Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Enabling Practical Nanoparticle Electrodeposition from Aqueous Nanodroplets

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I. Experimental Methods

Conductivity measurements: It was used a Thermo Scientific Orion Versa Star Pro using Orion 013005MD Conductivity Cell (epoxy/graphite) with a cell constant of 0.475 cm^{-1}. The electrode was submerged in the respective solutions and between each measurement, it was cleaned with ethanol and used air to dry the electrode.

II. Supporting Information Figures

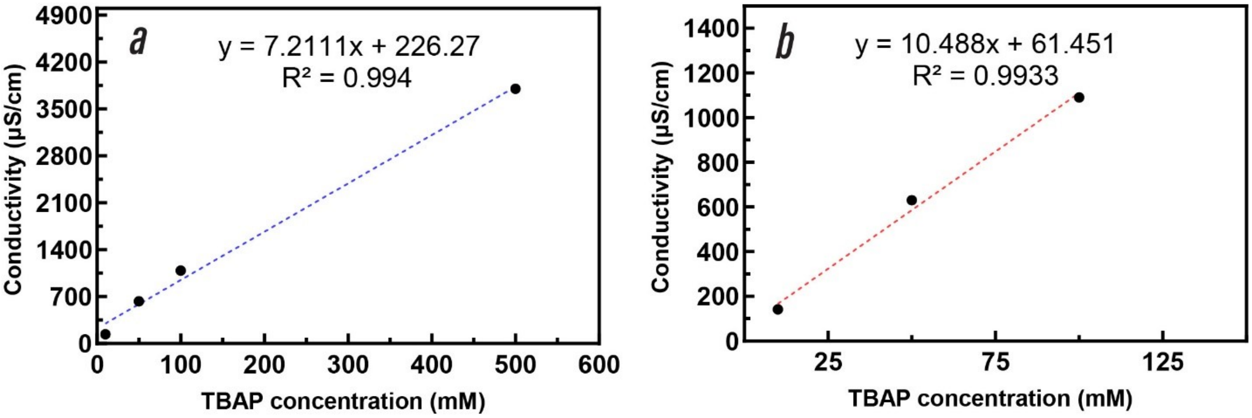

Figure S1. Conductivity measurements in a solution of 1,2-dichloroethane with the tetrabutylammonium perchlorate (TBAP) supporting electrolyte, including **a)** a point at which it begins to level out of linearity. The intercept serves as the conductivity of 1,2-dichloroethane at 226 µS/cm. **Figure S1b** represents a better fit, displaying the 1,2-dichloroethane conductivity as 61 µS/cm. Considering each figure, the fact that resistivity is inversely proportional to conductivity and the value of the cell constant is 0.475 cm^{-1}, the resistance ranges from 9.3 kΩ to 34.3 kΩ.

Table S1. Conductivity measurements of different concentrations of TBAP (tetrabutylammonium perchlorate) in 1,2-dichloroethane

Concentration (mM)	Run 1 (µS/cm)	Run 2 (µS/cm)	Run 3 (µS/cm)	Average (µS/cm)	Standard Deviation (µS/cm)
10	139.8	143.7	140.8	141.4	2.026
50	630.3	630.6	631.1	630.7	0.4041
100	1091	1087	1093	1090	3.055
500	3799	3798	3809	3802	6.083

