Supporting information

An Ultrasensitive Electrochemical Sensor for the Detection of Acetaminophen via a Three-Dimensional Hierarchical Nanoporous Gold Wire Electrode

Lanting Qian, Reem Elmahdy, Antony Raj Thiruppathi, Aicheng Chen*

Electrochemical Technology Centre, Department of Chemistry, University of Guelph, 50 Stone Rd E, Guelph, Ontario N1G,2W1 Canada

* Corresponding Author. E-mail: aicheng@uoguelph.ca, Tel: +1 5198244120 ext. 54764

Electrochemical active surface area (ECSA) and roughness factor (Rf) calculations:

The ECSA of the smooth and nanoporous gold electrodes were calculated by integrating the gold reduction peak at ~0.8 V, which was proportional to the ECSA of the gold electrodes. The Rf was calculated using the formula:

Rf = ECSA / Geometric area

Example:

ECSA for NP100 gold electrode:

Charge (Q) = Area (integrated from the reduction peak) / Scan rate

= 0.00297 / 0.1

= 0.0297 mC, which is 29.67 μC

ECSA = Q / 390μC cm^2

= 29.67 μC / 390μC cm^2

= 0.0759 cm^2

Note: A value of 390 μC cm^{-2} has been suggested for polycrystalline gold. Ref (Pure & Appl. Chem., 1991, 63, 711-734; Chem. Mater. 2007, 19, 3648-3653; J Mater Chem, 2012, 22, 6733).

Geometric area of the gold electrode = 0.0047 cm^2

RF = 0.0759 cm^2 / 0.0047 cm^2

= 16.15

Table S1. Estimation of the geometric area, electrochemically active surface area (ECSA), and roughness factor of the different Au electrodes prepared in the present study.

Electrodes	**Geometric area (cm^2)**	**Charge (μC)**	**ECSA (cm^2)**	**Roughness Factor**
Au	0.0047	1.91	0.0048	1.04
NPAu-50	0.0047	14.26	0.0359	7.63
NPAu-75	0.0047	22.85	0.0586	12.47
NPAu-100	0.0047	29.67	0.0759	16.15
NPAu-150	0.0047	55.16	0.1412	30.06
NPAu-200	0.0047	74.92	0.1905	40.53

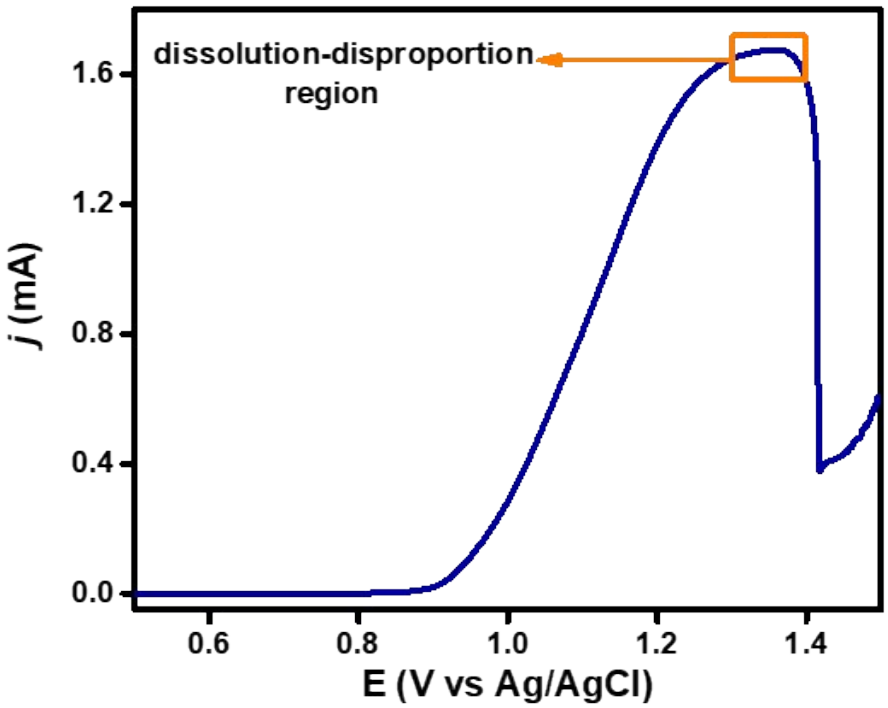

Fig. S1. LSV scan of smooth gold electrodes in 1M KCl solution in the range of 0.5V to 1.5V.

