

A low-temperature extraction–solvothermal route to the fabrication of micro-sized MoS₂ spheres modified by Cyanex 301

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Abstract

Mono-dispersed molybdenum disulfide micro-spheres with the diameter of 1–3 μm have been successfully synthesized via extraction–solvothermal method at 150 °C. The extractant Cyanex 301 (di-(2,4,4-trimethylpentyl) dithiophosphinic acid) acted as phase transferring agent, reductant, sulfur source and morphology-controlling agent in the whole procedure. The obtained MoS₂ micro-spheres were characterized by XRD, EDS, SEM, TEM, HRTEM, IR, UV-Vis and TG, respectively. The influences of reaction conditions were discussed while a mechanism was proposed to explain the formation of the micro-spheres. Moreover, the tribological properties of liquid paraffin (LP) containing Cyanex 301-modified MoS₂ micro-spheres were also evaluated on a four-ball machine, showing that the obtained MoS₂ product was an excellent oil additive in LP and such lubricant had good anti-wear and friction-reducing properties.

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1. Introduction

As a useful semiconductor, molybdenum disulfide generally crystallizes with a hexagonal lamellar structure (S–Mo–S) and is composed of sulfur layers between which Mo atoms are placed [1]. Each Mo atom is covalently bound to six sulfur atoms in a trigonal prismatic coordination environment. The layers are held together by van der Waals's interactions between sulfur atoms. The lamellar-type structures make MoS₂ a useful solid lubricant for high vacuum applications [2], scanning probe microscopy [3], an intercalation host to forming new materials [4] and electrochemical hydrogen storage [5].

Recently, lots of methods for the preparation of MoS₂ have been explored. Viswanath [6] reported the solid-state reaction of stoichiometrically mixed molybdenum and sulfur powders in vacuum at high temperature. Monteiro [7] prepared MoS₂ by the thermal decomposition of molybdenum dithiocarbamates, such as [MoO₂(S₂CNEt₂)₂], [Mo₂O₂(S₂CNEt₂)₂], [Mo₂O₄(S₂CNEt₂)₂], [Mo₂O₃S(S₂

CNEt₂)₂], [Mo₂O₂S₂(S₂CNEt₂)₂] and [Mo₂OS₃(S₂CNEt₂)₂]. Tenne et al. [8,9] reported the product of fullerene-like MoS₂ nano-tubes via the gas phase reaction between MoO_{3-x} and H₂S in a reducing atmosphere at elevated temperature (800–1000 °C), and the reaction mechanism was also extensively studied [10–12]. Nano-crystalline MoS₂ particles were also obtained by the reaction between MoO₃ and elemental sulfur with hydrazine as reducing agent at moderate temperature [13]. Electrochemical/chemical synthesis [14] method was also reported, in which MoO₂ “precursor” nano-wires were first electrodeposited size-selectively on the surface of a highly oriented pyrolytic graphite (HOPG) surface, then the “precursor” was converted to MoS₂ by exposing to H₂S at 800–900 °C. Gas-phase decomposition of Mo(CO)₆ in the presence of H₂S [15] and γ-irradiation [16] could also be used to make MoS₂. Many different morphologies of MoS₂ were obtained, such as nano-particles, nano-wires, nano-tubes and/or nano-particles with inorganic fullerene-like structures [17]. Xu [18] reported the preparation of MoS₂ hollow spheres with diameter of 400–600 nm via the reaction of (NH₄)₆Mo₇O₂₄ and thioacetamide with Fe powder as the reducing agent. Chen [19] obtained spherical MoS₂ with

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average diameter of 400 nm via a direct sulfidization of the oxides, using the formed H_2S from the reaction of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and CS_2 at 500°C . Afanasiev [20] prepared MoS_2 hollow spheres with uniform size of 200–300 nm from the solution reaction of the common precursor $(\text{NH}_4)_2\text{Mo}_2\text{O}_{12}$.

