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Synthesis and characterization of molybdenum disulfide micro-sized solid spheres

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Abstract Mono-dispersed molybdenum disulfide solid spheres with the diameter of 0.5–2 μm have been successfully synthesized by a solvothermal method with a homemade quaternary ammonium salt of 2-undecyl-1-dithioureido-ethyl-imidazoline (SUDEI) as surfactant. The obtained solid spheres are characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), respectively. The influences of reaction conditions are discussed while a mechanism is proposed to explain the formation of the peculiar morphology.

Introduction

Transition metal sulfides are a large family of materials that show many interesting properties. Some of them are superconductors [1], others produce fluorescence [2], and the others are good electrical conductors [3]. As a member of this family, MoS_2 has a sandwich interlayer structure formed by (S–Mo–S) layers in the direction [001] [4]. Within one layer its structure can be viewed as a two-dimensional macromolecule with each Mo ion surrounded by six sulfur anions. These layers are loosely bounded to each other by Van der Waals forces. Due to this structure, MoS_2 has numerous applications such as a useful catalyst for an electrode in high-energy density batteries [5], an intercalation host to forming new materials [6], and a useful solid lubricant for high vacuum applications [7]. For each of these applications, the important processes occur either at the surface or at the exposed edges of the MoS_2 layers [8].

Recently, completely amorphous hollow microtubes of molybdenum polysulfide and MoS_2 microspheres with uniform size of 200–300 nm were reported by Afanasiev et al. [9, 10]. Peng et al. [11] reported that they had synthesized tube-like and ball-like amorphous MoS_2 solvothermally in pyridine. Li et al. [12] synthesized MoS_2 with new morphological structure via a solution route, the as-prepared MoS_2 were uniform particles of 70 nm and exhibited randomly stacked layers at high magnification. Afanasiev et al. [13] prepared single-molecular-layer (SML) MoS_2 in aqueous solution in the presence of cetyltrimetylammonium chloride surfactant. Chen et al. [14] reported that they obtained spherical MoS_2 with average diameter of 400 nm by a sulfidization route from the oxides at 500 °C.

In order to improve the lubrication properties of MoS_2, it is supposed to be prepared with spherical structures. The sliding and rolling frictions exist simultaneously between the friction pairs to make the anti-wear and friction-reducing properties much better.

Here we report the synthesis of mono-dispersed solid spheres of micro-sized MoS_2 with the diameter of 0.5–2 μm by solvothermal method in the mixture of distilled water and ethanol in the presence of homemade surfactant SUDEI.

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Experimental

Preparation of surfactant SUDEI

The special surfactant—quaternary ammonium salt of 2-undecyl-1-dithioureido-ethyl-imidazoline (SUDEI) was synthesized by two steps. Firstly 2-undecyl-1-dithioureido-ethyl-imidazoline (UDEI) was synthesized based on the reference [15] in details, and then the preparation of its quaternary ammonium salt (SUDEI) was carried out in our lab: 15 g UDEI was dissolved in 40 ml toluene and the mixture was heated to 80 °C. Then 7.6 g epichlorohydrin was dropwised slowly into the system and the mixture was maintained at 80–85 °C for 3 h to give the needed surfactant—SUDEI after removing the solvent toluene by vacuum distillation.

Preparation of MoS_2 spheres

A typical procedure was as follows: 0.242 g sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), 0.182 g thiosemicarbazide (CH_5N_3S), 0.100 g hydrazinehydrade ($N_2H_4 \cdot H_2O$) and 0.280 g self-made SUDEI were put into a Teflon-lined stainless steel autoclave with capacity of 50 ml. Then 20 ml distilled water and 20 ml ethanol were used to fill the autoclave to 80% of its total volume. The autoclave was tightly sealed and maintained at 190 °C for 24 h, then cooled to room temperature naturally. The resulting dark powder was collected carefully and washed with distilled water and ethanol for several times to remove the residue of the reactants. Then the final products were dried in a vacuum at 50 °C for 5 h. The solid product was annealed under Ar flow at 500 °C for 2 h.

All the reagents used in the above procedures were of analytical grade without any further purification.

