Synthesis and tribological properties of hexagonal $NbSe_2$ nanoplates

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Published in Micro & Nano Letters; Received on 20th December 2012; Accepted on 4th April 2013

Hexagonal $NbSe_2$ nanoplates have been successfully prepared via solid-state reaction by a ball-milled mixture of Nb and Se powders. The as-prepared products are characterised by an X-ray diffractometer, scanning electron microscopy and transmission electron microscopy. The results showed that the $NbSe_2$ nanoplates have a hexagonal structure and the sizes of nanoplates are about 1 μm in diameter and 100–300 nm in thickness. The tribological properties of hexagonal $NbSe_2$ nanoplates as a lubrication additive in paraffin base oil were investigated by a UMT-2 ball-on-plate friction and wear tester. The wear scars were measured by a VEECO WYKO NT1100 non-contact optical profile testing instrument. The study shows that under determinate conditions, the friction coefficient of the base oil containing $NbSe_2$ nanoplates is lower than that of pure base oil, and it decreases with the increase of mass percent of $NbSe_2$ powders when its proportion is lower than 2 wt%.

1. Introduction: In recent years, much interest has been focused on the synthesis of transition metal dichalcogenides MQ_2 (M: Mo, W, Nb; Q: S, Se) nanomaterials because of their unique structure and superior properties. It is well known that transition metal dichalcogenides have a sandwich interlayer structure formed by stacking of the Q–M–Q layers [1, 2]. These layers are loosely bound to each other only by Van der Waals forces and easily cleaved. Owing to this unique structure, laminar MQ_2 has numerous applications such as superior solid lubricants [3], electron devices [4], catalysts [5], hydrogen storage bodies [6], super shock absorbers [7] and photosensitive film [8]. Particularly in the field of lubrication, ultralow-friction properties have been observed when MQ_2 materials were used as lubricants, which made them become one of the focuses of research.

Recently, MQ_2 nanomaterials have attracted considerable attention and have been synthesised by a great diversity of methods, for instance, gas-phase reactions, laser ablation, sonochemical process, hydrothermal synthesis, thermal decomposition and solid-state reaction [9–14]. Many research results indicated that transition metal dichalcogenides materials can provide excellent load-carrying capacity and good anti-wear and friction-reducing properties as lubricant additives [15, 16]. For example, Joly-Pottuz *et al.* [17] confirmed that WS_2 nanoparticles as additives in base oil significantly enhanced the anti-wear and friction reducing ability of base oil. Yang *et al.* [18] investigated the tribological properties of WSe_2 nanorods as additives in HVI500 base oil and demonstrated that the friction coefficient of the base oil containing WSe_2 nanorods was lower than that of the base oil, and decreased with increasing mass fraction of WSe_2 nanorods when the concentration of WSe_2 was lower than 7 wt%. In our previous research [19, 20], $NbSe_3$ and $NbSe_2$ nanofibres exhibited excellent tribological behaviour as a lubricant additive. It was found that the addition of the $NbSe_2$ and $NbSe_3$ fibres significantly decreased the friction coefficient of basic oil (HIV1500) in the range of experimental conditions, which indicates their excellent tribological properties. However, compared with sulphides, researches about the tribological properties of MSe_2 (M = Nb, Mo, W etc.) have rarely been reported. Herein, we report on the shape-selective synthesis of hexagonal $NbSe_2$ nanoplates by a facile solid-state reaction. The products were characterised by an X-ray diffractometer (XRD), an energy-dispersive X-ray spectrometer (EDS) and scanning electron microscopy (SEM). Moreover, the tribological properties of $NbSe_2$ nanoplates as additives in paraffin base oil were also investigated.

2. Experimental: Elemental selenium and molybdenum powders were purchased from SCRC Chemical Co., Shanghai, and used as received. In a typical preparation, a mixture of 2 g Nb and 3 g Se was energetically ball-milled at 400 rpm (rotation per minute) in the presence of ethanol for 10 h in a planetary ball mill. Then the ball-milled mixture was introduced into a 10 ml stainless steel reactor in a nitrogen-filled glove box. The filled reactor is tightly closed with the threaded plug and pushed into the tube furnace. The temperature of the tube furnace is raised to 750°C at a rate of 10°C/min and maintained at 750°C for 2 h. The closed reactor heated at 750°C is gradually cooled to room temperature and a black powder is obtained.