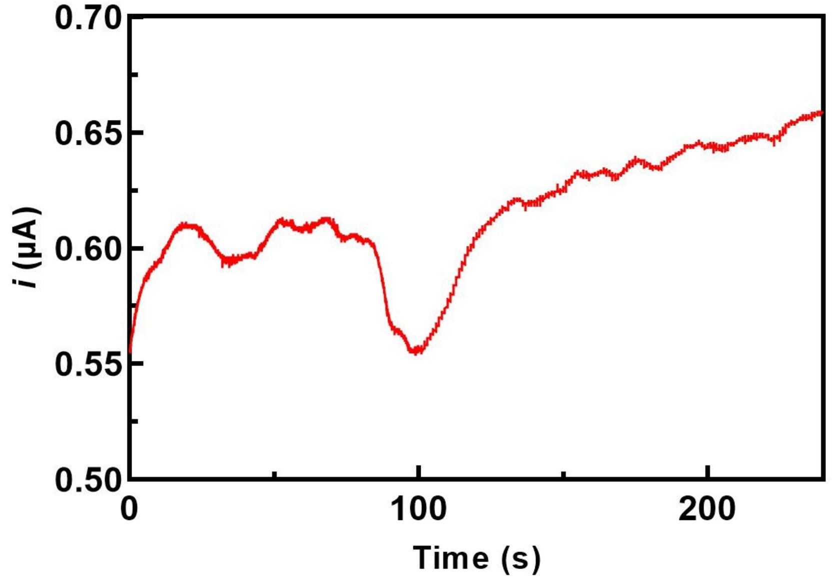

Figure S2. Amperometric *i-t* curve of the electrodeposition of Pt NPs at –0.1 V vs Ag/AgCl using a w/o emulsion. The water droplets contained 50 mM hexachloroplatinic acid with 250 mM $LiClO_4$ suspended in a 1,2-DCE solution without TBAP. The substrate used to electrodeposit the NPs was HOPG. Due to the resistance of the bulk phase (i.e., 1,2-DCE, between 9.3 kΩ to 34 kΩ), the current observed was attributed to the resistance of the solution, representing the *i*R drop. If Ohm's Law is taken to be V=*i*R, the *i*R drop approximation ranges from 9.3 mV to 34 mV. Despite taking into consideration a resistance measurement from the conductivity measurements in **Figure S1**, the standard reduction potential of chloroplatinic remains far away.

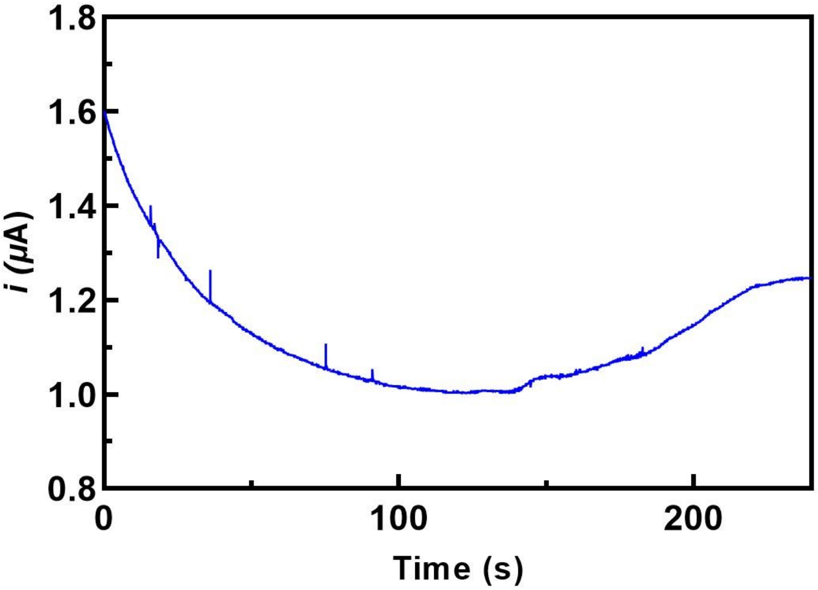

Figure S3. Amperometric *i*-*t*-curve of the electrodeposition of Pt NPs at –0.1 V vs. Ag/AgCl using a w/o emulsion with 50 mM hexachloroplatinic acid in water droplets suspended in 1,2-DCE with 0.1 M TBAP. The substrate was HOPG.

