

Hydrothermal synthesis of amorphous MoS₂ nanofiber bundles via acidification of ammonium heptamolybdate tetrahydrate

G. Nagaraju · C. N. Tharamani · G. T. Chandrappa · J. Livage

Received: 16 March 2007 / Accepted: 10 August 2007 / Published online: 1 September 2007
© to the authors 2007

Abstract MoS₂ nanofiber bundles have been prepared by hydrothermal method using ammonium molybdate with sulfur source in acidic medium and maintained at 180 °C for several hours. The obtained black crystalline products are characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectrometer (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The PXRD pattern of the sample can be readily indexed as hexagonal 2H-MoS₂. FTIR spectrum of the MoS₂ shows the band at 480 cm⁻¹ corresponds to the $\nu_{as}(\text{Mo-S})$. SEM/TEM images of the samples exhibit that the MoS₂ nanofiber exist in bundles of 120–300 nm in diameter and 20–25 μm in length. The effects of temperature, duration and other experimental parameters on the morphology of the products are investigated.

Keywords Hydrothermal · Nanofiber bundles · MoS₂ · Citric acid

Introduction

Nowadays, one-dimensional nanostructural materials (nanorods, nanowires, nanobelts and nanotubes) have attracted heightened attention because of their potential applications in nanodevices and functional materials [1]. Continuous effort has been devoted to the investigation on the crystalline phases of the layered transition metal dichalcogenides, because of their unusual crystal structure and unique physical and chemical properties [2]. In analogy to graphite, nanoparticles of many inorganic compounds such as MoS₂, WS₂ are not stable against folding, and can adopt nanotubular and fullerene-like structures [3]. As transition metal sulfides, MoS₂ has been the subject of significant research for applications including nonaqueous lithium batteries, catalytic hydride sulfurization of petroleum and wear resistance. For each of these applications, the important processes occur either at the surface or at the exposed edges of the MoS₂ layers [1]. MoS₂ is a layered semiconductor (band gap = 1.2 eV, indirect) that resists oxidation even in moist air at temperatures up to 85 °C [4]. This attribute makes MoS₂ an attractive semiconductor material for nanoscience applications. Recent studies have suggested that reducing the size of the MoS₂ crystals can improve their lubrication properties in bearings, O-rings or other heavy—wear applications [5].

Inorganic syntheses using organic surfactants are successfully applied for the preparation of various nanostructural materials [6, 7]. The subsequent template elimination without destruction of the mesoporous texture remains a difficult step [8]. Various methods of preparation includes chemical vapor deposition, sol–gel processing, spray pyrolysis, co-precipitation, sonochemical synthesis, metathesis reactions, two step electrochemical synthesis etc are having been in practice [9–12]. Tenne and co-workers

G. Nagaraju · G. T. Chandrappa (✉)
Department of Chemistry, Central College Campus, Bangalore
University, Bangalore 560001, India
e-mail: gtchandrappa@yahoo.co.in

C. N. Tharamani
Department of Chemistry, University of Saskatchewan,
Saskatoon, Canada SK S7N 5C9

J. Livage
Laboratoire Chimie de la Matière Condensée, Université Pierre
et Marie Curie, 4 place Jussieu, Paris cedex 05 75252, France

[13, 14] first reported the production of fullerene-like MoS₂ nanotubes via the gas phase reaction between MoO_{3-x} and H₂S in a reducing atmosphere at elevated temperature (800–1000 °C). Rao and co-workers obtained MoS₂ nanotubes by simple heating MoS₃ in a stream of hydrogen under high temperature [15]. Zelenski et al. [16] synthesized fibers and tubules of MoS₂ by the thermal decomposition of ammonium thiomolybdate precursors at 450 °C. MoS₂ nanotubes [17] were made by subliming 2H–MoS₂ powder in presence of H₂S at 1300 °C. Recently MoS₂ nanorods [18] were synthesized using α -MoO₃ nanorods with a mixture of H₂S · H₂ (15 vol% of H₂S) for 4 h at several temperatures. However, almost all the methods to obtain MoS₂ nanotubes and nanorods utilize high temperature gas-solid reaction under reducing gas atmosphere. Yumei et al. [1, 19] synthesized MoS₂ nanorods and nanospheres by hydrothermal method using ammonium molybdate with Na₂S in presence of NH₂OH · HCl as oxidizing agent. Hydrothermal synthesis is becoming popular for environmental reason, since water is used as reaction solvent than organics. This method has been widely used to prepare nanostructures due to its simplicity, high efficiency and low cost.

