

## Supporting Information

# The Electroneutrality Condition Allows for Electrodeposition of Gold Nanoparticles from Aqueous Nanodroplets

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## I. Experimental Procedures

## a. Materials

The chemicals lithium perchlorate (battery grade, 99.99 % trace metal basis), and gold chloride (III) hydrate (auric acid; 99.995 % trace metal basis), were obtained from Sigma-Aldrich. The organic phase 1,2- dichloroethane (99+%) was obtained from Alfa Aesar. The highly oriented pyrolytic graphite (HOPG) substrate was purchased from Momentive Performance Materials Quartz, Inc. The HOPG surface was exfoliated between experiments using adhesive tape to take out individual layers for exposing new cleaner layers. Nano-pure water (18.2 M $\Omega$ ·cm) was used to dissolve all the water-soluble chemicals. The glassy carbon electrode (r= 1.5 mm) and Ag/AgCl reference electrode was purchased from CH Instruments, Austin, TX. A 10 mL fluorinated ethylene propylene Oak Rids Centrifuge Tube was purchased from Thermo Scientific. TEM grid of carbon type-B, 200 mesh TH, Nickel was purchased from TED Pella, Inc.

## b. Preparation of solutions

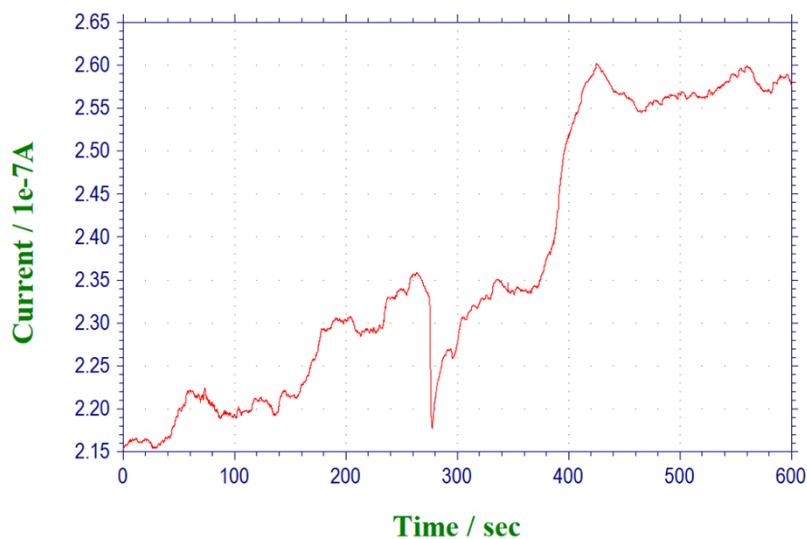
One main aqueous solution was prepared. The solution was 25 mM gold chloride (III) hydrate, and 0.25 M LiClO<sub>4</sub> in water. Water-in-oil emulsions were prepared by taking 25  $\mu$ L of the aqueous solution and then was added to 5 mL of 1,2-dichloroethane solvent in a 10 mL fluorinated ethylene propylene centrifuge tube. Then, the emulsion solution was sonicated with an ultrasonic processor. Sonication of the emulsion was performed applying a pulse 5 seconds ON and 5 seconds OFF with an amplitude of 40% for a total time of 1 minute.

