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COMMUNICATION

Facile synthesis of self-assembly mesoporous CuO nanospheres and hollow Cu₂O microspheres with excellent adsorption performance

11Cite this: DOI:
10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Self-assembly mesoporous CuO nanospheres (CuO NSs) and hollow Cu₂O microspheres (Cu₂O MSs) were synthesized by a facile ethylene glycol-water solvothermal method without any surfactants. The formation and evolution of copper oxides were investigated by controlling the synthesized condition. The as-prepared Cu_xO materials showed an excellent adsorption capability for the quick removal of Acid Orange 7 (AO7) dye in water.

As important functional materials, copper (Cu⁺ or Cu²⁺) oxides have been widely investigated in recent years, since they are inexpensive, environmentally benign, non-toxic and abundant.¹⁻⁴ Copper oxide (CuO and Cu₂O), typically, have potential applications in the field of solar energy conversion, adsorption, photo-degradation, electronics, and gas sensors.⁵⁻⁸ In our previous reports, it was reported that porous nano-size Cu₂O nanoparticles have a selective adsorption property for anionic dyes, showing a new potential application of Cu_xO in removing anionic dyes from waste water for environment treatment.^{9,10} It is well known that nanomaterials with spontaneous assembly and hierarchical structures show a strong correlation between their function and geometry.¹¹ Therefore, porous semiconductor materials endowed with a large number of reaction sites, high specific surface area, high specific strength and good permeability are particularly significant in the practical applications.

Recently, considerable research efforts have been undertaken to develop simple methods for the fabrication of low-dimensional copper oxide semiconductor materials. Yang's group have exploited the concept of nanostructures engineering on copper foil surface through a solution chemical route.¹² They have synthesized a series of copper-based materials on the surface of pure copper foil, such as CuO nanorods arrays and Cu₂O nanowires arrays.^{13,14} It has also been demonstrated that the crystal structure transformation among Cu, CuO and Cu₂O is practicable.¹⁵⁻¹⁷ As a more facile synthesis route, alcohol-based reduction method has been widely used to synthesize copper oxide materials. For example, Guo's group synthesized Cu₂O/GO and CuO/GO composite via a diethylene glycol reduction method which exhibited enhanced photo-electrocatalytic activity.^{18,19} However, capping agent is usually

indispensable in order to achieve satisfactory diversified structures. At present, capping agent or surface active agent, such as polyvinylpyrrolidone (PVP), cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS), were widely investigated to purposefully synthesize Cu₂O nanocubes,²⁰⁻²² multi-shelled Cu₂O^{23,24} and multi-aspect Cu₂O spheres.²⁵⁻²⁷ To obtain morphology-controllable and crystal-assignable copper oxide materials, complex experimental steps, strict reaction conditions and toxic reduction agent are often required. So far, among different methods reported for copper oxide nanocrystals, it is worth mentioning that a simple and suitable method for preparing porous copper oxide is still unsatisfactory. Therefore, it is necessary to develop a facile method to fabricate copper oxide with controllable structure.

In the current work, a simple water-ethylene glycol (EG) mixed solvothermal route for the formation of mesoporous CuO nanospheres (NSs) and hollow microspheres Cu₂O (MSs) has been investigated. The uniform and size controllable CuO NSs could be obtained via a spontaneous aggregation and crystallization processes in the absence of any surfactants or additives (even pH adjusting agency of NaOH). With the assistant of glucose, hollow Cu₂O MSs could be easily received. The possible growth process of CuO NSs nanocrystal was detected by investigating the relationship between the morphology changes and the growth temperatures. It was also found that, with the addition of reduction agent (glucose), the reaction temperature has strong influence on the final Cu₂O size-distribution and homogeneity. Finally, selective adsorption performances of the synthesized samples were also investigated. It was found that the as-prepared CuO NSs have a large BET specific surface area (around 168 m²/g) and show an excellent adsorption capability in the removal of AO7 dye from water.