In this article, as a part of our recent efforts on the investigation of 1-D materials [20], we report a simple low temperature hydrothermal method for preparation of MoS₂ nanofiber bundles with morphology control. We examined the effect of precursors (ammonium molybdate, sodium sulphide and citric acid) concentration, duration and the temperature on the morphology of the product. Finally, we discuss appropriate conditions for producing MoS₂ nanobundles.

Experimental section

Synthesis

The hydrothermal process was carried out like our previous report [21, 22] to prepare MoS₂ nanofiber bundles. In a typical synthesis of MoS₂ nanofibers, sodium sulfide and H₂S gas were used as sulfur sources in order to investigate the source effect on the morphology of the product.

In the first trail 1.235 g ammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄ · 4H₂O) was put into 25 mL distilled water under continuous stirring. After 10 min, 0.5 g citric acid monohydrate (C₆H₈O₇ · H₂O) was added to the above solution. To this solution mixture, 0.312 g sodium sulfide crystals were added. The initial greenish black color was changed to red after 1h stirring on a magnetic stirrer. In the subsequent trail, 0.5 g ammonium heptamolybdate tetrahydrate was put into 25 mL distilled water under continuous stirring. H₂S gas is passed in to the warmed acidified with dilute HCl solution for about 5–8 min.

The sealed 25 mL Teflon lined autoclaves containing above solution mixture were placed for hydrothermal treatment at 180 °C for several hours. The autoclaves were cooled and the resulted black solid was retrieved from the solution by centrifugation, washed with distilled water followed by ethanol to remove the ions possibly remaining in the end product, and finally dried in air.

Characterization

Powder X-ray diffraction data were recorded on Philips X'pert PRO X-ray diffractometer with graphite monochromatized Cu K α radiation ($\lambda = 1.541 \text{ \AA}$). The Fourier transform infrared spectrum of the samples was collected using Nicolet FTIR spectrometer. Scanning electron micrograph images were taken with JEOL (JSM—840 A) scanning electron microscope. X-ray photoelectron spectroscopy was carried out on an ESCA-3 Mark II X-ray photoelectron spectrometer, (VG Scientific, UK) using Al K α radiation (1486.6 eV) as the exciting source. The morphology of the samples was observed using (H-800EM Japan Hitachi) transmission electron microscope (TEM) equipped with EDS (Kevex Sigma TM Quasar, USA) to measure the elements contained in the samples.

Results and discussion

Figure 1a, b shows the PXRD patterns of the samples prepared using sodium sulfide and H₂S as sulfur sources in acidic medium at 180 °C for 48 and 24 h, respectively. It shows only a broad, weak envelope beginning at $2\theta = 30^\circ$ and continuing out above 60° , the two maxima approximately located at the *100* and *110* positions of bulk 2H–MoS₂ [23]. The PXRD patterns resemble that of the single-layer MoS₂ prepared by exfoliation method [24]. All the diffractions can be readily indexed as hexagonal 2H–MoS₂ [space group P6₃/mmc (194)] with lattice constants $a = 3.16116 \text{ \AA}$ and $c = 12.2985 \text{ \AA}$, identical to the reported data in the JCPDS cards (37–1492). At 180 °C only poor crystals were produced. The absence of the *002* diffraction at $2\theta = 14.4^\circ$ suggests that absence of stacking, thus the sample should be an aggregate of single sheets of MoS₂ [1, 8, 18, 23, 25].

Chemical analysis using EDS indicates the presence of Mo and S (elements of MoS₂), and no other elements existed as observed in Fig. 2. Furthermore, the quantification of the peaks shows that the atomic ratio of S to Mo is 1.92, which is very close to the stoichiometric MoS₂. From the IR spectrum (Fig. 3), it is observed that the band at 480 cm^{-1} corresponds to $\nu_{\text{as}}(\text{Mo-S})$. The bands above 600 cm^{-1} correspond to Mo–O vibrations and they indicate

