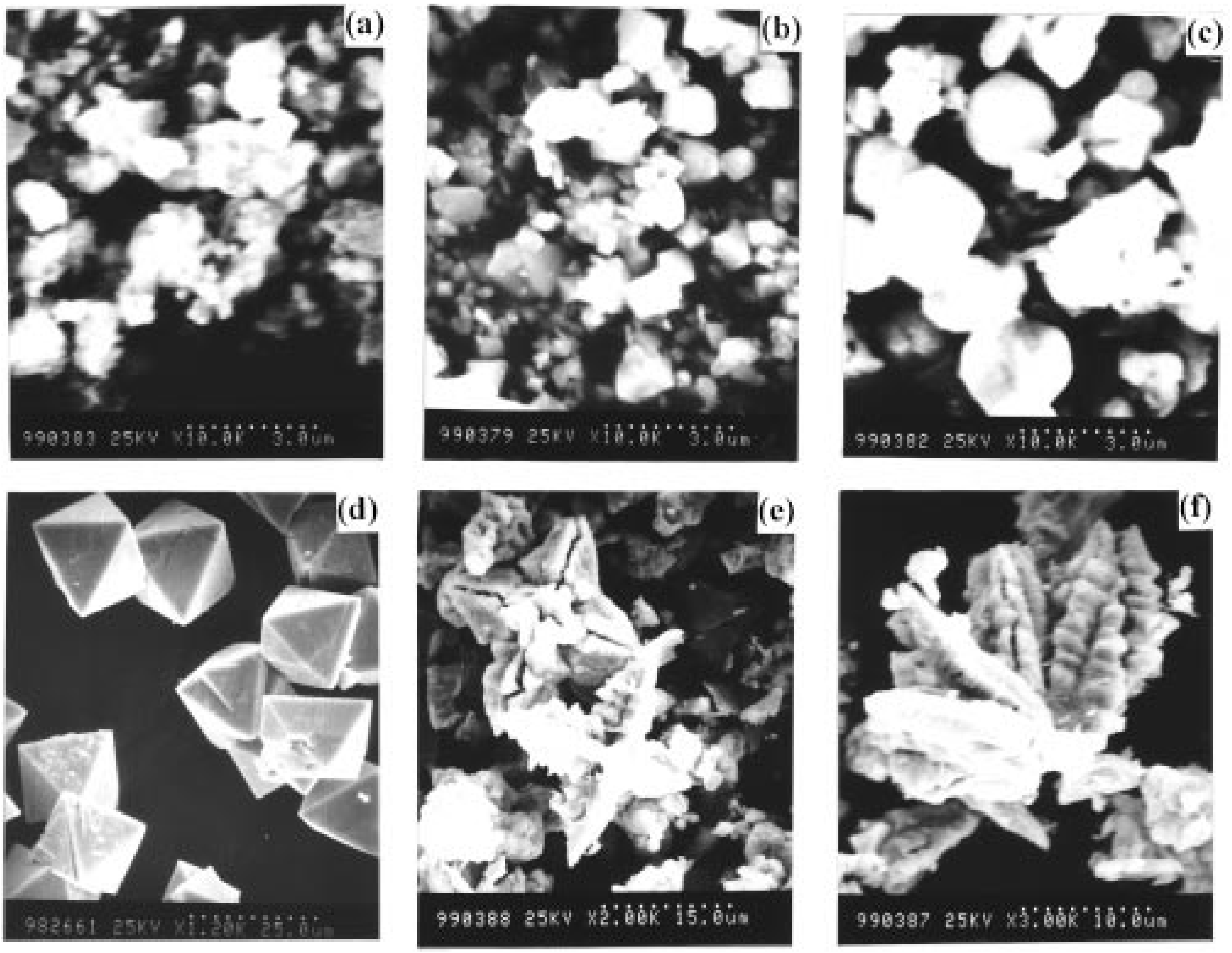

Figure 3. SEM images of phase-pure compounds obtained under various conditions: (a) $NiSe_2$ crystals grown in water at 180 °C; (b) $NiSe_2$ crystals grown in pyridine at 180 °C; (c) $NiSe_2$ crystals grown in THF at 170 °C; (d) $NiSe_2$ crystals grown in En at 170 °C; (e) $Ni_{0.85}Se$ crystals grown in En at 200 °C; (f) Ni_3Se_2 crystals grown in En at 220 °C.

in various solvents. Very alike to the results obtained in En, the single phases, besides $NiSe_2$, may also be produced in the other solvents through control over the Ni/Se ratio and reaction temperature.

