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SYNTHESIS AND CHARACTERIZATION OF MoS_2 NANOCOMPOSITES BY A HIGH PRESSURE HYDROTHERMAL METHOD

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In this paper, different morphologies of MoS_2 were successfully synthesized with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as precursor under hydrothermal conditions related with pressure in the range of 0.1-3.5 Mpa, the morphology and phase structure were examined by means of scanning electron microscopy, and X-ray diffraction. The effects of reaction time, imposed pressure on the evolution of phase and morphology were investigated. It was found that the pressure plays a significant role in the formation of "flower-like" balls, and "flower-like" plank. A possible mechanism was used to explain the formation of the resultant MoS_2. As claimed by the results, pressure could offer a very powerful way to synthesis of novel morphologies. The present study attempts to shed some light on the roles that pressure play in influencing the microstructures of the molybdenum disulfide particles.

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1. Introduction

Transition metal sulfide (MoS_2) crystal has a sandwich interlayer structure formed by stacking of the (S-Mo-S) layers in [001] direction [1]. These layers are loosely bound to each other only via van der waals forces, which accounts for easy cleavage of (S-Mo-S) layers in the direction of [001]. MoS_2 with the layered structure attracted considerable attention for the application as a solid lubricant [2], hydrodesulfurization catalyst [3], nonaqueous lithium batteries [4], and for special applications in space [5]. In last decades, many efforts have been contributed to prepare MoS_2 in a nanometer scale, and research theirs physicochemical properties and applications [6]. Various synthetic methods for the IF-MoS_2 have been brought forward, such as solid-gas or gas phase reactions [7, 8], electron-beam irradiation activation and arc discharge [9, 10], thermal decomposition [11], hydrothermal or solvothermal synthesis [12], sonochemical process [13], and template synthesis [14]. By these methods, peoples can obtain MoS_2 nanocrystalline with various morphologies, such as nanoparticles [15, 16], nanowires [17], nanotubes [18], nanorods [19] with inorganic fullerene-like structures. For example, Tenne and co-workers reported the production of

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IF-MoS_2 by the reaction between MoO_3 and H_2S in a stream of forming gas (typically 5% H_2 / 95% N_2) at high temperature (about 850 ^oC) [20, 21]. Li *et al* obtained MoS_2 nanotubes and fullerene-like nanoparticles by the reaction of MoO_3 nanobelts and S in an argon atmosphere at 850 ^oC [22]. Rao and co-workers obtained MoS_2 nanotubes by simple heating MoO_3 in a steam of hydrogen under a high temperature (1300 ^oC). MoS_2 nanorods have been successfully synthesized by sulfidation of the MoO_3 nanofibers under a H_2S/H_2 steam at 350~600 ^oC [23]. Recently, peoples devoted their works to synthesis the different sizes, morphologies, structures and properties of MoS_2 materials [24, 25]. In contrast, among the synthesis method mentioned above, the hydrothermal technique is an ideal route for synthesizing various nano-sized materials with high purity and controlled structure at relatively low reaction temperature [26]. However, because of the limitation of the equipments, most of the studies have only considerate the influence of the temperature, precursors and the time of reaction on the as-synthesized materials. Up to now, the influence of pressure in the stainless steel autoclave on the properties of MoS_2 has not been reported.

In this letter, we improved on the conformation of the autoclaves, obtained different morphologies MoS_2 nanoparticles (by a high pressure hydrothermal method) under certain pressure and investigated the physicochemical properties of as-prepared products by changing the imposed pressure of the autoclaves. The effects of reaction pressure on the evolution of MoS2 synthesis and the morphology are discussed.

2. Experimental

High-pressure hydrothermal synthesis was performed in a purpose-designed autoclave where pressure was provided by Argon. A typical synthetic procedures were as follows: 0.88 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and 2.64 g $NaS_2\cdot 9H_2O$ were mixed within 10 ml distilled water and then added into a 30 ml stainless steel autoclave which was filled with 0.6 M HCl solutions up to 70~80% of total volume. The autoclave was heated to and maintained at 200 ^oC with a certain constant pressure. The resulting products were separated from the solution by centrifugation, washed several times by distilled water and absolute ethanol, and dried in a vacuum at 80 ^oC.