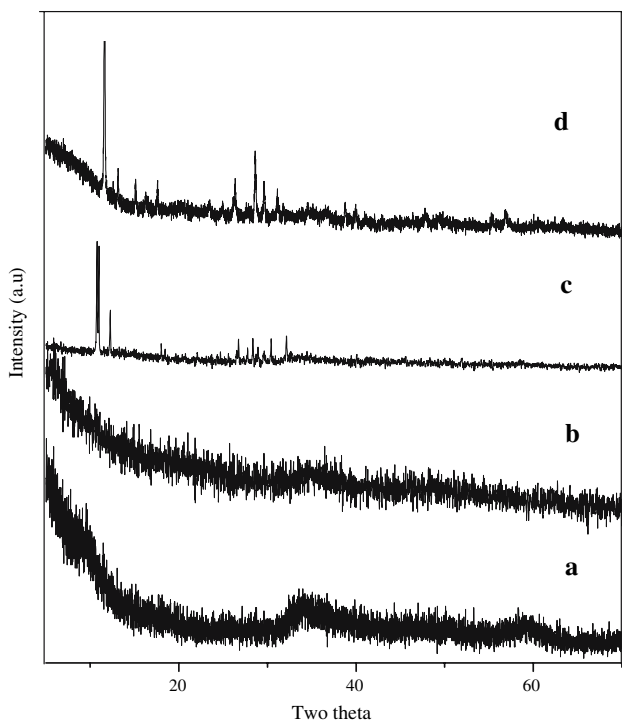


Fig. 1 Powder XRD pattern of MoS₂ nanofiber bundles prepared at (a) 180 °C for 48 h using Na₂S as sulfur source with 0.5 g citric acid. (b) 180 °C for 24 h using H₂S as sulfur source. (c) 180 °C for 48 h using Na₂S as sulfur source without citric acid. (d) 180 °C for 48 h using Na₂S as sulfur source with 1 g citric acid

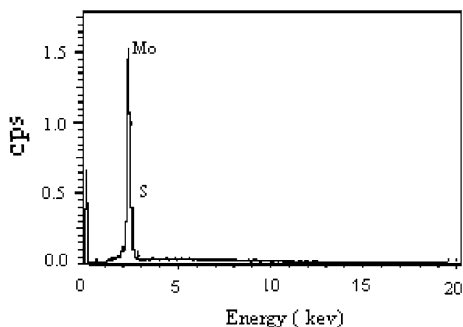


Fig. 2 EDS pattern of MoS₂ nanofiber bundles prepared at 180 °C for 48 h

that oxygen is present in similar types of coordination as in MoO₃. We assign the band at 941 cm⁻¹ to the $\gamma_{as}(\text{Mo-O})$ vibrations of terminal ($-\text{Mo}=\text{O}$) group and 693 cm⁻¹ to $\gamma(\text{Mo-O})$ vibrations. The frequency of the vibration is shifted to the lower wavenumber compare to its standard value in crystalline MoO₃, due to the presence of reduced Mo centers and sulfur as a ligand [26].

X-ray photoelectron spectra of Mo(3d) and S(2p) core level regions of as-prepared nanoparticles are shown in Fig. 4a and b and the values are tabulated in Table 1. Mo(3d) peaks in as-prepared nanoparticles were deconvoluted into

