

ELECTRONIC SUPPLEMENTARY INFORMATION

Electrochemical deposition of gold nanoparticles on carbon ultramicroelectrode arrays

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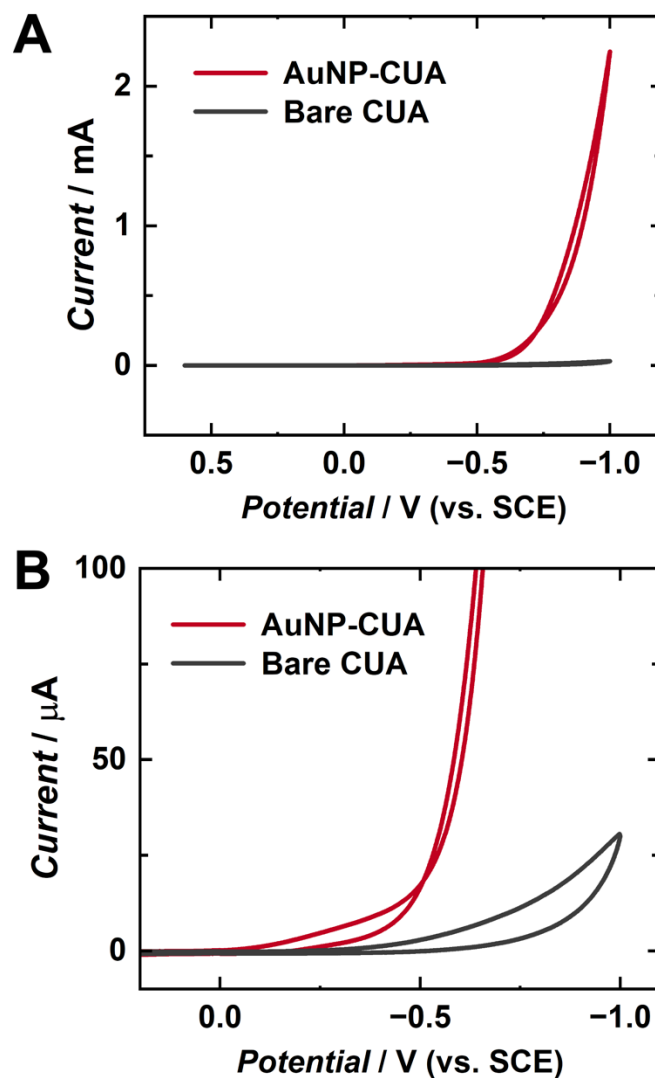
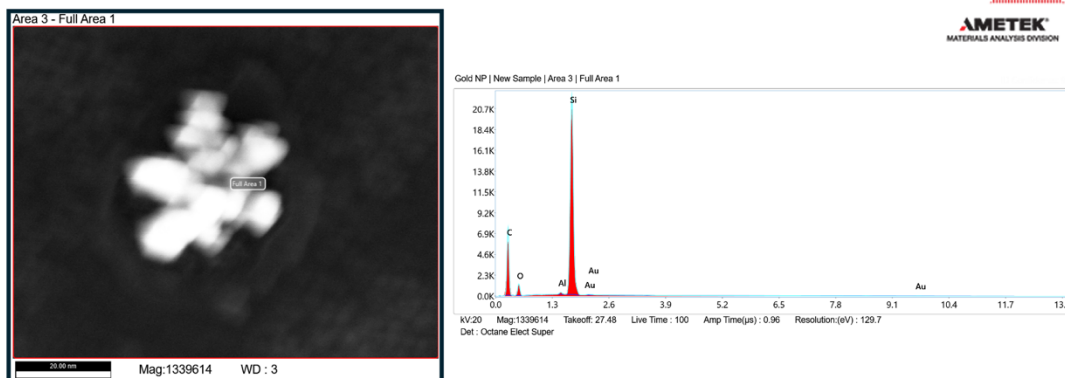


