

# Supporting Information

## Electrochemically mediated gradient metallic film generation

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### Experiment section

**Chemistry and Materials** Cupric sulfate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), lactic acid ( $\text{C}_3\text{H}_6\text{O}_3$ ), Sodium Hydroxide ( $\text{NaOH}$ ), Gelatin, sodium chloride ( $\text{NaCl}$ ), Borax, Phosphate mixture, acetone ( $\text{C}_3\text{H}_6\text{O}$ ), alcohol ( $\text{C}_6\text{H}_6\text{O}$ ),  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (2%), chloroauric acid ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), sodium chloride ( $\text{KCl}$ ), hexachloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ), boracic acid ( $\text{H}_3\text{BO}_3$ ), Nickel (II) sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ), indium tin oxide (ITO) glass (1 mm thickness, resistance valueless than  $100 \Omega$ ) was obtained from Isfahan Electro Optic Company.

**Preparation of ITO substrate** The ITO electrode was cleaned 10 minutes using a (KQ-100E) type ultrasonic cleaner from Kunshan Ultrasonic Instrument Company, with diluted ammonia, deionized water, ethanol and deionized water, respectively. The cleaned conductive glass was naturally dried in the air and set aside. Deionized water was used for all aqueous solutions and washing. Other chemicals used were of analytical grade and were purchased from sigma Adrich.

**Preparation of gradient metal film** The electrodeposition was performed with a standard three electrode system (CHI-601C) in an electrolytic cell. Indium doped tin oxide (ITO) glass slide ( $20 \text{ cm}^2$ ) was used as a substrate/working electrode. Platinum wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All of the chemicals were of analytical grade, used without further purification. Electrolyte were obtained by 0.3 mol/L  $\text{CuSO}_4$ +5 mL lactic acid+1 mL 0.02 g/L Gelatin and 1 mL 0.1 mol/L  $\text{NaCl}$  as an additive, adjust pH with 5 mol/L  $\text{NaOH}$ , the deposition was performed potentiostatically under conditions of -0.4 V vs. SCE for 20 min at room temperature (25 °C). AuNPs/ITO obtained by 0.1 mol/L  $\text{KCl}$ +0.5 mmol/L  $\text{HAuCl}_4$ , the deposition was performed potentiostatically under conditions of -0.4 V vs. SCE for 20 min at room temperature (25 °C). Au nanoparticles, Pt nanoparticles and Ni nanoparticles are deposited on ITO via constant voltage electrodeposition. After deposition, all of the films were rinsed with deionized water and dried in air.

### Characterization of Materials

**Ellipsometry.** Ellipsometric data was obtained on a SC620 ellipsometer from (Shanghai, China), equipped with a fixed  $60^\circ$  angle of incidence. Film calculations were performed using a commercial software package (Elli, Optrel GbR, Berlin, Germany).

**X-ray diffraction(XRD).** X-ray diffraction (XRD, Bruker D8 advance with  $\text{Cu K}\alpha$  radiation) was used to characterize the phase composition.

**Scanning electron microscope (SEM).** Morphologies and structures of samples were researched by scanning electron microscope (Hitachi S-4800). SEM emits electrons through a field emission or thermal emission electron gun, focuses the electron beam with an electromagnetic lens, excites various signals from the sample, such as secondary electrons, absorbs electrons, etc, and then receives and magnifies them to form a scanned image that reflects the surface morphology.

**X-ray photoelectron spectroscopy (XPS).** The chemical composition and elemental state were obtained via (XPS), XPS was collected by using a Thermo ESCALAB 250 instrument with a monochromated Al X-ray resource at 1486.6 eV.

## Method of electrodeposition

**Preparation of Gradient Electrodeposited Metal Films** Initially, fixed the conductive glass on the electrode holder and gradually immersed in the electrolyte, as the same time, adjust the distance between the auxiliary electrode and the working electrode is 2 cm, and adjust the flow rate so that the conductive glass does not touch the solution and slowly immersed in the solution, until it is immersed to 2 cm. This leads to controllable preparation of metal gradient films.