The final products were characterized by various techniques. The X-ray powder diffraction (XRD) were recorded with an X-ray diffractometer (XRD, Rigaku D/max-rA) using Cu Kα radiation (λ=1.5418 Å). Data was collected in steps of 0.05^o with a count time of 1 s, at an operating potential of 40 kV and a current of 100 mA. The morphologies of the products were observed by field emission scanning electron microscopy (FESEM, JEOL JSM-6700 F) and transmission electron microscopy (TEM, H-800 at an accelerating voltage of 200 kV). The optical properties of obtained MoS_2 were measured using an UV-vis spectrophotometer (Analytic jena AG, Specord 200) in the wavelength range of 300~800 nm.

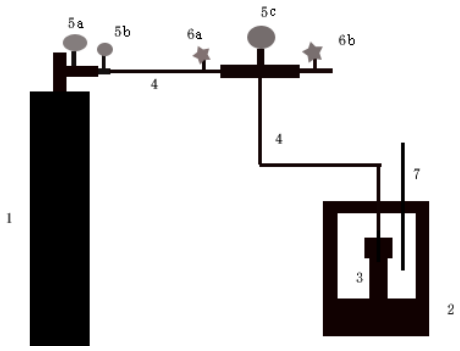

Fig. 1. Schematic diagram of the purpose-designed equipment in our research：1. Argon tank; 2. Furnace；3. Stainless steel autoclave；4. Copper tube；5. Vacuumatic pressure gauge； 6. Vacuum fold valve; 7. Thermocouple. (Part 1: It is the pressure source, which provides pressure to the stainless steel autoclave. Part 2: The furnace can provide and keep a certain temperature to the autoclave. Part 3: The stainless steel autoclave is the reaction container, which make sure the precursor solution tightly sealed. Part 4: This part is used as a tube, which can transport the argon to the autoclave. Part 5: The significance of this part is to indicate the magnitude of the pressure. Part 6: It is the leak valve that can make the argon leak out from the system after the reaction. Part 7: We can obtain the temperature of the autoclave from it.)

3. Results and discussion

The crystal structure and phase purity of the samples were characterized by XRD. Fig. 2 shows the XRD patterns of as-obtained MoS_2 samples under different imposed pressure. The major detectable diffraction peaks can be readily indexed to the hexagonal phase of MoS_2 consistent with the standard powder diffraction file of MoS_2 (JCPDS 37-1492), and there is no obvious peak from impurity. Moreover, the intensities of the diffraction peaks of MoS_2 changed significantly under different imposed pressures. With a further increase in the reaction pressure to 3.5 MPa, XRD pattern (Figure. 2e) shows that the intensities of diffraction peaks of MoS_2 increase. As shown in Fig. 2, the high and sharp peaks reveal that the sample was well crystallized. The higher the imposed pressure is, the better the crystallized products will be. The high and sharp diffraction peak of (002) of the as-prepared MoS_2 samples indicates the formation of well-stacked layered structure of MoS_2 during the hydrothermal process.

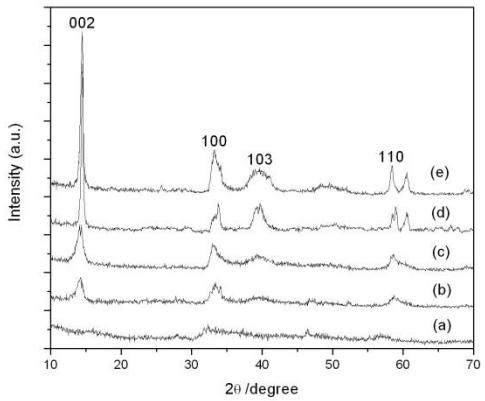

Fig. 2. XRD patterns of the MoS_2 prepared at different initial pressures: (a) 0.1 Mpa; (b) 1.0 Mpa; (c) 2.0 Mpa; (d) 3.0 Mpa; (e) 3.5 Mpa