In 1995, nano-fluid was put forward in American Arogonome State Lab, which was formed by dispersing nano-particles, such as metals and metal oxides, into polar or non-polar medium [21]. In order to reduce the surface energy of nano-particles, the synthesis of organic–inorganic composite materials has been paid much attention [22]. For example, nano-particles of MoS_2 [23], PbS [24], Ag_2S [25] and ZnS [26] modified by PyDDP (pyridin salt of dioctadecyl dithiophosphoric acid) were synthesized successfully, which could be dispersed into organic solvents because of the modification effects of DDP on their surface. Cyanex 301 (di-(2,4,4-trimethylpentyl) dithiophosphinic acid) is of the similar structure to DDP, which is one of the industrial extractants investigated extensively in the solvent extraction field and can extract a great deal of metals in a wide scope of aqueous acidity. Due to its high activity, extraction–solvothelmal method and extraction–reduction method have been reported recently to prepare nano-materials, which could be dispersed easily into non-polar organic solvents or used to prepare “organic nano-fluid” with high loading concentration. For example, Ag nano-particles modified by extractant Cyanex 302 [27] (di-(2,4,4-trimethylpentyl) monothiophosphinic acid) and Cyanex 301 [28] were prepared directly in alkane via extraction–reduction method by our group; CdS nano-wires and Bi_2S_3 nano-rods were also obtained by the thermal decomposition of the Cyanex 301– Cd^{2+} (or Bi^{3+}) complex in gasoline through extraction–solvothelmal method [29].

Zhang [30] considered that the spherical MoS_2 with the diameter of about $1.5\ \mu\text{m}$ might be a much better oil additive in lubricating oils. Thus, mono-dispersed molybdenum disulfide solid spheres with the diameter of $0.5\text{--}2\ \mu\text{m}$ were prepared in our lab [31] by a solvothelmal method with a self-prepared surfactant quaternary ammonium salt of 2-undecyl-1-dithioureido-ethyl-imidazoline (SUDEI) as surface-modifying agent at 190°C . In this paper, Cyanex 301-modified MoS_2 micro-spheres with the diameter of about $1\text{--}3\ \mu\text{m}$ have been prepared successfully at 150°C via extraction–solvothelmal method in gasoline. The as-prepared product could be well dispersed into organic solvents again and has a good friction-reducing and anti-wear properties in liquid paraffin (LP).

2. Experimental

2.1. Chemicals

Cyanex 301 was kindly supplied by Cytec Co. of Canada and used without further purification. The content of di-(2,4,4-trimethylpentyl) dithiophosphinic acid obtained

from our titration was 83.2% [32]. Hydrogenated gasoline was supplied by QiLu Petroleum Co. in China. Other reagents used in this work, such as heptane, LP and Na_2MoO_4 were of analytical purity. Water was distilled.

2.2. Preparation and characterization of MoS_2 micro-spheres

In a typical procedure, 50.00 ml aqueous solution containing $0.08\ \text{mol l}^{-1}$ Na_2MoO_4 and $0.75\ \text{mol l}^{-1}$ HCl , and 50.00 ml gasoline solution of $0.12\ \text{mol l}^{-1}$ Cyanex 301 were added into a flask, shaken for several minutes and equilibrated. After phase separation, 35.00 ml organic phase containing the Cyanex 301– MoO_2^{2+} complex was transferred into a 50 ml Teflon-lined stainless autoclave, then the autoclave was sealed and maintained at 150, 170 and 190°C for 24 h, respectively. The obtained MoS_2 products were filtered and washed by acetone and ethanol for several times, dried in vacuum at 70°C for 8 h, and collected for the further characterization. The solid product was calcined under Ar flow at 500 and 750°C for 2 h, respectively.

The morphologies and size of the MoS_2 micro-spheres were observed by transmission electron microscopy (TEM) (JEM-2000EX Electro-Microscope, Jeol Co., Japan) and scanning electron microscopy (SEM) (JSM-5600LV, Jeol Co., Japan) with energy-dispersive X-ray spectra (EDS) (Kevex Co., USA). The MoS_2 products were characterized by X-ray powder diffraction (XRD), using Rigaku (Japan) D/max r-B X-ray diffractometer with Cu/K radiation ($\lambda = 0.15418\ \text{nm}$) operating at 40 kV and 30 mA with 2θ ranging from 10° to 80° . The samples were also measured by ultraviolet-visible absorption spectra (UV-Vis) (756CRT UV-Vis Spectrophotometer, Shanghai Precision and Scientific Instrument Co. Ltd., China), infrared ray (IR) (510P Fourier Transform Infrared Spectrophotometer, Nicolet, USA) and thermal gravimetric analysis (TG) (TG-209 Thermal Analyzer, Netzsch, Germany).

