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**Template-free synthesis of complicated double-wall Cu<sub>2</sub>O hollow spheres with enhanced visible photocatalytic activities**

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In this study, complicated double-wall Cu<sub>2</sub>O hollow spheres have been successfully prepared by a facile hydrothermal process in a ternary solvent system including water, ethanol and glycerol. The obtained double-wall Cu<sub>2</sub>O hollow spheres have an average diameter of ~ 15 μm and the spheres assembled by irregular particles with an average diameter of ~ 500 nm. Scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the structure of synthesized products. The formation mechanism of the double-wall Cu<sub>2</sub>O hollow spheres is related to a self-assembly process accompanied with an Ostwald ripening process, during which the Cu<sub>2</sub>O spheres are first formed through the self-assembly of Cu<sub>2</sub>O nanoparticles and then gradually develop into double-wall hollow interiors by an Ostwald ripening process. Furthermore, the photocatalytic properties of as-obtained samples were investigated. It is found that such unique double-wall hollow architecture exhibits excellent photocatalytic efficiency for the degradation of MO under visible-light illumination, which is up to 90.3 % and this photocatalytic efficiency is higher than the Cu<sub>2</sub>O particles with irregular spherical structure (74.2%). The high photocatalytic performance of the double-wall Cu<sub>2</sub>O hollow spheres is associated with the plenty of nanopores which exist in the spheres, serving as transport paths for small molecules.

**Keywords:** Cu<sub>2</sub>O; Semiconductors; Double-wall hollow spheres ; Microstructure; Photocatalytic property

## 1. Introduction

Cuprous oxide (Cu<sub>2</sub>O) is an important p-type semiconductor with a direct band gap of about 2.17 eV and possesses unique optical and magnetic properties, which makes it a promising material with potential applications in electronics, catalysis, optical devices and gas sensors.<sup>1-4</sup> Extensive studies have been devoted to control the morphologies of Cu<sub>2</sub>O in the past few decades, such as nanowires,<sup>5</sup> nanocubes,<sup>6</sup>

hollow spheres,<sup>7</sup> octahedral<sup>8</sup> and the hollow structures are of particular interest. Recently, Wang et al.<sup>9</sup> have synthesized hollow Cu<sub>2</sub>O spheres with novel multishelled nanostructures with the assistance of CTAB vesicles. In addition, Zhang et al.<sup>10</sup> have fabricated double-wall Cu<sub>2</sub>O hollow spheres via a surfactant-assisted approach. However, these synthesis methods need to utilize surfactants as a soft-template, which could introduce some impurities bonded to the surface of Cu<sub>2</sub>O and complicate the fabrication process. Hence, it is necessary to explore effective template-free approaches to prepare multishelled hollow Cu<sub>2</sub>O structure.

Here, we put forward a simple but effective hydrothermal method to prepare Cu<sub>2</sub>O particles with a complicated double-wall hollow structure without using any sacrificial templates in a water, ethanol and glycerol ternary solvent system. The crystal structure, morphology evolution, and growth mechanism of the prepared samples are also studied. This interesting hollow structure significantly improves photocatalytic performance.

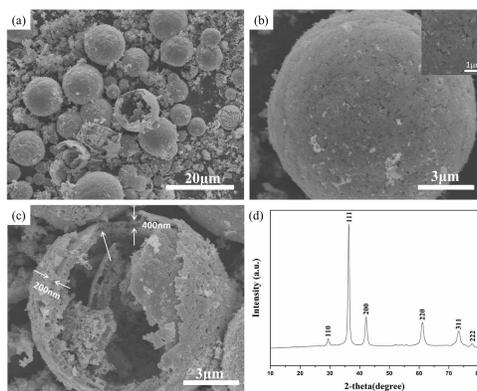
## 2. Experimental

In a typical procedure, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (1.0 g) was dissolved in 24 mL of ethanol-glycerol-water ternary solvent with ratios (v/v/v) (7:7:10) to prepare the precursor solution with a concentration 0.17 M. Then urea (0.5 g) was added to the cupric nitrate solution under constant stirring. After the solution was stirred for 30 min, it was transferred into a 50 mL Teflon-lined stainless steel autoclave, followed by a hydrothermal treatment at 170 °C for 0.5–7 h. After cooling to room temperature, the precipitate was centrifuged, washed with deionized water and ethanol several times, and then dried in a vacuum oven at 50 °C for 5 h.

