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A NOVEL ROOM TEMPERATURE METHOD TO NANOCRYSTALLINE Ag_2Se

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ABSTRACT

Nanocrystalline Ag_2Se was synthesized at room temperature through the reaction of $AgNO_3$, Se, and KBH_4 in pyridine. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). TEM revealed that the as-prepared Ag_2Se grains were homogeneous and spherical, and their average size was about 25 nm. XPS analysis showed that the purity was good. Different solvent media were tested, and pyridine was found to be the most suitable one. The possible mechanism of the formation of Ag_2Se grains is proposed. This novel mild method will be extended to prepare other nanocrystalline chalcogenides at room temperature. *© 1999 Elsevier Science Ltd*

KEYWORDS: A. chalcogenides, A. nanostructures, B. chemical synthesis, C. electron microscopy, C. photoelectron spectroscopy

INTRODUCTION

The preparation and characterization of selenides has attracted much attention because of the special properties of these materials. Ag_2Se is a well-known superionic conductor [1–3]. It has been used as thermochromic material for nonlinear optical devices [4], photochargeable secondary batteries [5], and multipurpose ion-selective electrodes [6]. Many methods have been used to obtain Ag_2Se, including mechanical alloying method using a high-energy ball

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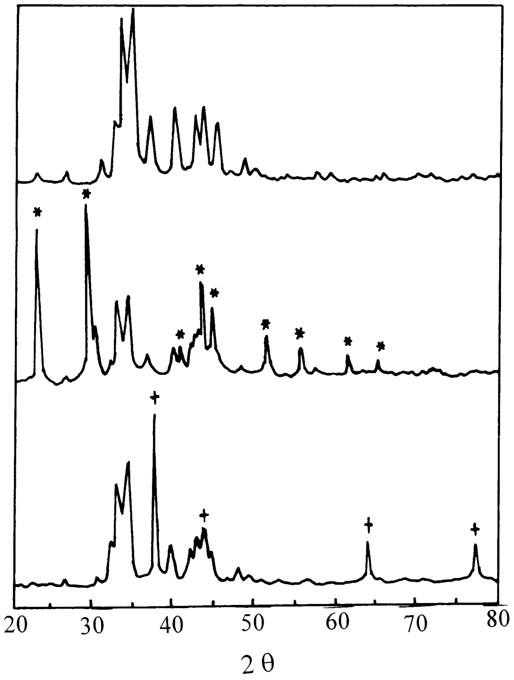

FIG. 1
XRD diffraction patterns of as-prepared samples: Ag_2Se, $Ag_2Se + Se$ (indexed by *), and $Ag_2Se + Ag$ (indexed by +).

mill [7], microemulsions [8], electrolysis [9], and a hydrothermal route at elevated temperature (>260°C) and pressure (100 atm) [10]. However, there are few reports that nanocrystalline Ag_2Se has been synthesized.

Since properties are known to vary with size, it has become important to decrease the size of materials to nanoscale. Most researchers are also seeking milder conditions for preparing nanocrystalline materials. This paper reports a novel method to obtain nanocrystalline Ag_2Se at room temperature, with the reduction of KBH_4. Compared with other methods, this method is simpler and milder, and it can be extended to obtain other chalcogenides.

In past years, most studies of the chemistry of BH_4^- reduction focused on preparing amorphous metals [11], nanocrystalline magnetic materials [12,13], catalysts [14], borides [15], and transition-metal oxides such as MoO_2, VO_2, Na_xWO_3, and K_xMO_3 [16–18]. In these studies, boron was always incorporated into the solid products [15,19]. Most products were amorphous or crystallized after post-treatment at high temperature (>350°C) in inert atmosphere [15–18]. To our knowledge, this is the first time that reduction of KBH_4 has been used to prepare nanocrystalline selenide at room temperature in organic solvent.

EXPERIMENTAL

Appropriate amounts of Se, $AgNO_3$, and KBH_4 powders were put into a flask, and the flask was filled with pyridine to 80% of its capacity. Next, the flask was sealed and the system was

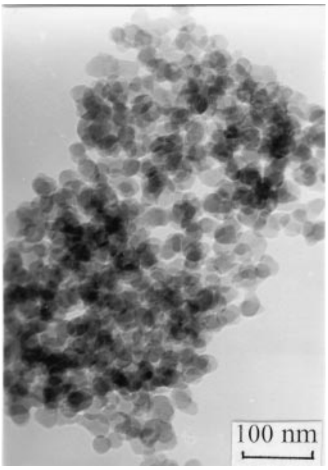

FIG. 2
TEM image of nanocrystalline Ag_2Se.

kept at room temperature (about 10°C) for 4 h. The black precipitate that formed was washed with distilled water, and the final product was collected for characterization.

