Front. Chem. China 2009, 4(2): 173–176
DOI 10.1007/s11458-009-0025-8

RESEARCH ARTICLE

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Flowerlike MoS_2 nanoparticles: solvothermal synthesis and characterization

Abstract Flowerlike MoS_2 nanoparticles have been successfully synthesized through a mild solvothermal reaction with the aid of ethanol aqueous solution, and the samples have been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and low temperature nitrogen adsorption-desorption. The nanometer flower MoS_2 is composed of ultrathin nanosheets of approximately 10 nanometers in thickness. The influence of the reaction temperature and the reaction time on the formation of the flowerlike MoS_2 nanoparticles were evaluated. The optimal experimental conditions were determined as follows: the molar ratio of 1∶1 between ethanol and water, the reaction temperature of 190°C, and the reaction time of 24 h.

Keywords nanometer flower MoS_2, solvothermal synthesis, characterization

Molybdenum disulfide (MoS_2) crystal has a sandwich interlayer structure formed by stacking of the (S–Mo–S) layers in the direction (001). These layers are loosely bound to each other only by Vander Waals forces, which account for easy cleavage of the (S–Mo–S) layers in the direction (001). This compound, due to its unique and unusual physical and chemical properties based on the extreme degree of anisotropy in their structures is known as hydrodesulfurization catalysts [1,2], lubricants due to exhibition of excellent friction and wear resistance and extended lifetime in vacuum [3,4], in photo electrochemical cells for solar energy conversion applications [5], an efficient electrode material in high energy density batteries [6], an intercalation host to form new materials with modification of physical properties [7,8], and for special applications scanning tunnel microscope [9].

In recent years, MoS_2 has received a considerable amount of attention due to its novel properties. A number of the preparation methods on promising MoS_2 materials including nanowires, nanotubes [10–16], microscale spherical [17], fullerenelike [18], hollow spheres [19], and nanometer flowers [20] have been reported during the last decade.

With the development of the preparation method and the mechanism research of the low-dimensional nanomaterials, it is realized that the crystal aeolotropic structure is very important to synthesize low-dimensional nanomaterials, and the external environment grows the regulative function to it. Li [20] synthesized MoS_2 nanometer flower with crystal aeolotropic structure using chemical vapor deposition (CVD) method. In this article, the nanometer flower MoS_2 has been prepared by solvothermal synthesis method using sodium molybdate, thiourea, and hydroxylamine hydrochloride as the precursors. In this low temperature approach, thiourea acts as a sulfur doner, and hydroxylamine hydrochloride is the reducing agent. The samples have been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and specific surface area (BET).

1 Experiments

1.1 Reagent and apparatus

The sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), thiourea ($CS(NH_2)_2$), hydroxylamine hydrochloride ($NH_2OH \cdot HCl$), and ethanol were analytical grade and were purchased from the Shanghai Chemistry Corporation. All chemicals were used without further treatment.

The products are characterized by XRD, SEM, and BET. The XRD patterns were recorded by a Japan Rigaku D/max B X-ray diffractometer using Cu (Ka) radiation operating at 40 kV and 30 mA with 2θ ranging from 10°C to 90°C. SEM images were taken with a JEOL-JSM-6700F

Translated from *Chinese Journal of Inorganic Chemistry*, 2008, 24(6) (in Chinese)

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scanning electron microscope. The nitrogen adsorption–desorption isotherm was measured on a Chemsorb-3000 apparatus.

1.2 Preparation of MoS_2 nanoflower

In the typical solvothermal synthesis, 4 mmol $Na_2MoO_4 \cdot 2H_2O$ was dissolved into 60 mL ethanol aqueous solution (the ratio of ethanol and water is 1 : 1) under stirring. 8 mmol $NH_2OH \cdot HCl$ and 8 mmol $CS(NH_2)_2$ were introduced into the above solution under continuous stirring for about 10 min. Finally, the total resultant solution was transferred into a teflon-lined stainless steel autoclave with a capacity of 100 mL and then sealed and maintained at 190°C for 24 h. After the solvothermal process, the autoclave was cooled to ambient temperature naturally. A black precipitate was retrieved from the solution, centrifuged, and then washed with distilled water for several times to remove the ions possibly remained in the final products and finally dried at 50°C in a vacuum drying oven. The dry sample was annealed in nitrogen atmosphere at around 500°C for 5 h.

2 Results and discussion

2.1 The influence of solvothermal synthesis conditions on the MoS_2 crystalline

In order to disclose the influence of the formation of nanometer flower MoS_2, the effects of the reaction temperature and the reaction duration were investigated, respectively.