The photocatalytic activity of the prepared samples was evaluated by degradation of methyl orange

(MO) aqueous (25 mg/L) under visible-light illumination. An amount of 0.1 g of the prepared  $\text{Cu}_2\text{O}$  particles was dispersed in 50 mL of MO aqueous solution (25 mg/L). Before irradiation, the suspension was stirred for 30 min in darkness to reach adsorption–desorption equilibrium. The photocatalytic process was irradiated by Xeno lamp (100 W). The concentration of MO during the degradation course was detected by UV–vis spectrophotometer measurement at 462 nm and the degradation rate is recorded as  $(C_0 - C)/C_0$ , where  $C$  is the concentration of MO for each irradiated time, and  $C_0$  is the starting concentration.

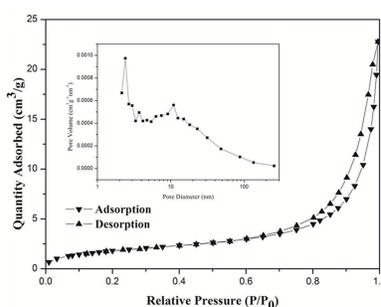
### 3. Results and discussion



**Fig. 1.** (a)–(c) SEM images of the complicated double-wall  $\text{Cu}_2\text{O}$  hollow spheres with different magnifications; the inset of Fig. 1(b) is enlarged SEM image of the corresponding individual microsphere; (d) XRD pattern of as-prepared sample.

Fig. 1a-c shows the typical scanning electron microscopy (SEM) images of the as-synthesized products at 170 °C for 7 h. As can be observed from Fig. 1a, the obtained samples are dominant by spherical particles with diameter of ~ 15  $\mu\text{m}$  and some broken spheres could also be observed from the image, confirming the existence of hollow interior in the spheres. The detailed exterior structure of the sphere could be clearly verified by the magnified SEM image in Fig. 1b. It is found that the surface of microsphere is full of tiny pores. The enlarged SEM image of this single sphere can also confirm this

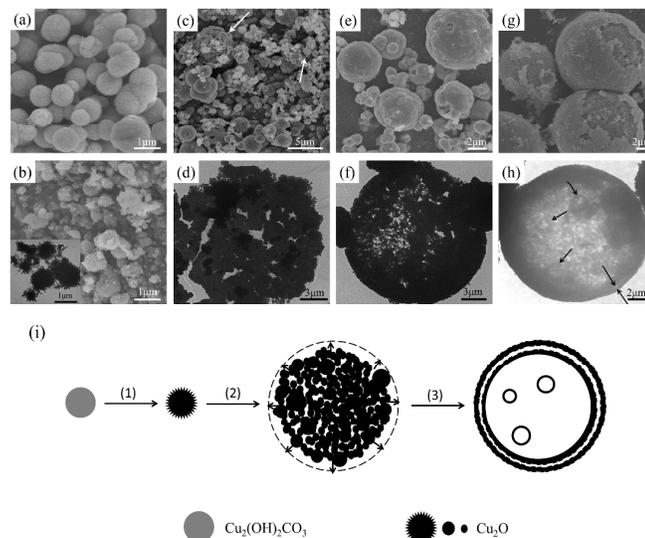
porous property (inset of Fig. 1b). Fig. 1c further confirms the microsphere consists of two layers and the internal structure exposes the second layer that shows the highly porous feature of the interior structure (marked by arrow). The thickness of the outer shell and inner shell are  $\sim 200$  nm and  $\sim 400$  nm, respectively. The phase and purity of the as-synthesized complicated hollow spheres were investigated by XRD. The characteristic peaks of XRD pattern (Fig. 1d) could match well with  $\text{Cu}_2\text{O}$  (JCPDS 65-3288), and no peaks of any other phases are detected, indicating that  $\text{Cu}_2\text{O}$  have been successfully prepared in this hydrothermal process.



