# Surfactant-free synthesis of Cu<sub>2</sub>O yolk-shell cubes decorated with Pt nanoparticles for enhanced H<sub>2</sub>O<sub>2</sub> detection

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### **Experimental section**

## Chemicals

Cupric chloride (CuCl<sub>2</sub>), sodium hydroxide (NaOH), zinc chloride (ZnCl<sub>2</sub>) sodium ascorbate (SA), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), mono potassium phosphate (KH<sub>2</sub>PO<sub>4</sub>), potassium hydrogen phosphate (K<sub>2</sub>HPO<sub>4</sub>), potassium chloride (KCl), sodium chloride (NaCl), ascorbic acid (AA), fructose and lactose were purchased from Aladdin Reagent. Potassium hexachloroplatinate (K<sub>2</sub>PtCl<sub>6</sub>) and methyl alcohol were obtained from Shanghai Sinopharm Chemical Reagent. 0.05% Nafion solution was diluted from 5% Nafion solution (Sigma-Aldrich) using ethanol as the solvent. All chemicals used in our work were of analytical grade and no further purification was processed. The deionized water (18.25 M $\Omega$ ·cm) was obtained from a MilliQ Academic water purification system (Millipore Corp.)

## Ont-pot synthesis of Cu<sub>2</sub>O hollow yolk-shell cubes

Typically, 1 ml CuCl<sub>2</sub> solution (0.1 M), 0.25 ml ZnCl<sub>2</sub> solution (0.1 M) and 1 ml of sodium hydroxide (0.4 M) were added into 42.75 ml deionized water under constant stirring. After 5 minutes stirring, 5 ml of sodium ascorbate (0.1 M) was injected into the beaker. Then the reaction was further processed for 60 minutes. The aforementioned reaction was controlled in the water bath at the temperature of 40 °C. Finally, the precipitates were collected by the centrifugation at the speed of 5000 rpm for 2 minutes, followed by the washing with water and ethanol for several times and dried at 50 °C for 12 hours in vacuum.

### Synthesis of Pt nanoparticles decorated Cu<sub>2</sub>O composites

Pt-Cu<sub>2</sub>O yolk-shell particles were synthesized by a photochemical reducing approach: Firstly, 10 mg of as-prepared yolk-shell Cu<sub>2</sub>O particles were dispersed in 10 ml of 20 % CH<sub>3</sub>OH aqueous solution containing 0.513 mM K<sub>2</sub>PtCl<sub>6</sub> by sonication. The suspension was stirred and illuminated by 200 W UV light for 60 minutes at room temperature. Then the composite precipitates were washed by deionized water and ethanol four times and dried in the vacuum at 50 °C for 12 hours.

#### Characterization

The X-ray diffractometer (Bruker-AXS D8 ADVANCE) with Cu K $\alpha$  as the radiation source ( $\lambda$ =1.54 Å) was utilized to characterize the crystal phases of the as-prepared products. The X-ray photoelectron spectroscopy (XPS) was measured by Thermo

Fisher ESCALAB Xi<sup>+</sup> spectrometer equipped with an Al mono K $\alpha$  X-ray source. The morphologies of yolk-shell Cu<sub>2</sub>O cubes and Pt-Cu<sub>2</sub>O yolk-shell cubes were characterized by the JSM-7000F field-emission scanning electron microscope (FE-SEM, JEOL, Japan). The transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were investigated by The JEOL JEM-2100 transmission electron microscope with an accelerating voltage of 200 KV. JEOL JEM-F200 microscope was used to acquire scanning transmission electron microscopy (STEM) of the Pt decoratedCu<sub>2</sub>O yolk-shell cubes.

#### Fabrication of the electrodes

Before the fabrication of the electrodes, alumina powders with size of 0.5  $\mu$ m and 50 nm were used to polish the surface of the bare glassy carbon electrodes (GCEs) ( $\Phi$  5 mm) to obtain the mirror-like surfaces. Then the GCE electrodes were ultrasonically cleaned in deionized water and ethanol for several times. The modification of electrodes were carried out as follows: 2 mg of as-prepared pristine yolk-shell Cu<sub>2</sub>O or Pt-Cu<sub>2</sub>O yolk-shell particles were dispersed in 2 ml of Nafion solution (0.05%) by sonication for 30 minutes to obtain the homogeneous suspensions. 20  $\mu$ L of the resulting suspensions were dropped on the GCEs (denoted as y-s Cu<sub>2</sub>O/Nafion/GCE and y-s Pt-Cu<sub>2</sub>O/Nafion/GCE, respectively), followed by the drying at room temperature.

