

Electronic Supplementary Information

Facile and shape-controlled electrochemical synthesis of gold nanocrystals by changing water contents in deep eutectic solvents and their electrocatalytic activity

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1. Chemicals

Choline chloride ($\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3\text{Cl}$, 98%), urea (NH_2CONH_2 , 99.5%), ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$, 99.0%), and glycerol ($\text{HOCH}_2\text{CHOHCH}_2\text{OH}$, 99.0%) were purchased from Sigma-Aldrich Co. LLC. Tetrachloroauric (III) acid tetrahydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) and ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 99.7%) were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification unless otherwise specified.

2. Preparation of DESs

Choline chloride (ChCl) was recrystallized from absolute ethanol, filtered, and dried under vacuum. Urea (U), ethylene glycol (EG), and glycerol (G) were dried under vacuum before use. DESs were formed by stirring choline chloride and urea (reline, molar ratio: $(\text{ChCl})/\text{U} = 1:2$), choline chloride and ethylene glycol (ethaline, molar ratio: $(\text{ChCl})/(\text{EG}) = 1:2$), or choline chloride and glycerol (glyceline, molar ratio: $(\text{ChCl})/\text{G} = 1:2$) at 80 °C until homogeneous and colorless liquids, respectively.¹⁻³ The prepared DESs, once formulated, were kept in a vacuum at 80 °C

prior to use.

3. Preparation of Au NCs in three DESs

The electrochemical synthesis of Au NCs in three DESs were carried out by using a standard three-electrode cell connected to a CHI 660D electrochemical workstation (Shanghai Chenhua Instrumental Co., Ltd), with a Pt wire counter electrode, a Pt quasi-reference electrode, and a glassy carbon electrode (GCE, 3 mm in diameter) as the working electrode. The GCE was polished with 1.0, 0.3, and 0.05 μm Al_2O_3 powder and rinsed thoroughly with ultrapure water. Then, the electrodes were subsequently washed in ethanol and ultrapure water by ultrasonication and dried by nitrogen before each experiment.^{4,5} In a typical procedure, different morphological Au NCs were electrodeposited directly on GCEs under the applied potential of -0.60 V (vs. Pt) in reline, -0.90 V in ethaline, and -0.85 V in glyceline at 90 °C for 600 s, respectively. These DESs containing 20 mM HAuCl_4 .

4. Effects of the experimental conditions

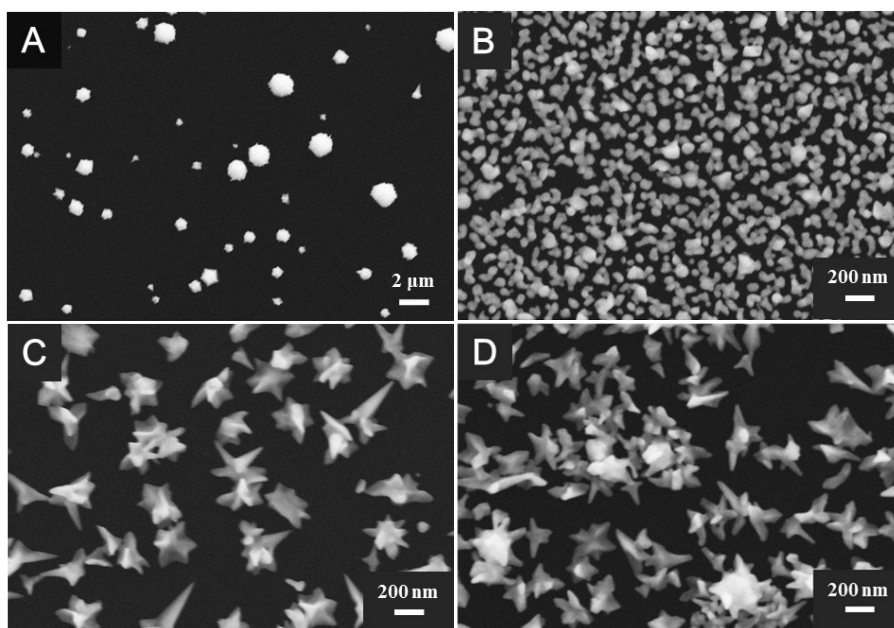


Fig. S1 FESEM images of the Au NCs in reline obtained at different applied potentials: (A) -0.40 V, (B) -1.40 V, (C) -0.55 V, and (D) -0.65 V.

