Supporting Information

Facile synthesis of self-assembly mesoporous CuO nanospheres and

hollow Cu₂O microspheres with excellent adsorption performance

Siyuan Yang^a, Shengsen Zhang^{a,b}, Hongjuan Wang^a, Hao Yu^a, Yueping Fang^b, Feng Peng^{*,a}

^aSchool of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510640 China.

^b College of Science, South China Agricultural University, Guangzhou, 510642, China.

*Corresponding author, Email address: cefpeng@scut.edu.cn (F. Peng), Fax: +86 20 87114916.

1. Experimental Section

1.1 Preparation of materials

All the reagents were used as received without any further purification.

(1) Synthesized of mesoporous CuO NSs

The CuO NSs were synthesized by a simple solvothermal route without the presence of any surfactants. In a standard synthesis process, 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), after stirring for 15 minutes, the homogeneous mixed solution then putted 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 final black CuO NSs were collected by centrifugation and washed with water and ethanol for several times to remove most of the EG.

(2) Synthesized of mesoporous Cu₂O MSs

The process for Cu_2O MSs synthesis was basically as the same as that of CuO NSs, except for 5 ml glucose solution (0.43 M) was injected into the initial mixed solution before the solvothermal reaction. Cu_2O MSs with different size distributions obtained at different reaction temperatures from 60 to 160 °C. The reddish-yellow Cu_2O MSs were collected by centrifugation and washed with water and ethanol for several times to remove most of the EG.

(3) Synthesized of Cu₂O polyhedron and Cu₂O cube

Cu₂O polyhedron and Cu₂O cube crystals also were obtained by another glucose added manner, in which, after the synthesized of CuO NSs, a same volume and concentration of glucose solution (5 ml, 0.43M) were added into the mixed CuO NSs solution, and then the mixed solution continue reacted for another 1 h at different temperature for the completely transformation of CuO NSs to Cu₂O polyhedron (140 °C) and Cu₂O cube (120 °C). The final products were collected by centrifugation and washed with water and ethanol for several times to remove most of the EG.

1.2 Catalyst characterization

The morphologies of the prepared samples were obtained in a field-emission scanning electron microscope (FESEM, LEO 1530VP) and transmission electron microscopy (TEM)

(FEI Tecnai 20 microscope). X-ray diffraction (XRD) patterns were recorded on an X-ray diffractometer (D/max-IIIA, Japan) using Cu Ka as the radiation source. Brunauer–Emmett–Teller (BET) surface area measurements were carried out by N_2 adsorption at 77 K using the volumetric adsorption analyzer (ASAP 2010, Micromeritics Ins. Corp.)

1.3 Adsorption test.

Adsorption performance of all the as-synthesized Cu_xO nanostructures and commercial Cu_xO materials were assessed by acid orange 7 (AO7, $C_{16}H_{11}N_2NaO_4S$), methyl orange (MO, $C_{14}H_{14}N_3SO_3Na$) and methyl blue (MB, $C_{16}H_{18}CIN_3S$). The experimental process was carried out in a dark box. Firstly, 0.02 g tested powders (samples of CuO NSs and Cu₂O MSs were received at 160 °C) were suspended in 50 ml 50 mg/l solution of pollutants. Subsequently, the mixture solution was continually stirring. Considering the adsorption behavior was immediately performed, the time sampling was carried out after the addition of powder samples. Each a determinate interval (such as 5 min), 5 ml of the suspension was sampled and separated by centrifugation at 8000 rpm for 10 min. The adsorption kinetics curves of different absorbents were determined through measuring the concentration of dye solution at different times by a UV-vis spectro photometer (Hitachi U3010). The typical max wavelength of AO7, MO and MB were 483 nm, 462 nm and 662 nm, respectively.

Removal ratio of dyes was calculated by the following equation (1):

 $X = (C_0 - C)/C_0 \times 100\%$. (1)

The adsorption capacity of Cu_xO was calculated by the following equation (2):

$$Q_{\rm m} = (C_0 - C) \times V/W(2)$$

Where, $Q_m (mg/g)$ is the adsorption capacity at a certain times, $C_0 (mg/L)$ is the initial concentration of the dyes solution, C (mg/L) is the concentration of the solution at different time, V(L) is the volume of the solution and W(g) is the weight of the sorbent.

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. The used CuxO nanomaterials were centrifuged and washed with alcohol-water mixed solution until the supernatant liquid was colorless, and then dried in vacuum at 60 °C.

2. Supplementary Figures and Table



A schematic diagram for the controllable synthesized procedure is given in Fig. S1.

Fig. S1 A schematic illustration of the overall successive synthesized procedure.

Fig. S2 shows Cu₂O polyhedron and Cu₂O cube crystals obtained by another glucose added manner. It can be proved that the as synthesized CuO NSs were susceptible to the added glucose solution accompany with the react temperature. Under the reaction temperature of 140 °C, glucose was added to the reaction solution containing CuO NSs and kept reaction for 1 hour, the solution became reddish yellow from brownish black and some precipitate was easy to deposit onto the bottom of the round bottom flask. Fig. S2A and B clearly indicate Cu₂O polyhedron with hollow interiors and geometrical symmetry. However, when the reaction temperature dropped to 120 °C, it was found that most of the CuO NSs transformed to Cu₂O cubic with smooth surfaces and a mean edge length of about 400 nm (Fig. S2C and D). The insets are corresponding TEM images.



Fig. S2 SEM images of Cu₂O polyhedron and Cu₂O cubes obtained at different reaction temperatures of 140 °C (A, B) and 120 °C (C, D). The insets are corresponding TEM images.

Table S1 Adsorptive removal ratios (X) and the adsorption capacities (Q_m) of the compared samples for all the examined dyes removal (in 15 min).

CuxO	AO7		МО		MB	
Samples	Х	Qm	Х	Q _m	X	Q_m
	(%)	(mg/g)	(%)	(mg/g)	(%)	(mg/g)
c-CuO	5.2	6.5	7	8.7	0	0
CuO NSs	97.5	121.9	55.2	68.9	0	0
c-Cu ₂ O	11.4	14.2	2.2	2.7	0	0
Cu ₂ O MSs	60.7	75.9	11.3	14.1	0	0
Cu ₂ O poly	55.7	69.7	8.5	10.6	0	0
Cu ₂ O cube	45.8	57.3	6.9	8.6	0	0



Fig. S3 UV/Vis absorbance spectra of all the samples (20 mg) in solution (50 ml) with AO7 (A) and MO (B) after 30 min.



Fig. S4 The Adsorption kinetics of the as prepared CuO NSs (A)and Cu₂O MSs (B) (20 mg) for AO7 (50 mg/L, 50 ml). C0 is the initial concentration of AO7 solution and C is the concentration of AO7 in the solution at different adsorption time.

As shown in Fig. S4, the reactivated samples can quickly adsorb AO7 from the contaminative solution every time and the adsorption performance are not significantly reduced. 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.