#### **Electrochemical measurements**

The electrochemical measurements were carried out on a standard three-electrode system (CHI-660E, Shanghai Chenhua, China) in room temperature. The as-prepared y-s Cu<sub>2</sub>O/Nafion/GCE and y-s Pt-Cu<sub>2</sub>O/Nafion/GCE electrodes served as the working electrodes, an Ag/AgCl electrode as the reference electrode and a Pt foil as the counter electrode. 100 ml of 0.1M PBS (pH=7.4) aqueous solutions with or without various concentrations of  $H_2O_2$  were served as the electrolyte solution for all the cyclic voltammetry (CV) and chronoamperometry (CA) measurements. Before the

test, the solutions were saturated with  $N_2$  for 15 minutes to fully remove the soluble  $O_2$  in the solution. Magnetic stirrings were processed in amperometric measurements to guarantee the thorough mixing of  $H_2O_2$  with the PBS solution. EIS was undertaken on a VersaSTAT MC workstation in 0.1 M KCl solution containing 0.01 M  $K_3$ [Fe(CN)<sub>6</sub>] and 0.01 M  $K_4$ [Fe(CN)<sub>6</sub>] at the open circuit potential.



**Figure s1** (a) XRD pattern, (b)Cu 2p, (c) Pt 4f and (d) Zn 2p XPS spectra of Pt-Cu<sub>2</sub>O yolk-shell cubes.



Figure s2 FESEM images of yolk-shell  $Cu_2O$  (a), TEM images of an individual yolk-shell (b).



**Figure s3** SEM images of products (yolk-shell  $Cu_2O$ ) obtained at different time: (a) 1 min, (b) 30 min, (c) 60 min, (d) 90 min and (e) 120 min. Insets of (b-e) show the individual  $Cu_2O$  at different reaction periods, scar bar: 200 nm.



**Figure s4** Size distributions of products  $Cu_2O$  obtained at different time: (a) 1 min, (b) 30 min, (c) 60 min, (d) 90 min and (e) 120 min. (f) The size change of the  $Cu_2O$  with the elongation of the reaction time.



**Figure s5** SEM images of products  $Cu_2O$  synthesized without the addition of the  $ZnCl_2$  (a) and with the flow of nitrogen (b), the reaction time is 3 hours.



Figure s6 Amperometric response of the Pt-Cu<sub>2</sub>O yolk-shell composites modified electrode under various potentials, from -0.30 V to -0.10 V, with the successive addition of 0.1 mM  $H_2O_2$ .

Electrode	Linear rang	Limit of	Sensitivity (µA	Reference
	(mM)	detection (µM)	mM <sup>-1</sup> cm <sup>-2</sup> )	
Cu <sub>2</sub> O/N-graphene	0.005-3.57	0.8	26.67	1
Cu <sub>2</sub> O-rGO	0.03-12.8	21.7	19.5	2
CQDs/octahedral	0.005-5.3	2.8	good	3
Cu <sub>2</sub> O				
Pt@UiO-66	0.005-14.75	3.06	75.33	4
PB@Pt/CNT	0.00025-1.25	0.2	720	5
Pt-TiO2/rGO	0.1-22.5	100	40	6
Pt/graphite	0.0005-2	0.0075	55.59	7
PtIr/MWCNTs	0.0025-0.075	2.5	58.8	8
PtCu/C	0-4	12.2	69.4	9
y-s Cu <sub>2</sub> O	0.01-6000	11.1	20.3	This work
	6000-14000		30.9	
y-s Pt-Cu <sub>2</sub> O	0.01-6000,	10.3	25.3	This work
	6000-16000		55.7	
GO - Graphene Oxide, CQD – Carbon Quantum Dot, PB – Prussian Blue, MWCNT				
– Multi-Wall Carbon nanotube.				

Table s1 The comparison with the reported H<sub>2</sub>O<sub>2</sub> nonenzymatic H<sub>2</sub>O<sub>2</sub> sensors

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