Characterization of samples

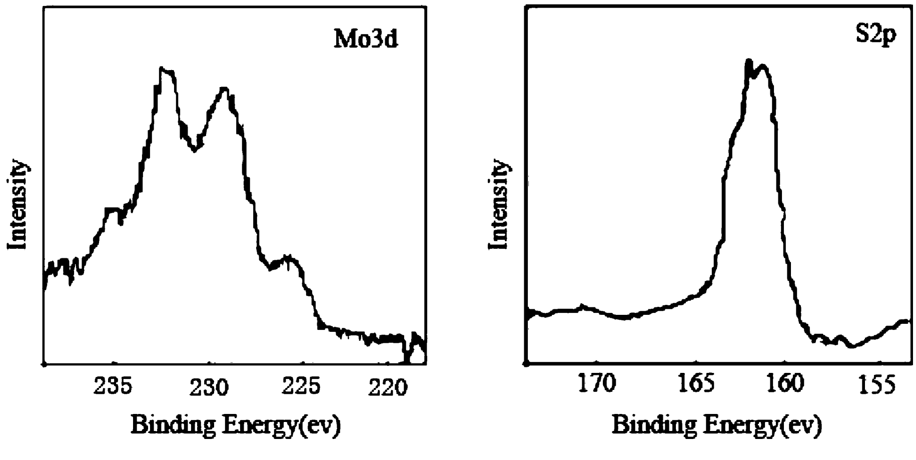
The X-ray photoelectron spectra (XPS) were performed on a PHI5702 X-ray photoelectron spectrometer. X-ray powder diffraction (XRD) patterns were recorded by a Japan Rigaku D/Max r-A X-ray diffractometer using Cu (Kα) radiation (λ = 1.54056 Å) operating at 40 kv and 30 mA with 2θ raging from 10 to 80°. The morphologies of the final products were observed by transmission electron microscopy (TEM) using a JEOLJEM-2000EX transmission electron microscope. The scanning electron microscopy (SEM) was taken on a JSM-5600LV microscope.

Results and discussion

XPS measurements of the so-prepared MoS_2 sample (see Fig. 1) indicate that the binding energies of Mo 3d 5/2 and 3/2 are 228.1 and 232.3 eV, respectively. Indeed, according to the literature [16], the signal with Mo 3d 5/2 Binding Energy (BE) of ~229 eV and lower can be attributed to Mo (IV) sulfide, whereas Mo (V) should have ~1 ev higher BE value. The peaks at 161.70 eV for S 2p is close to previous report [17]. The quantification of the Mo (3d) and S (2p) peaks gave the ratio of Mo:S of 1:1.89, close to the composition of MoS_2. The presence of surfactant SUDEI does not affect strongly the S/Mo ratio in above uncalcined sample.

The XRD patterns of the so-prepared MoS_2 samples with SUDEI (Fig. 2b) and without SUDEI (Fig. 2a) show only a broad weak envelope beginning at about 2θ = 30° and continuing out above 65°. The [002] peak at 2θ = 14.4° indicates the stacking of the single layers. The two maxima approximately locate at [100] and [110] positions of bulk 2H-MoS_2 [18]. However the absence of [002] diffraction at 2θ = 14.4° in Fig. 2b indicates that the stacking of the single layers has not

Fig. 1 XPS of the so-prepared micro-sized MoS_2



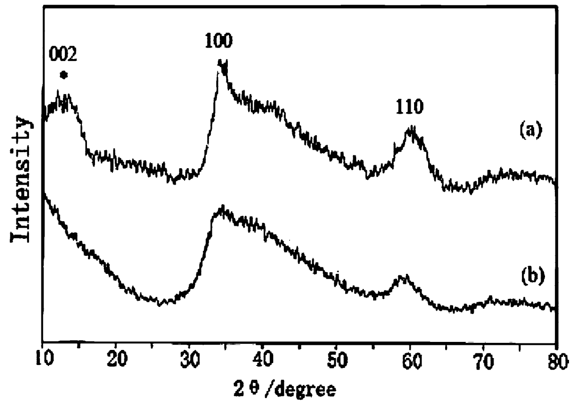


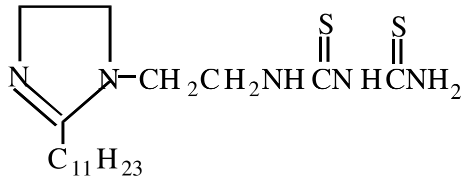
Fig. 2 Powder X-ray diffraction patterns of the products obtained by solvothermal method at 190 °C for 24 h then calcined at 500 °C for 2 h under Ar flow, (**a**) sample without SUDEI; (**b**) sample with 7 g/l SUDEI. Marked peak (*) indicates the (002) line, corresponding to the layer stacking

taken place when using surfactant SUDEI. The XRD pattern of the sample with 7 g/l SUDEI (Fig. 2b) is in good agreement with that of the single-molecular-layer MoS_2 [19]. According to the literature [13], the decrease of MoS_2 layer stacking due to the presence of organic compound seems to be a general phenomenon. The carbonaceous matter of any origin prevents the crystallization of the sulfide. The role of the organic molecule is rather that of scaffolding and preventing the agglomeration of layered MoS_2.