2.3. Tribological property of MoS_2 micro-spheres in LP

The MoS_2 samples obtained from the solvothelmal stage (after washing by ethanol and acetone and dried at 70°C) were dispersed into LP in the supersonic bath. The tribological experiments were performed on a four-ball machine (MMW-1, Jinan, China) and the tribological conditions were: load 300 N, rotating velocity 1450 r/min and test duration 30 min. The balls ($\Phi 12.7\ \text{mm}$, HRC 61–64) were made of GCr15 bearing steel (AISI-52100).

3. Results and discussion

3.1. The extraction of MoO_2^{2+} from HCl medium by Cyanex 301

Equal volume of $0.08\ \text{mol l}^{-1}$ Na_2MoO_4 aqueous solution and $0.12\ \text{mol l}^{-1}$ Cyanex 301 gasoline solution were

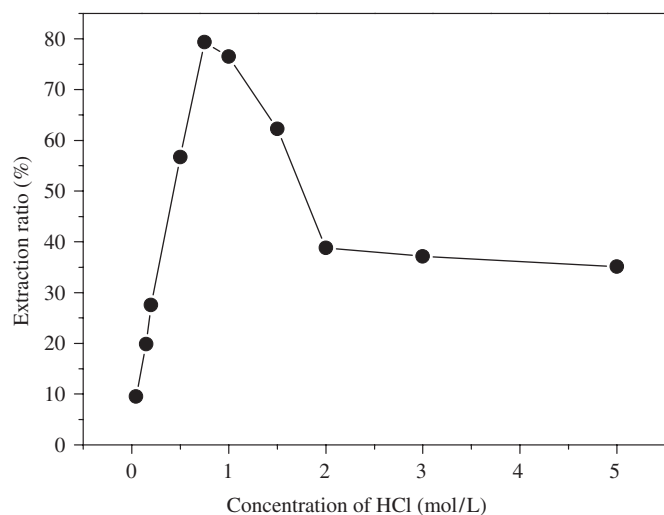
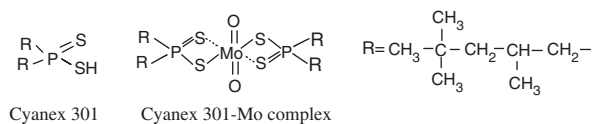


Fig. 1. Effect of HCl concentration in the aqueous phase on the extraction ratio of Mo.

mixed, shaken for several minutes and equilibrated for longer than 30 min at room temperature. The concentration of Mo in the aqueous solution before and after extraction was determined by the titration of EDTA. The effect of the initial concentration of HCl in the aqueous phase on the extraction ratio of Mo was shown in Fig. 1.

From Fig. 1, it could be seen that the extraction ratio reached about 80% when the acid concentration in the aqueous phase was about 0.75 mol l^{-1} . It was confirmed that the MoO_2^{2+} in the aqueous solution was efficiently transferred into the organic phase during the experiments. In the aqueous phase, Mo(VI) ions mainly existed in the form of MoO_4^{2-} at $\text{pH} > 6.5$ and MoO_2^{2+} at $\text{pH} < 1$. Only the form of MoO_2^{2+} could be extracted by Cyanex 301 under this condition due to the extraction mechanism of ion exchange [33]. The extraction equation is $\text{MoO}_{2(a)}^{2+} + 2\text{HA}_{(o)} \rightleftharpoons \text{MoO}_2\text{A}_{2(o)} + 2\text{H}_{(a)}^+$, where (a) and (o) represent aqueous phase and organic phase, respectively. The structures of Cyanex 301 and extracted complex MoO_2A_2 are shown as follows:



3.2. Characterization of the MoS_2 micro-spheres

Fig. 2 showed the XRD patterns of the as-prepared MoS_2 spheres via solvothermal synthesis at 150°C (a), calcined at 500°C (b) and 750°C (c), respectively for 2 h under Ar flow. It could be seen that the sample obtained directly in the autoclave (a) was of amorphous structure. While the main peaks of the calcined samples (b and c) matched well with the hexagonal MoS_2 standard positions (JCPDS Card No. 75-1593). The two maximal peaks in

