α -MoO₃@SiO₂ core-shell nanospheres: spatially confined synthesis and tribological properties

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Abstract

Molybdenum disulfide (MoS_2) is widely used in the field of lubrication due to its unique layered structure. But in a high temperature environment, MoS_2 can be greatly deteriorated by severe oxidation, showing a higher friction coefficient and a shorter service life. The modified Stöber method was used to coat SiO_2 on the surface of MoS_2 , so that MoS_2 was converted into layered $\alpha\text{-MoO}_3$ in a confined space at high temperature. The morphology, size and composition of the prepared $\alpha\text{-MoO}_3\text{@SiO}_2$ core-shell nanoparticles were investigated using transmission electron microscopy, scanning electron microscopy, x-ray diffraction and Raman spectroscopy. The tribological properties of the prepared nanoparticles were investigated by ball-disk friction experiments. The results show that the prepared nanoparticles have uniform particle size, high shell coverage and excellent anti-wear properties. Based on the analysis of the wear scars and the existing elements on the friction surface, the lubrication mechanism of the core-shell structure in the friction experiment was discussed.

1. Introduction

Molybdenum disulfide (MoS_2), an inorganic compound of the transition metal disulfides (TMDs) series, has received widespread attention in the field of tribology because of its unique layered structure[1, 2]. The MoS_2 molecular layers are bonded to each other by weaker van der Waals forces, while the covalent bonds between the layers are relatively strong. Many reports have confirmed that this layered two-dimensional structure material is very effective in lubrication[3–5].

Although MoS_2 has been widely used in lubricating materials, especially in the development of automobiles[6], aerospace[7] and machinery[8], its tribological behavior is extremely sensitive to environmental conditions. For example, molecular oxygen oxidizes the edge sites of MoS_2 at high temperature, destroys the shear properties of MoS_2 , and leads to the deterioration of lubricating properties[9, 10]. Generally, the maximum working temperature of MoS_2 lubricant is 400 °C[11]. The physical adsorption of water molecules in a humid environment destroys the shear-prone properties of MoS_2 sheets, thereby deteriorating the tribological behavior of MoS_2 [12, 13]. Therefore, MoS_2 lubricants have many limitations in practical applications.

Molybdenum trioxide (MoO_3) is a transition metal oxide with a layered crystal structure, and the layers are staggered and arranged by van der Waals force. This special layered structure makes MoO_3 have broad application prospects in optoelectronics[14], catalysis[15], lubrication[16], etc. MoO_3 and MoS_2 have a similar layered structure and therefore also share the same lubrication mechanism[17]. Compared with MoS_2 , MoO_3 have a wider temperature application range. However, when the temperature is higher than 600 °C, MoO_3 sublimates in the air, resulting in the failure of lubrication. Coating the MoO_3 with a layer of SiO_2 will hopefully solve its sublimation problem.

In this work, MoS₂ nanoflowers were first synthesized by a simple hydrothermal method. The core-shell MoS₂@SiO₂ nanospheres were prepared by depositing a layer of SiO₂ on the surface of MoS₂ nanoflowers by the modified Stöber method[18]. Finally, MoS₂@SiO₂ was baked in a tube furnace at 680 °C to obtain core-shell α-MoO₃@SiO₂ nanospheres. It shows that α-MoO₃@SiO₂ nanospheres have good lubricating properties. Due to the protection of the SiO₂ shell, MoO₃ still maintains a layered structure and no sublimation occurs. This study improves the application performance of MoO₃ and provides a new idea for high temperature solid lubricating materials.

2. Materials And Methods

2.1 Materials

The chemicals used in this work, including sodium molybdate (Na₂MoO₄·2H₂O, 99.0%), thioacetamide (CH₃CSNH₂, 99.0%), polyvinylpyrrolidone [K30, CH₂CH(NCH₂CH₂CO)_n], Molecular weight 58000), TEOS, aqueous ammonia (25 wt%), absolute ethanol (99.7% pure), and deionized water were purchased from Sinopharm Chemical Reagent Co., Ltd. (China).