Figure 3 show the images of the so-prepared samples. SEM (Fig. 3b) study suggests that mono-dispersed spherical morphology of MoS_2 is obtained. Transmission electron micrographs are displayed in Fig. 3a, c. The morphology of the samples modified by SUDEI (Fig. 3a) shows the micro-sized spherical structure. Figure 3c shows the TEM image of the so-prepared samples which calcined at 500 °C for 2 h under Ar flow. It is obvious that the morphology and the size of the product are kept during the annealing process. It is evident that the texture of the so-prepared MoS_2 spheres is stable, which might be attributed to the presence of surfactant SUDEI.

It is well-known that the regular morphology of MoS_2 is thin platelet. In order to disclose the forming mechanism of MoS_2 micro-sized spheres, the effects of the SUDEI concentration on the synthesis of MoS_2 are investigated. It can be found that when the concentration of SUDEI is varied systematically from 0 to 9 g/l under the same condition, the as-obtained samples are of different morphologies. As showed in Fig. 4a, the product obtained without SUDEI consists of the aggregation of MoS_2 particles with thick platelet morphology. As the SUDEI concentration is increased to 4 g/l, the obtained samples (Fig. 4b) are aggregation of particles similar to spheres. Figure 3a presents the typical TEM image of MoS_2 products obtained at the SUDEI concentration of 7 g/l, which are micro-sized spheres with diameter of 0.5–2 μm. If the SUDEI concentration is further increased to 9 g/l, we can see the product (Fig. 4c) is composed of large agglomerates and spheres structure is not clear. Therefore, we proposed that the amount of surfactant SUDEI added in the system is responsible for the formation of such unusual morphologies.

The synthesis of UDEI and its corrosion inhibiting effects on 20G, A_3 and X_{20} steels in the medium of hydrofluoric acid, hydrochloric acid and citric acid have been described in details in the reference [20]. As an excellent corrosion inhibitor, its corrosion inhibiting mechanism is based on the multi-centered chemical absorption sites. However, no study on its application in the preparation of nano-materials has been reported so far. Its structure is showed as following:



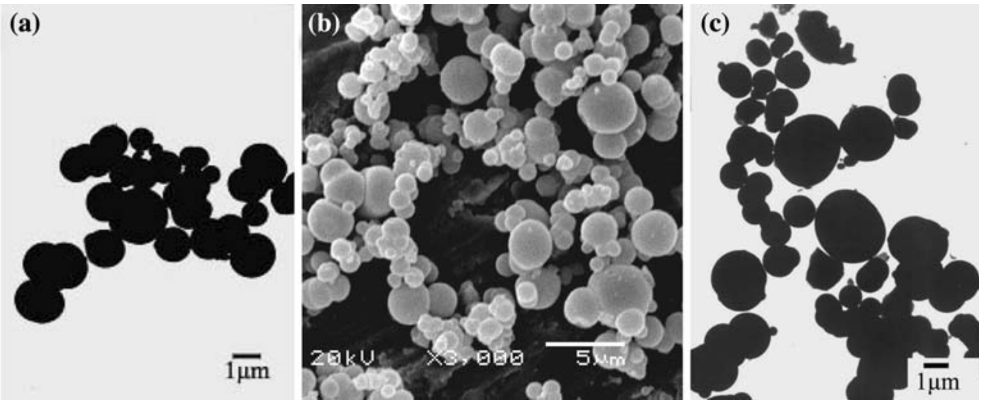


Fig. 3 Morphology of the micro-sized MoS_2 solid spheres: (**a**) TEM image of the sample with 7 g/l SUDEI; (**b**) SEM image of the sample with 7 g/l SUDEI; (**c**) TEM image of the sample with 7 g/l SUDEI after calcined at 500 °C for 2 h under Ar flow

