Electronic Supplementary Information

Facile preparation of Cu/Cu_2O nanoporous nanoparticles as a potential catalyst for non-enzymatic glucose sensing

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1. Experimental section

1.1 Synthesis of the Cu/Cu_2O nanoporous nanoparticles.

All of the chemical reagents used were of analytical grade. Prior to the experiment, all glass substrates used in preparation process were cleaned successively using detergent, deionized water, acetone, and boiling isopropyl alcohol, each under ultrasonication and then treated with nitrogen purging for 15 min. To prepare feed precursor solutions for a typical synthesizing Cu/Cu_2O nanoporous NPs, 0.115 mM $CuSO_4.5H_2O$ (in ethylene glycol solvent), and 0.197 mM long-chain poly-vinylpyrrolidone (PVP, dw=60000, in ethylene glycol solvent) were, simultaneously, injected dropwise into a round-bottom flask which was magnetically stirred at a rate of 45 mL h^{-1}. Subsequently, the mixture was stirred vigorously for 30 min and then sealed in a teflon lined stainless-steel autoclave (10 L capacity). The autoclave was allowed to be heated at 150℃ for 8 h. A hot dark brown Cu NPs suspension was first obtained and then was water cooled to 90℃. In this process, EG reduces Cu and PVP plays the key role as a structure-directing agent. Afterwards the hot suspension is put into a continuous flow reactor (CFR) at a flow rate of 5.0 ml/min per pump to complete the growth of nanoporous NPs with a mean residence time of 240 s. Meanwhile, the oxygen/nitrogen (volume ratio, 5:95) was introduced into CFR at a flow rate of 1.5 ml/min to allow the Cu nanocrystals suspended in solvent can be sectional oxidized to Cu_2O nanocrystals by dissolved oxygen. During reactions the entire column of CFR is thermally insulated to minimize heat loss. Once the reaction is completed, the final product is removed from the CFR, rinsed with ethanol, dried with a stream of N_2, and observed.

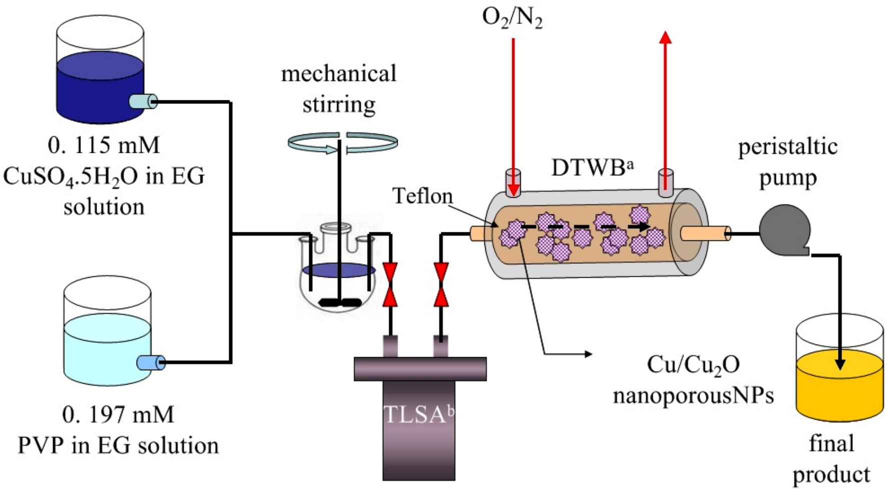
1.2 Preparation of the modified electrodes.

Bare glassy carbon electrode (GCE, 3-mm diameter) were polished before each experiment with emery paper and alumina slurry (CHI Instrument, Shanghai, China) in sequence, then rinsed successively with nitric acid, ethanol, distilled water using bath sonication for 10 min, followed by drying at room temperature. Subsequently, 4 mg Cu/Cu_2O nanoporous NPs were dispersed in 1.0 ml of ethanol suspension and 5 μL drop on the surface of GCE. After drying, 5 μL of Nafion (Nf, 0.4 wt%) was then cast on the layer of Cu/Cu_2O nanoporous NPs for the purpose of entrapment.