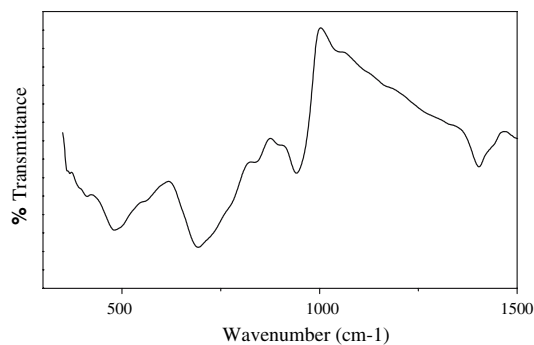


Fig. 3 FTIR spectrum of MoS₂ nanofiber bundles prepared at 180 °C for 48 h

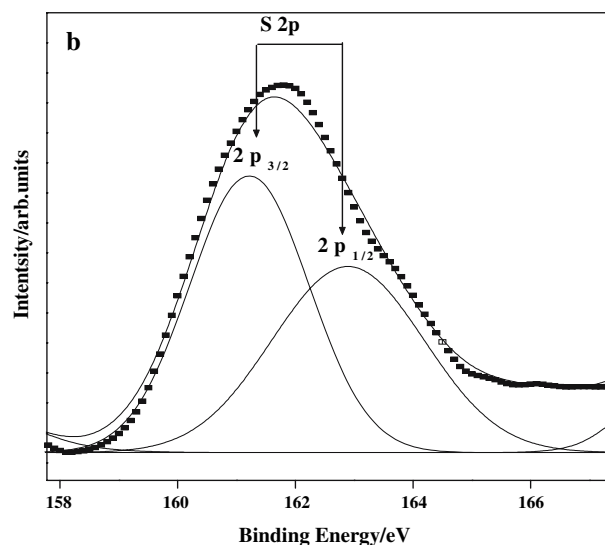
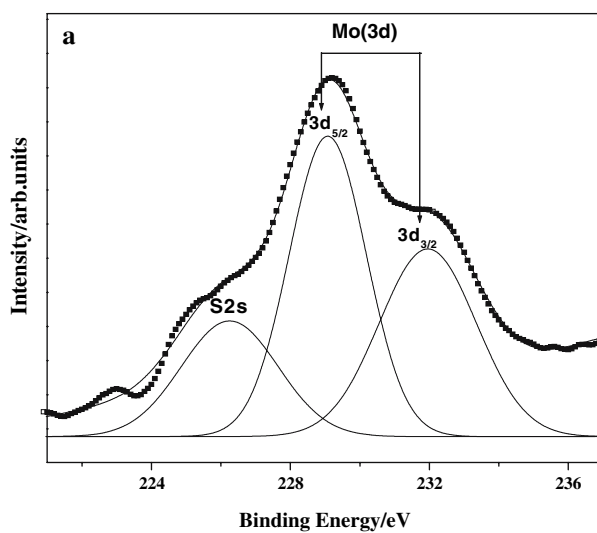


Fig. 4 XPS pattern of MoS₂ nanofiber bundles prepared at 180 °C for 48 h

Table 1 XPS data of Mo(3d) and S(2p)

Peak	Area	Binding energy (eV)	FWHM (eV)	Peak height (Intensity)
Mo3d _{3/2}	481.32	232.1	2.7661	138.84
Mo3d _{5/2}	612.97	229.1	2.1874	223.59
S2s	295.81	226.25	2.7571	85.605
S(2p _{3/2})	113.89	161.25	2.0538	44.248
S(2p _{1/2})	110.89	162.94	2.8032	31.562

WHM = Full Width Half Maximum

sets of spin-orbit doublet. Accordingly, the high intense Mo(3d_{5/2}) peaks at 229.1 and low intense Mo(3d_{3/2}) peak at 232.1 eV could be attributed to MoS₂. Whereas lower binding energy shoulder peak at 226.25 eV is because of S(2s) [27].

Figure 4b shows S(2p) doublet peak (2p_{3/2} and 2p_{1/2}) at 161.25 and 162.94 eV respectively in which 2p_{3/2} and 2p_{1/2} orbital peaks coincide with each other. It is to be noted that the peak positions of S(2p) and Mo(3d_{5/2}) for MoS₂ is in good agreement with the results on MoS₂ [28].

The chemical shifts of Mo(3d_{5/2}) and S(2p) in MoS₂ nanoparticle is +1.6 and −2.2 eV in comparison to elemental Mo and S [29]. The electronegativity of S being 2.5 is greater than that of Mo being 1.8. Therefore there occurs some partial electron transfer from molybdenum to sulfur. As a result, molybdenum becomes positively charged as shown by the increase in binding energy and sulfur becomes negatively charged as shown by the decrease in binding energy.

MoS₂ nanofiber of about 120–300 nm in diameter and 20–25 μm in length are identified from SEM images (Fig. 5). They are well aligned and occur in-group of

bundles with very high aspect ratio. It can be seen that the nanofiber self assembled into bundles and the nanofiber in a bundles had the same growth direction. The morphology and structure of individual MoS₂ nanorods have been characterized in further detail using TEM, which are shown in Fig. 6. It can be seen that the nanorods are straight and uniform along their entire length and thickness of about up to 300 nm. The ends of the nanorods are broken. Figure 6d is the high resolution TEM image of the MoS₂ nanorods and this image shows solid nanorods are uniform in thickness.

The reduction of transition metal ions by surfactant is useful for the production of ultra fine particles of metal sulfides. Unfortunately, molybdc compound reduction chemistry is quite complex and the nature of the products strongly depends on the reaction conditions. For example, Afanasiev et al. show that the reduction of aqueous ammonium molybdate at different temperatures and conditions yields binary sulfides such as MoS_{5,6}, MoS₆, and MoS₃ as well as binary oxides such as MoO₃ and MoO₂. In fact, the mechanism differs markedly in aqueous and in nonaqueous solutions. In order to disclose the transition

