

0D/1D Heterostructured Au@Cu₂O/CuO/Cu(OH)₂ with Multivalent Cu(I)/Cu(II) for Efficient and Bendable Glucose Sensing

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Experimental details:

1. Chemicals and reagents

Gold chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium oleate (NaOL), silver nitrate (AgNO_3), sodium borohydride (NaBH_4), hydrochloric acid (HCl, 37wt%), ascorbic acid (AA), Hexadecyl trimethyl ammonium Bromide (CTAB). Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), sodium hydroxide (NaOH), sodium dodecyl sulfate (SDS) and hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) were analytically pure and used directly without further purification. Glucose, D-fructose, α -lactose monohydrate, sodium ascorbate (SA), dopamine hydrochloride (DA), urea, sodium chloride (NaCl) and Nafion were purchased from Shanghai Aladdin Biochemical Technology Co. All solutions are freshly prepared with high-quality ultrapure water (resistivity = $18.25 \text{ M}\Omega \text{ cm}^{-1}$).

2. Synthesis of Au nanorods

Gold nanorods with a length of 110 nm and a diameter of 50 nm were prepared using the typical seed growth method in a binary-surfactant solution with some modifications.^[1] The seed solution was synthesized as followed: 0.6 mL of 0.01 M NaBH_4 was added into a solution containing 10 mL of 0.5 mM HAuCl_4 and 0.2 M CTAB. Then, the seed solution was aged at 25 °C for half an hour before use. The growth solution was prepared as followed: 2.8 g of CTAB and 0.49 g of NaOL were completely dissolved in 100 mL of ultrapure water at 30 °C. Subsequently, 7.2 mL of 4 mM AgNO_3 was added into the solution. 100 mL of 1 mM HAuCl_4 was added then the solution changed to colorless. After 90 minutes of low-speed stirring, 600 μL of HCl was added. After another 15 min of slower stirring, 0.5 mL of 0.064 M ascorbic

acid was added. Then, 0.16 mL of the aged gold seed solution was quickly injected into the growth solution. Finally, the solution was left undisturbed at 30°C for 12 hours. The nanorod solution was separated by centrifugation at 10,000 rpm for 20 minutes, washed 3 times with ultrapure water, and rediluted to 5 mM.

3. Characterization

The crystal structure of the prepared samples was characterized by X-ray diffraction spectroscopy (XRD, XRD-7000S), where the X-ray source was Cu-K α radiation ($\lambda=1.51$ Å) with a 2θ scan range of 20°-80°. X-ray photoelectron spectroscopy (XPS) spectra were measured by Thermo Scientific ESCALAB Xi+ with monochromatic Al K α radiation ($h\nu=1486.69$ eV) at high vacuum ($<5\times 10^{-10}$ mbar) chamber pressure. All binding energies are corrected by the C 1s peak at 284.6 eV. The morphology and structure of the samples were characterized by means of a JSM-7000F scanning microscope (SEM) and a transmission electron microscope (FEI Tecnai G2 F30 S-Twin) with an accelerating voltage of 300 kV. The Brunauer-Emmett-Teller (BET, Belsort-max) method was employed to measure the specific surface areas.

4. Electrochemical measurements

The electrochemical measurements and EIS were carried out on a CorrTest electrochemical analyzer. A standard three-electrode was used, in which the as-prepared material worked as the working electrode, Pt wire worked as the counter electrode and Ag/AgCl worked as the reference electrode. Cyclic voltammetry and amperometric response were chosen to test the electrochemical behavior of the

prepared materials, and the electrolyte was 0.1 M NaOH in all cases without special instructions. EIS was performed in an electrolyte solution of 0.5 M Na₂SO₄, in a frequency range from 0.1 Hz to 100 kHz with an ac probe amplitude of 5 mV.

Two reference samples, *i.e.*, Au/Cu(OH)₂ and Au@Cu₂O, were synthesized by controlling the added amounts of hydrazine hydrate. For Au/Cu(OH)₂, no hydrazine hydrate was added during the synthesis process, thus the Au nanorods were decorated on the Cu(OH)₂ nanowires, as shown in Figure S1a. While for Au@Cu₂O, excess hydrazine hydrate was used to ensure the Cu precursor was reduced into Cu₂O, thus forming the core-shell structured Au@Cu₂O with octahedral morphology (Figure S1b). The mean size of Au@Cu₂O NPs and Au@Cu₂O NPs in Au@Cu₂O/CuO/Cu(OH)₂ were 981.08 nm and 181.02 nm, respectively, as shown in Figure S1c-d. The smaller mean size of Au@Cu₂O NPs in Au@Cu₂O/CuO/Cu(OH)₂ was ascribed to the reduction of partial Cu(OH)₂ into Cu₂O.

