



ELSEVIER

Contents lists available at [ScienceDirect](http://ScienceDirect.com)

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Synthesis of MoS₂ nanoparticles using MoO₃ nanobelts as precursor via a PVP-assisted hydrothermal method

Xianzhong Zeng^{a,b,c}, Wei Qin^{a,b,*}^a Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research (YIC), Chinese Academy of Sciences (CAS), Yantai, Shandong, 264003, PR China^b Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong, 264003, PR China^c University of Chinese Academy of Sciences, Beijing, 100039, PR China

ARTICLE INFO

Article history:

Received 27 May 2016

Received in revised form

3 July 2016

Accepted 6 July 2016

Available online 6 July 2016

Keywords:

MoS₂

Nanoparticles

MoO₃ nanobelts

Surfactant assistance

Semiconductors

ABSTRACT

The synthesis of MoS₂ nanoparticles from MoO₃ with a certain morphology through a surfactant-assisted hydrothermal process is described in this paper. MoO₃, which has a nanobelt morphology with a width of 100–500 nm and a length from one to several micrometers, is used as the precursor, and poly(vinylpyrrolidone) (PVP) is used as the surfactant. The morphology of the resulting MoS₂ nanomaterial has been characterized by the field-emission scanning electron microscope, which shows that the obtained nanoparticles have diameters ranging from 50 to 100 nm with rough surfaces. Additionally, the composition and crystallinity as well as the phase information of the produced nanoparticles have been characterized by the energy-dispersive X-ray spectrometer and X-ray diffraction. Specifically, in this process, the presence of PVP plays a crucial role for the successful fabrication of the nanoparticle morphology, which may be due to the formation of PVP micelles leading to an oriented aggregation of MoS₂ nuclei. In addition, comparative experiments have been conducted and the possible reaction mechanism is proposed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

As a typical layered transition metal dichalcogenide, molybdenum disulfide (MoS₂) materials have received much attention due to their potential applications in transistors of electronics [1], catalysts for hydrodesulfurization [2] and hydrogen evolution [3], candidates for hydrogen storage [4], tribological lubricant [5] and optical response [6], as well as electrode components for supercapacitors [7] and lithium batteries [8]. Meanwhile, MoS₂ nanomaterials with various morphologies such as open-ended nanotubes [9], hollow nanospheres [2], flower-like microspheres [10], nanorods [11] and nanoparticles [12] have been reported. Among various morphologies, MoS₂ nanoparticles are promising due to their distinct physicochemical properties different from bulk materials. It has been found that MoS₂ nanoparticles show excellent shock-absorbing performance under a very high shock wave pressure [13] and ultra-low friction and wear [14]. In addition, MoS₂ nanoparticles exhibit enhanced catalytic [3], electronic [15] as well as optical [12] properties. As a result, it is essential to synthesize MoS₂ with a nanoparticle morphology in a controlled manner.

Nowadays, different strategies for the synthesis of MoS₂ nanoparticles have been explored. Zak et al. synthesized fullerene-like MoS₂ nanoparticles from MoO₃ powder via reaction with N₂, H₂, and H₂S gases at 850 °C [16]. Etzkorn et al. prepared the MoS₂ nanoparticles via a metal-organic chemical vapor deposition approach using Mo(CO)₆ and sulfur as initial materials with a homemade device [17]. Song et al. obtained the MoS₂ nanoparticles by employing a millisecond pulsed Nd: YAG laser to ablate a piece of Mo target in a dimethyl trisulfide atmosphere [6]. However, these aforementioned methods suffer from problems of high temperatures, complicated procedures and harsh conditions, which may largely restrict their wide applications. Therefore, it is highly desired to develop a new strategy for a mild, facile and cost-effective synthesis of MoS₂ nanoparticles.

