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GROWTH AND CHARACTERIZATION OF $NbSe_2$ SINGLE CRYSTALS VIA A SIMPLE CALCINATION PROCESS

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The $NbSe_2$ nanoplates with novel hexagonal morphology have been obtained via solid-state assembly of $NbSe_2$ ultrathin nanosheets, which were prepared by a simple calcination process using micro-sized Nb and Se powders as the precursors. The influence of high-temperature annealing upon morphology of single-crystal NbSe2 was investigated. On the basis of experimental results of different temperatures and time-dependent morphology evolution process, a possible reaction process and a growth mechanism were preliminarily proposed.

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1. Introduction

In recent years, interest in the synthesis and application of transition metal dichalcogenides MX2 (M: Mo,W, X = S,Se) nanomaterial has steadily grown because of their unique structure and superior properties [1]. As we know, transition metal dichalcogenides have a sandwich interlayer structure formed by the stacking of the X–M–X layers, which are loosely bound to each other only by van der Waals forces and are easily cleaved [2]. Moreover, MX2 exhibits unique physical, optical and electrical properties correlated with their layer structure. In addition, their electronic structure is such that band-edge excitation corresponds largely to a metal centred d-d transition. Owing to these features, laminar MX2 materials have numerous applications such as solid lubricants [3-12], catalysis, electrocatalysis, high-density batteries and efficient solar energy cells [13–16]. Among these layered materials, Outside graphene, so much focus on metal chalcogenide nanostructures which would bring out new replacement that can be competitive with and even better than the graphene.

Niobium diselenide (NbSe2) is one of the transitionmetal dichalcogenide layered compounds, and it is exceptionally attractive because of its super conductivity and the formation of a charge-density-wave (CDW) state [17]. To date, 1D NbSe2 nanostructures have been prepared by the intense electron irradiation of bulk NbSe2 [18]. Recently, Odom etal. [19] described the synthesis of 2D nanoplates and 1D nanowires of NbSe2 in high yield starting from a niobium chloride precursor and elemental Se via a solution-based synthesis. However, it is still a great challenge to develop a simple and novel method to synthesize NbSe2 nanomaterials with high yield, uniform size and shape and at acceptable prices for the real market needs.

Up to now, the synthesis of the regular self-assembly NbSe2 hexagonal nanostructures via a sintered process has rarely been reported. In this paper, we report a facile and a simple calcination process route for synthesis of single-crystal NbSe2 nanoplates using niobium and

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selenium powders as raw materials without any additives. In addition, a growth mechanism and morphology for NbSe2 products has been discussed in detail on the basis of the effect of the temperature annealing and reaction time. The approach also helps to produce a high yield of uniform nanostructure, which opens up possibilities for other nanomaterials.

