J|A|C|S
COMMUNICATIONS

Direct Synthesis of Mesostructured Lamellar Molybdenum Disulfides Using a Molten Neutral *n*-Alkylamine as the Solvent and Template

Britt A. Vanchura, Pingang He, Valentyn Antochshuk, Mietek Jaroniec,* Amy Ferryman, Dmytro Barbash, Julia E. Fulghum, and Songping D. Huang*

Department of Chemistry, Kent State University, Kent, Ohio 44240

Received February 1, 2002; Revised Manuscript Received July 8, 2002

Transition metal disulfides MS_2 (M = Ti, Zr, Hf, V, Nb, Ta, Mo, and W) constitute an important class of inorganic layered compounds. Their intercalation chemistry has been extensively studied due to the fundamental importance and technological utilities of the process and the related materials.[1] The crystal structures of metal disulfides feature a layer of metal ions sandwiched by two layers of hexagonally close-packed sulfur atoms. The metal ion in the structure has either octahedral (Oct) or trigonal prismatic (TP) coordination. Depending on both the $(n - 1)$d electron configuration and the coordination environment of the metal center, these compounds can have either a semi-metallic or metallic behavior.[2] It has been shown that the intercalation process in metal disulfides is directly associated with a charge transfer between the HOMOs of the guests and the appropriate low-lying bands with empty electronic states in the metal disulfide.[3] Consequently, the metal disulfides of groups 4 and 5 can undergo facile direct intercalation reactions with many inorganic and organic species to form intercalated phases. In contrast, both MoS_2 and WS_2 show intercalation inertness toward most guest species except the simple alkali metal ions.[4]

Thus far, the only established route for introducing inorganic or organic guest species into the layer galleries of molybdenum or tungsten disulfide is via exfoliation of Li_xMS_2 (M = Mo and W) and restacking dispersed single-layers in the presence of a guest species.[5] The exfoliation−restacking process entails treating solid Li_xMS_2 with water to obtain a colloidal suspension of single MS_2 layers. Upon exposure to water, hydrogen gas is emitted from the solution; this acts to expel the bulk host into dispersed single layers. In the presence of a suitable guest, the exfoliated layers can restack to form an intercalation compound. This technique has been successfully applied to a variety of guests including organic Lewis bases, aromatics, inorganic clusters, and polymers.[6−11]

To overcome the intercalation inertness of MS_2 (M = Mo and W) and circumvent the inconvenience of the exfoliation process, we developed a de novo one-step molecular self-assembly method for preparing intercalated MS_2 compounds. The reaction depends on the oxidative decarbonylation of $M(CO)_6$ (M = Mo and W) by elemental sulfur, which is known to produce bulk MS_2 in an organic solvent using sonochemical excitation.[12] When a strong Lewis base such as a molten neutral *n*-alkylamine is used as a solvent and a template, similar reactions can lead to the self-assembly of amine-templated, mesostructured lamellar metal disulfides. Thus, when $Mo(CO)_6$, elemental sulfur and *n*-dodecylamine (DDA) in the molar ratio of 1:2:1 are allowed to react in a Teflon-lined autoclave in the N_2 atmosphere at 140 °C for 12 h, a pure new phase designated as DDA-MoS_2 can be obtained in 95% yield based on $Mo(CO)_6$ after acetone and diethyl ether washing. The conventional elemental analysis of the as-synthesized DDA-MoS_2 combined with thermogravimetric analysis (TGA) showed the empirical formula to be $[(C_{12}H_{25}NH_3)_x(C_{12}H_{25}NH_3)_{0.46-x}]MoS_2$ (see Figure 1 of the Supporting Information).[13] The electrostatic interactions between the small portion of the protonated amine and the slightly negatively charged MoS_2 sheets give rise to the stability of the intercalated phase. This formulation is also consistent with the similar observations made in exfoliated−restacked MoS_2 materials.[14] Notwithstanding, the oxidation states of the metal center and sulfur atom in this material were revealed by X-ray photoelectron spectroscopy (XPS) to be 4+ and 2−. Specifically, the binding energies are Mo $(3d_{5/2}) = 229.5$ eV; S $(2p_{3/2}) = 162.3$ eV (Figure 2 of the Supporting Information). These binding energies are very close to those of bulk MoS_2 measured under the same conditions by us or reported in the literature.[15] We have found that the XPS technique is not sensitive enough to detect any change in binding energies of either molybdenum or sulfide caused by the slight negative charge that is essentially delocalized over the entire MoS_2 layer (Figure 3 of the Supporting Information). The average peak intensity ratio of S/Mo from the different spectral regions of the same sample batch as well as from those of a different sample batch is ca. 2.02. It is worthwhile to point out that no spectral signals of MoS_3 were detected in the XPS studies. Figure 1 shows the X-ray powder diffraction (XRD) patterns of the as-synthesized DDA-MoS_2. A single strong peak at $2\theta = 3.0°$, which corresponds to a *d* spacing of 29.5 Å, was observed. TEM imaging studies revealed long-range lamella mesoscopic ordering in the samples as depicted by the representative TEM graph shown in Figure 2. Thus, the low-angle diffraction peak in the XRD patterns can be indexed as the (001) reflection of a lamella phase. The repeat distance measured by TEM is consistent with the *d* spacing found in the XRD patterns. When