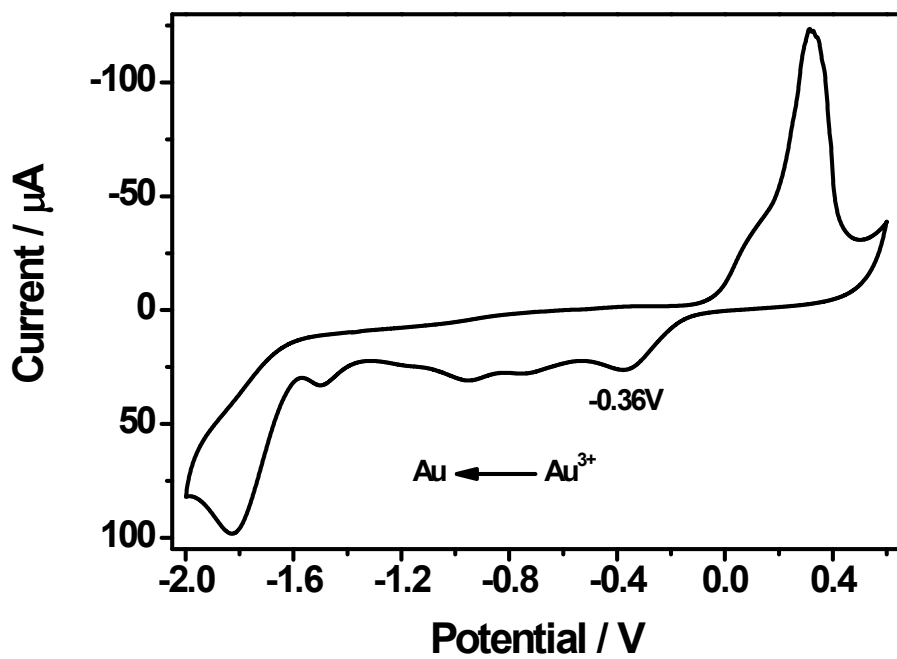


Fig. S2 Typical cyclic voltammogram of a GCE in reline containing 20 mM HAuCl₄. Scan rate: 50 mV·s⁻¹.

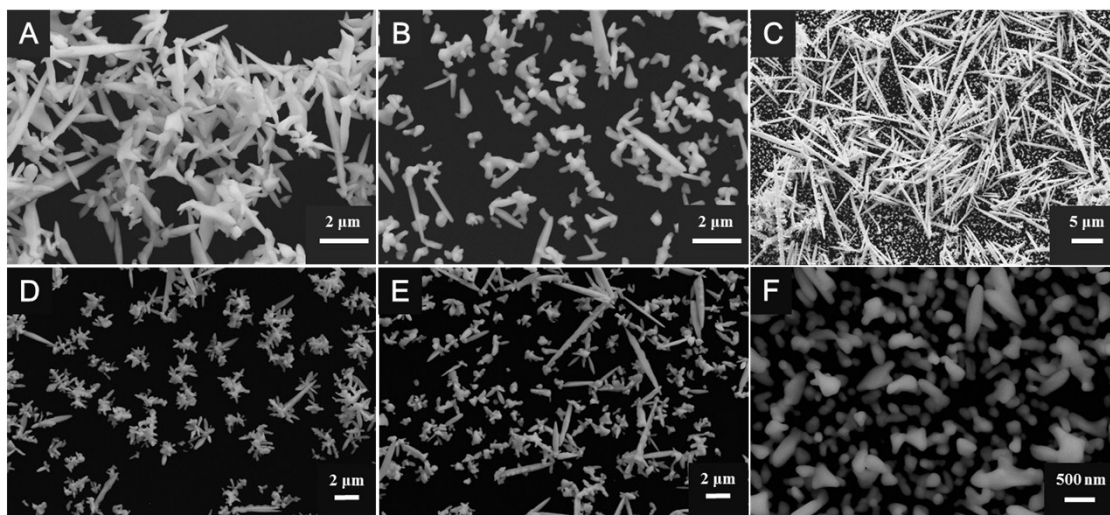


Fig. S3 FESEM images of synthesized Au NCs with water content of 20% (A), 50% (B), and 90% (C) in ethaline; 20% (D), 50% (E), and 90% (F) in glyceline.

