Sodium carbonate-assisted formation of hollow cadmium molybdate microspheres

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Hollow cadmium molybdate ($CdMoO_4$) microspheres with an average diameter of ~1000 nm have been successfully synthesised via a Na_2CO_3-assisted solution synthesis method without using any other surfactants or additives. X-ray diffraction pattern and scanning electron microscopy were used to characterise the samples. The photocatalytic property of hollow $CdMoO_4$ microspheres to degrade dye rhodamine B under the irradiation of UV light was evaluated, which was much better than that of solid microspheres obtained through the same solution synthesis method without the assistance of Na_2CO_3.

1. Introduction: Hollow micro/nanostructures have attracted much attention for the fascinating properties associated with the unique hollow structures, such as large surface area, low density, and high loading capacity [1–8]. Due to the existence of a hollow cavity, the surface area of hollow structures is significantly larger while the density is much lower than that of their solid counterparts with the same composition and size. Although the successful preparation of many hollow binary and tertiary compounds [9–12], it remains a challenge to refind and solve 'old question' using modern equipments for the design and synthesis of nanomaterials [13].

Cadmium molybdate ($CdMoO_4$) is an interesting material from several points of view, including its optical, chemical, and structural properties [14–17]. In the past decade, various methods from room temperature aqueous solution route to hydrothermal method have been developed to synthesise $CdMoO_4$ micro/nanostructures with versatile morphologies, such as hollow [18] and core–shell microspheres [19], nanorods [20], porous microspheres [21], nanoplates [22], nanoparticles [23], and so on. However, there has been no report on Na_2CO_3-assisted formation of hollow $CdMoO_4$ microspheres. Herein, we report a novel and facile yet efficient Na_2CO_3-assisted solution synthesis method to synthesise hollow $CdMoO_4$ microspheres with an average diameter of ~1000 nm. The Na_2CO_3 plays an important role in the formation process of hollow $CdMoO_4$ microspheres.

2. Experimental details: All reagents provided by Sinopharm Chemical Reagent Co. Ltd were of analytical grade and used as received without further purification. In a typical synthesis process, Na_2MoO_4 solution with 6 ml of 0.1 M in test tube was poured into a test tube containing 4 ml of 0.1 M $CdSO_4$ solution, then the suspension mixture was shaked for 10 s and transferred into a beaker containing 12 ml of deionised water. The beaker was kept at room temperature for 4 h, and the white product in the beaker was separated by centrifugation, washed several times with deionised water, absolute ethanol and acetone. After drying in air at 60°C for 60 min, the final solid $CdMoO_4$ microspheres were obtained. To obtain hollow $CdMoO_4$ microspheres, Na_2CO_3 solution with 12 ml of 0.05 M was used to replace deionised water for ripening of $CdMoO_4$ microspheres, and the product was kept in 1 M HCl solution for 30 min to dissolve $CdCO_3$.

The as-prepared samples, solid and hollow $CdMoO_4$ microspheres, were characterised using X-ray powder diffraction (XRD) (Bruker D8-advance, Cu Ka, $k = 0.154056$ nm) and field emission scanning electron microscopy (FESEM) (FESEM, S4800, Japan).

To evaluate the photocatalytic property of the products, RhB stock solution of 0.0167 mmol l^{-1} was prepared in 1000 ml of deionised water in a flask. Dye solution of 50 ml was mixed with 0.0734 mmol $CdMoO_4$ and the mixture was put into a beaker and agitated for 2 h in the dark to achieve the adsorption equilibrium on the product surface. A 300 W medium-pressure mercury lamp with a quartz condenser tube around was positioned in the middle of the beaker as light irradiation source. After a certain time interval, the absorbance of the solution after centrifugation was monitored instantaneously on a spectrometer. The percentages of dye in solution were calculated according to the absorbance.