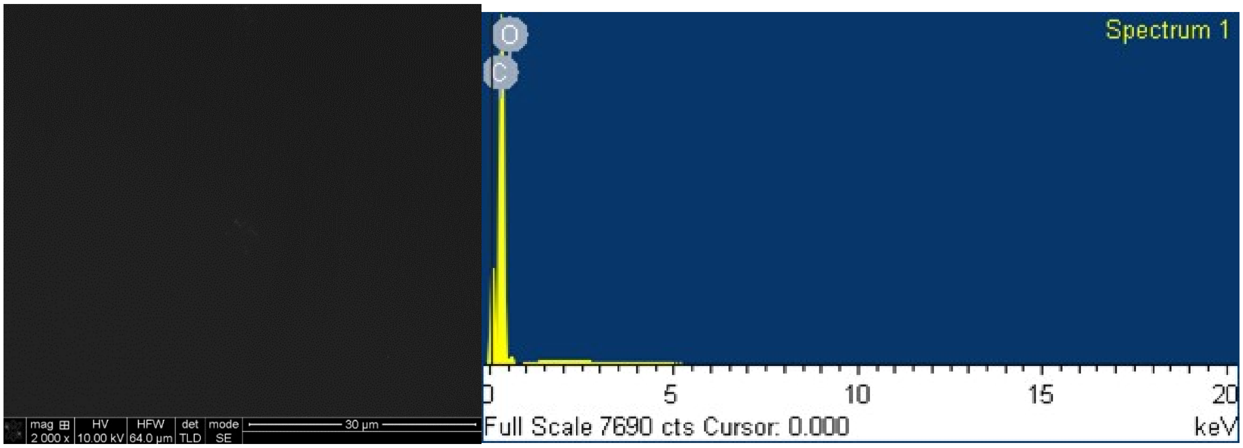

Figure S4. SEM and EDX data of a bare HOPG substrate. A control experiment was performed to assure that no previous nanoparticles were deposited on the surface. As expected, no Pt nanoparticles were observed. The SEM was performed at 10 keV and the EDX at 20 keV.

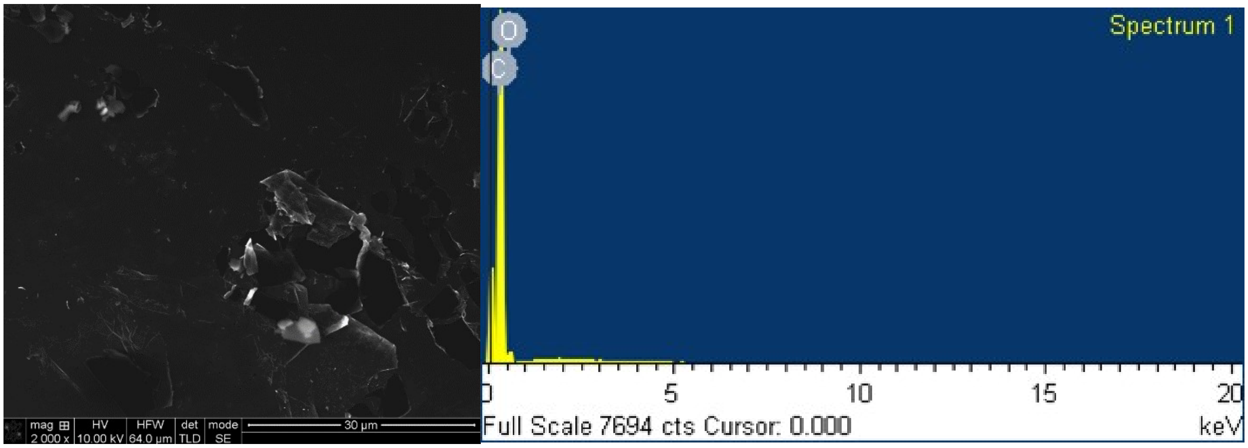

Figure S5. SEM and EDX data of HOPG substrate after the addition of a w/o emulsion. The emulsion was added to the substrate and all the electrodes were connected. After waiting for 240 seconds, the substrate was rinsed with water and ethanol for 5 minutes. The emulsion was composed of 50mM hexachloroplatinic acid with 250 mM $LiClO_4$ suspended in 1,2 DCE without TBAP. As presented in the EDX data, no nanoparticle formation was observed, and only carbon and oxygen were present. This control experiment was performed to show that the NPs formed are not attributed to a precipitation process of any spontaneous reaction without applying an external potential. The SEM was performed at 10 keV and the EDX at 20 keV.

