Formation and evaluation of electrochemically-active ultra-thin palladium–Nafion nanocomposite films†

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A simple method for producing electrochemically-active palladium nanoparticles within ultra-thin Nafion films is described.

The synthesis of nanometre-sized particles is of tremendous interest in different fields of chemistry and allied disciplines.[1] For catalytic applications, metal particles usually exhibit size-dependent reactivity, with smaller particles typically more active.[2] However, the synthesis of naked metal nanoparticles remains challenging, with the aggregation and sintering providing an obstacle in practical applications.[3] To overcome such problems, metal nanoparticles are often synthesized or immobilized on solid supports (zeolites, polymers)[4,5] or stabilized by capping with small organic ligands or polymers, in order to reduce agglomeration processes.[6] The dispersion of nanoparticles in polymer films is attractive, as it may enhance the processibility and allows a wider variety of surfaces and interfaces to be functionalised with nanoparticles.

Nafion is a perfluorinated ionomeric cation exchanger, well known for its thermal, chemical and electrochemical stability.[7] As a membrane, Nafion is used extensively as an electrolyte in methanol and hydrogen fuel cells.[8] Traditionally, Nafion films have been rather thick (> 1 μm), but recent developments have seen the use of the Langmuir–Schaefer (LS) technique[9] to produce Nafion films on solid supports on the nanometre and mesoporous scale. Such films have proved useful for incorporating different species such as metal oxides[10a] and redox mediators.[10b–d]

Pd nanoparticles are attracting considerable interest for hydrogen-related applications, such as hydrogenation, hydrogen evolution and hydrogen oxidation.[11] Several strategies have recently emerged for the preparation of nanostructured Pd films, including template electrodeposition at solid/liquid and liquid/liquid interfaces.[12] In this paper, we describe a simple strategy for fabricating relatively monodisperse palladium nanoparticles embedded in a Nafion ultra-thin polymeric film. The method takes advantage of the fact that Nafion films have a structure in which the hydrophilic sulfonated end groups aggregate in domains located within the hydrophobic matrix constituted by the fluorocarbon backbone.[7b,13] The hydrophilic domains can be loaded with Pd^{2+} which, upon reduction, facilitates the formation of small particles in these nanocompartments.

A schematic of the procedure used is illustrated in Fig. 1. Nafion LS films were deposited on indium tin oxide (ITO) electrodes using a well established procedure.[9,10c] Films were formed by depositing between 10 and 50 layers, corresponding to film thicknesses ranging from 15 to 75 nm, (a) in Fig. 1. Nafion LS films produced in this way were subsequently dipped for 30 min in a solution containing palladium nitrate (b). After removing the electrode from this loading solution, Pd^{2+} ions incorporated in the films were reduced to Pd using $NaBH_4$ as the reducing agent (c).

The morphology of the Pd produced in this way was investigated by transmission electron microscopy (TEM), with typical results for a 20-layer Nafion LS film shown in Fig. 2. This image shows clearly that Pd nanoparticles are formed and that although there is some clustering, the particles are discrete. The diameter of Pd nanoparticles measured by TEM was in the range 5 ± 1 nm.

Fig. 3 shows typical tapping mode AFM images of a 10-layer Nafion LS film before (a) and after (b) reduction of Pd^{2+} by $NaBH_4$: a relatively smooth and uniform film is evident for the pristine Nafion film, while features with a characteristic size of 20–30 nm are visible after treatment with $NaBH_4$, which is reasonably consistent with the scale of the nanoparticle clustering observed by TEM. This characteristic topography was further confirmed by analysis of the phase images of the AFM data (figure not shown).

Cyclic voltammetry (CV) was used to investigate whether the Pd nanoparticles formed were in electrical contact with the underlying ITO electrode. Fig. 4 reports a typical CV of a 40-layer nanocomposite film in 0.1 M KNO_3 at pH 3.

The CV shows a small broad oxidation wave at about 0.3 V and a sharp reduction peak at about −0.05 V (*vs.* Ag quasi-reference electrode, QRE). These peaks are attributed to the formation of palladium oxide (forward anodic scan), while on the return cathodic sweep, the surface oxide is reduced giving rise to a well-defined cathodic stripping peak.[12a] These results suggest that although Pd is embedded in the Nafion film, the surface activity is similar to that of naked Pd.

