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# A facile method to the cube-like MnSe<sub>2</sub> microcrystallines via a hydrothermal process

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#### Abstract

A convenient hydrothermal process was applied to prepare the cube-like  $MnSe_2$  microcrystallines through the reaction of  $MnSO_4 \cdot H_2O$  with Se and  $NaH_2PO_2 \cdot H_2O$  in aqueous solution at 160 °C for 12 h. Powder X-ray diffraction (XRD) analysis confirmed that the product was the cubic phase of  $MnSe_2$  with cell parameter a = 6.440 Å. The chemical composition of the  $MnSe_2$  was determined by XPS. The Raman spectrum of  $MnSe_2$  presented the peaks of the Se–Se stretching mode at 232.44 and 266.58 cm<sup>-1</sup>. The images of scanning electron microscope (SEM) and transmission electron microscope (TEM) showed the cube-like morphology of the product with the edge length ranging from 20 to 30  $\mu$ m. The formation mechanism of the  $MnSe_2$  microcrystallines was discussed as well. © 2006 Elsevier Ltd. All rights reserved.

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## 1. Introduction

Transition metal dichalcogenides  $MX_2$  (M=Mn, Fe, Co, Ni; X=S, Se) with pyrite structures have been paid much attention due to their electrical, magnetic, and optical properties [1–5]. A great number of experimental and theoretical studies have been reported on the so-called pyrites  $MX_2$  during the last decades [6–9]. For their application in rechargeable battery electrodes [10] and dilute magnetic semiconductors (DMSs) [11], the pyrites  $MX_2$  are very attractive to scientists.

Developing simple and convenient methods to prepare these pyrites are challenging to chemists. Traditionally, transition metal dichalcogenides are synthesized by the direct stoichiometric combination of elements in evacuated silica tubes [12]. But due to the limit of slow diffusion, the complete reaction requires intermittent grinding and heating at high temperature from 500 to 1200 °C. This process needs high energy and long time. The direct elemental reactions were improved by

\* Corresponding author. *E-mail address:* ytqian@ustc.edu.cn (Y. Qian). conducting them in liquid ammonia at room temperature, but the obtained product was a mixture of amorphous nickel selenide and crystalline nickel [13]. Then the mixture was heated at 300 °C and the crystalline NiSe<sub>2</sub> and NiSe were produced. Recently, hydrothermal synthesis has proved to be a useful method to produce pyrite crystallines. For example, NiSe<sub>2</sub> nanocrystallines, CoSe<sub>2</sub> nanorods, FeSe<sub>2</sub> nanocrystallines [14], MnSe<sub>2</sub> nanorods and microcrystallines [15] have been synthesized via the hydrothermal process.

Here, we report a facile hydrothermal method to prepare the cube-like MnSe<sub>2</sub> microcrystallines.

### 2. Experimental section

All the chemicals were analytical grade and purchased from Shanghai Chemical Reagents. In a typical procedure, 0.005 mol manganese sulfate monohydrate ( $MnSO_4 \cdot H_2O$ ) and 0.01 mol sodium hypophosphite ( $NaH_2PO_2 \cdot H_2O$ ) were dissolved in 40 ml distilled water, then 0.01 mol selenium metal powder (Se) were added into the solution. The mixture was transferred into a Teflon-lined autoclave with 60 ml capacity, which was sealed, maintained at 160 °C for 12 h, and then cooled to room temperature naturally. At last, the black product was collected by filtration, washed with distilled water and ethanol, and then dried at 60 °C in vacuum.

The samples were characterized by powder X-ray diffraction (XRD) employing a scanning rate of  $8.0000^{\circ}$  min<sup>-1</sup> in the  $2\theta$  range from 10 to 70° and using a MAX 18 AHF X-ray diffractometer (MAC Science) equipped with graphite-monochromatized Cu K $\alpha$ 1 radiation ( $\lambda$ =1.54056 Å). The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using a non-monochromatized Mg Ka (1253.6 eV) X-ray in high vacuum  $(5 \times 10^{-9} \text{ Pa})$  as the excitation source. The binding energy values were calibrated from that of C1s (284.6 eV). The Raman spectrum was recorded on a SPEX-1403 laser Raman spectrometer by means of back scattering technique at room temperature. The morphology was observed by scanning electron microscopy (SEM), which was operated on a Hitachi S-650 scanning electron microscope. Transmission electron microscope (TEM) images were performed on a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The samples for TEM were prepared by putting a few drops of absolute ethanol solution in which the crystalline samples were ultrasonically dispersed onto an amorphous carbon substrate supported on a copper grid and then allowing the solvent to evaporate at room temperature.

