Chinese Chemical Letters Vol. 14, No. 3, pp 312 – 315, 2003
http://www.imm.ac.cn/journal/ccl.html

Characterization of Nested Hollow Inorganic Fullerene-like Tungsten Disulfide Nanoparticles Prepared by Solid-Gas Reaction

Wei Xiang CHEN[1]*, Jiang Ping TU[2], Xiao Chun MA[3], Zhu De XU[1],
Reshef TENNE[4], Rita ROSENSTVEIG[4]

[1]Department of Chemistry, [2] Department of Material Science and Engineering, Zhejiang University, Hangzhou 310027
[2]Department of Material Science and Engineering, Zhejiang University, Hangzhou 310027
[3]College of Mechanical and Electronic Engineering, Zhejiang University of Technology, Hangzhou 310032
[4]Department of Materials Science and Interface, Weizmann Institute of Science, Rehovot 76100, Israel

Abstract: Non-carbon inorganic fullerene-like (IF) nanoscale materials have recently attracted intense interest due to their nested hollow and nanotube structures. In this letter, IF-WS_2 nanoparticles prepared by solid-gas reaction were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The results show that the IF-WS_2 nanoparticles have a nested hollow closed spherical structure with diameter of 100-150 nm.

Keywords: Inorganic fullerene-like, WS_2, nanoparticles.

Since the discovery of carbon fullerenes, such as C_{60} and C_{70}, and carbon nanotubes, a wide range of related fullerene-like and nanotube structures have been identified. It was proposed that generally nanoparticles of 2-D layered compounds are not stable in the planar form and they fold into closed-cage or tubular structures (IF), which are analogous to the carbon fullerenes and carbon nanotubes[1-2]. This concept has been verified and numerous inorganic compounds with fullerene-like and nanotube structures have been reported. These include transition metal disulfides (*e.g.* WS_2, MoS_2 and NbS_2)[3-5] and metal oxide (*e.g.* VO_x)[6].

It is believed that nanoparticles of transition metal disulfides with inorganic fullerene-like (IF) structure improve considerably the tribological properties of powdered materials in comparison to commercially layered compound (2H) particles[7, 8]. Thin film coating of IF-MoS_2 nanoparticles prepared by the arc-discharge method exhibited excellent tribological behavior, with a very low friction coefficient (0.005) even in humid atmosphere, while sputtered 2H-MoS_2 films deteriorated very rapidly[9]. Recently, IF-WS_2 nanoparticles were impregnated into metal-based composites prepared by powder metallurgy. It was demonstrated that IF-WS_2 could greatly improve the

*E-mail: weixiangchen@css.zju.edu.cn

tribological properties of the nanocomposite[10].

Inorganic fullerene-like WS_2 nanoparticles were synthesized by a solid-gas reaction, which is similar to the method described elsewhere[11]. In the present work, a powder of WO_3 nanoparticles was forced to go down into the reactor at a rate of 60 mg·min^{-1} by a carrier N_2 gas. A counteracting stream of nitrogen- hydrogen- sulfureted hydrogen mixture (N_2: H_2: H_2S = 90: 5: 5) was introduced into the reactor at a flow rate of 800 ml·min^{-1}. These WO_3 nanoparticles were sulfidized under the reducing atmosphere at 870°C, and inorganic fullerene-like (IF) WS_2 nanoparticles were formed on a substrate in the reactor. For the transmission electron microscopy (JEOL JEM2010), IF-WS_2 nanoparticles were dispersed in acetone by an ultrasonic method. **Figure 1** shows TEM images of IF-WS_2 nanoparticles prepared by this method. The shape of most IF-WS_2 nanoparticles is close to spherical with diameters ranging from 90 nm to 120 nm. As shown in the high resolution TEM (HRTEM) micrograph in **Figure 1**, IF-WS_2 has a nested fullerene-like structure, which is analogous to that of carbon nano-onions.

Figure 1 TEM and HRTEM images of IF-WS_2 nanoparticles

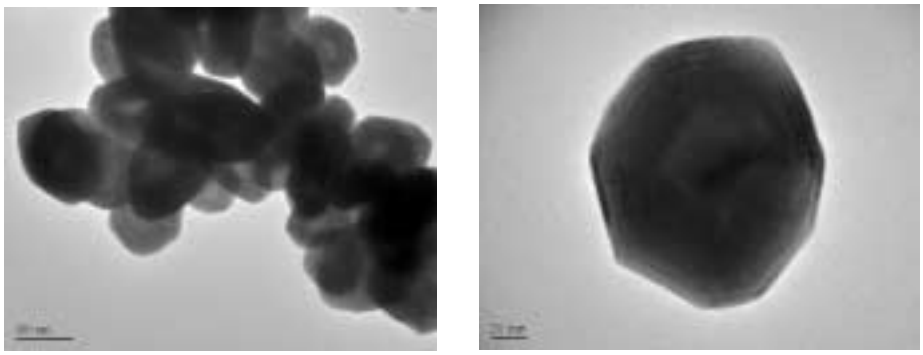
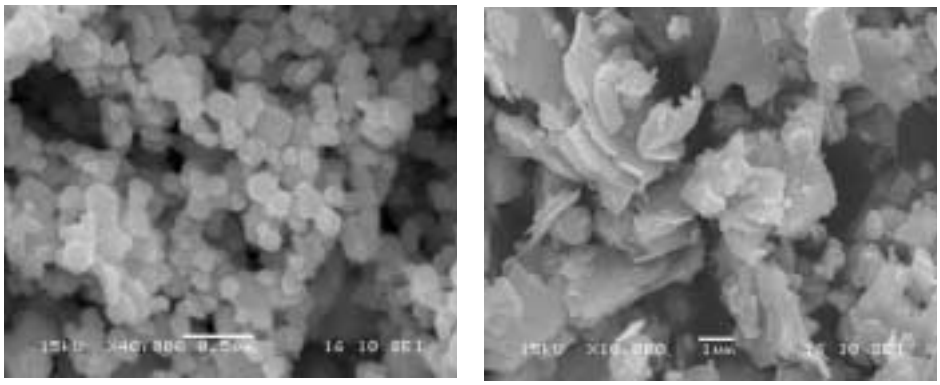