**Fig. 2.**  $\text{N}_2$  adsorption and desorption isotherms and pore size distribution for the complicated double-wall  $\text{Cu}_2\text{O}$  hollow spheres

Brunauer–Emmett–Teller (BET) gas-sorption measurement was conducted to determine the specific surface area and pore structures of the double-wall  $\text{Cu}_2\text{O}$  hollow spheres. The nitrogen adsorption–desorption isotherms are shown in Fig. 2. Hysteresis loops can be observed in the isotherms of the sample, indicating the presence of mesopores in all samples. The  $S_{\text{BET}}$  of samples calculated from  $\text{N}_2$  isotherms is  $6.92 \text{ m}^2 \cdot \text{g}^{-1}$ . The pore size distributions determined by the Barrett–Joyner–Halenda (BJH) method are displayed in inset of the Fig. 2. The pore size distribution of samples shows three peaks around 2.4 nm, 3.7 nm and 12.54 nm. The results indicate that this complicated double-wall hollow spheres possess various pores. This is important for expanding the application range of double-wall  $\text{Cu}_2\text{O}$

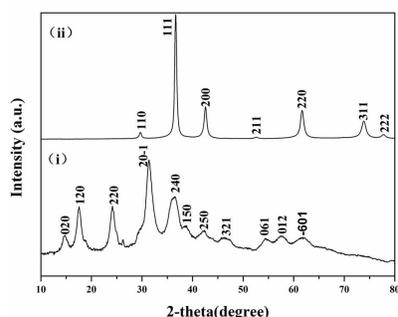
hollow spheres.<sup>[11]</sup>



**Fig. 3.** (a, b, c, e, g) SEM images of the samples prepared for different times: (a) 30 min; (b) 70 min (inset is the corresponding TEM image); (c) 100 min; (e) 4 h; (g) 7 h. (d, f, h) The corresponding TEM images of a single  $\text{Cu}_2\text{O}$  sphere prepared at 100 min, 4 h, 7 h. (i) Schematic illustration of the formation of complicated double-wall  $\text{Cu}_2\text{O}$  hollow spheres.

To study the morphological evolution of obtained double-wall  $\text{Cu}_2\text{O}$  hollow spheres, time-dependent experiments were conducted and products prepared at different growth stages were analyzed continuously by SEM and TEM observations. After the sample was heated for 30 min, uniform spheres with rough surfaces were formed, as shown in Fig. 3a. XRD analysis of the product indicated they were  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (JCPDS: 10-0399) (Fig. 4i). At this stage, the urea may play a key role in the formation of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  particles.<sup>12</sup> After being heated for 70 min, a brick red suspension was obtained, and the XRD pattern is shown in Fig. 4ii. All diffraction peaks can be indexed to the  $\text{Cu}_2\text{O}$ , indicating that  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  particles were reduced to  $\text{Cu}_2\text{O}$  particles. From Fig. 3b, we can see that these particles are a mixture of irregular spherical particles. The size of these particles shows no obvious change, but plenty

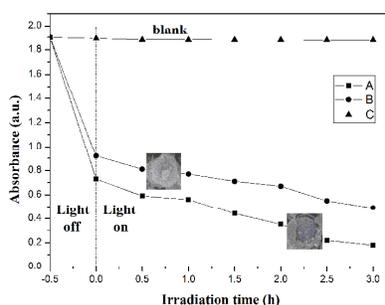
of small protuberances which spread all over the surfaces of these particles could be observed (inset of Fig. 3b). In this hydrothermal synthesis, glycerol is used as solvent and reducing agent for  $\text{Cu}^{2+}$ . It initially dehydrates to produce aldehydes and then reacts with  $\text{Cu}^{2+}$  generated from  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  intermediate to form primary  $\text{Cu}^+$ .<sup>13</sup> When the reaction time was prolonged to 100 min, the irregular spherical particles shape with uniform size of  $\sim 500$  nm agglomerate into larger spheres (marked by arrows). This assembled phenomenon may be due to these protuberances, which have relatively higher free energy.<sup>14</sup> And the driving force of the solvents also promotes the particles aggregation.<sup>15</sup> Actually, in addition to the scabbled incompact  $\text{Cu}_2\text{O}$  spheres, there are also a lot of dispersed small  $\text{Cu}_2\text{O}$  spheres in this product. A TEM image of the  $\text{Cu}_2\text{O}$  spherical structure assembled by irregular particles is shown in Fig. 3d. The resultant  $\text{Cu}_2\text{O}$  microspheres obtained at this stage were loosely packed and lots of tiny particles with different packing density also appeared on the surface of the microsphere. As the reaction proceeded, the ratio of the assembled spherical structure increased at the expense of small particles (Fig. 3e). Interestingly, as shown in Fig. 3f, the particles located in the inner core began to dissolve, and a hollowing effect was observed. As the reaction time was increased to 7 h, the resultant  $\text{Cu}_2\text{O}$  microspheres became compact and blunt, as shown in Fig. 3g. A TEM image of a single  $\text{Cu}_2\text{O}$  microsphere obtained at this stage is shown in Fig. 3h, from which we can see that the product is well-defined double-wall hollow microstructure and some small hollow spheres could be further observed in the hollow inside (marked by arrows), which can be referred to the Ostwald ripening process.<sup>16</sup>



