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Synthesis of gold-decorated latexes *via* conducting polymer redox templates

M. Akif Khan,[a] Christian Perruchot,[a] Steven P. Armes*[a] and David P. Randall[b]

[a]*School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, East Sussex, UK BN1 9QJ*
[b]*School of Biological Sciences, University of Sussex, Falmer, East Sussex, UK BN1 9QJ*

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The efficient electroless deposition of gold from aqueous solutions has been achieved *via* redox interaction between Au(III) ions and conducting polymers such polypyrrole, polyaniline and poly(3,4-ethylenedioxythiophene). When using the doped, conductive bulk powder forms of these polymers, the average size of the gold deposits decreased from *ca.* 10 to *ca.* 1 μm as the initial pH of the reaction solution was increased from pH 0 to 7. In experiments conducted at neutral pH, pH drift down to pH 3 occurred during the redox reaction. However, if the base-treated, non-conductive forms of the polymers were added to $AuCl_3$ solutions at pH 7, the solution pH remained close to neutral, and finely dispersed gold deposits of 100–400 nm were obtained, strongly suggesting that the gold nucleation is pH-dependent. These findings were then used in attempts to prepare gold-clad latex particles by using micrometer-sized, conducting polymer-coated polystyrene latexes as redox templates for the reduction of gold from solution. Although it was not possible to obtain homogeneous gold coatings, a series of latex particles randomly decorated with 40–60 nm gold nanoparticles was obtained, with gold loadings of up to 12.5 wt% as measured by TGA. XPS studies confirmed the presence of metallic gold at the latex surface, in addition to an increase in the oxidation state of the conducting polymer overlayer, thus confirming that a redox interaction had indeed occurred. Disk centrifuge studies clearly indicated a marked decrease in the colloidal stability of the latexes after gold decoration. Finally, pressed pellet solid-state conductivity measurements showed the composite particles to be non-conductive, which is no doubt due to the discrete, well-sepa0rated nature of the gold nanoparticles on the latex, which prevents efficient charge transport.

Introduction

The metallization of non-conducting materials such as plastics or glass is of great importance, notably in the electronics industry. The metal coating processes used in the manufacture of printed circuit boards (PCBs) often rely on the initial formation of a thin metallic layer *via* electroless deposition, which can then be used as an electrode to facilitate the electrodeposition of subsequent metallic layers.[1] However, two obvious disadvantages of conventional electroless deposition techniques are the use of expensive noble metal catalysts and environmentally-unfriendly chemicals such as formaldehyde. In the past decade, though, it has been shown that thin films of organic conducting polymers (OCPs) can be employed as electrodes for metallization, thus negating the need for the undesirable electroless coating solutions. For example, it has been demonstrated that soluble polyaniline (PANI) dip-coated onto PCBs could be employed as a thin conducting electrode for the subsequent electrodeposition of copper.[1] Alternatively, *in situ* polymerization of other conducting polymers such as polypyrrole (PPY)[2–4] and poly(3,4-ethylenedioxythiophene) (PEDOT)[5] has been shown to be an effective method by which to establish the initial electrode. Huang *et al.* used PANI as an electrode to facilitate the electrodeposition of copper onto PCBs, and noted that spontaneous deposition of noble metals such as platinum and silver onto the OCP occurred on immersing the substrate into an aqueous solution containing the appropriate metal salt.[1] Although this was rationalized in terms of the electrode potentials of the PANI and metal salts, no actual experimental evidence was presented to show that reduction to zero-valent metal had in fact occurred.

More recently, Kang and co-workers have studied this phenomenon in some detail and reported a novel method for the electroless deposition of palladium and gold by utilizing the redox chemistry of conducting polymers.[6–9] They demonstrated that exposing films of PANI or PPY to aqueous chloroauric acid solutions led to the efficient reduction of Au(III) ions to elemental gold, as demonstrated by the two half-reactions shown below [eqn. (1) and (2)]:

$$\mathrm{Au(III)} + 3\mathrm{e}^- \rightarrow \mathrm{Au(0)} \qquad (1)$$

$$\mathrm{OCP}^{n+} \rightarrow \mathrm{OCP}^{m+} + (m-n)\mathrm{e}^- \qquad (2)$$

Despite the reactions being carried out in 0.5 M HCl, it was postulated that "in the presence of the Au(III) ions, spontaneous deprotonation will result in an increase in the intrinsic oxidation state of the polymer and the reduction of Au(III) to Au(0)".[6] The oxidised polymer could then be reprotonated and reduced in the acidic media, allowing the process to be sustained. By using UV–vis absorption spectroscopy, it was clearly shown that the concentration of Au(III) ions in solution rapidly decreased after exposure to the conducting polymer film. Moreover, XPS studies confirmed that zero-valent gold had been deposited onto the polymer films. Although a self-sustaining catalytic mechanism was proposed, the rate of formation of metallic gold was shown to decrease with time. This was attributed to the decrease in the contact surface area between the polymer and solution as the quantity of deposited gold increased. Subsequent work by the Singapore group involved the reduction of gold from solution using colloidal PANI– and PPY–silica nanocomposites.[10] It was clearly shown

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that the increased surface area of these nanocomposites relative to the conducting polymer films led to vastly increased rates of gold reduction.

The work of Kang and co-workers clearly demonstrates that the removal of metal ions from solution can be accomplished using OCPs. However, with the exception of a single AFM study to assess the surface roughness of PANI films used in the reduction of Pd ions,[9] no attempts were made to examine the morphology of the reduced/adsorbed metals. Furthermore, since Holdcroft and Abdou have demonstrated that conductivities of up to 11 000 S cm^{-1} can be achieved as a result of the electroless deposition of elemental gold onto poly(3-hexylthiophene) films,[11,12] it is perhaps surprising that no conductivity measurements were undertaken by the Singapore group. Finally, in the light of claims that the conducting polymer–silica nanocomposites apparently increased in size from approximately 500 to >2000 nm due to the accumulation of elemental gold,[10] it would be interesting to examine the effect that the deposition of gold has on the colloidal stability of the conducting polymer particles after deposition.

In the present work, we attempt to address the issues raised above by carrying out a systematic study to examine the morphology of metallic gold overlayers deposited onto conducting polymer bulk powders *via* the electroless method described by Kang and co-workers.[6–10] The effect of parameters such as reaction temperature and pH upon the gold morphology has been systematically investigated with a view to obtaining the most homogeneous metallic coating on the conducting polymer. Finally, the feasibility of synthesizing metal-clad latex particles by using conducting polymer-coated polystyrene latexes[13–15] is investigated (see Fig. 1).

Unlike conducting polymer–silica nanocomposites, which possess silica-rich surfaces,[16] conducting polymer-coated latexes should be well suited to the synthesis of metal-clad colloidal particles as their surface compositions are conducting polymer-rich.[17–19] In principle, such metal-clad latex particles might exhibit conductivities in the metallic regime, yet possess densities far lower than pure metallic particles of comparable size.