Atomic absorption spectroscopy of samples indicates that the atomic ratios for most of the compounds are in agreement with the ideal stoichiometries within experimental errors. However, $NiSe_2$ obtained in En or water is evidently selenium-rich. XPS spectra also reveal that the surfaces of $NiSe_2$ and $Ni_{0.85}Se$ are abundant in selenium, whereas nickel is in excess on the surface of Ni_3Se_2, which may be caused by the nickel-rich reaction system.

SEM images of single-phase powders obtained in various solvents are provided in Figure 3. It reveals that $NiSe_2$ particles prepared in water are nearly spherical. The $NiSe_2$ particles produced from pyridine or THF exhibit an octahedral shape. Comparatively, those formed in En appear to be nearly perfect octahedrons. The starfish-like $Ni_{0.85}Se$ and dendritic Ni_3Se_2 show striking differences in morphology compared to $NiSe_2$.

It is very interesting that the mixed particles of $NiSe_2$ and $Ni_{0.85}Se$ obtained in En possess a unique shape, as indicated in Figure 4a. The special morphology of the mixture could be viewed as the hybrid of the morphologies of the two crystals. Analogously, the SEM image shown in Figure 4b reveals that the mixture of $Ni_{0.85}Se$ and Ni_3Se_2 exhibits the hybrid morphology of $Ni_{0.85}Se$ and Ni_3Se_2, instead of owning their individual morphologies.

The solvents and the growth behavior of different crystals are believed to be responsible for the distinctive morphologies. Although all the selected solvents provide a circumstance to $NiSe_2$ formation, they bring different influences. En favors the crystal growth mostly and hence gives crystals with larger sizes. In contrast, distilled water benefits their growth least, which affords small particles. Mass diffusion probably also exerts an impact on the crystal growth. The intergrowth of different crystals may result in the hybrid morphologies of mixtures. Despite the observation of various morphologies of crystals before,[9] and the Monte Carlo simulations of growth in two dimensions as a mathematical function of the driving potential,[10] the influential mechanics of the solvent on the morphology of crystals still remains obscure now.

Due to their unusual morphologies, the nickel selenides are expected to find unique applications, such as solar cells[11] or catalysts for the removal of sulfur or oxygen from the source gas.[12] As for $NiSe_2$, elevating the temperature and extending the reaction period may grow bigger single crystals, which provide an opportunity to investigate its fundamental properties.

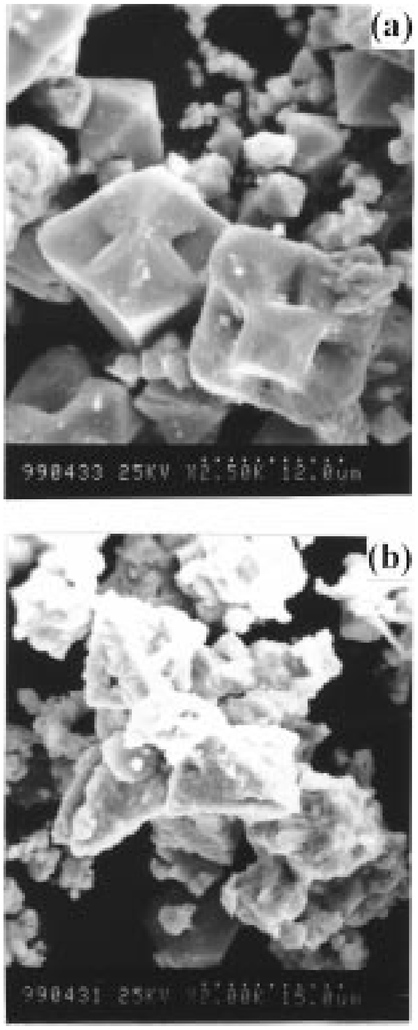

Figure 4. SEM images of mixtures obtained in En: (a) $NiSe_2$ and $Ni_{0.85}Se$; (b) $Ni_{0.85}Se$ and Ni_3Se_2.

Conclusion

The convenient solvothermal process has been employed to synthesize nickel selenides with different morphologies for the first time. The single phases can be conveniently obtained under controlled conditions. Similarly, sulfur or tellurium substitutes for selenium will most probably afford nickel sulfides or tellurides. In an extensive sense, this one-step route may be applicable to the other transition metal chalcogenides with special morphologies.

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