Synthesis and structure of multi-layered WS$_2$(CoS), MoS$_2$(Mo) nanocapsules and single-layered WS$_2$(W) nanoparticles

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Multi-layered MoS$_2$ (or WS$_2$) nanocages stuffed with Mo (or CoS/CoO) nanocrystals have been synthesized by using the reaction between metal nanoparticles and sulfur powders. This simple synthesis method, different from the conventional methods for synthesizing pure inorganic fullerenes, is also potentially important for large-scale synthesis of nanoparticles of other metal dichalcogenide. Besides the multi-layered WS$_2$ nanocapsules, we have successfully fabricated nanocapsules with a single-layered WS$_2$ sheet encapsulating W by using the arc-discharge method. We discuss possible mechanisms for the formation of the unique core-shell structured nanocapsules.

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1. Introduction

The encapsulation of nanocrystallite materials is important, not only in scientific research because of the novel properties induced by size-, surface- and interface-effects, but also in many technologies, ranging from cluster protections, catalysts to biomedical applications [1]. Recently, one focuses on encapsulation on materials with a layered structure because of their bendable layers in nanoscale. To date, a great number of nanoscale materials have been successfully engaged in curled-up graphite and $h$-BN layers [1–3]. However, it is still difficult for synthesis reasons to have a universal encapsulation of foreign nanoparticles with metal dichalcogenides (MX$_2$, M = W, Mo, Nb, Ta; X = S, Se, Te), even though they show analogous layered structures to graphite and $h$-BN. On the other hand, the most effective method for synthesizing pure fullerene-like WS$_2$ and MoS$_2$ materials are based on solid-gas reactions, in which a large amount of H$_2$S and/or H$_2$ are used as reducing agents in conjunction with metal compounds as precursors [4, 5]. For example, by annealing oxide precursors in flowing H$_2$S + H$_2$, one can produce about one gram of hollow WS$_2$ nanoparticles with a relatively broad size distribution [5]. Although recent modifications to this method have to some extent scaled up the production, a large amount of H$_2$S and H$_2$ are still needed to provide elemental sulfur and reducing agents [6]. Other techniques, including electron-beam irradiation [7], sonoeclectrochemical bath reaction [8], electron chemical deposition [9], and C$_60$ catalyzed self-assembly process [10], have also been developed to grow a small amount of pure inorganic fullerenes. In a word, most of the research in this field is focused on the synthesis of multi-layered pure inorganic fullerenes, which are spherical or tubular in shape.

In this work, we report a novel method for the large-scale synthesis and the structural properties of nanocapsules with WS$_2$ (or MoS$_2$) shell material encapsulating CoS/CoO (or Mo) cores, and show that the rapidity of this method, simplicity of the reactors, nonuse of H$_2$ and minimized usage of H$_2$S make the present method a powerful synthesis route. In the following, we annotate the shell core structure by setting the shell composition before the core composition in brackets “shell (core)”. Besides the multi-layered WS$_2$(CoS/CoO) and MoS$_2$(Mo) nanocapsules, single-layered WS$_2$(W) nanocapsules have been fabricated by using the arc-discharge method.

2. Experimental procedure

2.1. Synthesis of multi-layered WS$_2$(CoS/CoO) nanocapsules

Nanocapsules consisting of multi-layered WS$_2$ shells which encapsulate CoS/CoO nanoparticles (hereafter S1) were produced by reaction between cobalt (doped with elemental tungsten) nanoparticles and sulfur powders. In analogy with our previous work [2, 3], the W-doped cobalt nanoparticles were prepared via the arc-discharge method, in which a cobalt cylinder compacted with 99 wt% purity Co powders was used as anode while a 1.5 mm-diameter W needle was used as cathode, an arc-discharge with a typical current of 300 A was maintained for 2 h in an argon atmosphere. The W-doped cobalt nanoparticles generated by arc discharge were then mixed with excess commercial.
sulfur powders in an ultrasonic alcohol bath. After the mixing process, the alcohol was evaporated in a boiling water bath. Finally, the dried mixture was heated up to about 600°C for 1 h, using a resistance heater placed in a water-cooled chamber (Φ28 cm × 40 cm) filled with an atmosphere of Ar (10000 Pa) + H2S (4000 Pa).