Fig. S1 Cyclic voltammetric (CV) comparison of 0.5 M H_2SO_4 at a scan rate of 100 mV s^{-1} at gold nanoparticle-modified carbon ultramicroelectrode arrays (AuNP-CUAs) versus a bare CUA surface, displayed as the red and gray traces, respectively. The electrodeposition parameters for the AuNP-CUA were -0.5 V vs. SCE for 5 s in a solution of $50 \text{ } \mu\text{M HAuCl}_4$ with $0.5 \text{ M H}_2\text{SO}_4$. Different CV current (x -axis) and potential (y -axis) windows were plotted to observe changes in kinetics and applied potential in the system: (A) Large window of full CV displaying a significant increase in cathodic current and (B) Narrow CV window showing a positive potential shift in the onset of hydrogen evolution reaction (HER).


eZAF Quant Result - Analysis Uncertainty: 11.92 %

Element	Weight %	MDL	Atomic %	Error %	Net Int.	R	A	F
C K	67.1	0.29	79.7	10.9	406.5	0.9250	0.0554	1.0000
O K	10.4	0.23	9.3	11.6	77.9	0.9340	0.0555	1.0000
Al K	0.2	0.04	0.1	10.6	17.6	0.9500	0.6269	1.0208
Si K	21.4	0.04	10.8	3.9	1852.2	0.9526	0.7351	1.0032
Au L	0.9	1.63	0.1	52.7	2.6	0.9909	0.9978	1.0737

Fig. S2 Energy Dispersive X-Ray Spectroscopy (EDX) was performed on gold nanoparticles (AuNPs) on a single electrode in the carbon ultramicroelectrode arrays (CUAs) to ensure that the material being imaged via scanning electron microscopy (SEM) was gold. Several other elements were detected in addition to Au, including carbon (C) from the electrode material, oxygen and aluminum (O and Al) from the alumina layer, and silicon and oxygen (Si and O) from the quartz substrate.