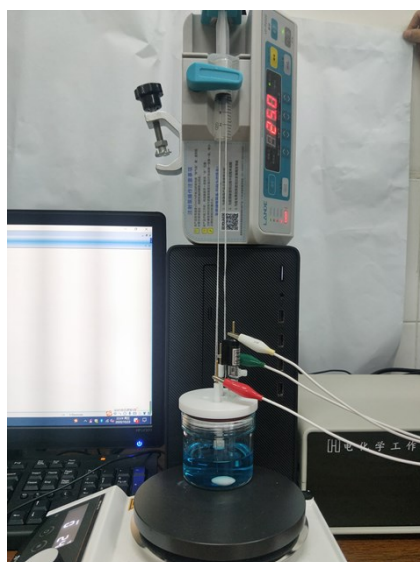
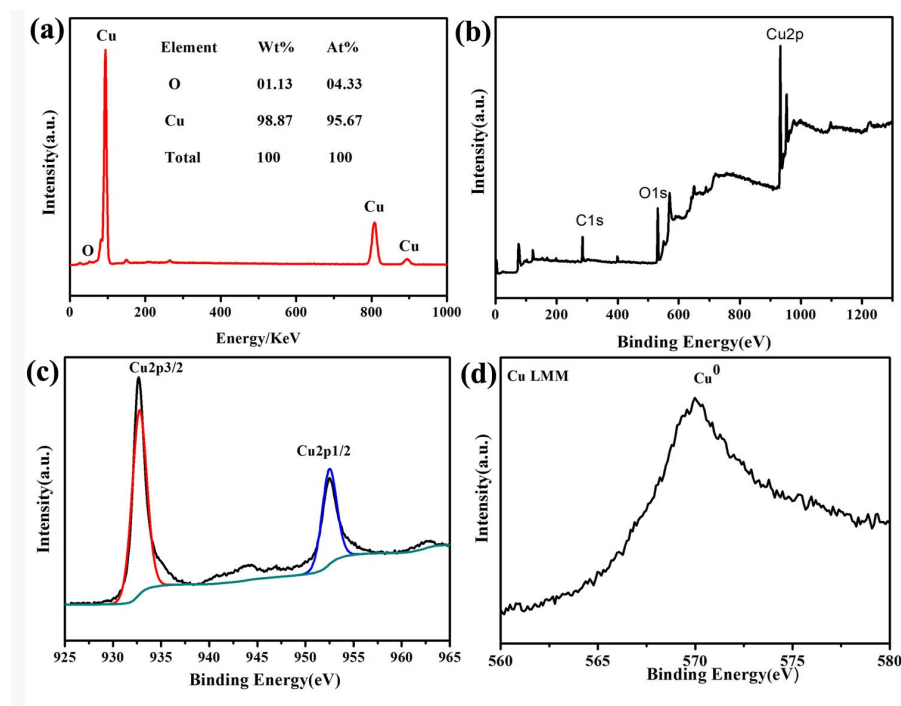


Fig. S1 Diagram of electrodeposition experimental apparatus.

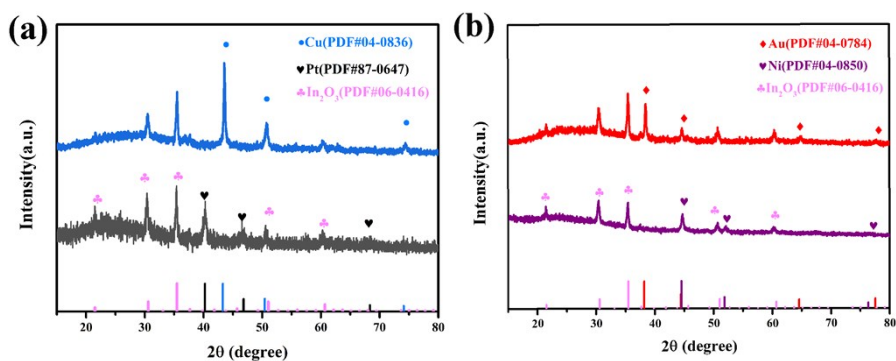
**Syringe pump** The injection rate was controlled through tuning the injection rate of LD-P2020 syringe pump (Shanghai, China). Connect the working electrode and control the electrodeposited gradient metal film by adjusting the flow rate. The experimental device are shown in the Fig. S1.