1.3 Characterization and electrochemical measurements.

The powder X-ray diffraction (XRD) patterns were obtained from powder samples mounted on glass slides in a PANalytical D/max-IIIA XRD instrument operating with Cu Kα radiation (λ=1.5406 nm). The morphology and elemental composition of the prepared products were characterized by scanning electron microscopy (SEM, Netherlands FEI.Co Sirion 200) and energy dispersive X-ray spectroscopy (EDX), respectively. The internal structure and the progress of the synthesis were assessed by transmission electron microscopy (TEM; JEM-2100) performed at an acceleration voltage of 200 kV. Samples were sonicated in ethanol before being dropped on a copper mounted holey carbon film and dried. The statistical characterization of the diameter size distribution of each sample was performed based on the TEM images. Thermalgravimetric analysis (TGA) and was conducted on a TA Instruments Q500 thermal analyzer apparatus under an ambient atmosphere. The infrared (IR) spectrum instrument is a TENSOR 27 instrument. The surface area (BET) and pore volume and size (BJH) of the materials was determined by nitrogen sorption (Tristar 3000, Micromeritics Instrument Corporation, U.S.A) at -195.7°C. Cyclic voltammetric (CV) and amperometric measurements were performed in a dual channel electrochemical workstation (CHI832C) with which a conventional three electrode cell was connected. A Cu/Cu_2O nanoporous NPs-modified electrodes, a platinum wire electrode and a Ag/AgCl (3M NaCl) electrode served as the working electrode, counter electrode, and reference electrode, respectively. 0.1 M NaOH solution was applied as the electrolyte in the study, which would provide a general view regarding the electrochemical behavior of the modified electrodes.

2. Supporting figures.



[a]DTWB-digital thermostat water bath, [b]TLSA-teflon lined stainless-steel autoclave

Scheme S1. Scheme of the synthesis and controlled-growth processes of the Cu/Cu$_2$O nanoporous NPs in a CFR system.

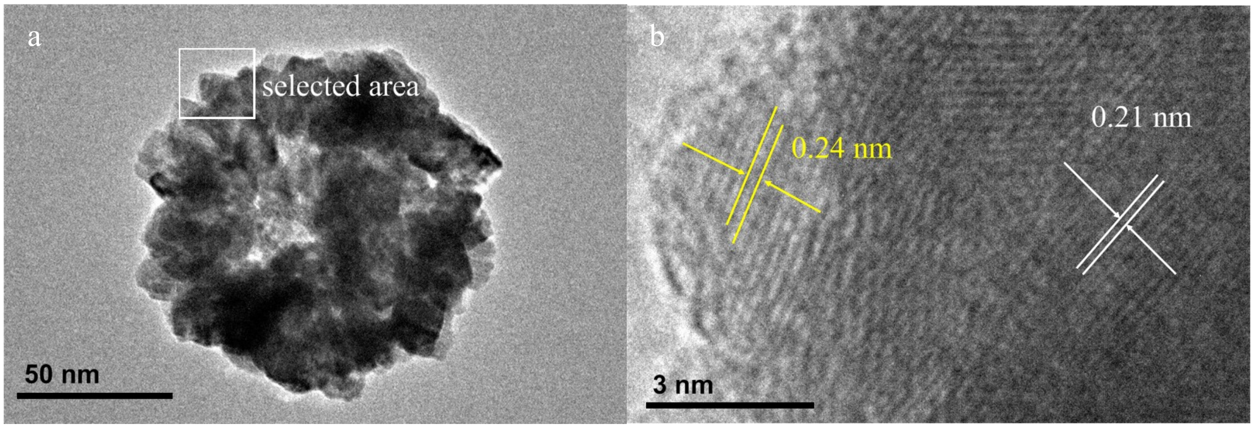


Fig S1. (a) TEM image of an as-prepared Cu/Cu$_2$O nanoporous NP and (b) HRTEM observation from selected area in (a).

