

## Supporting Information

# Dispersing Pt Atoms onto Nanoporous Gold for High Performance Direct Formic Acid Fuel Cells

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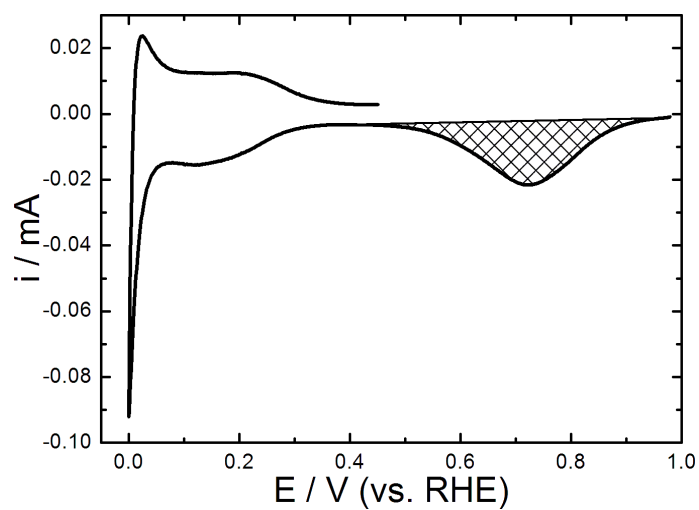
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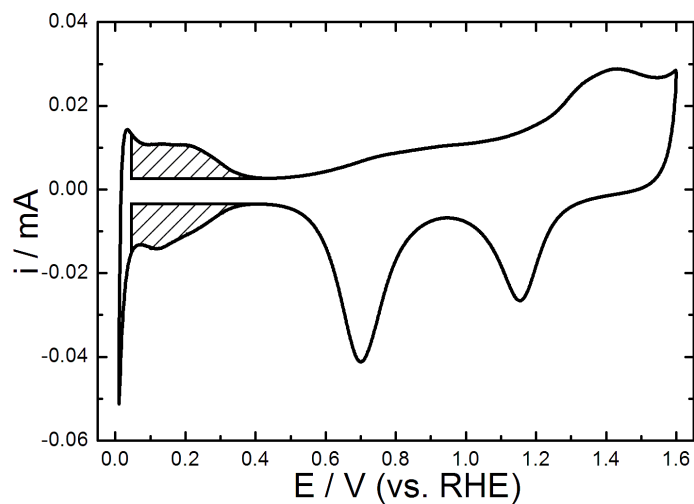
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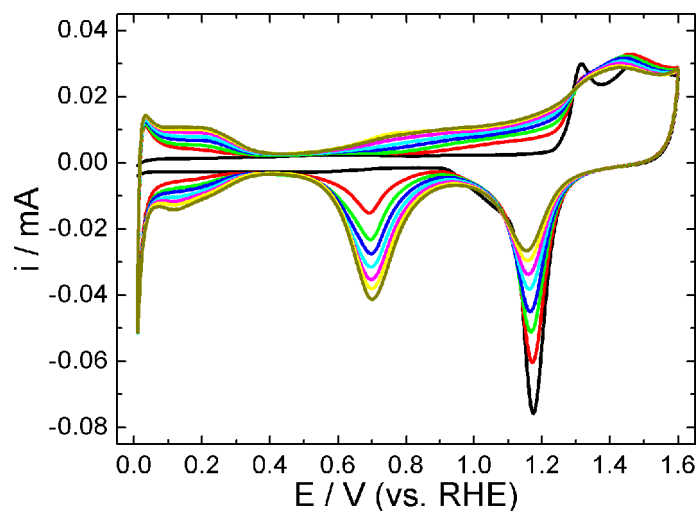
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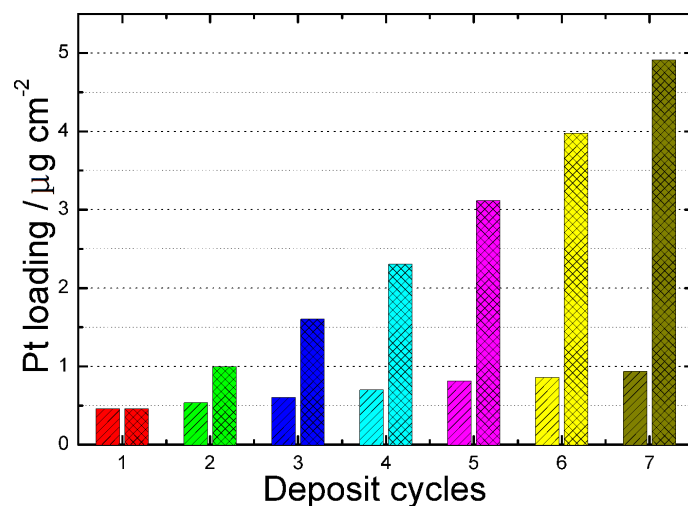
**Figure S1.** CV curve of  $\text{PtCl}_6^{2-}$  electro-reduction onto the ligament surface of NPG leaf. The integrated charges used for Pt loading calculation were illustrated by tilted grids.



