Solvothermal Synthesis to Nanocrystalline $Ni_{0.85}Se$ and $NiSe_2$ at Low Temperature

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Nanocrystalline $Ni_{0.85}Se$ and $NiSe_2$ were prepared through the reaction between $NiCl_2{\cdot}6H_2O$ and elemental selenium at 50 °C, using $N_2H_4{\cdot}H_2O$ as reductant and pyridine as solvent. TEM images showed that the $Ni_{0.85}Se$ and $NiSe_2$ particles were both spherical in shape with sizes of about 20 nm. Solvent pyridine plays an important role in the formation of nanocrystalline nickel selenides due to its appropriate N-chelation ability and alkalescence.

Transition metal chalcogenides have gained much attention in the field of materials science, due to their special electronic properties and interesting chemical behaviors.[1–3] As typical representatives of the great number of transition metal chalcogenides, nickel selenides, which exhibit a wide range of physical and chemical properties, have been investigated extensively in various aspects.[4–9] For example, $NiSe_2$ is a good electrical conductor and Pauli paramagnetic metal compound. Its magnetic susceptibility is weakly paramagnetic ($\cong 1 \times 10^{-6}$ emu/g) and increases very weakly with temperature.[10,11]

Traditionally, nickel selenides have been synthesized by solid state reaction, which requires elevated temperature and inert atmosphere protection, and need a relative long duration.[12,13] A low-energy approach is the precipitation of selenides from aqueous solution of the metal cation using H_2Se.[14] However, this method includes the use of the very toxic reagent H_2Se and the formation of impurities in the product. Recently, Parkin and coworkers reported a room-temperature liquid ammonia route to metal chalcogenides through elemental reactions, but the obtained nickel selenides were amorphous. To obtain crystalline material, the postheat treatment at 250–300 °C is needed, and the product is a mixture of $NiSe_2$ and NiSe.[15] In addition, crystalline nickel selenide films can be prepared by metal–organic chemical vapor deposition method (MOCVD).[16]

In previous works of our laboratory, microcrystalline nickel selenides with different morphologies were synthesized using different solvents at 170–220 °C, and nanocrystalline $NiSe_2$ with particle size ranging from 20 to 25 nm was prepared at 90–100 °C through a hydrothermal method.[17,18] In this work, nanocrystalline $Ni_{0.85}Se$ and $NiSe_2$ with particle size ranging from 15 nm to 20 nm were synthesized at near room temperature (50 °C) in pyridine using $N_2H_4{\cdot}H_2O$ as reductant.

A typical procedure is as follows. Analytically pure elemental selenium (0.01 mol) with 8 mL $N_2H_4{\cdot}H_2O$ (80%, v/v) were put in Teflon-lined stainless steel autoclaves, 0.01 or 0.006 mol $NiCl_2{\cdot}6H_2O$ was also added in to produce $Ni_{0.85}Se$ and $NiSe_2$, respectively. Then they were filled with pyridine up to 90% of the capacity (50 mL). The autoclaves were maintained at 50 °C for 12 h and then were cooled to room temperature naturally. The precipitates were filtered and washed with distilled water and ethanol successively. The final black products were dried in a vacuum at 70 °C for 2 h.

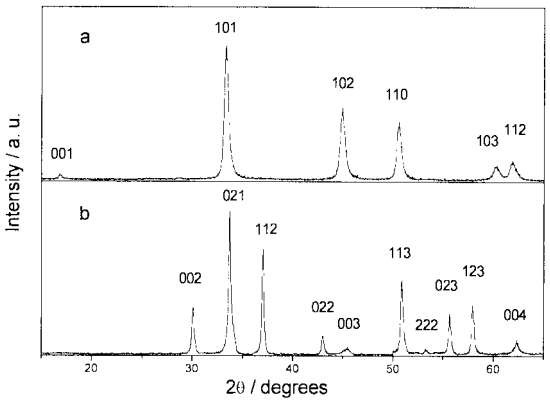

Figure 1. XRD patterns of nanocrystalline (a) $Ni_{0.85}Se$, (b) $NiSe_2$.