Mesoporous CuO NSs were synthesized by a simple solvothermal route without the presence of any other reagent addition. In a standard synthesis, 10 ml of copper acetate (Cu(Ac)₂, 0.1 M), 5 ml of H₂O and 45 ml of ethylene glycol (EG) were mixed to form a solution in a round-bottom flask (100 ml), the homogeneous mixed solution was then put into an 160 °C oil bath and stirred under reflux for one hour. Varied reaction temperatures were performed to investigate the spontaneous aggregation and crystallization processes

of CuO NSs. The process for Cu₂O MSs synthesis was basically as the same as that of CuO NSs except that 5 ml glucose solution (0.43 M) was injected into the initial mixed solution before the solvothermal reaction, Cu₂O MSs with different size distributions can be obtained at different reaction temperatures. The final black CuO NSs and reddish-yellow Cu₂O MSs were collected by centrifugation and washed with water and ethanol for several times to remove most of the EG. Two kinds of Cu₂O crystals with different morphology were also obtained by a controlled glucose added manner, which were denoted as Cu₂O polyhedron and Cu₂O cube (See ESI, Experiment section and Fig. S1-S2).

The nanostructure transformation of the CuO NSs and Cu₂O were examined by SEM, TEM and XRD. It is found that the reaction temperature is a crucial condition for the growth of copper oxides crystals in the EG reduction progress, which affects the morphology and constructions of copper oxides. A group of typical SEM imagines of CuO NSs obtained at different reaction temperatures are presented in Fig.1, which clearly shows the growth procedure of the products. At a relative low temperature (80 °C), after 1 h reaction, the light blue mixed solution turned to olive green, which indicated the formation of irregular CuO nanoparticles (Fig. 1A). Uniform spindle-shaped CuO nanorods with sharp ends formed from tiny nanosheets spontaneously assembled at a little higher reaction temperature of 100 °C (Fig. 1B). When the reaction temperature was improved to 140 °C, small amounts of CuO NSs appeared (Fig. 1C). With the temperature of 160 °C, the nearly monodisperse nanospheres formed in large scale as shown in Fig. 1D and E. The corresponding TEM imagine is given in Fig. 1F. The mean CuO NSs size was determined by randomly selecting 500 CuO NPs from Fig. 1E. It is found that the average diameter of CuO NSs is 412 nm and the histogram of the size distribution is inserted in Fig. 1E. Looking carefully at the feature of samples from the four different reaction temperature periods, it is conclude that: (i) the final monodispersed mesoporous CuO NSs with wavy-like surface (sample in Fig.1 D) are composed of many self-assembly schistose CuO (samples in Fig. 1A, B and C), and (ii) the reaction temperature obviously influences the final morphology of CuO and a higher temperature could effectively enhance the aggregation of CuO piece-like crystallites; the higher reaction temperature is favorable for the more uniform crystallite size distribution of CuO NSs.

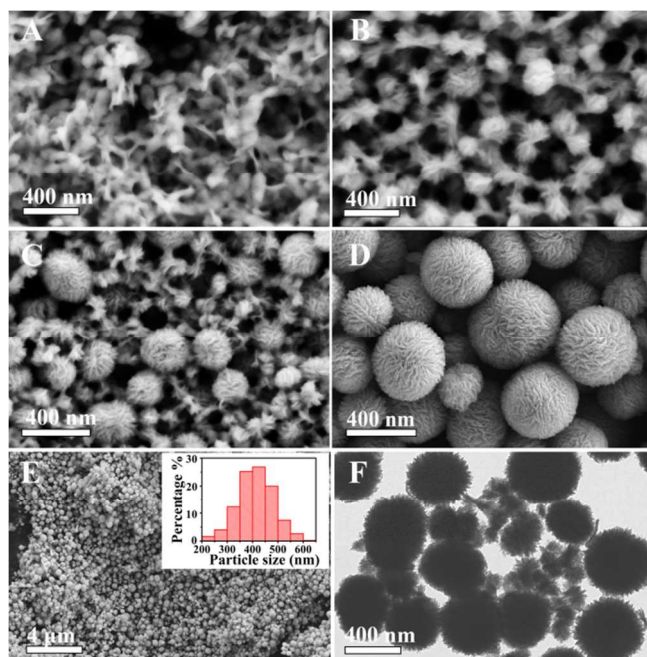


Fig. 1 The morphological transformation of synthesized CuO NSs at different reaction temperatures of 80 °C (A), 100 °C (B), 140 °C (C) and 160 °C (D, E). (F) is the corresponding TEM imagines of (D). The inset in (E) is a histogram of the size distribution from the as synthesized CuO NSs.