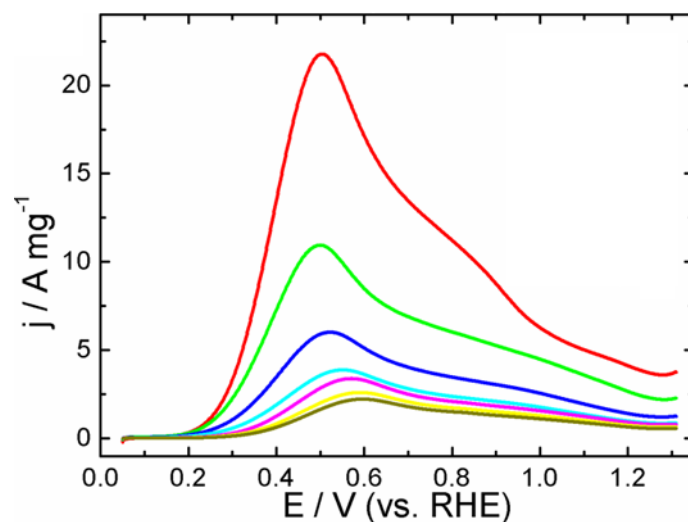
**Figure S2.** Method of H-UPD charge integration. The integrated charges used for ECSA calculation were illustrated by tilted lines.



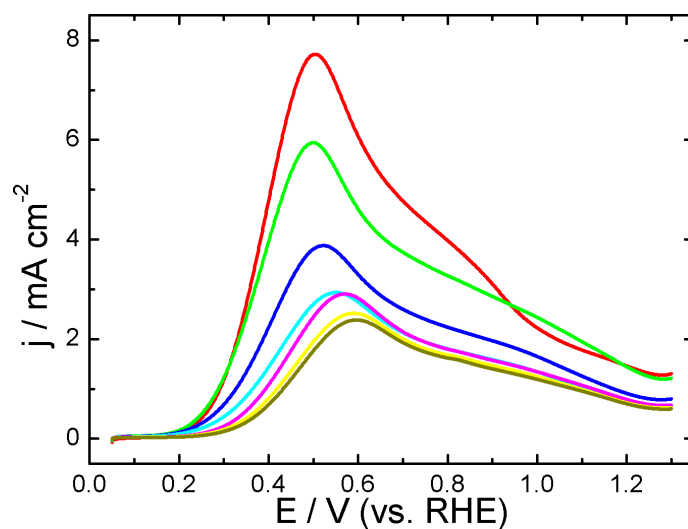
**Figure S3.** Cyclic voltammetry (CV) curves of NPG and NPG-Pt electrodes prepared for 1-7 deposition cycles (black-brown) in 0.1 M  $\text{HClO}_4$  (sweep rate:  $50 \text{ mV s}^{-1}$ ). The ordered changes in hydrogen adsorption/desorption, Pt and Au oxidation/reduction can be clearly seen.