3. Results and discussion: Fig. 1 shows XRD pattern of $CdMoO_4$ microspheres. The main peaks in the curves can be indexed to be the typical tetragonal phase of $CdMoO_4$ (JCPDS Card No. 07-0209). No characteristic peaks from other impurities can be detected from the XRD pattern, indicating that the as-synthesised products have high phase purity.

Fig. 2 shows FESEM images of two $CdMoO_4$ samples. Among the four images, Fig. 2*a* shows the low-magnification SEM image of the hollow $CdMoO_4$ microspheres obtained in the presence of Na_2CO_3. It can be observed that some of the particles are pressed spheres rather than round spheres. It may be caused by the formation of cavities in the original microspheres. Fig. 2*b* shows the image of an individual hollow $CdMoO_4$ microsphere. The microsphere has a diameter of ~1000 nm as well as those of the particles in Fig. 2*a*. Fig. 2*c* shows the low-magnification SEM image of the solid $CdMoO_4$ microspheres obtained in the absence of Na_2CO_3. All of the particles in Fig. 2*c* are round spheres rather than pressed spheres for no formation of cavities. It can be observed that the average diameter of solid $CdMoO_4$ microspheres aggregated by smaller particles is also ~1000 nm. Fig. 2*d* shows the image of an individual solid $CdMoO_4$ microsphere. Compared with the observation of hollow and solid $CdMoO_4$ microspheres, it could be concluded that the particles contained in hollow ones are smaller and closer than those in solid ones.

Fig. 3 presents photodegradation curves of RhB by the as-synthesised products upon ultraviolet light irradiation. From Fig. 3, it is found that after 180 min, the degradation percentage

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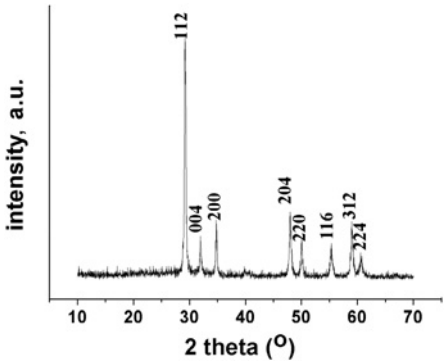

Fig. 1 *XRD pattern of the $CdMoO_4$ microspheres*

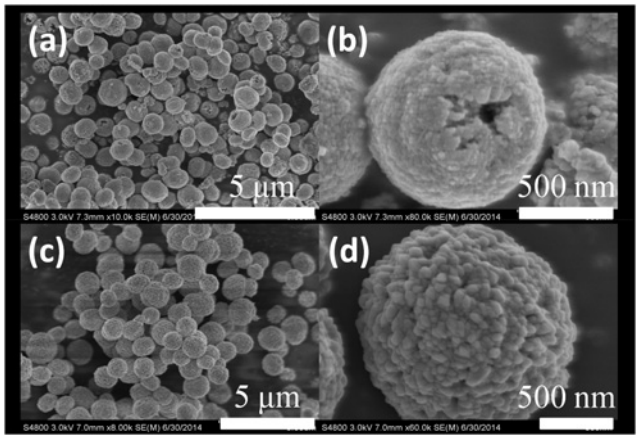

Fig. 2 *FESEM images of $CdMoO_4$ ripening*
a In the presence of Na_2CO_3 – low magnification
b In the presence of Na_2CO_3 – single hollow microsphere
c In the absence of Na_2CO_3 – low magnification
d In the absence of Na_2CO_3 – single solid microsphere

