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### Hierarchical flowerlike magnesium oxide hollow spheres with extremely high surface area for adsorption and catalysis

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Three-dimensionally hierarchical flowerlike MgO hollow spheres with extremely high surface area of 343 m<sup>2</sup> g<sup>-1</sup> were prepared through a facile and environmentally friendly solvothermal route. The maximum adsorption capacity at natural pH reached 569.7 mg/g for removal of arsenic in water, which is the highest among all of reported adsorbents. In addition, flowerlike MgO hollow spheres also displayed excellent catalytic activity and stability for the Claisen-Schmidt condensation reaction as a solid base catalyst.

#### **1. Introduction**

Self-assembly of low-dimensional nanomaterials into threedimensionally (3D) hierarchical architectures with wellcontrolled morphologies have attracted much attention due to their particular structures and properties.1-5 It has been demonstrated that 3D hierarchically nanostructured materials often exhibit enhanced properties compared to their bulk counterparts or their building blocks.<sup>6,7</sup> To date, great efforts are being made on the preparation of these complex 3D hierarchical nanostructures.<sup>8-11</sup> In our previous works, 3D flowerlike hierarchical architectures of iron oxide,<sup>12,13</sup> ceria<sup>14</sup> and magnesium oxide<sup>15,16</sup> prepared through an ethylene glycol (EG)-mediated method showed impressive performance in catalysis and heavy metal ions adsorption. However, nearly all of them are solid structures. There were very rarely reports about 3D flowerlike hollow hierarchical nanostructures, which have higher surface area and more channels for mass transportation. These are two important features for adsorption and catalysis.

As a nontoxic, low-cost, and environmental-friendly material, MgO has already been widely used in toxic wastewater treatment and catalysis.<sup>17-20</sup> In the past years, various MgO nanostructures, including microspheres,<sup>16,21,22</sup> nanocrystals,<sup>23</sup> nanoparticles,<sup>24-26</sup> nanocubes,<sup>27,28</sup> nanowires,<sup>29</sup> nanoflowers<sup>15,30-32</sup> and nanosheets<sup>32,33,34</sup> have been fabricated successfully. Though these great advances had been made, it is a great challenge to develop a facile and environment-friendly method to produce MgO with 3D hierarchical hollow structures through a template-free method.

Herein, we report a facile solvothermal route to synthesize 3D hierarchical flowerlike MgO hollow sphere precursors, which are then transformed to MgO by simple calcination. In particular, none expensive or toxic chemicals are used, making the synthesis route economical and environmentally benign. A plausible formation mechanism based on Oswald ripening has been proposed for the formation of hollow nanostructures. The as-obtained flowerlike MgO hollow spheres have extremely high surface area of  $343 \text{ m}^2/\text{g}$  and exhibit very impressive performance in adsorption and catalysis. When used as adsorbents for removal of arsenic in water, maximum adsorption capacity at natural pH is 569.7 mg/g, which is highest among all of reported adsorbents. In addition, flowerlike MgO hollow spheres also display excellent catalytic activity and stability for the Claisen-Schmidt condensation reaction as a solid base catalyst.

#### 2. Experimental section

# 2.1 Preparation of hierarchical flowerlike hollow magnesium glycolates

In a typical experiment, 0.166 g PVP K-30 was dissolved into 20 mL ethylene glycol, then 100  $\mu$ L ammonium hydroxide (28%) was added drop by drop. Next, 0.214 g Mg(OAc)<sub>2</sub>•4H<sub>2</sub>O (1 mmol) was introduced into the above-mentioned solution. After stirring for 30 min, the obtained clear solution was transferred to a 50 mL Teflon autoclave, and heated at 185 °C in an electric oven for 5 h. After cooling to room temperature, the obtained white precipitates were washed four times with ethanol and dried under vacuum for 6 h.

### 2.2 Preparation of hierarchical flowerlike magnesium oxide hollow spheres

Firstly, the above obtained magnesium glycolates product was calcined at 500  $^{\circ}$ C with heating rate of 1  $^{\circ}$ C/min for 1h in a tubular furnace under argon condition, then argon flow was changed to air atmosphere for another 2 h to remove the carbon generating from the first step.