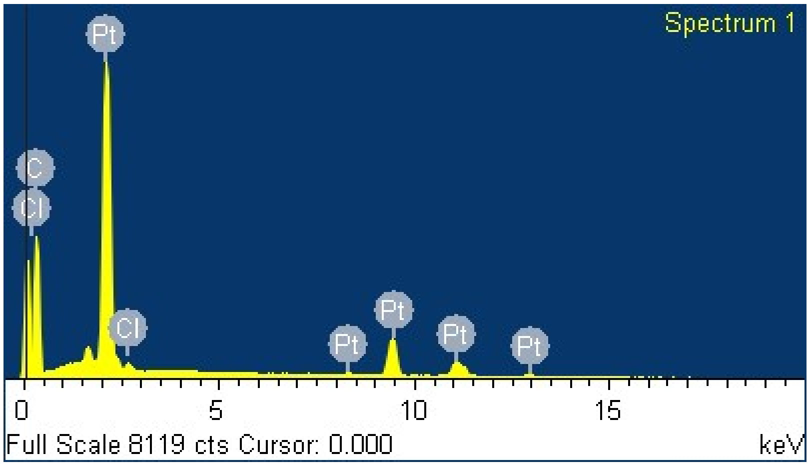

Figure S6. EDX data for a HOPG substrate with Pt NPs. The solution used was a w/o emulsion with 50 mM hexachloroplatinic acid with 250 mM $LiClO_4$ in water droplets suspended in 1,2-DCE. The applied potential was -0.1 V vs Ag/AgCl for 240 seconds. EDX was performed at 20 keV. This figure displays evidence of the presence of Pt NPs observed in the main manuscript in **Figure 1** (**a-c**).

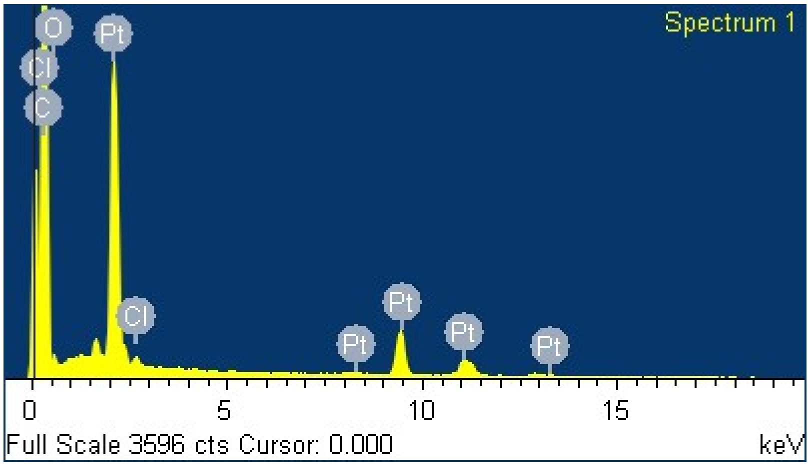

Figure S7. EDX data for a HOPG substrate with Pt NPs. The solution used was a w/o emulsion of 50 mM hexachloroplatinic acid in water droplets suspended in 1,2-DCE with 0.1 M TBAP. The applied potential was -0.1 V vs Ag/AgCl for 240 seconds. EDX was performed at 20 keV. This figure exhibits evidence of the presence of Pt NPs observed in the main manuscript in **Figure 1** (**d-f**).