5. Characterization of Au NCs

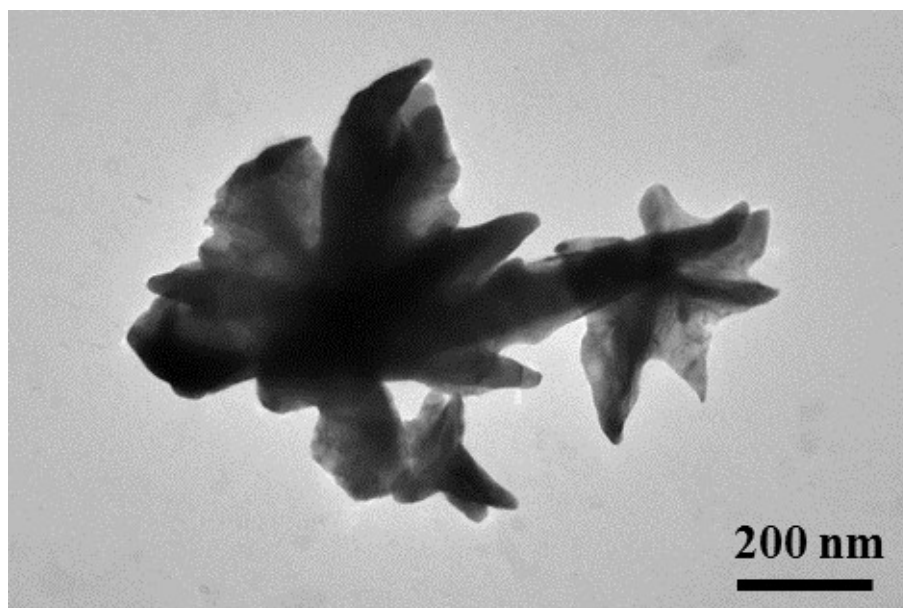


Fig. S4 TEM image of synthesized Au NSs in relin.

The as-prepared Au NCs were examined by transmission electron microscopy (TEM, JEOL JEM 2100).

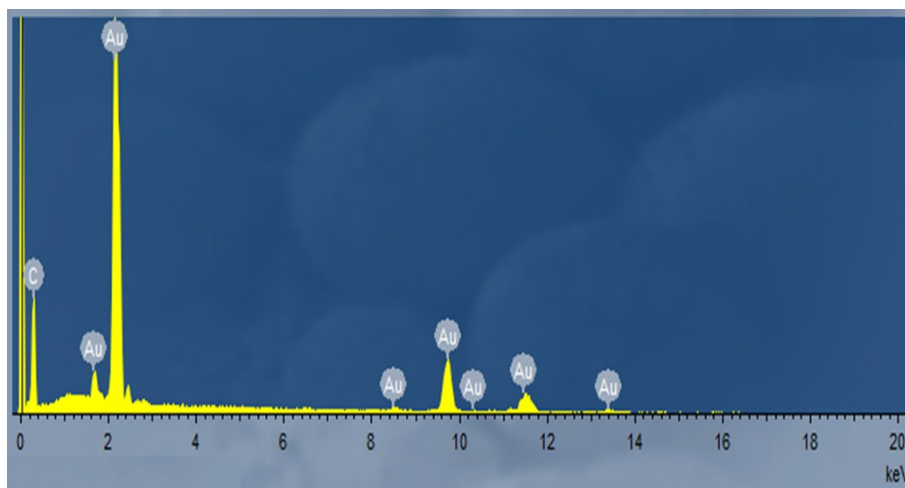


Fig. S5 EDS spectrum of synthesized Au NSs in reline.

To characterize the chemical composition of prepared Au NCs, energy dispersive spectroscopy (EDS, Oxford) spectrograms were recorded and analyzed (Fig. S5). The spectrogram of the EDS measurement shows that the characteristic peaks of the metallic Au and carbon (the carbon present here is ascribed to the GCE). The synthesized Au NCs were not treated specially. These results demonstrate that the prepared Au NCs only include Au element, revealing high purity of Au NCs.