Different mass fractions of the as-prepared $NbSe_2$ powder were dispersed in paraffin base oil via 2 h ultrasonication without any active reagent, and then a series of suspended oil samples were obtained. The tribological properties of the base oil containing $NbSe_2$ nanoplates were evaluated on a UMT-2 ball-on-plate friction and wear tester. The testing of friction reduction and wear resistance was conducted at rotating speed of 100–500 rpm and load of 10–100 N for 30 min. The material of the upper sample is a 440C stainless steel ball with a diameter of 10 mm, hardness of 62 HRC and the counterpart is a 45 steel disc of Φ40 mm × 3 mm in size.

The X-ray diffraction patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu Kα radiation ($\lambda = 0.1546$ nm). The morphologies and structures of the samples were characterised by SEM (JEOL JXA-840A) and transmission electron microscopy (TEM) with a Japan JEM-100CX II TEM. The wear scars were measured by a VEECO WYKO NT1100 non-contact optical profile testing instrument.

3. Results and discussion: The crystalline structure and phase purity of $NbSe_2$ nanoplates were confirmed by XRD and EDS. As shown in Fig. 1*a*, all observed diffraction peaks can be systematically indexed to those of the hexagonal phase of $NbSe_2$, which are in good agreement with the values of the standard card (JCPDS No. 65-7464). No peaks from other impurities were detected in the XRD pattern, indicating that the sample was highly pure. The EDS result is shown in Fig. 1*b*, which reveals that the nanoplates consist of element Nb and Se, no other element was observed. Furthermore, the quantitative energy dispersive X-ray analysis shows that the atom ratio between Nb and Se is about 1:1.98, which is close to 1:2 by the atomic ratio of $NbSe_2$.

Micro & Nano Letters, 2013, Vol. 8, Iss. 6, pp. 294–297
doi: 10.1049/mnl.2012.0958

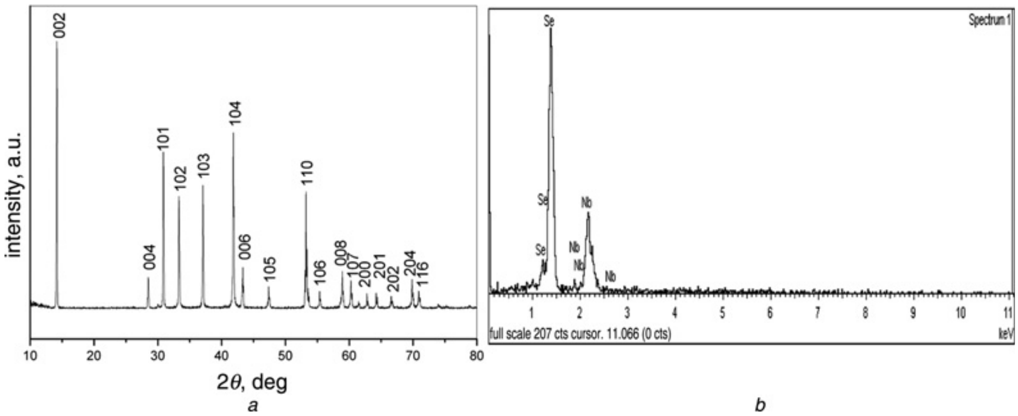

Figure 1 *XRD pattern and EDS of the as-prepared $NbSe_2$ nanoplates*
a XRD
b EDS

The size and morphology of $NbSe_2$ samples were identified by SEM and TEM. Figs. 2*a* and *b* show typical SEM images of the $NbSe_2$ nanoplates. The low magnification image in Fig. 2*a* shows that the samples consist of a large number of smooth hexagonal $NbSe_2$ sheets, indicating that high-yield and good uniformity of products could be readily achieved through this approach. From the magnified SEM images (Fig. 2*b*), it is clearly found that the sizes of the $NbSe_2$ nanoplates are about 1 μm in diameter and 100–300 nm in thickness. The morphology and structure of the as-synthesised $NbSe_2$ nanoplates were further characterised using TEM. Fig. 2*c* is a typical TEM image of $NbSe_2$ nanoplates, which clearly shows the hexagonal structure; the results were consistent with the above SEM results. The inserted selected area electron diffraction pattern in Fig. 2*c* further indicates the single crystalline nature of the hexagonal flake.

