

Fabrication and electrocatalytic properties of polyaniline/Pt nanoparticle composites

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Polyaniline (PANI)/Pt nanoparticle composites can be prepared by the spontaneous redox reaction of K_2PtCl_4 with PANI, to yield thin films that show electrocatalytic properties in both acidic and neutral aqueous media.

Electrically conducting polymers (ECPs) with dispersed metallic nanoparticles have received much attention recently^{1–5} for many applications including biosensors,^{6,7} electrochemical capacitors,⁸ protective coatings against corrosion⁹ and as electrocatalysts.^{10–14} The ECP polyaniline (PANI) is of particular interest due to its environmental stability, large conductivity range¹⁵ and the different redox states it possesses: the leucoemeraldine base (reduced form); emeraldine base (EB, half-oxidised form); emeraldine salt (ES, half-oxidised, protonated form); and pernigraniline base (fully oxidised form). Platinum nanoparticles are attracting attention as efficient catalysts for the oxidation of small organic molecules.^{10–14}

While the dispersion of Au nanoparticles in polymer films is readily achieved,^{2,4,5,16} the processing of Pt nanoparticles has proved more difficult. The most popular method for fabricating PANI/Pt composites has involved the electropolymerisation of aniline at an electrode, followed by the electrodeposition of Pt from a precursor salt, by either a pulsed or potential cycle program.^{11–14} This has tended to produce relatively thick films (of the order of 1 μm), with large Pt particles, at loadings of up to 200 $\mu\text{g cm}^{-2}$.

Here, we report a simple two-step method for fabricating PANI/Pt nanoparticle composite thin films that show good electrocatalytic activity for hydrazine oxidation in acidic and neutral media. In the first step a solution of PANI(EB) (1 wt%) and a solution of K_2PtCl_4 (10 mM), both in formic acid, were mixed in equal volumes and sonicated for 1 h. The treatment of the EB form with acid produces the doped conducting ES form. Fig. 1(a) shows a tapping mode AFM image of a spin cast film (2000 rpm, 60 s, 1 s ramp time) deposited from this PANI/Pt solution. Pt particles can clearly be seen both at the surface of the film and embedded within it (film thickness of 25 nm determined from AFM). The particles are quite well dispersed and have diameters ranging from 30 to 90 nm, with most particles having a diameter of 50 nm. While these films showed encouraging electrocatalytic characteristics for the oxidation of hydrazine in acidic media, the optimal activity was achieved by carrying out further Pt deposition. Thus, the PANI/Pt film formed in the first step was immersed into a neutral aqueous solution of K_2PtCl_4 (10 mM) for 30 min. This second Pt deposition

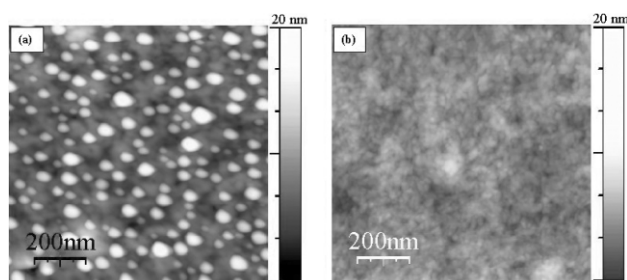


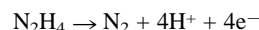
Fig. 1 Tapping mode images ($1 \times 1 \mu\text{m}$) of (a) PANI/Pt spin cast film and (b) same film after immersion in 10 mM K_2PtCl_4 for 30 min.

step appears to have caused a levelling of the surface topography.

In both steps the driving force for Pt formation is that PANI(ES) acts as an electron donor and the platinum salt as an electron acceptor, resulting in the oxidation of PANI(ES) to the pernigraniline form and the reduction of K_2PtCl_4 to metallic Pt. In acidic media, the pernigraniline form may undergo reduction back to the ES form,¹⁷ thereby promoting the further reduction of the Pt complex to metallic Pt.

To investigate further the material formed after step 2, transmission electron microscope (TEM) images were obtained of a PANI/Pt film after immersion in the Pt salt solution. Sample preparation involved dipping a TEM grid in a PANI/Pt formic acid solution (0.1 wt% PANI and 1 mM K_2PtCl_4), allowing the grid to dry in air, followed by immersion in an aqueous solution of 10 mM K_2PtCl_4 for 10 s. The lower concentration of the PANI/Pt solution ensured that a sufficiently thin film was formed after the dipping procedure, to allow TEM analysis. The TEM images in Fig. 2 show that (dark) particles of the order of 1–2 nm diameter are formed over the entire region of the film (Fig. 2(a) and (b)), with a lower density of larger clusters, up to 50 nm diameter, also produced (Fig. 2(a)). It is worth noting that closer inspection reveals these clusters to comprise of 1–2 nm diameter particles.

