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Chemical deposition of palladium on leucoemeraldine from solutions: state and distribution of palladium species

Jinggong Wang,[a] **K. G. Neoh,***[a] **E. T. Kang**[a] **and K. L. Tan**[b]

[a]*Department of Chemical and Environmental Engineering, National University of Singapore, Kent Ridge, Singapore 119260. E-mail: Chenkg@nus.edu.sg; Fax: +65 7791936; Tel: +65 8742186*
[b]*Department of Physics, National University of Singapore, Kent Ridge, Singapore 119260*

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The reactions of polyaniline in its lowest oxidation state, leucoemeraldine (LM), with palladium ions in $PdCl_2$, $Pd(NO_3)_2$, mixed solutions of $PdCl_2$ and $Pd(NO_3)_2$ and mixed solutions of $PdCl_2$ and $AuCl_3$ were investigated. The amount of Pd deposited on the leucoemeraldine film was calculated from the decrease in Pd ion concentration in solution as determined by inductively coupled plasma emission spectroscopy. The state and distribution of the Pd species on the film surface was analysed using X-ray photoelectron spectroscopy and atomic force microscopy, respectively. The results showed that a much faster and more complete reduction of Pd ions to Pd^0 occurred in the $Pd(NO_3)_2$ solution as compared to the $PdCl_2$ solution and the explanation for this difference in reactivity has been offered from an electrochemical and coordination chemistry point of view. The mixing of $Pd(NO_3)_2$ with $PdCl_2$ appears to affect the Pd coordination states in solution which in turn affects the Pd uptake rate and the manner in which the Pd is deposited on the LM surface. In mixed solutions of $PdCl_2$ and $AuCl_3$, it was clearly seen that the presence of a small amount of $AuCl_3$ (molar ratio of $AuCl_3/PdCl_2$ of 0.1) can greatly accelerate the uptake of Pd and complete removal of Pd ions from $PdCl_2$ can be accomplished.

Introduction

The interesting redox properties of polyaniline associated with the chain nitrogens[1,2] provide an approach for the reduction of precious metal ions. The fact that polyaniline can exist in a large number of inter-convertible intrinsic oxidation states[3] suggests that by coupling the metal reduction process in acid solution with an increase in the intrinsic oxidation state of the polymer, and the subsequent reprotonation and reduction of the oxidized polymer in the acid medium,[2] spontaneous and sustained reduction of certain metals to their elemental form can be achieved. The electroless precipitation of gold in elemental form from acid solution can be readily achieved using polyaniline as well as polypyrrole.[4,5] Chemical deposition of palladium from its acid solution has also been demonstrated,[6,7] and the deposition process and the state of the deposited palladium were found to be dependent on the nature of the anions in solution, the acidity of the solution and the redox degree of polyaniline.[8] A number of recent articles on the catalytic properties of electroactive polymers modified by platinum or palladium particles[9–14] attest to the interest in such systems since electroactive polymers can provide an efficient route for the shuttling of electronic charges to the catalyst centres and hence be an attractive host medium.[15]

In this paper, we used polyaniline in its lowest oxidation state, leucoemeraldine (LM), in film form rather than as powder or nanocomposites supported by SiO_2 particles as used previously[16] for investigating the effects of using mixed solutions of $PdCl_2$ and $Pd(NO_3)_2$ as well as $PdCl_2$ and $AuCl_3$. Of particular interest in our investigation is whether the uptake of Pd by LM from the mixed solutions proceeds in a manner similar to that observed in the "pure" solution since Pd can form a number of complexes. The use of the film form of LM also readily enables the investigation of how the state and the distribution of the metal species on the surface are affected by the reaction conditions. These issues are of interest since the catalytic properties of such polyaniline–Pd systems can be expected to be dependent on the state of the palladium as well as the manner in which the particles are distributed.

Experimental

Preparation of polyaniline

Polyaniline was synthesized *via* the oxidative polymerisation of aniline by ammonium persulfate in 0.5 M H_2SO_4 at 0 °C for 5 hours. The collected solid particles were then washed with excess 0.05 M H_2SO_4 and then dried under reduced pressure. The as-synthesized polyaniline in the form of a powder was undoped by treatment with excess 0.5 M NaOH for 1 hour in order to obtain the emeraldine (EM) or 50% oxidized base and then washed with excess deionised water. Free-standing EM films of about 20 μm in thickness were prepared by exhaustive pumping of the concentrated *N*-methylpyrrolidinone (NMP) solution containing 8% EM base powder by weight at room temperature for about 24 hours.