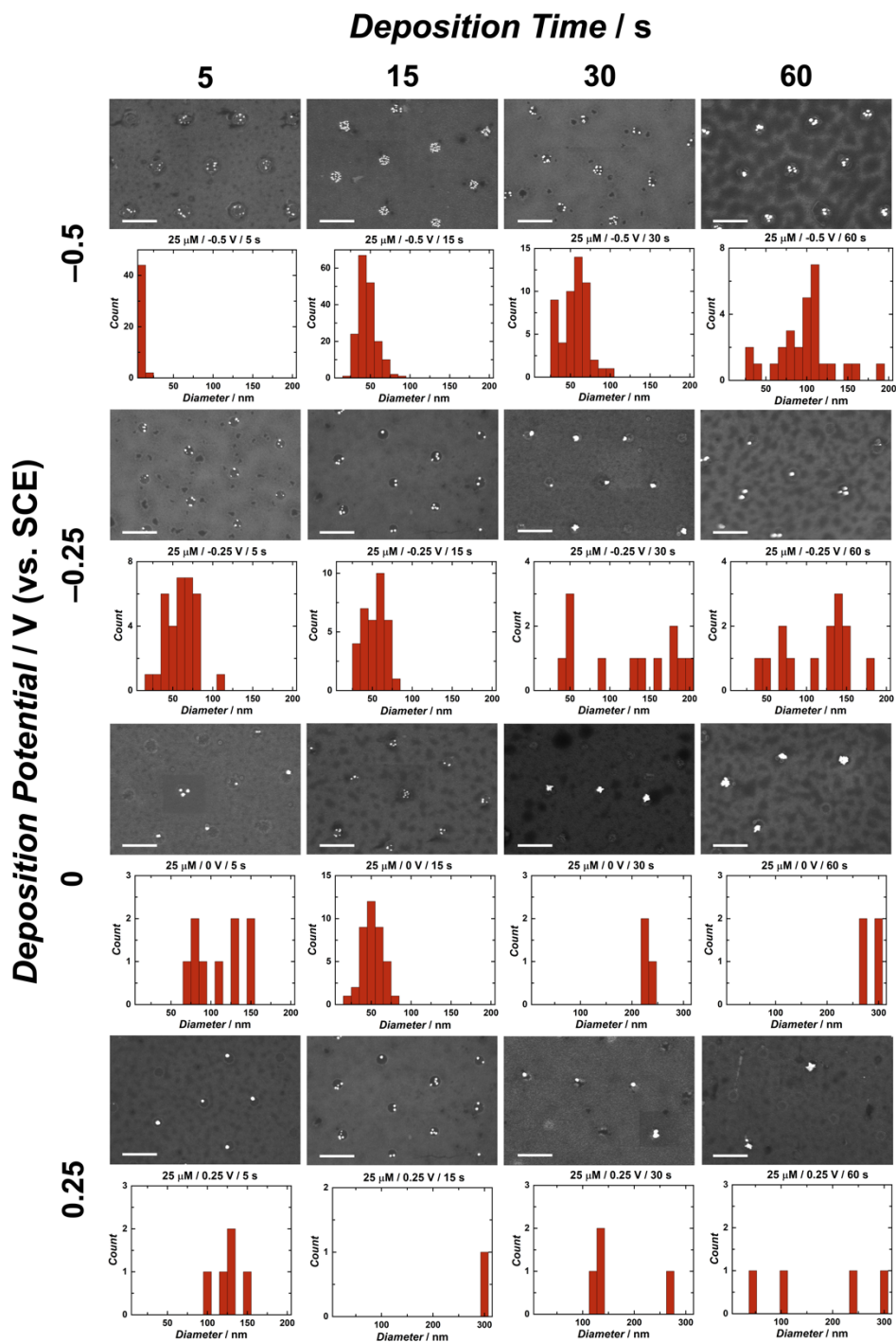


Fig. S3 Representative scanning electron microscopy (SEM) images and particle size distribution histograms for all time and potential parameters for the electrodeposition of gold nanoparticles (AuNPs) on carbon ultramicroelectrode arrays (CUAs) in $25 \mu\text{M}$ HAuCl_4 and 0.5 M H_2SO_4 solution. The SEM micrographs and histogram plots are arranged in order of increasing deposition time (from left to right) and decreasing reductive potential (from top to bottom). The scale bars represent $1 \mu\text{m}$ for all SEM images. Particle diameter measurements were taken from nine individual electrodes in the CUA of the same area as shown in the respective SEM images for each.