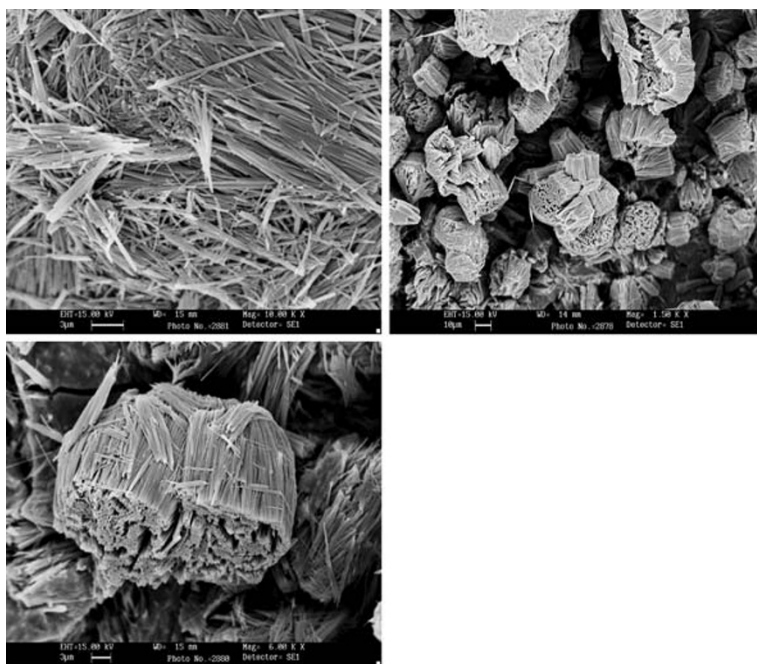
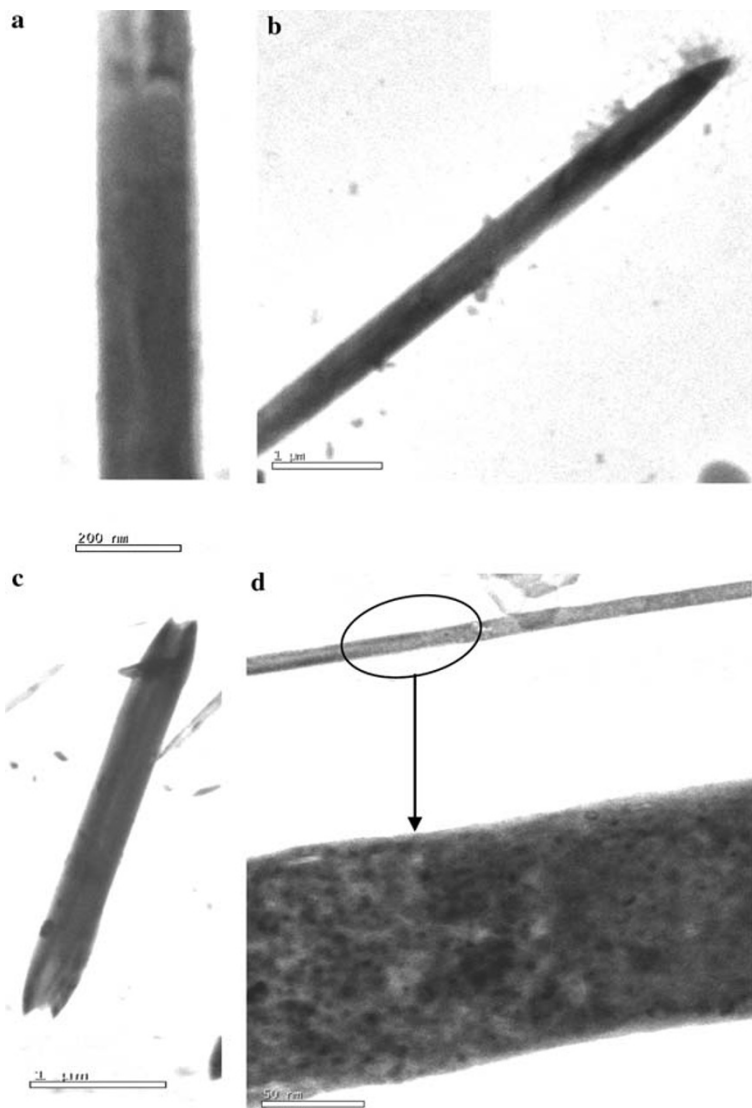
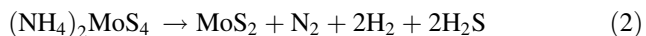
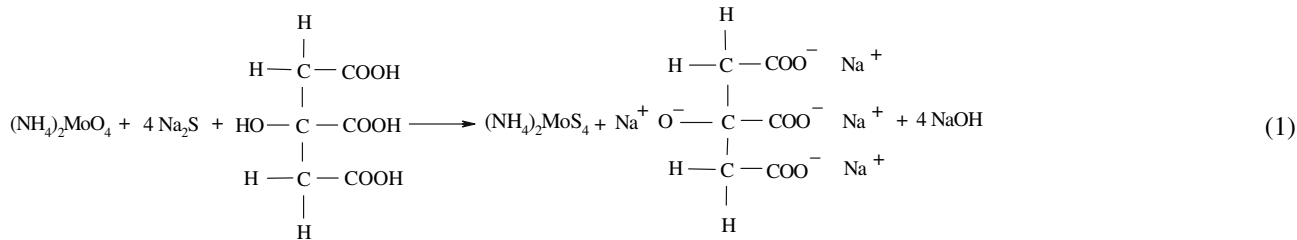
Fig. 5 SEM images of MoS₂ nanofiber bundles prepared at 180 °C for 48 h