**Fig. 4.** XRD patterns of the sample obtained at different reaction times: (i) 30 min; (ii) 70 min.

After analysis of the SEM and TEM images, we speculated that the complicated double-wall hollow  $\text{Cu}_2\text{O}$  spheres were formed via self-assembly and Ostwald ripening process. A schematic representation is shown in Fig. 3i. The forming process involves three steps: (1) reduction of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  particles to  $\text{Cu}_2\text{O}$ ; (2) formation of scabbled  $\text{Cu}_2\text{O}$  microspheres by assembly of dispersed small  $\text{Cu}_2\text{O}$  spherical particles; (3) Ostwald ripening of the scabbled  $\text{Cu}_2\text{O}$  microspheres. Generally, Ostwald ripening involves the formation of aggregation with primary crystallites and followed outward mass transfer through the growth of larger crystals from those of smaller size, which have a higher solubility than the larger ones, and the migration of crystallites from the inner core to the outer shell causes the formation of the hollow structure. Typically, the core components are formed and serve as “template” in the initial stage, then the tiny particles are deposited on the surface of the core approach to form the capsule structures. In the ripening process, the tiny particles with different packing density on the surface of microsphere are likely to be less stable (Fig. 3d), it will be dissolved and serve as starting points to re-engineer surface structures for the subsequent recrystallization process, which lead to the formation of new layer on the outer surface.<sup>17</sup> At the same time, the outward evacuation from the inner core leads to the formation of an interior cavity in the central region. Since the inner larger particles have a lower solubility than the smaller ones, and the migration rate of larger particles from the inner core to the outer

shell is relatively slow. Hence, several small hollow spheres can be further created in the hollow core and it is believed that localized Ostwald ripening should be the main driving force for this self-transformation. The followed ripening process will start at the outermost surface of the microspheres and loosely packed core simultaneously, which leads to the formation of complicated double-wall hollow structure. But in this special double-wall hollow spheres structure, the inner shell can also be seen as the interior part of the spheres compared with the outer shell. During the formation of outer shell, the inner shell also followed the Ostwald ripening process, *i.e.* outward mass transfer for the growth of larger crystals through consuming the inner shell, which lead to much more porous inner shell than the exterior one.



**Fig. 5.** Curves of absorbance (A) vs. irradiation time (t) for the Cu<sub>2</sub>O particles with different morphologies (samples A and B correspond to the Cu<sub>2</sub>O particles showed in Fig. 3 g and b; C: blank).

