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ScienceDirect
Materials Letters 61 (2007) 1303 – 1306
materials letters
www.elsevier.com/locate/matlet

Spray drying process to synthesize multiple fullerene-like MoS_2 particles

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Received 8 May 2005; accepted 6 July 2006
Available online 26 July 2006

Abstract

Multiple inorganic fullerene-like (IF) molybdenum disulfide hollow spheres were synthesized through spray drying method. The molybdenum trisulfide precursor, which was prepared by the mixed solution of ammonium molybdate ($(NH_4)_2MoO_4$) and ammonium disulfide ($(NH_4)_2S$) with a spray drying method, was desulfurized at 850 °C in a mixture of hydrogen and argon, and subsequently multiple fullerene-like molybdenum disulfide hollow spheres were obtained. The samples were identified and characterized by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM), and the mechanism of formation is also discussed based on the experimental result. The spray drying process would be an effective method to synthesize large-scale of inorganic fullerene-like materials.

Keywords: Spray drying process; Molybdenum disulfide; Fullerene-like

1. Introduction

The stimulus for the formation of carbon fullerenes [1] and carbon nanotubes [2] structures stems from the high energy of the dangling bonds at the edge of graphite planes. Using a similar reasoning, Tenne and his co-workers [3,4] firstly synthesized inorganic nested fullerene-like compounds MS_2 (M = W, Mo), which have the similar layered structure to graphite, as with stacks of S–M–S sandwiches held together via weak Van der Waals interactions. They also formulated the general trend that nanoparticles of 2-D layered compounds are inherently unstable in the planar form and adopt to form polyhedral (fullerene-like) topologies, which is not unique to carbon. And the fullerene-like WS_2 and MoS_2 nanoparticles were first formed by heating the corresponding metal thin films in the presence of H_2S gas. These materials were generally named inorganic fullerene-like materials (shortly named IF).

The IF materials have generated intense scientific interest owing to their distinctive properties and wide ranges of promising applications. IF-MoS_2 and WS_2 nanoparticles are excellent lubricants [5–7], MoS_2 and WS_2 nanoparticles or nanotubes were used as heterogeneous catalysts [8,9], WS_2 nanotubes had been tested successfully as scanning probe microscope tips [10], and some other applications such as solid-state secondary lithium battery cathodes and lithium intercalation materials have also been reported [11,12]. In the view of encouraging results, more works on the mechanical, electrochemical, catalytic, photochemical, and chemical reactivity are expected.

To date, several methods have been reported to prepare the novel IF structure materials and nanotubes. High yields of IF-MS_2 (M: Mo, W) nanoparticles were developed by heating MO_3 precursor powders at about 850 °C under H_2S/H_2 flow [13]. And some other methods have also been developed to synthesize inorganic fullerenes and nanotubes: electron irradiation of MoS_2 layered crystal [14], laser ablation of MoS_2 targets [15], high-pressure arc discharge [16] and solution low-temperature route [17], etc. Although a lot of research has been carried out globally, scientists still meet great challenge to synthesize large-scale IF materials via a much more effective method, which enables scientists to extensively investigate the properties and the applications of the IF materials. Feldman

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doi:10.1016/j.matlet.2006.07.018

et al. have synthesized macroscopic quantities of IF MoS_2 and WS_2 via a fluidized bed reactor [18]. In the present work, we report the synthesis and characterization of large-scale multiple IF-MoS_2 particles by means of spray drying pyrolysis method. Here, ammonium tetrathiomolybdate solution ($(NH_4)_2MoS_4$) which was prepared by the mixed solution of ammonium molybdate ($(NH_4)_2MoO_4$) and ammonium disulfide ($(NH_4)_2S$), was decomposed to the molybdenum trisulfide (MoS_3) with a spray drying method, then the MoS_3 precursor was transformed to megranate-shaped multiple IF-MoS_2 hollow spheres when pyrolyzed at 850 °C in a mixture of hydrogen and argon.

2. Experimental

Stoichiometric amounts of $(NH_4)_2MoO_4$ and $(NH_4)_2S$ were mixed in distilled water. $(NH_4)_2MoS_4$ aqueous solution (typical 0.01 M) was subsequently obtained according to the following reaction:

$$(NH_4)_2MoO_4 + 4(NH_4)_2S + 4H_2O \rightarrow (NH_4)_2MoS_4 + 8NH_4 \cdot OH$$

The resulting $(NH_4)_2MoS_4$ aqueous solution was dried via a spray-dryer. Then $(NH_4)_2MoS_4$ was decomposed to MoS_3 at elevated temperature, which was X-ray amorphous (not shown). In the process, the solution was atomized via a sprinkler under an air pressure of 0.2 MPa, and the spray was carried into a preheated quartz tube where the inlet air temperature was 220 °C, and the exit air temperature was 110 °C. The product MoS_3 was collected in the cooler region, the water was vaporized and went out along with the airflow.