Fig. 3 shows the effect of paraffin basic oil and the base oil containing 2 wt% at different loads under a speed of 50 rpm for 1 h. It is observed that the friction coefficient of the base oil containing $NbSe_2$ nanoplates was lower than that of the base oil, and decreased with increasing mass fraction of the additives. Especially, the base oil with 2% $NbSe_2$ nanoplates have lower friction coefficient compared with other mass fraction of the additives. The lubrication of $NbSe_2$ as oil additive is mainly dependent on the formation of tribofilm in the friction process. However, a continuous tribofilm only begins to be formed under an optimal concentration. For the lower concentrations (<0.5 wt%), the formed tribofilm is incomplete, and can be easily damaged under high normal loads, and result in a drastic increase of the friction coefficient. Fig. 4 shows the friction coefficient as a function of concentration of the $NbSe_2$ nanoplates from 0.5 to 2 wt% at 50 N load under diverse speeds for 1 h. The friction coefficient of the paraffin basic oil containing $NbSe_2$ nanoplates is lower and more stable than that of basic oil at rotating speed. At a lower sliding velocity, the friction coefficient decreased as the sliding velocity increased. This can be attributed to the fact that with the increase of sliding velocity, the shear stress increased, which is beneficial for the formation of tribofilm. Hence, a decreased friction coefficient was reached. Nevertheless,

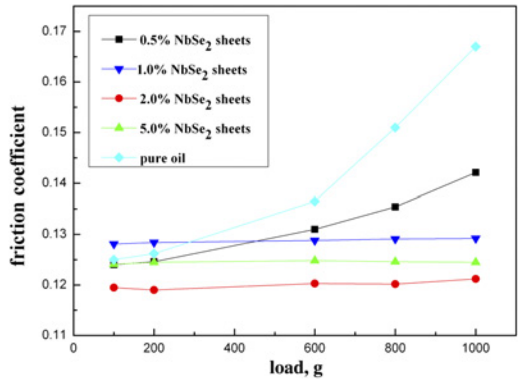

Figure 3 *Variations of friction coefficient of lubricant with increasing load for the paraffin base oil and the paraffin base oil containing 0.5, 1, 2 and 5 wt% at 50 rpm for 1 h*

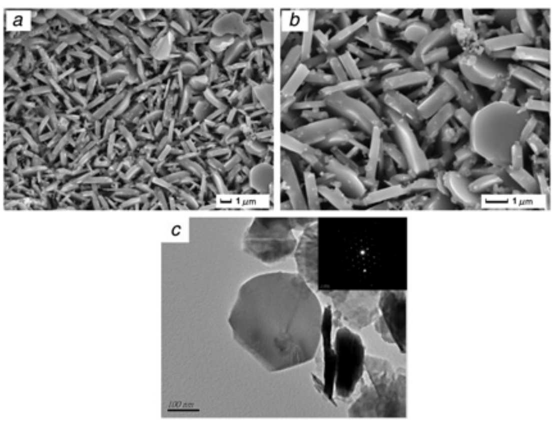

Figure 2 *SEM and TEM images of the as-prepared $NbSe_2$ nanoplates*
a, *b* SEM
c TEM