The fully reduced form of the polyaniline (leucoemeraldine or LM base) film was obtained by reduction of the EM base film with anhydrous 98% hydrazine (Aldrich) for 3 hours followed by thorough washing with deionised water. The LM film obtained was then pumped dry under reduced pressure. Since the LM film is very easily oxidized, the Pd uptake experiments were conducted soon after the preparation of the LM films.

Uptake of Pd from solutions

The as-synthesized LM film was cut into small strips of 2 cm × 1 cm × 0.02 mm in size. For all the Pd uptake experiments using $PdCl_2$, $Pd(NO_3)_2$ and their mixed solutions, the initial molar ratio of N (in LM) to Pd^{2+} in solutions was fixed at 4 : 1. Standard solutions of 100 mg dm^{-3} of Pd^{2+} in 0.5 M acids were obtained by diluting the concentrated $PdCl_2$ (Aldrich, 5 wt.% in 10 wt.% HCl) and $Pd(NO_3)_2$ (Merck,

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1000 mg L^{-1} $Pd(NO_3)_2$ in 0.5 M HNO_3) with HCl and HNO_3 respectively. According to the weight of LM strips and the fixed initial molar ratio, the volume of Pd^{2+} acid solution to be used was calculated. Mixed solutions of $PdCl_2$ and $Pd(NO_3)_2$ with molar ratios of $Pd(NO_3)_2$ to $PdCl_2$, R, of 10, 3.33, 1, 0.33 and 0.1 were also used. The uptake of Pd from its acid solutions was carried out at room temperature by adding the LM strips to the Pd^{2+} acid solution which was shaken at a constant rate (50 rpm).

For Pd uptake experiments from mixed solutions of $PdCl_2$ and $AuCl_3$, the initial molar ratio of $N:(Pd^{2+}+Au^{3+})$ was fixed at 4 : 1. The volumes of $PdCl_2$ and $AuCl_3$ acid solution (BDH Laboratory Supplies, 1000 ± 5 mg L^{-1} $AuCl_3$ in 0.5 M HCl) were mixed to obtain different mixtures of molar ratio of Au^{3+} to Pd^{2+}, r, of 0.1, 0.2, 0.3, 0.4 and 0.5. The process for metal uptake was carried out as described above.

Measurement of metal ion concentration and film characterization

The concentration of palladium ions in solution was determined using an inductively coupled plasma (ICP) emission spectrometer (Perkin Elmer Optima 3000DV) at a wavelength of 340 nm. To investigate the rate of uptake of palladium from solution, the palladium ion concentration in solution was measured at time intervals of 0, 15, 30, 60, 120, 180, 240 and 300 minutes. The gold ion concentration was measured in a similar manner using ICP at a wavelength of 243 nm.

The polyaniline films after metal uptake were characterized by angle-resolved X-ray photoelectron spectroscopy (XPS). XPS measurements were made on an Axis His 165 (Kratos Analytical) spectrometer with a MgK_α X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The core-level signals were obtained at a photoelectron take-off angle (α) of 75° with respect to the sample surface. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). All binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV. In peak synthesis, the linewidth (full width at half maximum or FWHM) of the gaussian peaks was maintained constant for all components in a particular spectrum. Surface elemental stoichiometries were determined from peak-area ratios, after correcting with the experimentally determined sensitivity factors, and were accurate to within $\pm10\%$. The elemental sensitivity factors were determined using stable binary compounds of well-established stoichiometries.

The surface morphology of the films after metal uptake was investigated using an atomic force microscope, Nanoscope IIIa (Digital Instruments). The scan area was fixed at 5 μm × 5 μm. The average roughness (R_a) of the film surface was directly calculated from the whole sample images automatically.