The electrochemically active surface area of Pd nanoparticles was estimated by integrating the charge passed in the Pd oxide stripping reaction at low scan rate (10 mV s^{-1}, figure not shown),

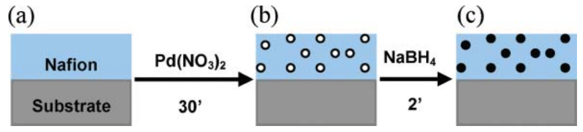

Fig. 1 Schematic of the fabrication of palladium nanoparticles within a Nafion LS film.

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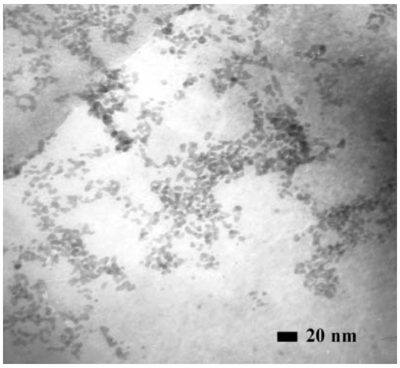

Fig. 2 TEM image of palladium nanoparticles in a 20-layer Nafion LS film.

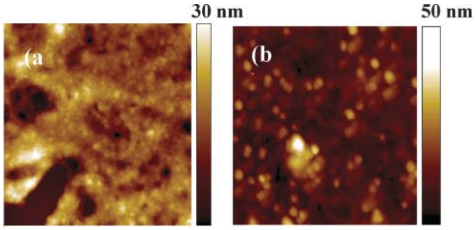

Fig. 3 AFM topography images of a 10-layer Nafion LS film before (a) and after (b) formation of Pd nanoparticles. The scale is 1 μm × 1 μm.

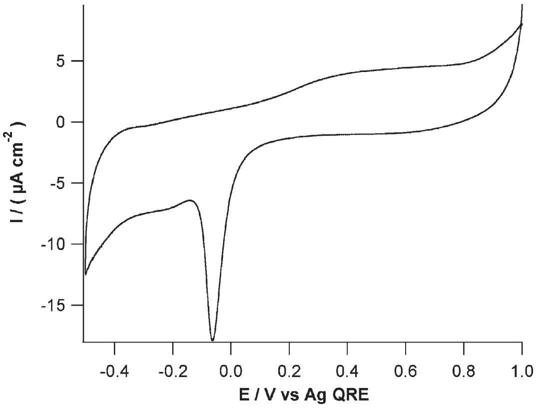

Fig. 4 CV of a 40-layer Pd–Nafion LS film in 0.1 M KNO_3, pH 3 (HNO_3), scan rate 50 mV s^{-1}.

following the procedure of Rand and using a conversion factor of 424 μC cm^{-2}.[14] For the data in Fig. 4, the surface area was 6.1×10^{-2} cm^2 Pd/cm^2 ITO. However, even though the effective surface area of Pd is only 6% of the geometric area of the ITO electrode, the modified electrode shows regular macroscopic behaviour in voltammetric experiments (*vide infra*). Considering 5 nm as the average diameter of the Pd nanoparticles, as estimated by TEM, the number density of nanoparticles in Nafion is approximately 1.3×10^{16} cm^{-3}. Since each particle, on average, comprises 4.4×10^3 atoms, the Pd^{2+} concentration in the film that is converted to Pd is ~ 0.1 mol dm^{-3}. This value is typical of the concentration of cationic redox mediators,[10c,d] suggesting that much of the Pd^{2+} is converted to Pd nanoparticles that are electroactive. Studies on other thickness films suggested a close correlation of the magnitude of the oxide stripping peak with film thickness. The activity of the ultra-thin composite films was further considered through studies of hydrogen oxidation. Palladium is receiving considerable attention in fuel cell technologies due to low cost, greater availability compared to platinum and its ability to absorb large quantities of hydrogen.[11] Fig. 5 reports typical CVs for various modified ITO electrodes, specifically functionalised with a pristine 40-layer Nafion film (dotted line) and a 40-layer Pd–Nafion film, before (dashed line) and after (solid line) purging an aqueous 0.1 M KNO_3 solution with H_2.