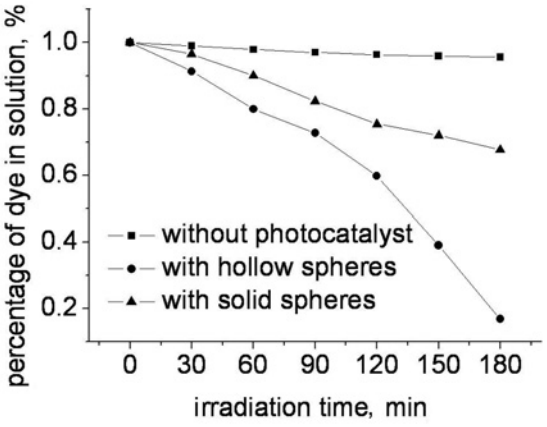

Fig. 3 *Photoinduced degradation of RhB dye in aqueous $CdMoO_4$ suspensions with UV irradiation. Condition: photocatalyst of 0.0734 mmol dispersed in 50 ml of 0.0167 mmol/l dye solution*

of RhB dye with the presence of hollow $CdMoO_4$ microspheres is more than 85%, while those of the RhB photolysis and the one with the presence of solid $CdMoO_4$ microspheres were ~0% and <30%, respectively. The comparison of the photocatalytic efficiencies shown in Fig. 3 reveals that the hollow $CdMoO_4$ microspheres exhibit more excellent photocatalytic activity for RhB under UV light. The reason is the higher surface area and lower density for hollow ones in the same composition and size.

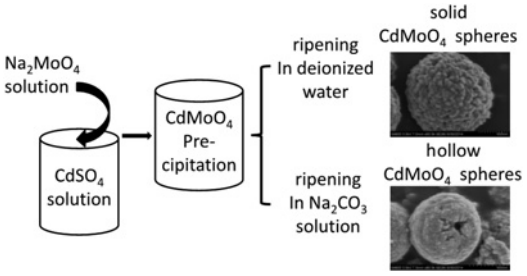

Fig. 4 *Simplified schematic diagram of hollow $CdMoO_4$ microspheres*

Fig. 4 shows a simplified diagram for the formations of $CdMoO_4$ microspheres ripening in different environments. When the fresh $CdMoO_4$ precipitation was poured into deionised water to ripen, solid $CdMoO_4$ microspheres were obtained; while ripen in Na_2CO_3 solution, hollow $CdMoO_4$ microspheres were reached. It is necessary to briefly discuss the possible mechanism for Na_2CO_3-assisted formation of hollow $CdMoO_4$ microspheres. First, a quantity of $CdMoO_4$ nuclei was formed rapidly when Na_2MoO_4 solution was mixed with $CdSO_4$ solution. According to [24], these formed nuclei grow by a diffusive mechanism into the primary particle units, which will self-assemble to form much larger particles in a process dominated by the irreversible capture of single particles. These larger particles adopt a spherical structure due to the main driving force being the tendency to decrease the high surface energy and finally form $CdMoO_4$ solid microspheres. It is believed that the interactions between primary particles may be affected by several factors, such as van der Waals forces, electrostatic and dipolar fields associated with the aggregates, crystal-face attraction, hydrogen bonds, hydrophobic interactions, and so forth [25–27]. In this Letter, Ostwald ripening should be the main driving force for the following hollowing process. In deionised water, Ostwald ripening did not happen obviously in 4 h. However, in Na_2CO_3 solution, the CO_3^{2-} in the solution could accelerate the dissolution of inner primary $CdMoO_4$ particles for the combination between CO_3^{2-} and Cd^{2+} from $CdMoO_4$. To purify the product obtained from Na_2CO_3 solution, HCl solution was used to dissolve $CdCO_3$. More efforts are going on to explore the detailed mechanism for the formation of hollow nanospheres caused by Na_2CO_3.

4. Conclusion: In summary, $CdMoO_4$ microspheres with an average diameter of ~1000 nm were synthesised by a solution synthesis method. The microspheres become hollow with the assistance of Na_2CO_3 which provides a suitable chemical environment to direct the specific nucleation and ripening of $CdMoO_4$ microspheres. The hollow $CdMoO_4$ microspheres show a better photocatalytic property to degrade rhodamine B in solution under the irradiation of UV light.

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6 References

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