Results and discussion

Pd uptake from $PdCl_2$, $Pd(NO_3)_2$ and their mixed solutions

The amounts of Pd deposited on the LM films as calculated from the reduction in Pd ion concentration in $Pd(NO_3)_2$ and $PdCl_2$ solutions are shown in Fig. 1. The results shown are the average of two runs and the reproducibility is close to 5%. This figure shows that $Pd(NO_3)_2$ reacts more effectively with LM than $PdCl_2$. In the former case, essentially all the Pd ions have been removed from solution after 300 minutes (initial ratio of Pd ions in solution to N in LM is 0.25). From the electrochemical and coordination chemistry point of view, we can offer the following explanation for the difference in the reactivity of $Pd(NO_3)_2$ and $PdCl_2$ with LM. The coordination states of palladium chloride in acid solution depend on the acid concentration, in other words, on the molar ratio of Cl to Pd.[8] In our experiments, the acid concentration was fixed at 0.5 M. As such, the molar ratio of Cl to Pd for the solutions used is much higher than 4 and the dominant states are anionic complexes, such as $[PdCl_4]^{2-}$ and $[PdCl_3(H_2O)]^{-}$.[8,17,18] For the $Pd(NO_3)_2$ solution, the dominant metal ion species in solution is Pd^{2+}. The electrode potentials of the Pd^{2+}–Pd pair (reaction (1)) and the $[PdCl_4]^{2-}$–Pd pair (reaction (2)) are 0.951 V and 0.591 V, respectively.[19]

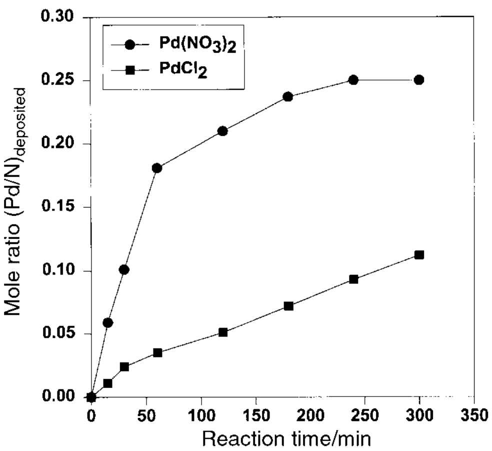

Fig. 1 Mole ratio of Pd deposited per mole of LM at an initial mole ratio of Pd^{2+} in solution to LM of 1 : 4.

$$Pd^{2+}+2e^{-}\rightarrow Pd^{0} \quad (1)$$

$$[PdCl_4]^{2-}+2e^{-}\rightarrow Pd^{0}+4Cl^{-} \quad (2)$$

It is well known that polyaniline can be used as a non-metal electrode with the following electrode reactions (3) and (4):[20]

$$[(C_6H_4)NH(C_6H_4)NH(C_6H_4)NH(C_6H_4)NH]_x-(2x)e^{-}\rightarrow [(C_6H_4)NH(C_6H_4)NH(C_6H_4)N^{+}H(C_6H_4)N^{+}H]_x \quad (3)$$

$$[(C_6H_4)NH(C_6H_4)NH(C_6H_4)N^{+}H(C_6H_4)N^{+}H]_x-(2x)e^{-}\rightarrow [(C_6H_4)N(C_6H_4)N(C_6H_4)N(C_6H_4)N]_x+(4x)H^{+} \quad (4)$$

The potentials of the above reactions (3) and (4) are about 0.1 V and 0.7 V *vs.* SCE respectively.[20] For a redox reaction to be possible and spontaneous, the cell potential must be positive. A comparison of the cell potential was carried out considering the reactions of the Pd^{2+}–Pd and $[PdCl_4]^{2-}$–Pd systems with those of polyaniline as given by reactions (3) and (4). The spontaneity of all the reactions except the combined reactions of (2) and (4) was confirmed. Thus, the reduction of Pd^{2+} from $Pd(NO_3)_2$ to Pd^0 by LM can be expected to be more readily accomplished than that of $[PdCl_4]^{2-}$ from the $PdCl_2$ solution.

Furthermore, after the coordination of Pd ion with Cl^- and/or water molecules, the Pd units are at the centre of the entire coordination units which are much bigger than the original Pd units. Such ligands can adversely affect the reaction of the Pd units with the nitrogen of LM, the reaction centre, for the following reasons. Firstly, the two possible configurations are tetrahedral and square planar when palladium is coordinated with Cl^- and/or water molecules.[17,18] These two states can keep the Pd units stable, especially in the square planar case.[17,18] Secondly, the spatial effects should also be considered. The tetrahedral and square planar configurations can impede the reaction of the Pd unit with nitrogen due to the placement of too many atoms and other large groups, such as the phenyl groups, between the Pd units and nitrogen.

