Journal Name

Dynamic Article Links ▶

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Supplimentary Material for Selective Localisation of Platinum Nanoparticles at Gold Nanocavity Arrays

Colm T. Mallon, Elaine Spain, Tia E. Keyes* and Robert J. Forster*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Full experimental details. Polystyrene spheres (600 nm diameter) were purchased from Duke Scientific. Cysteamine (98%) were purchased from Sigma. Electrochemistry was performed in a standard three electrode cell, using a platinum mesh counter electrode and a Ag/AgCl (sat. KCl) reference electrode at 23 ± 2 ^{0}C. All potentials are quoted with respect to this reference. Raman spectroscopy was carried out on a Horiba Jobin Yvon HR800UV microscope using 633 nm excitation line, focused through a 100x objective lens. The acquisition time was 15 seconds and 3 acquisitions were performed to acquire a spectrum. Scanning electron microscopy was performed using a Hitachi S-3000N scanning electron microscope.

Nano-cavity preparation. Nano-cavity arrays were fabricated in a method similar to that described by Bartlett and co-workers.[1] Gold (400 nm) coated silicon wafers were cleaned in piranha solution before immersion in a solution of 1 mM cysteamine in ethanol overnight. The adsorption of cysteamine results in a more hydrophilic surface. The slides were then placed upright in an aqueous solution containing 0.01% W/W 820 nm polystyrene spheres. Evaporation of the solvent at ambient temperature creates a 2-dimentional array of spheres on the gold surface as the solution meniscus slowly moves down the slide. Electrochemical deposition through this template was achieved using a commercially available gold salt solution (Technic Inc, TG-25 RTU) at a potential of -0.95 V. Deposition continued until sufficient charge had been passed to create a 500 nm thick gold film. Monolayers of 11-undecanonic acid were formed on the top surface of the arrays by immersion of the slide for 12-14 hours in 1 mM solutions of COOH-C_{11}-SH in ethanol.

Nano-particle preparation. A gold disk electrode was washed with ethanol and then placed in a 1 mM solution of dodecanethiol in ethanol and monolayer self-assembly allowed to proceed for 7 hours. After the formation of the monolayer, the substrate was rinsed 4 to 5 times with ethanol and dried under a N_2 stream. Platinum nanoparticles, PtNPs, were electrodeposited from 1 mM hydrogen hexachlorideplatinate (IV) hydrate, H_2PtCl_6, in 0.5 M H_2SO_4 using the defects within the self-assembled monolayer as templates. A 20 ms nucleation pulse was applied to the gold disc electrode at a potential of -1600 mV followed by a growth pulse

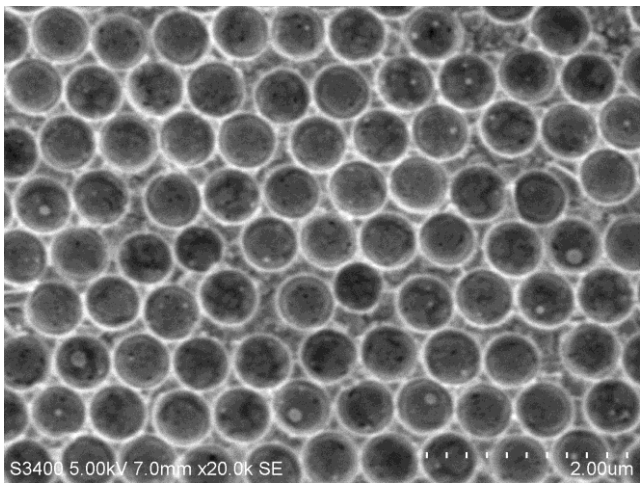

Fig. S1 Scanning electron micrographs of gold nano-cavity array with selectively localised commercially available platinum particles within the cavities.

at – 200 mV for 60 s. Following deposition, the electrode was removed from the electrolyte, rinsed with Milli-Q water and dried under a stream of high purity argon. Platinum nanoparticles, PtNPs, were electrodeposited on the nucleation sites within the self-assembled monolayer as templates. The PtNPs were functionalized with probe oligo (5' thiolate) by immersing the nanoparticle functionalized electrode in a 10 µM solution of the probe DNA strand dissolved in 1 M NaCl-TE buffer for 2 hours. The modified electrodes were then washed with deionized water for 15 s to remove loosely bound oligo and immersed in 0.01 M H_2SO_4. The oligo functionalized platinum nanoparticles were then desorbed by applying a current of +0.01 A (reductive) for 120 seconds.

Hybridisation conditions. *Step 1: Monolayer of Capture Strand DNA.* A monolayer of capture strand DNA was prepared on a freshly polished and electrochemically cleaned gold disk electrode by immersing it in a 10 µM solution of the capture strand DNA dissolved in 1 M NaCl-TE Buffer. After 5 hours, the electrode was rinsed with deionized water for 15 s to remove loosely bound oligo.
Step B: Hybridization of target oligo to the capture surface. Hybridization of the target at concentrations between 10 pM and 1 µM to the immobilized capture strand was performed at

37°C in 1 M NaCl-TE Buffer for 90 min. Following hybridization, the modified electrode was rinsed thoroughly with buffer.

Step 3: Probe Hybridization. The nanoparticle labelled probe DNA was then hybridized to the complementary section of the target not used for binding to the capture strand for 2 hours at 37 °C in 1 M NaCl-TE Buffer. Finally, before quantitation, it was thoroughly washed with deionized water.

Commerical nano-particle binding. Platinum nanoparticles (diameter 50-70 nm) for uniform functionalization with probe strand DNA were purchased from Particular GmbH.