Surfactant-free synthesis of Cu₂O yolk-shell cubes decorated with Pt nanoparticles for enhanced H₂O₂ detection

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Experimental section

Chemicals

Cupric chloride (CuCl₂), sodium hydroxide (NaOH), zinc chloride (ZnCl₂) sodium ascorbate (SA), hydrogen peroxide (H₂O₂), mono potassium phosphate (KH₂PO₄), potassium hydrogen phosphate (K₂HPO₄), potassium chloride (KCl), sodium chloride (NaCl), ascorbic acid (AA), fructose and lactose were purchased from Aladdin Reagent. Potassium hexachloroplatinate (K₂PtCl₆) 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 Ω ·cm) was obtained from a MilliQ Academic water purification system (Millipore Corp.)

Ont-pot synthesis of Cu₂O hollow yolk-shell cubes

Typically, 1 ml CuCl₂ solution (0.1 M), 0.25 ml ZnCl₂ 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 Cu₂O composites

Pt-Cu₂O yolk-shell particles were synthesized by a photochemical reducing approach: Firstly, 10 mg of as-prepared yolk-shell Cu₂O particles were dispersed in 10 ml of 20 % CH₃OH aqueous solution containing 0.513 mM K₂PtCl₆ 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 α as the radiation source (λ =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⁺ spectrometer equipped with an Al mono K α X-ray source. The morphologies of yolk-shell Cu₂O cubes and Pt-Cu₂O 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 decoratedCu₂O yolk-shell cubes.

Fabrication of the electrodes

Before the fabrication of the electrodes, alumina powders with size of 0.5 μ m and 50 nm were used to polish the surface of the bare glassy carbon electrodes (GCEs) (Φ 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 Cu₂O or Pt-Cu₂O yolk-shell particles were dispersed in 2 ml of Nafion solution (0.05%) by sonication for 30 minutes to obtain the homogeneous suspensions. 20 μ L of the resulting suspensions were dropped on the GCEs (denoted as y-s Cu₂O/Nafion/GCE and y-s Pt-Cu₂O/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 Cu₂O/Nafion/GCE and y-s Pt-Cu₂O/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)₆] and 0.01 M K_4 [Fe(CN)₆] at the open circuit potential.



Figure s1 (a) XRD pattern, (b)Cu 2p, (c) Pt 4f and (d) Zn 2p XPS spectra of Pt-Cu₂O 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-Cu₂O 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 ⁻¹ cm ⁻²)	
Cu ₂ O/N-graphene	0.005-3.57	0.8	26.67	1
Cu ₂ O-rGO	0.03-12.8	21.7	19.5	2
CQDs/octahedral	0.005-5.3	2.8	good	3
Cu ₂ 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 ₂ O	0.01-6000	11.1	20.3	This work
	6000-14000		30.9	
y-s Pt-Cu ₂ 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 H₂O₂ nonenzymatic H₂O₂ sensors

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