Fig. 6 TEM images of MoS₂ nanofiber bundles prepared at 180 °C for 48 h



process from (NH₄)₆Mo₇O₂₄ · 4H₂O to MoS₂, the role of citric acid [30–32] on phase of products was investigated. The possible reaction mechanism can be written as

reduction reaction under hydrothermal conditions. Thus by the addition of 1 g of citric acid or without citric acid, sulfureted reaction and reduction reaction do not react



Step 1 is a sulfureted reaction, in which an intermediate phase (NH₄)₂MoS₄ is produced [33], and step 2 is a

reduction reaction under hydrothermal conditions. Thus by the addition of 1 g of citric acid or without citric acid, sulfureted reaction and reduction reaction do not react completely so that the products consist of much MoO₃ phase as shown in the Fig. 1c, d. Therefore during the formation of MoS₂ nanofiber bundles, citric acid plays a very prominent role. Figure 7a, b gives the SEM images of

Fig. 7 SEM images of MoS₂ nanofiber bundles prepared at (a) 180 °C for 48 h with 1 g citric acid and (b) without citric acid

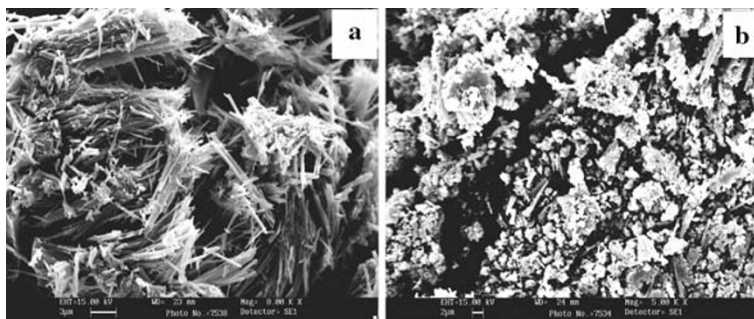
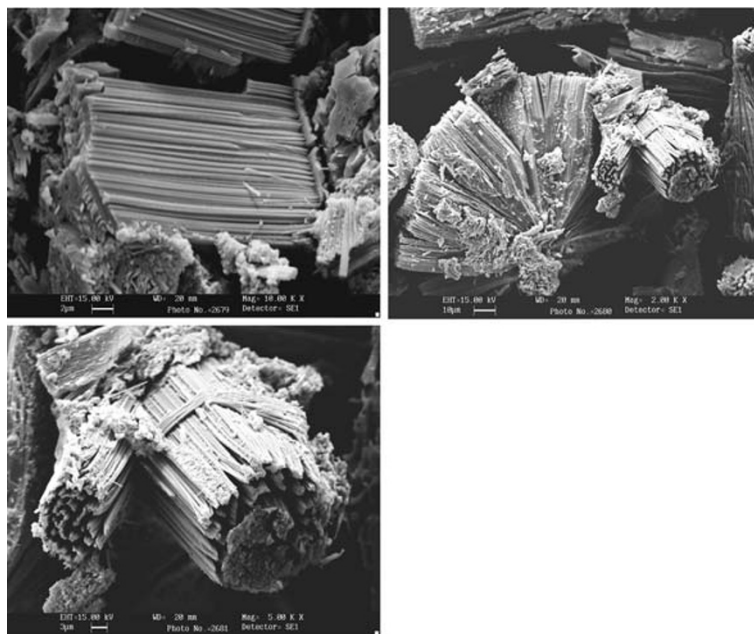


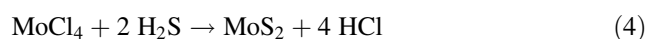
Fig. 8 SEM images of MoS₂ nanofiber bundles prepared at 180 °C for 24 h using H₂S as sulfur source



the product prepared with and without citric acid. We evaluate the effect of temperature and duration on the morphology of the products. But there was no interesting morphology of the product obtained.