2.2 Synthesis of MoS₂ Nanoflowers

MoS₂ nanoflowers were synthesized by hydrothermal method. Dissolve 0.15g of sodium molybdate (Na₂MoO₄·2H₂O), 0.2g of thioacetamide (CH₃CSNH₂) fully in distilled water. Then polyvinylpyrrolidone [CH₂CH(NCH₂CH₂CH₂CO)_n] was added and stirred for 1 h. Subsequently, after 30 min of ultrasonic shaking, the solution was transferred to a stainless steel reactor and placed in an electric oven at 220 °C for 20 h. After cooling to room temperature, the black precipitate was collected from the solution. It was washed several times and dried under vacuum at 60 °C for 8 h. MoS₂ nanoflowers were obtained.

2.3 Preparation of α-MoO₃@SiO₂ Nanoflowers

First, MoS₂@SiO₂ nanospheres were prepared by a modified Stöber method. 0.05 g of the above-prepared MoS₂ powder was dissolved in 40 ml of anhydrous ethanol and then 8 ml of deionized water was added. Then the solution was sonicated for 30 min and transferred to a beaker. Add 1.5 ml of ammonia and 1.0 ml of TEOS to the solution. Amorphous SiO₂ shells were synthesized on the surface of MoS₂ nanoflowers by base-catalyzed hydrolysis and condensation using TEOS as raw material. After stirring continuously for 20 h to complete the reaction, the gray-black precipitate was collected from the solution, washed several times and dried under vacuum at 60 °C for 8 h. The MoS₂@SiO₂ nanospheres was obtained. Finally, the MoS₂@SiO₂ nanospheres were placed in a tube furnace at 680 °C for 10 min, and the α-MoO₃@SiO₂ nanospheres were obtained after cooling. The synthetic route is shown in Fig. 1.

2.4 Characterizations

The morphology of the samples was characterized by scanning electron microscope (SEM, Zeiss, Gemini SEM 300). The structure and dimensions of the samples were observed by transmission electron microscopy (TEM, JEOL, JEM-2100F) at an accelerating voltage of 200 KV. X-ray diffraction (XRD, Rigaku, D/max2200Pc) was performed using a Ni-filtered Cu K α diffractometer (40 kV, 40 mA) in the range of 2 θ (10°-90°) at a rate of 8°/min to show the crystal structure and crystallinity of the samples. Chemical composition and content were investigated by energy dispersive spectroscopy (EDS) mapping scans using field emission TEM (JEOL, JEM-2100F). Raman spectroscopy (Dxr 2Xi) was performed using a 532 nm excitation laser line to show the vibrational modes of the sample lattice. Thermal analysis was performed by thermogravimetric analysis/differential scanning calorimetry (TG-DSC, Nicolet, ISQ 7000 Nicolet iS50) in flowing air heated from room temperature to 900 °C to study the oxidation mechanism of the samples. The heating rate was 10 °C/min.

2.5 Tribological Test

Glass sheets (20mm×20mm) are used as the substrate, and the substrate is ultrasonically cleaned with acetone and absolute ethanol to remove possible contamination and obtain a clean substrate. In order to fully understand the intrinsic properties of the samples, no binder was added, and deionized water was used as the dispersion. The concentration of each dispersion was 0.005 g/mL. Finally, 50 μ L was added dropwise to the glass sheet for friction experiment. Fig. 2 is a schematic of measuring the tribological properties of the prepared nanomaterials using a ball-to-disk friction tester.

The tribological properties were tested on a ball-on-disk friction tester (MS-T3001) in the air at 25 °C. The load is 8 N, the speed is 80 r/min, the ball is GCr15 (ϕ = 6 mm, Ra=20 nm), and the rotating radius is 3 mm. The friction test continues for 600 revolutions. Each experiment was repeated more than three times. Meanwhile, the friction test results of SiO₂ nanospheres prepared by Stöber method and MoS₂ nanoflowers after baking at 680 °C are used as a comparison.