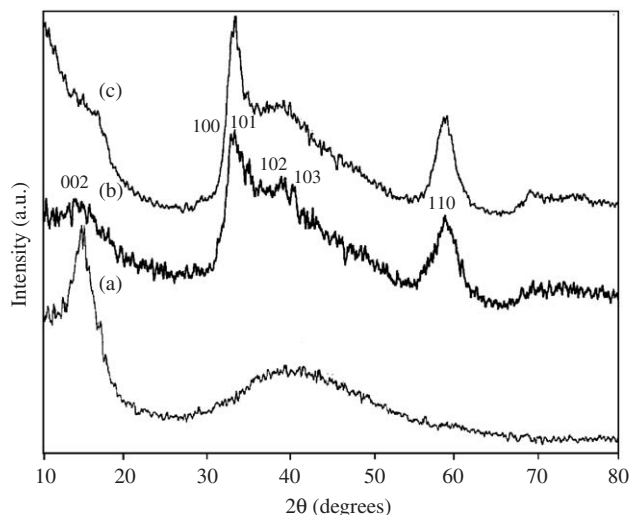


Fig. 2. XRD patterns of the as-prepared MoS_2 spheres at 150°C (a), calcined at 500°C (b) and 750°C (c) for 2 h under Ar flow.

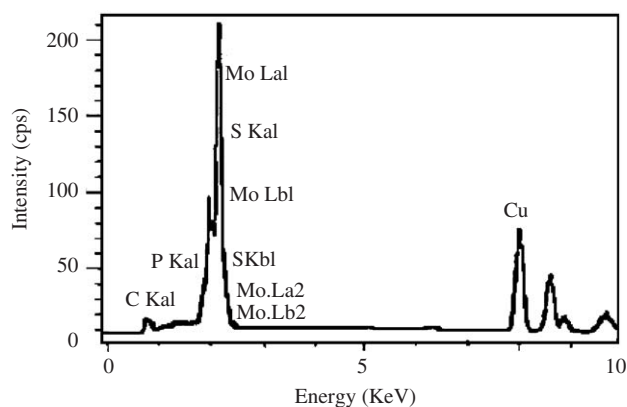


Fig. 3. EDS pattern of the as-prepared MoS_2 micro-spheres.

Fig. 2(b) and (c) approximately located at the 100 ($d = 2.7201$) and 110 ($d = 1.5628$) position of bulk 2H-MoS_2 . The absence of 002 diffraction ($d = 6.2750$) in Fig. 2(c) indicated that the stacking of the single layers did not take place [34], which was in good agreement with that of the single-molecular-layer MoS_2 [35,36], while a relatively weak 002 diffraction peak appeared at the corresponding position in Fig. 2(b), revealing the layer stacking of MoS_2 . From the XRD patterns, it could be observed that annealing had some effects on the crystal growth of MoS_2 and the crystallinity of the products could be greatly increased by high-temperature treatment.

Fig. 3 showed the EDS pattern of the as-prepared MoS_2 micro-spheres obtained from the solvothermal stage at 150°C . The sample was composed of S and Mo with the chemical ratio of about 2.16:1 (the Cu signal arose from the copper grid [37]). It also could be seen that the elements of phosphorus and carbon existed with relatively low concentration on the surface of MoS_2 . In other words, the obtained MoS_2 product was well-modified by the

