Mn²⁺-mediated construction of rhombicuboctahedral Cu₂O nanocrystals enclosed by jagged surfaces for enhanced enzyme-free glucose sensing

Haoqi Ren,^{*a,b*} Xin Zhang,^{*a*} Xiaochuan Zhang,^{*a*} Jie Cui,^{*a*} Qing Yang,^{*a*} Chuncai Kong,^{*c*} Zhimao Yang^{*c*} and Shaodong Sun*^{*a*}

^a Engineering Research Center of Conducting Materials and Composite Technology, Ministry of Education; Shaanxi Engineering Research Centers of Metal-based Heterogeneous Materials and Advanced Manufacturing Technology; Shaanxi Province Key Laboratory for Electrical Materials and Infiltration Technology; School of Materials Science and Engineering, Xi'an University of Technology, Xi'an 710048, Shaanxi, People's Republic of China.

E-mail: sdsun@xaut.edu.cn (S. D. Sun).

^b Materials Science & Engineering Divison, Boston University, 15 St. Mary's St., Boston MA 02215, USA

^c School of Science, State Key Laboratory for Mechanical Behavior of Materials, MOE Key Laboratory for Non-Equilibrium Synthesis and Modulation of Condensed Matter, Center of Suzhou Nano Science and Technology, Xi'an Jiaotong University, Xi'an 710049, ShaanXi, People's Republic of China.

Experimental Sections

Chemicals

Cupric chloride (CuCl₂), cupric nitrate (Cu(NO₃)₂), cupric sulfate (CuSO₄), cupric acetate (Cu(Ac)₂), manganous acetate (Mn(Ac)₂), ferric chloride (FeCl₃), cobaltous chloride (CoCl₂), magnesium chloride (MgCl₂), aluminium chloride (AlCl₃), nickel chloride (NiCl₂), stannous chloride (SnCl₂), sodium ascorbate (SA, C₆H₇NaO₆), sodium hydroxide (NaOH), glucose, uric acid (UA), sodium chloride (NaCl), fructose, lactose and sucrose were purchased from Aladdin Reagent. All chemicals were of analytical grade without any further purification. The deionized water (18.25 M Ω ·cm) was from a MilliQ Academic water purification system (Millipore Corp.).

Synthesis of jagged Cu₂O rhombicuboctahedral nanocrystals

All Cu₂O materials were prepared through a facile wet chemical route in aqueous phase at room temperature (25°C). In the typical procedure, 1 mL CuCl₂ solution (0.1 M), was mixed together with 1 mL sodium hydroxide solution (0.4 M) as well as 50 mL $Mn(Ac)_2$ solution (0.002 M) under stirring at room temperature. After a continuous stirring for 5 minutes, 5 mL SA solution (0.1 M) was added dropwise into the beaker, and then stirring was constantly processed for 20 minutes. Finally, the precipitates were completely washed with water and ethanol for several times. Then the products were dried in a vacuum oven at 50 °C for 12 h. Different kinds of metal salts can be utilized to replace $Mn(Ac)_2$.

Instruments

The crystal phases of the as-obtained Cu₂O structures were characterized with the X-ray diffractometer (Bruker-AXS D8 ADVANCE) equipped with Cu K α radiation source (λ =1.54 Å). The chemical composition and purity of the products were tested by electron energy dispersive X-ray (EDX) analysis. The transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) analysis and selected-area electron diffraction (SAED) analysis were conducted on a JEOL JEM-2100 transmission electron microscope at an accelerating voltage of 200 kV. Samples for the TEM analysis were dispersed in 3 mL ethanol by ultrasonic for 5 min. Next, the ethanol solutions of samples were dropped onto a carbon-coated copper grid, which were dried in air before TEM analysis. The JSM-7000F field-emission scanning electron microscope (FE-SEM, JEOL, Japan) was utilized to observe the different morphologies of Cu₂O materials.

Preparation of Cu₂O electrode and electrochemical measurement

A non-enzymatic amperometric electrochemical sensor was fabricated by dropping Cu_2O ethanol solution onto a glassy carbon electrode with Nafion as binding agent. The modified electrodes were prepared as follows: 5 mg of the jagged Cu_2O powders was dispersed in 5 mL Nafion solution (0.05 %, Sigma–Aldrich) by sonication. 20 µL of the well-dispersed Cu_2O suspension was casted on the pre-treated glassy carbon electrode (denoted as $Cu_2O/Nafion/GCE$) by two times, and then dried at room temperature. Before the fabrication of sensors, the bare GCE ($\phi = 5$ mm) was polished into a mirror-like surface by 0.5 µm and 50 nm alumina slurry, and subsequently cleaned in deionized water, 50% (v/v) nitric acid solution, ethanol, and deionized water for a few minutes,

respectively. The as-prepared Cu₂O/Nafion/GCE was used as the working electrode with a platinum foil as the counter electrode and an Ag/AgCl as the reference electrode. Electrochemical measurements were carried out on an Ametek VMC-4 electrochemical analyser with a three-electrode system in a 0.1 M KOH aqueous solution. For comparison, Cu₂O microcrystals with smooth surfaces were synthesized according to our previous work [1].

 S. Sun, X. Song, Y. Sun, D. Deng, Z. Yang, The crystal-facet-dependent effect of polyhedral Cu₂O microcrystals on photocatalytic activity, Catal. Sci. Tech., 2 (2012) 925-930.



Fig. S1 (a) XRD patterns of the as-obtained 26-facet Cu_2O . (b) EDX result of the as-obtained 26-facet Cu_2O . (c) TEM mapping of the as-obtained 26-facet Cu_2O .



Fig. S2 (a) SEM and (b) TEM images of Cu_2O cubes synthesized without Mn^{2+} ions.



Fig. S3 SEM images of Cu_2O synthesized with (a) $CuSO_4$, (b) $Cu(NO_3)_2$ and (c) $Cu(CH_3COO)_2$, respectively.



Fig. S4 SEM images of Cu₂O cubes synthesized with (a) Fe³⁺, (b) Ni²⁺, (c) Al³⁺, (d) Sn²⁺, (e) Co²⁺ and (f) Mg²⁺, respectively.



Fig. S5 TEM image of the final product with superfluous $Mn^{2+}(5 \text{ times higher})$.



Fig. S6 SEM and TEM images of Cu_2O with different amount of SA (a) 0.5 mL, (b) 1 mL, (c) 2 mL, (d) 3 mL, (e) 10 mL, (f) 15 mL.



Fig. S7 CV curves of the jagged 26-facet Cu₂O nanocrystals/Nafion/GCE electrode at different concentration of glucose solution (0.1 M KOH).



Fig. S8 Amperometric responses of the as-prepared electrodes detecting low concentration of glucose at +0.65 V vs Ag/AgCl.



Fig. S9 N_2 adsorption/desorption isotherms for the 26-facet rough Cu_2O nanocrystals and smooth microcrystals.