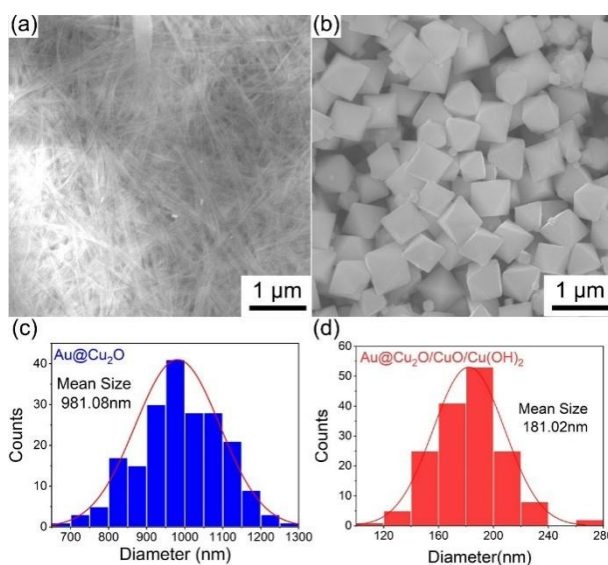


Figure S1. SEM images of (a) unreacted Au/Cu(OH)₂ NWs and (b) fully reduced Au@Cu₂O NPs, which were prepared by adding the same amount of Au NR (100 μL) as that was used for Au@Cu₂O/CuO/Cu(OH)₂; the size distribution of (c) fully reduced Au@Cu₂O NPs and (d) Au@Cu₂O NPs in Au@Cu₂O/CuO/Cu(OH)₂.

The size of Au@Cu₂O NPs and the length of Cu(OH)₂ NWs in Au@Cu₂O/CuO/Cu(OH)₂ can be adjusted by controlling the amount of hydrazine hydrate, as shown in Figure S2. When the amount of hydrazine hydrate was 46 μL (Figure S2a), the mean size of Au@Cu₂O in Au@Cu₂O/CuO/Cu(OH)₂ was 150.55 nm (Figure S2c). While an increased usage of hydrazine hydrate of 54 μL led to the formation of Au@Cu₂O with a mean size of 210.5 nm in Au@Cu₂O/CuO/Cu(OH)₂.

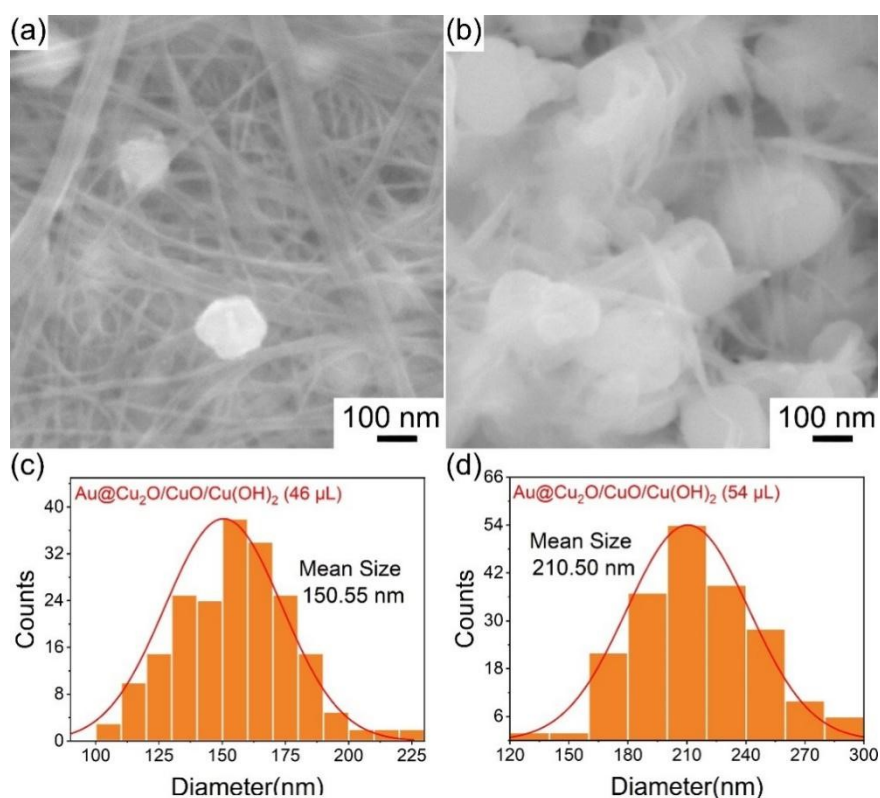


Figure S2. SEM images and size distribution of Au@Cu₂O/CuO/Cu(OH)₂ nanostructure prepared by different amounts of hydrazine hydrate: (a, c) 54 μL; (b, d) 64 μL