## c. Instrumentation

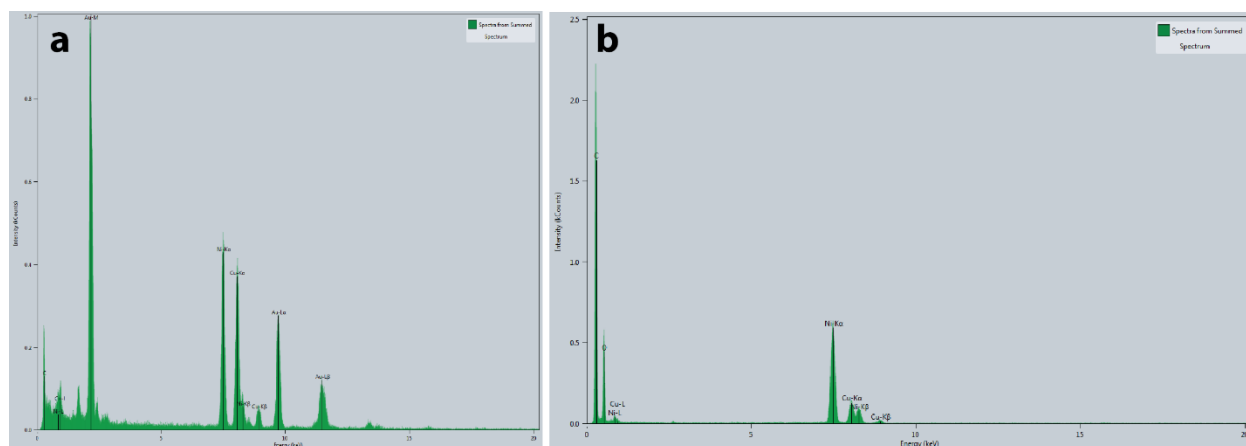
Chronoamperometry and cyclic voltammetry was performed using a CHI model 601D potentiostat (CH Instruments, Austin, TX), where a polarographic notation (Texas) was used. We implicate oxygen reduction to the change in current density as a function of time in our chronoamperograms. For the electrodepositions, we have previously shown that the coulombic efficiency for metal nanoparticle electrodeposition from aqueous nanodroplets is 100%.<sup>1</sup> A PTFE cell with a 2 mm diameter Viton O-ring was used with the HOPG to expose only a 2 mm diameter of the carbon substrate as the working electrode. An Ag/AgCl was stored in a solution of 1 M KCl with a salt bridge, and a glassy carbon rod was used as the reference and counter electrodes,

respectively. The water-in-oil emulsions were prepared using a Q500 ultrasonic processor (Qsonica, Newtown, CT) with a microtip probe. An inductively coupled plasma-mass spectrometer was used for partition coefficient determination in the work here presented, with all spectra and concentration measurements being obtained on a NexION 300D Inductively Coupled Plasma-Mass Spectrometer (PerkinElmer, Waltham, MA), having all samples be prepared and diluted using a 2 % HNO<sub>3</sub>. Internal standards were used for comparison, with an Yttrium internal standard used in the work here presented. Helios 600 Nanolab dual beam system (FEI, Hillsboro, OR) and INCA PentaFET-x3 (Oxford, Abingdon, UK) were used for Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) to obtain images of nanoparticles and to confirm the presence of certain elements. The voltage and current during SEM and EDX were 5 keV, 20 keV, and 0.69 nA. An Thermo Scientific Talos F200X were used for Transmission Electron Microscopy (TEM) at 200 kV to obtain the diffraction pattern of the nanoparticles. ImageJ was used to obtain the d-spacing from the selected area diffractogram.