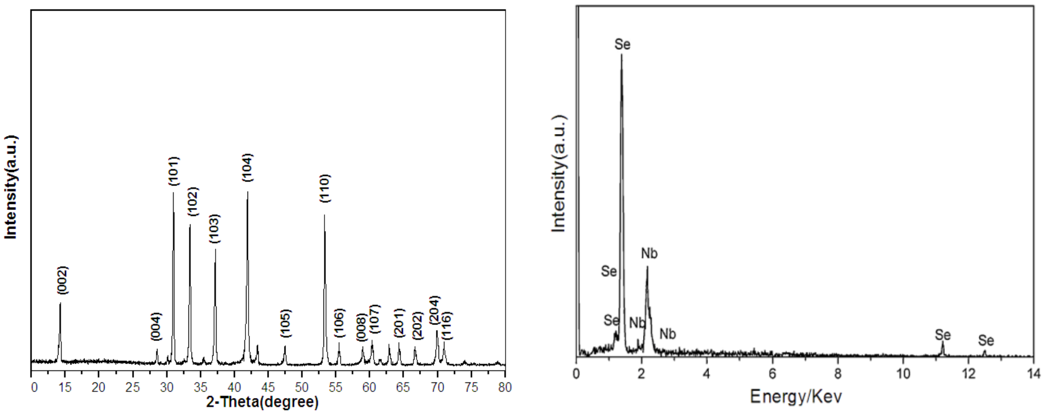
2. Experiment

Synthesis of NbSe2 samples. The elemental selenium (99.9%, 300 mesh), and niobium (99.8%, 200 mesh) powders (mole ratio Nb:Se, 1:2.2, Se excess 5%) were mixed in planet ball-milling at 400 rpm (rotation per minute) in the presence of ethanol for 8 h. Then the ball-milled mixture was introduced into 10-ml stainless steel reactor in a nitrogen-filled glove box. The filled reactor is tightly closed with the threaded plug and quickly pushed into the hot zone of the tube furnace. The temperature of the tube furnace was heated to 750°C at a rate of 10°C/min and kept at 750°C for 2 h, then cooled to room temperature and a black powder is obtained.

Characterization of NbSe2 samples. The X-ray diffraction were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu Ka radiation (λ=0.1546 nm, scan rate: 0.08°/s, scanning range:10°-80°). The structure and morphology of the samples were characterized by scanning electron microscopy (SEM, JEOL JXA-840A) and transmission electron microscopy (TEM) with a Japan JEM-100CX II transmission electron microscopy.

