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Preparation of Nanocrystalline MoS_2 Hollow Spheres

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Abstract: Nanocrystalline MoS_2 with hollow spherical morphology has been prepared by the hydrothermal method. The products are characterized by means of X-ray powder diffraction, transmission electron microscopy and high-resolution transmission electron microscopy. The experimental results give the evidence that the sample is consists of hollow spheres 400~600 nm in diameter, and there is much whisker on the surface of MoS_2 hollow sphere.

Keywords: Nanocrystalline MoS_2, hollow spheres, whisker, hydrothermal method.

Molybdenum disulfide (MoS_2) crystal has a sandwich interlayer structure formed by stacking of the (S-Mo-S) layers in the direction [001][1]. These layers are loosely bound to each other only by Van der Waals forces, which accounts for easy cleavage of the (S-Mo-S) layers in the direction [001]. Due to this structure, laminar molybdenum disulfide has numerous applications as a solid state lubricant[2], as a hydrodesulfurization catalyst[3], nonaqueous lithium batteries[4], and for special applications in space[5]. Especially, the MoS_2 with inorganic fullerene-like structures was found, it has been focused on the research field of preparation and structure properties[6-11]. In last years, many efforts have been contributed to prepare materials on a nanometer scale, and research theirs structure properties and applications[12]. There are many methods to prepare nanocrystalline MoS_2, by the different methods, peoples can obtain MoS_2 nanocrystalline with the different morphologies, such as nanoparticles[13~14], nanowires[15], nanotubes and / or nanoparticles with inorganic fullerene-like structures[6~8,16~17]. Herein, we report a simple route to synthesize the nanocrystalline MoS_2 hollow spheres by a hydrothermal method. The reaction is carried out in an acid aqueous solution at 280°C, using metal Fe powders as reducing reagent.

Experimental

The analytically pure $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$ (>99%, 1.5 mmol), thioacetamide (>99%, 31 mmol) and a sufficient amount of metal Fe power (>99%, 12 mmol) were put into a 200 mL teflon liner autoclave, then 1.2 mol/L (molar solution) hydrochloric acid (HCl) was

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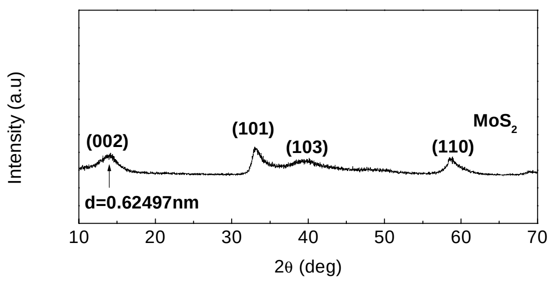
used to fill the tank to 80% of the total volume, then the autoclave was tightly sealed and maintained at 280°C for 48 h, then allowed to cool to room temperature. The resulting powders were filtered and washed with 1.2 mol/L HCl, distilled water and absolute ethanol several times. After drying in a vacuum at 80°C for 4 h, the corresponding sample was obtained.

The phases and the crystallographic structure of the products were determined by X-ray powder diffraction **(**XRD**),** using a Japan Rigaku D / max-B X-ray diffraction with Cu Kα radiation (λ=1.5418 Å). To examine the morphology and particle size of molybdenum compounds obtained, the transmission electron microscope (TEM) images were taken on a Hitachi model H-800, using an accelerating voltage of 200 KV. The strongest evidence for the hollow spheres is the direct observation of a single hollow sphere was carried out by high-resolution transmission electron microscopy (HRTEM) on a JEOL-2010 transmission electron microscope.

Results and Discussion

Figure 1 shows the XRD patterns of the as-prepared samples, all of the diffraction peaks can be indexed to 2H-MoS_2 (JCPDS card, 37-1492), which correspond to the (002), (101), (103), and (110) plane of model 2H-MoS_2. However, it is found that the XRD patterns of the as-prepared sample is very weak in relative intensity of the (002) plane with model MoS_2, meanwhile, the shift of (002) Bragg diffraction peek toward lower angles and the simultaneous broadening of this peek. All of that is similar to the most pronounced evidence for the formation of fullerene-like particles reported in literature[6].