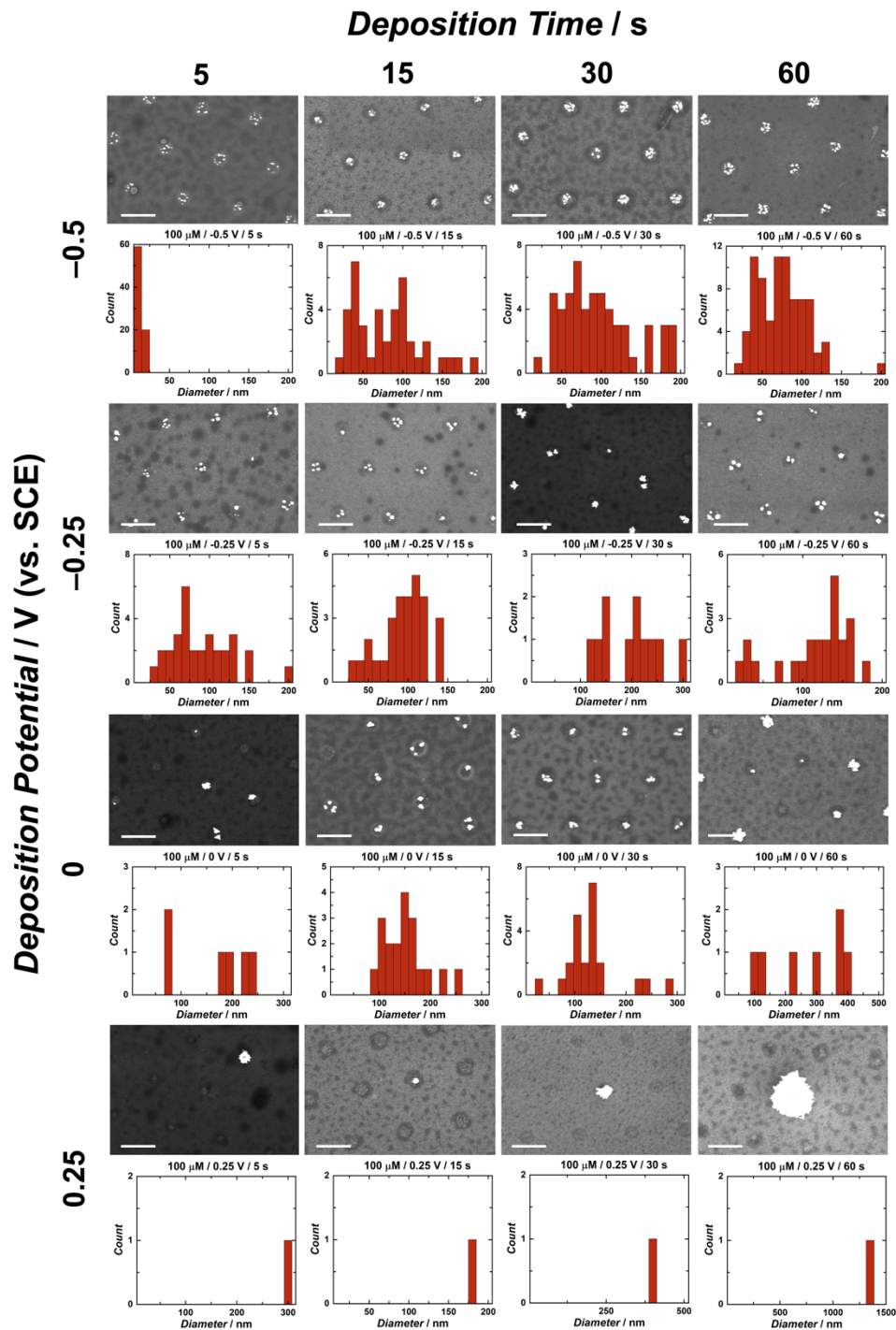


Fig. S4 Representative scanning electron microscopy (SEM) images and particle size distribution histograms for all time and potential parameters for the electrodeposition of gold nanoparticles (AuNPs) on carbon ultramicroelectrode arrays (CUAs) in 100 μM HAuCl_4 and 0.5 M H_2SO_4 solution. The SEM micrographs and histogram plots are arranged in order of increasing deposition time (from left to right) and decreasing reductive potential (from top to bottom). The scale bars represent 1 μm for all SEM images. Particle diameter measurements were taken from nine individual electrodes in the CUA of the same area as shown in the respective SEM images for each.

