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Characterization and adsorption characteristics of mesoporous molybdenum sulfide microspheres

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ABSTRACT

Bioinspired hierarchical mesoporous MoS_2 microspheres are prepared by using pollen grains as biotemplate. Physicochemical properties of the as-prepared microspheres are characterized in detail by X-ray diffraction analysis, scanning electron microscopy and Fourier transform-infrared spectroscopy. Results indicate that the as-prepared products have a similar structure with the pollen grains, which maintain the ellipsoidal shape and the open pores networks on reticular shells. In addition, the products calcined at 800 °C have an excellent adsorption activity of methyl orange (MO), which is probably related to a similar structure with the pollen grain.

1. Introduction

Mesoporous materials, which have a crystalline framework, high specific surface area, excellent transport behavior and tunable pore size, have received significant research attention [1–4]. To achieve a high surface area and meso or microporous structure, the fabrication of the desired morphologies and structures as well as the control in crystallinity, porosity and composition are important [5–7]. Especially, lots of efficient hierarchical micro/nanomaterials have been prepared by biotemplates for a long time. Among them, the pollen grains have been extensively used as the male gametophytes in higher plants; also the pollen grains are one of typical reactors. To fulfill the reproduction of next generation, their extracellular surface must be capable of ruling the complex bioreactions in the pollen–stigma recognition and fertilization or the defense mechanism. So the pollen grains can be and have been used as the biotemplates in preparing mesoporous materials [8–10]. Recently, bioinspired hierarchical mesoporous TiO_2 and SnO_2 nanoparticles were prepared by using the pollen grains as biotemplate as reported in Refs. [11,12]. Results indicate that the as-prepared products have a similar structure with the pollen grains, which maintain the ellipsoidal shape and the open pores networks on reticular shells [12].

Molybdenum disulfide (MoS_2) has received particular attentions because of its unique layered crystal structure, which is beneficial for the intercalation of guest species, such as Li^+, atoms and even large molecules [6]. As a result, various MoS_2 nanostructures have attracted considerable interest in several applications including rechargeable lithium-ion batteries [6], hydrogen storage [13], catalysts [14], and lubricants [15]. Herein, we reported the preparation of the mesoporous MoS_2 nanoparticles by using pollen grains as biotemplate and investigated on the morphology, crystal structure, and absorption characteristics of the as-prepared samples. Due to its large size, the products can be easy collected by sedimentation or centrifugation, also the biotemplate from nature is a potential way to synthesize functional mesoporous materials.

2. Experimental section

Synthesis of MoS_2 microspheres using pollen grains as biotemplate: The pollen grains were used as a biotemplate to prepare mesoporous MoS_2 nanoparticles. The pollen grains were rinsed in ethanol and then dried naturally. For a typical synthesis, 0.883 g ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and 3.020 g sodium sulfide ($Na_2S\cdot 9H_2O$) were added to 100 mL of ethanol and water (volume ratio of ethanol to water is 1:1) solution. Then, 1.0 g pollen grains were immersed into the solution by vigorous stirring and the pH was adjusted to 7 by an addition of hydrochloric acid. After stirring for 10 h, the as-immersed pollen grains were then separated from the solution by filtration, cleaned by ethanol three times, rinsed in distilled water, dispersed in ethanol, and dried at 80 °C for 24 h. Finally, the templated products were further calcined at different temperatures for 3 h to remove the biotemplate. Thus, the resulting black powders were collected and used for characterization.

Characterization: Crystalline properties of the as-prepared samples were characterized by a powder X-ray diffractometry

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(XRD, D/max-2200, Rigaku, Japan) using Cu Kα radiation. The morphology and grain size of the products were examined by scanning electron microscopy (SEM, FEI Quatan250FEG, American). Absorption spectra of the products were measured by using a JASCO model V-570 UV/VIS/NIR spectrometer in the wavelength range from 200–800 nm. Fourier transform infrared (FT-IR) spectra of the prepared powders were measured by the KBr pellet method with a VERTEX-70 infrared spectrometer.

Adsorption experiments: 0.04 g of MoS_2 powders were put into a conical flask containing 100 mL of aqueous solution of methyl orange (MO) with different concentrations. The flask was covered well and shaken in the water bath shaker at room temperature for different time. Then, the samples were collected using a centrifugal. The adsorption capacity was different between the initial and final concentration of aqueous solution of MO. Residual concentration of the MO solution was determined by measuring its absorbance at 463 nm using an UV–vis spectrophotometer (UV-2550).

3. Results and discussion

Fig. 1 shows the XRD patterns of the mesoporous MoS_2 products. It can be seen that the as-obtained product is amorphous, and the calcined products become rhombohedra phase structure. As seen from the patterns of the calcined samples, the peaks at scattering angles of 14.53°, 33.03°, 34.06°, 38.37° and 58.31° correspond to the reflections from the (003), (101), (012), (104) and (110) crystal planes of the molybdenite-3R MoS_2, respectively, and all these diffraction peaks in the patterns can be indexed as rhombohedra phase MoS_2 (JCPDS no. 17-0744). The lattice constants of MoS_2 calculated from the XRD patterns are $a=b=3.16$ Å and $c=18.33$ Å. MoS_2 crystal structure is composed of vertically stacked and weakly interacting layers, which held together by van der Waals interactions as shown in right of Fig. 1. These results indicate that the distance between neighboring MoS_2 layers is 6.15 Å and their in-plane structure is preserved.