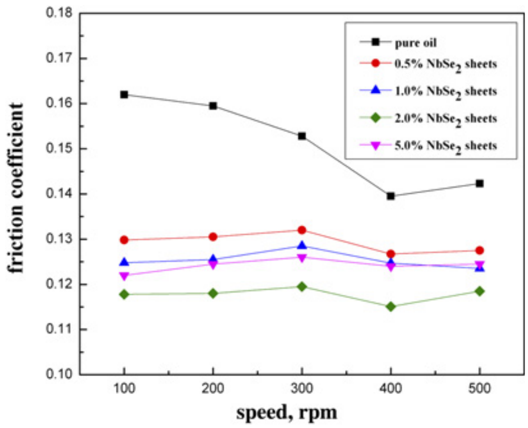

Figure 4 *Curves of friction coefficient against rotational speed for the paraffin base oil and the paraffin base oil containing 0.5, 1, 2 and 5 wt% under 10 N load for 1 h*

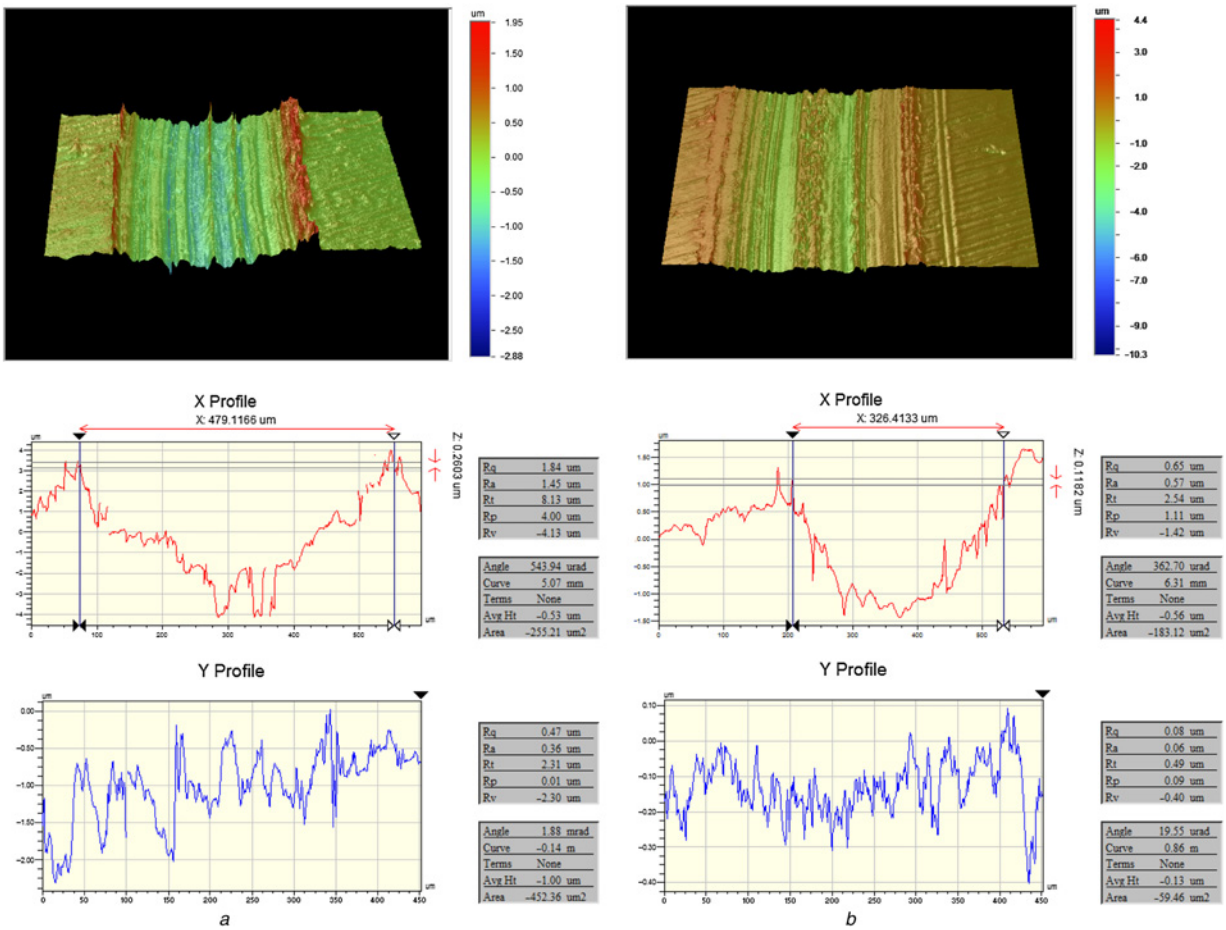

Figure 5 *Non-contact optical profile testing instrument images of wear scar at 50 rpm under 10 N loads for 1 h*
a Pure base oil
b 5 wt% $NbSe_2$ nanoplates + base oil

