

Electronic Supplementary Information

For

Electrochemical Fabrication of Nanoporous Gold Electrodes in Deep Eutectic Solvent for Electrochemical Detections

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Experimental section

Reagents

Zinc chloride, urea, nitrobenzene, sodium dihydrogen phosphate dihydrate, disodium hydrogen phosphate dodecahydrate, concentrated sulfuric acid (98%), concentrated hydrochloric acid (36%) were purchased from Beijing Chemical Company (A. R. analytical reagent grade). Hydrazine hydrate was purchased from Beijing Yili Fine Chemicals Corporation. Mercury chloride was purchased from Jiangyan Huanqiu Chemicals Corporation. The conductive ITO glass (Transmittance > 83 %, Sheet resistance < 15 Ω /sq) were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd., China.

Aqueous solutions of NaH_2PO_4 and Na_2HPO_4 were mixed to prepare 0.1 M phosphate buffer solution (PBS) with pH of 7.4 and 7.0. Urea was dried in vacuum at 60 °C before use. All other reagents were used without further purification.

Apparatus

X-ray powder diffraction (XRD) patterns were recorded on a D8 Advance (Bruker, Germany) diffractometer using $\text{Cu-K}\alpha$ radiation with a Ni filter ($\lambda = 0.154059$ nm at 30 kV and 15 mA). Thermal gravimetric analysis (TGA) patterns were collected on Pyris Diamond TGA/DTA (PerkinElmer, U.S.). Scanning electron microscopy (SEM) images were collected on an S-4800 field emission scanning electron microanalyzer (Hitachi, Japan). Electrochemical detection experiments were carried out by using a CH Instruments model 660e electrochemical workstation (Shanghai Chenhua Equipments, China).

Experimental

Synthesis of ZnCl₂-urea deep eutectic solvent (DES):

The preparation of ZnCl₂-urea DES follows Abbott's work.¹ The DES was prepared by mixing ZnCl₂ and urea (molar ratio, 1:3.5) under stirring at 60 °C to form transparent liquid.

Electrochemical Fabrication of Nanoporous Gold Electrodes:

A three-electrode electrochemical system was used. The reference and the counter electrode were a zinc wire and a zinc foil, respectively. The gold plate working electrode (3.0 mm in diameter) was polished, rinsed and dried before use.

Potentiostatic electrodeposition of zinc was firstly carried out on gold electrodes in DES at -0.2 V (vs. Zn). Equivalent amount of zinc ($Q = 0.07$ C) was electrodeposited on gold electrodes at different temperatures. Subsequently, anodic stripping of Zn in the same electrolyte at 1.0 V (vs. Zn) was performed until an ignorable steady anodic current ($<1 \mu\text{A}$) was reached. The electrode color changed from glossy gold to dull yellow due to the formation of NPG. Finally, the NPG electrodes was electrochemically cleaned by cycling for 100 cycles between 0.0 to 1.6 V (vs. Ag/AgCl) in 1 M H₂SO₄ aqueous (scan rate: 100 mV/s) for further use.

Fabrication of ITO-Au electrodes for XRD characterization:

Due to the weak Au-Zn alloy diffraction signals are difficult to observe on the bulk gold, bare ITO glasses electrodeposited with a thin layer of Au were used as working electrodes. The method of fabrication ITO-Au electrodes was reported by a previous literature.² ITO glass was firstly washed with acetone, ethanol and water for 5 min successively and dried with nitrogen flow. The cleaned surface of ITO electrode was reduced into a thin film of In-Sn by applying a constant potential of -1.15 V (vs. Ag/AgCl) for 200 s in PBS (pH=7.4). The In-Sn layer on ITO electrode was subsequently destroyed by immersing into aqua regia for 2 s. After that, the double-pulse electrodeposition method (positive potential: 0.5 V, 0.5 s; negative potential: -0.2 V 1 s; 20 cycles) was used to fabricated ITO-Au electrodes in 10 mM chloroauric acid aqueous solution. Finally, ITO-Au electrodes washed and dried for further electrodeposition and stripping experiments like Au plate electrode.

