

Supporting Information

Exploring Nanoparticle Porosity Using Nano-Impacts: Platinum Nanoparticle Aggregates

Xue Jiao,^a Stanislav V. Sokolov,^a Eden E. L. Tanner,^a Neil P. Young^b and Richard G. Compton,^{*a}

Experimental

4-Nitrobenzenethiol (NTP) (80%, O₂NC₆H₄SH), perchloric acid (70%, HClO₄) and sodium perchlorate monohydrate (98%, NaClO₄ · H₂O) were obtained from Sigma-Aldrich, Dorset, U.K. Citrate-capped platinum nanoparticles (PtNPs) were provided by NanoComposix, San Diego, CA, U.S.A with a reported diameter 50 nm and concentration of 3.3×10^{13} particles L⁻¹.¹ All solutions were prepared with ultrapure water from Millipore with a resistivity of not less than 18.2 MΩ cm at 298 K.

TEM (JEOL JEM-3000F FEGTEM, 300 kV accelerating voltage) was performed to determine the size of PtNPs. Samples were prepared by depositing a drop of the stock PtNP suspension (3.3×10^{13} particles L⁻¹) onto holey carbon grids (Agar Scientific, Stansted, U.K), followed by drying in air prior to imaging. ImageJ software² (National Institutes of Health, U.S) was used to analyse the TEM images.

PtNPs were tagged by NTP via mixing a PtNP suspension (3.3×10^{13} particles L⁻¹, directly from the manufacturer) with 0.5 mM NTP aqueous solution with a volume ratio of 1:1 for 1 to 30 hr. The excess NTP molecules were removed by centrifuging and the tagged nanoparticles were washed three times with water.

A three electrode system in a Faraday cage was employed for all electrochemical experiments, with a μAutolab III (Metrohm Autolab B.V., Utrecht, The Netherlands) or an in-house potentiostat.³ The working electrode was a glassy carbon macrodisk (3 mm diameter; BASi, West Lafayette, IN, U.S.A) or a carbon fibre microdisc (33 μm diameter; BASi, West Lafayette, IN, U.S.A) electrode. Both electrodes were polished with alumina powders (Buehler, Lake Bluff, IL, U.S.A) in a size sequence: 1.0 μm, 0.3 μm and 0.05 μm. The reference electrode was a saturated calomel electrode (SCE) [Hg/Hg₂Cl₂, saturated KCl] (+ 0.241 V vs standard hydrogen electrode, SHE; BASi, West Lafayette, IN, U.S.A) or a silver/silver chloride electrode [Ag/AgCl, 1.0 M KCl] (+ 0.235 V vs SHE; Cypress Systems, Lawrence, KS, U.S.A). The counter electrode was a graphite rod (6 mm diameter; Sigma-Aldrich, Dorset, U.K) or a platinum foil (Goodfellow, Cambridge, U.K). All experiments were conducted under a nitrogen atmosphere. All electrochemical measurements were thermostatted at 25 ± 0.5 °C.

In the experimental data reported in the manuscript, potentials are quoted on the SCE or the Ag/AgCl (1.0 M KCl) scales.

The glassy carbon macroelectrode was modified first by adsorption of molecular NTP directly on the electrode surface, and second by drop casting NTP-tagged PtNPs onto the surface. For direct adsorption, the electrode was immersed in a NTP solution (0.5 mM) for 1 h, then rinsed with water and sonicated before experiments to remove the excess molecules from the electrode surface. For modification with previously modified PtNPs, a NTP-tagged PtNP suspension (3 μL) was drop casted onto the electrode surface, which was subsequently allowed to dry under flowing nitrogen prior to experimentation.

Potentiostatic control and impact current measurement were achieved through an in-house built low noise potentiostat.³ A NI USB-6003 data acquisition (DAQ) device (National Instruments, Austin, TX, U.S.A) was connected to a computer interface via USB for analogue-digital conversion. Python 2.7 was employed to write a script to control the DAQ device, which was run through the IDE Canopy (Enthought, Austin, TX, U.S.A). Currents were measured at the working electrode (running to ground) by a low-noise current amplifier LCA-4K-1G (FEMTO, Messtechnik GmbH, Germany), within a limited output bandwidth of two cascaded passive RC-filters (100 Hz). The

DAQ device oversampled the outgoing signal and converted it from analogue to digital at a stream rate of 4 kHz. To allow potentiostatic control, a highly stabilized (1 kHz bandwidth) classic adder potentiostat⁴ was used. Importantly, for the reference buffer a high quality operational amplifier, LMC6001 (Farnell, Leeds, U.K) with an ultra-low-input bias (25 fA) was selected; and for potential control at the counter electrode a high quality low-noise operational amplifier, AD797 (Farnell, Leeds, U.K) was adopted.

References

- 1 NanoComposix, 50 nm Citrate NanoXact™ Platinum Nanoparticles (Certificate of Analysis Examples): [http://50.87.149.212/ Specification%20Sheets/Platinum%20Spec%20Sheets/PT50-NX-CIT-MGM1553.pdf?2581746](http://50.87.149.212/Specification%20Sheets/Platinum%20Spec%20Sheets/PT50-NX-CIT-MGM1553.pdf?2581746).
- 2 J. M. M. Pérez and J. Pascau, *Image Processing with ImageJ*, Packt Publishing, 2013.
- 3 C. Batchelor-McAuley, J. Ellison, K. Tschulik, P. L. Hurst, R. Boldt and R. G. Compton, *Analyst*, 2015, **140**, 5048-5054.
- 4 R. M. Souto, *Electroanalysis*, 1994, **6**, 531-542.