When glucose as a reduction agency was injected into the original mixed solution (H₂O: EG: Cu(Ac)₂) in the solvothermal reaction, Cu₂O microspheres could be achieved. Based on the examination of the reaction temperature-dependent formation of CuO NSs, the Cu₂O MSs at different reaction temperatures were also synthesized. As can be seen from Fig. 2A-D, All of the synthesized samples at the reaction temperature from 60 to 140 °C have sphere structures. With the increase of reaction temperature, the average diameter of the spheres increases and the spheres become more homogeneous. Figs. 2E(1)-(4) are the corresponding size distribution histograms calculated from samples in Fig. 2A-D, which clearly reveals that the mean diameter increases from 320 nm to 1 μm.

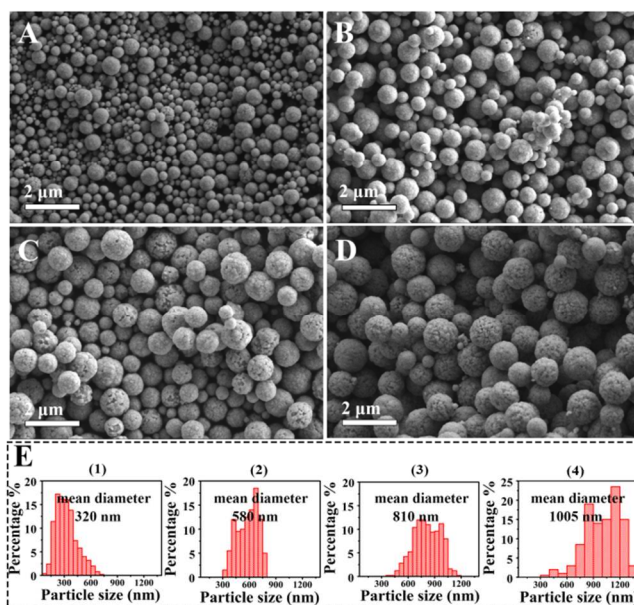


Fig. 2 SEM images of Cu₂O samples obtained at different synthesis temperatures of 60 °C (A), 80 °C (B), 100 °C (C) and 140 °C (D). E is the corresponding size distribution histogram calculated for A, B, C and D samples.

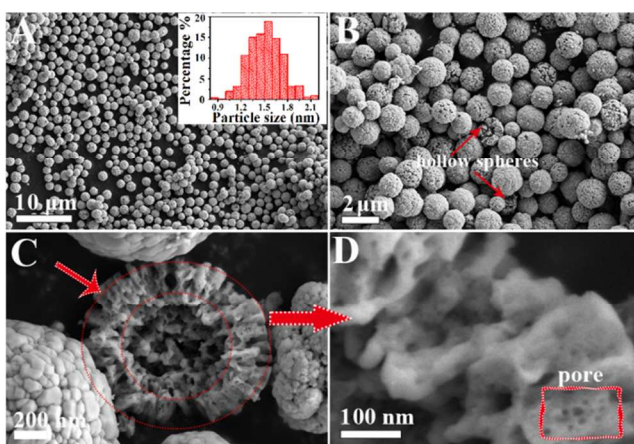


Fig. 3 SEM images with different magnifications of the as-synthesized Cu₂O MSs at the synthesis temperature of 160 °C.