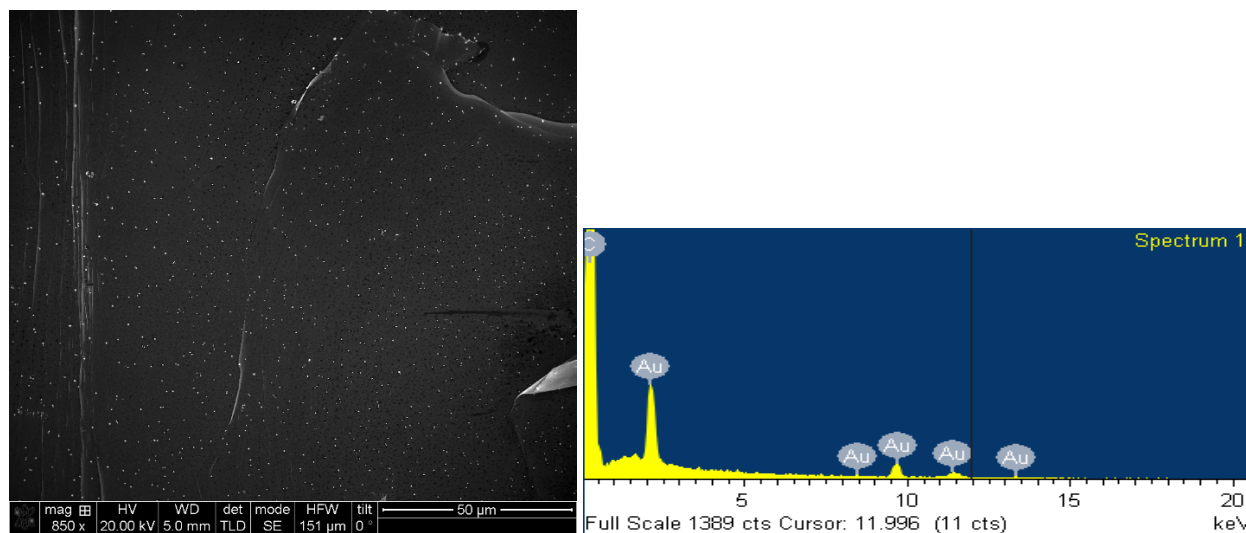
## II. Supporting Information Figures



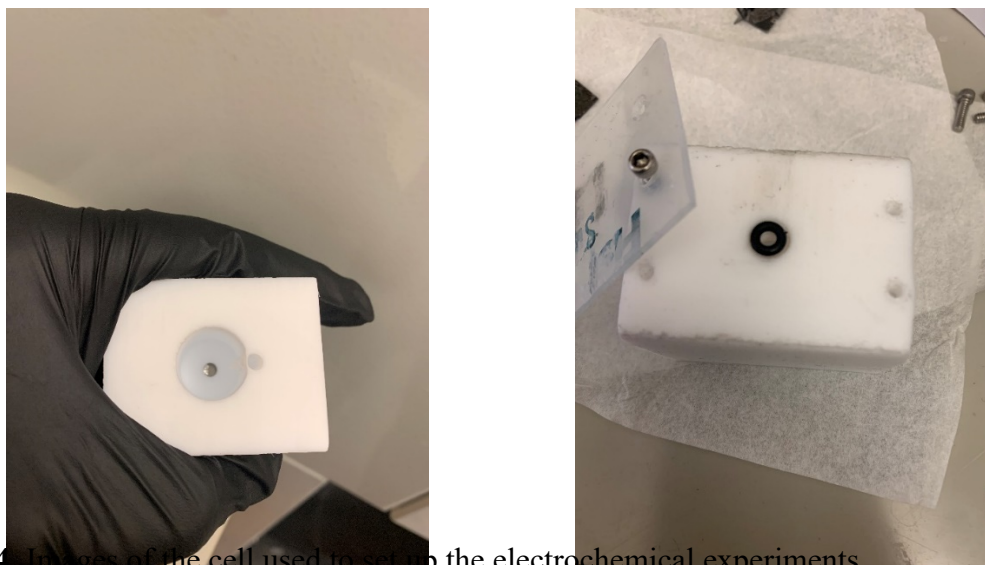
**Figure S1.** Representative chronoamperometric *i-t* curve of the electrodeposition of Au nanoparticles using water droplets suspended in 1,2-dichloroethane. The applied potential was – 0.1 V vs Ag/AgCl. The water droplets contained 25 mM auric acid and 250 mM LiClO<sub>4</sub>. The 1,2-dichloroethane phase did not had any supporting electrolyte.