Figure 1 XRD pattern of as-prepared sample



The transmission electron microscopy (TEM) images of as-prepared samples are shown in **Figure 2a** and **2b**. The sample is consists of hollow spheres 400~600 nm in diameter. Some twin spheres were also observed. The strong contrast between the dark edge and pale center is evidence for its hollow nature[18~19]. Broken spheres are also observed, providing further proof of their hollow nature. **Figure 2c** is the electron diffraction (ED) of the hollow spheres; it reveals that the shell is composed of hexagonal MoS_2 polycrystals. However, the strongest evidence is the direct observation of a single hollow sphere by high-resolution transmission electron microscopy (HRTEM) as shown in **Figure 3a**. The HRTEM images under higher magnification of selected area are shown in **Figure 3b** and **3c,** they reveal the fabrication of the sphere wall. **Figure 3b** shows that the wall of nanocrystalline MoS_2 hollow sphere has irregularly oriented lattices, which is different from the inorganic fullerence-like structure[6]. In addition, it is found that there is much whisker on the surface of hollow sphere (see **Figure 3c**). All of that illustrate the grown mechanism of hydrothermal route is different from ones of gas-solid-phase (GSP) reaction[6-8] method. A detailed study of the mechanism of the hydrothermal method is underway and will be reported elsewhere.

Figure 2 ED and TEM images of as-prepared sample

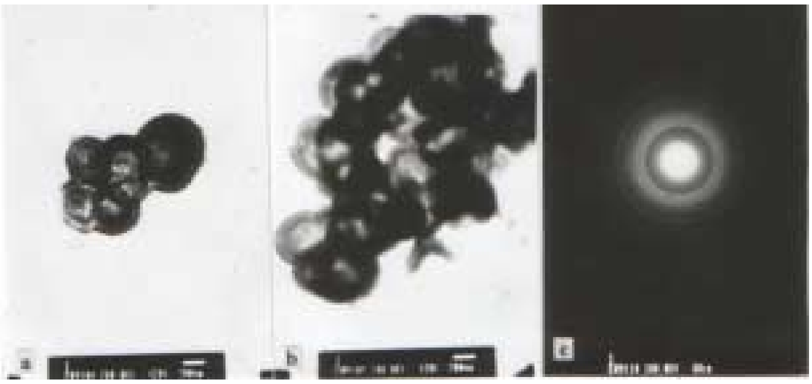
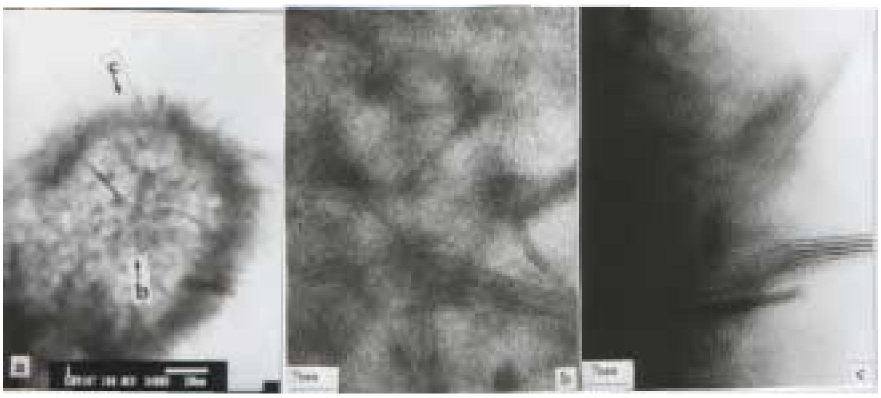


Figure 3 HRTEM image and images of selected area under higher magnification for a single MoS_2 hollow sphere



Conclusion

In conclusion, the nanocrystalline MoS_2 hollow sphere has been synthesized successfully from the $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$ and CH_3CSNH_2, in an acid aqueous solution, using metal Fe powers as reducing reagent by the hydrothermal method. MoS_2 particles were in the form of hollow spheres with a particle size distribution in range from 400 to 600 nm.

Meanwhile, hydrothermal conversion perhaps affords a simple route to synthesize the nanocrystalline MoS_2 hollow spheres.

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