The two-step spin casting preparation method was employed to coat an indium tin oxide (ITO) electrode with the PANI/Pt film. The electrocatalytic oxidation of hydrazine was investigated:



This surface-controlled reaction is of interest, as it is catalysed by platinum only; neither PANI nor the underlying ITO electrode promote the reaction. The reaction is of practical importance, as hydrazine has been investigated as a fuel for a zero emission fuel cell.¹⁸ Electroanalytical methods for determining hydrazine are also of interest, as hydrazine has been identified as a carcinogen and a hepatotoxin.¹⁹

Fig. 3 shows typical cyclic voltammograms for the oxidation of 0.1 M hydrazine in 1 M H_2SO_4 at both a PANI/Pt composite electrode and Pt wire electrode (0.5 mm diameter). In both cases, a three electrode setup was used, with a saturated calomel reference

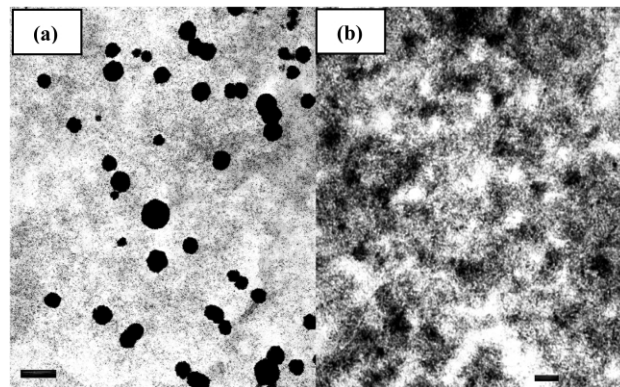


Fig. 2 (a) TEM image (100 nm scale bar) of a PANI/Pt film after immersion in 10 mM K_2PtCl_4 for 10 s. (b) Higher resolution (20 nm scale bar) image showing the formation of nm-particles (dark spots).

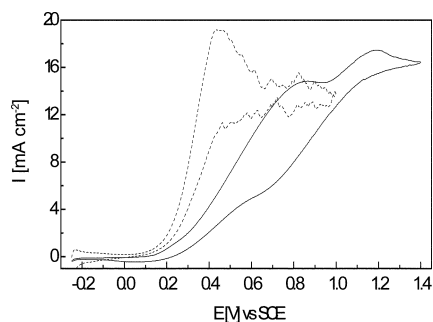


Fig. 3 Cyclic voltammograms for the oxidation of 0.1 M N_2H_4 (1 M H_2SO_4) at PANI/Pt composite (—) and Pt wire (---) electrodes, recorded at a scan speed of 50 mV s^{-1} .

electrode (SCE) and a Pt counter electrode. The response of the composite electrode is comparable to that of the Pt wire, although the onset potential for hydrazine oxidation is slightly more positive than for the wire electrode. To compare the two responses, we attempted to measure the real surface area of Pt in the composite electrode by CO stripping, but the signal was much too low to be measured. Consequently, in comparing the current densities at the two electrodes, we have used the overall geometric area. It can be seen that the current densities are quite similar, which is particularly noteworthy, given the relatively small amount of Pt in these films. This similarity suggests the formation of a well packed film of Pt nanoparticles over the entire electrode after the second step of the fabrication method, which is supported by the TEM images in Fig. 2(b).

In neutral media ($\text{pH} = 7.3$, 0.1 M phosphate buffer), the PANI/Pt composite remained active for hydrazine oxidation, with a current density of 4 mA cm^{-2} at 0.4 V (SCE), even when the film had been annealed on a hot plate (50°C , 2 min) to remove any residual formic acid that would dope PANI. This is a surprising result as PANI is appreciably conducting only in the ES form at $\text{pH} < 4$.¹⁷ To understand the redox characteristics of the PANI/Pt composite at neutral pH, we compared its activity to a PANI electrode. The PANI/Pt electrode was redox active at $\text{pH} 7$, as seen in Fig. 4(a), which shows the oxidation–reduction waves for the conversion of the fully reduced leucoemeraldine form of PANI to the EB form. Moreover, this well-defined response was evident from the first scan and was stable to repetitive cycling. In contrast, an annealed PANI electrode showed quite different characteristics (Fig. 4(b)). In the first cycle there was an oxidation peak at 0.4 V with no cathodic counterpart. After 5 cycles the redox activity of the PANI film became stable and resembled that of Fig. 4(a), but a significant break-in procedure was required, in contrast to the PANI/Pt. This is a significant result, as it opens up the potential use of PANI/Pt composites at neutral pH without any need for pre-treatment of the electrode.

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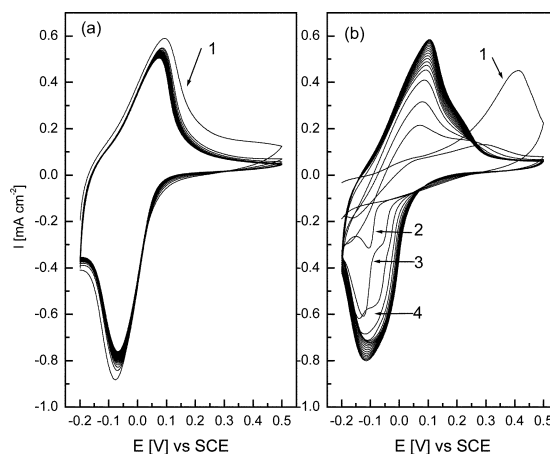


Fig. 4 Cyclic voltammograms (20 cycles) of (a) PANI/Pt electrode and (b) PANI electrode in 0.1 M phosphate buffer ($\text{pH} = 7.3$).

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