Experimental

Materials

Aniline hydrochloride (Aldrich) and 3,4-ethylenedioxythiophene (kindly donated by Bayer AG, Germany) were used as received, whereas pyrrole monomer (Aldrich) was distilled under reduced pressure. Styrene (Aldrich) was passed through a column of neutral activated alumina to remove inhibitor. All monomers were stored at −15 °C prior to use. Poly(*N*-vinylpyrrolidone) (Fluka; molecular mass 360 000) and α-azoisobutyronitrile (BDH Laboratory Supplies) were used without further purification. $FeCl_3 \cdot 6H_2O$ and $AuCl_3$ were obtained from Aldrich and used as received.

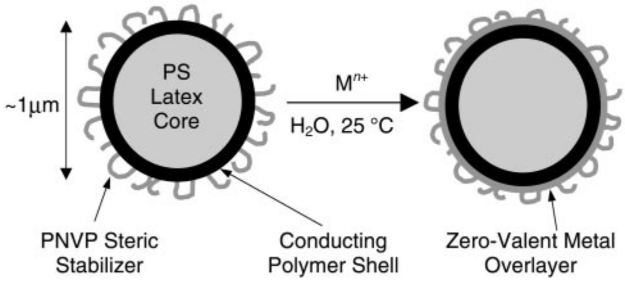


Fig. 1 Schematic representation of the proposed formation of metal-clad latex particles *via* electroless deposition using the conducting polymer overlayer as a redox template.

Synthesis of conducting polymer bulk powders

Polypyrrole. 10.0 ml (144.1 mmol) of pyrrole monomer was added *via* syringe to a solution of 90.8 g (335.8 mmol) $FeCl_3 \cdot 6H_2O$ in 1000 ml distilled water. The solution rapidly turned black and was stirred at room temperature for 24 h. The reaction mixture was then filtered under vacuum and the black filtrate was copiously rinsed with water, before being dried overnight under vacuum to give 10.7 g (90%) black powder.

Polyaniline. 10.0 g (77.2 mmol) of aniline hydrochloride was added to a solution of 22.0 g (96.5 mmol) $(NH_4)_2S_2O_8$ in 1000 ml distilled water. The solution rapidly turned dark green and was stirred at room temperature for 24 h. The reaction mixture was then filtered under vacuum and the dark green filtrate was copiously rinsed with 1.2 M HCl until the washings were colourless, before being dried overnight under vacuum to give 7.9 g (92%) dark green powder.

Poly(3,4-ethylenedioxythiophene). 30 ml of an EDOT–methanol solution (1 : 2 v/v; 93.8 mmol EDOT) was added to a solution of 59.1 g (218.6 mmol) $FeCl_3 \cdot 6H_2O$ in 980 ml distilled water at 85 °C. The solution rapidly turned dark blue and was stirred for 24 h. The reaction mixture was then centrifuged at 5000 rpm and the sediment was redispersed in a H_2O–MeOH mixture (1–1 v/v). The centrifugation–redispersion procedure was repeated four times before the sediment was dried overnight under vacuum to give 13.9 g (75%) dark blue powder.

Polystyrene latex synthesis

The poly(*N*-vinylpyrrolidone) (PNVP) steric stabilizer (7.5 g) was dissolved in 600 ml isopropanol in a round-bottomed flask equipped with mechanical stirrer, reflux condenser and thermometer. The solution was heated to 70 °C and purged under a nitrogen blanket overnight. Then a solution of α-azoisobutyronitrile (0.75 g) pre-dissolved in cold styrene monomer (75 g) was added with vigorous stirring and the polymerization allowed to proceed for 24 h. After cooling to room temperature, the milky latex was purified by centrifugation at 5000 rpm for 50 min. The resulting supernatant was replaced by deionized water. This centrifugation–redispersion procedure was repeated three times. The polystyrene latex particles were sized using disk centrifuge photosedimentometry (DCP). Measurements were obtained using a Brookhaven BI-DCP instrument operating in the line start mode. The dispersions were prepared for analysis by adding a few drops of latex to 3 ml of a H_2O–MeOH mixture (2 : 1 v/v). The particle density, which is an essential parameter required for DCP analysis, was measured by helium pycnometry (Accupyc 1330, Micromeritics) to be 1.05 g cm^{-3}. DCP confirmed that the latex had a relatively narrow size distribution, with a weight-average particle diameter, D_w, of 1.03 ± 0.05 μm. Scanning electron microscopy (SEM) studies confirmed that the latex particles were spherical and near-monodisperse, with a smooth, featureless surface morphology. Nitrogen microanalysis indicated that the latex contained around 2.9 wt% PNVP stabilizer. Assuming that all the stabilizer is present at the surface of the latex particles, the adsorbed amount of stabilizer was calculated to be 10.5 mg m^{-2}.

Conducting polymer-coating protocol

Polypyrrole. 71.1 g of an aqueous dispersion of a 1.03 μm diameter polystyrene latex (solids content 21.1%, corresponding to 15.0 g dry latex) was added to 70.0 ml H_2O in a 250 ml screw-capped bottle equipped with a magnetic stirrer. To this was added 12.7 g $FeCl_3$ (47.0 mmol), and the resulting milky orange solution was stirred for 20 min. 1.4 ml (20.0 mmol) of pyrrole was then added *via* syringe, bringing the total pyrrole monomer concentration to 1 v/v%. The solution turned grey and then black over a period of minutes. The reaction mixture was then stirred at room temperature for 24 h prior to centrifugation at 4000 rpm. The supernatant was replaced with distilled water and the sediment redispersed, and this centrifugation–redispersion procedure was repeated four times. A small portion of latex was dried overnight at 50 °C to yield a grey powder for analysis by TGA and pressed-pellet conductivity measurements. Nitrogen microanalyses of the PPY-coated latex and PPY bulk powder indicated a PPY loading of approximately 10.2 wt%. The nitrogen content of the uncoated latex due to the PNVP stabilizer was allowed for in this calculation.

Poly(3,4-ethylenedioxythiophene). 71.1 g of an aqueous dispersion of a 1.03 μm diameter polystyrene latex (solids content 21.1%, corresponding to 15.0 g dry latex) was added to 70.0 ml H_2O in a 250 ml round-bottomed flask equipped with reflux condenser and magnetic stirrer, and heated to 85 °C using an oil bath. To this solution was added 8.2 g $FeCl_3$ (30.0 mmol), and the resulting milky orange solution was stirred for 20 min. Then 4.3 ml of an EDOT–MeOH solution (1 : 2 v/v; 13.0 mmol EDOT) was added *via* syringe, producing a total EDOT monomer concentration of 1 v/v%. The solution turned blue over a period of minutes. The reaction mixture was then stirred at room temperature for 24 h prior to centrifugation at 4000 rpm. The supernatant was replaced with distilled water and the blue sediment was redispersed, and this centrifugation–redispersion procedure was repeated four times. A small portion of latex was dried overnight at 50 °C to yield a light blue powder for analysis by TGA and pressed-pellet conductivity measurements. On the basis of sulfur microanalyses of the PEDOT-coated latex and PEDOT bulk powder, the PEDOT loading of the latex was estimated to be 8.1 wt%.

Base-treatment of conducting polymer powders and conducting polymer-coated latexes

The conducting polymer powders and conducting polymer-coated latexes (typically 1 g batches) were stirred in 100 ml 0.5 M NaOH for 3 h. The powder (or latex) was then isolated by centrifugation and the supernatant was replaced with fresh NaOH and stirred for a further 2 h. The powder (or latex) was then centrifuged and successive supernatants were replaced with distilled water until neutral pH was achieved. After one more centrifugation run the base-treated powder (or latex) was dried overnight under vacuum.