Figure 2 shows scanning electron microscope (SEM) images of IF-WS_2 nanoparticles and layered WS_2 (2H) particles. To eliminate charging of the particles and blurring of the image in high magnifications, the IF-WS_2 and 2H-WS_2 samples were coated with a platinum film before the SEM observation (JEOL JSM-5600LV). This comparison clearly shows that, while macroscopic particles of this compound (right) favor the 2H platelike morphology, the IF-WS_2 nanoparticles (left) represent a spherical closed-cage structure. X-ray diffraction (XRD) patterns of IF-WS_2 and 2H-WS_2 powders are shown in **Figure 3**. Most of the XRD peaks of the IF-WS_2 powder coincide with those of 2H-WS_2. However, in comparing the XRD patterns of IF-WS_2 and 2H-WS_2 some differences are discernible, like the shape and relative intensity of the peaks. Most importantly, the (002) peak of the IF nanopowder is shifted to a lower angle, compared to the (002) peak of the 2H-WS_2 powder. This shift is caused by a 2-3% lattice expansion in the IF-WS_2 powder along the c-axis compared to the bulk 2H-WS_2 form. As shown also in **Figure 3**, the FWHM of the diffraction peaks of IF-WS_2 are larger than that of 2H-WS_2. For the (002) peak, the FWHM of IF-WS_2 is 0.545 degree, while that of 2H-WS_2 is 0.158 degree, suggesting a size difference of about

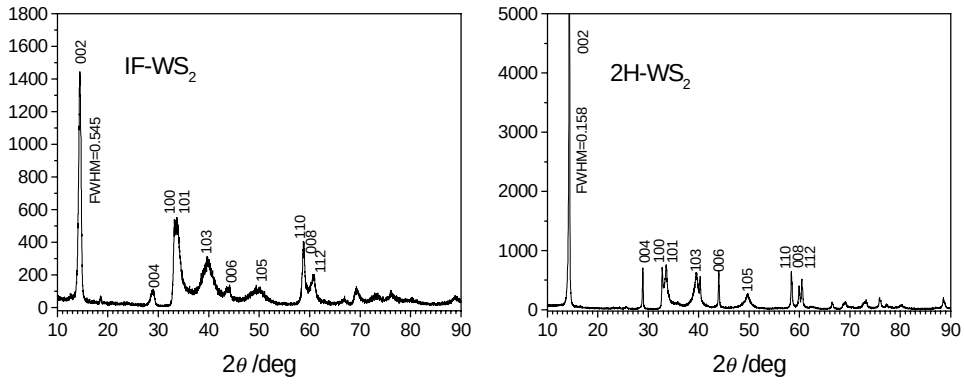
one order of magnitude between the particles of the two phases.

Figure 2 SEM images of IF-WS_2 nanoparticles and 2H-WS_2 particles



(a) IF-WS_2 nanoparticles (b) 2H-WS_2 particles

Figure 3 XRD partterns of IF-WS_2 nanoparticles and 2H-WS_2 particles



Acknowledgments

This work was supported by the National Natural Science Foundation of China (50171063, 20171039, 20003009), the Zhejiang Provincial Natural Science Foundation of China (501074, 200053), the Israeli Ministry of Science (Tashtiot) and the Israel Science Foundation, the Minerva Foundation (Munich)

References

1. R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature*, **1992,** *360*, 444.
2. R. Tenne, M, Homyonfer, Y. Feldman, *Chem. Mater*., **1998,** *10*, 3226.

3. A. Zak, Y. Feldman, V. Alperovich, R. Rosentsveig, R. Tenne, *J. Am. Chem. Soc*., **2000**, *112*, 11108.
4. Y. Feldman, G.L. Frey, M. Homyonfer, R. Tenne, *J. Am. Chem. Soc*., **1996**, *118*, 5632.
5. M. Nath, C. N. R. Rao, *Chem. Commun*., **2001,**: *21*, 2236.
6. P.M. Ajayan, O.Stephan, P. Redlih, C.Colliex, *Nature*, **1995**, *375*, 564.
7. L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S. R. Cohen, R. Tenne. *Nature*, **1997**, *387*, 791.
8. L. Rapoport, Y. Feldman, M. Homyonfer, H. Cohen, J. Sloan, J. L. Hutchison, R. Tenne, *Wear*, **1999**, *225*, 975.
9. M. Chhowalla and G.A. J. Amaratunga, *Nature*, **2000**, *407*, 164.
10. L. Rapoport, M. Lvovsky, I. Lapsker, V. Leshchinsky, Yu Volovik, Y. Feldman, A. Zak, R. Tenne, *Adv. Eng. Mater*., **2001,** *3*, 71.
11. L. Rapoport, M. Lvovsky, I. Lapsker, V. Leshchinsky, Yu Volovik, Y. Feldman, R. Tenne, *Wear*, **2001,** *249*, 150.

Received 24 April, 2002