the friction coefficients slightly increase with a further increase in the sliding velocity at a higher sliding velocity. We believe that the increase of friction coefficients may be related to the following factors. On the one hand, the shear stress increased with increase of the sliding velocity. On the other hand, the higher velocity surely provokes an increase in the contact temperature, which causes reduction of lubricant oil viscosity. Therefore the increase of shear stress and decrease of lubricant oil viscosity cause reduction of tribofilm thickness, which leads to the increase of friction coefficient.

To determine the wear resistance properties of $NbSe_2$ nanoplates, a VEECO WYKO NT1100 non-contact optical profile testing instrument was used to measure the grinding track. The three-dimensional interactive display images show the wear scar at 50 rpm under 10 N loads for 1 h. Obviously, the grinding track for the base oil is composed of wide grooves and irregular pits along the sliding direction (Fig. 5*a*). It can be seen from Fig. 5*b* that the depth and width of wear scar caused by the base oil with 5.0 wt% $NbSe_2$ nanoplates are about 1.0 and 200 µm. It demonstrates that the base oil with 5.0 wt% $NbSe_2$ nanoplates represented better anti-wear capability than paraffin base oil. In addition, the topography of the worn scar lubricated by $NbSe_2$ nanoplates was investigated using a common optical microscope, as shown in Fig. 6. The SEM image also shows that the rubbed surface lubricated by the base oil had lots of wide and deep furrows; this result was concordant with the above results of the non-contact optical profile test. It is well known that the morphology of materials have a certain influence on its tribological properties. This result might be caused by $NbSe_2$ nanoplates. The $NbSe_2$ sheets will more easily penetrate into the interface with base oil and form a continuous film in the concave of the rubbing face, which can decrease shearing stress, and therefore give a low wear [21].

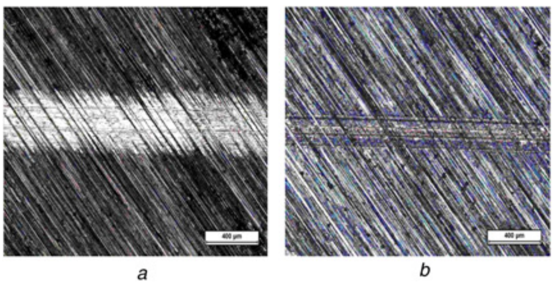

Figure 6 *Wear scar of plate*
a Paraffin base oil
b Paraffin base oil with 5.0 wt% $NbSe_2$ nanoplates

4. Conclusion: $NbSe_2$ nanoplates of 1 µm in diameter and 100–300 nm in thickness were successfully prepared via solid-state reaction by a ball-milled mixture of Nb and Se powders. The paraffin base oil with the addition of $NbSe_2$ nanoplates showed the best friction-and-wear properties. The introduction of $NbSe_2$ nanoplates was able to improve the tribological properties of base oil as lubrication additives, especially in terms of friction reduction and wear resistance. The base oil has a friction coefficient that decreases as the mass percentage of the $NbSe_2$ nanoplates additives increases. The excellent anti-wear and friction-reducing properties indicate that the as-prepared $NbSe_2$

doi: 10.1049/mnl.2012.0958

nanoplates will be useful for its further industrial application as a good oil additive in the future.

5. Acknowledgments: This work was financially supported by the National Natural Science Foundation of China (grant number 51275213), the Jiangsu National Nature Science Foundation (grant number BK2011534), the Open Project of Key Laboratory of Tribology of Jiangsu Province (grant numbers Kjsmcx2011002 and Kjsmcx1005) and the Senior Intellectuals Fund of Jiangsu University (grant number 09JDG009).

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