Figure 1 displays the X-ray diffractogram of the samples obtained under solvothermal conditions at 190°C for durations of 6, 12, 18, and 24 h and subsequently annealed at 500°C for 5 h under nitrogen atmosphere. It clearly indicates that after the 6, 12, and 18 h duration, the products contain diffraction peaks due to the presence of MoO_2 as impurity (JCPDS Card 5–452). It is also observed from Fig. 1 (a–d) that the intensity of the diffraction peaks due to MoS_2 keeps on increasing, and the intensity of the diffraction peaks of MoO_2 keeps on decreasing with the duration for the formation of hydrothermal products. When the reaction time is 24 h, the diffraction peaks of MoO_2 disappear, and some diffraction peaks at $2\theta = 13.9°$, 34.5°, and 60.4° could be indexed on the basis of 2H-MoS_2.

Therefore, it appears that at the initial stage of reaction, hydroxylamine hydrochloride, which acts as a reducing agent, reacts with a part of the sodium molybdate giving MoO_2. This MoO_2 subsequently reacts with S^{2-} obtained from the reaction of thiourea in ethanol aqueous media transforming MoO_2 to MoS_2 [21].

The reaction temperature dependence of the formation of nanometer flower MoS_2 in solvothermal products was obtained for the temperatures 150, 170, 190, and 210°C

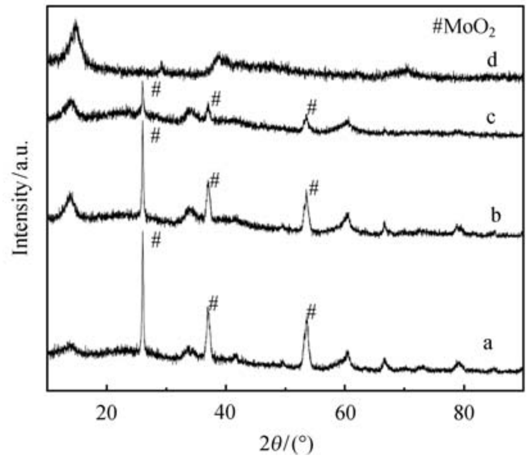

Fig. 1 XRD patterns of MoS_2 prepared under different reaction time. (a) 6 h; (b) 12 h; (c) 18 h; (d) 24 h

and was subsequently annealed at 500°C for 5 h under nitrogen atmosphere. The corresponding XRD patterns are shown in Fig. 2 (a–d). All the reflections except the one obtained at 150°C can be readily indexed as hexagonal 2H-MoS_2, identical to the reported data in the JCPDS cards (37–1492). As to the sample obtained at 190°C, there was a small peak with 2θ of 13.9° corresponding to diffraction from the (002) plane of crystalline MoS_2. The data showed that only several layers of MoS_2 layers stack along this direction. The diffraction peaks of MoO_2 were comparatively much more imperfect. It suggested that the transformation from MoO_2 to MoS_2 at 190°C took place entirely.

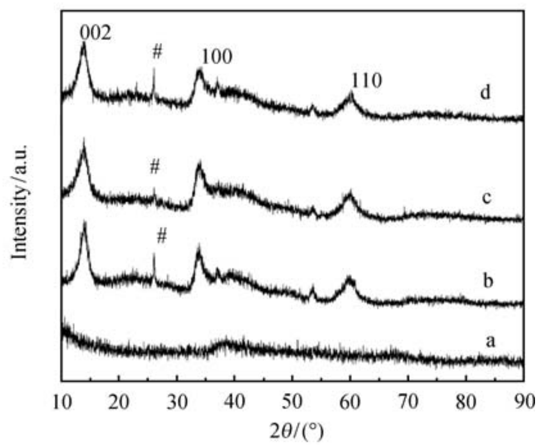

Fig. 2 XRD patterns of MoS_2 prepared under different temperature. (a) 150°C; (b) 170°C; (c) 190°C; (d) 210°C

Under the experimental conditions, the formation of flowerlike MoS_2 nanoparticles is a slow and mild process. For obtained well-crystalline product, the optimum reac-

