硫粉为硫源，多元醇辅助合成硫化钼纳米片

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摘要：本文以普通硫粉和钼酸钠为原料，通过两相法在 170–200 °C 下经 8 h 制备得到二硫化钼纳米片，同时基于聚集-聚并模型提出其三步法生长机理。其中，硫粉的再组装保证了其向 H₂S 的转化，使钼酸钠得以还原，因此在本方法中起到关键作用。本法制备得到的硫化钼纳米片富含可能由于各种位错引起的未饱和硫原子，有利于其在催化加氢等领域的应用。此外，由于二维过渡金属硫族化合物结构相似，所以本方法及其机理可能同样适用于其他二维过渡金属硫族化合物。本方法为绿色、便捷制备二硫化钼纳米片提供了一个选择。

关键词：二硫化钼纳米片；硫粉；聚集和聚并模型；乙二醇；两相法

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Polyol-Mediated Synthesis of MoS₂ Nanosheets Using Sulfur Powder as the Sulfur Source

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Abstract: MoS₂ nanosheets are prepared with sulfur powder and Na₂MoO₄ by a one-pot two-phase method at 170–200 °C for 8 h. In addition, a three-step growth mechanism based on the aggregation and coalescence model is proposed. The reassembly of sulfur powder ensures the transformation from sulfur powder to H₂S to reduce Na₂MoO₄ and plays a key role in the successful preparation of MoS₂ nanosheets. The as-prepared MoS₂ nanosheets are rich in unsaturated sulfur atoms, probably resulting from the dislocation cores of the MoS₂ nanosheets, which have been found to be beneficial for hydrogen evolution reaction catalysis. The method and growth mechanism adopted in this study may be applied to other transition metal dichalcogenides for similar structures. The facile and green method provides an alternative for the preparation of MoS₂ nanosheets.

Key Words: MoS₂ nanosheet; Sulfur powder; Aggregation and coalescence model; Ethylene glycol; Two-phase method

1 Introduction

Molybdenum disulfide (MoS₂) nanosheets have received increasing attention as a promising material for Hydrogen evolution reaction (HER) catalysis, energy storage, and semiconductor device because of its excellent chemical, physical, optical and

electrical properties and low cost during the last decades^{1–4}. However, the HER activity of MoS₂ nanosheets, as has been reported by both experimental and theoretical studies, are limited to the density per unit surface area and turnover frequency of catalytically active edge sites^{5–13}. Therefore, many efforts have been

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devoted to prepare MoS₂ nanosheets with abundant exposed edge sites^{13–25}. However, the effective scale-up of MoS₂ nanosheets still remains a major challenge.

Currently, four main approaches have been employed to obtain MoS₂ nanosheets in laboratories^{14–25}, including micromechanical cleavage, chemical vapor deposition, Li ion intercalation, and liquid-phase exfoliation. The micromechanical cleavage method is reported to have low yield and time-consuming¹⁴. Chemical vapor deposition method, in spite of good crystallinity of the resulting MoS₂ nanosheets also has the limitation of its high cost, poor transferability and complex manipulation¹⁵. The latter two methods can be achieved by taking advantage of the sandwiched S-Mo-S layer structure of MoS₂ that are held together by weak van der Waals interaction. The interaction and hydration of lithium cations combined with the strong affinity of organic solvents or surfactants give rise to the exfoliation of MoS₂ in organic solvents^{16–20}, whereas it is still challenging for effective scale-up because of expensive intercalating agents used, long reaction time (at least several days), strict storage, high sensitivity to environment conditions, and possible structure deformations. The liquid-phase exfoliation of MoS₂ powder is achievable in appropriate organic solution or aqueous surfactants solution by means of sonication and centrifugation^{21–25}. Nevertheless, both organic solvents and aqueous surfactant exfoliated MoS₂ usually show multilayer stacks with size as large as 200–400 nm, which results in the reducing number of active sites. Moreover, the dispersed concentrations of resulting MoS₂ nanosheets are generally too low to require large quantities of exfoliated MoS₂ nanosheets. Due to the aforementioned limitations of approaches to obtain MoS₂ nanosheets, a green, convenient, low-cost, and large-scale approach for preparing MoS₂ has been pursued for a long time.