In this paper, a novel wet chemistry approach for the synthesis of MoS₂ nanoparticles is described. MoO₃ with a certain morphology is used as the precursor and poly(vinylpyrrolidone) (PVP) is employed as the surfactant to produce MoS₂ nanoparticles through a facile hydrothermal process. To get the nanoparticle morphology, the presence of surfactant PVP is proved to be important and the possible mechanism has been discussed. The proposed method is promising for controllable synthesis of MoS₂ nanoparticles via a facile, mild and cost-effective process.

* Corresponding author.

E-mail address: wqin@yic.ac.cn (W. Qin).

2. Experimental

In this experiment, all the chemical reagents were analytical grade and used directly without further purification. The MoS₂ nanoparticles were synthesized via two hydrothermal processes including the preparation of MoO₃ nanobelts and the subsequent transformation of MoO₃ nanobelts to MoS₂ nanoparticles. The MoO₃ nanobelts were prepared according to the previous report [18] with some modifications. Briefly, 3.3604 g Na₂MoO₄ · 2H₂O was dissolved in 70 mL of distilled water to make a precursor solution, and then 4 M nitric acid solution was added to acidify the initial solution to a pH of 1. The resulting solution was transferred into a 100 mL of Teflon-lined stainless steel autoclave and was treated at 180 °C for 24 h. The resultant white products were collected via centrifugation and were washed with distilled water. Eventually, the obtained MoO₃ nanomaterials were dispersed in water solution for further experiments.

For synthesis of MoS₂ nanoparticles, 25 mg PVP was added into 30 mL of the water solution which contains 25 mg of the MoO₃ nanobelts. The mixture was stirred for 10 min to obtain a uniform suspension. Then, 50.67 mg of NaSCN was added. After vigorous stirring for another 10 min, the resulting mixture was transferred into a 50 mL of Teflon-lined stainless steel autoclave, and heated at 180 °C for 24 h. The obtained black product was centrifuged and washed thoroughly with water and ethanol, respectively. Finally, the collected product was dried at 80 °C for 12 h under a vacuum.

To analyze the composition and phase purity of the as-synthesized samples, the X-ray diffraction (XRD) measurements were done by using a Shimadzu XRD-7000 X-ray diffractometer, operating at 40 kV and 50 mA with Cu K α radiation at a scanning rate of 2°/min. The general size and morphology of the obtained materials were characterized by a field-emission scanning electron microscope (FESEM, Hitachi, S-4800), which was coupled with an energy-dispersive X-ray spectrometer (EDS, HORIBA, EX-350).

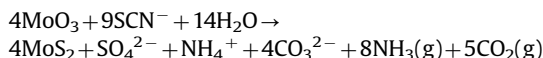
3. Results and discussion

The XRD and EDS data show the crystallinity and phase characteristics of the synthesized nanoparticles. Fig. 1a indicates the representative XRD pattern of the produced MoS₂ nanoparticles. All the diffraction peaks in the XRD pattern can be readily matched with a pure hexagonal MoS₂ phase (JCPDS NO. 37-1492). The pronounced diffraction peaks at 2 theta values of 14.38, 32.68, 39.54 and 58.33 are attributed to (002), (100), (103) and (110) reflections, respectively. Notably, any other characteristic peaks are

not observed, indicating a high purity of the as-synthesized nanoparticles. Additionally, the broadness of diffraction peaks can be observed probably due to the small size of the crystallites [10,19]. The EDS results shown in Fig. 1b confirm that the nanoparticles are mainly composed by the elements of Mo and S. The molar ratio was calculated to be 1:2 corresponding well with the stoichiometry of MoS₂, which is consistent with the XRD result. The presence of C and O elements could be due to the residual PVP on the surface of the MoS₂ nanoparticles.