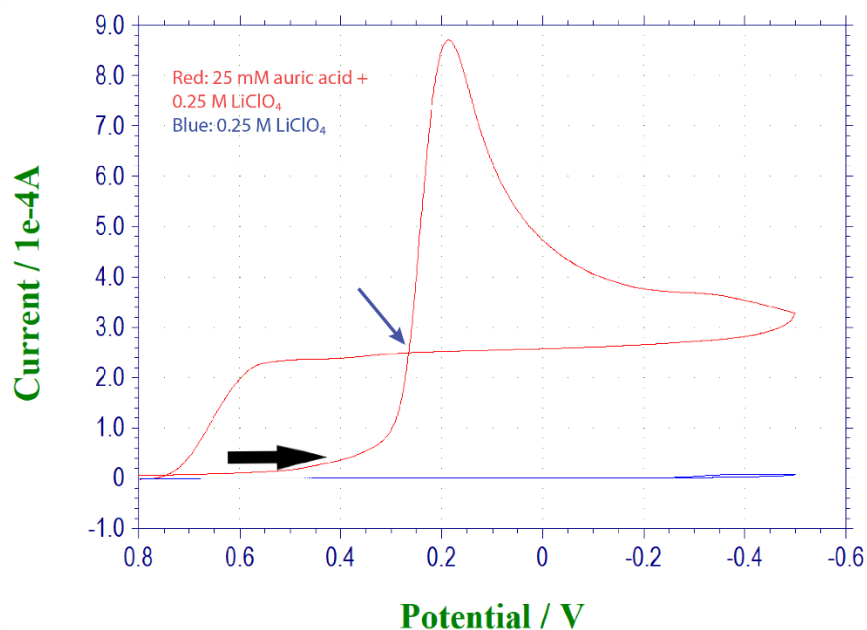
**Figure S2.** EDX data of a) Au nanoparticles on Carbon Type-B, 200 mesh TH, Nickel TEM grid, and b) just the TEM grid. Different elements could be observed because of the composition of the TEM grid as presented in the methodology section. However, Cu can be observed due to the production procedure of the grids that usually has a small percentage of Cu.



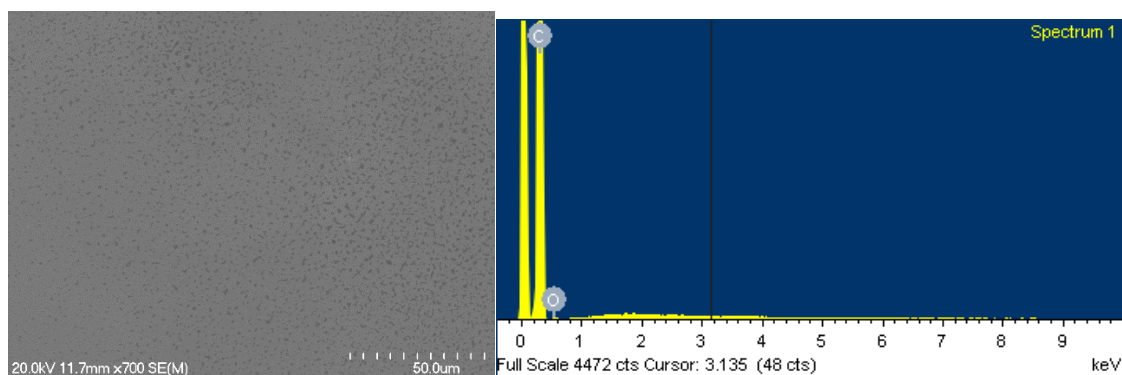
**Figure S3.** Representative SEM and EDX data of Au nanoparticles showing a higher coverage on the HOPG surface. The lines presented in the SEM image are just defects from the carbon substrate.



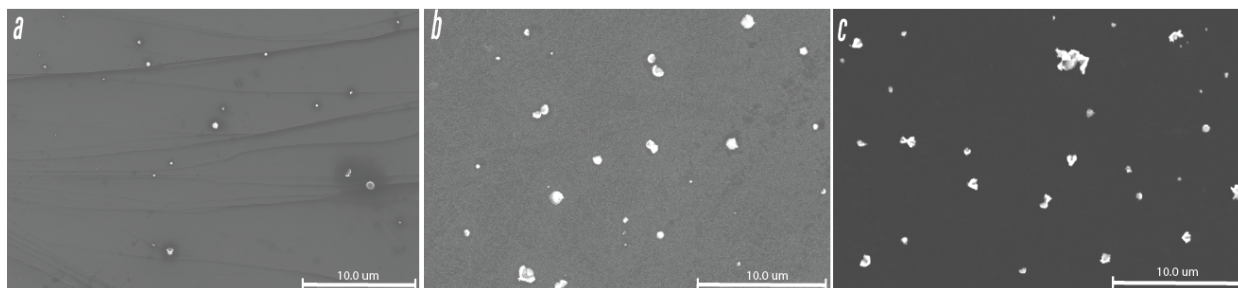
**Figure S4** Images of the cell used to setup the electrochemical experiments.