3. Results And Discussion

3.1 Composition Structure and Microstructure of MoS₂@SiO₂

The morphology, structure and dimensions of the synthesized samples are shown in Fig. 3. From Fig. 3a, it shows that the MoS₂ formed nanoflower-shaped particles with an average diameter of 250 nm and dispersed well. The morphology of the particles can be directly observed in the corresponding TEM image (Fig. 3c). From Fig. 3b, it shows that the surface of the sample became smooth after the silica shell was deposited. At the same time, it can be clearly observed from Fig. 3d that the bright outer layer contains dark cores, indicating that a core-shell structure of silica-coated MoS₂ is formed. Two main findings are obtained in the figure: (1) The previous MoS₂ nanoflowers structure was completely preserved; (2) The edges of the "petals" of MoS₂ nanoflowers are covered by SiO₂ to form a spherical shape with good dispersibility. From these results it can be demonstrated that SiO₂ was successfully deposited on the

surface of MoS₂ nanoflowers during the reaction. Apparently, a clear core-shell structure can be seen for all these MoS₂@SiO₂ nanospheres, and the average thickness of the SiO₂ shell is about 30 nm.

The XRD patterns of the synthesized MoS₂ and MoS₂@SiO₂ are shown in Fig. 3e. The diffraction peaks of MoS₂ at $2\theta = 13.94^\circ, 33.14^\circ, 38.7^\circ, 46.06^\circ$ and 69.88° correspond to the (002), (004), (110), (103) and (110) planes of the hexagonal MoS₂, respectively (JCPDS No.37-1492)[19, 20]. From the diffraction pattern of MoS₂@SiO₂, the characteristic diffraction peaks of MoS₂@SiO₂ at 38.7° and 69.88° respectively correspond to the (100) and (110) planes of MoS₂. In addition, the broad diffraction peak at $20\text{-}30^\circ$ is amorphous SiO₂, respectively (JCPDS No.29-0085)[21, 22]. The results confirmed that the MoS₂ nanoflowers were coated with amorphous SiO₂.

As shown in Fig. 3f, Raman spectroscopy is used to further characterize the samples. From the fitted results, MoS₂ nanoflowers had characteristic peaks at 380.3 cm^{-1} and 402.7 cm^{-1} , which correspond to the E1 2g and A_{1g} modes of MoS₂. E1 2g mode is the in-plane vibration of Mo-S bond and A_{1g} is the out-of-plane vibration of S atom[23]. Since the layer number of a MoS₂ flake can be identified based on the frequency difference between E1 2g peak and A_{1g} peak[24], it indicates that each petal of the MoS₂ nanoflowers prepared in this work was composed of 2 layers of MoS₂. For the MoS₂@SiO₂ nanospheres, due to the influence of Si and O atoms on the vibration of MoS₂, the E1 2g peak and A_{1g} peak were slightly shifted to 378.7 cm^{-1} and 402.8 cm^{-1} , respectively. Thus, the Raman results show that the SiO₂ shell coating did not affect the structure of MoS₂ nanoflowers.

To further confirm the characterization results, the composition and content of MoS₂@SiO₂ nanospheres were investigated. EDS map scanning spectra reflecting the spatial elemental distribution of Silicon, oxygen, sulfur and molybdenum. Fig. 4b and Fig. 4c show that the Si and O elements were distributed throughout the outer layer of the particle; while in Fig. 4d and Fig. 4e, the S and Mo elements were only distributed in the core part. This result proves the existence of the core-shell structure, which means that the outer layer and the inner core are composed of different materials. Fig. 4f illustrates that the atomic ratios of Si to O and Mo to S were both approximately 1:2, which proves the presence of SiO₂ and MoS₂. All the results indicate that MoS₂@SiO₂ core-shell structure was prepared by depositing amorphous SiO₂ shells on the crystalline MoS₂ nanoflowers.