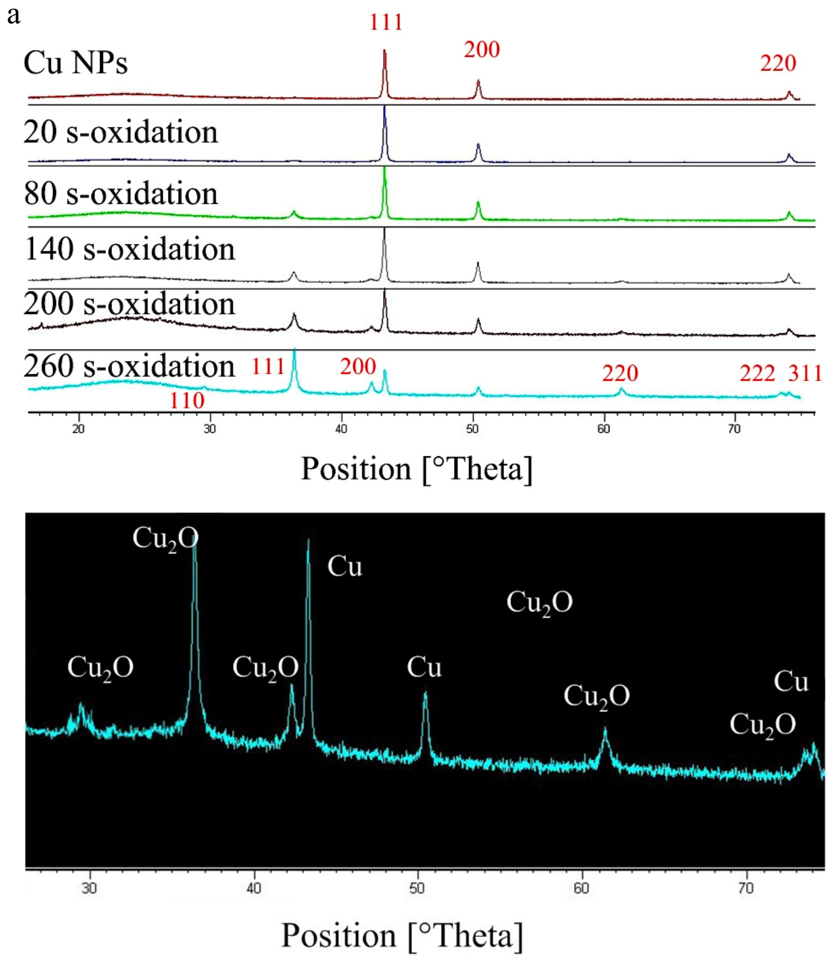


Fig S2. (a) XRD patterns of samples at different oxidation stages to reflect the growth process of the Cu/Cu_2O nanoporous NPs. (b) XRD pattern of as-obtained Cu/Cu_2O nanoporous NPs for 240 s oxidation.