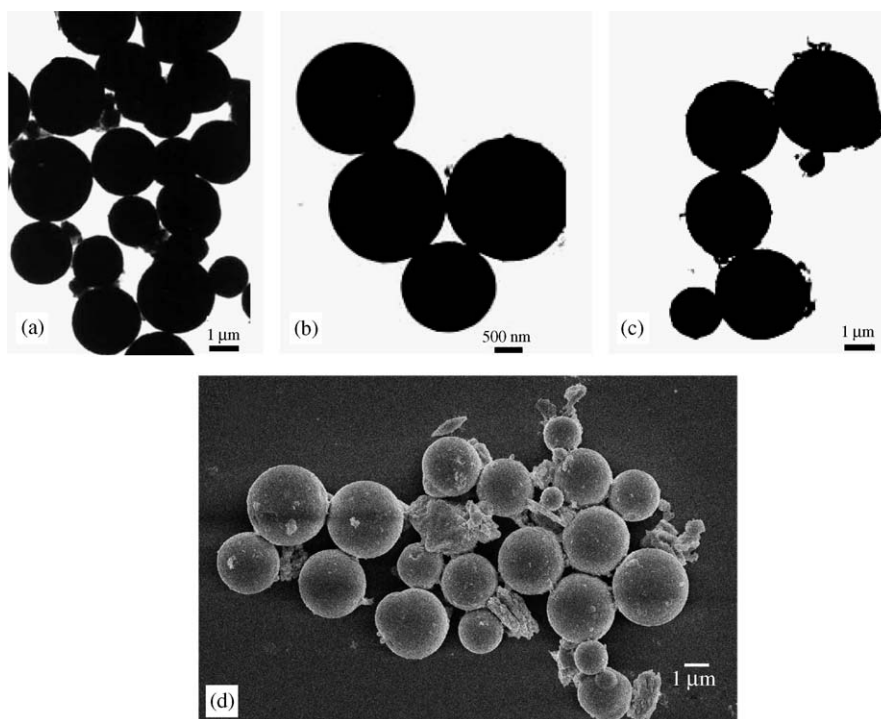


Fig. 4. TEM images of the as-prepared MoS₂ micro-spheres obtained at 150 °C (a), 170 °C (b) and 190 °C (c) and SEM image of the sample obtained at 150 °C (d).

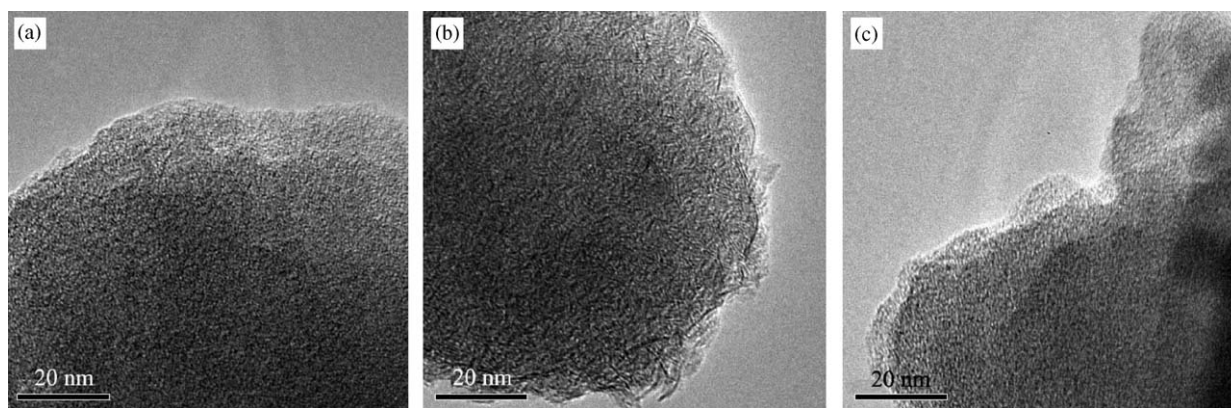


Fig. 5. HRTEM images of the as-prepared MoS₂ (a), calcined at 500 °C (b) and 750 °C (c) for 2 h under Ar flow.

extractant Cyanex 301, which could give rise to its good dispersion and stability in organic solvents and keep off air.

Fig. 4 showed the morphologies of the MoS₂ micro-spheres synthesized at 150, 170 and 190 °C, respectively. Both TEM and SEM images suggested that mono-dispersed MoS₂ spheres were obtained with the diameter of 1–3 μm.

Fig. 5 showed the HRTEM images of the so-prepared sample via solvothermal synthesis at 150 °C (a), calcined at 500 °C (b) and 750 °C (c) for 2 h under Ar flow. It was obvious that the morphology and size of the products were kept well during the calcined process. From Fig. 5(a), it could be seen that the uncalcined sample was mainly small-sized particles, which could further confirm that the broad

peak in the XRD curve shown in Fig. 2(a) was mainly caused by some combination of these particles, the disorder in the crystallinity and the strain in the crystallites [37]. However, there was a little difference between the samples calcined at 500 and 750 °C, i.e., the layered crystals appeared on the surface and inside of sample (b) disappeared in sample (c). The clear appearance of the layered crystals on (and in) the sample indicated that the adsorbed extractant was decomposed totally at 500 °C, and the layered crystals structure might be destroyed at 750 °C.

Fig. 6 showed the UV-Vis spectra of the extractant Cyanex 301 (a), Cyanex 301–MoO₂²⁺ complex (b) and MoS₂ micro-spheres (c) in *n*-heptane, respectively. It could be seen that the absorption spectrum of MoS₂