The samples were characterized by X-ray powder diffraction (XRD) using a MAX 18 AHF X-ray diffractometer (MAC Science Co., Ltd.) with Cu $K\alpha_1$ radiation (λ = 1.54056 Å). Figures 1a and 1b show the XRD patterns of as-prepared nanocrystalline $Ni_{0.85}Se$ and $NiSe_2$. All peaks in the patterns can be indexed as pure hexagonal $Ni_{0.85}Se$ and cubic $NiSe_2$, respectively.[19] The calculated lattice parameter of $Ni_{0.85}Se$ is a = 3.624 Å, c = 5.298 Å, and that of $NiSe_2$ is a = 5.961 Å, which are very close to the reported values.[19] The average sizes of $Ni_{0.85}Se$ and $NiSe_2$ powders obtained from the Scherrer formula based on the XRD line-width were 17 and 20 nm, respectively.

The compositions of the samples were determined by inductively coupled plasma–atomic emission spectra (ICP–AES), which were carried out on an Atomscan Advantage spectrometer (Therma Jarrell Ash Corp.). The results show that the Ni : Se ratios of $Ni_{0.85}Se$ and $NiSe_2$ are 0.86 : 1.00 and 0.52 : 1.00, respectively, which are close to the stoichiometry of $Ni_{0.85}Se$ and $NiSe_2$.

Figures 2a and 2b show the transmission electron microscopy (TEM) images of $Ni_{0.85}Se$ and $NiSe_2$, which were recorded on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 KV. TEM images indicate that both $Ni_{0.85}Se$ and $NiSe_2$ consist of uniform spherical particles with the particle size ranging from 15 to 20 nm, which is consistent with the XRD results. The electron diffraction (ED) patterns of the samples (the ED pattern of Figure 2a is shown in Figure 2c) furthermore identify that the obtained $Ni_{0.85}Se$ and $NiSe_2$ have good crystallinity.

To study the effect of solvent, the contrast experiments using other solvents were done at present reaction temperature. When distilled water was used as solvent, the crystalline product was only $Ni(OH)_2$, which were determined by XRD. EDX analysis showed that amorphous nickel selenide also existed in the prod-

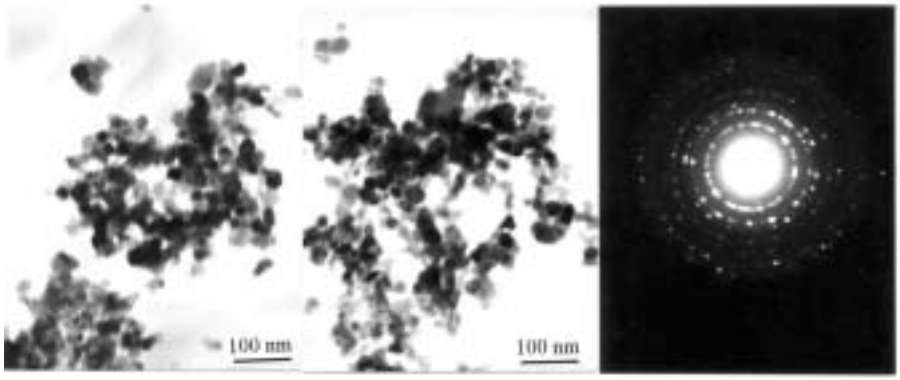

Figure 2. TEM images of nanocrystalline (a) $Ni_{0.85}Se$, (b) $NiSe_2$, (c) the ED pattern of (a).

uct. These results indicate that at this temperature in water the hydrolysis of Ni^{2+} could not be avoided in alkalescent environment and the crystal growth of nickel selenide is bad. When ethylenediamine was used as solvent, molecular precursor containing Ni and Se instead of nickel selenide was obtained. After considering the special properties of ethylenediamine, such as strong polarity, strong chelation and certain reduction, this result is reasonable. With cooperation of $N_2H_4{\cdot}H_2O$, ethylenediamine can not only bind to and stabilize Ni^{2+}, but also dissolve Se and produce complex, just like some amine solvents form complex with S and Se.[20] But the complex cannot decompose to nickel selenide at the present reaction temperature due to its strong chelation ability. Relatively speaking, pyridine is the suitable solvent for this reaction at 50 °C due to its appropriate coordinative ability and alkalescence. In this reaction, $NiCl_2{\cdot}6H_2O$ can dissolve in pyridine to form complex, and elemental selenium can be reduced to Se^{2-} at 50 °C because $N_2H_4{\cdot}H_2O$ is a strong reductant and alkalescence of pyridine can increase its reducing ability too. Then Se^{2-} and the complex of Ni^{2+} can gradually react to form nanocrystalline nickel selenides ($Ni_{0.85}Se$ and $NiSe_2$), because the coordinative ability of pyridine is not too strong. The products in pyridine are single phase and the hydrolysis of Ni^{2+} can be avoided.