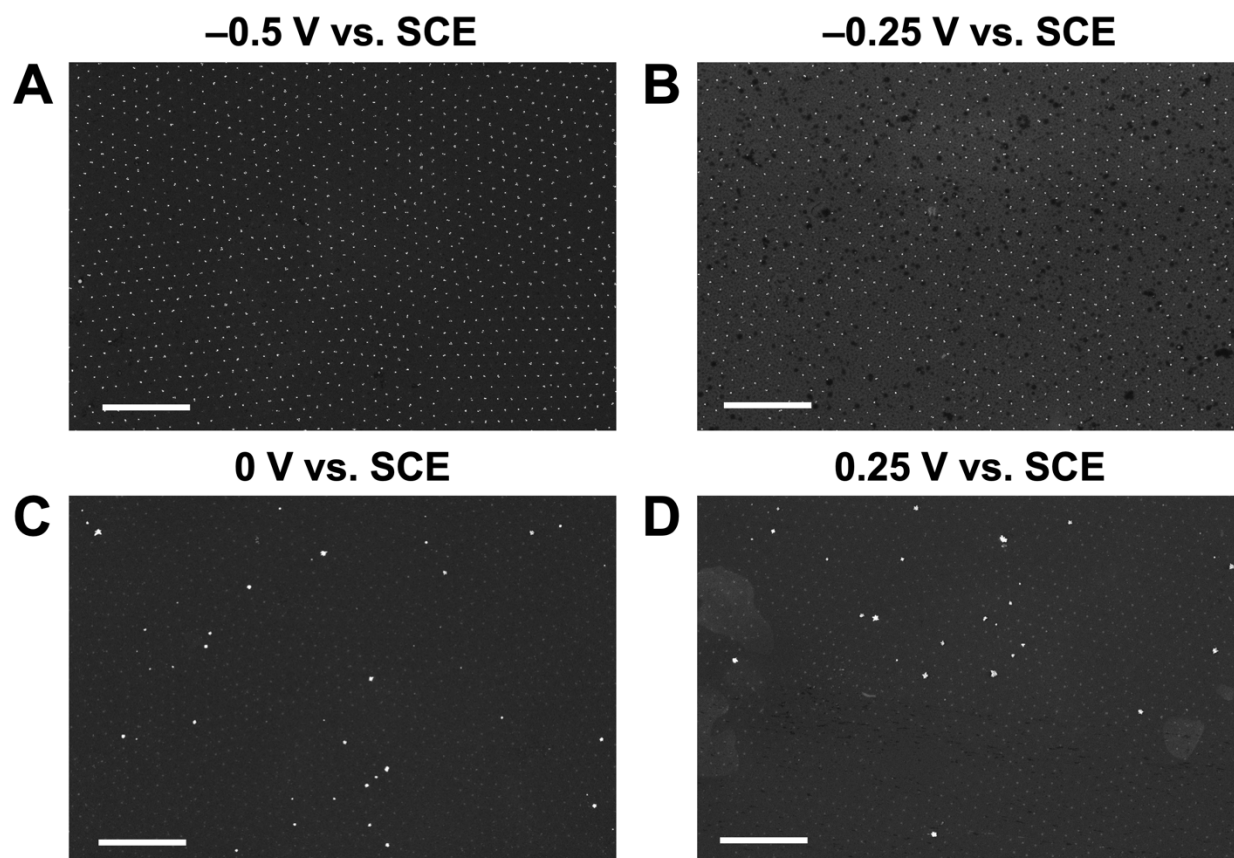


Fig. S5 Representative scanning electron microscopy (SEM) images of gold nanoparticles (AuNPs) illustrating the coverage on the carbon ultramicroelectrode array (CUA) surfaces at electrodeposition potentials of (A) -0.5 V, (B) -0.25 V, (C) 0 V, and (D) 0.25 V vs. SCE. Deposition times of 30 s and HAuCl_4 concentrations of 50 μM were the same for all four samples. Scale bars represent 10 μm for all SEM images. Note: In part (A), a few ultramicroelectrodes in the CUA array may appear less bright at this SEM resolution; however, SEM images at higher resolution confirm that they still have AuNPs deposited on them.

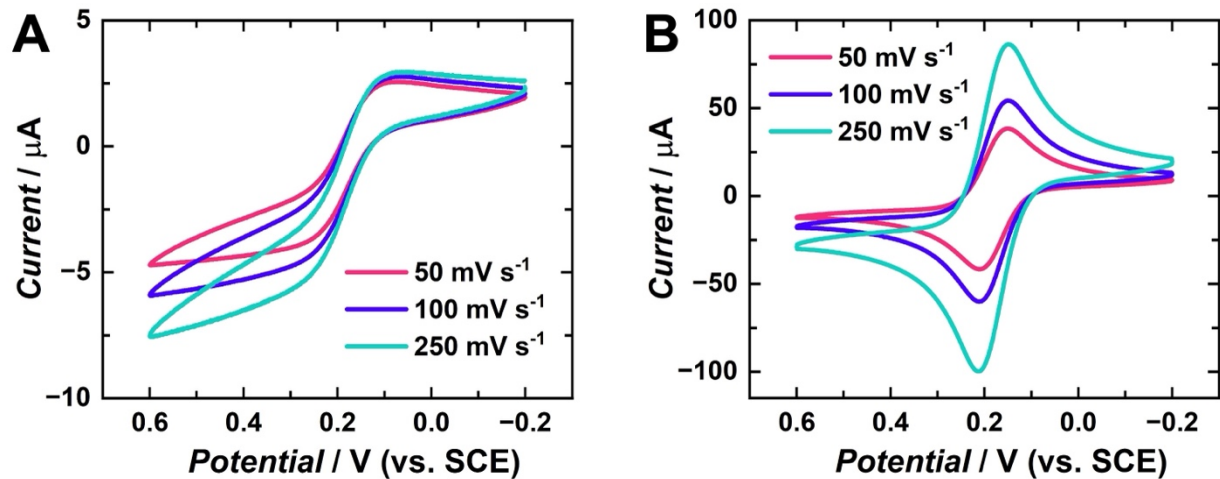


Fig. S6 Cyclic voltammograms of the (A) carbon ultramicroelectrode arrays (CUAs) (1.4 % exposed carbon electrode area) and (B) planar, carbon Macro electrodes (100% exposed carbon electrode area) at scan rates of 50, 100, and 250 mV s^{-1} using 500 μM ferrocenemethanol in a supporting electrolyte solution containing 0.5 M KCl.