Fig. 2 shows a comparison of the uptake of Pd from solutions of different $Pd(NO_3)_2$ to $PdCl_2$ molar ratios (R). As in Fig. 1, the amount of Pd deposited on the LM film was calculated from the amount of Pd remaining in solution as measured by ICP. This figure clearly shows that as more $Pd(NO_3)_2$ was added, the amount of palladium deposited

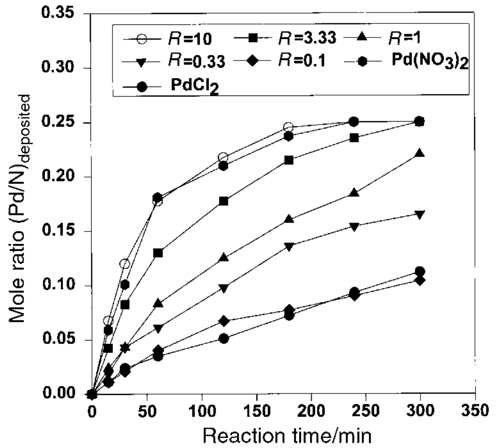

Fig. 2 Mole ratio of Pd deposited from mixed $PdCl_2$ and $Pd(NO_3)_2$ solutions per mole of LM at an initial mole ratio of Pd^{2+} in solution to LM of 1 : 4.

increases. Very interestingly, the highest uptake was observed at a molar ratio of $R=10$, not from the pure $Pd(NO_3)_2$ as would be expected. It was also clearly observable that some changes involving the Pd complexes occurred when the $Pd(NO_3)_2$ solution (yellow) was mixed with the $PdCl_2$ solution (off-white) to obtain the $R=10$ solution, since there was an immediate colour change of the solution to a deeper yellow. In Fig. 3, the measured amounts of Pd deposited on LM from the various mixtures (data from Fig. 2) are plotted against the values predicted based on the sum of the amounts deposited from the indicated proportions of pure $PdCl_2$ and $Pd(NO_3)_2$ solutions (Fig. 1), assuming that the uptake from each solution in the mixture proceeds independently. Fig. 3 shows that in general, when the uptake is low (*i.e.* short time or low R), the actual amount deposited is either close to or lower than the predicted value. However, the trend is reversed when the uptake is high. In particular, for the $R=10$ solution, the actual uptake is higher than the predicted value for all the reaction times tested. The interaction between $PdCl_2$ and $Pd(NO_3)_2$ not only affects the Pd uptake rate but also the manner in which the Pd deposit is distributed on the film surface as indicated by the AFM data (which will be discussed below).

The LM films after reaction with $PdCl_2$ and $Pd(NO_3)_2$ solutions are visually different. After a reaction time of 15 minutes, the film in the $Pd(NO_3)_2$ solution has a shiny metallic sheen while the film in the $R=10$ mixed solution is dull light gray, and the film reacting with $PdCl_2$ more or less retains its original colour. With increasing reaction time, the colour of each film generally does not change significantly from that after 15 minutes, although an increase in the thickness of the deposited layer is obvious. The exception is the film reacting with $PdCl_2$. As the reaction progresses, the film gradually looks more metallic, especially the sample taken near the end of the reaction (300 minutes), but it is also visually obvious that the deposited layer is very thin, compared to that seen after reaction with $Pd(NO_3)_2$. These colour differences indicate clearly that the state and distribution of the Pd on the LM surface are affected by the composition of the Pd solutions.

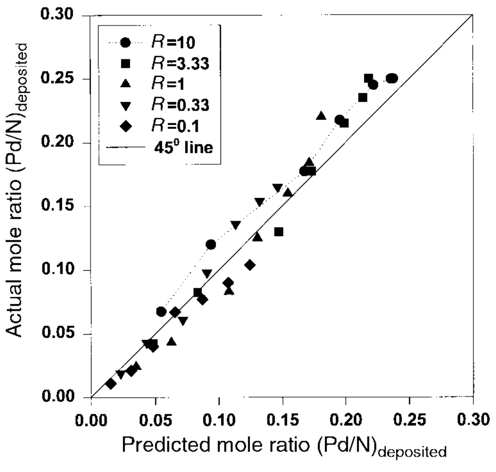

Fig. 3 Comparison of the actual and predicted values of $(Pd/N)_{deposited}$.