When an increased amount of Au NR (600 μ L) was used, a smaller mean size of 186.94 nm for octahedral Au NR@Cu₂O NPs was achieved, as shown in Figure S3.

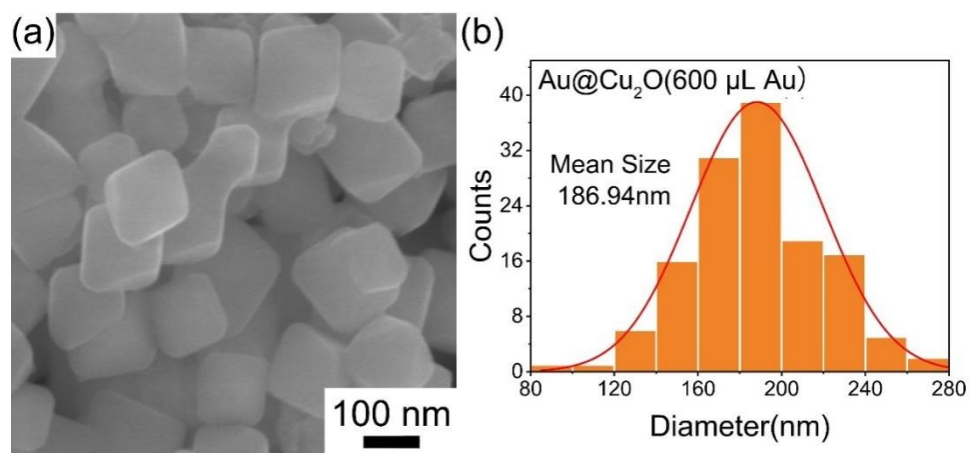


Figure S3. (a) SEM images and (b) size distribution of fully reduced Au@Cu₂O NPs prepared by adding 600 μ L Au NR

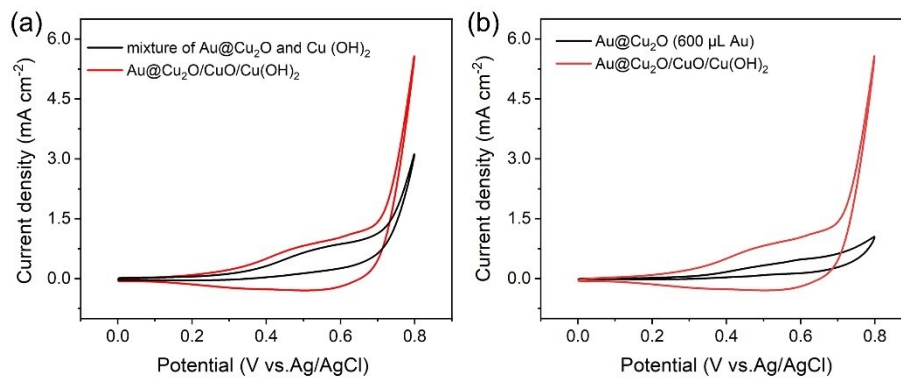


Figure S4. (a) The CV curves of mechanically mixed Au@Cu₂O NPs and Cu(OH)₂ electrode and Au@Cu₂O/CuO/Cu(OH)₂ electrode, (b) The CV curves of fully reduced Au@Cu₂O NPs prepared by adding 600 μL Au NR electrode and Au@Cu₂O/CuO/Cu(OH)₂ electrode. All of the experiments were conducted in 0.1 M NaOH electrolyte with 1 mM glucose

