

Electronic Supplementary Information (ESI)

Materials

Nafion[®] 117 solution (5% w/v mixture of low molecular weight alcohols), Pd(NO₃)₂ in 10% wt solution in 10% wt HNO₃, NaBH₄, NaCl were purchased from Sigma-Aldrich. All aqueous solutions were prepared from Milli-Q reagent grade water (Millipore Corp.) with a resistivity $\geq 18 \text{ M}\Omega \text{ cm}$ at 25 °C.

Film Fabrication Procedure

Nafion LS films were fabricated using the procedure of Bertocello et al.¹ Briefly, a stock solution of Nafion was prepared by dilution of the commercial solution with methanol to obtain a final concentration of 0.85 mg mL⁻¹. Nafion Langmuir monolayers were formed using a Langmuir trough (Nima Instruments, Coventry, UK). The surface pressure was measured by means of a Wilhemy balance with an accuracy of $\pm 0.1 \text{ mN m}^{-1}$. The volume of Nafion added to the subphase varied between 200-300 μL . A period of two minutes was allowed to elapse before compression of the floating films. Based on our previous work¹, the conditions used for the fabrication of Nafion LS films were surface pressure of 20 mN m⁻¹ and 0.1 M NaCl as subphase. Nafion LS films were deposited on indium-tin oxide glass plates (ITO, Delta Technologies Ltd. (USA) with resistivity, $R_s \leq 10 \text{ }\Omega/\text{square}$. These substrates were cleaned by sonication in isopropanol, acetone and chloroform for at least 5 minutes before use. The pristine Nafion LS films were then dipped in a solution containing 5 mM Pd(NO₃)₂ for 30 minutes. This allowed the electrostatic incorporation of Pd(II) ions into negatively charged Nafion films. Pd²⁺ ions incorporated within the Nafion films were reduced to Pd⁰ by exposure to a freshly

prepared solution containing 10 mM NaBH₄ in water for 2 minutes. After each step, the samples were gently washed with water.

Methods

For TEM analysis, Nafion LS films were deposited onto bespoke ion-beam thinned silicon substrates (3 mm diameter) prepared in-house, while for AFM analysis the substrates used for deposition were 300 nm oxidized silicon substrates (IDB Technologies Ltd., UK). Bespoke TEM samples were made by ion-beam milling of thinned silicon samples. The centre of square pieces (~ 3 mm) of a thin (200 μm) Si wafer was thinned down to ~ 50 μm using a Model 515 South Bay Technology Precision Dimpling Instrument, and then ion milled to electron transparency by a Model 691 Gatan Precision Ion Polishing System.

TEM images were obtained using a JEOL 2000fx TEM. TM-AFM images were taken in air using Si tips (Lot-Oriel, UK) with a Digital Instruments Multimode AFM and Nanoscope IIIa controller (Veeco). Cyclic voltammetry (CV) and linear sweep (LSV) measurements were performed using an electrochemical analyzer (CH Instruments, model CHI730A). A typical three electrode configuration was used, where the working electrode was an ITO coated glass plate on which a Nafion/Pd LS film had been deposited. A platinum gauze was used as the counter electrode and an Ag wire served as a quasi-reference electrode. The area of the working electrode was typically between 0.5 - 0.6 cm² and kept constant for each set of CV measurements.

[1] P. Bertonecello, M.K. Ram, A. Notargiacomo, P. Ugo and C. Nicolini, *Phys.Chem.Chem.Phys.*, 2002, **4**, 4036