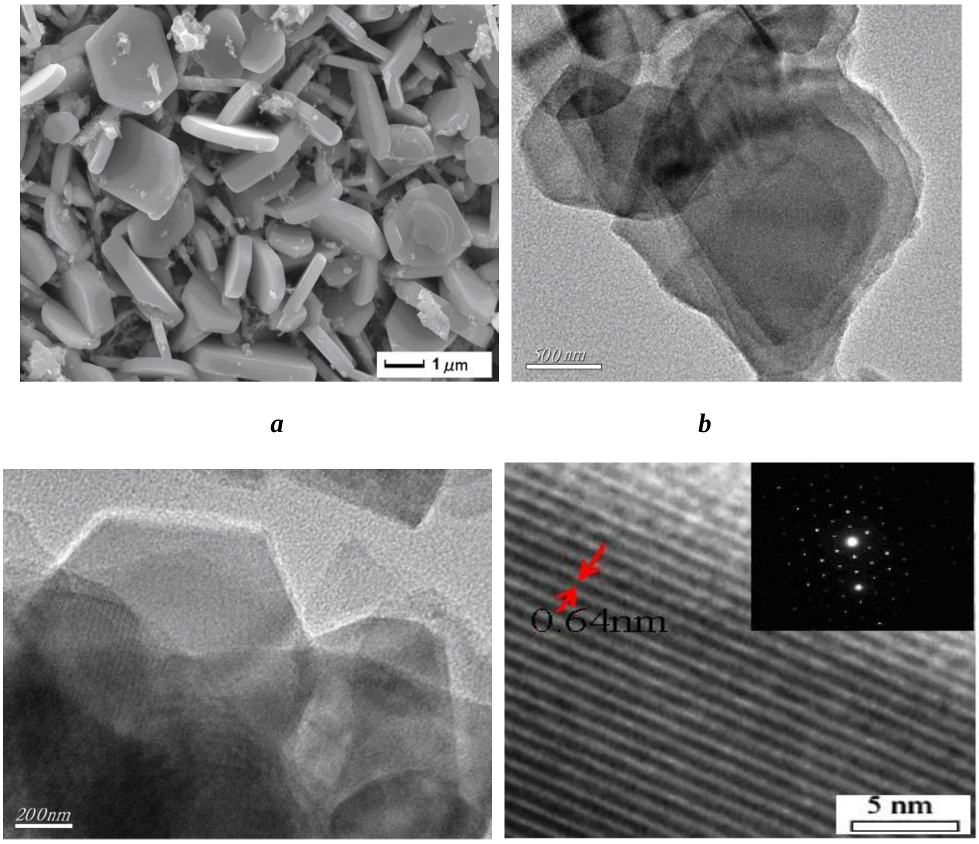
3. Results and discussion

The crystallinity, structure, and phase purity of the prepared samples were confirmed by XRD and EDS. As shown in Fig. 1a, all observed diffraction peaks can be exactly indexed to the hexagonal phase of NbSe2 with lattice constants a = 3.445 Å and c = 12.55 Å (PDF No. 65-7464). No characteristic peaks were observed, and the sharp diffraction peaks imply a good crystallinity of the obtained NbSe2 products under current synthesis conditions. The Energy-dispersive X-ray Spectrometer (EDS) result (Fig. 1b) demonstrates that the samples are consisted of elements Nb and Se, while no other elements was observed. Furthermore, the quantification of the peaks shows that the atom ratio of Nb:Se is about 1:1.98, which is close to 1:2 by atomic ratio of NbSe2. The morphology and size of NbSe2 products were further identified by SEM and TEM.



a *b*

Fig. 1(a) XRD pattern and (b) EDS of the NbSe2 product obtained at 750°C.



a *b*

c *d*

Fig. 2. SEM (a), TEM (b,c) and HRTEM (d) images of NbSe2 nanosheets.

As it is shown in Fig. 2a, it is evident that the NbSe2 particles are dispersed nanoplates with diameters of about 1μm and the thickness of only 100-200nm. From Fig. 2b and c, they show that NbSe2 nanoplates are assembled with a few multiple sheets which clearly show the hexagonal structure. Obviously, the results were in accordance with the SEM observation. Furthermore, according to the high resolution TEM image (Fig. 2d), it is observed that the lattice spacing paralleled to the nanosheet edge is 0.64nm, corresponding to the [002] lattice planes of NbSe2 single crystals [20]. The inserted the selected area electron diffraction (SAED) pattern in Fig. 1d further indicates the single crystalline nature of the hexagonal nanosheets.