The morphologies and sizes of the synthesized MoO₃ precursor and MoS₂ nanoparticles were characterized by FESEM and the results are shown in Fig. 2. An overall view of the morphology of the produced MoO₃ nanomaterials shown in Fig. 2a illustrates that the products are composed by isolated nanobelts with a length of one to several micrometers. Fig. 2b shows a high resolution image of MoO₃ nanobelts. It can be seen that each nanobelt has a smooth surface with an average width of 100–500 nm. A panoramic picture of the as-prepared MoS₂ is exhibited in Fig. 2c. Nanoparticles with a diameter of 50–100 nm are observed. Notably, some particles seem to be aggregated but still have distinct boundaries. A higher magnification of FESEM image (Fig. 2d) shows a rough surface of each MoS₂ nanoparticle. This may be attributed to the stacking of the single MoS₂ layer, which is reasonable in good agreement with the high density of the (002) diffraction peak in XRD [20,21].

According to the previous report [22], MoO₃ could be converted to MoS₂ through the following reaction:



Experiments show that the MoS₂ product has a morphology of quasi-flower with thick layers in the absence of PVP. In addition, the presence of an acid could induce three-dimensional MoS₂ nanoflowers with thin layers [23]. The corresponding FESEM images are shown in Fig. 3a and b, respectively. These results verify that the presence of PVP is crucial for the synthesis of MoS₂ nanoparticles. A surfactant-induced reaction mechanism is illustrated in Fig. 3c for the synthesis of MoS₂ nanoparticles from MoO₃ nanobelts in the presence of the PVP. With the addition of SCN⁻, the MoS₂ nuclei can be formed at the surface of the MoO₃ nanobelts and released into the solution because of the anisotropy between them. The MoS₂ nuclei are further grown by an oriented growth to produce nanosheets, and the quasi-flowers with thick layers can be self-assembled. However, in the presence of the hydrochloride acid, the three-dimensional MoS₂ nanoflowers with thin layers are formed. This is probably due to the fact that H⁺

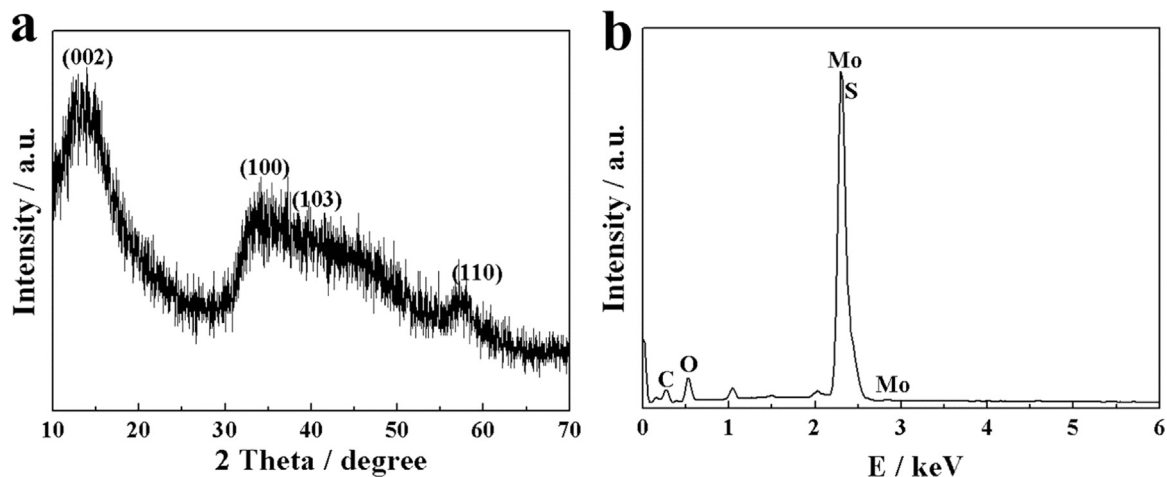


Fig. 1. (a) XRD and (b) EDS patterns of the as-synthesized MoS₂ nanoparticles.