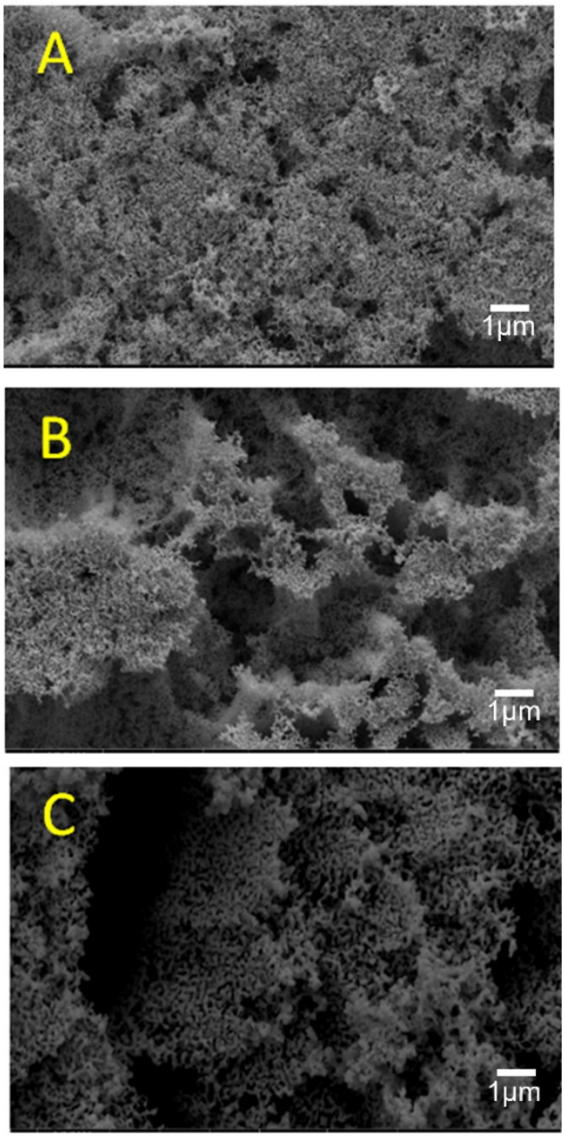

Fig. S2. Scanning electron microscopy (SEM) images of (**A)** NPAu-50 **(B)** NPAu-100 and **(C)** NPAu-150 at 30,000X magnification.