Fig. S2(a) shows the EDS of Cu/ITO nanoparticles, and 4.33% of oxygen atoms may come from indium tin oxide on the surface of conductive glass, it is further proved that the gradient film is composed of pure copper. The chemical states of the Cu film in the near-surface region were investigated by XPS analyses. As shown in Fig. S2(b), the elements C, O, and Cu appeared in the XPS spectrum, in which the element C came from the hydro-carbons in XPS instrument, the element O came from the indium tin oxide (ITO) substrate. Fig. S2(c) shows the high resolution XPS of Cu 2p. Two peaks at 932.7 eV and 952.2 eV were assigned to Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> of Cu<sup>+</sup> or Cu<sup>0</sup> owing to the absence of a satellite peak at approximately 943 eV in Fig. 1(c). Cu LMM X-ray induced Auger electron spectroscopy (XAES) is an effective analysis method to distinguish

these two states, and the peak at 570.3 eV in Fig. S2(d) inset was related to  $\text{Cu}^0$ , indicating that  $\text{Cu}_2\text{O}$  does not exist in the film.



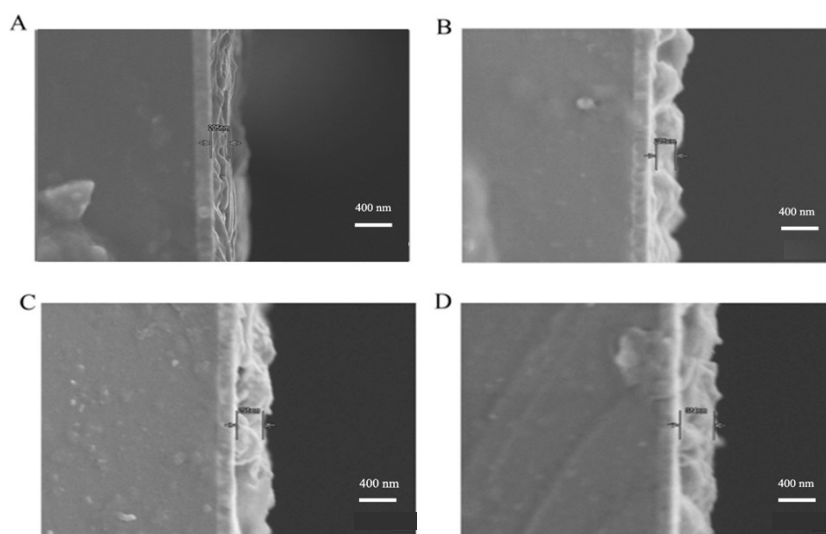
**Fig. S2.** (a) EDS patterns of Cu/ITO; XPS analysis of the copper film; (b) full spectrum in the binding energy region from 0 to 1300 eV, (c) detailed spectrum of C 1s, (d) detailed spectrum of Cu 2p, (d) is Cu LMM spectrum.



**Fig. S3** XRD pattern of the Cu metal nano-particle, Pt metal nano-particle, Au metal nano-particle and Ni metal nano-particle on the surface of conductive glass.