#### 2.3 Adsorption experiments

Solutions with different concentrations of arsenate were prepared using Na<sub>2</sub>HAsO<sub>4</sub>•7H<sub>2</sub>O (98%, Alfa) as the sources of heavy metal ions. All the initial solutions were adjusted to pH 7.0 using diluted 0.2 mol/L HCl solution. The batch adsorption experiments were carried out in 50 mL polyethylene tubes with 8 mg adsorbents and 16 mL arsenate solutions of different concentrations at room temperature. After stirring for 12 h, the solutions were separated from suspensions by centrifugation. Then the upper solutions were filtered through a PTFE membrane with 0.2  $\mu$ m pore diameter and analyzed by Inductively Coupled Plasma- Atomic Emission Spectroscopy (ICP-AES). The solids were dried under vacuum for 24 h for further characterizations. The amount of special adsorbate ions adsorbed per unit weight of the adsorbent at equilibrium (mg g<sup>-1</sup>), *q*<sub>e</sub> was calculated according to the following equation:

$$q_e = (C_0 - C_e)V/m$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of adsorbate ions (mg L<sup>-1</sup>), respectively, V is the volume of the solution (L) and m is the mass of adsorbent (g).

The Langmuir model is applicable for uniform adsorption processes, where each adsorption site on the surface has identical binding sites and is described as monolayer adsorption. Langmuir model can be described as follows:

$$q_{\rm e} = q_{\rm m} b C_{\rm e} / (1 + b C_{\rm e})$$

where  $C_e$  (mg g<sup>-1</sup>) and  $q_e$  (mg g<sup>-1</sup>) are the equilibrium concentration of adsorbate ions in the supernatant and the amount of adsorbate ions adsorbed on per weight of MgO at equilibrium, respectively.  $q_m$  (mg g<sup>-1</sup>) is the maximum adsorption capacity associated with complete monolayer coverage, and *b* (L mg<sup>-1</sup>) is a Langmuir constant related to the energy and affinity of the sorbent. These adsorption capacities were obtained at pH=7.0, which is similar to the real underground water condition.

#### 2.4 Catalytic tests

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For a typical experiment, a mixture of acetophenone (3 mmol), benzaldehyde (2.5 mmol), dry toluene (10 mL), and catalyst (175 mg) was put into a 25 mL Schlenk tube. Then, the tube was evacuated and backfilled with argon three times to avoid benzaldehyde oxidation to benzoic acid. The mixture was stirred in a preheated 110 °C oil bath for desired time. Samples were taken periodically and analyzed by a gas chromatograph (Shimadzu GC-2010) equipped with a flame ionization detector (FID) and a Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). The identity was ascertained by GC-MS (Shimadzu GCMS-QP2010S).

### 2.5 Regeneration experiments of hierarchical flowerlike magnesium oxide hollow spheres

After the  $3^{rd}/5^{th}$  run, the solid catalyst was separated via centrifugation. The recovered catalyst was washed with toluene for two times and dried under vacuum for 5 h. The obtained powder was calcined at 500 °C with heating rate of 1 °C/min for 1h in a tubular furnace under argon condition, then argon flow was changed to air atmosphere for another 2 h to remove the carbon generating from the first step.

#### 2.6 Characterization

The morphologies of all samples were characterized by highresolution transmission electron microscopy (HRTEM, JEOL

2100F) and scanning electron microscopy (HITACHI S-4800 SEM). X-ray diffraction (XRD) patterns were performed on a Rigaku D/max-2500 diffractometer with Cu K $\alpha$  radiation ( $\lambda$ = 1.5418 Å) at 40 kV and 200 mA. The content of arsenate (As (V)) was determined by ICP-AES (Shimadzu ICPE-9000). EDS mappings of the materials were conducted using scanning TEM (STEM) equipped with an EDS detector (JEOL 2100F). XPS measurement was performed on the VG Scientific ESCALab220i-XL spectrometer using Al Ka radiation. Thermogravimetric (TG) analysis was carried out on a Shimadzu DTG-60H instrument under a flow of air with a temperature ramp of 10 °C/min from room temperature to 600 °C. Nitrogen adsorption-desorption isotherms were obtained on Quantachrome Autosorb AS-1 at 77 K. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer using pressed KBr pellets to test the chemical bonding of the products from 400 to 4000 cm<sup>-1</sup>.