Metal deposition protocol on conducting polymer bulk powders

In a typical experiment, 46.1 mg (0.6 mmol) chloride-doped PPY was added to 30 ml of 0.01 M $AuCl_3$ solution in 1.0 M HCl, thus giving a N : Au ratio of 2.0. The reaction mixture was stirred for 3 h at room temperature before being centrifuged at 4000 rpm for 15 min. The supernatant was then analyzed by UV spectroscopy, and the sediment was dried overnight under vacuum prior to characterization by SEM and TGA.

Metal deposition protocol on conducting polymer-coated latexes

In a typical experiment, 3.2 g of PPY-coated polystyrene latex (solids content 9.4%, corresponding to 300 mg dry latex), pre-adjusted to pH 7 using 0.5 M NaOH, was added to 20.2 ml of 0.012 M $AuCl_3$ solution, also pre-adjusted to pH 7 using 0.5 M NaOH, to create a solution with an overall $AuCl_3$ concentration of 0.01 M, and giving a N : Au ratio of 2.0. The reaction mixture was stirred at room temperature for 3 h before being centrifuged at 4000 rpm for 10 min. The sediment was redispersed in distilled water. This centrifugation–redispersion procedure was repeated twice. A portion of the redispersed latex was kept for analysis by DCP; the remainder was dried overnight under vacuum prior to characterization by SEM, TGA and pressed-pellet conductivity measurements.

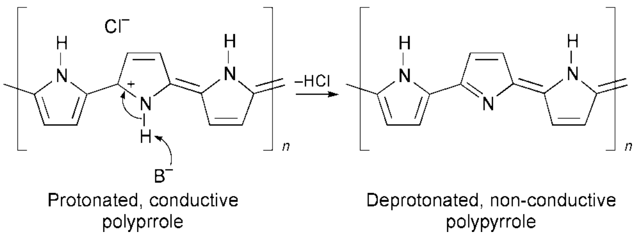
Characterization

Thermogravimetric analyses were carried out in air using a Perkin Elmer TGA 7 instrument operating from room temperature up to 800 °C at a scan rate of 20 °C min^{-1}. UV spectra were obtained using a Perkin Elmer Lambda 2S spectrometer. SEM images were obtained using a Leo S420 Stereoscan instrument at an accelerating voltage of 20 kV and probe current of 25 pA. Samples for secondary images were sputter-coated with gold using an Edwards S150 Sputter Coater. Samples for back-scattered images and energy dispersive X-ray spectroscopy (EDXS) were left uncoated. Back-scattered images were obtained using a two segment back-scattered electron detector with an accelerating voltage of 20 kV and probe current of 100 pA. EDXS was performed using an Oxford Instruments ISIS Analyzer and software using an accelerating voltage of 20 kV and a probe current of 1 nA. Electrical conductivity measurements were made on pressed pellets of dried latexes using a home-made four-point probe apparatus.[20–22] XPS measurements were carried out using a VG Scientific ESCALAB Mk. II spectrometer (interfaced to a VGS 5000S data system based on a DEC PDP 11/73 computer) using an Al-Kα X-ray source operating at a power of 340 W (34 mA and 10 kV).

Results and discussion

Gold deposition on conducting polymer powders

As Kang and co-workers have demonstrated, the redox chemistry of PANI and PPY can be utilized to reduce Au(III) ions from acidic solution to obtain elemental gold.[6–8,10] However, the morphology of this deposited gold has never been investigated. In the present work, a systematic study has been carried out to examine the efficacy of various conducting polymers for the electroless reduction of Au(III) from aqueous solution. Each conducting polymer was evaluated in its doped state and also after base treatment with NaOH. It is well known that base treatment of conducting polymers leads to much lower conductivities.[23–25] In the case of PANI and PPY, this reduced conductivity is due to deprotonation of the OCP backbone, as shown in Scheme 1 below:



Scheme 1

This involves the removal of mobile positive charges (holes) from the OCP backbone. Since charge compensation by the dopant anion is no longer required, this species is no longer electrochemically bound and diffuses out; hence this process is often called ‘dedoping’, although no change in the oxidation state of the OCP backbone has occurred. In the case of thiophene-based OCPs such as PEDOT, the precise role played by the base is more difficult to rationalise as there are no acidic (labile) protons available on the polymer backbone. However, like PPY and PANI, base treatment of PEDOT also resulted in an essentially non-conductive ($<10^{-6}$ S cm^{-1}) powder. Foot *et al.* postulated that treatment of polythiophene films with ammonia led to disproportionation of the base, with the electrons released in this process compensating the mobile holes on the polymer backbone.[24] However, the mechanism by which NaOH renders PEDOT non-conductive remains unclear.

Doped and base-treated conducting polymer powders were added to 0.01 M $AuCl_3$ solutions at either pH 0 or 7. After stirring for 3 h, the conducting polymer powder was isolated by centrifugation and the quantity of gold deposited onto the conducting polymer powders was assessed using TGA. For reactions carried out at pH 0, any decrease in the solution concentration of $AuCl_3$ was measured by UV spectroscopy on the supernatant, using the strong absorbance peak at 314 nm.[10] However, this approach was problematic at higher pH, since the absorption maximum at 314 nm first shifts to lower wavelength (pH 4–5) and then disappears (pH 6–7), presumably due to changes in the nature of the Au species in solution. Results are summarized in Table 1.

At pH 0 PANI and PEDOT are clearly more effective at reducing Au(III) to Au(0) than PPY. There appears to be little difference between using either the doped or base-treated form of PANI. However, the doped forms of PPY and PEDOT gave markedly better results. This is perhaps surprising, as rapid reprotonation (redoping) might reasonably be expected of each of the base-treated polymers under the highly acidic reaction conditions. In all cases there is fairly good agreement between the incombustible residues as measured by TGA and the gold contents expected on the basis of the UV assays. At pH 7, it is apparent that the doped conducting polymers are always more effective reducing agents than the corresponding base-treated conducting polymers, with quantitative removal in the case of doped PEDOT and over 93% removal in the case of doped PPY. Similarly, for reactions carried out at pH 0, the doped forms of PPY and PEDOT are clearly more effective. In addition, both PPY and PEDOT proved to be more effective at pH 7 than at pH 0, regardless of their sample history.