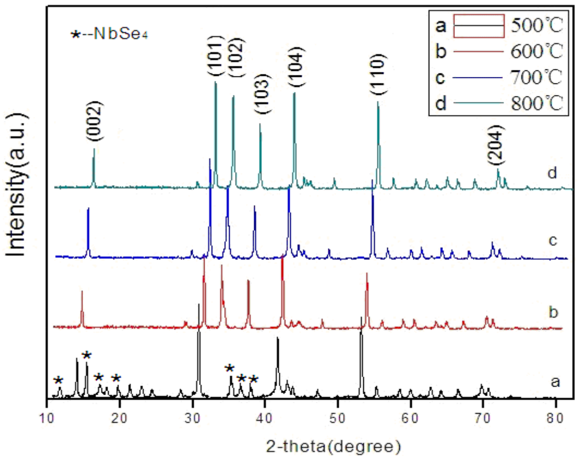


Fig. 3. XRD patterns of the products obtained at different reaction temperatures

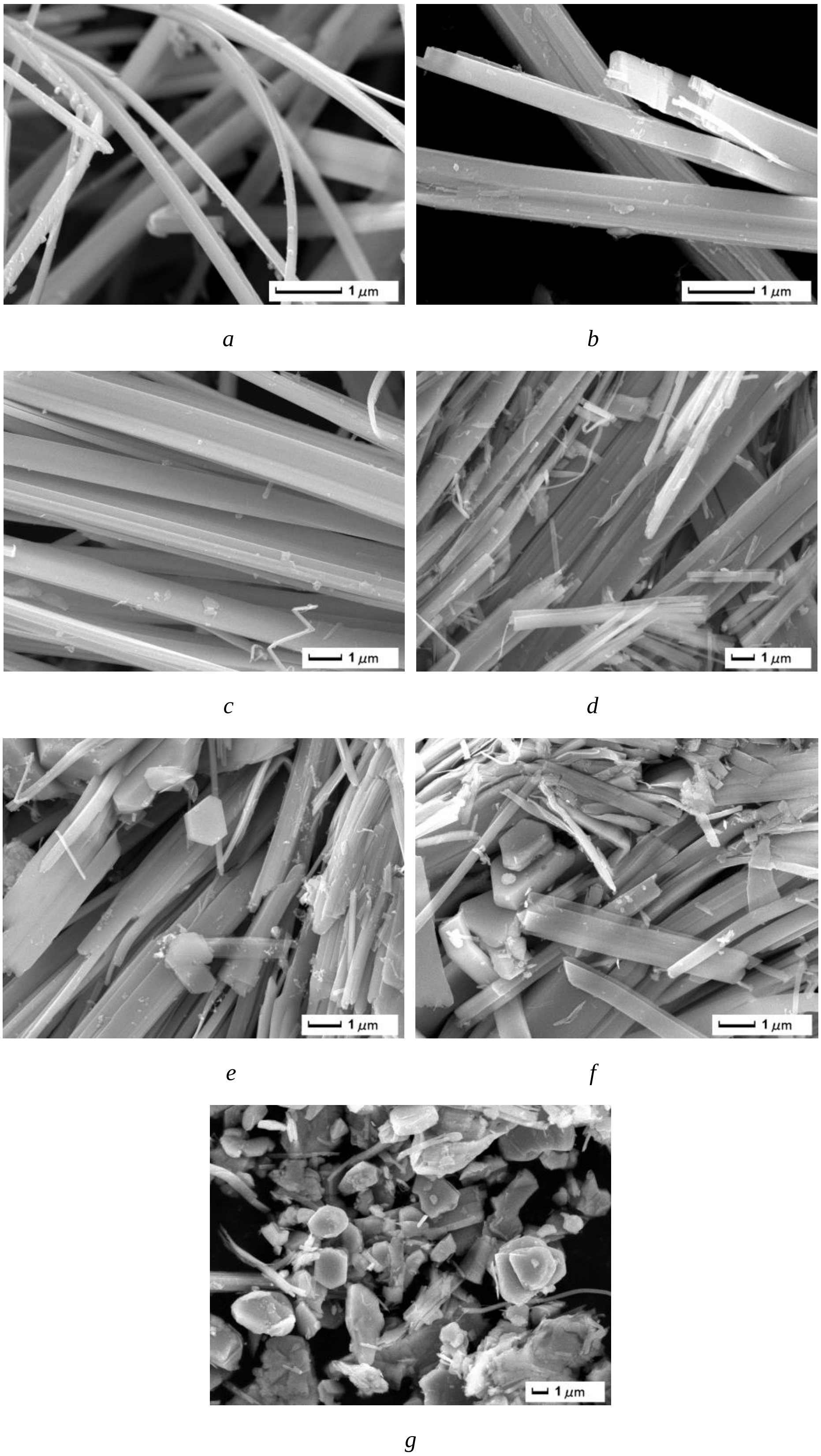
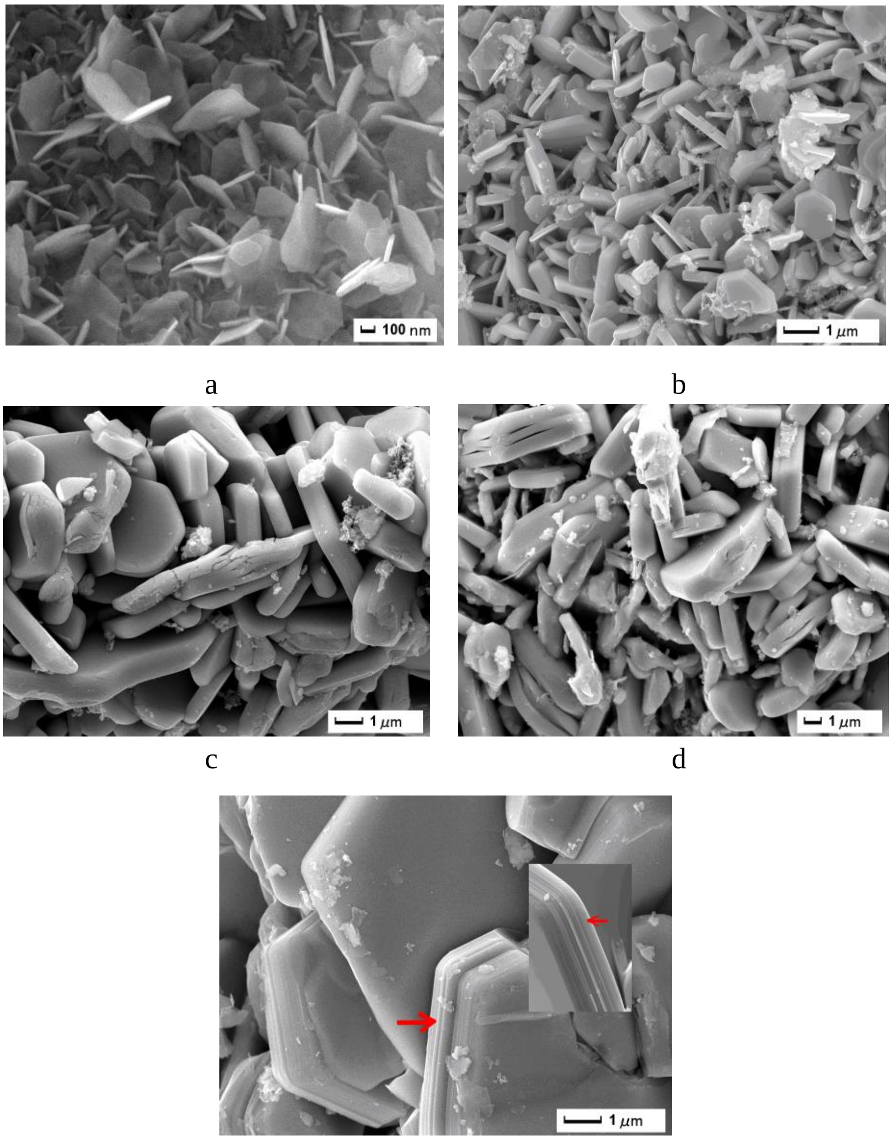