3.2 Effect of confined space on the formation of α -MoO₃

The thermal stability and oxidation behavior of MoS₂ and MoS₂@SiO₂ nanoflowers were investigated by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) to reveal their high-temperature reaction processes. TG and DSC curves are presented in Fig. 5. It can be seen that there are four weightless stages on the TG curve of MoS₂. The 10% weight loss before 100°C is due to the volatilization of water molecules in the sample. The organic molecules in the sample are oxidized to CO/CO₂, and an exothermic peak appears at about 350°C . MoS₂ was oxidized to α -MoO₃ at 440°C to

550 °C. The DSC curve had a clear exothermic peak at about 525°C, at which the oxidation rate was the fastest. The stage after 650 °C is the sublimation of MoO₃ and the sample begins to lose weight rapidly.

The DSC curve of MoS₂@SiO₂ shows that the oxidation temperature of organics is delayed from 300 °C to 400 °C, while the violent oxidation process of MoS₂ originally at 500 °C disappeared. This shows that the shell composed of SiO₂ can slow down the chemical reaction at high temperature, so that MoS₂ can be converted into α-MoO₃ while keeping its structure unchanged. From the TG curve, it can be seen that, the produced α-MoO₃ is still confined in the SiO₂ shell, so that the existence of core-shell structure prevents α-MoO₃ from sublimation at high temperature.

Based on the above analysis, the α-MoO₃@SiO₂ material required for lubrication was obtained after baking the MoS₂@SiO₂ nanospheres at 680 °C for 10 min. XRD patterns and Raman spectroscopy were used to characterize the chemical composition of the fired samples, as shown in Fig. 6. MoS₂ nanoflowers were also baked at 680 °C under the same conditions. However, without the protection of the silica shell, α-MoO₃ has sublimated at 680 °C. So the powder left after MoS₂ baking is the intermediate oxidation product, MoO₂.

Figure 6a shows the XRD patterns of MoO₂ and α-MoO₃@SiO₂. The diffraction peaks at $2\theta = 26.05^\circ$, 37.04° , 53.57° and 66.71° correspond to the (011), (-211), (-311) and (-402) planes of MoO₂ (JCPDS No. 73-1249). It can be seen from the results of thermal analysis that MoS₂ is oxidized to MoO₃ and volatilized after being baked at 680°C. Only the intermediate oxide MoO₂ remains in the sample, which is consistent with the XRD results. From the diffraction pattern of α-MoO₃@SiO₂, the diffraction peaks at 12.85° , 23.38° , 27.38° , 33.81° and 49.33° correspond to the (020), (110), (021), (111) and (002) planes of MoO₃ (JCPDS No. 76-1003). The broad diffraction peak corresponding to amorphous SiO₂ (JCPDS No.29-0085) still exists. It is proved that MoS₂ is completely oxidized to α-MoO₃ during high temperature baking, and α-MoO₃ is not sublimated under the protection of SiO₂ shell. In addition, the inset of Figure 6a shows the TEM image of the α-MoO₃@SiO₂ nanospheres. It can be seen that the core-shell structure is obvious, and the morphology and size are consistent with MoS₂@SiO₂. The core-shell α-MoO₃@SiO₂ nanospheres were successfully prepared.

Figure 6b shows the Raman spectroscopy of MoO₂ and α-MoO₃@SiO₂. For MoO₂, there is no characteristic peak of MoS₂ in the spectrum, indicating that MoS₂ in the sample is completely sublimated. From the result, it can be found that the spectrum of α-MoO₃@SiO₂ is consistent with that of layered orthorhombic α-MoO₃[25, 26]. The peak at 285 cm^{-1} is attributed to the peaks of the B_{2g} and B_{3g} vibrational modes of the Mo-O bond. The peak at 819 cm^{-1} is attributed to the peaks of the A_g and B_{1g} vibrational modes of the Mo-O-Mo bond, and the peak at 994 cm^{-1} is attributed to the peaks of the A_g and B_{1g} vibrational modes of the Mo=O bond[27, 28]. The results show that the core in the core-shell MoO₃@SiO₂ is layered α-MoO₃.