**Figure S5.** Red trace shows the cyclic voltammogram of 25 mM auric acid with 0.25 M LiClO<sub>4</sub> in water. First segment is pointed out by the black arrow. Voltammogram starts at 0.8 V vs Ag/AgCl and goes in the negative direction. The reduction peak around 0.2 V vs Ag/AgCl corresponds to the formation of gold nanoparticles. Additionally, a nucleation loop can be observed as evidence of gold formation (blue arrow). The working, reference, and counter electrodes used were glassy carbon, Ag/AgCl, and glassy carbon rod respectively. The scan rate was 50 mV/s. The quiescent solution was purged with nitrogen gas for 10 minutes before performing the experiment.



**Figure S6.** Representative SEM and EDX data of a HOPG surface. Electrodeposition was performed in water-in-oil emulsion with 25 mM auric acid in water suspended in 1,2-dichloroethane without any supporting electrolyte with chronoamperometry at  $-0.1$  V vs Ag/AgCl for 600 seconds. No gold nanoparticles were observed.



**Figure S7.** SEM-EDX images of Au nanoparticles electrodeposited in the presence of a) 5 mM  $\text{LiClO}_4$ , b) 75 mM  $\text{LiClO}_4$ , and c) 0.5 M  $\text{LiClO}_4$ . The electrodeposition was performed using chronoamperometry at  $-0.1$  V vs Ag/AgCl for 600 seconds. The emulsion was prepared as explained in the methodology section, but with varied concentrations of  $\text{LiClO}_4$ . The average nanoparticle diameter when using 5 mM, 75 mM, and 0.5 M  $\text{LiClO}_4$  was  $490 \text{ nm} \pm 254 \text{ nm}$  ( $N=137$ ),  $403 \text{ nm} \pm 334 \text{ nm}$  ( $N=116$ ), and  $548 \text{ nm} \pm 217 \text{ nm}$  ( $N=113$ ), respectively. Additionally, the working electrode was HOPG.

**Table S1.** Data for the determination of the partition coefficient of  $\text{HAuCl}_4$  using ICP-MS. Gold standards of known concentrations were used and diluted by the instrument, with all samples being diluted with 2 %  $\text{HNO}_3$  prior to measurement on ICP-MS. Concentrations for standards shown are plotted against raw intensity counts and have arbitrary units (a.u.). All calibration curve measurements were taken at an  $N=5$ .

Conc. (ppm)	Intensity (a.u)	RSD	Std. Dev. (a.u)
0.0	145.5	12.4%	0.180949973
0.5	140.1	8.0%	0.11209236
1	984.0	14.8%	1.46009252
2.5	12204.6	5.9%	7.187161419
10	52749.7	0.8%	4.039240972
50	271080.2	7.7%	209.9908336
100	554851.5	5.1%	280.8024779

**Table S2.** Miller indices obtained by comparing the selected area diffractogram with theoretical values.

$1/2r(1/\text{nm})$	$1/r(1/\text{nm})$	$r$ (nm)	$d$ (Å)	(hkl)
9.667	4.8335	0.206889	2.068894	200
17.766	8.883	0.112575	1.125746	222

### III. References

1. Glasscott, M. W.; Dick, J. E., Fine-Tuning Porosity and Time-Resolved Observation of the Nucleation and Growth of Single Platinum Nanoparticles. *ACS Nano* **2019**, *13* (4), 4572-4581.