Powder X-ray diffraction (XRD) was performed on a Rigaku D/max γA rotation anode X-ray diffractometer using Ni-filtered Cu Kα radiation, to characterize the products. The morphology and grain size were determined by transmission electron microscopy (TEM). TEM images were taken with a Hitachi H-800 transmission electron microscope. The purity and composition of the as-prepared nanocrystalline X-ray photoelectron spectra (XPS) were recorded on an ESCALab MK2 using Al Kα as the exciting source. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s to 284.50 kV.

RESULTS AND DISCUSSION

The XRD pattern of a typical sample (Fig. 1a) revealed that the as-prepared nanocrystalline Ag_2Se was orthorhombic and matched the literature data perfectly [20]. After refinement, the cell parameters were $a = 0.43$, $b = 0.71$, and $c = 0.78$ nm, which were also in accordance with reported values [20]. The average crystallite size was 25 nm, which was determined by the Scherrer equation based on the half-widths of XRD peaks. No impurities, such as Ag and Se, were detected.

The TEM image of the grains of the as-prepared nanocrystalline Ag_2Se is shown in Figure 2. From this microphoto, it is obvious that the grain morphology was homogeneous and spherical; the grain sizes varied from 20 to 30 nm and the average size was about 25 nm.

XPS analysis results are shown in Figure 3. The two strong peaks, at 368.1 and 373.9 eV, correspond to Ag 3d binding energy for Ag_2Se. The strong peak at 53.6 eV corresponds to Se 3d binding energy for Ag_2Se. These results are close to that of bulk Ag_2Se. No impurities, such as Ag, Ag_2O, Se, SeO_2, or B, were detected; the product purity was good. From the XPS analysis, Ag and Se contents were quantified by Ag 3d and Se 3d peak areas and the composition of the product was determined to be $Ag_{2.1}Se$.

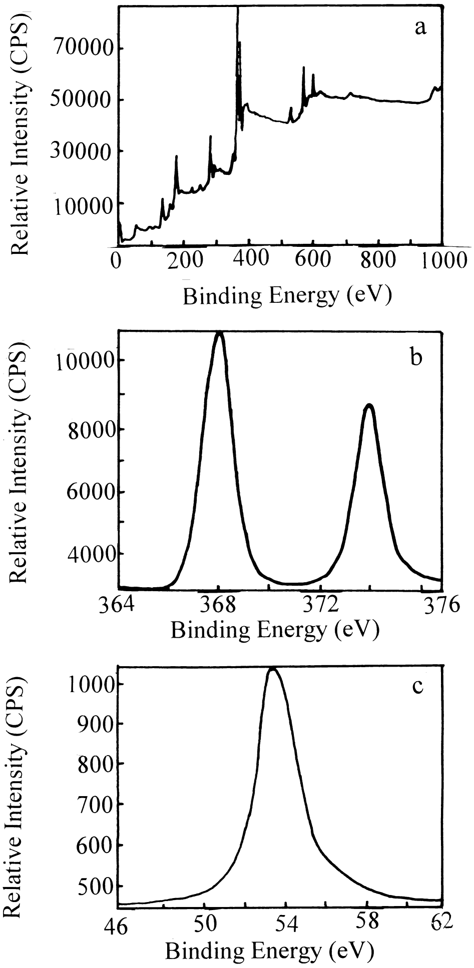

FIG. 3
XPS analysis of as-prepared nanocrystalline Ag_2Se.

Different solvent media were tested to investigate their influence on the quality of the nanocrystalline Ag_2Se product. Pyridine is known to produce complex $S(Py)_2$ with sulfur, due to its base and N-chelation [21–23]. Possibly a similar complex $Se(Py)_2$ is produced when Se is put into pyridine, because many properties of Se are similar to those of S. This was supported by the fact that when only selenium powder was added into pyridine, the solution color slowly changed to brown and the selenium powder disappeared. This increased the activity of the reactants and ensured the complete conversion of selenium and Ag to Ag_2Se, without high temperature; thus, this method differs greatly from solid-state reaction. When other solvents were used, e.g., benzene, which have no chelation and cannot produce a complex with selenium, a large amount of unreacted selenium remained in the product even when the system temperature was elevated to 180°C for 3 days. (To ensure safety in these experiments, a stainless steel autoclave with Teflon-liner was used instead of the flask, because the system pressure and temperature greatly increased.) The results are shown in Figure 1b. Peaks indexed by an asterisk belong to Se. These experiments showed that pyridine was the most suitable solvent.