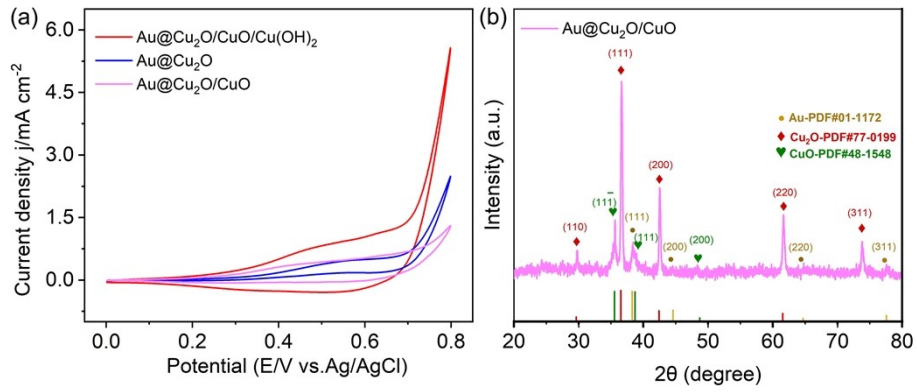


Figure S5. (a) The CV curves of surface oxidized Au@Cu₂O/CuO electrode, Au@Cu₂O electrode and Au@Cu₂O/CuO/Cu(OH)₂ electrode (b) XRD of prepared Au@Cu₂O/CuO sample

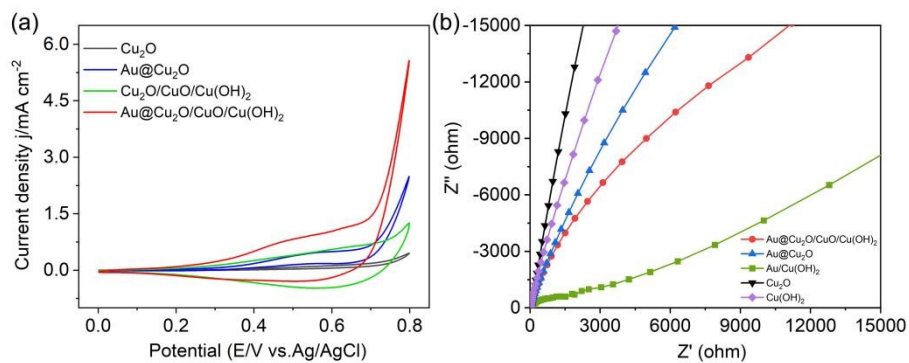


Figure S6. (a) The CV curves of bare Cu_2O , $\text{Au@Cu}_2\text{O}$ electrode, $\text{Cu}_2\text{O/CuO/Cu(OH)}_2$ electrode and $\text{Au@Cu}_2\text{O/CuO/Cu(OH)}_2$ electrode (b) EIS (Nyquist) plots of prepared bare Cu_2O , bare Cu(OH)_2 , Au/Cu(OH)_2 , $\text{Au@Cu}_2\text{O}$ and $\text{Au@Cu}_2\text{O/CuO/Cu(OH)}_2$ electrode

The test voltage were optimized by testing the i-t curve of Au@Cu₂O/CuO/Cu(OH)₂ at 0.5 ~ 0.7 V, as shown in Figure S7. It can be found that 0.6 V vs. Ag/AgCl was the most suitable potential for characterizing i-t performance.