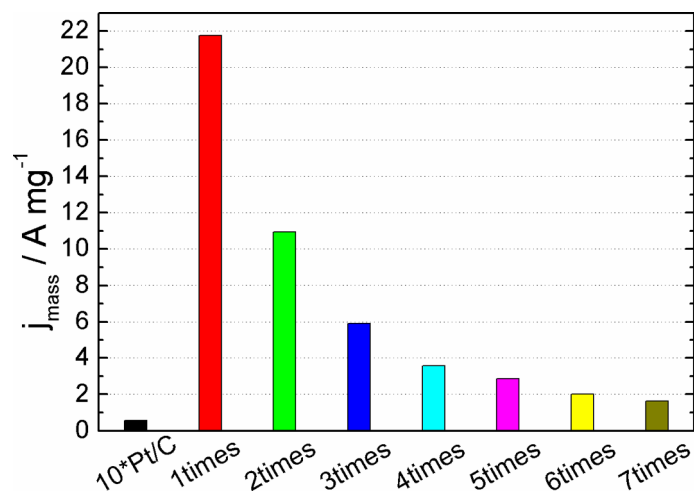
**Figure S4.** Pt loading after specific cycles' deposition using 100 nm NPG membrane as support. Tilted lines: Pt loading at each single deposition cycle; Tilted grids: the total Pt loading.



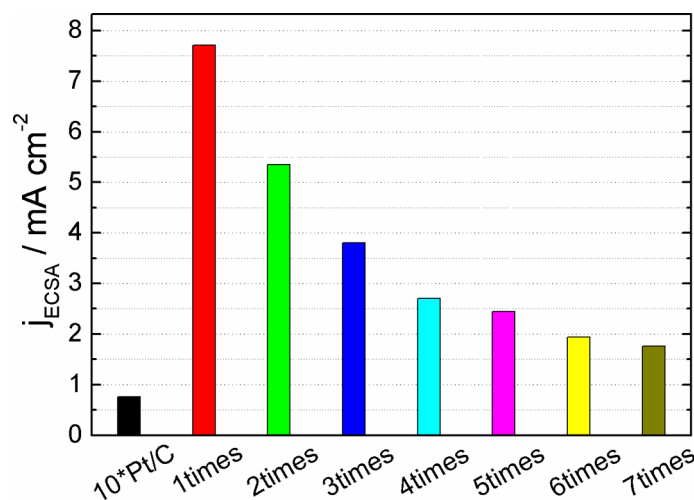
**Figure S5.** Electrocatalytic properties of NPG-Pt<sub>x</sub>. Pt mass specific catalytic activities of NPG-Pt electrodes prepared for 1-7 deposition cycles (red-brown) in 0.1 M HClO<sub>4</sub>+0.05 M HCOOH. Only forward segments were given for clarity. Sweep rate: 50 mV s<sup>-1</sup>.



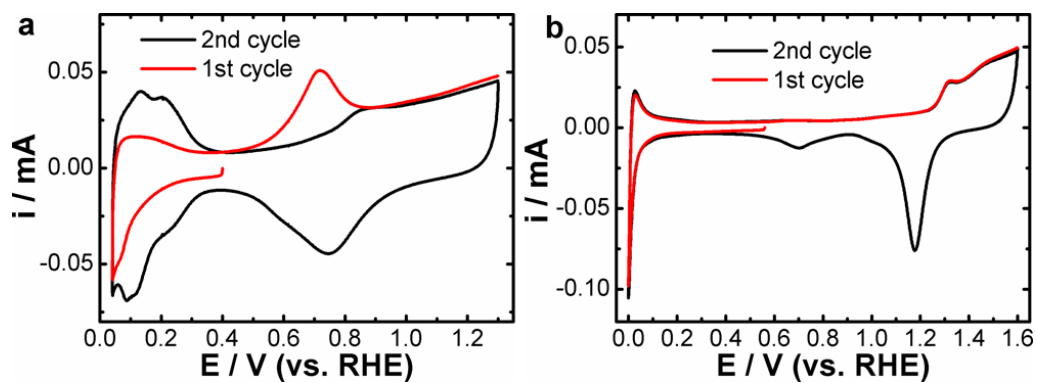
**Figure S6.** Electrocatalytic properties of NPG-Pt<sub>x</sub>. ECSA specific catalytic activities of NPG-Pt electrodes prepared for 1-7 deposition cycles (red-brown) in 0.1 M HClO<sub>4</sub>+0.05 M HCOOH. Only forward segments were given for clarity. Sweep rate: 50 mV s<sup>-1</sup>.