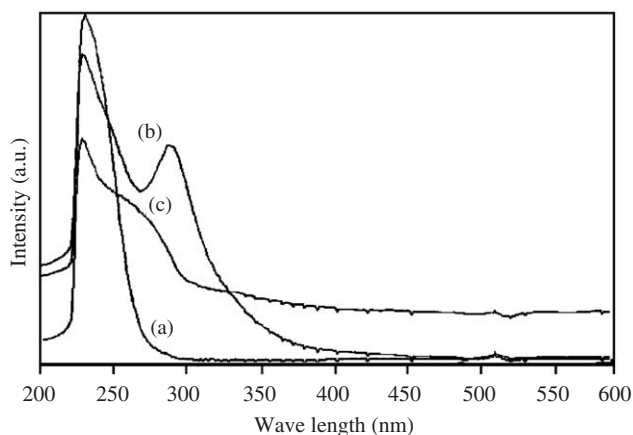


Fig. 6. UV-Vis spectra of Cyanex 301 (a), Cyanex 301–MoO₂²⁺ complex (b) and MoS₂ micro-spheres (c) in *n*-heptane.

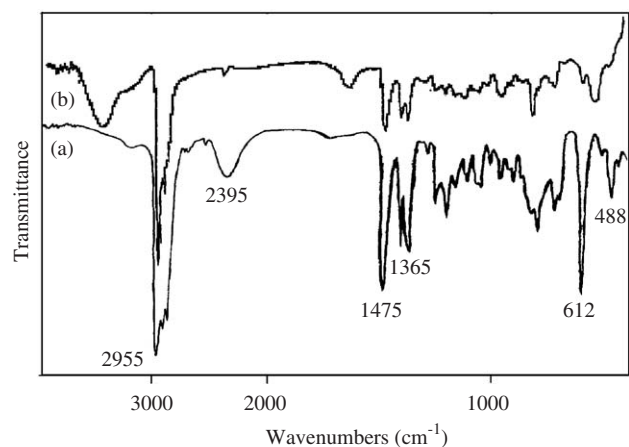


Fig. 7. IR spectra of Cyanex 301 (a) and the as-prepared MoS₂ micro-spheres (b).

micro-spheres (c) was apparently different from those of Cyanex 301 and Cyanex 301–MoO₂²⁺ complex in *n*-heptane, indicating that Cyanex 301 had reacted with molybdenum and a novel product different from Cyanex 301–MoO₂²⁺ complex was formed. The strong coordination effect between P=S bond in Cyanex 301 and MoS₂ particles could give rise to the good stability of the prepared MoS₂ particles in organic solvents. In addition, the UV-Vis spectrum of MoS₂ micro-spheres was identical with that of the bulk semiconductor MoS₂ [38]. From the UV-Vis analysis, it could be primarily concluded that the product was MoS₂ micro-spheres modified by Cyanex 301 rather than Cyanex 301–MoO₂²⁺ complex.

Fig. 7 showed the IR spectra of the extractant Cyanex 301 (a) and the as-prepared MoS₂ micro-spheres (b). In Fig. 7(a), the absorption peaks at 2955 and 2395 cm⁻¹ were attributed to the stretched vibration of C–H and S–H, respectively. The absorption peaks at 1475 and 1365 cm⁻¹ were attributed to the splitting of *tert*-butyl. The typical peaks of Cyanex 301 [39] also existed in Fig. 7(b), indicating that a little amount of Cyanex 301 was adsorbed

onto the surface of the MoS₂ micro-spheres to form a modification layer and could not be washed off totally by acetone and ethanol. Moreover, the absorption peak of P=S at 612 cm⁻¹ in Fig. 7(a) weakened in Fig. 7(b), showing that there was a strong coordination effect between P=S bond in Cyanex 301 and MoS₂ particles.

Fig. 8 showed the TG (in N₂ atmosphere) curve of the prepared solid sample of MoS₂ micro-spheres. There was only one main weight loss at about 348.6 °C, corresponding to the decomposition of Cyanex 301 coated onto the surface of MoS₂ micro-spheres. So it was considered that MoS₂ micro-spheres were well modified by the extractant Cyanex 301, giving rise to the good dispersion in organic solvents, such as gasoline, LP, base oil 500 SN and gear oil, etc. Moreover, it was described in the specification brochure of the extractant Cyanex 301 [40] that its decomposition temperature was about 220 °C, which was consistent with the initial decomposition temperature of the experimental results in the TG-DTG curve.

In order to investigate the formation mechanism of MoS₂ solid spheres and the effects of experimental conditions on the morphology, such as the reaction time, temperature and the solvents polarity, some additional experiments have been further conducted, and the results indicated that the amount of the MoS₂ product obtained at 190 °C was larger than that at 150 °C within the same reaction time. The amount of the product increased with the increasing of reaction time from 12 to 24 h at the same temperature (150 °C). Furthermore, there was no MoS₂ products formed in the autoclave at 130 °C, which might be because that the extractant and/or Cyanex 301–MoO₂²⁺ complex could not decompose at lower temperature, therefore there was no sulfur source for the reduction of Mo(VI)–Mo(IV).