2.2. Synthesis of multi-layered MoS2(Mo) nanocapsules

In analogy to the preparation of sample S1, nanocapsules consisting of multi-layered MoS2 shells which encapsulate Mo nanoparticles (hereafter S2) were prepared by reaction between Mo nanoparticles and sulfur powders. The Mo nanoparticles precursor was also prepared via an arc discharge method, in which bulk Mo and a 4 mm-diameter W needle were used as anode and cathode, respectively. The Mo nanoparticles prepared this way were mixed with excess sulfur powders in an ultrasonic alcohol bath. Then the alcohol was evaporated in a boiling water bath. After that, the dried mixture was heated up to about 600°C for 1 h, using a resistance heater placed in a water-cooled chamber (Φ28 cm × 40 cm) filled with an atmosphere of Ar (10000 Pa) + H2S (4000 Pa). In fact, the reaction processes to generate S1 and S2 were carried out using the same heater and at the same time.

2.3. Synthesis of single-layered WS2(W) nanocapsules

The W nanoparticles coated with single-layered WS2 sheet (hereafter S3) were synthesized via an arc-discharge method. An arc-discharge with a typical current of 300 ampere, maintained for 2 h, was struck between the bulk tungsten anode and tungsten needle cathode in an atmosphere of Ar (12000 Pa) + H2S (3000 Pa). After the experiments, the waste gas in the chamber was pumped out and then the powder products on the chamber wall were collected in air and used in the further experiments.

2.4. Characterization

X-ray powder diffraction (XRD) experiments on S1, S2, W-doped cobalt nanoparticles, and Mo nanoparticles, respectively, were conducted to identify the phases in the products and lattice parameters. The shell-core structures of the nanocapsules S1, S2, and S3 were investigated by using high-resolution transmission electron microscopy (HRTEM) (Jeol type JEM2010).

3. Results and discussion

3.1. Multi-layered WS2(CoS/CoO) nanocapsules

Fig. 1 shows the XRD spectra of the precursor metal nanoparticles and the final sulfuration products. Cobalt and cobalt oxide could be indexed in the XRD spectra of the precursor cobalt nanoparticles, as shown in Fig. 1c. The presence of the cobalt oxide in the precursor should be mainly ascribed to the evaporation of oxide in the commercial cobalt powders. Of course, when exposed to air, the atoms on the fresh surface of the metallic cobalt nanoparticles would also be partially oxidized by oxygen. Although no tungsten has been detected by XRD in the cobalt nanoparticles, nonetheless, both the XRD and TEM results of S1 verified the presence of elemental tungsten in the precursor. In fact, during the arc discharge process, the 1.5 mm-diameter tungsten needle had been obviously shortened after the experiment, indicating the tungsten evaporation and thus doping to the cobalt nanoparticles.

Sample S1 consists of three phases, i.e. WS2, CoS and CoO, as shown in Fig. 1d. The HRTEM observations shown in Fig. 2, illustrate the structure and the phase distribution of the S1 nanoparticles. It is revealed that most of the S1 particles have core/shell structures, where the shell is the layered WS2. Although different shapes of the WS2 (CoS/CoO) nanocapsules are observed (Fig. 2.), their sizes are usually less than 95 nm, while the shells consist of 4–10 layers of WS2 sheets. For nanoparticles with polyhedral shape, WS2 sheets spread over the particle surfaces and thus apexes are formed (Fig. 2a). A smaller spherical nanocapsule (Fig. 2b) suggests that the spherical shape might be more stable for very small nanocapsules, owing to the annihilation of the WS2 dangling bonds. We attribute the formation of the elongated tubular nanocapsules to the large original particle size or possibly the contact of different particles (Fig. 2c). It is noticed that mismatch and breakdown of WS2 sheets are frequently observed at the apex areas and quite small nanocapsules. We attribute this phenomenon to the occurrence of internal pressure. The strain relief of the folding structure and the volume expansion during the sulfuration process may result in an internal pressure.

The growth mechanism of the WS2 (CoS/CoO) nanocapsules is not fully understood yet. However, it is clear that most of the WS2 phase is presented on the