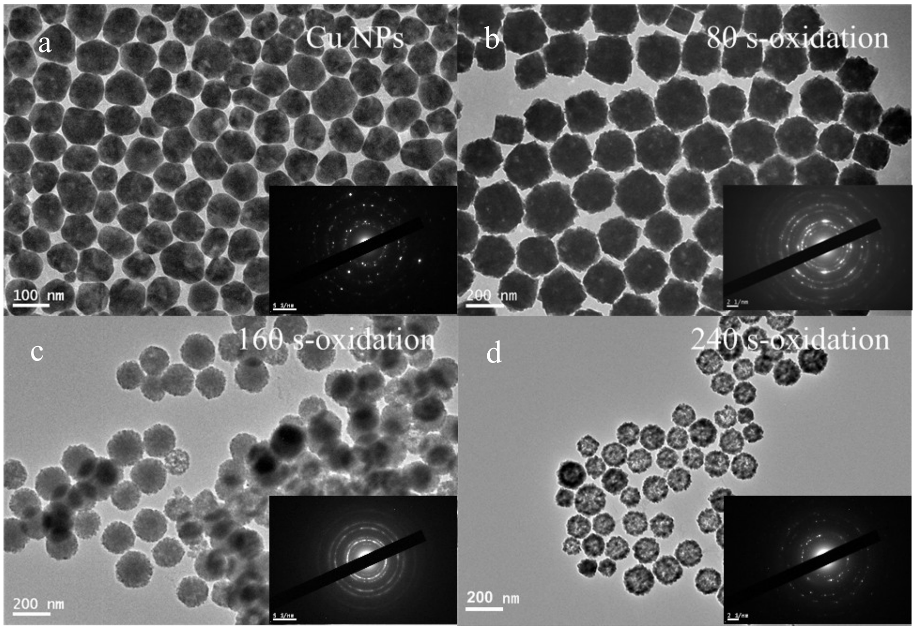
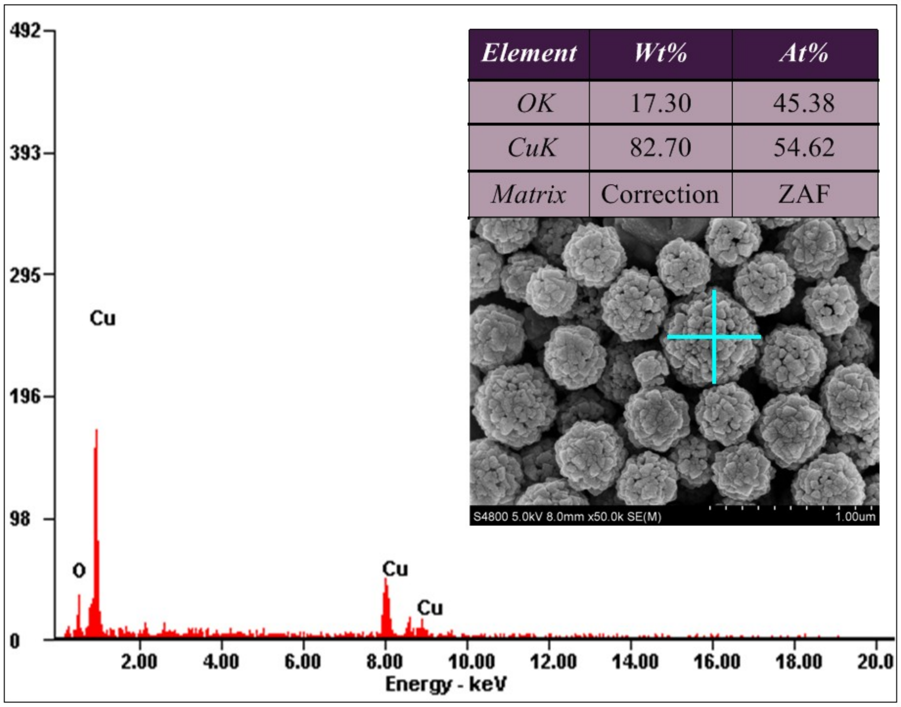


Fig S3. TEM images of samples via solvothermal treatment by introducing oxygen at various time: (a) 0 s, (b) 80 s, (c) 160 s, (d) 240 s, and inset are in situ SAED patterns of (a-d), respectively.



Element	*Wt%*	*At%*
OK	17.30	45.38
CuK	82.70	54.62
Matrix	Correction	ZAF

Figure S4. EDS-analysis of fresh obtained NPs from selected area.