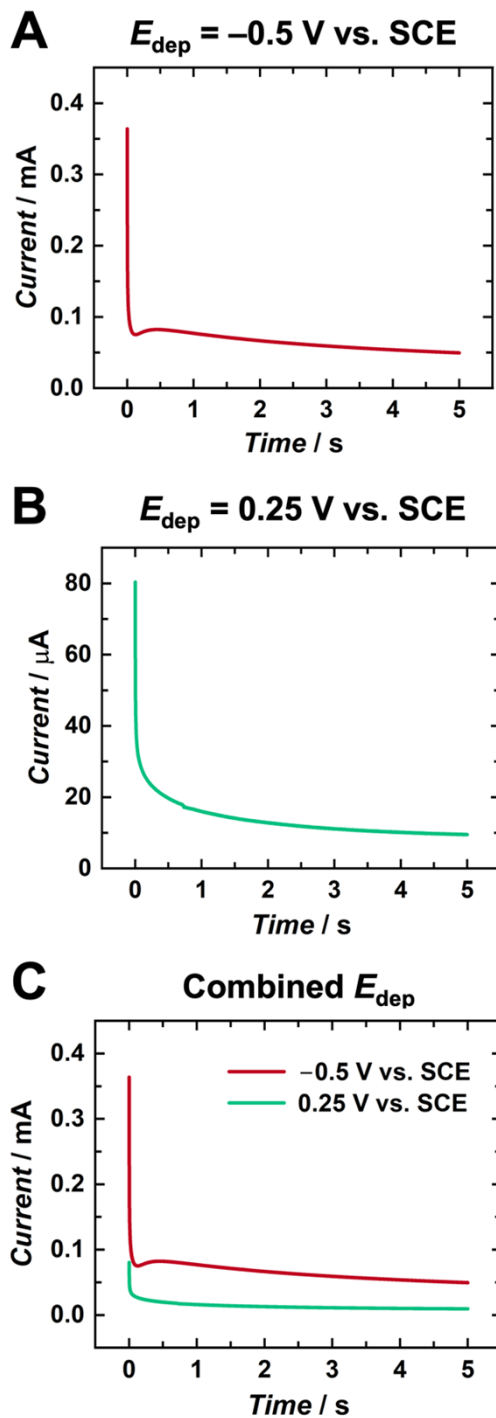


Fig. S7 Amperometric current-time ($i-t$) profiles for the electrodeposition of gold nanoparticles (AuNPs) on carbon ultramicroelectrode arrays (CUAs) with 1.4% exposed carbon area. The potential was stepped to (A) -0.5 V and (B) 0.25 V vs. SCE for a deposition time of 5 s in a solution containing $0.5 \text{ M H}_2\text{SO}_4$ and $50 \mu\text{M HAuCl}_4$. (C) Overlay of amperograms from (A) and (B) to display the dependence of the resulting current output, charged passed, and amount of gold deposited, on the applied electrodeposition potential. This data at the two different electrodeposition potentials was used to determine amounts of gold deposited on the CUA electrodes, which are reported in Table 1.