Fig. 4. SEM images of NbSe2 obtained under temperatures and duration time
(a: 500°C,1h; b:500°C,2h; c: 600°C,1h; d:600°C,2h; e: 650°C,1h; f:650°C,2h; g:700°C,2h.)

In order to understand the formation mechanism of these nanoplates, the structures and morphologies of intermediate materials have been investigated under certain temperatures for different reaction hours. The XRD results and SEM images of the as-prepared samples were shown in Figs. 3 and 4, respectively. Combined with the XRD and SEM results, the obtained products were mainly composed of a great amount of NbSe4 (Fig. 3) nanoroads with the average diameter about 100 nm at the temperature of 500°C for 1 h(Fig. 4a). The nanoroads with the diameter of 100-500nm were appeared at 500°C heated for 2h (Fig. 4b). When the reaction temperature reached 600°C and stayed for 1h, the NbSe4 transformed to NbSe2 (Fig. 3) nanorods (Fig. 4c). By increasing the reaction time to 2h at 600°C, microrods were forming nanobelts widths of 2-3μm (Fig. 4d). When it comes to 650°C for 1h, part of nanobelts transformed to nanosheets (Fig. 4e) with only 1 hour. Moreover, the lengths of the nanobelts were decreased and the thickness were increased when heated to 2 h. Additionally, the sizes of nanosheets were also increased (Fig. 4f). Particularly, with the temperature of 700°C for 2h, the nanorods gradually disappeared and transformed into nanosheets (Fig. 4g).



a b

c d

e

Fig. 5. SEM images of NbSe2 obtaine dunder temperatures and duration time (a:750°C,0.5h; b:750°C,1h; c:800°C,2h d: 850°C,2h and e:900°C,2h).