A very homogeneous and completely monodispersed Cu₂O MSs were obtained at a higher reaction temperature of 160 °C. The morphology and hierarchical porous structure of the as-prepared

Cu₂O MSs were observed by SEM. Fig. 3A-C show SEM images of the as-synthesized Cu₂O MSs at different magnifications, it can be seen from Fig. 3A that bulk quantities of Cu₂O MSs were fabricated with relatively uniform diameters. A histogram of the size distribution of the Cu₂O is shown as inset in Fig. 3A. It is found that the diameters of Cu₂O MSs are in the range of from 0.9 to 2.1 μm and the mean diameter is 1.5 μm . Figs. 3B-C reveal that these monodisperse Cu₂O MSs have a hollow spherical structure with the shell thickness of about 400 nm. More interestingly, there are a lot of mesoporous in the Cu₂O MSs shell walls (Fig. 3D), which proves that the as-synthesized Cu₂O MSs are composed of center hollow monodispersed microspheres with abundant mesoporous on the wall. We speculate that the reduction effect of glucose led to the formation of Cu₂O hollow structure. Especially, in higher reaction temperature of 160 °C, glucose was decomposed to produce carbon dioxide gas, resulting in the prominent hollow structure.

The crystal structure of all the final obtained samples was verified by XRD. Fig. 4 shows the XRD patterns for both the CuO NSs and Cu₂O MSs received at 160 °C. From Fig. 4a and b, it can be seen that all the diffraction peaks for CuO NSs and Cu₂O MSs can be readily indexed to the monoclinic symmetry of CuO (JCPDS 45-0937) and face-centred cubic Cu₂O (JCPDS 05-0667), respectively. No obvious impurities were detected, indicating the purity of the synthesized samples.

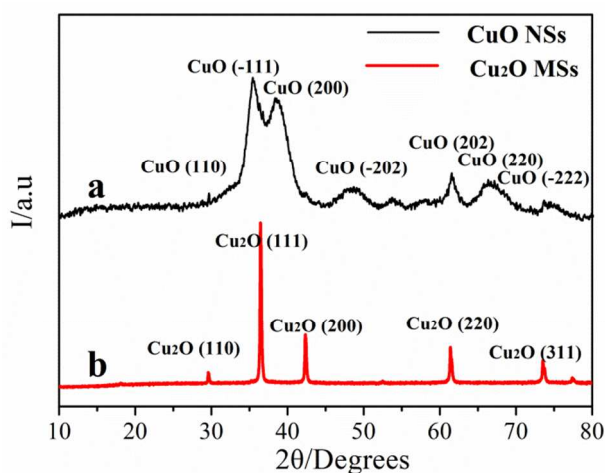


Fig. 4 XRD patterns of the CuO NSs (a) and Cu₂O MSs (b) respectively.

As it is known to all, the size and morphology of nanomaterials have a great effect on their chemical and physical properties and therefore their applications. The synthesized Cu_xO materials with different morphology were employed as efficient adsorbents to effectively remove dyes from water and thus could be used for the environment treatment. For comparison, the adsorptive capability of commercial CuO (*c*-CuO) and Cu₂O (*c*-Cu₂O) were also investigated. Adsorption performances of all samples were assessed with AO7, methyl orange (MO) and methyl blue (MB). The results showed the as-synthesized Cu_xO nanostructures had a highly selective adsorption characteristic for anionic dyes MO and AO7, especially AO7, but no adsorption was observed for cationic dye MB (See ESI, Table S1 and Fig. S3). The zeta potential of the synthesized CuO NSs and Cu₂O MSs samples were measured to be +31 mV and +28 mV, respectively. The positive zeta potential of Cu_xO surfaces have also been found in our previous reports.¹⁰ Here, we presume the mechanism of selective adsorption can be attributed to the electrostatic adsorptions. The adsorption kinetics of the CuO NSs and Cu₂O MSs received at 160 °C for AO7 is shown in Fig. 5A. It can be seen that all the synthesized materials arrived adsorptive

equilibrium within 30 min. CuO NSs can rapidly remove AO7 over 97.5% in 15 min, at the same time, Cu₂O MSs also reach 60.7%. Both of them are much higher removal rate than the commercial CuO and Cu₂O, which only have a low removal rate for AO7 (5.2% and 11.4%, respectively). The adsorption capacity of Cu_xO were further calculated from the statistical chart of AO7 adsorption in 15 min. Fig. 5B apparently shows that the as-synthesized CuO NSs and Cu₂O MSs samples both have higher adsorption capacities for AO7 dye, which are almost 20 times and 5 times those of commercial CuO and Cu₂O, respectively. To test the reusability of copper oxides particles (CuO NSs and Cu₂O MSs) for dye adsorption, we carried out the bleaching experiment for AO7 repeatedly five times. As shown in Fig. S4, the reactivated samples can quickly adsorb AO7 from the contaminative solution every time and the adsorption performances are not significantly weakened. These results further proved that the as-synthesized CuO NSs and Cu₂O MSs are effective and stable for quickly removal of AO7 dye in water.