That KBH_4 was selected as the reductant was a key factor in Ag_2Se being obtained at room temperature in a short time. The existence of active H^- in KBH_4 activates the reaction between Se and $AgNO_3$ and makes the reaction happen easily at room temperature. Excessive KBH_4 was used to ensure that selenium and $AgNO_3$ were completely converted. When KBH_4 was substituted by other reductants, such as sodium, no obvious reactions happened under identical conditions.

Experiments demonstrated that when stoichiometric $AgNO_3$ was added to the system, only Ag_2Se was produced, as evidenced by the XRD pattern (Fig. 1a). When $AgNO_3$ was excessive, Ag peaks appeared in the XRD pattern and Ag and Ag_2Se coexisted in the product. In Figure 1c, the peaks indexed by the plus-sign belong to Ag. These results reveal that KBH_4 might reduce $AgNO_3$ to Ag first. The newly formed Ag grains dispersed in the solution; they had a high surface area and were very active. They reacted with Se to produce nanocrystalline Ag_2Se at room temperature. To test this hypothesis, stoichiometric Ag powder was used directly instead of $AgNO_3$. The result was a large amount of Ag remained in the product and little Ag_2Se was produced. This may be due to the low activity of silver powder.

CONCLUSIONS

The reduction route discussed here has the advantage of obtaining metal selenides directly at room temperature. XPS indicated that no boron was incorporated into the products when KBH_4 was used for the reduction. Furthermore, preparation of metal selenides through this method does not require extreme precursors, such as the easily hydrolyzable Na_2Se or toxic H_2Se.

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REFERENCES

1. F. Shimojo and H. Okazaki, *J. Phys. Soc. Jpn.* **62** (1), 179 (1993).
2. K. Honma and K. Iida, *J. Phys. Soc. Jpn.* **56** (5), 1828 (1987).
3. T. Sakuma, K. Iida, K. Honma, and H. Okazaki, *J. Phys. Soc. Jpn.* **43** (2), 538 (1977).
4. K.L. Lewis, A.M. Pitt, T. Wyatt-Davies, and J.R. Milward, *Mater. Res. Soc. Symp. Proc.* **374**, 105 (1994).
5. T. Akoto, Y. Hasuda, M. Ishizawa, and T. Horie, Jpn. Kokai Tokkyo Koho JP 04,171,681 [92,171,681].
6. B. Nesie and M.S. Jovanovic, *J. Serb. Chem. Soc.* **56** (6), 353 (1991).
7. T. Ohtani, K. Maruyama, and K. Ohshima, *Mater. Res. Bull.* **32**, 343 (1997).
8. Ph. Monnoyer, J.B. Nagy; V. Buschmann, A. Fonseca, L. Jeunieau, P. Piedigrosso, and G. Van Tendeloo, *NATO ASI Ser.*, Ser. 3, 18, 505, 1996.
9. A.M. De Becdelievre, J. Amosse, and M.J. Barbier, *Mater. Res. Bull.* **5**, 367 (1970).
10. L. Cambi and M. Elli, *Chim. Ind.* **50** (1), 94 (1968).

11. R. D. Rieke, *Science* **246**, 1260 (1989).
12. L. Yiping, G.C. Hadjipanayis, C.M. Sorensen, and K.J. Klabunde, *J. Magn. Magn. Mater.* **79**, 321 (1989).
13. J. Van Wontergham, S. Morup, C.J.W. Koch, S.W. Charlds, and S. Wells, *Nature* **322**, 1986 (1986).
14. A. Corrias, G. Ennas, G. Licheri, G. Marongui, and G. Paschian, *Chem. Mater* **2**, 263 (1990).
15. G.N. Glavee, K.J. Klabunde, C.M. Sorensen, and G.C. Hadjipanayis, *Inorg. Chem.* **34**, 28 (1995).
16. Y.T. Zhu and A. Manthiram, *J. Solid State Chem.* **110**, 187 (1994).
17. A. Manthiram, A. Dananjay, and Y.T. Zhu, *Chem. Mater.* **6**, 1601 (1994).
18. C. Tsang, A. Dananjay, J. Kim, and A. Manthiram, *Inorg. Chem.* **35**, 504 (1996).
19. J. Shen, Z. Li, Q. Yan, and Y. Chen, *J. Phys. Chem.* **97**, 8504 (1993).
20. JCPDS No. 24-1041.
21. C.O. Kienitz, C. Thone, and P.G. Jones, *Inorg. Chem.* **35**, 3990 (1996).
22. Y. Cheng, T.J. Emge, and J.G. Brennan, *Inorg. Chem.* **35**, 342 (1996).
23. Y. Cheng, T.J. Emge, and J.G. Brennan, *Inorg. Chem.* **35**, 7339 (1996).