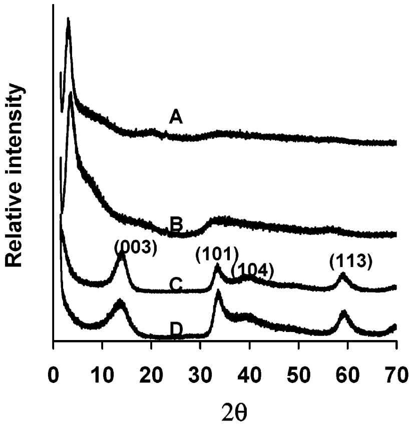

Figure 1. XRD patterns of the as-synthesized DDA-MoS_2 (A), DDA-WS_2 (B), complete calcined samples of DDA-MoS_2 (C), and DDA-WS_2 (D).

---

* To whom correspondence should be addressed. E-mail: shuang1@kent.edu.

10.1021/ja025786a CCC: $22.00

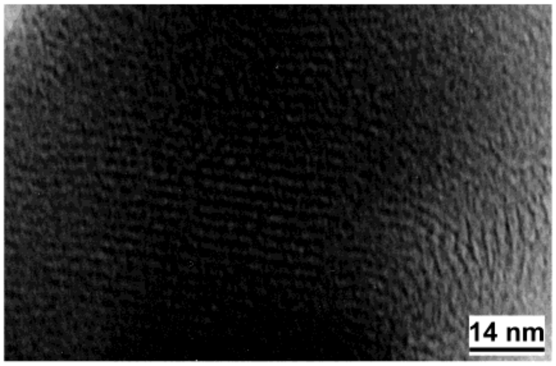

Figure 2. Transmission electron micrograph of DDA-MoS_2.

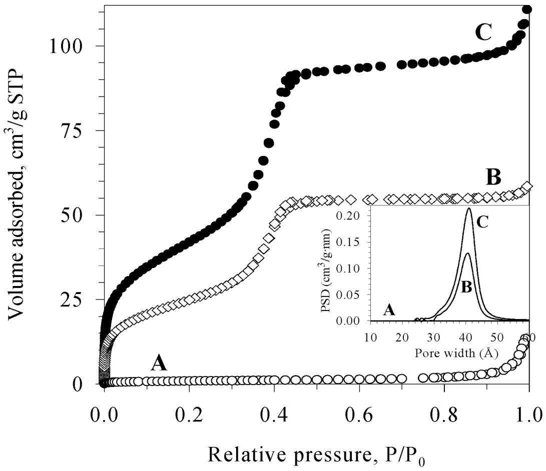

Figure 3. Nitrogen adsorption isotherms for nonporous MoS_2 (A), mesoporous WS_2 (B), and mesoporous MoS_2 (C). The inset shows the differential pore size distributions calculated according to the KJS method for the two samples.

the reaction was carried out in other molten *n*-alkylamines such as *n*-hexylamine (HA), *n*-octylamine (OA), and decylamine (DA), a series of mesostructured lamellar phases, designated as HA-MoS_2, OA-MoS_2, DA-MoS_2, were obtained. The XRD patterns of these materials all contain similar features with the d_{001} peak position at 17.7, 21.9, and 24.7 Å, respectively. Similarly, the use of $W(CO)_6$ in place of $Mo(CO)_6$ also gave a complete series of mesostructured lamellar phases whose d_{001}-spacings are essentially identical to those of the corresponding molybdenum disulfide series. Finally, this synthetic technique can further be extended to introduce a variety of other Lewis bases such as 4,4′-bipyridine and 1,10-phenanthroline into the MS_2 layers.[16]

In an attempt to remove the template from $[(C_{12}H_{25}NH_3)_x(C_{12}H_{25}NH_3)_{0.46-x}]MoS_2$ by slow thermal treatments under a nitrogen atmosphere for a week at 200 °C, we found that both compounds were transformed into mesoporous materials with a concomitant increase of the *d* spacing by ca. 9 Å. The resulting mesoporous MoS_2 and WS_2 have the BET specific surface areas of 155 and 91 m^2/g, and the corresponding pore volumes of 0.19 and 0.10 cm^3/g, respectively. Note that the framework densities of $MoS_2 = 4.8$ g/cm^3 and $WS_2 = 7.5$ g/cm^3 are much higher than that of silica (2.2 g/cm^3). If one takes into account a correction for the density difference, these materials have surface areas and pore volumes comparable to those of mesoporous silicates. Preliminary data also showed that the mesopores are narrowly distributed around 40.5 Å (see inset in Figure 3). Nitrogen adsorption isotherms measured at −196 °C shown in Figure 3 are very similar for both materials and resemble those obtained for highly ordered MCM-41 materials.[17] Tenne and co-workers recently reported on the synthesis of nested fullerene-like MoS_2 and WS_2 particles or nanotubes.[18] However, the accessibility to the mesopores in these hollowed materials has not been demonstrated. To the best of our knowledge, the compounds obtained in this work are the first metal sulfide-based materials to exhibit highly uniform pores.[19] Further heating of both mesoporous materials at 500 °C for 12 h gave dense 3R-MoS_2 and 3R-WS_2 (see Figure 1). Detailed formation mechanisms, structural characterization, and porosity studies on such mesoporous metal disulfides are currently under way (see Figure 4 of the Supporting Information).[20]