In order to investigate the morphology of the deposited gold, the conducting polymer powders were examined by both conventional SEM and also with a back-scattering detector to examine the morphology of the metallic deposits. The back-scattering technique detects back-scattered electrons, rather than secondary electrons as in conventional SEM. The propensity of an element to scatter electrons depends on its atomic number. Elements of higher atomic number will scatter more electrons, and so will give rise to stronger signals in the back-scattering image. Fig. 2(a) shows the conventional SEM image (left) and the back-scattered image (right) of the doped PPY after treatment with $AuCl_3$ at pH 0, resulting in the incorporation of 37.0 wt% incombustible residue by TGA. The back-scattered image clearly shows discrete areas of high contrast, suggesting the presence of an element with high atomic number. Energy dispersive X-ray spectroscopy (EDXS) was used to produce an X-ray map (not shown) of this sample. A far greater gold signal was obtained from the areas of high contrast than from the surrounding polymer. Regardless of conducting polymer type and sample history, identical results were obtained at pH 0: ill-defined, polydisperse (*ca.* 1–10 μm) gold-containing particles were observed. However, deposition is certainly not homogeneous, and this is most likely due to strong nucleation occurring after the initial reduction of a small fraction of Au ions. These metallic gold particles then act as nucleation sites for further reduction/deposition, leading to the formation of the observed polydisperse, micrometer-sized gold particles. No chlorine signal was detected from these gold features, which strongly suggests that the particles are metallic gold rather than $AuCl_3$, as expected if the reduction of gold ions from solution has taken place. This interpretation is in good agreement with the previous results reported by Kang and co-workers.[6–8,10]

The conducting polymer powders exposed to $AuCl_3$ at pH 7 were similarly characterized in terms of their morphology. Fig. 2(b) shows the conventional SEM image and back-scattering image for doped PPY powder after exposure to $AuCl_3$ at pH 7 (54.5 wt% gold by TGA). The back-scattered image clearly shows that there are discrete areas of high contrast, which were confirmed to be gold by EDXS analysis. Moreover, these gold features are considerably smaller (*ca.* 1 μm) and more highly dispersed than the ill-defined metallic deposits obtained at pH 0 [see Fig. 2(a)]. However, these improvements in the degree of dispersion of the gold are increased dramatically when base-treated PPY is used at pH 7 (43.5 wt% gold), see Fig. 2(c), with the back-scattered image revealing even smaller (*ca.* 100–400 nm) gold deposits. Finer metallic deposits are also clearly observed in the SEM images of both the base-treated PANI and PEDOT powders at pH 7 (not shown). Overall, these results clearly show a strong correlation between the morphology of the deposited gold obtained at pH 7 and the sample history of the conducting polymer, with the base-treated polymers leading to smaller, more finely dispersed gold deposits. In addition, TGA shows that the base-treated polymers are not as effective at reducing gold from solution as their doped counterparts. Similar differences in behaviour between the doped and base-treated powders were apparent from the UV and TGA analyses at pH 0, but under these conditions there was no obvious trend in the morphology of the deposited gold, perhaps due to the very rapid reprotonation of the polymer at pH 0, which would be expected to obscure any differences. Reactions were repeated at 0 and 50 °C, but although there were the expected changes in the rate of reaction, no apparent difference in the morphology of the deposited gold was observed.

In order to investigate further why the morphology of the deposited gold differed depending on whether doped or base-treated OCPs were used at pH 7, the reactions using doped and base-treated PPY were repeated and the solution pH was

Table 1 Summary of gold contents as determined by UV spectroscopy and TGA analyses after treating conducting polymer powders with 0.01 M $AuCl_3$ at pH 0 and pH 7 at 25 °C for 3 h

	pH 0			pH 7	
Conducting polymer	% Decrease in [Au][a]	Calculated TGA residue (wt%)[b]	Actual TGA residue (wt%)	Actual TGA residue (wt%)	Calculated % decrease in [Au][c]
Doped PPY	58.3	42.7	37.0	54.5	93.8
Base-treated PPY	44.2	40.1	34.5	43.5	50.9
Doped PANI	85.4	43.5	35.2	38.8	70.5
Base-treated PANI	86.5	48.5	37.6	22.5	26.8
Doped PEDOT	90.7	37.0	32.5	39.4	100.5
Base-treated PEDOT	69.7	32.9	34.5	36.2	76.9

[a] As measured by UV–vis absorption spectroscopy. [b] Based on the decrease in [$AuCl_3$] in the supernatant as measured by UV spectroscopy and assuming all TGA residue is metallic Au. [c] As calculated from the TGA residue assuming that all of the incombustible residue is metallic Au reduced from Au(III) in the supernatant.

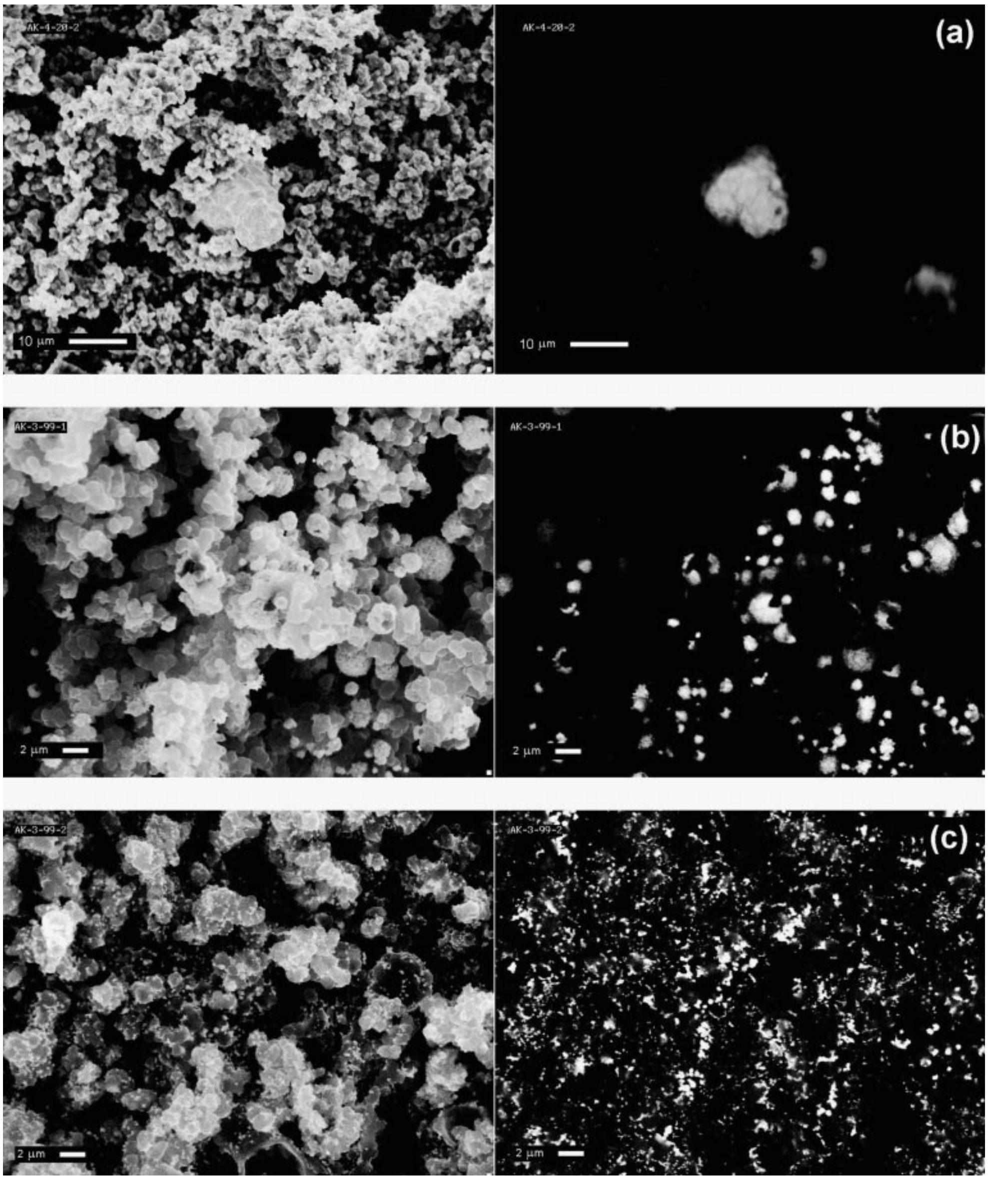


Fig. 2 Conventional SEM (left) and back-scattered (right) images of: (a) doped PPY powder stirred in 0.01 M $AuCl_3$ at pH 0; (b) doped PPY powder stirred in 0.01 M $AuCl_3$ at pH 7 and; (c) base-treated PPY powder stirred in 0.01 M $AuCl_3$ at pH 7. In all cases the N : Au molar ratio was 2.0, and reactions were carried out for 3 h at 25 °C.