The morphology of the product prepared at 180 °C for 24 h (Fig. 8) using H₂S resembles with the morphology of the product prepared at 180 °C for 48 h (Fig. 5) using sodium sulfide as sulfur source. Here, there is a regular arrangement of MoS₂ fibers takes place to form bundles. The thickness of the fiber is found to be about 300 nm and length is about 12 μm. From the SEM images, we observed that the length of all fibers is found to be same with sharp ends having voids in each MoS₂ bundles.

The possible reaction mechanism can be written when H₂S as sulfur source is



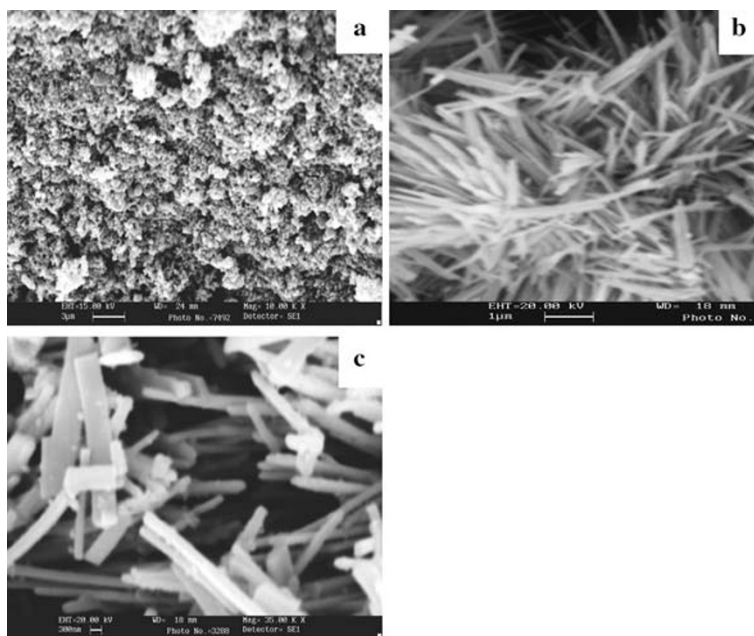
Step 3 is a reduction reaction, in which an intermediate phase MoCl₄ is produced [19], and step 4 is a sulfureted reaction under hydrothermal conditions.

Figure 9a, b shows the SEM images of MoS₂ prepared at 180 °C for 16 and 20 h. When the duration is increased to 48 h, nanorods (Fig. 9c) are obtained. The thickness of the nanorods is found to be in the range of 200–600 nm.

Conclusion

Nanofiber of MoS₂ bundles with 150–300 nm in diameters and 20–25 μm in length have been successfully synthesized by a simple low temperature hydrothermal method. PXRD pattern indicated the amorphous MoS₂ was made up of single layer and layer stacking had not taken place. The

Fig. 9 SEM images of MoS₂ nanofiber bundles prepared at 180 °C h using H₂S for (a) 16 h (b) 20 h and (c) 48 h



nanofiber self assembled into bundles and the nanofiber bundle had the same growth direction. SEM study reveals the formation of bundles of well-aligned MoS₂ nanofiber with very high aspect ratio. Since the MoS₂ nanomaterials are often very difficult to prepare and the search for more simple routine is quite valuable with regard to energy-saving and less pollution. It can be demonstrated that the optimum conditions for preparing MoS₂ nanofiber are at 180 °C for 48 h using citric acid and 180 °C for 24 h by passing H₂S in presence of HCl. Under these conditions the morphology of the products resembles to one another.

Acknowledgments The author G. T. Chandrappa thankful to the Department of Science and Technology, NSTI Phase-II, New Delhi, Government of India for financial support to carryout this research work. We also thank the Central Facility, Dept. of Physics and Dept. of Metallurgy, Indian Institute of Science, Bangalore for collecting XRD data and SEM images.