Herein, we report the preparation of MoS₂ nanosheets of with abundant active sites by a revised one-pot, polyol-mediated method for the first time and propose a three-step growth mechanism of the MoS₂ nanosheets based on the aggregation and coalescence model. Compared with the aforementioned methods, this method is proved to be able to prepare scale-up MoS₂ nanosheets more easily without any hazardous chemicals in 8 h, in which only sulfur powder, polyol (ethylene glycol, diethylene glycol), and

Na₂MoO₄ were used. Meanwhile, the size of nanosheets could be adjusted by changing the polyol-to-water ratio. More importantly, the growth mechanism may be suitable for other transition metal dichalcogenides (TMDCs).

2 Experimental

2.1 Chemicals and materials

Ethylene glycol (EG, ≥ 95%), diethylene glycol (DEG, ≥ 99%), absolute ethyl alcohol (≥ 99.7%), sublimed sulfur (≥ 98%), Na₂MoO₄ (≥ 99%) were purchased from Beijing Reagent Company. All chemicals were used as received, except for sublimed sulfur slightly ground before use. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was used as well, and MoS₂ syntheses were conducted in 50 mL PTFE-lined stainless autoclaves.

2.2 Synthesis of MoS₂ nanosheets

In a standard synthesis, 0.14 g ground sublimed sulfur and 0.36 g Na₂MoO₄ were added into a 50 mL PTFE-lined autoclave with 30 mL mixture of H₂O and polyol. Then the autoclave was sealed and heated at 170 °C in an electric drying oven for 24 h. The final black products were precipitated with DI water and absolute ethyl alcohol by centrifugation at 4000 rpm for 30 min thrice to wash out polyol and possible sulfur particles. The average yield is about 92%.

2.3 Characterization

X-ray diffraction (XRD) patterns of the samples were recorded with Cu K_α radiation (Bruker/AXS D8 Advance, Netherlands). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained by Hitachi SU8020 (Japan) and FEI Tecnai G2 F20 S-TWIN TMP (U. S. A.), respectively.

3 Results and discussion

3.1 Synthesis of MoS₂ nanosheets

Fig.1A shows that all the diffraction peaks of the MoS₂ nanosheets agree well with the hexagonal MoS₂ phase (JCPDS CARD No. 37-1492). These peaks are at approximately 2θ = 14.3°, 32.8°, 39.5°, 49.6°, 58.3°, 69.0°, which correspond to the (002),

Fig.1 (A) XRD patterns of obtained MoS₂ nanosheets at 170 °C for 8 h (red line: after calcination in N₂ at 400 °C for 4 h, black line: before calcination); (B) TEM image of obtained MoS₂ nanosheets at 170 °C for 8 h (color online)

(100), (103), (105), (110), (201) crystal planes, respectively. The high intensity of (002) peak implies the good stack of MoS₂ nanosheets. The broadened peaks (as black line shown) suggest the poor crystallinity of as-prepared sample. Fig.2B shows that the average length of as-prepared MoS₂ sheets are ca 150 nm with different width, when react at 170 °C for 8 h. The nanosheets are rich in unsaturated sulfur atoms due to the dislocations, which present as tiny rings^{11,26}, resulted from the random overlap of small nanoflakes composing nanosheets according to the aggregation and coalescence model^{27–35}. Similar structure had been proved to be beneficial for the HER catalysis^{11,12}, and Zhou *et al.*²⁶ has also provided a detailed classification for the dislocations.