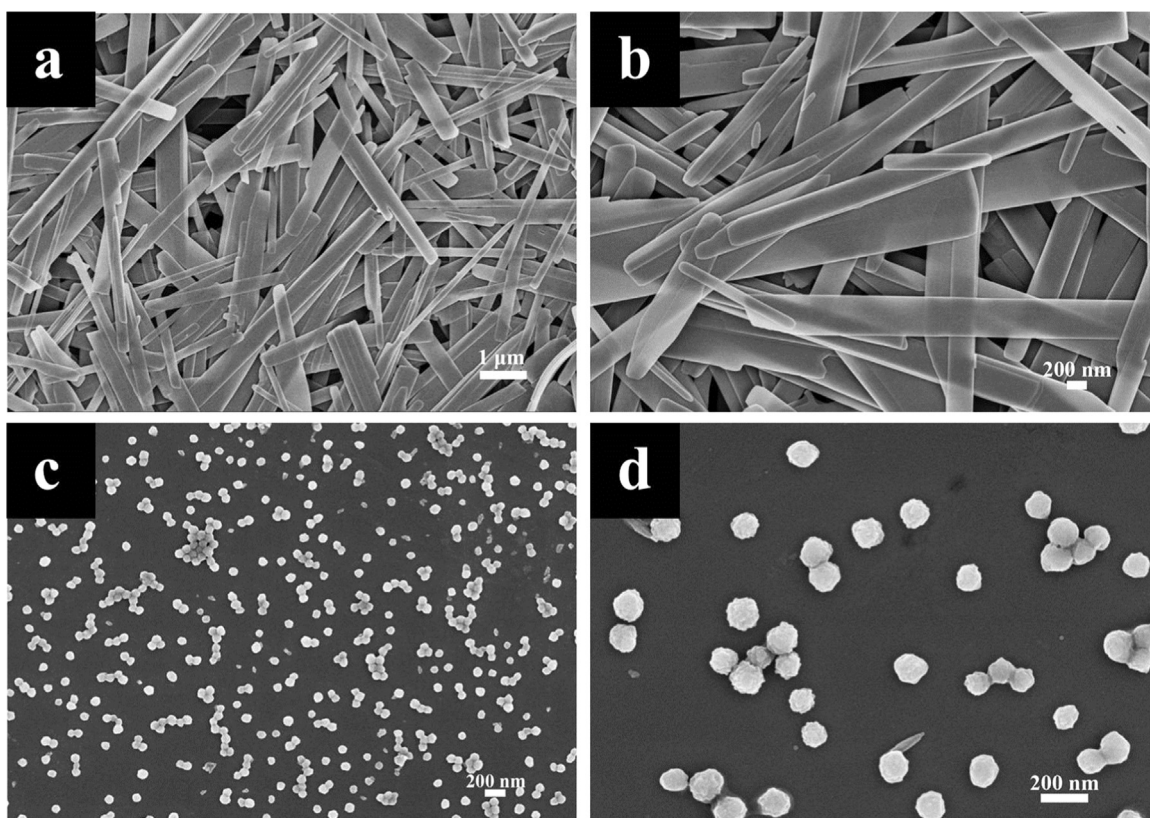


Fig. 2. FESEM images of the obtained MoO_3 nanobelts (a, b) and MoS_2 nanoparticles (c, d).