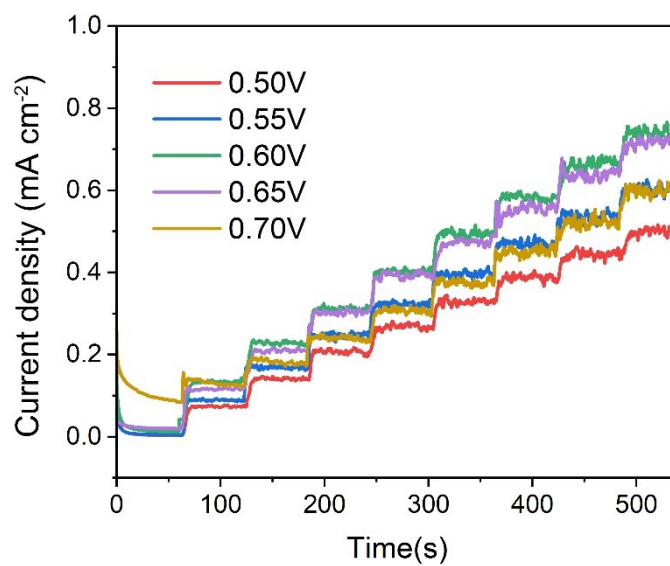


Figure S7. The i-t curve of Au@Cu₂O/CuO/Cu(OH)₂ at 0.5 ~ 0.7 V vs. Ag/AgCl

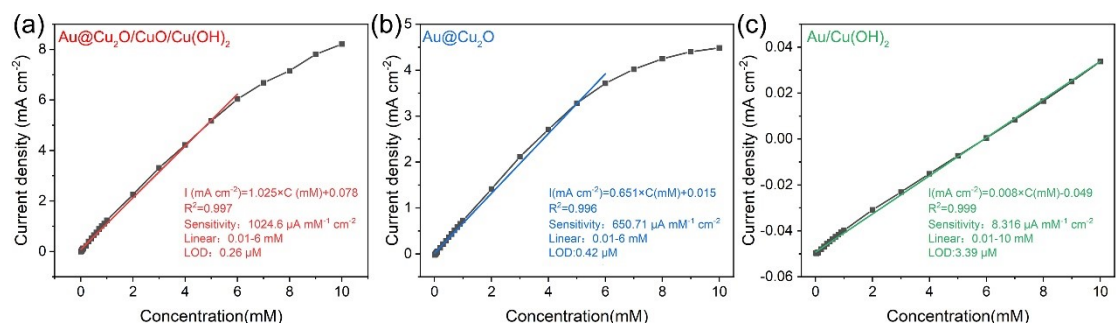


Figure S8. The fitted linear lines of current-concentration relationships over (a)

Au@Cu₂O/CuO/Cu(OH)₂, (b) Au@Cu₂O, and (c) Au/Cu(OH)₂

Table S1. BET results of Au@Cu₂O/CuO/Cu(OH)₂, Au@Cu₂O, and Au/Cu(OH)₂

Sample	BET surface area S_{BET}/(m²·g⁻¹)	Pore volume V/(cm³·g⁻¹)	Pore size (nm)
Au@Cu ₂ O/CuO/Cu(OH) ₂	10.282	0.045	17.620
Au@Cu ₂ O	9.996	0.046	18.464
Au/Cu(OH) ₂	47.901	0.329	27.506

The effect of scan rates on the glucose oxidation over the as-prepared electrodes were performed at different sweep rates from 10 to 200 mV/s, as shown in Figure S9. The cathodic and anodic peaks over the as-prepared electrodes all increased with the increase of the sweep rates. The higher scanning speed led to a slowing down of the electrocatalytic reaction kinetics during the adsorption of glucose molecules, indicating a typical surface-controlled adsorption/diffusion process during the sensing process.

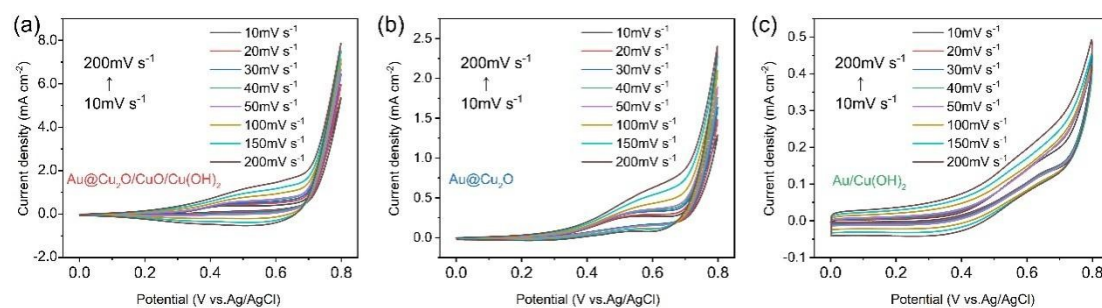


Figure S9. The CV curves at different scanning rates from 10 to 200 mV s⁻¹ for the prepared electrode in 0.1 M NaOH solution with 1 mM glucose: (a) Au@Cu₂O/CuO/Cu(OH)₂, (b) Au@Cu₂O NPs, and (c) Au/Cu(OH)₂ NWs