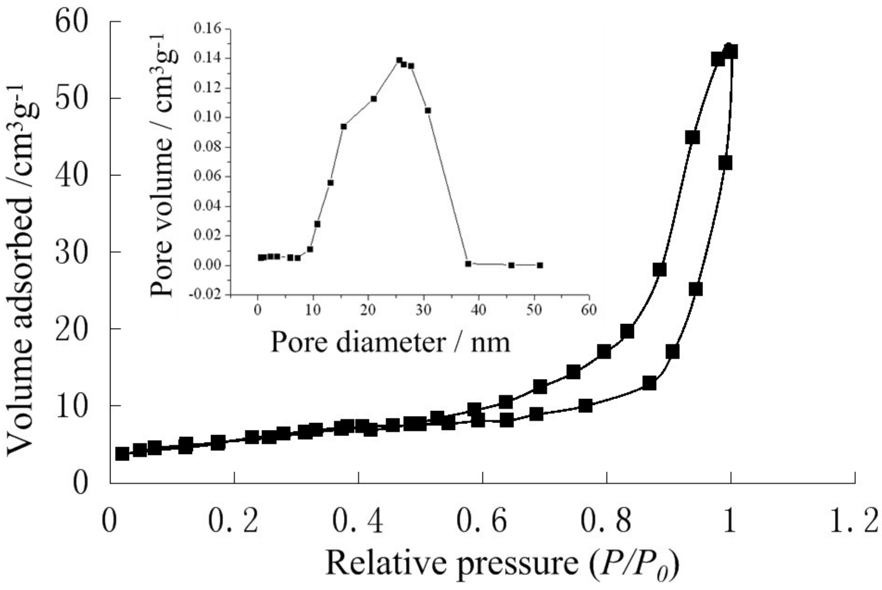


Fig S5. The N_2 adsorption and desorption isotherms and the pore size distribution curve (inset) of the Cu/Cu_2O nanoporous NPs.

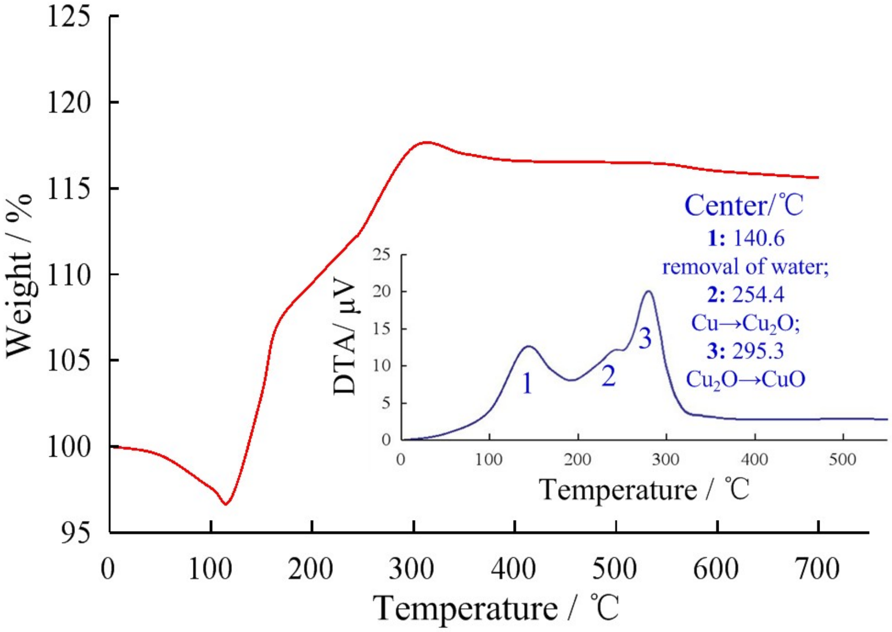


Fig S6. Differential thermal analysis (DTA) and thermogravimetry (TG) of Cu/Cu_2O nanoporous NPs as performed in air atmosphere. Component 1 in DTA mainly concern the combustion of absorbed water in first state, component 2 and 3 concern the oxidation heat liberation corresponding to Cu→Cu_2O and Cu_2O→CuO respectively.