Acknowledgment. S.D.H. acknowledges financial support by an NSF CAREER award (DMR-9996287). M.J. and V.A. are supported by an NSF Grant (TS-0086512). Additional funds were provided by a Research Challenge Grant administered via Kent State University. We thank Mr. Charles Liu for his contribution in the initial stage of this project.

Supporting Information Available: Additional figures showing TGA, XPS, and single-crystal structure determination results (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Jacobson, A. J. Intercalation Reactions of Layered Compounds. In *Solid State Chemistry: Compounds*; Cheetham, A. K., Day, P., Eds.; Oxford University Press: New York, 1992; , Chapter 6, pp182−233.
(2) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41−99.
(3) Friend, R. H.; Yoffe, A. D. *Adv. Phys.* **1987**, *36*, 1−94.
(4) (a) Hermann, A. M.; Somoano, R.; Hadek, V.; Rembaum, A. *Solid State Commun.* **1973**, *13*, 1065−1068. (b) Somoano, R. B.; Hadek, V.; Rembaum, A. *J. Chem. Phys.* **1973**, *58*, 697−701. (c) Murphy, D. W.; Christian, P. A. *Science* **1979**, *205*, 651−656.
(5) Gee, M. A.; Frindt, R. F.; Joensen, P.; Morrison, S. R. *Mater. Res. Bull.* **1986**, *21*, 543−549.
(6) Bissessur, R.; Kanatzidis, M. G.; Schindler, J. L.; Kannewurf, C. R. *Chem. Commun.* **1993**, 1582−1585.
(7) Lemmon, J. P.; Lerner, M. M. *Chem. Mater.* **1994**, *6*, 207−210.
(8) Golub, A. S.; Shumilova, I. B.; Zubavichus, Y. V.; Jahncke, M.; SussFink, G.; Danot, M.; Novikov, Y. N. *J. Mater. Chem.* **1997**, *7*, 163−167.
(9) Dungey, K. E.; Curtis, M. D.; Penner-Hahn, J. E. *Chem. Mater.* **1998**, *10*, 2152−2161.
(10) Ollivier, P. J.; Kovtyukhova, N. I.; Keller, S. W.; Mallouk, T. E. *Chem. Commun.* **1998**, 1563−1564.
(11) Kosidowski, L.; Powell, A. V. *Chem. Commun.* **1998**, 2201−2202.
(12) Mdleleni, M. M.; Hyeon, T.; Suslick, K. S. *J. Am. Chem. Soc.* **1998**, *120*, 6189−6190.
(13) Elemental analysis of DDA-MoS_2: Calcd for $(C_{12}H_{25}NH_2)_{0.46}MoS_2$: C, 27.0; H, 5.1; N, 2.6; S, 26.2 Found: C, 26.9; H, 5.3; N, 2.5; S, 26.3.
(14) Heising, J.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *121*, 11720−11732.
(15) Mcdevitt, N. T.; Bultman, J. E.; Zabinski, J. S. *Appl. Spectrosc.* **1998**, *52*, 1160−1164.
(16) The *d* spacings for $(4,4'\text{-bipy})_xMS_2$ and $(1,10\text{-phen})_xMS_2$ (M = Mo and W) are 16.3 and 9.9 Å, respectively.
(17) Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir* **1997**, *13*, 6267−6273.
(18) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222−225.
(19) For other representative mesostructured metal sulfides, see: (a) Huo, Q. S.; Margolese, D. I.; Ciesla, U.; Demuth, D. G.; Feng, P. Y.; Gier, T. E.; Sieger, P.; Firouzi, A.; Chmelka, B. F.; Schuth, F.; Stucky, G. D. *Chem. Mater.* **1994**, *6*, 1176−1191. (b) Li, J. Q.; Delmotte, L.; Kessler, H. *Chem. Commun.* **1996**, 1023−1024. (c) Zelenski, C. M.; Dorhout, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 734−742. (d) MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *397*, 681−684. (e) Rangan, K. K.; Trikalitis, P. N.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2000**, *122*, 10230−10231.
(20) We isolated a cluster compound $[Mo_4S_8(en)_4]$ which shows mechanistic relevance to the formation of mesostructured lamellar MoS_2.

JA025786A