The solvent polarity was another important factor to the shape controlling of the final morphology of the MoS₂ product. The interfacial properties and the aggregation behavior of surface-active species in this system were also dependent on the solvent polarity. The solvent gasoline was evaporated firstly from the extracted organic solution containing Cyanex 301–MoO₂²⁺ complex, then the complex was dispersed into a mixture of ethanol and water (*V*_{ethanol}:*V*_{water} = 3:1) and heated to 150 °C in an autoclave for 24 h. The final hollow spherical morphology of the MoS₂ product with diameter of about 50 nm could be observed and shown in Fig. 9.

3.3. Discussion of the formation mechanism

From the above results we could see that the extractant Cyanex 301 played several roles in the whole procedure: the extractant for metal ions, the sulfur source for metal sulfides, the reductant to reduce Mo(VI) for Mo(IV), the growth controlling agent for the spherical crystals and the surface-modifying agent for the products. So the easy process of extraction–solvothermal method and the multi-functions of the acidic thiophosphinic extractant Cyanex

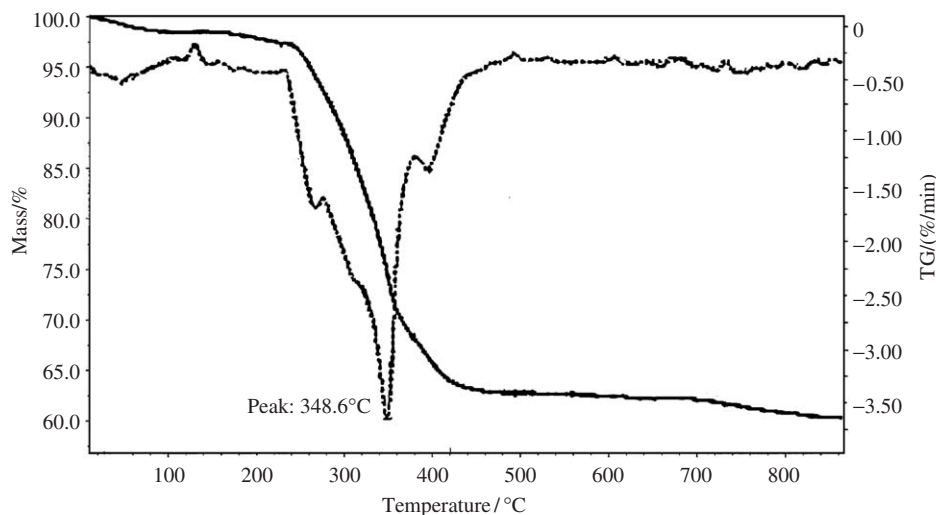


Fig. 8. TG curve of the as-prepared MoS₂ micro-spheres in N₂ atmosphere.

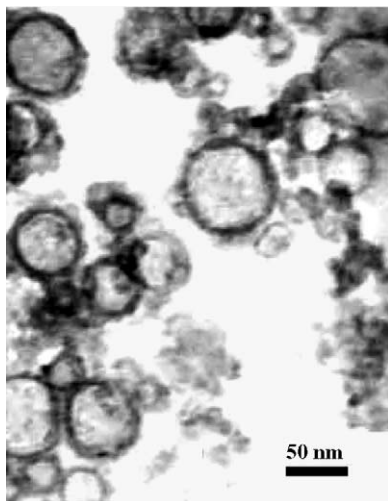


Fig. 9. TEM image of MoS₂ hollow spheres obtained in the mixture of ethanol and water ($V_{\text{ethanol}}:V_{\text{water}} = 3:1$) at 150 °C for 24 h.

301 could be of extensive applications in the preparation of other materials and have significant sense in the manufacture production.

The probable formation mechanism of MoS₂ micro-spheres is put forward as following:

Firstly, Mo(VI) ions existed in the form of MoO₂²⁺ in the aqueous phase at $C_{\text{HCl}} = 0.75 \text{ mol l}^{-1}$ were extracted into the organic phase by the extractant Cyanex 301. The amphiphilic structure of the formed Cyanex 301–MoO₂²⁺ complex could be analogous to a surfactant, which would aggregate to some degree in the organic phase to form “water in oil micelle” because of that a few H₂O molecules were brought into the organic phase simultaneously during the extraction process. The hydrophilic segment of MoO₂²⁺ would assemble in the “water core”.