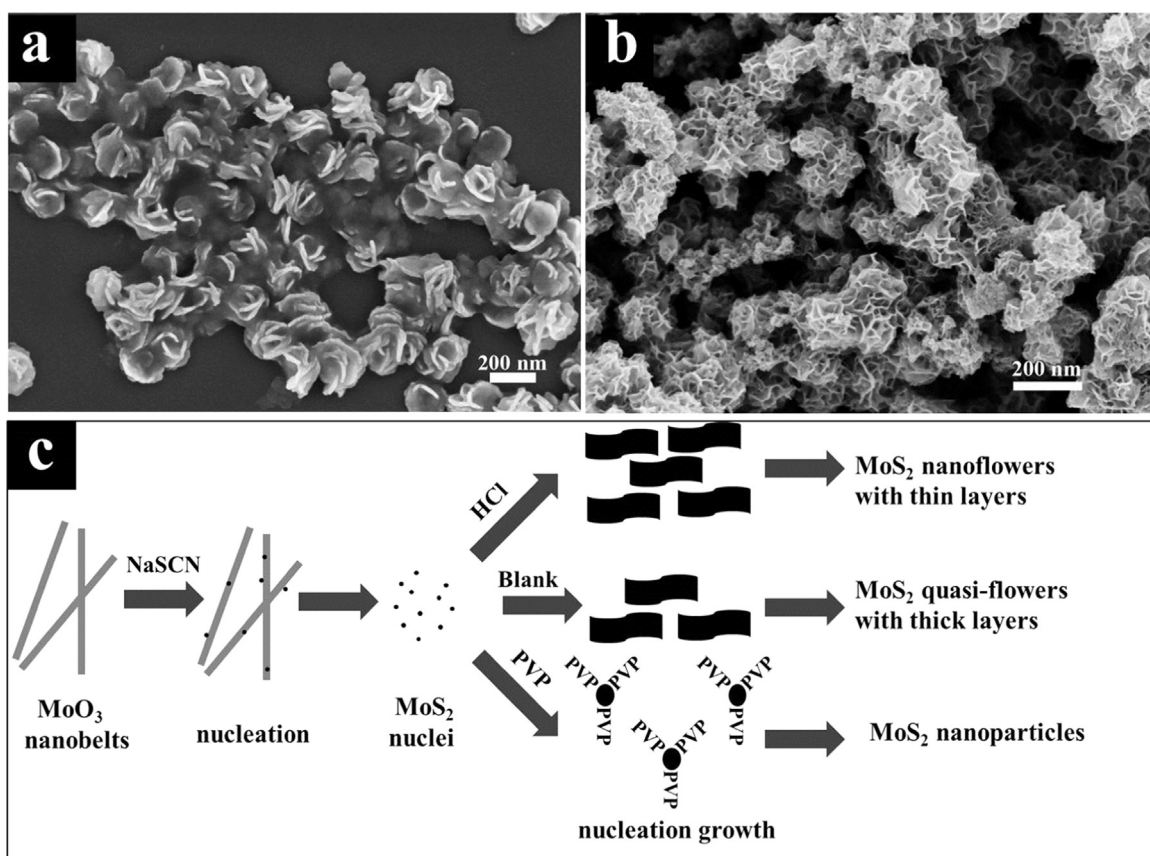


Fig. 3. FESEM images of the produced MoS_2 from MoO_3 nanobelts through different processes: (a) direct reaction to NaSCN; (b) further addition of HCl. (c) Schematic illustration of the mechanisms for the formations of MoS_2 with different morphologies.

with small diameters can access into the layered structures of the MoS₂ nanosheets, thus leading to the exfoliation of MoS₂ [24,25]. Interestingly, when PVP was added, PVP as a nonionic surfactant could induce micelles in the solution, thus preventing the further nucleation growth to nanosheets. In this case, the nanoparticles are produced through the oriented aggregation to reduce surface activities of the MoS₂ nuclei [26].

4. Conclusions

We have demonstrated a novel method for preparation of MoS₂ nanoparticles using MoO₃ nanobelts as the precursor via a surfactant-assisted hydrothermal process. The obtained MoS₂ nanoparticles are single-crystallines having a hexagonal phase structure with a diameter ranging from 50 to 100 nm. The possible mechanism of this process is proposed. The present method allows the controllable synthesis of MoS₂ nanoparticles in a facile, mild and cost-effective way.

Acknowledgments

This work was financially supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA11020702), the National Natural Science Foundation of China (21475148), and the Taishan Scholar Program of Shandong Province (TS20081159).