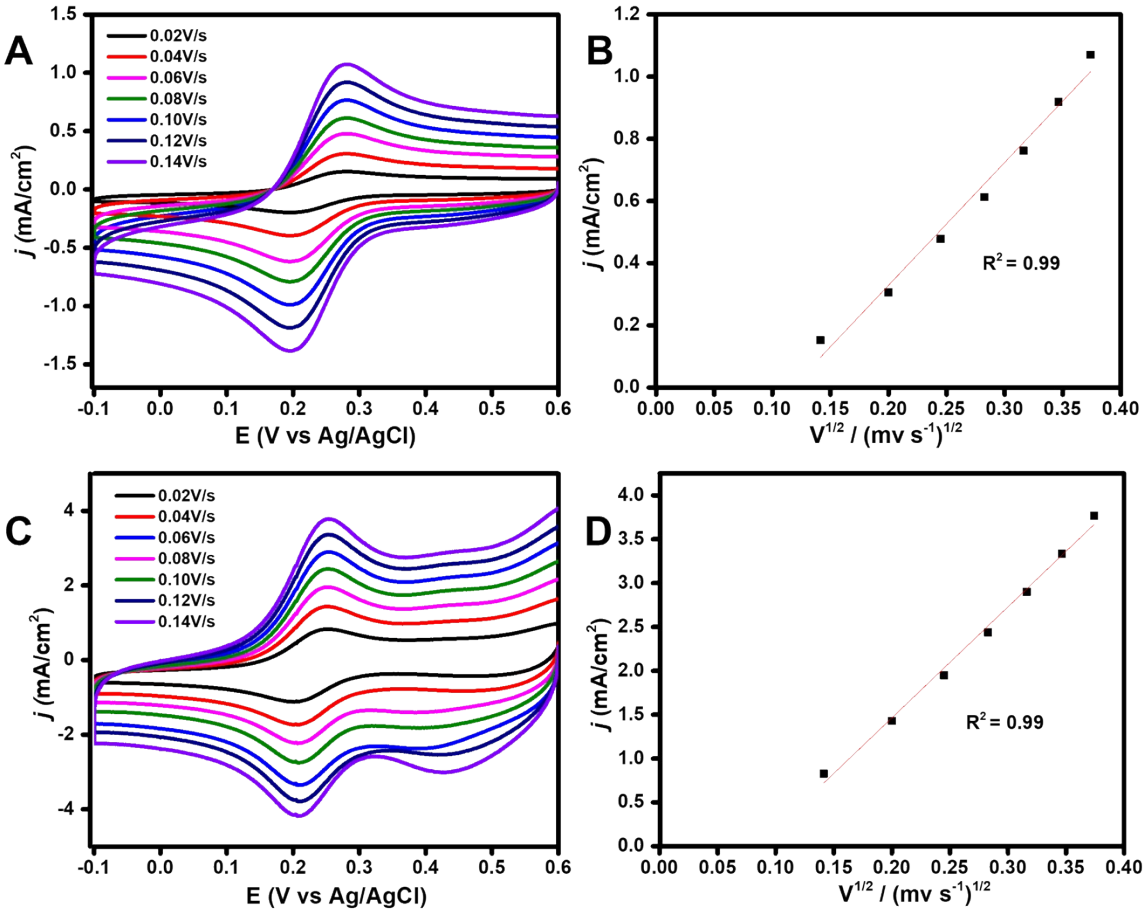

Figure S3. Cyclic voltammogram (CV) curves (left) and their dependence of peak current density as a function of the square root of the scan rate (right) (0.02 V/s to 0.14 V/s): (A) Au; (B) NPAu-50; and (C) NPAu-150 scanned in the KNO_3-ferricyanide media (1mM $K_3[Fe(CN)_6]$ in 0.2 M KNO_3 at different scan rates.

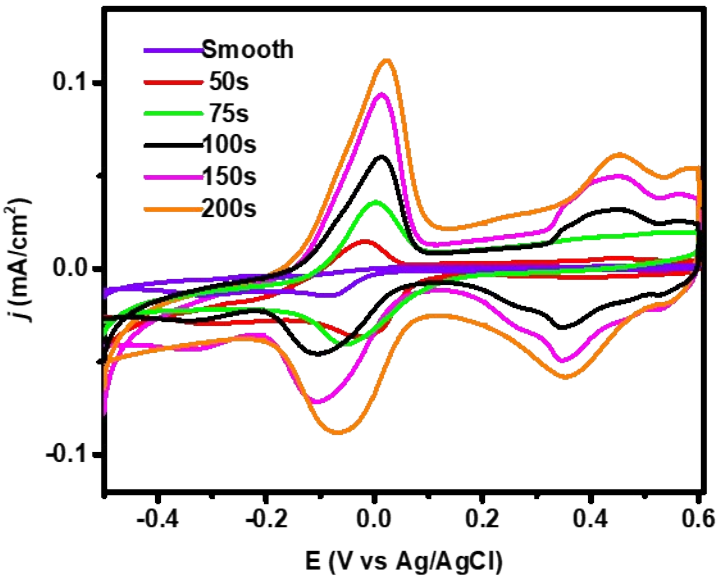

Figure S4. Cyclic voltammograms of Au, NPAu-50, NPAu-75, NPAu-100, NPAu-150 and NPAu-200 in a 0.01 M $KClO_4$ solution containing 50 μM $Pb(NO_3)_2$ at 20 mV s^{-1}.