Secondly, as the reaction temperature and the pressure increased gradually during the solvothermal stage, Mo(VI)

in the Cyanex 301–MoO₂²⁺ complex was reduced to Mo(IV) by S or H₂S coming from the decomposition of extractant HA or extracted complex MoO₂A₂ [41] and small MoS₂ particles were formed. The new-formed MoS₂ molecules would aggregate in the “water core”. Based on the micelle morphology and the growth habit of MoS₂ crystal, MoS₂ would aggregate to form small particles or plates immediately.

Thirdly, the new-formed small particles were very active under the solvothermal conditions although their surface could be protected by the adsorbed extractant or extracted complex as a surfactant to a certain degree. The new-formed MoS₂ particles, the free extractant and the extracted complex would aggregate together to form so-called “organic–inorganic hybrid micelle” [42]. At the same time, all the reactions including the decomposition of HA and MoO₂A₂ and the formation of new MoS₂ would go on, the hybrid micelles would grow up to a definite morphology in the solvothermal stage. The final morphology would be certainly dependent on the solvent polarity. That is why the product prepared from gasoline was micro-sphere with the diameter of 1–3 μm, while it was hollow spheres obtained from a mixture of alcohol and water.

The adsorbed force of the extractant molecules on the MoS₂ surface is very strong. The extractant cannot be washed off totally from the MoS₂ spheres by ethanol and acetone. This has been confirmed by the above characterization results of UV-Vis, IR and TG analysis. The EDS pattern (Fig. 3) also indicates that the chemical ratio of S and Mo on the sample surface is about 2.16:1 (more than 2:1), which further confirms the strong interaction force between the extractant Cyanex 301 and the MoS₂ product.

3.4. Tribological property of MoS₂ micro-spheres in LP

Fig. 10 showed the friction coefficient and wear scar diameter (WSD) values of Cyanex 301–MoO₂²⁺ complex

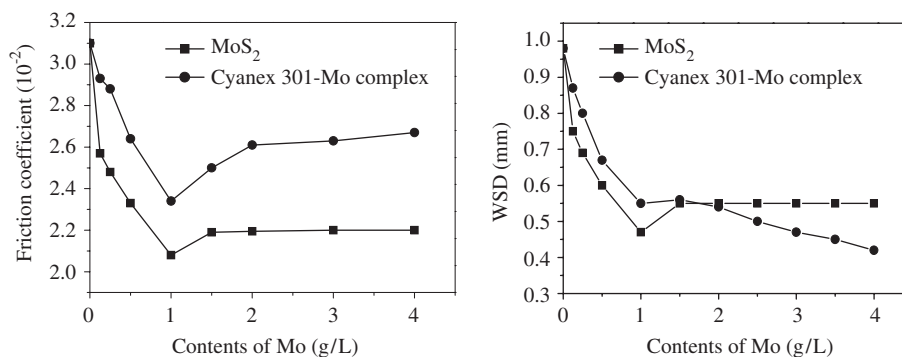


Fig. 10. Variations in friction coefficient and wear scar diameter (WSD) with different contents of Cyanex 301–Mo complex or MoS₂ micro-spheres in LP.

and MoS₂ micro-spheres as additives in LP. The primary results indicated that both anti-wear and friction-reducing properties of complex and MoS₂ modified by Cyanex 301 were much better than those of the pure LP under the experimental conditions. When the mass content of MoS₂ additive in LP was 1 g l⁻¹, the friction coefficient and WSD values were decreased about 33% and 51%, respectively. This might be resulted from the spherical structure of MoS₂, changing sliding friction into rolling friction partially, thereby reducing the friction coefficient. The R groups of Cyanex 301 on the surface of MoS₂ could also make the friction coefficient reduced, owing to “the brush mechanism” [38].

4. Conclusions

Mono-dispersed MoS₂ micro-spheres with the diameter of 1–3 μm have been successfully synthesized via extraction–solvothermal method at 150 °C. The extractant Cyanex 301 acted as phase transfer agent, reductant, sulfur source and morphology controlling agent during the whole procedure. The lubricant system of MoS₂ micro-spheres in LP had good anti-wear and friction-reducing properties because that the sliding and rolling frictions existed simultaneously in the lubrication process.

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