monitored throughout the reaction. In addition, aliquots were taken at regular intervals, centrifuged immediately, and the sedimented powders were dried under vacuum. TGA was then performed on the dry powders and the decrease in the gold solution concentration calculated from the measured gold residues. The results are shown in Fig. 3. It can clearly be seen that there is greater depletion of Au(III) from solution when using the doped rather than base-treated PPY, and the final concentrations after 3 h are in excellent agreement with the results from earlier experiments (see Table 1). However, the pH of the reaction solution decreases markedly from pH 7 to pH 3 when using doped PPY. The pH of the reaction involving base-treated PPY, on the other hand, only drops slightly from pH 7 to 6.4. Further control experiments were carried out in which doped and base-treated PPY powders were added to distilled water and gave similar time-dependent pH curves, suggesting that the change in pH shown in Fig. 3 is due to the presence of the polymer rather than due to any reaction with the $AuCl_3$ itself. Control experiments carried out with the doped and base-treated forms of PANI and PEDOT in distilled water also resulted in similar pH changes.

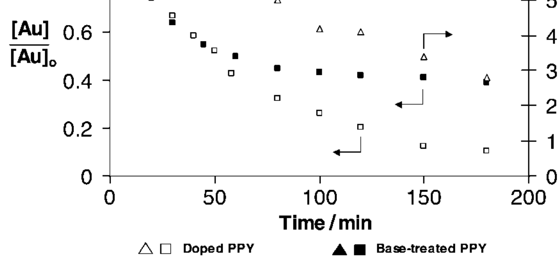


Fig. 3 Variation of solution pH and gold solution concentration with time for the reaction of doped and base-treated PPY bulk powder at 25 °C. The initial $AuCl_3$ concentration was 0.01 M at pH 7.

During the acidic conditions of the conducting polymer syntheses, one would expect the polymer chains to become highly protonated. This would obviously be expected for PANI since it is synthesized in 1.2 M HCl, and the use of $FeCl_3$ as oxidant for the PPY and PEDOT syntheses leads to reaction mixtures with a solution pH of less than one. It has been shown that in such acidic media, conductive PPY films can be protonated to a greater degree than one would expect from their idealized structure, with some of the pyrrole ring nitrogens accepting a second proton.[25] Similarly, at such low pH it may be possible that PEDOT becomes protonated to some degree through either the ring sulfur atom or the ether oxygen(s). On addition of distilled water, however, these highly protonated, doped OCP powders should release these weakly bound protons, leading to a lower solution pH. However, the base-treated polymers should have very few, if any, labile protons and hence not be capable of lowering the pH of a neutral aqueous solution.

It can be postulated that the observed changes in the morphology of the deposited gold are dictated mainly by the solution pH during reaction. At pH 0, the deposited gold particles are *ca.* 10 μm in diameter. When the doped OCPs are added to solutions of $AuCl_3$ at pH 7, which actually results in an effective solution pH of 3–5, the gold deposits are *ca.* 1 μm in diameter. However, when base-treated OCPs are added to neutral $AuCl_3$ solutions, the solution pH decreases only slightly to pH 6.4–6.6 and the gold deposits are well-dispersed and are approximately 100–400 nm in diameter. The reason for such a trend remains unclear at the present time, but it may well be related to the variation in the precise nature of the Au(III) species as the pH changes. As mentioned earlier, the UV absorbance of an $AuCl_3$ solution changes markedly as the solution pH is adjusted from pH 0 to pH 7. This clearly suggests that the chemical structure of the Au(III) species is pH-dependent. There is no literature evidence for the simple aqua ion $[Au(OH_2)_4]^{3+}$, but various mixed chloro–aqua and chloro–hydroxo complexes have been suggested, with the actual species present depending on the solution pH.[26] It is also likely that such structural changes will influence the electrode potential of the reduction of Au(III) to Au(0). The electrode potentials of OCPs have been investigated,[1,27] and it is known that these are affected by pH.[28] We suggest that the pH dependence of the electrode potentials of the OCP and Au(III) species significantly affects the rate at which the redox chemistry occurs, and hence affects the morphology of the deposited gold.

Gold deposition on conducting polymer-coated latexes

Given the increased degree of dispersion of the gold deposits achieved by using base-treated OCPs at pH 7, similar protocols were used in attempts to synthesize gold-clad latex particles. A polystyrene latex was synthesized *via* dispersion polymerization, and SEM studies [see Fig. 4(a)] confirmed that the uncoated latex particles were spherical and had a smooth, featureless morphology. Batches of the polystyrene latex were