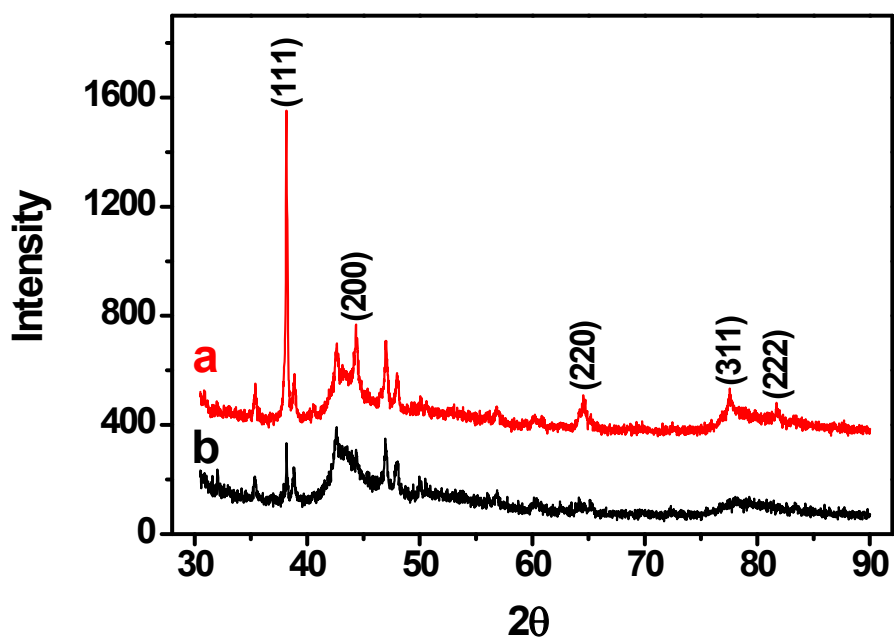


Fig. S6 XRD patterns of the as-prepared Au NSs obtained in reline (curve a) and GCE (curve b).

X-ray diffraction (XRD, Bruker D8 Advance) analysis was recorded to characterize chemical composition and crystal structure of the synthesized Au NSs (Fig. S6). There are five sharp and strong diffraction peaks of Au NSs observed at 38.2° , 44.4° , 64.6° , 77.6° , and 81.7° , which are assigned to the (111), (200), (220), (311), and (222) planes of the face-centered cubic (fcc) Au (JCPDS 04-0784), respectively. The XRD results suggest that the obtained Au NSs include pure and well-crystallized gold nanocrystals.

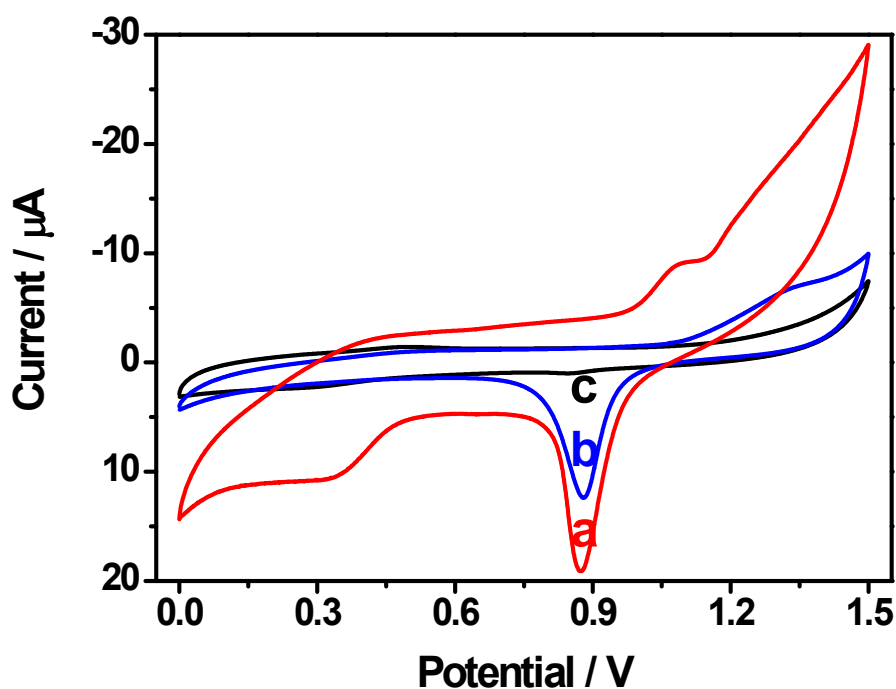


Fig. S7 CVs of the Au NSs modified electrode (curve a), commercial Au electrode (curve b), and bare GCE (curve c) in 0.5 M H_2SO_4 with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