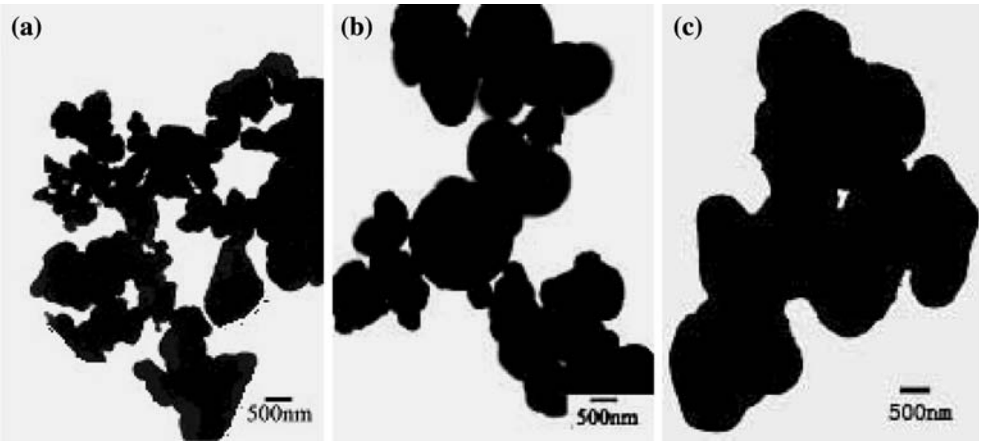


Fig. 4 TEM images of prepared MoS_2 at various concentration of SUDEI (**a**, without SUDEI; **b**, with 4 g/l SUDEI; **c**, with 9 g/l SUDEI)

After adding epichlorohydrin to UDEI, we have synthesized the surfactant—SUDEI used in this paper. Based on the special structure–property relationship of SUDEI, we infer that the mechanism for the formation of the spherical MoS_2 is probably as follows:

(1) The length of the hydrophilic segmer in SUDEI is similar to that of the lipophilic segmer. The hydrophilic segmer with seven non-carbon atoms has multi-centered chemical absorption sites, which have strong absorbing force on the formed MoS_2 particles. Due to the p-π conjugative structure between the two C = S π bandings, the p-π effect make the new formed MoS_2 particles absorbed at many places on the hydrophilic segmer, and imidazoline ring.
(2) During the absorption of MoS_2 initial particles on the SUDEI, more new-formed MoS_2 particles will be absorbed simultaneously. The large-volumed hydrophilic segmer and the long slim lipophilic segmer make the aggregated structure produce a certain curvature in the polar solvent.
(3) The successful preparation of MoS_2 micro-sized spheres can be guaranteed by reasonable materials ratio and solvothermal conditions. When the concentration of SUDEI is 4 g/l, spheres-like MoS_2 aggregates are formed as showed in Fig. 4b. While in the system of 7 g/l SUDEI showed in Fig. 3b, mono-dispersed spheres with the diameter of 0.5–2 μm are obtained. When the concentration of SUDEI is further increased to 9 g/l (Fig. 4c), large agglomerates occur, which might be attributed to the aggregation of large amount of SUDEI.

In a word, the three processes (the aggregation of SUDEI, the formation of MoS_2 particles and the absorption of SUDEI on MoS_2) take place simultaneously to give so-called ‘‘organic–inorganic hybrid micelle’’ [21]. Our lab has discussed the forming mechanism of ZnS hollow spheres by solvothermal method from pure ethanol solution in the presence of SUDEI in details [21], where the concentration of SUDEI played also an important role in controlling the morphology of the products. When the concentration of SUDEI was 2 g/l, ZnS hollow spheres could be obtained; while the hollow structure disappeared at 4 g/l SUDEI and the ZnS products became submicro-sized spheres. In this article, we have obtained mono-dispersed MoS_2 spheres at 7 g/l SUDEI and no hollow structure appears. We infer that SUDEI has different aggregation behavior in different solvents (here is alcohol: water = 1:1(v/v)). The different aggregation behavior and concentration of SUDEI as well as the different absorbing effects of SUDEI on MoS_2 result in the different morphology from that of ZnS.

Conclusions

We have presented here a solvothermal method to obtain micro-sized MoS_2 spheres. The presence of the homemade surfactant SUDEI was crucial to obtaining the interesting spherical morphology of the product MoS_2. XRD patterns indicated that the so-obtained MoS_2 was made up of single layer and layer stacking had not taken place. TEM images revealed that if the concentration of SUDEI was appropriate, mono-dispersed MoS_2 spheres could be obtained. The optimum concentration of SUDEI for the micro-sized spherical morphology of MoS_2 is 7 g/l. We expect that this convenient synthetic route to spherical MoS_2 may be extended to the synthesis of other materials.

The tribological behaviors of the so-obtained MoS_2 sphere and its application in the lubrication field have been investigated in our lab, showing an excellent anti-wear and coefficient reducing properties. Investigations of this aspect will be reported in our next paper.

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