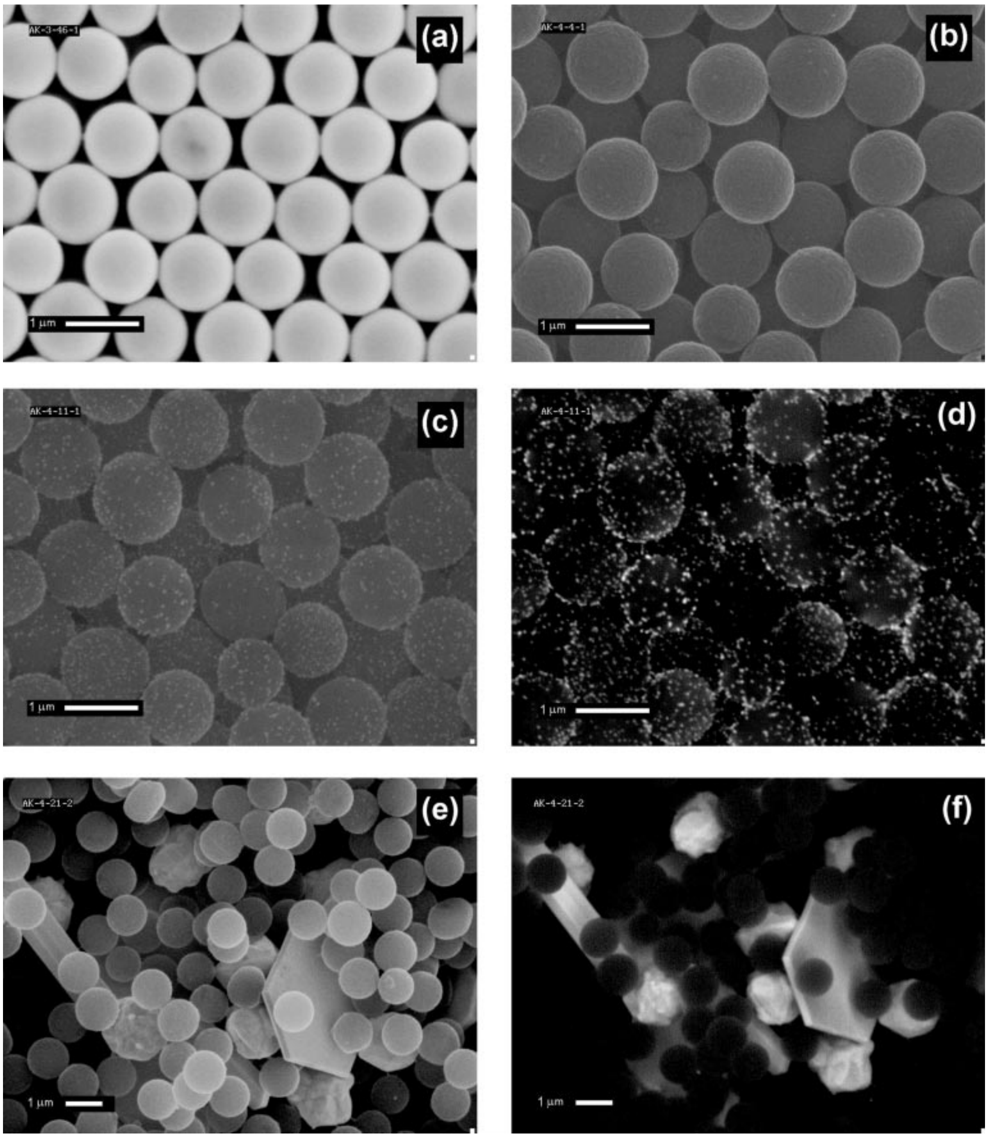


Fig. 4 (a) SEM image of uncoated 1.03 μm diameter polystyrene latex; (b) SEM image of the same latex coated with 10.2 wt% PPY followed by base treatment; (c) SEM image of this base-treated, PPY-coated latex after exposure to 0.01 M $AuCl_3$ at pH 7; (d) back-scattered image of the base-treated, PPY-coated latex after exposure to 0.01 M $AuCl_3$ at pH 7; (e) SEM image of the base-treated, PPY-coated latex after exposure to 0.01 M $AuCl_3$ at pH 0; (f) back-scattered image of the base-treated, PPY-coated latex after exposure to 0.01 M $AuCl_3$ at pH 0.

coated with PPY and PEDOT, respectively. However, the results obtained for the OCP bulk powders at pH 7 suggested that PANI was not a suitable choice for coating the polystyrene latex due to its low efficacy at reducing gold from solution. The synthesis and extensive characterization of such core–shell particles has been described in detail in our previous publications.[13,15,17,19] Since a more homogeneous deposition of gold was clearly evident when using base-treated conducting polymers (as judged from the images presented in Fig. 2) the coated latexes were stirred in 0.5 M NaOH overnight. Characterization data are summarized in Table 2. The pH of the first supernatant after centrifugation of the reaction mixture was measured, and in all cases was typically between pH 6.6 and 6.9, suggesting that the pH had not decreased significantly during reaction. A series of such experiments was carried out, and characterization data are summarized in Table 3.

As the amount of $AuCl_3$ is increased relative to the conducting polymer, a greater amount of gold is deposited onto the latex particles. However, in no case is there quantitative removal of gold from solution. It is worth emphasizing that when a control experiment was carried out in which uncoated polystyrene latex was stirred in 0.01 M $AuCl_3$ at pH 7 for 3 h, no change in either the gold solution concentration or the colloidal stability of the latex was observed. Furthermore, TGA of this latex revealed no incombustible residues, thus demonstrating that the conducting polymer component is essential for the spontaneous reduction of $AuCl_3$ to occur. The SEM image in Fig. 4(b) shows the base-treated, PPY-coated latex before treatment with $AuCl_3$. As expected, the conducting polymer overlayer is relatively smooth at this low loading.[13] The back-scattered image of this untreated latex (not shown) is completely featureless, confirming that no elements of high atomic number are present. Conventional SEM and back-scattered images of the same latex after exposure to $AuCl_3$ at pH 7 with a N : Au ratio of 2.0, resulting in a gold loading of 9.4 wt%, are shown in Fig. 4(c) and 4(d), respectively. Similar results were achieved using the PEDOT-coated latex. The SEM and back-scattered images clearly show that the latex surface has become randomly decorated with very small deposits (*ca.* 40–60 nm in size) of a heavy element, which was confirmed to be gold using EDXS.

It is unclear from these images whether the gold deposits actually adhere to the latex surface, or whether free colloidal gold particles co-exist with the latex and adsorb onto the latex surface during SEM sample preparation. However, further studies of the gold-decorated latexes were carried out in which very dilute samples in water were allowed to evaporate in air before examination by SEM (image not shown). If any free colloidal gold particles co-existed with the latex some fraction would be expected to be well-separated from the latex particles upon evaporation. However, gold nanoparticles were again only located on the surfaces of the well-separated latex particles, suggesting good adhesion to the latex surface. Moreover, the dispersions have been through repeated centrifugation–redispersion cycles, in which any discrete gold and latex particles would be expected to separate within the centrifuge tube due to differences in their size and mass (simple calculations show that the mass of a 1 μm polystyrene latex particle is approximately 500 times greater than that of a 50 nm gold particle). Since this separation does not occur, there must be some form of attractive interaction between the deposited gold and the latex.

It was believed that the ultrafine morphology of the gold deposits on the base-treated conducting polymer-coated latexes was a direct result of carrying out the reactions at neutral pH, as illustrated with the conducting polymer powders in Fig. 2. In order to confirm this hypothesis, a control experiment was carried out in which the base-treated, PPY-coated polystyrene latex was stirred in 0.01 M $AuCl_3$ at pH 0 for 3 h, resulting in the incorporation of 2.1 wt% gold, by TGA. The SEM and back-scattered images, in Fig. 4(e) and 4(f) respectively, clearly show that the latex particles remain undecorated; the gold is only present as polymorphic, micrometer-sized crystalline deposits.

In order to verify that reduction to zero-valent gold had occurred, XPS studies were carried out on the gold-decorated latexes. Fig. 5(a) shows the survey spectrum for the base-treated, PPY-coated polystyrene latex. Signals due to C and N from the latex and PPY overlayer are clearly apparent, as well as an O signal arising from the PNVP steric stabilizer[17] and over-oxidation[29] of the conducting polymer. In addition to this, a small amount of Cl is detected, suggesting that the dedoping process was not completely efficient. The Si signal suggests some pump oil or glass contamination. The survey spectrum of the same latex after treatment with 0.01 M $AuCl_3$ at pH 7, resulting in the incorporation of 9.4 wt% gold, is shown in Fig. 5(b). It is clear that, in addition to the peaks shown in Fig. 5(a), a strong pair of doublets can be detected at *ca.* 85 and

Table 2 Summary of characterization data for 1.03 μm PNVP-stabilized polystyrene latex coated with thin overlayers of either PPY or PEDOT

OCP type	OCP loading (wt%)	Theoretical OCP overlayer thickness/nm	Conductivity of doped OCP/S cm^{-1}	Conductivity after base-treatment/S cm^{-1}	Colloidal stability[a]
None[b]	0.0	—	$<10^{-6}$	$<10^{-6}$	Stable
PPY	10.2	13.7	0.9	$<10^{-6}$	Minimal aggregation
PEDOT	8.1	9.7	2×10^{-3}	$<10^{-6}$	Minimal aggregation

[a]Assessed qualitatively using DCP. [b]Uncoated polystyrene latex.