3.3 Tribological Properties of $\alpha\text{-MoO}_3\text{@SiO}_2$

The tribological properties of the $\alpha\text{-MoO}_3\text{@SiO}_2$ and other reference samples were tested using a ball-to-disk tester. As shown in Fig. 7a, the friction coefficient of $\alpha\text{-MoO}_3\text{@SiO}_2$ is low, about 0.2. The friction coefficient of MoO_2 is 0.7. It shows that $\alpha\text{-MoO}_3\text{@SiO}_2$ generated at high temperature still has lubricating properties, while MoO_2 does not have lubricating properties. The $\alpha\text{-MoO}_3$ composites formed in the confined space of the core-shell structure can be used in high-temperature lubrication. The friction coefficient of SiO_2 is 0.58 on average, which is significantly higher than that of $\alpha\text{-MoO}_3\text{@SiO}_2$. Compared with silica alone, it shows that the lubricating properties of $\alpha\text{-MoO}_3\text{@SiO}_2$ come from MoO_3 . In addition, the friction coefficients of MoS_2 and $\text{MoS}_2\text{@SiO}_2$ can be kept around 0.05, showing excellent lubricating properties. It shows that the prepared SiO_2 shell will not reduce the lubricating performance.

To explore the surface morphology, SEM images show the wear scar morphologies of different lubricated surfaces. As shown in Fig. 7b, when $\alpha\text{-MoO}_3\text{@SiO}_2$ is used as lubricant, the wear scar has a rough morphology and fine wear debris on the surface, and slight abrasive wear occurs during the friction process. It can be seen from Fig. 7c that the wear scars when lubricated by MoS_2 are very shallow and smooth. Combined with the friction coefficient in Fig. 7a, it can be demonstrated that the prepared MoS_2 nanoflowers have excellent lubricating properties. For $\text{MoS}_2\text{@SiO}_2$, the wear scar area in Fig. 7d is relatively flat with some small wear scars. The wear scar in Fig. 7e has a rough surface and abrasive grains. MoO_2 has no lubricating effect in friction. In Fig. 7f, the wear scar is severe under pure SiO_2 lubrication, and the surface has obvious grooves. This is abrasive wear caused by flaking debris.

The wear scar width can also show the anti-wear advantage of the core-shell structure. When $\text{MoS}_2\text{@SiO}_2$ is used as a lubricant, although the friction coefficient is not the lowest, it has the smallest wear scar width of 256 μm . It shows that the prepared composite material has excellent wear resistance and wear resistance. The wear scar widths of MoS_2 and $\text{MoS}_2\text{@SiO}_2$ are 325 μm and 256 μm , respectively. Although their friction coefficients are similar, the wear scar widths are quite different. The core-shell structure was found to be responsible for the decrease in wear. MoO_2 and pure SiO_2 wear a lot due to their lack of lubricating ability, and their wear scar widths are 409 μm and 352 μm , respectively. This also shows that SiO_2 alone cannot reduce the wear, while the 2D material and SiO_2 will have a synergistic effect when they work together, so that the wear rate is significantly reduced.

3.4 Tribological Mechanism

As the morphology and structure of the sample changed during the friction process, in order to further explore the friction mechanism, the surface element distribution changes of the sample after friction were further studied. The SEM image of the wear scar and the EDS analysis (the substrate is SiO_2) are shown in Fig. 8. For MoS_2 , a dense lubricating film is formed on the friction surface, and a small amount of agglomeration of MoS_2 occurs. No ball flower was observed, indicating that the ball flower structure assembled by the nanosheets is easy to peel off under the action of friction. Due to the unique two-

dimensional structure of the MoS₂ nanosheet, interlayer sliding occurs and spreads on the friction surface to achieve a good lubricating effect. For MoS₂@SiO₂, MoS₂ agglomeration also exists on the friction surface. No spherical structure was observed, combined with EDS analysis and low friction coefficient, it is speculated that the SiO₂ shell ruptured during the friction process to release MoS₂ to achieve a good lubricating effect.