To futher obtain a better understanding of the self-assembly growth mechanism of the hexagonal nanoplates, we collected samples annealed at higher temperatures for SEM investigation. When the reaction time was controlled to 0.5 h at 750°C (Fig. 5a), it is evident that the NbSe2 particles are dispersed ultrathin nanosheets with diameters of about 200-500nm and the thickness of only about 10nm, indicating that the nanosheets are very suitable for the self-assembly of ordered nanostructures. But the diameter of NbSe2 nanosheets changed to 500–800nm at 750°C for 1h (Fig. 5b). As noted in Fig. 2a, it is heated for 2h, so the size and thickness increased slightly. Obviously, there is a solid-state transformation from the nanosheets into the hexagonal nanoplates during annealing.

When the temperature rised to 800°C and 850°C for 2h, the thickness and the size of the nanoplates were changed obviously (Fig. 5c and 5d). Up to 900°C, it shows the details of individual plates in Fig.5e, which demonstrated that well-defined hexagonal NbSe2 nanoplates with smooth surface were constructed from the ultrathin nanosheets via the Ostwald ripening process [21,22]. From the observation made above, it is clear that the morphology of the obtained samples were affected by the reaction temperature and time.

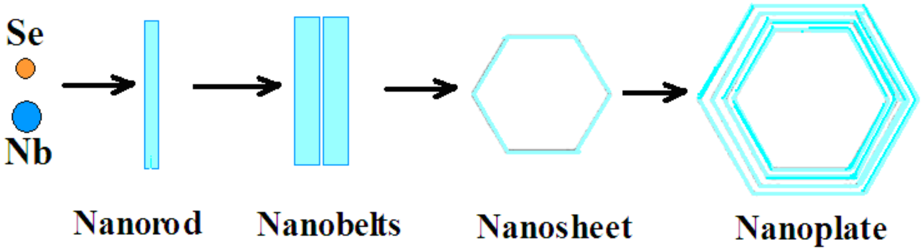


Fig. 6. Schematic illustration of the formation process to obtain hexagonal NbSe2 nanoplates.

Based on the above experimental results, it can be concluded that the formation process of NbSe2 nanoplates undergoes four stages of morphological evolution, schematically illustrated in Fig. 6. In the first stage, the NbSe4 nanorods began to form between the melted Se and Nb particles at 500°C. In the second stage, the NbSe4 nanorods gradually transformed to NbSe2 nanbelts with increasing temperature to 600°C. The reaction can be formulated as:

$$\mathrm{Nb} + 4\mathrm{Se} \xrightarrow{500^{0}\,\mathrm{C}} \mathrm{NbSe4} \qquad (1)$$

$$\mathrm{NbSe4} + \mathrm{Nb} \xrightarrow{600^{0}\,\mathrm{C}} 2\mathrm{NbSe2} \qquad (2)$$

In the third stage, the ultrathin hexagonal nanosheets were obtioned when the temperature was up to 750°C. In the final stage, the nanosheets aggregated to form the final hexagonal nanoplates through stacking along the c-axis for the minimization of surface energy with higher and higher temperatures.

4. Conclusions

In summary, the regular NbSe2 nanoplates with hexagonal morphology have been successfully prepared by a single-step, straightforward, and environmentally friendly solid-state reaction without any additives. The possible reaction process and growth mechanism were discussed with the assistance of temperature experiments. Obviously, the reaction temperature plays a crucial role in the formation of NbSe2 nanoplates. It is our hope that this efficient and simple solid phase synthetic route can be used on growing uniform and excellent crystalline during the growing process for the preparation of other nanomaterials.

Acknowledgements

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