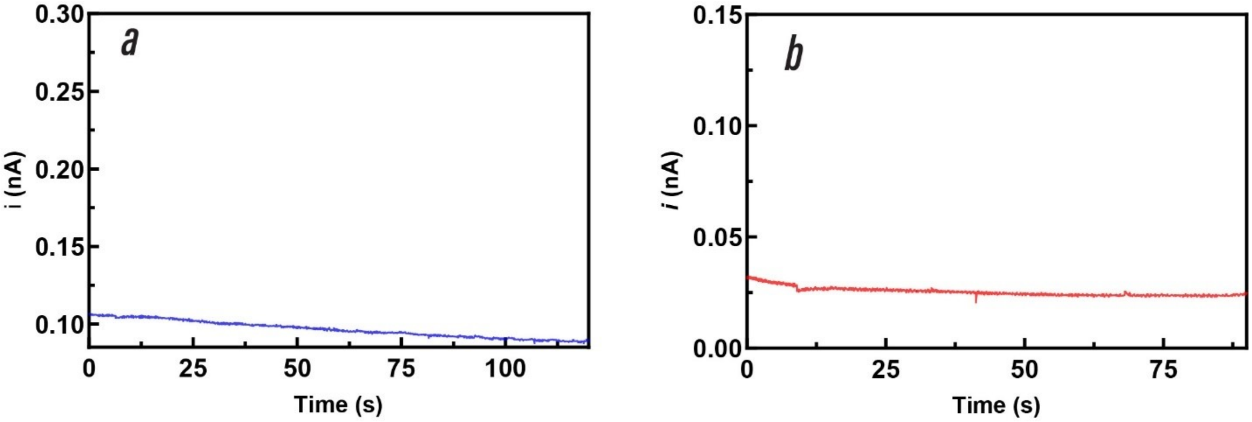

Figure S8. Amperometric i-t curves of a water-in-oil emulsion with **a)** 20 mM $LiClO_4$ in water droplets suspended in 1,2-DCE and **b)** water droplets suspended in 1,2-DCE with 0.1 M TBAP. The applied potential was -0.2 V vs Ag/AgCl using an Au UME as the working electrode. Both figures serve as a control experiment for **Figure 3a** and **3b** in the main manuscript. As expected, no collisions were observed due to the lack of redox molecules in the water droplets. The current response window was selected based on the current window of **Figure 3a** and **3b**.

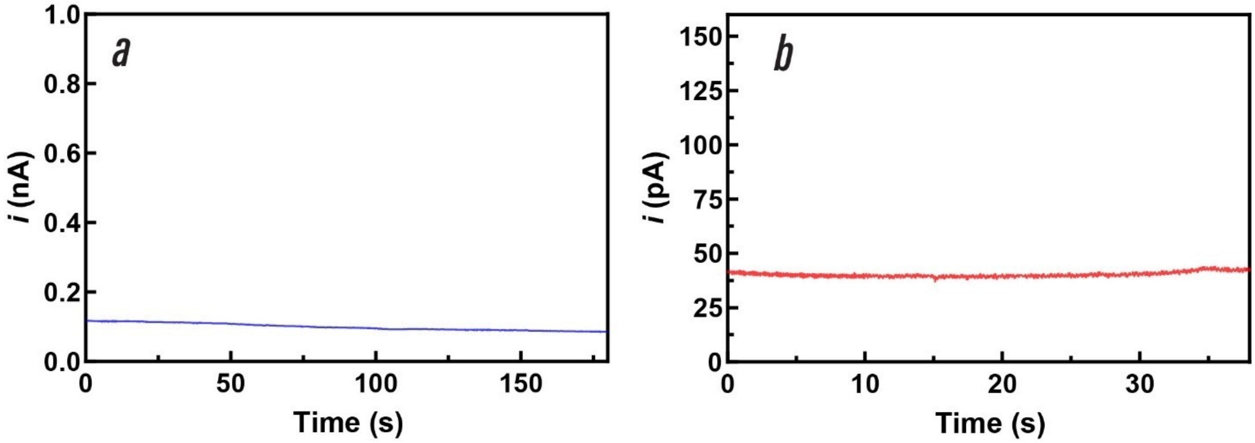

Figure S9. Amperometric i-t curves of a water-in-oil emulsion with **a)** 250 mM $LiClO_4$ in water droplets suspended in 1,2-DCE and **b)** water droplets suspended in 1,2-DCE with 0.1 M TBAP. The applied potential was -0.3 V vs Ag/AgCl using an Au UME as the working electrode. Both figures serve as a control experiment for **Figure 4a** and **4b** in the main manuscript. As expected, no collisions were observed due to the lack of redox molecules in the water droplets. The current response window was selected based on the current window of **Figure 4a** and **4b**.