The CV for Nafion alone on ITO after purging with H_2 reveals that the electrode is essentially inert with respect to the oxidation of H_2 over the potential range shown. The CV of the 40-layer Pd–Nafion film before purging with H_2 shows the presence of the typical peak for the cathodic stripping of Pd oxide at about −0.22 V (*vs.* Ag QRE). Note that the potential of the cathodic peak is shifted cathodically by about 0.2 V compared to the peak evidenced in Fig. 4, because the pH of the solution was *ca.* 6, causing the stripping of palladium oxide to occur at a more negative potential. A dramatic change in the response was observed when the solution was purged with H_2: the CV reveals an oxidation peak at about 0.1 V (*vs.* Ag QRE), characteristic of the oxidation of hydrogen.[15] Note that the peak current density value of 30 μA cm^{-2} is about half that expected for a diffusion-limited reaction, assuming 10^{-3} mol dm^{-3} as the concentration of H_2 after saturation in aqueous solution and a diffusion coefficient of 5×10^{-5} cm^2 s^{-1}.[16] At potentials beyond the peak value, the current magnitude decreases significantly and then, surprisingly, increases during the reverse scan. This behaviour can be attributed to the fact that during the oxidation scan there is the concomitant formation of Pd oxide with hydrogen oxidation. Oxide formation leads to passivation of the Pd nanoparticles, thus resulting in a decrease in the rate of hydrogen oxidation. Thus, during the reverse (reduction) scan, the electrode is bathed in hydrogen and, as oxide is removed from the surface, the hydrogen oxidation reaction is able to occur at driving potentials.

The results in Fig. 5 suggested that it might be beneficial to precondition the electrode by forming Pd oxide at anodic potentials, quickly stripping it from the surface, followed by an anodic sweep for hydrogen evolution. The beneficial effect is clearly visible in Fig. 6 which reports the forward anodic

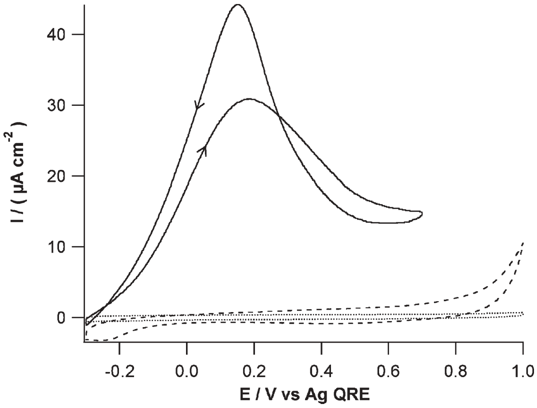

Fig. 5 CVs of a 40-layer Pd–Nafion LS film before (dashed line) and after saturation with H_2 (solid line) in 0.1 M KNO_3 supporting electrolyte, scan rate 20 mV s^{-1}. The dotted line shows a CV of a 40-layer Nafion LS film on ITO after saturation of the solution with H_2.

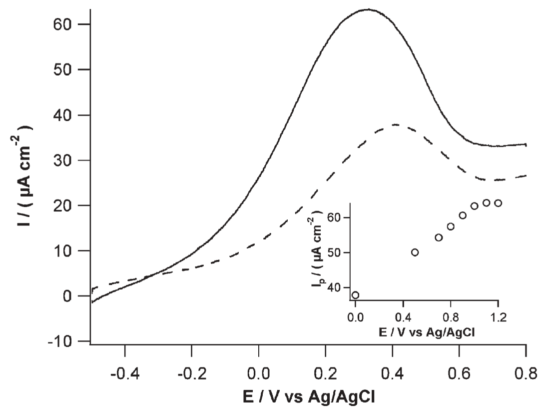

Fig. 6 Linear sweep voltammetry (LSV) of a 40-layer Pd–Nafion film, supporting electrolyte 0.1 M KNO_3, scan rate 100 mV s^{-1}, after saturation with H_2: without preconditioning (dashed line) and with preconditioning at 1 V for 30 s (solid line). Inset: LSV peak current magnitude, I_p, *vs.* preconditioning potential; other conditions as indicated above for the solid line.

voltammograms for hydrogen oxidation related to the same 40-layer Pd–Nafion film without (dashed line) and with (solid line) the application of a conditioning anodic potential (+1.0 V, 30 s duration). The magnitude of the anodic peak current under these conditions increased with increasingly anodic preconditioning potentials, reaching a maximum value at 1 V and beyond (see Inset of Fig. 6). Coupled with our earlier observations, these results suggest that the procedure herein produces electrochemically active Pd nanoparticles, without any protecting group, which are characterised by the usual oxide formation/stripping of naked Pd nanoparticles.

In summary, we have developed a very simple procedure for functionalising ultra-thin Nafion films with relatively monodisperse Pd nanoparticles. The nanoparticles have characteristics typical of naked Pd and are electrochemically active towards the catalytic oxidation of hydrogen. Further work is underway to further explore the electroanalytical and electrocatalytic properties and applications of these films.

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