References

- [1] B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, *Nat. Nanotechnol.* 6 (2011) 147–150.
- [2] A.N. Dhas, K.S. Suslick, *J. Am. Chem. Soc.* 127 (2005) 2368–2369.
- [3] Y.G. Li, H.L. Wang, L.M. Xie, Y.Y. Liang, G.S. Hong, H.J. Dai, *J. Am. Chem. Soc.* 133 (2011) 7296–7299.
- [4] J. Chen, N. Kuriyama, H.T. Yuan, H.T. Takeshita, T. Sakai, *J. Am. Chem. Soc.* 123 (2001) 11813–11814.
- [5] R. Rosentsveig, A. Margolin, A. Gorodnev, R. Popovitz-Biro, Y. Feldman, L. Rapoport, et al., *J. Mater. Chem.* 19 (2009) 4368–4374.
- [6] S.T. Song, L. Cui, J. Yang, X.W. Du, *ACS Appl. Mater. Interfaces* 7 (2015) 1949–1954.
- [7] M. Acerce, D. Voiry, M. Chhowalla, *Nat. Nanotechnol.* 10 (2015) 313–318.
- [8] T. Stephenson, Z. Li, B. Olsen, D. Mitlin, *Energy Environ. Sci.* 7 (2014) 209–231.
- [9] J. Chen, S.L. Li, Q. Xu, K. Tanaka, *Chem. Commun.* 16 (2002) 1722–1723.
- [10] X.H. Zhang, X.H. Huang, M.Q. Xue, X. Ye, W.N. Lei, H. Tang, et al., *Mater. Lett.* 148 (2015) 67–70.
- [11] H.T. Lin, X.Y. Chen, H.L. Li, M. Yang, Y.X. Qi, *Mater. Lett.* 64 (2010) 1748–1750.
- [12] L. Muscuso, S. Cravanzola, F. Cesano, D. Scarano, A. Zecchina, *J. Phys. Chem. C* 119 (2015) 3791–3801.
- [13] Y.Q. Zhu, T. Sekine, Y.H. Li, M.W. Fay, Y.M. Zhao, C.H.P. Poa, et al., *J. Am. Chem. Soc.* 127 (2005) 16263–16272.
- [14] M. Chhowalla, G.A.J. Amaratunga, *Nature* 407 (2000) 164–167.
- [15] T.S. Li, G. Gallii, *J. Phys. Chem. C* 111 (2007) 16192–16196.
- [16] A. Zak, Y. Feldman, V. Alperovich, R. Rosentsveig, R. Tenne, *J. Am. Chem. Soc.* 122 (2000) 11108–11116.
- [17] J. Etzkorn, H.A. Therese, F. Rucker, N. Zink, U. Kolb, W. Tremel, *Adv. Mater.* 17 (2005) 2372–2375.
- [18] X.W. Lou, H.C. Zeng, *Chem. Mater.* 14 (2002) 4781–4789.
- [19] X.F. Zhang, X.X. Song, S. Gao, Y.M. Xu, X.L. Cheng, H. Zhao, et al., *J. Mater. Chem. A* 1 (2013) 6858–6864.
- [20] G.G. Tang, Y.J. Wang, W. Chen, H. Tang, C.S. Li, *Mater. Lett.* 100 (2013) 15–18.
- [21] B.B. Sheng, J.S. Liu, Z.Q. Li, M.H. Wang, K.J. Zhu, J.H. Qiu, et al., *Mater. Lett.* 144 (2015) 153–156.
- [22] Y. Tian, Y. He, Y.F. Zhu, *Mater. Chem. Phys.* 87 (2004) 87–90.
- [23] X.Z. Zeng, S.Y. Yu, Q. Yuan, W. Qin, *Sens. Actuators B Chem.* 234 (2016) 80–83.
- [24] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M.W. Chen, M. Chhowalla, *Nano Lett.* 11 (2011) 5111–5116.
- [25] P. Joensen, R.F. Frindt, S.R. Morrison, *Mater. Res. Bull.* 21 (1986) 457–461.
- [26] C. Graf, D.L.J. Vossen, A. Imhof, A. Blaaderen, *Langmuir* 19 (2003) 6693–6700.