Electrochemical detections:

All the electrochemical experiments were conducted with CH Instruments model 660e electrochemical workstation. We used a conventional three-electrode system, NPG electrodes served as the working electrode, and a platinum foil and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and the reference electrode, respectively.

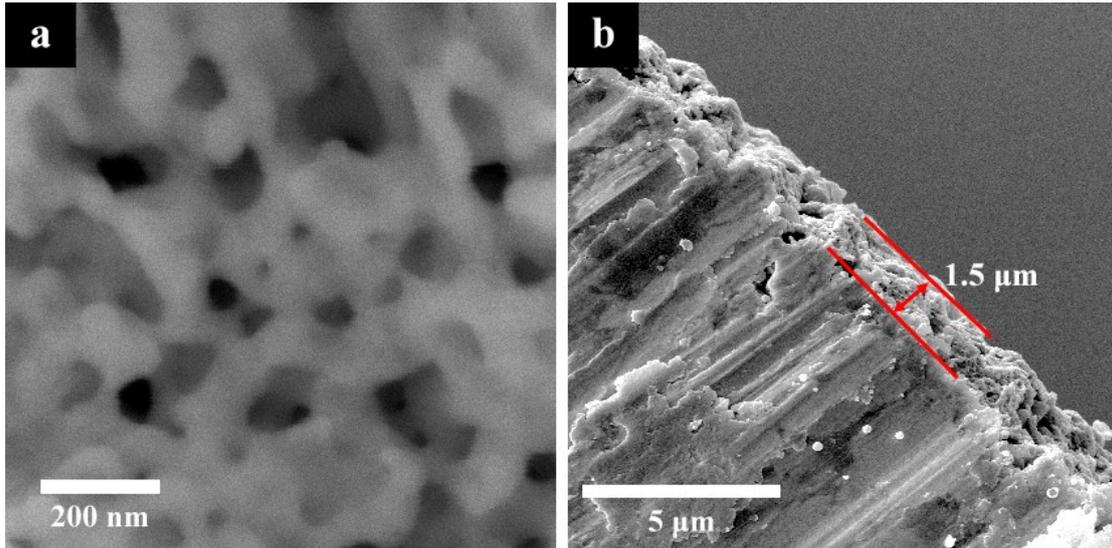


Fig. S1 (a) High resolution scanning electron microscopy (SEM) images of NPG-120; (b) SEM images of cross-sectional view of a gold wire after alloying/dealloying in ZnCl₂-urea DES at 120 °C