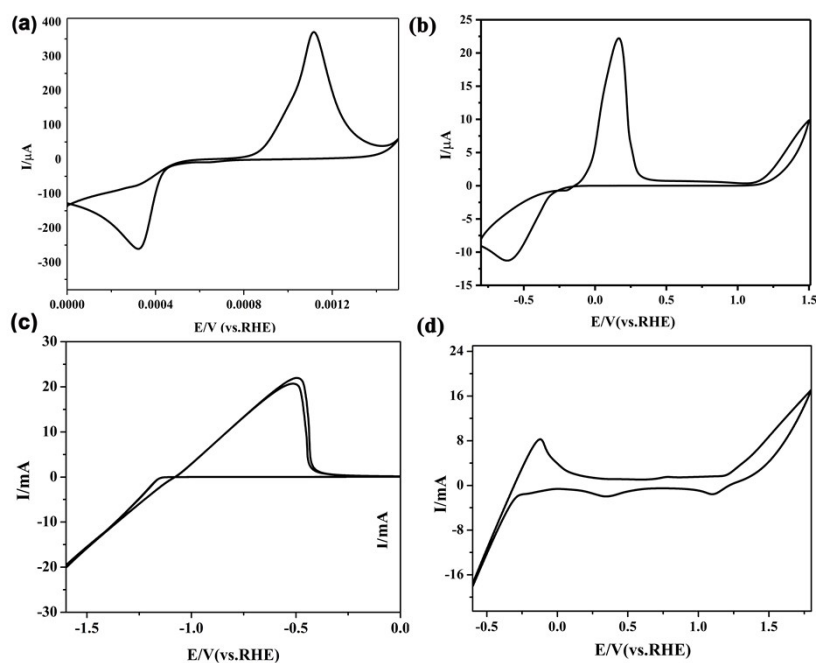
Fig. S3(a) shows the XRD patterns of the Cu/ITO and the Pt/ITO. The peaks at  $2\theta$  of  $43.3^\circ$ ,  $50.4^\circ$  and  $74.1^\circ$ , corresponding to the Cu (111), Cu (200) and Cu (220) reflection planes of the face-center-cubic (fcc) structure  $\text{Cu}^0$  (JCPDS No. 04-0836). The peaks at  $2\theta$  of  $40.3^\circ$ ,  $46.8^\circ$ ,  $68.3^\circ$ , corresponding to the Pt (111), Pt (200) and Pt (220) reflection planes of the cubic phase of Pt (JCPDS No. 87-0647). Fig. S3(b) shows the XRD patterns of the Au/ITO and the Ni/ITO. The peaks at  $2\theta$  of  $38.2^\circ$ ,  $44.4^\circ$ ,  $64.6^\circ$  and  $77.5^\circ$  belong to the (111), (200), (220), (311), and (222) planes of the cubic phase of Au (JCPDS No. 04-0784); The peaks at  $2\theta$  of  $44.5^\circ$ ,  $51.8^\circ$  and  $76.3^\circ$  belong to the (111), (200) and (220) planes of the cubic phase of Ni (JCPDS No. 04-0850). The

diffraction lines at  $2\theta = 21.5^\circ$ ,  $30.6^\circ$ ,  $35.5^\circ$ ,  $51^\circ$ , and  $60.7^\circ$  correspond to the (211), (222), (400), (440), and (622), respectively, can be ascribed to  $\text{In}_2\text{O}_3$  atomic plane from conductive glass surface (JCPDS No. 06-0416).



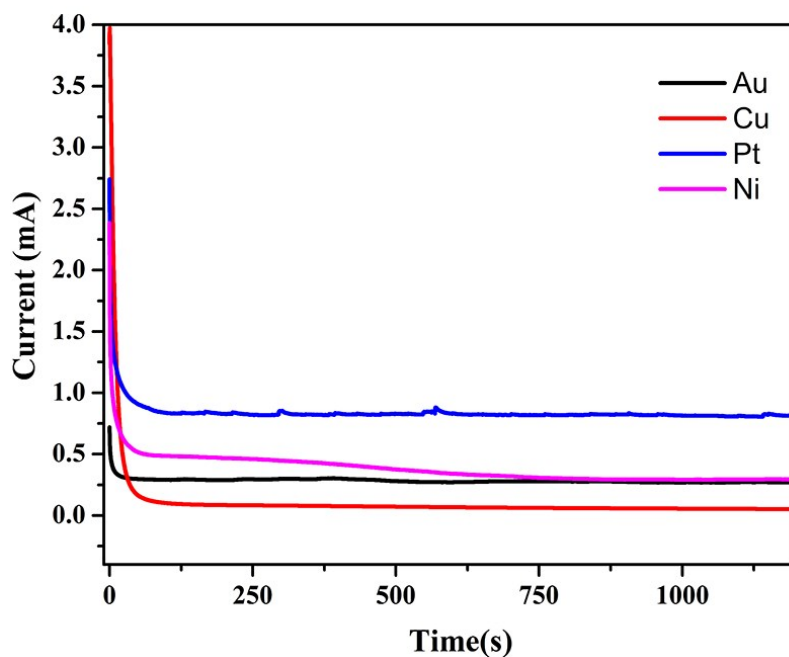
**Fig. S4** SEM of the thickness of the copper metal film on the surface of conductive glass at an immersion rate of 0.2 cm/min.