XPS measurements were performed to determine the state of the Pd deposited on the LM. In Fig. 4, the XPS Pd 3d spectra of LM films after reaction in $Pd(NO_3)_2$ and $PdCl_2$ solutions for varying periods of time are shown. A Pd $3d_{5/2}$ component peak with a binding energy, BE, of about 338 eV is characteristic of Pd^{2+} species while that at 335 eV is attributable to the Pd^0 species.[21] When $Pd(NO_3)_2$ is used, it is quite clear that Pd^0 is the main state of the palladium deposited on the surface of the LM film. This result was also found by Huang *et al.* for an LM powder.[16] For $PdCl_2$, Pd^{2+} is the predominant state on the LM surface at the beginning of the reaction; but after 3 hours, almost all the Pd is in the Pd^0 state on the surface of the LM film. Either the palladium which have already been deposited continue to react to reach the lowest redox state, or the palladium is deposited onto the surface as Pd^0 after some time. This result is rather different from the earlier work of Huang *et al.*[16] and this difference may be due to the different forms of the LM and the methods of making the LM. In our present experiment, 98 wt.% hydrazine was used as the reducing agent for 3 hours to obtain the LM film whereas in the earlier work, 80 wt.% hydrazine was used for a treatment time of 1 hour and the LM was in powder form.[16] It was also reported earlier that a third Pd $3d_{5/2}$ component peak at 336.5 eV was present in the Pd 3d spectrum of an LM film after reaction with Pd solution. The exact nature of this third Pd species is not known. The presence of this component peak at 336.5 eV was once again confirmed in our experiment (Fig. 4) and further investigation is desired.

Fig. 5 shows the fraction of Pd deposited as Pd^0 onto the LM film surface as calculated from the XPS analysis for the different reaction mixtures. From this figure, it can be seen that regardless of the reaction time in $Pd(NO_3)_2$, about 75% of the total Pd deposited is Pd^0. Of the remaining Pd species, a large proportion is the yet-to-be determined third Pd species with a BE of 336.5 eV in the XPS Pd 3d spectra. This may indicate some form of complexation of Pd with the imine nitrogens which resulted from the oxidation of the amine nitrogens in LM. Complexation of Ag^+ ions with imine nitrogens of

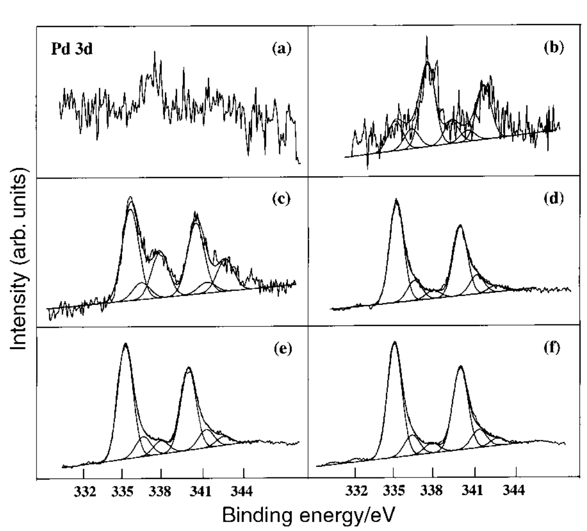

Fig. 4 XPS Pd 3d core-level spectra of LM base film after reaction with: (a) $PdCl_2$ for 10 min; (b) $PdCl_2$ for 30 min; (c) $PdCl_2$ for 300 min; (d) $Pd(NO_3)_2$ for 10 min; (e) $Pd(NO_3)_2$ for 30 min; (f) $Pd(NO_3)_2$ for 300 min.

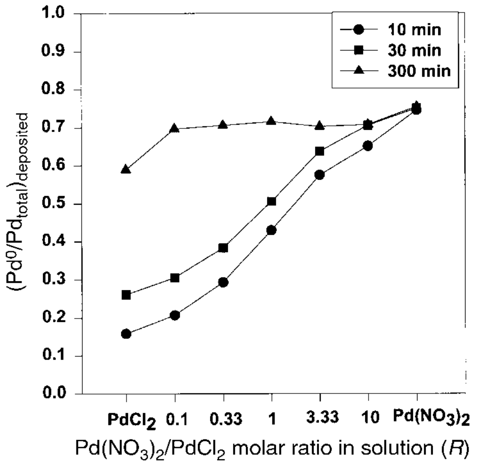

Fig. 5 Mole ratio of $(Pd^0/Pd_{total})_{deposited}$ at an initial mole ratio of Pd^{2+} in solution to LM of 1 : 4.

polyaniline, and the formation of other complexes of Pd with ethylenediamine have been reported earlier.[22,23]

For the mixed solutions of $PdCl_2$ and $Pd(NO_3)_2$, as expected, the fraction of Pd deposited as Pd^0 increases as R increases (Fig. 5). In fact, the value obtained experimentally is quite close to the value calculated from the respective combination from $PdCl_2$ and $Pd(NO_3)_2$. For example, for $R = 1$ at a reaction time of 10 minutes, the experimental $(Pd^0/Pd_{total})_{deposited}$ is 0.43 while the calculated value is 0.45.