## 3. Results and discussions

Fig. 1 shows the pyrite structure of the  $MnSe_2$  microcrystallines. The pyrite structure is a face-centered cubic phase and resembles the NaCl structure. The Mn atoms replace the Na atoms and occupy all the octahedral sites which are formed by six nearest  $Se_2$  groups. The dumbbell-shaped  $Se_2$  groups replace the Cl atoms, being surrounded by six nearest Mn atoms as well. Fig. 1 also gives out the growth directions of the cube-like MnSe<sub>2</sub> microcrystallines.

The XRD pattern of the product without being ground is shown in Fig. 2(a). All the diffraction peaks can be indexed as the pure cubic MnSe<sub>2</sub> phase. The lattice parameter can be calculated as a=6.440 Å, being close to the standard value a=6.417 Å (JCPDS 73-1525). Compared to the standard XRD pattern, the peak of {200} is much stronger, which indicates the growth direction of the product. In the pyrite structure, the {200} equivalent planes contain the three planes (200), (020),



Fig. 1. Crystal structure of the MnSe<sub>2</sub>.



Fig. 2. XRD pattern of the cube-like  $MnSe_2$  microcrystallines (a) and the grinded  $MnSe_2$  powders (b).

(002) which are perpendicular to the three directions [100], [010], [001] which have been presented in Fig. 1. The as-prepared  $MnSe_2$  microcrystallines grow along the three directions at an equal speed, as a result, the cubic morphology of the product is obtained. The preferential growth can be observed at {400} peak as well. Fig. 2(b), which is the XRD pattern of the grinded  $MnSe_2$  powders, shows the standard XRD pattern (JCPDS 73-1525).

The XPS surface analysis of the product is given out in Fig. 3. The survey spectrum shows the sample consists of Mn and Se, as well as the absorbed carbon and oxygen on the sample surface. High-resolution spectra are preformed at Mn



Fig. 3. XPS of the  $MnSe_2$  survey spectrum (a) and the high resolution spectrum for Mn (b) and Se (c) core shell regions, respectively.



Fig. 4. Raman spectrum of MnSe<sub>2</sub> at room temperature.

and Se core regions. The binding energy of Mn2p3 is at 640.95 eV and that of Se3d is at 54.95 eV, which are in good agreement with the reported value in the literature [14a,16].

The Raman allowed modes in the pyrite structure are mainly caused by the intraionic stretching modes of the dumbbell-shaped Se<sub>2</sub> units. The intraionic Se–Se stretching mode of pyrite-type compounds exhibits the information about the strengths of the intraionic Se–Se bonds. In our experiment, the peaks of the Se–Se stretching mode is observed at 232.44 and 266.58 cm<sup>-1</sup> in Fig. 4, being close to the values in the previous reports [17].

Fig. 5 shows the SEM and TEM images of the as-prepared  $MnSe_2$  microcrystallines. It can be observed that the sample is composed of a number of cube-like microcrystallines. The edge length of the  $MnSe_2$  microcrystallines is in the range from 20 to 30 µm and the volume is from 8000 to 27,000 µm<sup>3</sup>. The surfaces of the cube-like  $MnSe_2$  microcrystallines are very smooth, which is quite different from the  $MnSe_2$  microcrystallines.



Fig. 5. SEM (a)-(c) and TEM (d) images of the MnSe<sub>2</sub>.

$$H_2PO_2^- + Se + H_2O = Se^2^- + HPO_3^2^- + 3H^+$$
 (1)

$$Se + Se^{2^{-}} = Se_2^{2^{-}}$$
 (2)

$$Se_2^2 + Mn^2 = MnSe_2$$
 (3)

Scheme 1. Chemical reactions in the experiment.

tallines which have desquamation phenomenon on the surfaces [15b]. The smooth surfaces demonstrate that the product is well crystallized.