#### 3. Results and discussion

#### 3.1 Preparation and structure characterizations

In a typical experiment, 0.166 g PVP K-30 was dissolved into 20 mL ethylene glycol, then 100 µL ammonium hydroxide (25 wt%) was added drop by drop. Next, 0.214 g Mg(OAc)<sub>2</sub>•4H<sub>2</sub>O (1 mmol) was introduced into the above-mentioned solution. After stirring for 30 min, the obtained clear solution was transferred to a 50 mL Teflon autoclave and heated at 185 °C for 5 h. After cooling to room temperature, the precipitants were collected by centrifugation and washed three times by ethanol (About the details, please see the supporting information). The X-ray diffraction (XRD) pattern of the asobtained solid products (Fig. S1a, ESI<sup>†</sup>) showed strong peak located in the low-angle region at around 10.7°, similar to those of other metal alkoxide reported in the literatures.<sup>35</sup> Fourier Transform IR (FT-IR) spectrum (Fig. S1b, ESI<sup>†</sup>) showed two bands at 1113 cm<sup>-1</sup>, and 2850 cm<sup>-1</sup>, which could be assigned to  $v_{C-O}$  and  $v_{C-H}$  absorptions, respectively. When the magnesium precursor was calcined under argon atmosphere, products with black color were obtained (Fig. S2, ESI<sup>†</sup>), which should be ascribed to the carbonization of glycol. All the above results confirmed that the obtained precursors should be magnesium glycolates, not the magnesium hydroxide.



Fig. 1 (a-b) SEM and (c-d) TEM images of as-obtained hierarchical flowerlike magnesium glycolates hollow spheres.

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The morphology of magnesium glycolates was further characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. 1, magnesium glycolates precursors consisted of hierarchical flowerlike hollow spheres assembled from twisted nanosheets as the building blocks. The inner and outer diameters of the flowerlike hollow spheres were about 500 nm and 1  $\mu\text{m},$ respectively.

To investigate the formation process of this interesting hierarchical flowerlike hollow sphere structures, samples prepared at different reaction times were collected and characterized by SEM and TEM. As shown in Fig. 2a, some nanosheets agglomerated to form flowerlike structures at the early stage of the reaction (1 h). When the reaction time was further increased to 2 h, the petals continued to grow to form twisted nanosheets, which connected to each other to form the rugged surface (Fig. 2b). At the first two stages, the obtained magnesium glycolate was still solid. When the reaction time was 3 h, the hollow morphology began to appear (Fig. 2c), and the cavity became more obvious when the time was further extended to 4 h (Fig. 2d). The well-defined flowerlike hollow spheres with a hierarchical shell were obtained after hydrothermal reaction for 5 h. (Fig. 1). Interestingly, this welldefined flowerlike hollow architectures were well preserved even the reaction time was prolonged to 24 h, which implied that the flowerlike hollow frameworks were stable (Fig. S3, ESI†).



Fig. 2 TEM images of the morphological evolution during the timedependent experiments: (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h.

Based on the above experimental observations, a plausible formation mechanism of the hierarchical flowerlike hollow magnesium glycolates is proposed (Fig. 3). Firstly, magnesian ions coordinate with ethylene glycol molecules to form Mg(II)glycol complexes (Step (I)).<sup>35,36</sup> Then, the formation of Mg(II)glycol precursors aggregate to form solid flowerlike magnesium glycolates (Step (II)). Finally, through a wellknown Ostwald ripening process, the hierarchical flowerlike hollow spheres were obtained (Step (III)).37,38 In fact, the XRD peaks of Mg(II)-glycol precursors became more and more obvious with elongation of the reaction time, which was agree with the Ostwald ripening process (Fig. S4, ESI<sup>†</sup>). Such an Ostwald ripening mechanism can also explained well the effects of reaction temperature on the formation of hollow spheres. At the lower temperature, for example, 140 °C, only solid products were obtained (Fig. S5, ESI<sup>+</sup>). This is because Ostwald ripening needs a higher temperature to proceed.<sup>37</sup>



Fig. 3 Schematic illustration of the formation process of hierarchical flowerlike hollow magnesium glycolates spheres.

The alkalis effects on the morphologies of MgO precursors were also explored. Interestingly, it was found that ammonium hydroxide played a vital role for the formation of hollow spheres. Only solid flowerlike structures were obtained without ammonium hydroxide (Fig.S6, ESI<sup>+</sup>). Under the basic condition, a relatively fast nucleation rate for precipitation may be responsible for the formation of hollow architecture. When 5 times ammonium hydroxide (500 µL) was introduced, no specific morphology products were obtained (Fig. S7, ESI<sup>†</sup>). Furthermore, when K<sub>2</sub>CO<sub>3</sub> was introduced to replace ammonium hydroxide, large amount of magnesium precursor nanowires were produced (Fig. S8, ESI<sup>+</sup>). This interesting discovery provided an easy way to prepare different magnesium precursor nanostructures through changing species of the base.