The pollen grain can be considered as a unique genetic microorganism of independency, which shows a core–shell structure. The shells are composed of the specific hierarchical scaffolds and cover the pollen coats [8–12]. Herein, the pollen grains washed by ethanol are taken as a representative. FESEM image of their typical scaffolds is shown in Fig. 2a. It can be observed that they show fine ellipsoids and reticular shell surrounding entirely and the main particle size is about 15×20 μm^2. It can be also seen in the inset of Fig. 2a that the reticular shells are actually composed of open pore networks, which are just like the open doors. Such pores not only give a large and connective surface for the covering of biosensitive pollen coats, but also provide open doors and connective channels for the entering and transporting of the reactants [11,12].

Fig. 2b–d exhibits FESEM images of the obtained MoS_2 products and Fig. 2e–f is for the products calcined at 700 °C for 3 h, revealing that the hierarchical scaffolds of the pollen grains can be faithfully mimicked during the synthesized or calcined process. As shown in Fig. 2b, the product maintains the ellipsoid shape of the pollen grains. In comparison with natural pollen grains, the open pores′ networks on reticular shells are still there as shown in Fig. 2c, and the pore size is about 400–500 nm. The cross section of the MoS_2 shells as observed in Fig. 2d further shows that the hierarchical scaffolds well construct the hollow reticular shells and the foot layers from the surface to the inner side. A formation of the core–shell structure suggests a successful replacement of the pollen coats with MoS_2 coats, which is about 900 nm thick as shown in Fig. 2e–f. That means the open pore networks extend from the surface to the inner side to form barrel-shape networks as shown in the inset image of Fig. 2c, which indicates that such networks are just like thoroughly open doors to allow facile mass transport to form a core in the shell.

Fourier transform infrared spectra of the samples are shown in Fig. 3. The peak at about 3400 is associated with the stretching vibration of water molecules (O–H), including hydroxyl groups and molecular water on the surface of the microspheres [5]. The peak around 1680 cm^{-1} with similar intensities can be reasonably attributed to stretching vibration of C=O bonds. Another peak located around 1115 cm^{-1} is reasonably attributed to the C–O–C bonds [16], and the peak at 880 cm^{-1} in the spectrum of the as-obtained sample is mainly associated with bending vibration of C–H bonds.

The as-prepared MoS_2 microspheres express very different adsorption speeds and different maximum adsorption capacities for MO. As can be seen from Fig. 4, the concentration of MO sharply decreases at the first 30 min, with further passage of time, the concentration of MO decreases slightly. The physical adsorption of organic molecule is a noncovalent functionalization involving stacking interaction and corresponding to a weak binding energy, the π–π bonding interaction between organic molecules and the MoS_2 microspheres are affected by the relative position of benzene ring or C=C double bond of organic molecules to the hexagons on the their surface [17]. A little decrease of MO during 30–180 min may be attributed to photocatalytic degradation, where the MoS_2 microspheres are used as photocatalyst. In addition, the products calcined at 800 °C show the best adsorption capacity due to the specific surface area and unique structure mimicked from the pollen grains.

4. Conclusions

In summary, we have successfully presented a bio-inspired strategy, which mimics bioreactors′ scaffolds of the pollen grains,

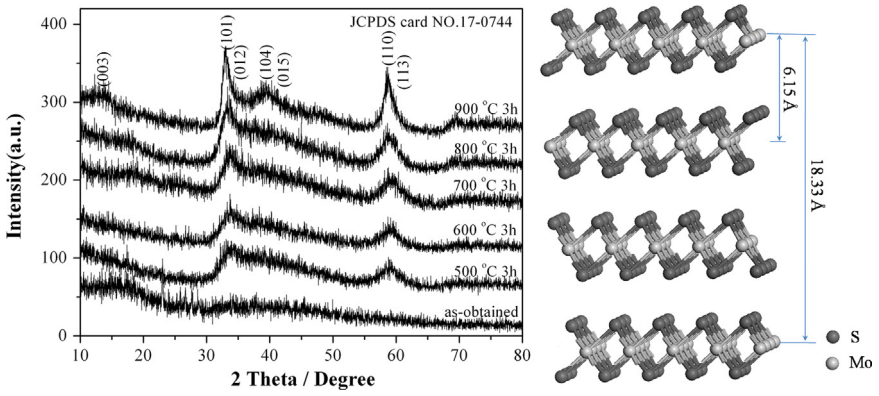

Fig. 1. XRD patterns of the mesoporous MoS_2 microspheres. The right shows the lamellar structure of MoS_2 crystals.