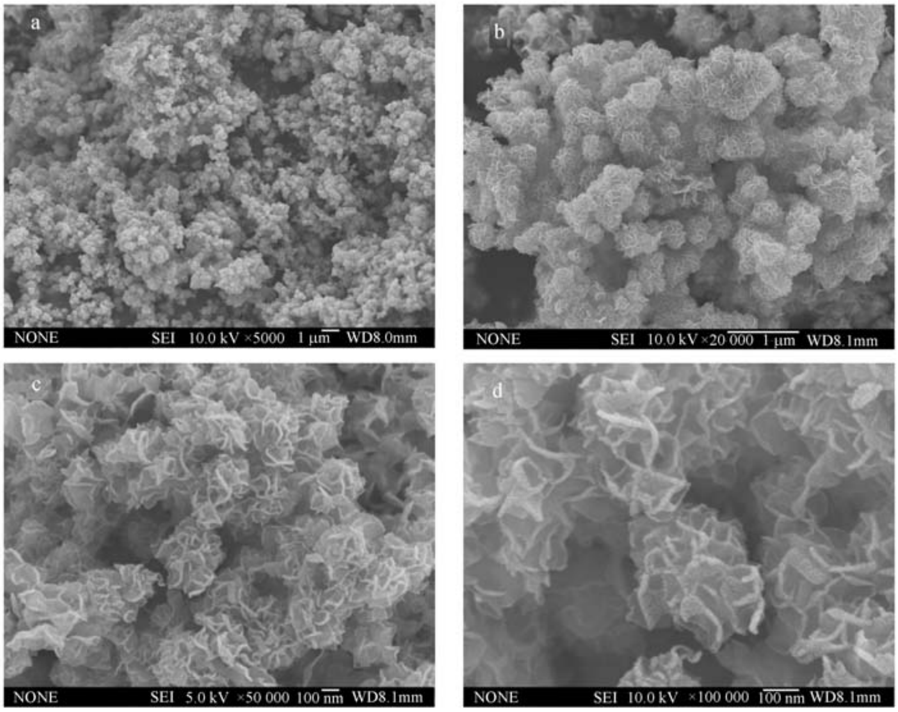

Fig. 3 SEM images of MoS_2 flowers at different magnifications

tion temperature was 190°C, and the optimum reaction time was 24 h.

2.2 Characterization of the flowerlike MoS_2 nanoparticles

Figure 3 represents the typical SEM images of samples at low and high resolution respectively taken for the optimum experimental conditions when subjected to the heat treatment at 500°C in nitrogen atmosphere. It can be seen that the as-prepared sample consists of a large quantity of fairly uniform particles with the average size of about 200–300 nm in diameter [Fig. 3(a)]. The high magnification SEM images [Fig. 3 (b–d)] reveal that all the MoS_2 particles have flowerlike morphology. The flower-like MoS_2 nanoparticle is composed of the ultrathin nanosheets of about 10 nanometers in thickness; some small nanosheets random situate in the center of the flower, and some large nanosheets surround these small ones. The nanosheets intersect with each other.

It can be seen from the XRD patterns of sample showed in Fig. 2(c) that all these diffraction peaks could be indexed on the basis of 2H-MoS_2 (space group P63/mmc). After refinement, the cell constants ($a = 0.31616$ nm, $c = 1.22985$ nm) are in agreement to the reported values in the JCPDS cards (JCPDS Card 37–1492). The presence of a (002) peak of high intensity in this thermally treated sample indicates the presence of well-stacked layered structure. A relative shift in the peak position of the (002) reflection from $2\theta = 13.9°$ to $2\theta = 14.4°$ is observed. This can be correlated in terms of the strain relief of the folded structure [22].

Figure 4 shows the N_2 adsorption-desorption isotherm of the as-synthesized nanometer flower MoS_2. It is found that the specific surface area of the nanometer flower MoS_2 is about 18 m^2/g calculated by the Brunauer–Emmett–Teller (BET) method. BET measurement results indicated that the MoS_2 has comparatively large surface area [23].

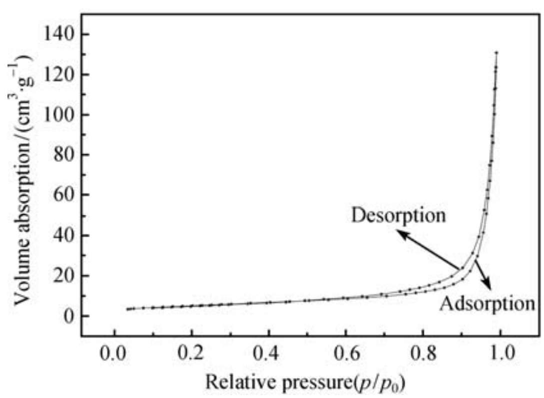

Fig. 4 N_2 adsorption–desorption isotherm of the MoS_2 flowers

3 Conclusion

An alternative route for the synthesis of nanometer flower MoS_2 through a mild solvothermal reaction with the aid of ethanol aqueous solution has been developed. The flowerlike MoS_2 nanoparticle is composed of the ultrathin nanosheets of about 10 nm in thickness. The nanometer flower MoS_2 has a specific surface area of round about 18 m^2/g. The optimum experimental conditions for the synthesis of the flowerlike MoS_2 nanoparticles were determined as follows: the molar ratio of 1:1 between ethanol and water, the reaction temperature of 190°C, and the reaction time of 24 h. The product has a special flowerlike architecture and a relatively large surface area.

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