The possible chemical reactions to form the cube-like MnSe<sub>2</sub> microcrystallines are presented in Scheme 1. In the first reaction, Se is reduced to  $Se^{2-}$  by the reductant NaH<sub>2</sub>PO<sub>2</sub>. H<sub>2</sub>O. Secondly, the obtained  $Se^{2-}$  combines with Se to form  $Se_2^{2-}$ , like the formation of polysulfide ions in aqueous solution. At last, the produced  $\text{Se}_2^{2-}$  reacts with the  $\text{Mn}^{2+}$  to precipitate the MnSe<sub>2</sub> as the final product. During the whole process, reaction (1) is the crucial step for the formation of the wellcrystallized cubic MnSe<sub>2</sub> microcrystallines. In reaction (1), the positive electrode potential  $\varphi^{\theta}$ Se/Se<sup>2-</sup> is -0.92 eV and the negative electrode potential  $\varphi^{\theta}$ H<sub>3</sub>PO<sub>3</sub>/H<sub>3</sub>PO<sub>2</sub> is -0.499 eV, that is, the reductant  $NaH_2PO_2$  cannot reduce Se to Se<sup>2-</sup> spontaneously at room temperature (298 K). The whole system needs high temperature to conquer the high activation energy Ea of the reaction (1) and make the reaction happen. So, reaction (1) determines the lowest reaction temperature. Meanwhile, it should be pointed out that the high activation energy Ea of reaction (1) makes the formation of  $Se^{2-}$  very slow, as a result, the formations of  $\text{Se}_2^{2-}$  and the MnSe<sub>2</sub> nuclei become very slow as well. The slow growth of the MnSe<sub>2</sub> nuclei benefits the growth of the well-crystallized cube-like MnSe<sub>2</sub> microcrystallines. Other reductants such as ethylenediamine and sodium sulfite anhydrous are also used to reduce Se in reaction (1), but the cube-like MnSe<sub>2</sub> microcrystallines cannot be produced. So, the reductant NaH<sub>2</sub>PO<sub>2</sub> is not substituted due to its suitable reducing ability.

Temperature is an important factor for the system, when the temperature is lower than 140 °C, the reaction (1) cannot happen and the precipitates are still selenium powder. To some extent, 140 °C is the lowest temperature determined by the high activation energy Ea of reaction (1). When the temperature is higher than 180 °C, a kind of so-called  $MnP_xO_y$  white-gray precipitates which is discussed below begin to turn out. If the system is heated to 200 °C for 24 h, the black  $MnSe_2$  microcrystallines will disappear and the white-gray  $MnP_xO_y$  precipitates will become the only product. In general, the temperature should be controlled in the range of 140–180, and 160 °C is an appropriate temperature to prepare the cube-like  $MnSe_2$  microcrystallines. As another important factor, time should be as long as 12 h in order to make the reactions complete at 160 °C.

According to the previous reports, the obtained  $MnSe_2$  will transform into  $\alpha$ -MnSe, which is the thermodynamic stable phase when the temperature is increased. However, the so-called  $MnP_xO_y$  white-gray precipitates turn out instead of  $\alpha$ -MnSe in our experiment. This phenomenon may be due to the following two reasons. First,  $H^+$  can be obtained in



Fig. 6. XPS spectrum of the MnP<sub>x</sub>O<sub>y</sub> precipitates.



Fig. 7. SEM images of the  $MnP_xO_y$  precipitates.

reaction (1) and the PH value is about 2, which is measured by the special indicator paper. The  $\alpha$ -MnSe can be dissolved by the acid solution at high temperature. Secondly, either the O<sub>2</sub> in the solution or the disproportional reaction of the P element in itself is able to engender a more complex  $P_x O_y^{2-}$  anion at higher temperature. The obtained  $P_x O_y^{2-}$  combines with Mn<sup>2+</sup> to form the white-gray MnP<sub>x</sub>O<sub>y</sub> precipitates. Unfortunately, the phase of MnP<sub>x</sub>O<sub>y</sub> cannot be characterized by XRD for without the corresponding standard PCPDF cards. XPS in Fig. 6 describes the precipitates include the three elements Mn, P and O. So, the white-gray precipitates can be called MnP<sub>x</sub>O<sub>y</sub> temporarily. Confirming the phase of the white-gray MnP<sub>x</sub>O<sub>y</sub> precipitates is being studied in our following work. Fig. 7 gives out the rodlike morphology of the so-called MnP<sub>x</sub>O<sub>y</sub> white-gray precipitates.