3.2 Effects of reaction temperature and holding time on the formation of MoS₂ nanosheets

In our scheme, the reaction temperature plays a major role on the transformation of sulfur powder and the growth of MoS₂ nanosheets, and the holding time also matters much as it affects the density of unsaturated sulfur atoms. Generally, sublimed sulfur tends to aggregate into insoluble sulfur above 159 °C in open or close systems and totally precipitate owing to their large size (ca 20 μm). To avoid such case, the sublimed sulfur was ground for ca. 10 min were used in our protocol. The transformation of sulfur powder (composed of S₈) into low reactive liquid sulfur beads with appropriate holding temperatures in airtight autoclaves makes the preparation of MoS₂ nanosheets successful (detailed in Fig.S1 (Supporting Information (SI))). The liquid sulfur beads contains abundant long free radical chains (S_n), whose reactivity decreased with enhancing reaction temperature, which can reach to a maximum at ca. 190 °C³⁶. The liquids beads spread evenly in the whole polyol at last and subsequently reacted with polyol gradually, generating H₂S for reducing Na₂MoO₄. Therefore, a length nucleation occurred mainly due to the slow reaction between the low-activity (S_n) and polyol. For EG, the reaction begins at 160 °C and can be expressed as³⁷:

Fig.2(A–D) shows the improved crystallinity of the as-prepared MoS₂ nanosheets with increasing holding time. When the holding time was less than 7 h, most of time no MoS₂ nanosheet was obtained, but grey solutions. After 8 h, smaller black nanosheets with poor crystallinity appeared at the bottom of the autoclave in a grey solution as shown in Fig.2A. Fig.2B shows that many or-

dered rings emerged after 12 h to reduce surface energy without obvious improvement in crystallinity. Fig.2C shows the crystal planes realign to reduce total system energy and crystal defects during the 12–16 h, which has been detailed by Wang³⁸. At 16–20 h, some regions with good crystallinity appeared as shown in Fig.2D, which can improve the electrical conductivity of MoS₂ nanosheets.

3.3 Influence of polyol and volume ratio of polyol to water

EG and DEG have been widely used in polyol process as solvents, reducing and stabilizer agents^{39,40} to prepare various NPs such as metals, alloys, oxides, and Metal chalcogenides^{41–48} due to their excellent physical and chemical properties. Fig.3(A–F) shows that the MoS₂ nanosheets prepared with EG and DEG differ significantly in dispersity and length at the same condition, which can be attribute to their different reducing powers and viscosities. As shown in Fig.3(A, C, F) the volume ratio of EG to water affects slightly on the size of as-prepared MoS₂ nanosheets, and the average all are ca 70–100 nm in length. The case can be attributed to the dramatical decrease of EG viscosity when the temperature increased to 170–200 °C. Moreover, every EG molecule only possess two hydrogen bond acceptors, therefore, the affinity of EG molecule on the MoS₂ nanosheets (or nanoflakes) is poor, giving rise to the free movement of MoS₂ nanosheets (or nanoflakes) at high temperature. In other words, the thermal energy of MoS₂ nanosheets is comparable to the aggregation barrier of the systems according to Jolte's stability hypothesis³⁵, thus all the MoS₂ nanosheets have a similarly final average size. However, as shown in Fig.3(B, D, F), the average size of the MoS₂ nanosheets prepared with DEG are roughly proportional to the increasing volume ratio of DEG to water, which increased from ca. 70 to 150 nm. The higher viscosity and more hydrogen bond acceptors (three) may account for the difference between the MoS₂ nanosheets prepared with EG and DEG. However, when the volume ratio of EG or DEG to water decreased to 1 : 4–1 : 5, high uniform MoS₂ nanospheres were obtained as Fig.3G (prepared with EG) and Fig.3H (prepared with DEG) show.

3.4 Growth mechanism

The three-step formation process of MoS₂ nanosheets can be expressed as follows: the reassembly of ground sublimed sulfur, the reduction of Na₂MoO₄ to MoS₂ nuclei, the formation of MoS₂ nanoflakes, and the formation of MoS₂ nanosheets (Fig.4). To take

Fig.2 TEM images of MoS₂ nanosheets prepared with different holding time at 170 °C for (A) 8 h, (B) 12 h, (C) 16 h, (D) 20 h

The inseted images are selected area electron diffraction (SAED) patterns of the matching samples.