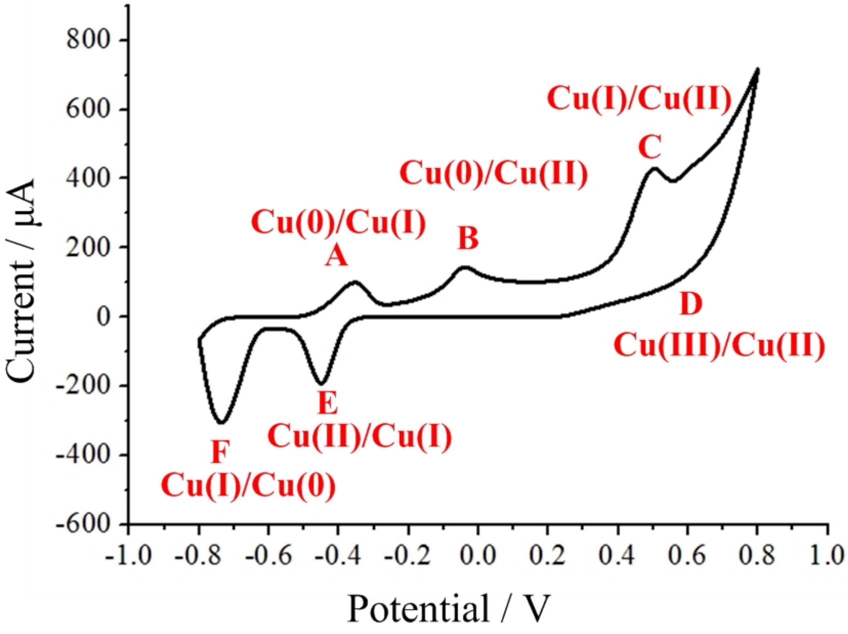


Fig S7. Cyclic voltammograms of the Nafion/(Cu/Cu_2O)-nanoporous NPs /GCE in the presence of 5 mM glucose. The electrolyte is 0.1 M NaOH and the scan rate is 5 mV/s.

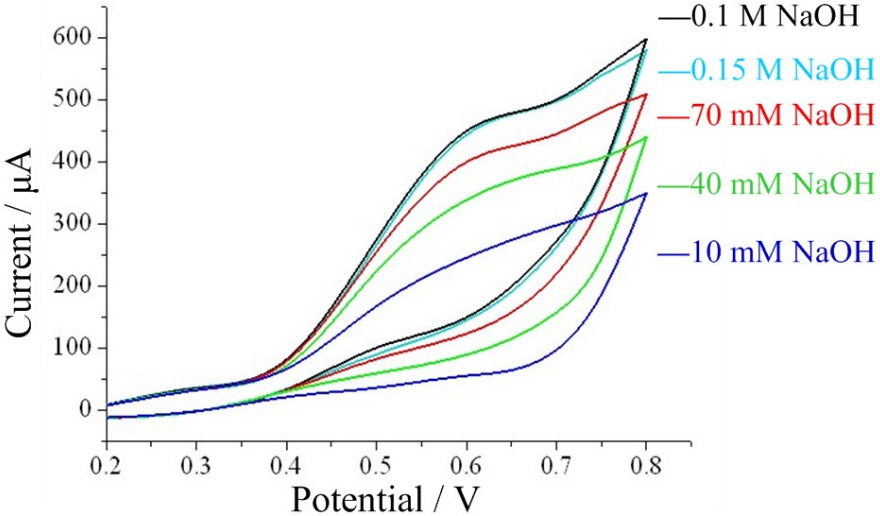


Fig S8. Cyclic voltammograms of the Nafion/(Cu/Cu_2O)-nanoporous NPs /GCE in different concentrations of NaOH from 10 mM to 0.15 M with 5 mM glucose concentration at a scan rate of 50 mV/s.

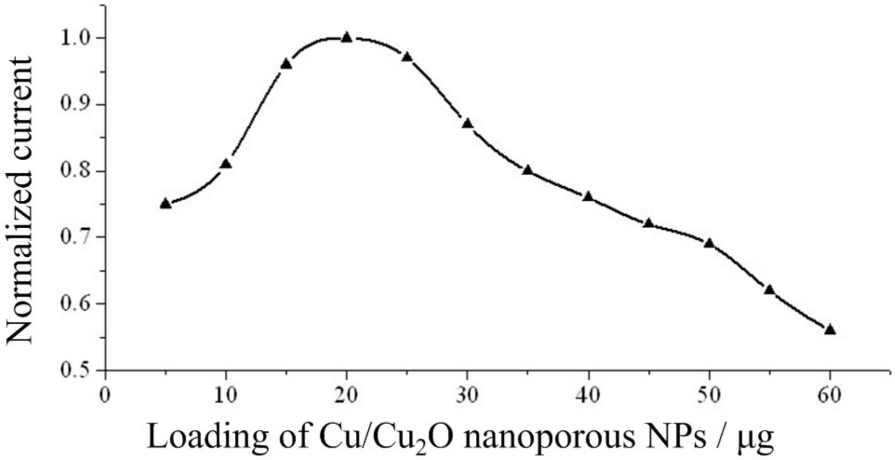


Fig S9. The normalized current response versus the loading of Cu/Cu_2O nanoporous NPs.