## 4. Conclusions

In summary, the cube-like  $MnSe_2$  microcrystallines have been synthesized by a convenient hydrothermal method. Temperature is a crucial factor to obtain the cube-like  $MnSe_2$  microcrystallines and the reductant NaH<sub>2</sub>PO<sub>2</sub> cannot be replaceable. The convenient hydrothermal synthetic method can be applied to synthesize other transition metal selenides.

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## References

- [1] S. Ogawa, S. Waki, T. Teranishi, Int. J. Magn. 5 (1974) 349.
- [2] H.S. Jarrett, W.H. Cloud, R.J. Bouchard, S.R. Butler, C.G. Frederick, G.L. Gilson, Phys. Rev. Lett. 21 (1968) 617.
- [3] P. Panissod, G. Krill, M. Lahrichi, M.F. Lapierre, Phys. Lett. A 59 (1971) 221.
- [4] S. Marcus, T.A. Bither, Phys. Lett. A 32 (1970) 363.
- [5] K. Adachi, K. Sato, M. Takeda, J. Phys. Soc. Jpn. 26 (1969) 631.
- [6] G. Krill, A. Amamou, J. Phys. Chem. Solids 41 (1980) 531.
- [7] S. Ogawa, Physica B&C 86-88 (1977) 977.
- [8] V.H. McCann, J.B. Ward, J. Phys. Chem. Solids 38 (1977) 991.
- [9] W. Folkerts, G.A. Sawatzky, C. Hass, R.A. de Groot, F.U. Hillebrecht, J. Phys. C 20 (1987) 4135.
- [10] (a) M.K. Aydinol, A.F. Kohan, G. Ceder, K. Cho, J. Joannopoulos, Phys. Rev. 56 (1997) 1354;
  - (b) M.S. Whittingham, Prog. Solid State Chem. 12 (1978) 41.
- [11] (a) D.J. Norris, N. Yao, F.T. Charnock, T.A. Kennedy, Nano Lett. 1 (2001) 3;
  - (b) L. Levy, N. Feltin, D. Ingert, M.P. Pileni, J. Phys. Chem. B 101 (1997) 9153;
  - (c) J.F. Suyver, S.F. Wuister, J.J. Kelly, A. Meijerink, Nano Lett. 1 (2001) 429.
- [12] (a) R.M.A. Leith, J.C. Terhell, Transition metal dichalcogenides in: R.M.A. Leith, D. Reidel (Eds.), Preparation and Crystal Growth of Materials with Layered Structures, Dordrecht, The Netherlands, 1977;
  - (b) G. Braveer, Second ed. Handbook of Preparative Inorganic Chemistry, vols. 1 and 2, Academic Press, New York, 1965;
  - (c) P. Wang, P. Somasundaram, J.M. Honig, T.M. Pekarek, Mater. Res. Bull., 32 (1997) 1435.
- [13] G. Henshaw, I.P. Parkin, G.A. Shaw, J. Chem. Soc., Dalton Trans. (1997) 231.
- [14] (a) J. Yang, G.H. Cheng, J.H. Zeng, S.H. Yu, Y.T. Qian, Chem. Mater. 13 (2001) 848;
  - (b) W.Z. Zhang, Z.H. Hui, Y.W. Cheng, L. Zhang, Y. Xie, Y.T. Qian, J. Cryst. Growth 209 (2000) 213;
  - (c) W.X. Zhang, Z.H. Yang, J.W. Liu, Z.H. Hui, W.C. Yu, Y.T. Qian, G.E. Zhou, L. Yang, Mater. Res. Bull. 35 (2000) 2403.
- [15] (a) M.Z. Wu, Y. Xiong, N. Jiang, M. Nan, Q.W. Chen, J. Cryst. Growth 262 (2004) 567;
  - (b) Q. Peng, Y.J. Dong, Z.X. Deng, H.Z. Kou, S. Gao, J. Phys. Chem. B 106 (2002) 9261.
- [16] H. Van Der Heide, R. Hemmel, C.F. Van Bruggen, C. Haas, J. Solid State Chem. 33 (1980) 17.
- [17] T. Suzuki, K. Uchinokura, T. Sekine, E. Matsuura, Solid State Commun. 23 (1977) 847.