The AFM images of the surface of the LM films after immersion in $PdCl_2$ and $Pd(NO_3)_2$ solutions for 10 minutes are shown in Fig. 6(a) and (b) respectively. The higher roughness value (R_a) for the film treated in $Pd(NO_3)_2$ is consistent with the ICP results showing a larger amount of Pd deposited on this film. However, the results obtained from the mixed solutions given in Fig. 6(c)–(g) show that the roughness value does not depend solely on the amount of Pd deposited. Contrary to expectation, the roughness of the LM films after reaction in mixed solutions is generally higher than that obtained with pure $Pd(NO_3)_2$ (with the exception of $R = 0.1$), even though the amount of Pd deposited is not higher. From Fig. 6, it can also be seen that after reaction in $Pd(NO_3)_2$, the distributed units of Pd on the LM surface look more rounded and more closely packed whereas for mixed solutions containing $PdCl_2$, the units are distributed in a more discrete, peak-like manner which accounts for the higher roughness of the latter. Previous X-ray diffraction analysis of palladium deposited onto a PANi surface from $PdCl_2$ shows the possibility of the co-existence of one-dimensional ordering of the Pd–polyaniline systems as well as crystals of metallic palladium.[8] From the AFM results, it may then be postulated that the manner in which the Pd deposit is built up on the LM surface is dependent on the distribution of metallic Pd and $PdCl_2$ complexes (which can be expected to be of different sizes) on the surface.

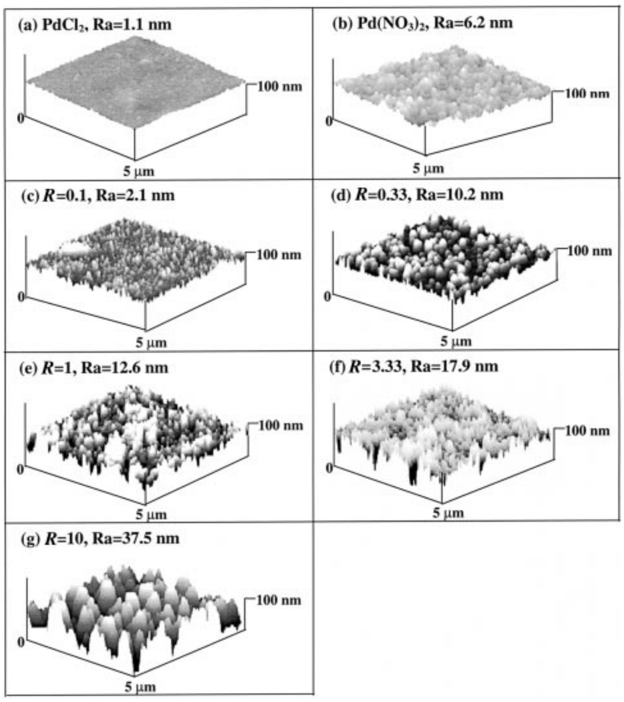

Fig. 6 AFM images of LM films after reaction in solutions of different mole ratios of $Pd(NO_3)_2/PdCl_2$, R, for 10 min.

Pd uptake from mixed solutions of $PdCl_2$ and $AuCl_3$

The spontaneous deposition of Au on PANi has been reported earlier[5,24] and the overall reaction can be represented as

$$[(C_6H_4)NH(C_6H_4)NH(C_6H_4)NH(C_6H_4)NH]_x + Au^{3+} \rightarrow$$
$$[(C_6H_4)N(C_6H_4)N(C_6H_4)N(C_6H_4)N]_x + Au + 6H^+ + 3e^- \quad (5)$$

The uptake of Au from $AuCl_3$ by LM proceeds much more readily than the equivalent process observed with $PdCl_2$. However, as shown in Fig. 7, when a small amount of $AuCl_3$ is added to the $PdCl_2$ solution, *e.g.* at a mole ratio of $AuCl_3/PdCl_2$ (r) of 0.1, the rate of uptake of Pd increases very significantly. For this particular condition, almost all the Pd is removed from solution after about 200 minutes. From Fig. 7, it can be similarly concluded that there is no further uptake of Pd from solution by 240 minutes for the other values of r (from 0.1 to 0.5).