The FESEM images of as-prepared samples were presented in Fig. 3. The given pressure was investigated from 0.1 to 3.5 Mpa. From Fig. 3a, it can be seen that when the autoclave did not imposed pressure (the initial pressure is 0.1 Mpa), the final pressure for balance in the autoclave was 1.2 Mpa, the morphologies of MoS_2 were disordered, and nanorods, nanospheres and nanoflakes were included. When putting 1.0 Mpa Ar into the autoclaves, the final pressure is 2.5 Mpa (Fig. 3b). The nanorods and nanoflakes disappear, the products are spherical with an average diameter of 400 nm, and the surfaces of the MoS_2 spheres are composed of nanoflakes. Fig. 3c shows the morphology of the product with the initial pressure and balance pressure are 2.0 Mpa and 3.6 Mpa, respectively. The morphologies of the products are all the same with Fig. 3b except the width of the nanoflakes is 20 nm, which thinner than that with the initial pressure is 2.0 Mpa (Fig. 2b). Fig. 3d shows the situation of the initial pressure is 3.0 Mpa, and the balance pressure is 4.9 Mpa, the morphologies of the samples mainly contain nanoflowers and few nanospheres with the nanoflakes on the surface are also exist (shown in Fig. 3d). When the initial pressure increased to 3.5 Mpa (the balance pressure came to 5.8 Mpa (fig. 3e)), all the morphologies of products are nanoflowers with a width of 10~20 nm. Fig. 3f is the amplificatory image of the Fig. 3e.

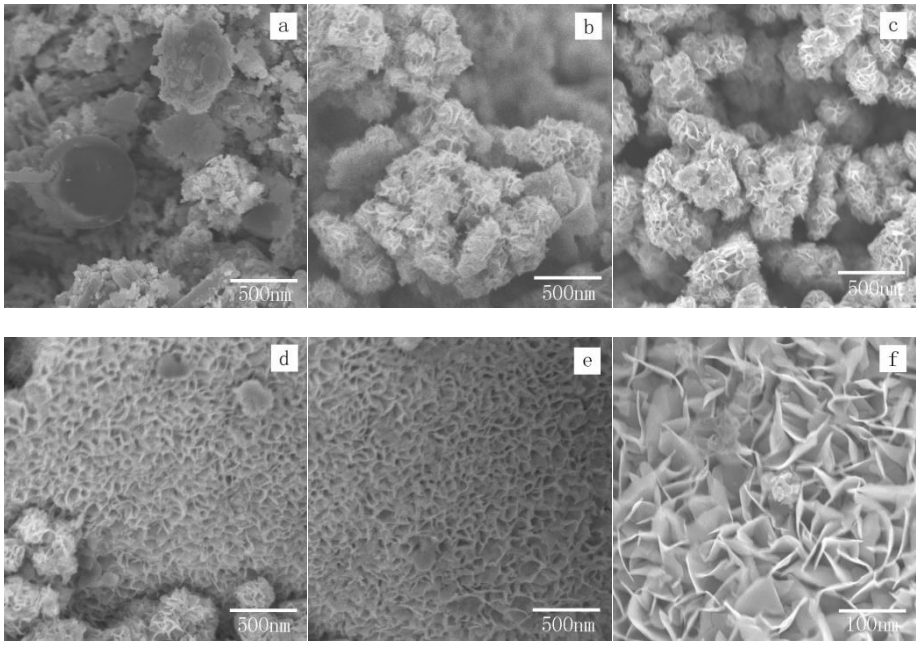

Fig. 3. FESEM images of as-prepared sample prepared under different initial pressure. (a) 0.1 Mpa; (b) 1.0 Mpa; (c) 2.0 Mpa; (d) 3.0 Mpa; (e) 3.5 Mpa; (f) amplificatory image of 3.5 Mpa

Fig. 4 shows the TEM images of as-synthesized products with irregular shapes at high pressure (3.0 and 3.5 Mpa). It can be noted that both of samples have similar "rag-like" morphologies just like those reported by Yiya Peng *et al* [27], which looked like aggregates of flocculate. Fig. 4a and Fig. 4b are the TEM images of samples which has fabricated at the pressure of 3.0 Mpa and 3.5 Mpa, respectively. It can be seen that the "rag-like" in Fig. 4b is thinner than that in Fig. 4a, which is agree with the results mentioned from the FESEM images.