As shown in Fig. 8, there is a small amount of lubricant on the friction surface of MoO₂. EDS results show that the friction surface is free of elements and MoS₂ is completely oxidized. Combined with the XRD pattern, MoO₃ sublimates at high temperature, and there is only a small amount of MoO₂ on the friction surface, resulting in insufficient lubrication. For MoO₃@SiO₂, no spherical structure was observed on the friction surface. Combining the Raman spectroscopy of Fig. 6b with the EDS results, during the baking process, MoS₂ is oxidized to layered MoO₃, but the SiO₂ shell protects α -MoO₃ from sublimation and still maintains a layered structure. During the friction process, the SiO₂ shell ruptures and releases layered α -MoO₃, which continues to work as a lubricant.

Based on the above results, the mechanism of the core-shell structure samples during the lubrication process is summarized. As shown in Fig. 9a, for MoS₂@SiO₂, the SiO₂ shell cracks during friction, releasing MoS₂. MoS₂ lamellar structure has excellent lubricating properties and synergizes with nano-sized SiO₂, which has good anti-wear and anti-friction properties. As shown in Fig. 9b, for α -MoO₃@SiO₂, the existence of the SiO₂ shell has two functions: (1) It protects MoO₃ from sublimation at high temperature and greatly reduces the weight loss rate. (2) The broken SiO₂ shell and layered α -MoO₃ work together to still provide a good lubricating effect. The presence of the core-shell structure plays a crucial role in improving the tribological properties of the lubricant.

4. Conclusion

In summary, this work has successfully developed a feasible strategy for preparing SiO₂ coated MoS₂ nanoflowers by hydrothermal assisted Stöber method. Relying on the confinement and protection of the SiO₂ shell, the α -MoO₃@SiO₂ composite was successfully prepared, which can be used for lubrication at 680 °C or even higher. Experiments show that the core of the prepared core-shell α -MoO₃@SiO₂ is layered α -MoO₃, and this composite has excellent anti-wear properties during friction due to the synergistic effect of 2D materials and SiO₂. This method can be extended and transitioned to other lubricants, providing new ideas for future lubrication above 1000 °C.

Declarations

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

In this work, Tong Wu and Yuan Gao contributed to the conception of the study; Tong Wu and Zang Pan performed the experiments; Yuan Gao and Tong Wu contributed significantly to analysis and manuscript preparation; Shengliang Zhao and Wei Wang helped perform the analysis with constructive discussions.

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Figures

Figure 1

Schematic of the preparation of MoO₃@SiO₂.

Figure 2

Schematic of the the ball-on-disk friction tester.

Figure 3

(a,b) SEM images of MoS₂ and MoS₂@SiO₂; (c,d) TEM images of MoS₂ and MoS₂@SiO₂. (e) XRD patterns of MoS₂ and MoS₂@SiO₂. (f) Raman spectrum of MoS₂ and MoS₂@SiO₂.

Figure 4

(a) EDS map scanning profile of the $\text{MoS}_2@\text{SiO}_2$, (b-e) The EDS element distribution diagram of (b)Si,(c) O ,(d) Mo and (e)S, (f) EDS spectrum of $\text{MoS}_2@\text{SiO}_2$.

Figure 5

TG and DSC curves of MoS₂ and MoS₂@SiO₂. Heating rate is 10°C/min.

Figure 6

(a) XRD patterns of MoO_2 and $\alpha\text{-MoO}_3\text{@SiO}_2$; the inset is the TEM image of the $\alpha\text{-MoO}_3\text{@SiO}_2$. (b) Raman spectrum of MoO_2 and $\alpha\text{-MoO}_3\text{@SiO}_2$.

Figure 7

(a) Friction coefficient of MoO₃@SiO₂, MoO₂, MoS₂, MoS₂@SiO₂ and SiO₂. Sample dispersion concentration is 0.005 g/mL, and rotation speed is 80 r/min. SEM images of wear track after friction test of different lubricants: (b) α-MoO₃@SiO₂, (c) MoS₂, (d) MoS₂@SiO₂, (e) MoO₂, (f) SiO₂.

Figure 8

The SEM images and the EDS mapping images of S, Mo, Si and O on the worn surfaces of the specimen.

Figure 9

Lubrication Mechanism of (a) $\text{MoS}_2@\text{SiO}_2$ and (b) $\text{MoO}_3@\text{SiO}_2$.

Supplementary Files

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