By plotting the ratio of $(Pd/N)_{deposited}$ to the maximum (Pd/N) (maximum Pd/N is the mole ratio of the amount of Pd originally in solution to LM) as in Fig. 8, the complete removal of Pd from the solution by 240 minutes can be more easily seen. The very significant enhancement of Pd uptake by the addition of a small amount of $AuCl_3$ is also clearly illustrated for all reaction times and there appears to be no further advantage of adding more $AuCl_3$ beyond $r = 0.1$. The corresponding plot of $(Au/N)_{deposited}$ to the maximum (Au/N) is given in Fig. 9. By comparing Fig. 8 and Fig. 9, it can be clearly seen that the uptake of Au proceeds much more rapidly than that of Pd from the respective chloride solution. The addition of $PdCl_2$ to $AuCl_3$ decreases the rate of Au uptake due to the decreasing Au concentration and the possible interaction of $PdCl_2$ and $AuCl_3$ to form complexes, as discussed below.

The LM films after reaction in the mixed solutions of $PdCl_2$ and $AuCl_3$ have a shiny golden sheen. The AFM image of the LM film after reaction in the mixed solution of $r = 0.1$ for

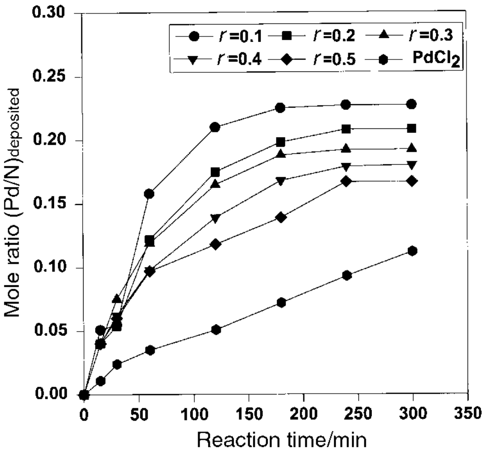

Fig. 7 Mole ratio of Pd deposited from mixed $PdCl_2$ and $AuCl_3$ solutions per mole of LM at an initial mole ratio of $(Pd^{2+} + Au^{3+})$ in solution to LM of 1 : 4.

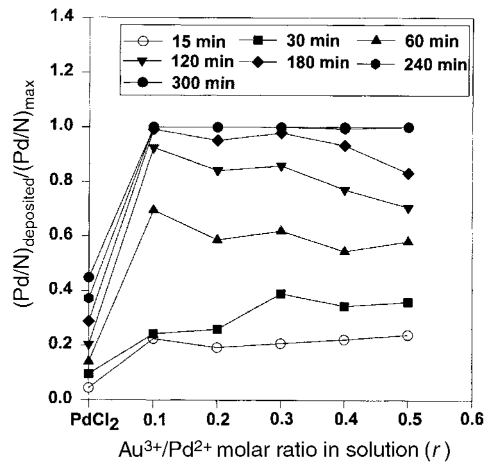

Fig. 8 Effect of Au on the deposition of Pd on LM film. Initial mole ratio of ($Au^{3+}+Pd^{2+}$) in solution to LM is 1 : 4.

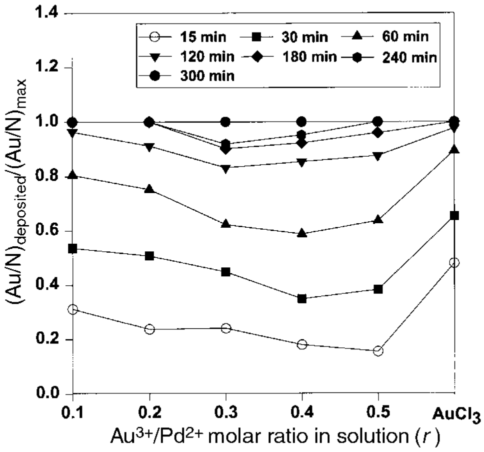

Fig. 9 Effect of Pd on the deposition of Au on LM film. Initial mole ratio of ($Au^{3+}+Pd^{2+}$) in solution to LM is 1 : 4.