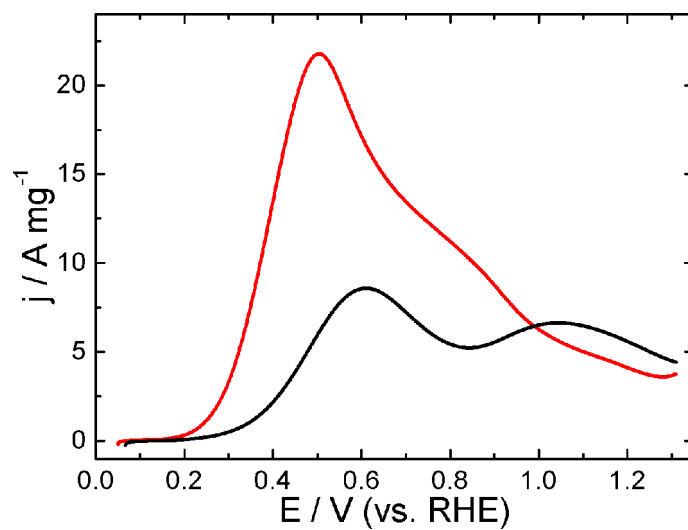
**Figure S7.** Pt mass specific catalytic activities of NPG-Pt electrodes prepared for 1-7 deposition cycles (red-brown) and Pt/C (black, magnified by 10-fold for clarity) at 0.5 V in 0.1 M HClO<sub>4</sub>+0.05 M HCOOH. Sweep rate: 50 mV s<sup>-1</sup>.



**Figure S8.** ECSA specific catalytic activities of NPG-Pt electrodes prepared for 1-7 deposition cycles (red-brown) and Pt/C (black, magnified by 10-fold for clarity) at 0.5 V in 0.1 M HClO<sub>4</sub>+0.05 M HCOOH. Sweep rate: 50 mV s<sup>-1</sup>.



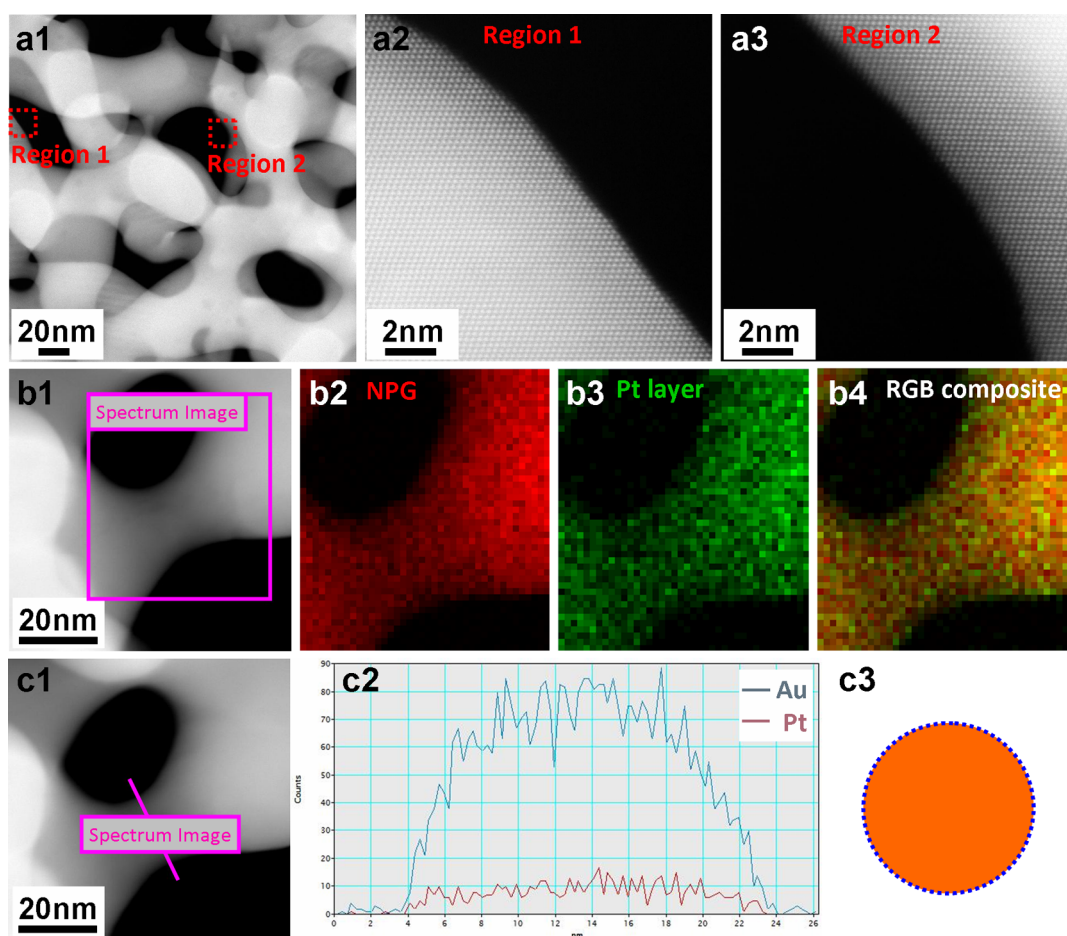
**Figure S9.** CV curves of a, Pt/C and b, NPG-Pt<sub>1</sub> in 0.1 M HClO<sub>4</sub> after dipping in 0.1 M HClO<sub>4</sub>+0.2 mM HCOOH for 5 min.