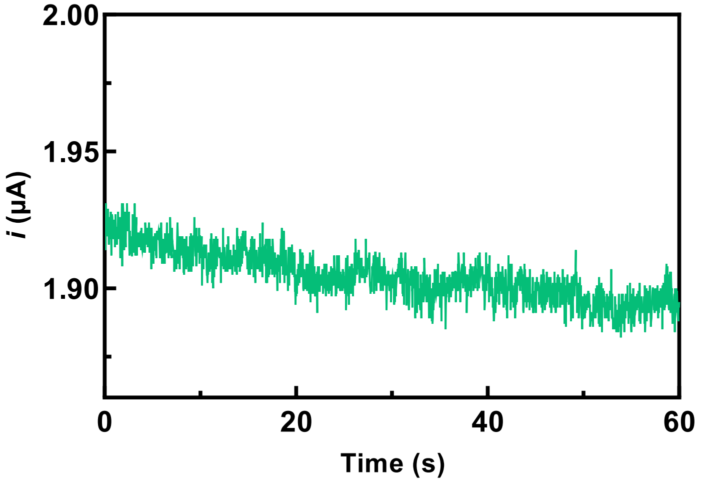

Figure S10. Amperogram of a water-in-oil emulsion of 50 mM hexachloroplatinic acid with 250 mM $LiClO_4$ in water droplets suspended in 1,2-dichloroethane using a glassy carbon macroelectrode as the working electrode. The applied potential was -0.3 V vs Ag/AgCl.

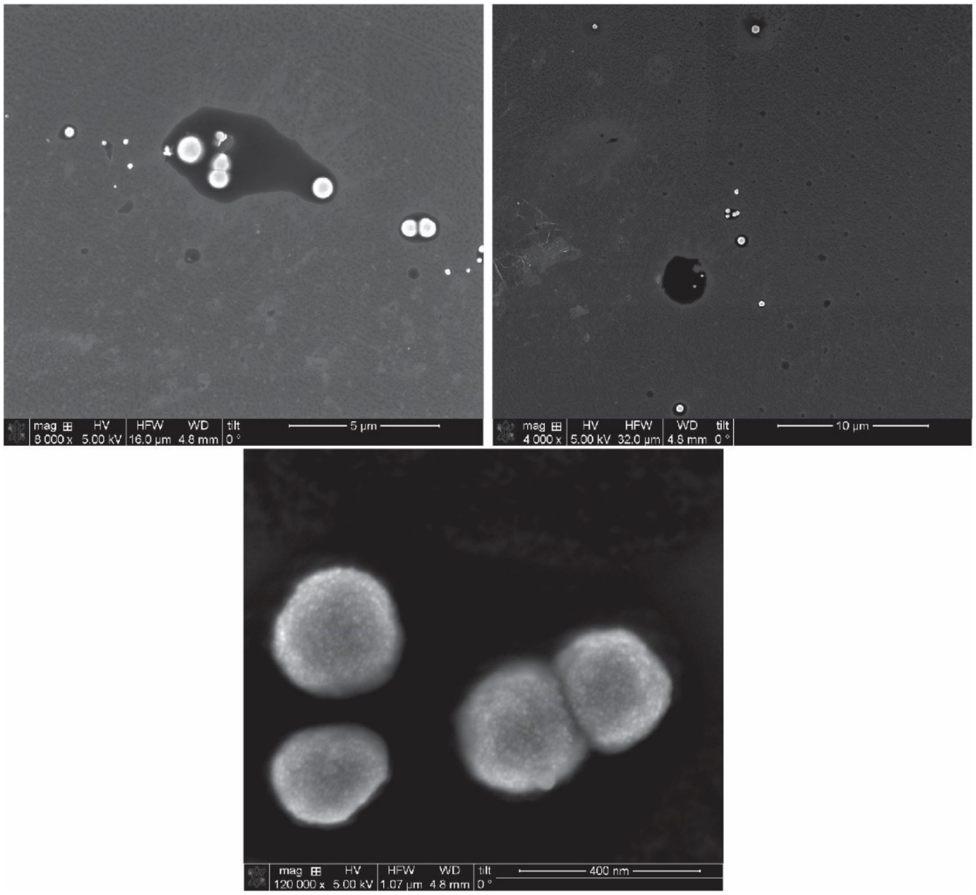

Figure S11. Representative SEM data of Pt particles on a HOPG substrate where it is shown multiple particles in a bigger area. The Pt particles were obtained in the presence of $LiClO_4$ in the water droplets. The emulsion used was 50 mM hexachloroplatinic acid with 250 mM $LiClO_4$ in water droplets suspended in 1,2-DCE. The applied potential was -0.1 V vs Ag/AgCl for 240 seconds.