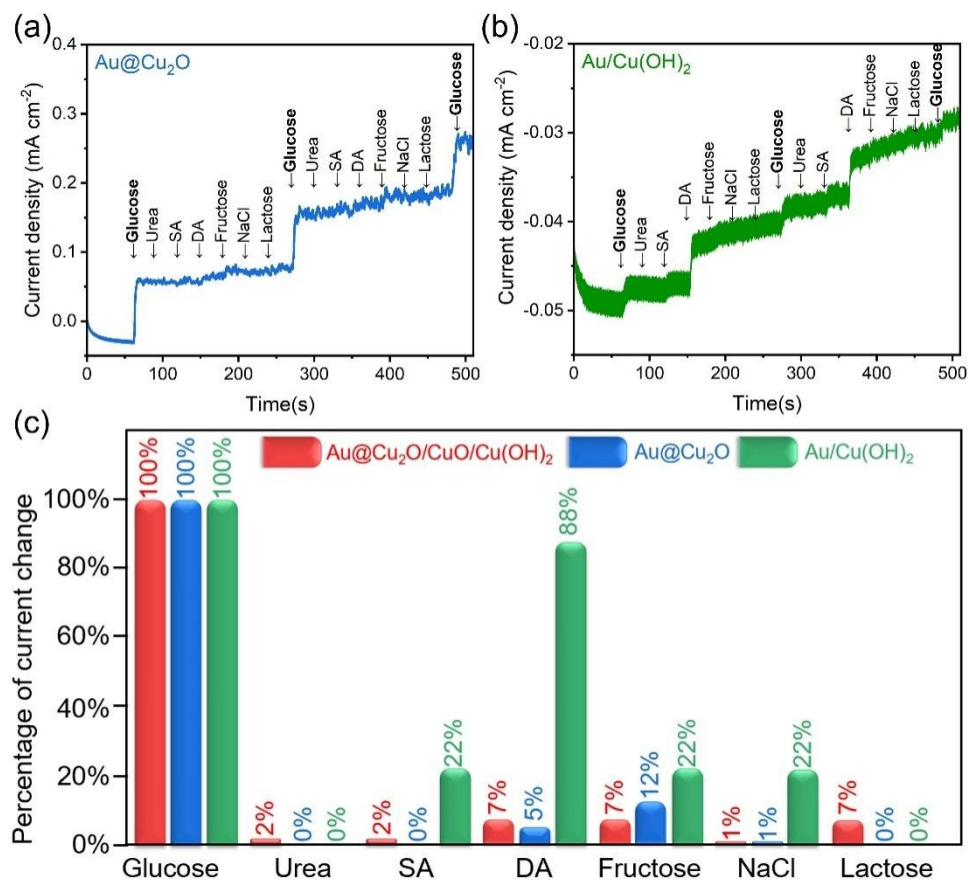


Figure S10. Amperometric response of (a) Au@Cu₂O NPs and (b) Cu(OH)₂ NWs to 0.1 mM glucose and different interference solutions in 0.1 M NaOH at an applied potential of 0.60 V vs. Ag/AgCl, (c) histogram of the percentage of current change after adding different interference solutions

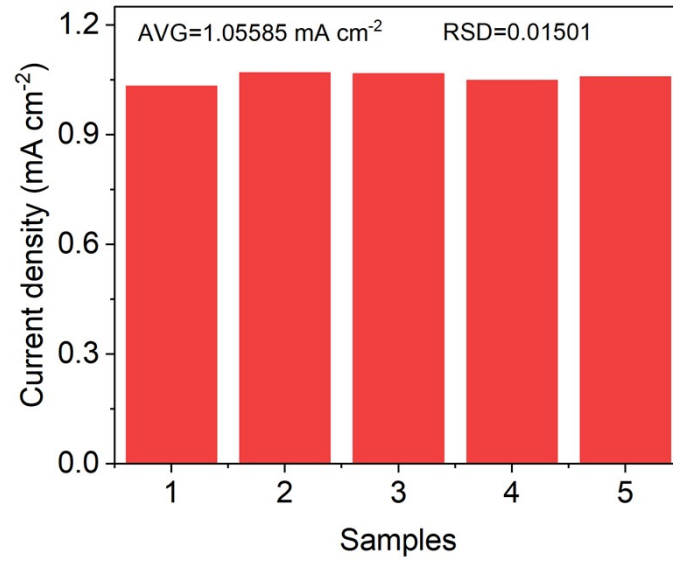


Figure S11. Reproducibility of five individually prepared Au@Cu₂O/CuO/Cu(OH)₂ electrodes which were tested in 1 mM glucose solution, at an applied potential of 0.60 V vs. Ag/AgCl

References

- [1] Ye X, Zheng C, Chen J, Gao Y, Murray CB. Using Binary Surfactant Mixtures To Simultaneously Improve the Dimensional Tunability and Monodispersity in the Seeded Growth of Gold Nanorods[J]. *Nano Letters*, **2013**, 13 (2): 765-771.