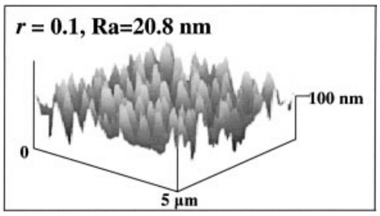

Fig. 10 AFM image of LM film after reaction in a mixed $PdCl_2$ and $AuCl_3$ solution of $r=0.1$ for 15 min.

15 minutes (Fig. 10) is distinctly different from that observed with pure $PdCl_2$. The former shows a distribution of sharp distinct peaks and the roughness factor is an order of magnitude higher. This can be attributed to the rapid build-up of Au and Pd deposits on the surface in the mixed solution. The XPS analysis of the LM film after reaction in the $r=0.1$ solution for 15 minutes confirms the presence of Au^0 (Au $4f_{7/2}$ component peak at 84 eV in Fig. 11(a)). However, for the Pd 3d spectrum (Fig. 11(b)), the proportion of the different Pd species is not clear since the Au 4d component peaks overlap with those of Pd 3d. At longer reaction times, there is no change in the Au spectrum (Fig. 11(c)) and the predominant species remains as Au^0. However, there is a noticeable change in the Pd spectrum (Fig. 11(d)). However it is not possible to deconvolute this spectrum due to the interference of the Au 4d signals, as mentioned above.

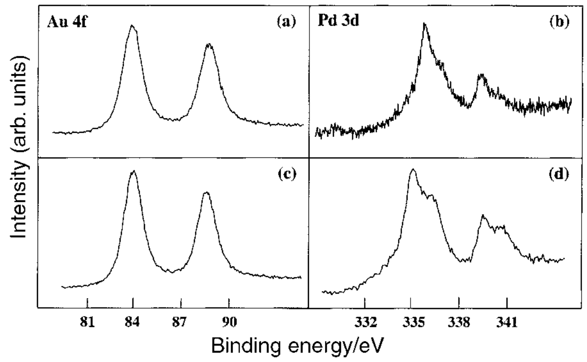

Fig. 11 XPS Au 4f and Pd 3d core-level spectra of LM base film after reaction in mixed solutions of $Au^{3+}/Pd^{2+}=0.1$: (a) Au 4f, after reaction for 15 min; (b) Pd 3d, after reaction for 15 min; (c) Au 4f, after reaction for 300 min; (d) Pd 3d, after reaction for 300 min.

Although from the XPS analysis, it is not clear if the states of the Pd deposited from the mixed solutions are different from those observed in pure $PdCl_2$, we postulate that complexation of Au and Pd occurs in the mixed solutions which accelerated the metal uptake. It is known that in $AuCl_3$ solution, the most probable coordination states are the anionic species, $[AuCl_3OH]^-$ and $[AuCl_4]^-$.[17,18] These states are very similar to the corresponding anionic states existing in $PdCl_2$ solution and in the mixed solutions, bridged complexes can be formed.[17,18,25] These bridged complexes can be subsequently cleaved by the attack on the nitrogen of the polyaniline chain, resulting in the deposition of the Au and Pd units. From our results (Fig. 8), it appears that only a small amount of $AuCl_3$ is needed for the formation of the bridged complexes. An increase in $AuCl_3$ concentration beyond the threshold value may result in a decrease in Pd uptake rate (Fig. 8) due to the decreasing Pd concentration ($(Au^{3+}+Pd^{2+})_{total}/N$ is kept constant) and/or the interference of the gold–gold bridged complexes on the gold–palladium complexes during the attack on the polyaniline nitrogen.

Conclusion

The uptake of Pd from $PdCl_2$ and $Pd(NO_3)_2$ solutions by leucoemeraldine film proceeds at different rates and results in different Pd states being deposited on the film. This is attributed to the presence of anionic Pd complexes existing in the $PdCl_2$ solutions. The reaction in $Pd(NO_3)_2$ solution results in the deposition of predominantly Pd^0 species for all the reaction times tested whereas in $PdCl_2$ the distribution of Pd states deposited on the film is dependent on the reaction time. The mixing of $Pd(NO_3)_2$ with $PdCl_2$ affects the coordination states of Pd in solution which in turn affects the Pd uptake rate and the manner in which Pd is deposited on the film surface. A significant acceleration of Pd uptake from $PdCl_2$ solution is observed when a small amount of $AuCl_3$ ($AuCl_3/PdCl_2=0.1$) is added and complete removal of Pd ions from $PdCl_2$ can be accomplished. This is attributed to the formation of gold–palladium bridged complexes in solution which react with the polyaniline nitrogens.

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