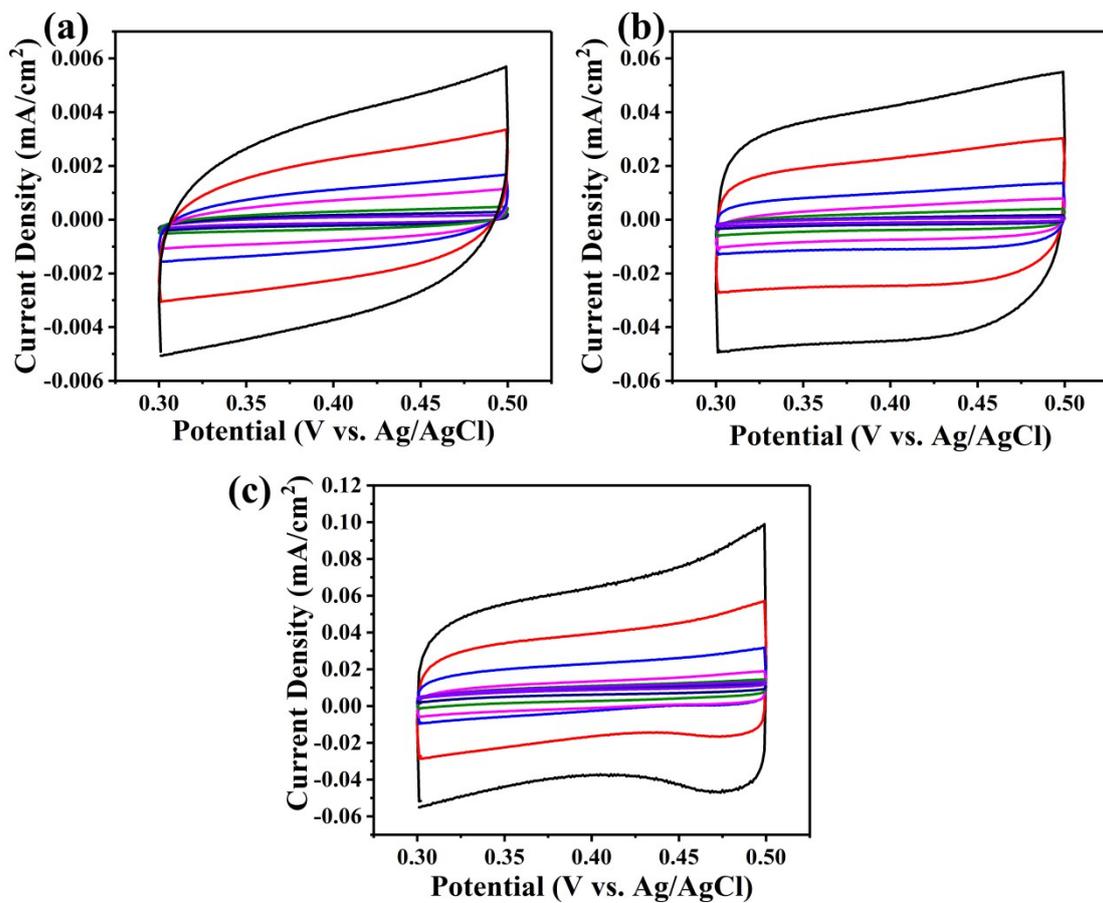


Fig. S2 Typical CVs of (a) bare gold electrode; (b) NPG-RT; (c) NPG-60 in 1 M H₂SO₄ at different scan rates (1, 2, 5, 10, 20, 50, 100, 200 mV/s).