**Figure S10.** Electrocatalytic property of NPG-Pt<sub>1</sub> (red) compared with Au<sub>bulk</sub>-Pt<sub>1</sub> (black).

Experiments were performed in 0.1 M HClO<sub>4</sub>+0.05 M HCOOH with a sweep rate of 50 mV

s<sup>-1</sup>.



**Figure S11.** HAADF TEM images of NPG-Pt<sub>5</sub> and the corresponding EDS mappings and line scans. a1, HAADF TEM image. a2-a3, HAADF HRTEM images. b1, HAADF TEM image. b2, EDS mapping for Au. b3, EDS mapping for Pt. b4, EDS mapping overlay for Au and Pt. c1, HAADF TEM image. c2, EDS line scans for Au and Pt. c3 is the schematic cross-section view for NPG-Pt<sub>5</sub> ligament.

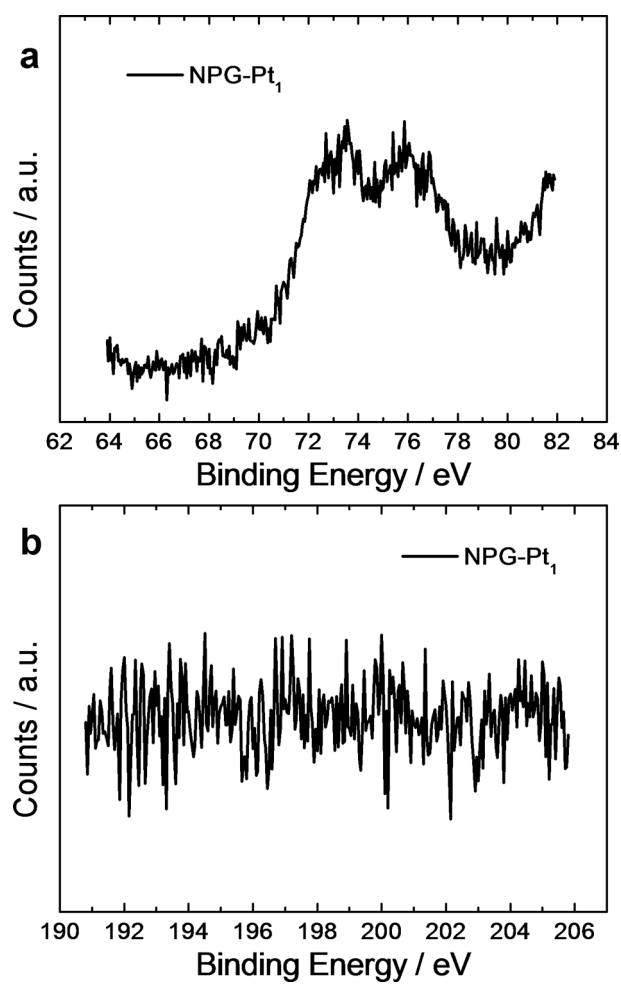
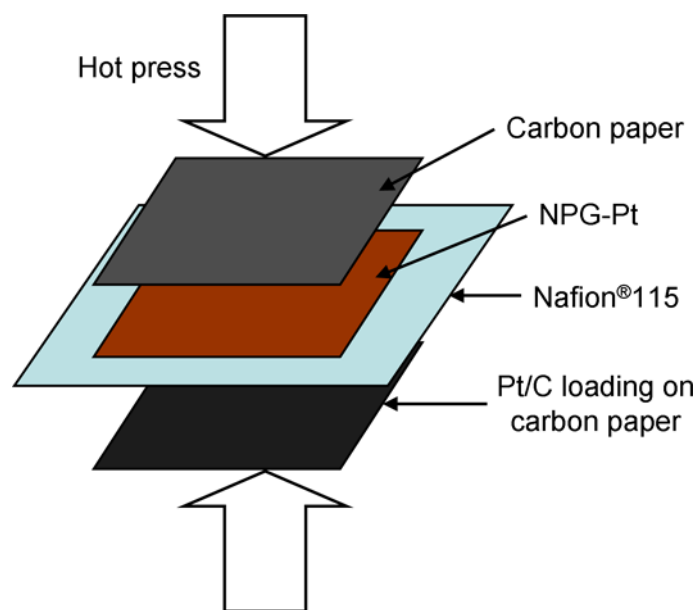
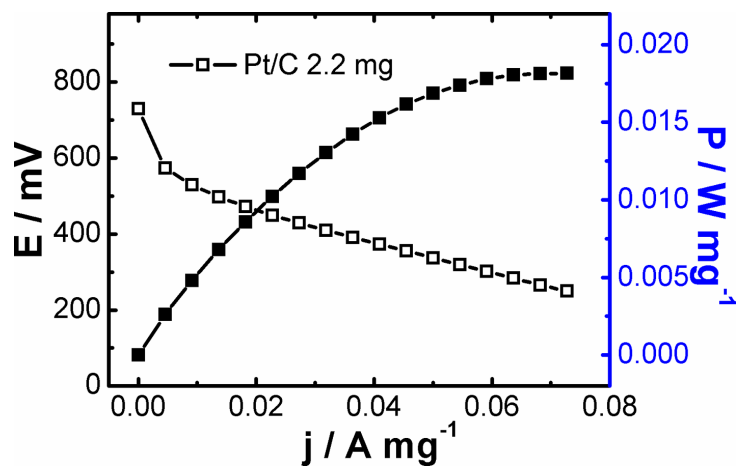