Fig.3 MoS₂ nanosheets prepared with EG (A, C, E) and DEG (B, D, F) with different volume ratio of EG/DEG to water at 170 °C heating for 8 h
(A, B) 1 : 1, (C, D) 1 : 2, (E, F) 1 : 3, (G, H) 1 : 5

Fig.4 Scheme of the three-step growth mechanism of MoS₂ nanosheets

EG as an example for further details. Before heating, most of the ground sulfur powder floated on the interface of the mixture of water and EG. At approximate 100 °C, the sulfur powder adsorbed on foams stemming from the boiling water was sprayed on the inner wall of autoclave because of the burst of foams. When the temperature reached to 120 °C, the water and EG separated with Na₂MoO₄ in water, and the sulfur powder began to melt into liquid beads. Then with the rising temperature, the high viscous liquids beads, which are insoluble in water, slipped into EG by gravity spread evenly in EG finally. At the critical polymerization temperature 159 °C, the S₈ composing of liquid sulfur beads began to transfer into low active insoluble sulfur (S₈)_n. Meanwhile, EG surmounted the onset potential of oxidation (160 °C)⁴⁰, and began to react with S₈ and (S₈)_n, followed by the generation of H₂S. Increasing H₂S then migrated to the water-EG interface gradually, which result in the reduction of Na₂MoO₄ into MoO₄²⁻ ions gradually (detailed in SI 2). By the aid of sub-critical water, the MoO₄²⁻ ions transferred into MoS₃ nuclei^{49,50}, which would be aggregated or coalesced due to van der Waals forces and violent collisions caused by Brownian movement because of the high density of MoS₃ nearby the water-EG interface^{33–35}. The MoS₃ then was trapped in EG and decomposed into MoS₂ soon for their poor thermostability. As a result, the MoS₂ and NPs grew into MoS₂ nanoflakes with poor crystallinity according to Kotov *et al.*²⁸ just as displayed in Fig.2A. Then, the nanoflakes grew larger gradually until to the maximal size determined by the aggregation barrier of the system³⁵. In the process, the crystallinity of MoS₂ nanosheets improved by the rearrange of atoms and special crystal planes to reduce defects and the total system energy, as elaborated in a latest research of Wang³⁸. However, the crystallinity improvement of

MoS₂ was limited by low reaction temperature, indicated by the discolations shown in Fig.2(B–D) and the small white rings on the nanosheets shown in Fig.4. We speculated that the growth mechanism may be applicable to other TMDCs because of their similar structure and properties.

4 Conclusions

MoS₂ nanosheets were successfully prepared with a novel one-pot, two-phase method with sulfur powder and Na₂MoO₄ at 170–200 °C for 8 h without transfer agents. The as-prepared MoS₂ nanosheets are rich in unsaturated S atoms that are crucial to the HER catalysis. Moreover, a possible three-step growth mechanism was proposed, which may be employed for other TMDCs for their similar structures. We hope this facile, green, low-cost method may be an effective method to prepare scale-up TMDCs in the near future.

Supporting Information: available free of charge via the internet at <http://www.whxb.pku.edu.cn>.

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硫粉为硫源，多元醇辅助合成硫化钼纳米片

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SI 1 The simple simulation of the initial transformation of sulfur powder in sealed sebc bottles

Fig.S1 Simple simulation of the assembly of ground sublimed sulfur in a sealed sebc bottle at different heating times of (A) 0 min, (B) 10 min, (C) 15 min, (D) 30 min

Sublimed sulfur are composed of S_8 with the melting point of ca. 120 °C. They will polymerize at 159 °C and reaches to a maximum at 190 °C¹. In the polymerization, the reactivity of sulfur powders decreased gradually, which can contribute to regulate the reduction rate of MoO_4^{2-} .

SI 2 The reduction process of MoO_4^{2-}

The overall reduction process of MoO_4^{2-} can be expressed as reactions 1-6²:

References

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