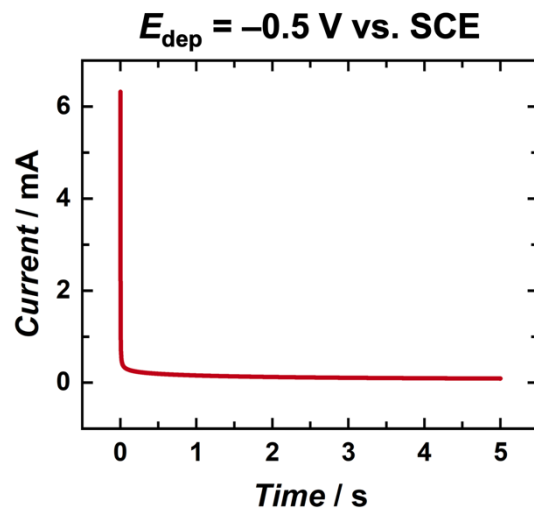


Fig. S8 Amperometric current-time (i - t) profile for the electrodeposition of gold nanoparticles (AuNPs) on carbon Macro electrode (pyrolyzed photoresist film only) with 100% exposed carbon area. The potential was stepped to -0.5 V vs. SCE for a deposition time of 5 s in a solution containing $0.5 \text{ M H}_2\text{SO}_4$ and $50 \mu\text{M HAuCl}_4$. Data was used to determine amounts of gold deposited on Macro electrode, which are reported in Table 1.

Determination of gold nanoparticle (AuNP) amount

Faraday's law was utilized to determine the amount of gold on the CUA surfaces.^{1, 2} Faraday's law, displayed in **Equation S1**, establishes a correlation between charge and amount of chemical substance in moles:

$$Q = nNF \quad \text{(Eq. S1)}$$

In this equation, Q represents total charge passed through the system in Coulombs (C), n indicates the number of electrons transferred in the associated redox reaction, N symbolizes the amount of species present in moles (mol), and F designates Faraday's constant (96,485 C mol⁻¹). The total charge was determined experimentally by integrating the area under amperometric curve from 0.5–5 s (**Figure S6**). The first 10% of points in this curve were excluded from the calculation due to contributions from non-faradaic, charging current early in the amperometric trace.¹ The number of electrons (n) equals 3, given the redox reaction of Au³⁺ to solid Au⁰ (**Equation 1**).

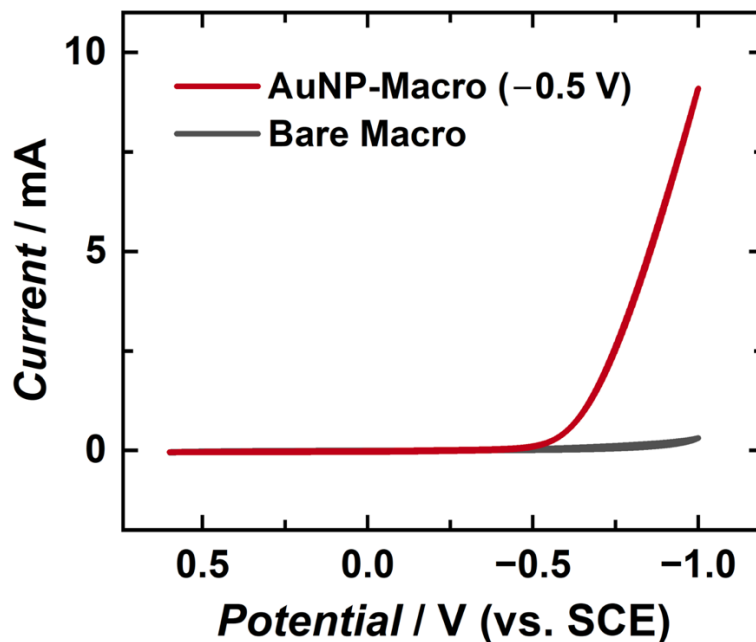


Fig. S9 Cyclic voltammetric current-potential (i - E) traces of the hydrogen evolution reaction (HER) in 0.5 M H_2SO_4 . The bare Macro electrode (gray trace) does not contain AuNPs. For the AuNP-modified Macro electrode (red trace), the deposition potential, deposition time, and HAuCl_4 concentration were -0.5 V vs. SCE, 5 s, and 50 μM , respectively. The voltammograms are representative average from $n=3$ total replicates.

References

1. O. Simoska and S. D. Minter, *Techniques in electroanalytical chemistry*, American Chemical Society, ACS In Focus, 2022.
2. A. J. Bard, L. R. Faulkner and H. S. White, *Electrochemical methods: fundamentals and applications*, John Wiley & Sons, Inc., 3rd edn., 2020.