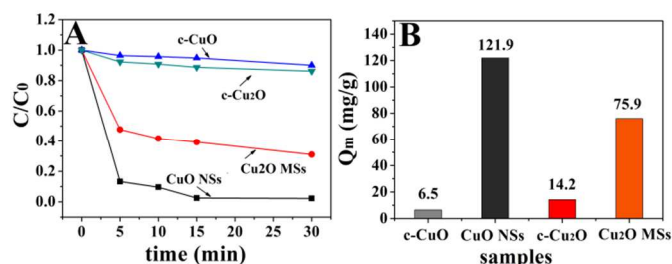


Fig. 5 (A) Adsorption kinetics of the as prepared Cu_xO materials (20 mg) and the commercial CuO and Cu₂O (20 mg) for AO7 (50 mg/L). C₀ is the initial concentration of AO7 solution and C is the concentration of AO7 in the solution at different adsorption time. (B) Adsorption capacity of all the samples for AO7.

The mechanism of selective adsorption had been demonstrated in our previous report, which was mainly attributed to the electrostatic adsorption¹⁰. In fact, the porous structure of the as-synthesized CuO NSs and Cu₂O MSs may affect the adsorption capacity and rate. Herein, the N₂ adsorption/desorption isotherms and pore size distributions of CuO NSs and Cu₂O MSs were tested. As show in Fig. 6A and B, the BET surface areas of the two samples are 168.2 and 36.5 m²g⁻¹ for CuO NSs and Cu₂O, respectively, which are far larger than those of *c*-CuO (5.1 m²g⁻¹) and *c*-Cu₂O (3.2 m²g⁻¹). The insets in Fig. 6A and B show that the pore-size distribution centres are at 5 nm for CuO NSs and 50 nm for Cu₂O MSs. In addition, the large pores (diameter > 150 nm) in the Cu₂O sample can be attributed to the centre hollow structure in Cu₂O MSs, as shown in the Fig. 3C. All these results are matched well with the SEM and TEM images. The effectively enhancement of the adsorption capacity mainly is attributed to the increase of surface physical adsorption active sites on the Cu_xO spheres, which are supplied by the porous structure. This study has developed a facile and practical pathway for the preparing Cu_xO porous materials, which are promising and interesting for potential applications of anionic dyes adsorption from waste water quickly.

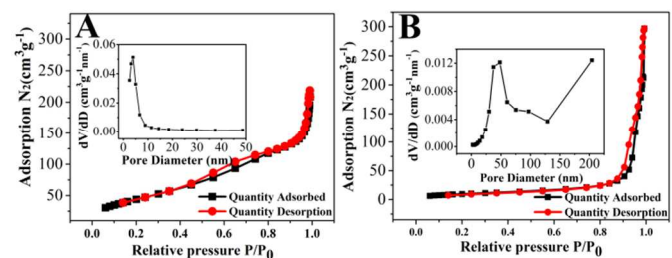


Fig. 6 (A) and (B) N₂ adsorption curves of the as-obtained CuO NSs and Cu₂O MSs; the inset shows the pore size distribution for the two samples respectively.

Conclusions

The uniform and size controllable CuO NSs and Cu₂O MSs can be obtained via a spontaneous aggregation and crystallization processes in the absence of any surfactants or additives. The growth progress and conditions were studied in detail by controlling the reaction temperature; the as-prepared Cu_xO materials show excellent adsorption capability for the quick removal of AO7 dye in water.

Acknowledgements

This work was supported by the financial support from the National Natural Science Foundation of China (No. 20873044), the Guangdong Provincial Science and Technology Project of China (2011B B050400014) and the China Postdoctoral Science Foundation (No. 2012M521606; 2014T70808).

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and supplementary figures. See DOI: 10.1039/b000000x/

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