As shown in Fig. S4, dividing the conductive glass into four equal parts under an immersion rate of 0.2 cm / min, as shown in Fig.S4 A-D, the thickness of the copper film are 115 nm, 248 nm, 358 nm, 416 nm. the scanning electron microscope's picture agrees with ellipsometric thickness.

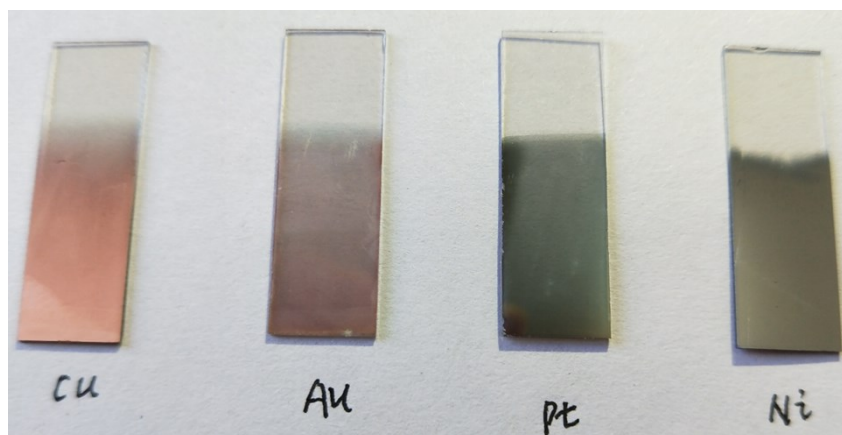


**Fig. S5** (a) **Fig. S5** (a) CVs of Au in  $0.1 \text{ mol L}^{-1} \text{ KCl}$  and  $0.5 \text{ mmol/L HAuCl}_4$  solution at a scan rate of  $100 \text{ mV s}^{-1}$ ; (b) CVs of Cu in  $0.3 \text{ mol L}^{-1} \text{ CuSO}_4$  electrolyte at a scan rate of  $100 \text{ mV s}^{-1}$ ; (c) CVs of Ni in  $0.3 \text{ mol L}^{-1} \text{ HBO}_3$  and  $0.1 \text{ mol L}^{-1} \text{ NiSO}_4$  solution electrolyte at a scan rate of 100

$\text{mV s}^{-1}$ ; (d) CVs of Pt in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{PtCl}$  solution electrolyte at a scan rate of  $100 \text{ mV s}^{-1}$ .



**Fig. S6** CA responses of Au nanoparticles, Cu nanoparticles, Pt nanoparticles and Zn nanoparticles the surface of conductive glass.



**Fig. S7** The photo of gradient copper film, Au film, Pt film and Ni film.

#### References

1. Z. Xi, H. Lv, D. P. Erdosy, D. Su, Q. Li, C. Yu, J. Li and S. Sun, *Nanoscale*, 2017, **9**, 7745.
2. N. Tavakkoli, N. Soltani, Z. K. Tabar and M. R. Jalali, *Chem. Pap.*, 2019, **73**, 1377.
3. L. Han, L. Tang, D. Deng, H. He, M. Zhou and L. Luo, *Analyst*, 2019, **144**, 685.
4. L. Shen, M. Fan, M. Qiu, W. Jiang and Z. Wang, *Appl. Surf. Sci.*, 2019, **483**, 706.