In this reaction, although Ni^{2+} and $N_2H_4{\cdot}H_2O$ were in excess, the corresponding elemental Ni was not detected by XRD. This indicates that Ni^{2+} can not be reduced to elemental Ni by $N_2H_4{\cdot}H_2O$, which is similar to the report that Zn^{2+} can not react with $N_2H_4{\cdot}H_2O$ to form elemental zinc in ammonia solution.[21] The experimental result also showed that the reaction time should be no less than 10 h, otherwise the reaction could not proceed completely. With the increase of reaction temperature and reaction time, the products did not change but the particle sizes increased.

In summary, nanocrystalline $Ni_{0.85}Se$ and $NiSe_2$ were prepared through the reaction of $NiCl_2{\cdot}6H_2O$ and elemental selenium at 50 °C, using $N_2H_4{\cdot}H_2O$ as reductant and pyridine as solvent. XRD, ICP-AES, and TEM were used to characterize the samples. It was found that the $Ni_{0.85}Se$ and $NiSe_2$ particles were both spherical in shape with average size of about 20 nm. Solvent pyridine plays an important role in the formation of nanocrystalline nickel selenides due to its appropriate coordinative ability and alkalescence.

References

1 W. S. Sheldrich and M. Wachhold, *Angew. Chem., Int. Ed. Engl.*, **36**, 206 (1997).
2 P. Bottcher, *Angew. Chem., Int. Ed. Engl.*, **27**, 759 (1988).
3 M. A. Haase, J. Qiu, J. M. DePuydt, and H. Chen, *Appl. Phys. Lett.*, **59**, 1272 (1991).
4 Y. Ueda and K. Kosuge, *Bull. Inst. Chem. Res. Kyoto Univ.*, **64**, 186 (1986).
5 M. G. Kanatzidis, *Angew. Chem., Int. Ed. Engl.*, **34**, 2109 (1995).
6 R. A. DeGroot and F. U. Hillebrecht, *J. Phys. C*, **20**, 4135 (1987).
7 M. G. Kanatzidis and S. P. Huang, *Coord. Chem. Rev.*, **130**, 509 (1994).
8 J. Barstad and E. Vestersjo, *Acta Chem. Scand.*, **20**, 2865 (1966).
9 I. Masaaki and F. Tsutomu, *X-ray Spectrum*, **16**, 73 (1987).
10 S. Ogawa, *J. Appl. Phys.*, **50**, 2308 (1979).
11 N. Inoue, H. Yasuoka, and S. Ogawa, *J. Phys. Soc. Jpn.*, **48**, 850 (1980).
12 P. R. Bonneau, R. F. Jarvis, and R. B. Kaner, *Nature*, **349**, 510 (1991).
13 I. P. Parkin, *Chem. Soc. Rev.*, **25**, 199 (1996).
14 H. C. Metcalf, J. E. Williams, and J. F. Caskta, "Modern Chemistry," Holt, Reinhart, Winston, New York (1982), p 54.
15 G. Henshaw, I. P. Parkin, and G. A. Shaw, *J. Chem. Soc., Dalton Trans.*, **1997**, 2689.
16 X. J. Song and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, **1997**, 231.
17 Z. H. Han, S. H. Yu, Y. P. Li, H. Q. Zhao, F. Q. Li, Y. Xie, and Y. T. Qian, *Chem. Mater.*, **11**, 2302 (1999).
18 W. X. Zhang, Z. H. Hui, Y. W. Cheng, L. Zhang, Y. Xie, and Y. T. Qian, *J. Cryst. Growth*, **209**, 213 (2000).
19 JCPDS files, No. 18-888, No. 6-507.
20 Y. Cheng, T. J. Emge, and J. G. Brennan, *Inorg. Chem.*, **35**, 7339 (1996).
21 J. Yang, S. H. Yu, X. L. Yang, and Y. T. Qian, *Chem. Lett.*, **1999**, 839.