References

1. Y. Tian, J. Zhao, W. Fu, Y. Liu, Y. Zhu, Z. Wang, *Mater. Lett.* **59**, 3452 (2005)
2. J.A. Wilson, F.J. Di Salvo, S. Majumdar, *Adv. Phys.* **24**, 117 (1972)
3. C.N.R. Rao, Manish Nath, *Dalton Trans.* **1** (2003)
4. S. Ross, A. Sussman, *J. Phys. Chem.* **59**, 889 (1995)
5. C.L. Stender, E.C. Greyson, Y. Babayan, T.W. Odom, *Adv. Mater.* **17**, 2837 (2005)
6. F. Krumeich, H.J. Muhr, M. Neiderberger, F. Bieri, B. Schner, R. Nesper, *J. Am. Chem. Soc.* **121**, 8324 (1999)
7. O. Durupthy, M. Jaber, N. Steunou, J. Maquet, G.T. Chandrappa, J. Livage, *Chem. Mater.* **17**, 6395 (2005)
8. P. Afanasiev, G.-F. Xia, G. Berhault, B. Jouguet, M. Lacroix, *Chem. Mater.* **11**, 3216 (1999)
9. M.R. Close, J.L. Petersen, E.L. Kugler, *Inorg. Chem.* **38**, 1535 (1999)
10. M.M. Mdleleni, T. Hyeon, K.S. Suslick, *J. Am. Chem. Soc.* **120**, 6189 (1998)
11. P.R. Bonneau, R.F. Jarvis Jr., R.B. Kaner, *Nature* **349**, 510 (1991)
12. Q. Li, J.T. Newberg, E.C. Walter, J.C. Hemminger, R.M. Penner, *Nano Lett.* **4**, 277 (2004)
13. R. Tenne, L. Margulus, M. Genut, G. Hodes, *Nature* **36**, 444 (1992)
14. Y. Feldman, G.L. Frey, M. Homyonfer, V. Lyakhovitskaya, L. Margulus, H. Cohen, G. Hodes, J.L. Hutchison, R. Tenne, *J. Am. Chem. Soc.* **118**, 5362 (1996)
15. M. Nath, A. Govindaraju, C.N.R. Rao, *Adv. Mater.* **13**, 283 (2001)
16. C.M. Zelenski, P.K. Dorhout, *J. Am. Chem. Soc.* **120**, 734 (1998)
17. W.K. Hsu, B.H. Chang, Y.Q. Zhu, W.Q. Han, H.M. Terrones, N. Grobert, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, *J. Am. Chem. Soc.* **122**, 10155 (2000)
18. M.A. Albitar, R. Huirache-Acuna, F. Paraguay-Delgado, J.L. Rico, G. Alonso-Nunez, *Nanotechnology* **17**, 3473 (2006)
19. Y. Tian, X. Zhao, L. Shen, F. Meng, L. Tang, Y. Deng, Z. Wang, *Mater. Lett.* **60**, 527 (2006)
20. B. Nagappa, G.T. Chandrappa, Jacques Livage, *Pramana-J. Phys.* **65**, 917 (2005)
21. G.T. Chandrappa, N. Steunou, S. Cassaignon, C. Bisvais, P.K. Biswas, J. Livage, *J. Sol-Gel Sci. Tech.* **26**, 593 (2003)
22. G.T. Chandrappa, J. Livage, *Syn. React. Inorg. Met.-Org. Nano-Met. Chem.* **36**, 23 (2006)
23. P. Joensen, R.F. Frindt, S.R. Morrison, *Mater. Res. Bull.* **21**, 457 (1986)
24. Y. Peng, Z. Meng, C. Zhong, J. Lu, W. Yu, Z. Yang, Y. Qian, *J. Solid State Chem.* **159**, 170 (2001)
25. Y. Tian, Y. He, Y. Zhu, *Mater. Chem. Phys.* **87**, 87 (2004)
26. Th. Weber, J.C. Muijsers, J.H.M.C. Van Wolput, C.P.J. Verhagen, J.W. Niemantsverdriet, *J. Phys. Chem.* **100**, 14144 (1996)
27. D. Briggs, M.P. Seah, *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy* (Wiley New York 1984), p. 503
28. J. Pouzet, H. Hadouda, J.C. Bernede, R. Le Ny, *Phys. Chem. Solids* **57**, 1363 (1996)

29. W. Wang, P. Skeldon, G.E. Thompson, *Surf. Coat. Technol.* **91**, 200 (1997)
30. M. Matzapetakis, C.P. Raptopoulou, A. Tsohos, V. Papaefthymiou, N. Moon, A. Salifoglou, *J. Am. Chem. Soc.* **120**, 13266 (1998)
31. J.-d. Tsay, T.-t. Fang, *J. Am. Ceram. Soc.* **82**, 1409 (1999)
32. M. Kakihana, T. Nagumo, M. Okamoto, H. Kakihana, *J. Phys. Chem.* **91**, 6128 (1987)
33. W. Pan, M.E. Leonowicz, E.I. Stiefel, *Inorg. Chem.* **22**, 612 (1983)