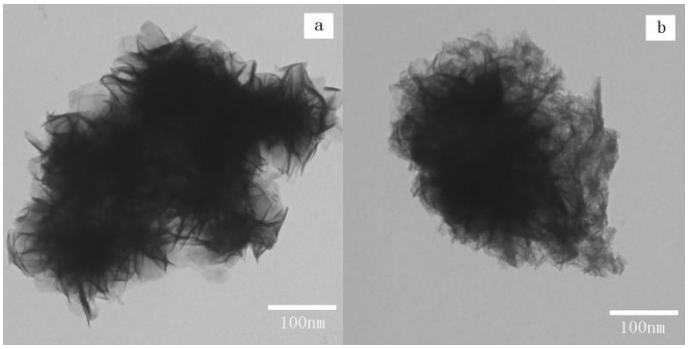

Fig. 4. TEM images of the sample prepared at different reaction pressure: (a) 3.0 Mpa; (b) 3.5 Mpa

The optical absorption property was investigated with room temperature UV-vis spectroscopy, and Fig. 4 shows the optical absorption spectra of the samples prepared at different imposed pressures. As shown in Fig. 4a, there are no obvious characteristic absorption spectra of

MoS_2 except a weaker absorbance at 350~400 nm with the initial pressure of 1.0 Mpa. Fig. 4b-4d represent the optical absorption spectra of the products at different initial pressures of 2.0, 3.0, 3.5 Mpa. As the pressure increasing, the absorption band at 380 nm became more intense, a weak and noisy peak at 610 nm appears when the initial pressure promoted to 3.0 Mpa (Fig. 4c). When the initial pressure is up to 3.5 Mpa, it typically display a strong, broad absorption with a maximum centered at 365 nm and two weaker absorptions at 610 and 650 nm. The spectral data are similar to the reported results by Tenne [28], who described two peaks in the region at 616.3 and 667 nm, as well as a strong absorption centered at 380 nm. As the pressure increasing, however, the spectra of as-prepared MoS_2 in our case appear to be blue shift in contrast with respect to the data obtained by Tenne. This spectra transition behavior of nanocrystalline could be explained as a function of the particle "size and shape" [29], which is consistent with the result of the foregoing statement. From Fig. 4, it can be concluded that the initial pressure of the autoclave plays a key role on the optical absorption properties of products.

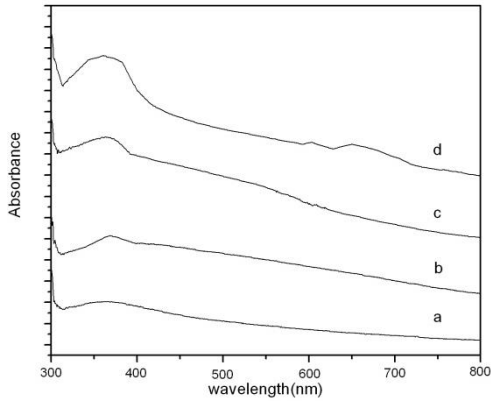

Fig. 5. UV-vis absorption spectra of as-prepared samples prepared with different initial pressures: (a) 1.0 Mpa; (b) 2.0 Mpa; (c) 3.0 Mpa; (d) 3.5 Mpa

In our case, we observed that the physicochemical properties of the as-prepared products were closely related to the initial pressure. We thought that the changing of the initial pressure have a significant effect on the morphologies and optical properties of the products. Considering the structure of the single-layer MoS_2 prepared by this method, the mechanism could be explained as follows. The single layers of the as-prepared MoS_2 had the ability to adsorb substances on their surface, such as H_2O and NH_3, and some substances could stabilize the single layers. As the pressure increasing, however, the interaction between the adsorbed substances and the single layers became stronger and stronger and prevented the single layers from stacking. In this case, the morphologies of the products would be changed to fit in with the circumstance which influenced by the pressure. Thus, it can be seen from the FE-SEM images, the morphologies of the as-prepared MoS_2 have changed from the nanorods and nanospheres to the nanoflowers, and the petal of the nanoflowers became thinner and thinner with the initial pressure increasing.

If the model actually reflects what happened in the autoclaves. It seems to indicate that when a pressure is acted on nanomaterials, the effects may be different from the bulk. Therefore, the high pressure hydrothermal synthesis is an important method to research nanomaterials under

high pressure, especially those with layered structure. New properties of materials, even new structures, may be found through this method.

4. Conclusion

In summary, MoS_2 nanocrystals with different morphologies have been synthesized by changing the reaction initial pressure at 200 ^{o}C under hydrothermal condition. The products were investigated by XRD, FESEM and TEM. The UV-vis absorption spectra were performed to study the optical properties of the products, and the spectra characters of blue shift have been found. A mechanism of the phenomenon in our experiments was also proposed.

Acknowledgments

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