Fig. 4 (a) XRD pattern, (b) SEM and (c-e) TEM images of flowerlike MgO hollow spheres.

Calcination is a simple route to turn metal alkoxide into metal oxide. TG analysis of magnesium glycolate exhibited a major weight loss of around 49.2% from room temperature to 600 °C in air, which can be attributed to the loss of water and the combustion of organic components (Fig. S9, ESI<sup>†</sup>). After calcination of magnesium glycolate precursors at 500 °C for 2 h in air, all the XRD diffraction peaks of products matched well with the periclase phase MgO (JCPDS No. 45-0946) (Fig. 4a).<sup>31</sup> The morphology of the obtained MgO was characterized by SEM and TEM. As shown in Fig. 4b, the SEM images revealed the same flowerlike architecture of MgO as that of the

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precursors. TEM image (Fig. 4c) displayed that the obtained MgO maintained hollow structure, indicating the cavity did not collapse during the calcination process. A higher-magnification TEM image displayed the petals of the flowerlike MgO were consist of many small nanocrystals (Fig. 4d). A representative high-resolution TEM (HRTEM) image showed that the lattice fringes were clearly visible with a spacing of 0.21 nm, corresponding to (200) lattice plane of periclase MgO (Fig. 4e).

 $N_2$  adsorption-desorption measurement was conducted to investigate surface structure and porosity of flowerlike MgO hollow spheres. As shown in Fig. 5, a typical type-IV with a distinct hysteresis loop was observed for  $N_2$  adsorptiondesorption isotherms, suggesting the presence of mesopores of flowerlike MgO hollow spheres.<sup>39</sup> The BJH pore size distributions (inset in Fig. 5) obtained from the isotherm suggested that the samples contained broadly distributed pores with sizes generally below 30 nm.<sup>40</sup> Specifically, flowerlike MgO hollow spheres had an extremely high surface area of 343 m<sup>2</sup>/g and a total pore volume of 1.90 cm<sup>3</sup>/g, which were also higher than many reported MgO materials.<sup>17,19,29,31,32,41-43</sup> Such high surface area and pore volume is very beneficial for mass transformation, which makes the flowerlike MgO hollow spheres have special advantage in absorption and catalysis.



Fig. 5  $N_2$  adsorption-desorption isotherms and mesopore size distribution curve (the inset) of the obtained flowerlike MgO hollow spheres.

## **3.2** Adsorption and catalysis properties of the flowerlike MgO hollow spheres

Organic and inorganic pollutants in the environments have received tremendous attention in modern society.44-46 As one of the top 20 hazardous substances in the world, arsenic is a huge threat to the health of human beings.<sup>47,48</sup> Among the inorganic arsenic species, arsenate (As (V)) is considered to be more dangerous and poisonous than the organo-arsenic. As a nontoxic, low-cost, and environmentally friendly material, MgO has been widely used to remove organic dyes,<sup>27</sup> arsenic,<sup>32</sup> fluoride,<sup>41,43</sup> lead and cadmium<sup>15</sup> from wastewater. For heavy metal ions adsorption, surface area is one of the most important factor. Because of extremely high surface area of our prepared flowerlike MgO hollow spheres, we first test their adsorption properties for arsenate (As (V)) from waste water. The adsorption rates of As (V) ions on flowerlike MgO hollow spheres and commercial MgO were displayed in Fig. 6a with an initial concentration of 114 mg  $L^{-1}$ . It can be seen that the adsorption process of flowerlike MgO hollow sphereswas much faster than that of commercial MgO. To our delight, the maximum adsorption capacities for As (V) was as high as 569.7 mg/g based on the Langmuir adsorption model (Fig. 6b), which

is 7.6 times of the commercial available magnesium oxide. This value is also the highest for MgO materials, and much higher than other nanomaterials reported in the literatures (Table S1, ESI<sup>†</sup>). <sup>8,12,29,32,37,46-55</sup>

X-ray photoelectron spectroscopy (XPS) was used to analyze the surface chemistry of the flowerlike MgO after arsenic absorption. As seen in Fig. S10, the 3p and 3d peaks of element arsenic could be well detected. It means that the As (V) was adsorbed on the flowerlike MgO's surface successfully. Energy-dispersive spectroscopy (EDS) mapping results showed that arsenic element was distributed on MgO's surface uniformly (Fig. S11, ESI<sup>†</sup>). The high adsorption performance of the flowerlike hollow MgO for As (V) adsorption should ascribe to the high surface area from the hierarchical hollow porous nanostructures. Moreover, zeta potential analysis of the flowerlike hollow MgO was +12.3 mV. This positive charge on the surface of MgO is also benefit for the anion adsorption such as arsenate through electrostatic interaction.