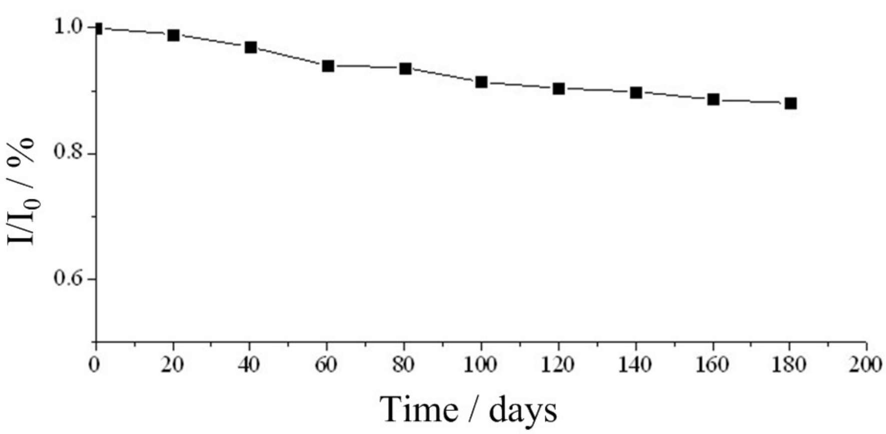


Fig S10. Long-term stability of the Cu/Cu_2O nanoporous NPs modified sensors stored at ambient conditions over six months in 0.1 M NaOH with addition of 5 mM glucose at 0.6 V.

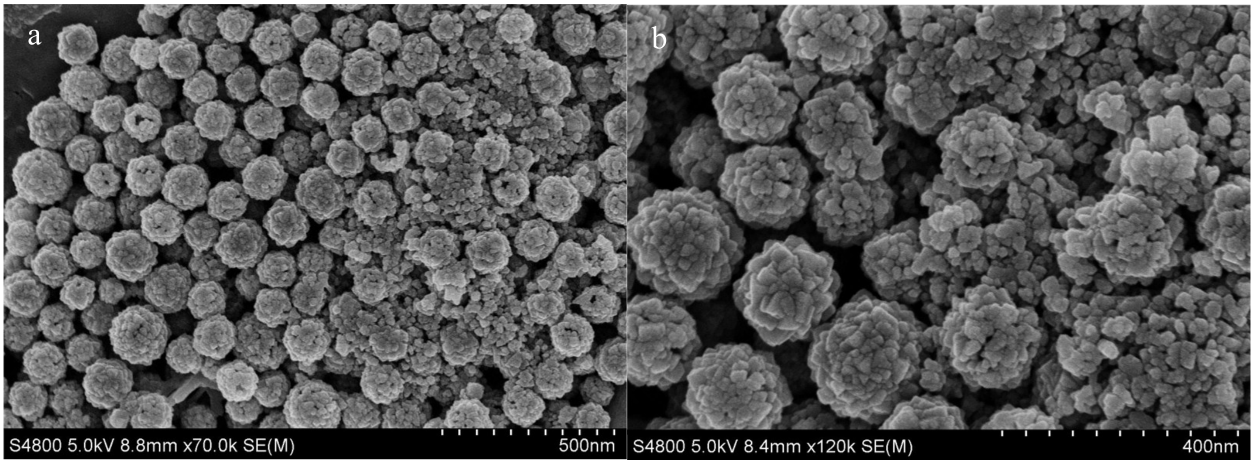


Fig S11. (a) A typical SEM image of the Cu/Cu_2O nanoporous NPs are broken up to smaller nanoparticles through repeated applications. (b) Local enlarged SEM image of (a).