The Au NCs were characterized by electrochemical methods. Fig. S7 shows the typical cyclic voltammograms (CVs) recorded in 0.5 M H_2SO_4 solution. The CVs of the Au NSs modified electrode (curve a) displays the characteristic peaks of Au, revealing the Au oxide formation and dissolution region. In the forward scan, the characteristic oxidation peaks of Au are detected at 1.10 V — 1.40 V (*vs.* SCE). These peaks are assigned to the oxidation from metallic Au to Au^{3+} ion. On the other hand, the enhanced cathodic peak current is at 0.87 V (*vs.* SCE). The characteristic redox peak intensity of Au NCs modified electrode significantly is higher than commercial Au electrode (Fig. S7, curve b). It is demonstrated that Au NCs modified electrode possessed high electroactive surface area.

6. Electrocatalytic performance measurements

The electrocatalytic performances of the Au NCs modified electrodes toward ethanol oxidation were evaluated by cyclic voltammetry in 0.5 M NaOH solution at room temperature. A saturated calomel electrode (SCE) was used as reference electrode, and all potentials in the electrochemical performance tests are quoted versus the SCE scale.

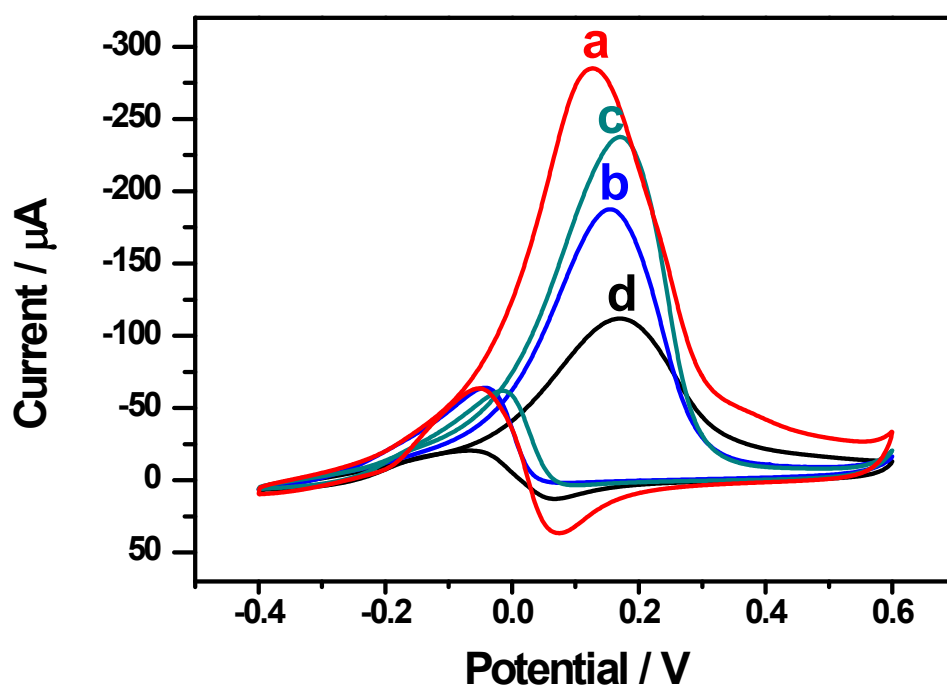


Fig. S8. CVs of the Au NSs modified electrode (curve a), Au NDs modified electrode (curve b), Au NFs modified electrode (curve c) and commercial Au electrode (curve d) in 0.5 M NaOH solution containing 0.50 M ethanol with a scan rate of $50 \text{ mV}\cdot\text{s}^{-1}$.

References

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