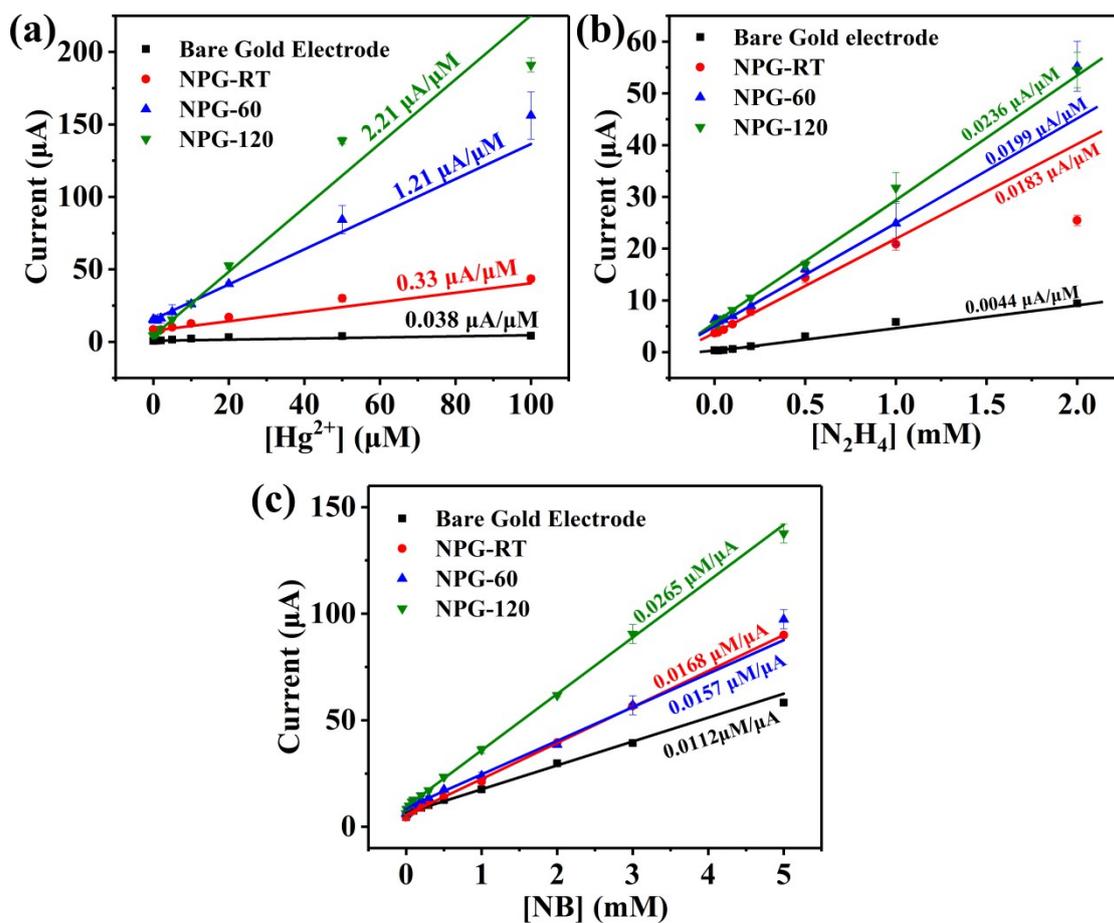


Fig. S3 The linear dependence of current responses and sensitivities of bare gold electrode and NPG electrodes with the different concentration of (a) Hg^{2+} (b) N_2H_4 (c) NB.

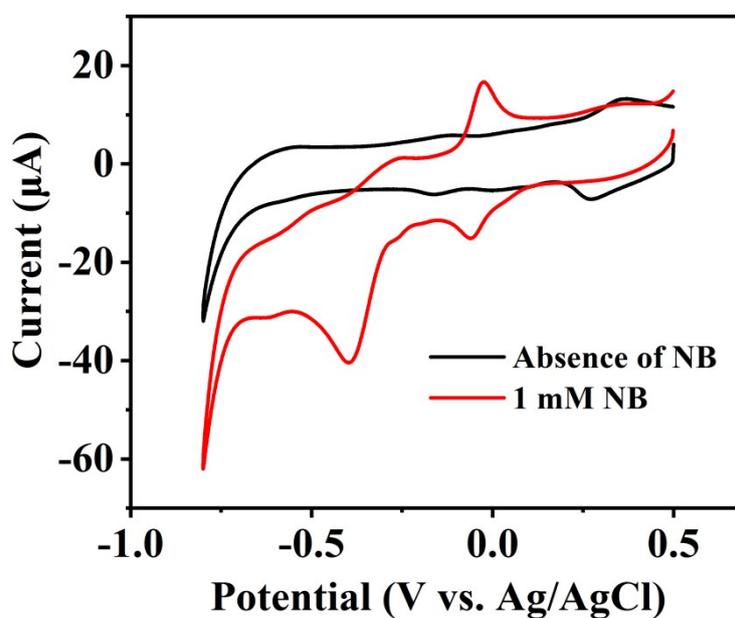


Fig. S4 CV of NPG-120 electrodes in the absence of NB and in the presence of 1 mM NB in PBS (pH=7.0) at the scan rate of 50 mV/s.

References

- 1 A. P. Abbott, J. C. Barron, K. S. Ryder and D. Wilson, *Chem. Eur. J.*, 2007, **13**, 6495-6501.
- 2 X. Zhang, B. Lou, D. Li, W. Hong, Y. Yu, J. Li and E. Wang, *Chem. Commun.*, 2015, **51**, 6788-6791.