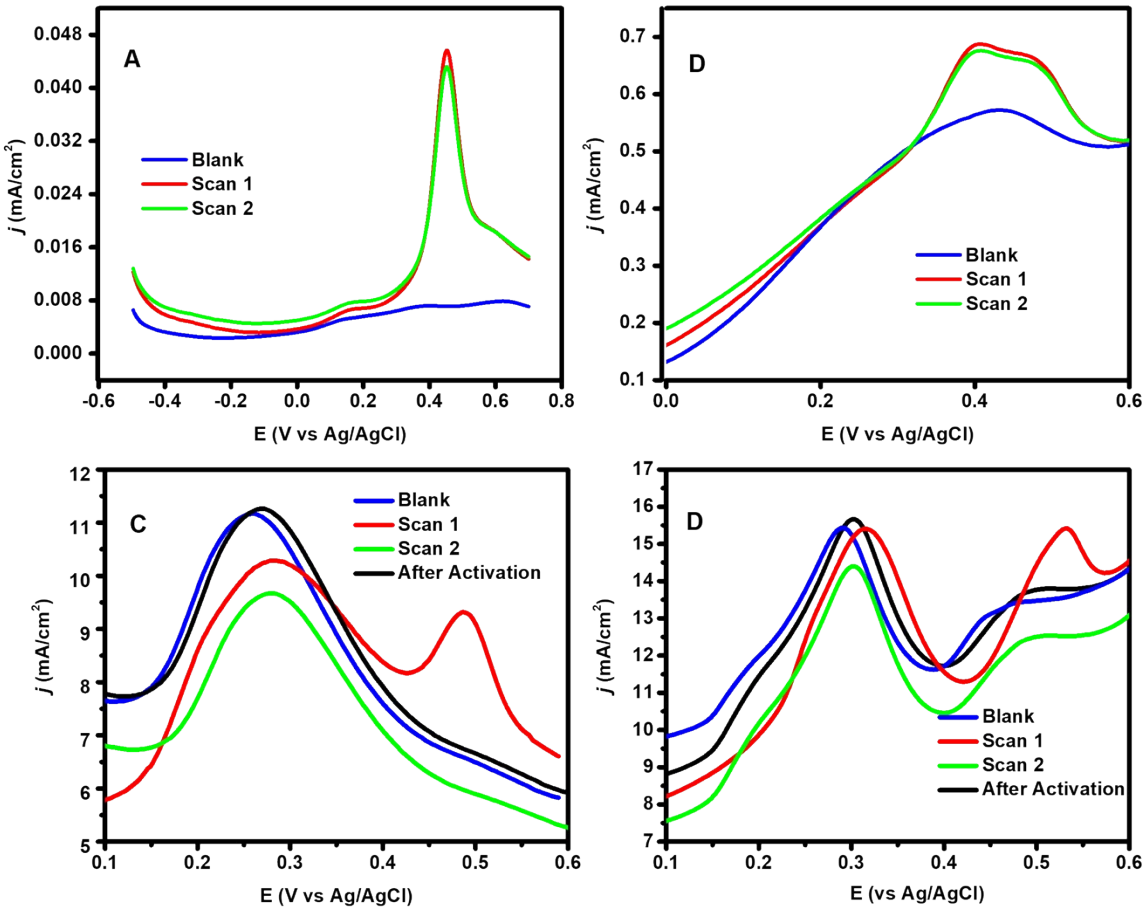

Figure S5. Square wave voltammogram (SWV) curves of (A) smooth Au and (B) NPAu-50 and NPAu-150 (C) and NPAu-200 (D) recorded in a 0.1M PBS solution in the presence of acetaminophen.

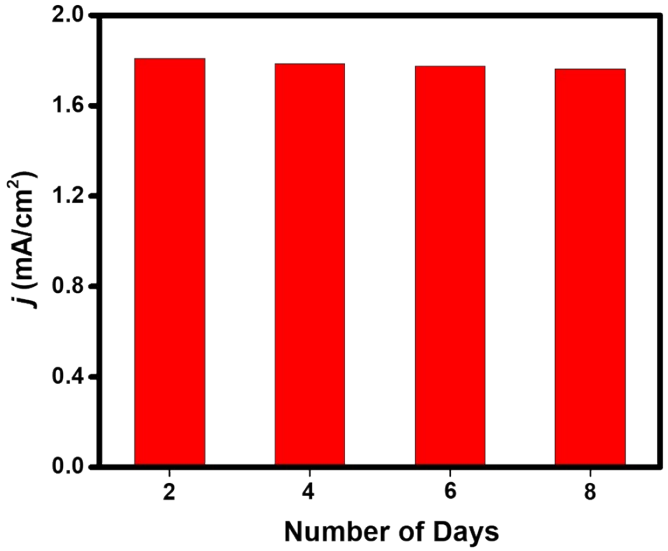

Figure S6. SWV wave responses of NPAu-100 measured in 0.1 M PBS containing 30 nM of acetaminophen tested over a span of 8 days.

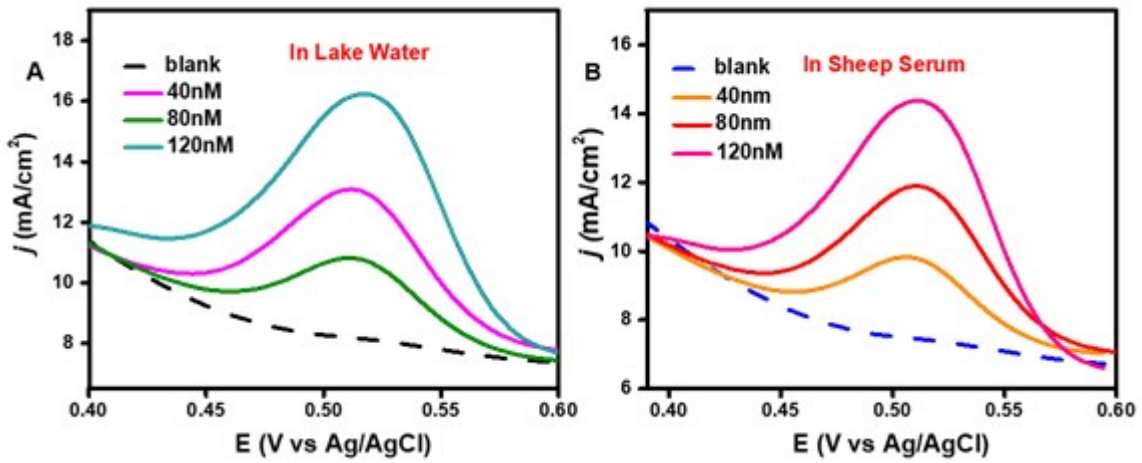

Figure S7. Square wave voltammogram (SWV) curves of acetaminophen detection using NPAu-100 electrode recorded in (A) lake water and (B) sheep serum.