Figure S12. XPS results of NPG-Pt<sub>1</sub> sample.

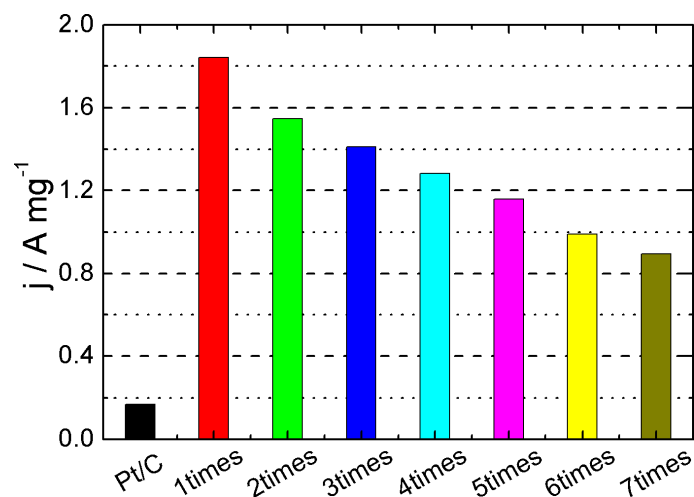




**Figure S13.** Fabrication procedure of MEA.



**Figure S14.** Zoomed in curves for Pt/C 2.2 mg shown in Figure 3c.



**Figure S15.** Electrocatalytic property of NPG-Pt<sub>x</sub> toward ethanol. Pt mass specific peak current densities of NPG-Pt electrodes prepared for 1-7 deposition cycles (red-brown) in 0.1 M HClO<sub>4</sub>+0.1 M CH<sub>3</sub>CH<sub>2</sub>OH. Result on Pt/C was also given for comparison. Sweep rate: 50 mV s<sup>-1</sup>.

#### References to Supporting Information:

S1. Brummer, S. B., Makrides, A. C. Surface oxidation of gold electrodes. *J. Electrochem. Soc.* **111**, 1122-1128 (1964).

S2. Trasatti, S., Petrii, O. A. Real surface area measurements in electrochemistry. *Pure Appl. Chem.* **63**, 711-734 (1991).