Table 3 Summary of characterization data for base-treated, PPY-coated and PEDOT-coated polystyrene latexes after stirring in 0.01 M $AuCl_3$ solution at 25 °C for 3 h at pH 7

OCP type	X : Au ratio[a]	Theoretical TGA residue (wt%)[b]	Actual TGA residue (wt%)	Conductivity/ S cm^{-1}	Colloidal stability[c]
PPY	3.0	9.4	6.9	$<10^{-6}$	Minimal aggregation
	2.0	13.3	9.4	$<10^{-6}$	Minimal aggregation
	1.0	23.7	11.2	$<10^{-6}$	Aggregation
	0.5	38.0	12.5	$<10^{-6}$	Aggregation
PEDOT	3.0	3.7	1.6	$<10^{-6}$	Minimal aggregation
	2.0	5.3	4.8	$<10^{-6}$	Aggregation
	1.0	10.2	5.4	$<10^{-6}$	Aggregation
	0.5	18.6	8.3	$<10^{-6}$	Aggregation

[a]Where X = N for PPY, and X = S for PEDOT. [b]Assuming quantitative reduction of gold from solution. [c]Assessed qualitatively using DCP.

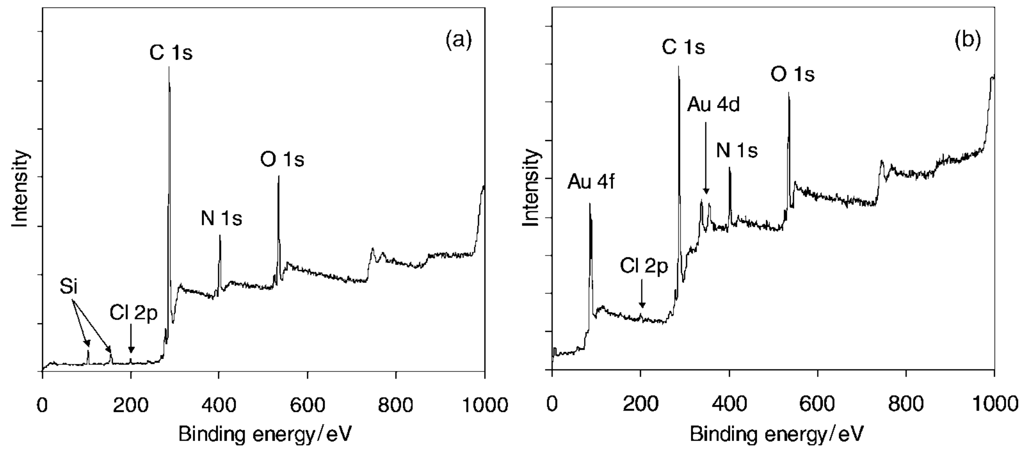


Fig. 5 XPS survey spectra of (a) base-treated, PPY-coated PS latex; (b) the same latex after exposure to 0.01 M $AuCl_3$ at pH 7 for 3 h, resulting in the incorporation of 9.4 wt% metallic gold.

340 eV, which are assigned to photoelectrons originating from Au 4f and Au 4d energy levels, respectively.

Close inspection of the peak-fitted Au 4f core-line spectrum for the base-treated, PPY-coated polystyrene latex [see Fig. 6(a)] after exposure to $AuCl_3$ reveals two strong signals due to electrons from Au $4f_{5/2}$ and $4f_{7/2}$ energy levels. Each signal is adequately peak-fitted with only one component, indicating that only one gold species is present. The $4f_{7/2}$ peak is centred at *ca.* 84 eV, and the accompanying $4f_{5/2}$ peak at *ca.* 87.6 eV. This doublet is characteristic of zero-valent gold.[30] In addition, there is no sign of any signal due to Au(III), for which a $4f_{7/2}$ peak would be expected at *ca.* 86–87 eV.[30] This proves unambiguously that reduction of Au(III) to Au(0) has indeed taken place, and is in excellent agreement with the work of Kang and co-workers.[7,10] Similar results were observed for the base-treated, PEDOT-coated latex after exposure to $AuCl_3$.

The peak-fitted N 1s core-line spectrum of the base-treated PPY-coated polystyrene latex before treatment with $AuCl_3$ is shown in Fig. 6(b). Three nitrogen environments are present, centred at 398.3, 400.1 and 401.5 eV, which are assigned to =N–, –NH–, and –N^+–, respectively.[29] The fact that a signal can be detected from the –N^+– species indicates that base treatment was not completely effective. After treatment with $AuCl_3$ at pH 7, leading to the deposition of 9.4 wt% gold onto the latex, the N 1s core-line spectrum appears to be subtly different [see Fig. 6(c)]. Although the peak-fitting and binding energies are similar, the relative peak area due to the –N^+– species compared to the total area of the N 1s peak increased

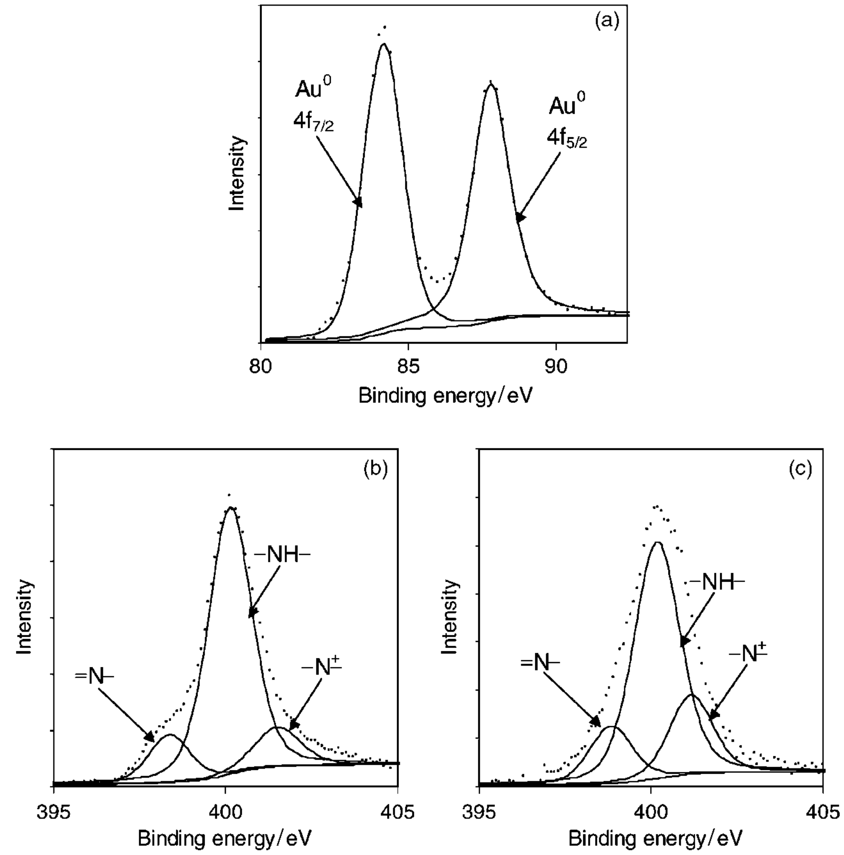


Fig. 6 (a) Au 4f XPS core-line spectrum for the base-treated, PPY-coated latex decorated with 9.4 wt% gold; (b) N 1s core-line spectrum for the base-treated, PPY-coated latex; (c) N 1s core-line spectrum for the base-treated, PPY-coated latex after exposure to 0.01 M $AuCl_3$ at pH 7.