The thermal decomposition of $(NH_4)_2MoS_4$ occurs according to the reaction [19]:

$$(NH_4)_2MoS_4 \rightarrow MoS_3\downarrow + H_2S\uparrow + NH_3\uparrow$$

Finally, the as-prepared MoS_3 precursor powders were desulfurized at 850 °C for 5 h in a gas mixture of argon and hydrogen (Ar: H_2 = 95: 5). The reaction involved is:

$$MoS_3 + H_2 \rightarrow MoS_2 + H_2S$$

The structure and morphology of the precursor and synthesized powders were examined by means of X-ray diffraction (XRD, Thermo X'TRA, Cu K_α radiation), field-emission scanning electron microscopy (SEM, HITACHI S-4700), and transmission electron microscopy (TEM, JOEL JEM 2010).

3. Results and discussion

Fig. 1a shows a SEM image of the MoS_3 precursor, which reveals that the products of the spray drying process are micrometer-sized hollow spheres with very thin spherical shells, and the spherical shell has a typical nanoscale wall thickness. The particle size varies because the spray process generates a unimodal droplet size distribution with a large standard deviation. The SEM image of obtained MoS_2 particles is shown in Fig. 1b. It is obvious that the MoS_2 particles are also hollow spheres, and they have the same diameter range as the MoS_3 precursor, which demonstrates that the size of MoS_2 particle is fully determined by the MoS_3 precursor. In addition, many much smaller nanoparticles are seen yielded on the inner surface of the hollow spherical shell irrespective of the sphere size, forming a multiple structure.

Fig. 2 shows the typical XRD pattern of the obtained MoS_2 particles. It is well known that the standard hexagonal MoS_2 (2H–MoS_2) has a two-dimensional layered structure, which would result in much stronger and sharper (002) diffraction peak compared to other peaks in its XRD spectrum. However, in this XRD spectrum, it appears quite different, the peak responding to the (002) lattice plane shows only a little stronger intensity compared to other peaks. In addition, the peak responding to the (002) lattice plane of MoS_2 is shifted to a lower 2θ degree (higher d-spacing) in comparison with the standard hexagonal (2H) MoS_2. The lattice expansion is attributed to the introduction of strain owing to the curvature of the layers. Moreover, the spectrum shows very broad diffraction, demonstrating that the MoS_2 has very small grain size. According to the reported literature, these characteristics provide the most obvious evidence for the formation of fullerene-like structure [20]. Therefore, it can be concluded that the smaller nanoparticles are supposed to be fullerene-like MoS_2, which grow correlatively to form multiple fullerene-like structures, as is clear from the Fig. 1b.

The morphological characterization of the hollow spheres was further investigated using TEM (Fig. 3). A large amount of nanoparticles are seen to grow correlatively, and these IF-MoS_2 nanoparticles have diameters ranging from tens to hundreds of nanometers. Fig. 4(a and b) shows the higher magnification of the IF-MoS_2

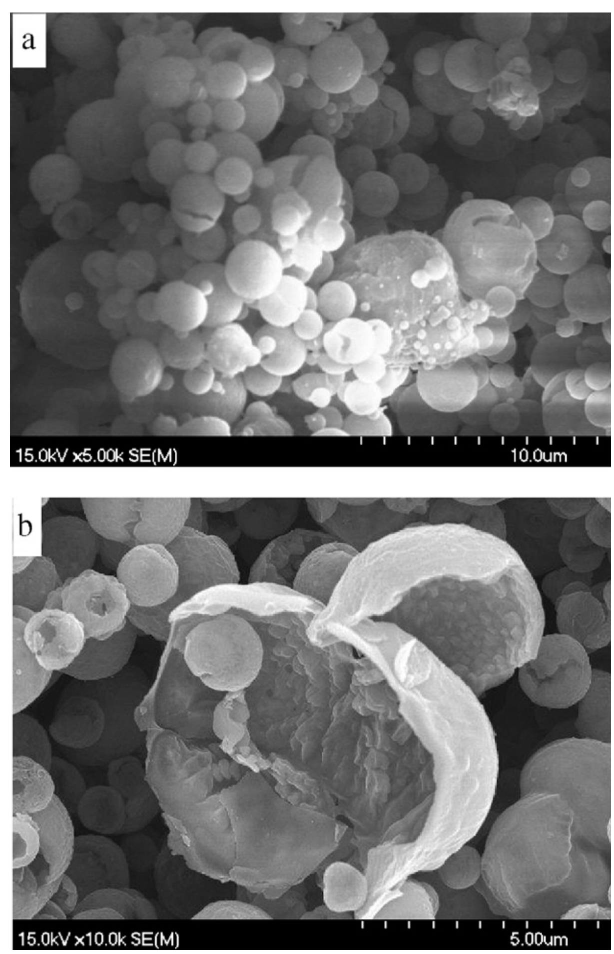

Fig. 1. a) SEM image of MoS_3 precursor, the particles are hollow spheres. b) SEM image of MoS_2 hollow spheres.