The photocatalytic activity of different samples was examined by the degradation of MO solution, and the results were shown in Fig. 5. The control experiment shows that the absorbance of MO is extremely slow without photocatalyst. After illumination by Xeno lamp for 180 min, it can be seen that, the photocatalytic activity of complicated double-wall Cu<sub>2</sub>O hollow spheres is much higher than the sample produced at 70 min and the degradation rates approached to 90.3% (7h) and 74.2% (70min), respectively. This double-wall hollow structure with high photocatalytic performance has at least three advantages: 1) the double-wall hollow architecture has a larger surface area ( $S_{\text{BET}}$  is  $6.92 \text{ m}^2 \cdot \text{g}^{-1}$  for double-wall Cu<sub>2</sub>O

hollow spheres, and it is  $2.22 \text{ m}^2 \cdot \text{g}^{-1}$  for the control one) and more active sites than the bulk material, which is advantageous for photocatalytic reactions, and 2) double-wall hollow structures enable multiple light reflection and scattering between spherical shells, and can effectively make use of the light, which can further increase the photocatalytic activity 3) these hollow spheres with numerous nanopores on the shell may represent an ideal candidate for improving the photocatalytic properties since the nanopores can be considered as transport paths for small molecules.<sup>[18-20]</sup>

#### 4. Conclusions

In the present work, the complicated double-wall  $\text{Cu}_2\text{O}$  hollow spheres were synthesized through a solvothermal method without using any templates. By careful analysis of the products at different growth stages, it is demonstrated that Ostwald ripening plays a major role in formation of this novel hollow structure. In addition, the investigation on photocatalysis properties indicates that as-synthesized double-wall  $\text{Cu}_2\text{O}$  hollow spheres exhibit outstanding photocatalytic activity for the photodegradation of MO.

#### REFERENCES

- [1] Tan Y, Xue X, Peng Q, Zhao H, Wang TH, Li YD, *Nano Lett*, 2007, 7, 3723-8.
- [2] Mao BG, Chu DQ, Wang LM, Wang AX, Wen YJ, Yang XZ, *Mater Lett*, 2013, 109, 62-5.
- [3] Zhang JT, Liu JF, Peng Q, Wang X, Li YD, *Chem Mater*, 2006, 18, 867-71.
- [4] Chang Y, Teo JJ, Zeng HC, *Langmuir*, 2005, 21, 1074-9.
- [5] Hafez M, Al-Marzouki F, Mahmoud W, *Mater Lett*, 2011, 65, 1868-70.
- [6] Gou L F.; Murphy CJ, *Nano Lett*, 2003, 3, 231-4.
- [7] Yu H, Yu J, Liu S, Mann S, *Chem Mater*, 2007, 19, 4327-34.
- [8] Zhang XJ, Wang GF, Wu HB, Zhang D, Zhang XQ, Li P, Wu HQ, *Mater Lett*, 2008, 62, 4363-5.
- [9] Xu H, Wang W, *Angew. Chem. Int. Ed*, 2007, 46, 1489-92.
- [10] Wang WZ, Tu Y, Zhang PC, Zhang GL, *CrystEngComm*, 2011, 13, 1838-42.

- [11] Li DY, Yang J, Tang WX, Wu XF, Wei LD, Chen YF, RSC Adv, 2014, 4, 26796-803.
- [12] Deng CH, Hu HM, Zhu WL, Han CG, Shao GQ, Mater Lett, 2011, 65, 575-8.
- [13] Fievet F, Lagier JP, Figlarz M, MRS Bull, 1989, 14, 29-34.
- [14] Ni XM, Zhao QB, Zheng HG, Li BB, Song JM, Zhang DE, Zhang XJ, Eur J Inorg Chem, 2005, 23, 4788-93.
- [15] Hu P, Han N, Zhang X, Yao MS, Cao YB, Zuo AH, Yang G, J Mater Chem, 2011, 21, 14277-84.
- [16] Jin L, Xu LP, Morein C, Chen CH, Lai M, Suib SL, Adv Funct Mater, 2010, 20, 3373-82.
- [17] Yec CC, Zeng HC, J Mater Chem A, 2014, 2, 4843-51.
- [18] Wang DA, Hisatomi T, Takata T, Pan CS, Katayama M, Domen k, Angew. Chem. Int. Ed, 2013, 52, 11252-56.
- [19] Wang WS, Zhen L, Xu CY, Shao WZ, Chen ZL, CrystEngComm, 2013, 15, 8014-21.
- [20] Dong ZH, Lai XY, Halpert J, Yang NL, Yi LX, Zhai J, Wang D, Tang ZY, Jiang L, Adv Mater, 2012, 24, 1046-49.