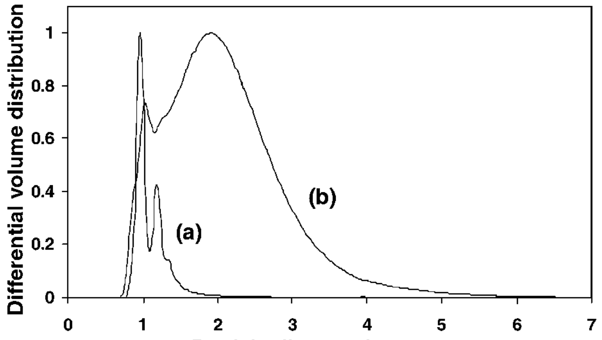


Fig. 7 Particle size distribution curves obtained using the disk centrifuge for (a) base-treated, PEDOT-coated polystyrene latex (8.1 wt% PEDOT), and (b) the same latex decorated with 4.8 wt% metallic gold.

from 11 to 20% after treatment with $AuCl_3$. This is further evidence that redox chemistry has occurred, and that the PPY backbone becomes more oxidized as the Au(III) ions in solution are reduced to Au(0). A similar change is evident in the N 1s core-line spectra of PPY–silica nanocomposites after stirring in $AuCl_3$ in 0.5 M HCl, but this was not discussed by Kang and co-workers.[10] Similar changes can also be observed in the S 2p spectrum (not shown) of the base-treated, PEDOT-coated latex, with the signal due to the S^+ species increasing in relative intensity after exposure to $AuCl_3$.

The colloidal stability of the latexes was assessed qualitatively using DCP. Fig. 7(a) shows the DCP curve for the base-treated, PEDOT-coated polystyrene latex before treatment with $AuCl_3$. The shape of this curve indicates two populations: the major population is discrete, singlet particles and the minor population represents doublet particles. This is in excellent agreement with previous results obtained for conducting polymer-coated latexes at similar conducting polymer loadings.[13–15] The high degree of dispersion is possible because the conducting polymer is located *within* the solvated PNVP steric stabilizer layer.[19] However, once the base-treated, PEDOT-coated polystyrene latex is decorated with 4.8 wt% gold, the degree of aggregation increases significantly, with far more doublets and higher aggregates being detected [see Fig. 7(b)]. The gold deposits are *ca.* 40–60 nm in diameter, which is greater than the estimated 20–30 nm thickness of the PNVP steric stabilizer layer, and gold, like all metals, has a high Hamaker constant.[31] This suggests that the surface-confined gold nanoparticles act as heteroflocculants for the latex particles.

It should be noted that although the latex surface appears to be fairly evenly decorated with gold nanoparticles, these metallic deposits do not form a homogeneous coating or shell. Pressed-pellet conductivity measurements confirmed that all of the gold-decorated latexes were non-conductive (see Table 3). This is not surprising, as the base-treated conducting polymer overlayers are non-conductive, and although the composites contain up to a maximum of 12.5 wt% gold, this corresponds to only 0.8 vol%, which is well below the percolation threshold for conductivity. The discrete, well-separated gold particles clearly do not form a conductive pathway to allow efficient charge transport.

Finally, it has been shown that metallic particles supported on a conducting polymer matrix can act as catalytic sites for multi-electron transfer processes.[32,33] For example, PANI films were examined by Lamy and co-workers, who showed that modification of a film with platinum nanoparticles formed by electrochemical reduction facilitated the electro-oxidation of methanol and carbon monoxide.[34] The catalytic activity of gold nanoparticles has also been demonstrated.[35] Tateishi and co-workers have shown that 1–12 nm gold particles deposited onto glassy substrates *via* vacuum evaporation techniques showed excellent electrocatalytic activity towards the oxidation of ethanol, formaldehyde and acetaldehyde in alkaline media.[36,37] More recently Hammache *et al.* reported that *ca.* 400 nm gold particles electrochemically deposited onto PPY/Fe electrodes acted as catalysts for the electrochemical oxidation of methanol in acidic media.[38] Other workers have shown that metal nanoparticles supported on latex particles exhibit high catalytic activity. Akashi and co-workers demonstrated that 1–2 nm platinum colloids immobilized upon 500 nm poly(*N*-isopropylacrylamide)-stabilized polystyrene particles were stable, active heterogeneous catalysts for the hydrogenation of allyl alcohol in water.[39] Thompson and co-workers, on the other hand, showed that 500 nm diameter poly(2-vinylpyridine) particles acted as an excellent support for 1–4 nm diameter palladium colloids. These composite particles were shown to be good catalysts for Suzuki-, Heck- and Stille-type carbon–carbon bond forming reactions.[40] In the latter example, the strong catalytic activity of the system was partly attributed to the high degree of dispersion achieved using a colloidal support.

In the light of the above reports on the effectiveness of precious metal particles within conducting polymer matrices and on latex supports as catalysts in various reactions, we suggest that the gold-decorated, conducting polymer-coated latex particles synthesized in this study could potentially be useful as novel supported catalysts.

Conclusions

A systematic study has been carried out to examine the morphology of elemental gold obtained from redox interaction between conducting polymer bulk powders and Au(III) ions in solution. When using the doped forms of the conducting polymers, SEM and back-scattering studies clearly showed that the size of the deposited gold particles decreased from *ca.* 10 to *ca.* 1 μm as the pH was increased from pH 0 to 7. However, the smallest gold particles (100–400 nm) and greatest degree of dispersion were obtained when using the base-treated forms of the polymers at pH 7. This trend in morphology is believed to be linked to the solution pH during reaction, which remains close to neutral when using the base-treated polymers at pH 7 and seems to suppress nucleation. These optimized parameters were then used to assess the feasibility of depositing gold overlayers onto the surfaces of conducting polymer-coated polystyrene latexes. A series of latexes was obtained, containing up to 12.5 wt% gold, the surfaces of which were randomly decorated with 40–60 nm gold nanoparticles. However, in no cases were homogeneous gold overlayers obtained and the composite particles were shown to be non-conductive. This is understandable given the low volume fraction of gold (only *ca.* 0.8 vol%) and its discrete, well-separated nature on the latex surface. XPS studies confirm that reduction to zero-valent gold had indeed taken place, and this was accompanied by an observed increase in the oxidation state of the conducting polymer overlayer. The colloidal stability of the coated latexes, as assessed by DCP, decreased after decoration with gold, most probably due to the surface-confined metallic nanoparticles acting as heteroflocculants. Finally, it is believed that these gold-decorated, conducting polymer-coated latexes may be useful as novel supported catalysts.

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