**Fig. 6** (a) Adsorption rates and (b) adsorption isotherm curves of As (V) adsorption on the flowerlike MgO hollow spheres (red line) and commercial MgO (violet line).

Because  $O^{2-}$  sites on MgO could act as the Lewis base, MgO could also be used as a solid base catalyst to catalyze Claisen-Schmidt condensation reaction to synthesize chalcone from benzaldehyde and acetophenone.<sup>16,20</sup> Therefore, we further test the catalytic property of flowerlike magnesium oxide hollow spheres for Claisen-Schmidt condensation reaction. As shown in Table 1, flowerlike magnesium oxide hollow spheres displayed a substantially higher activity than commercial MgO under the same conditions. The conversion of benzaldehyde reached 99% after 2 h, whereas commercial MgO reached only 6% benzaldehyde conversion during the same period of time (Table 1, entries 1-2).

Moreover, it is noteworthy the prepared hierarchical flowerlike MgO hollow spheres also exhibited much higher catalytic activity than the previous reports.<sup>16,56-58</sup> It was obvious that a wide range of benzaldehydes with varied substituents underwent condensation with several diversely substituted ketones by this procedure to produce the corresponding chalcones with excellent yields (Table 1, entries 3-8). The excellent activity can be ascrible to the particular structures of flowerlike hollow MgO hollow spheres: the high surface area is benificial for adsorption of substrates, while porous and hollow nanostructures is helpful for mass transportation.

Besides high catalytic activity of flowerlike MgO hollow spheres, they also exhibited impressive stability through a simple calcination after used for Claisen-Schmidt condensation reaction. From Fig. 7, it can be seen that after the 3rd run, the catalytic activity of flowelike MgO decreased obviously. XRD analysis and TEM images of the used sample revealed the crystal structure and morphlogy of flowerlike MgO hollow spheres did not change after 3 runs (Fig. S12). Digital photo of the used sample displayed that the color of used catalyst Journal of Materials Chemistry A Accepted Manuscri

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became pale yellow (Fig. S13a). The slight color change from white to festucine should come from coke during the recycle process, resulting in the catalytic activity loss.<sup>59-60</sup> In order to confirm this point, a simple calcination treatment was made. After calcination, the catalyst's color changed back to white (Fig. S13b). Gratifyingly, the catalytic activity of flowerlike MgO recovered and 99% conversion can be reached. Similarly, the catalytic activity recovered again through the same calcination process after the 5th run (Fig. 7).

**Table 1.** Claisen-Schmidt condensation reaction of aldehydes with ketones by using flowerlike MgO as catalysts<sup>[a]</sup>.



[a] Reaction conditions: catalyst (87 mg), benzaldehyde derivatives (1.25 mmol), ketone derivatives (1.5 mmol), toluene (5 mL), 110 °C, under Ar atmosphere. [b] Conversion was determined by GC, and the identity was ascertained by GC-MS. [c] Commercial MgO was used as the catalyst.



Fig. 7 Recycle performance of flowerlike MgO hollow spheres using the benzaldehyde and acetophenone as the substrates in 6 h. Green columns mean a simple calcination treatment was adopted to recover the activity of flowerlike MgO hollow spheres.

#### 4. Conclusions

In summary, 3D hierarchical flowerlike magnesium oxide hollow spheres were prepared successfully through a facile and environmentally friendly solvothermal route. A plausible formation mechanism based on Oswald ripening has been proposed for the formation of hollow nanostructures. The asobtained flowerlike MgO hollow spheres had a surface area as high as 343  $m^2/g$ , which is higher than most of reported MgO materials. When used as adsorbents for removal of arsenic in water, maximum adsorption capacity at natural pH reached as high as 569.7 mg/g, which is the highest among all of reported adsorbents. In addition, flowerlike MgO hollow spheres also displayed excellent catalytic activity and stability for the Claisen-Schmidt condensation reaction as a solid base catalyst. The impressive performance in adsorption and catalysis can be attributed to their paticular structures of flowerlike MgO hollow spheres.

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### Table of Contents (TOC)



3D hierarchical flowerlike MgO hollow spheres with extremely high surface area showed excellent adsorption property for heavy metal ions and catalytic property for the Claisen-Schmidt condensation reaction.