Electroless Reduction and Precipitation of Gold from Acid Solution by Polypyrrole

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SYNOPSIS

The oxidation of the 25% intrinsically oxidized polypyrrole, containing 25% [$=$ N $-$] and 75% [$-$ NH $-$], and the subsequent reprotonation and reduction of the highly intrinsically oxidized polymer in acid gold solution were utilized for the spontaneous and sustained reduction of gold. The X-ray photoelectron spectroscopic (XPS) results indicate that only elemental gold [or Au(0)] accumulates on the polymer film or powder surfaces. The N1s core-level spectra of the protonated and deprotonated polypyrrole after metal reduction suggest that the intrinsic structure of the polymer at the polymer/Au interface remains intact, even at [Au]/[N] mol ratios substantially above 1. The process, however, is limited by the decreasing effective surface area of the polymer due to Au coverage. The Au reduction behavior of polypyrrole was also compared to that of polyaniline. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Gold has always been a precious metal in high demand for its decorative and ornamental purposes for centuries. Together with other precious metals, such as platinum and palladium, these metals are of strategic importance for the present-day high-technology and electronic industries. Thus, gold recovery from primary and secondary sources, such as ores, leach solutions, electronic scraps, and waste electroplating solutions, has become an important technology.[1] Gold recovery by less energy-intensive processes, such as electroless plating,[2] activated carbon,[3] biomass and biomaterials,[4-6] and polymeric adsorbents,[7,8] has also been actively explored. Gold extraction from chloride solution has risen to prominence during the last two decades,[9] as this recovery process does not have the adverse environmental effects of cyanidation. As the demand for gold increases, extraction of the metal from the acid solutions needs to be accomplished with greater efficiency.

Our recent study[10] on the century-old aniline family of polymers[11] has suggested that the oxidation of the fully reduced leucoemeraldine (LM, containing all amine, $-$ NH $-$, nitrogens) and the 50% intrinsically oxidized emeraldine (EM, containing 50% amine and 50% imine, $=$ N $-$, nitrogens) states of the polymer and the subsequent reprotonation and reduction of the 75% oxidized nigraniline (NA) and the fully oxidized pernigraniline (PNA) in acid gold solution can be utilized for the spontaneous and sustained reduction of gold. In view of the fact that polypyrrole (PPY) has similar intrinsic redox properties associated with the chain nitrogens,[12,13] it should be interesting to explore the potential application of this polymer in the process of self-sustained electroless precipitation of gold in elemental form from acid solutions. The chemical structures resulting from the interconversion between some redox and protonated states of PPY are depicted in Figure 1. It should be noted that polymers with intrinsic oxidation states approaching 50% can be readily prepared.[12] However, as their environmental stability is not yet well characterized, they are not used in the present study.

EXPERIMENTAL

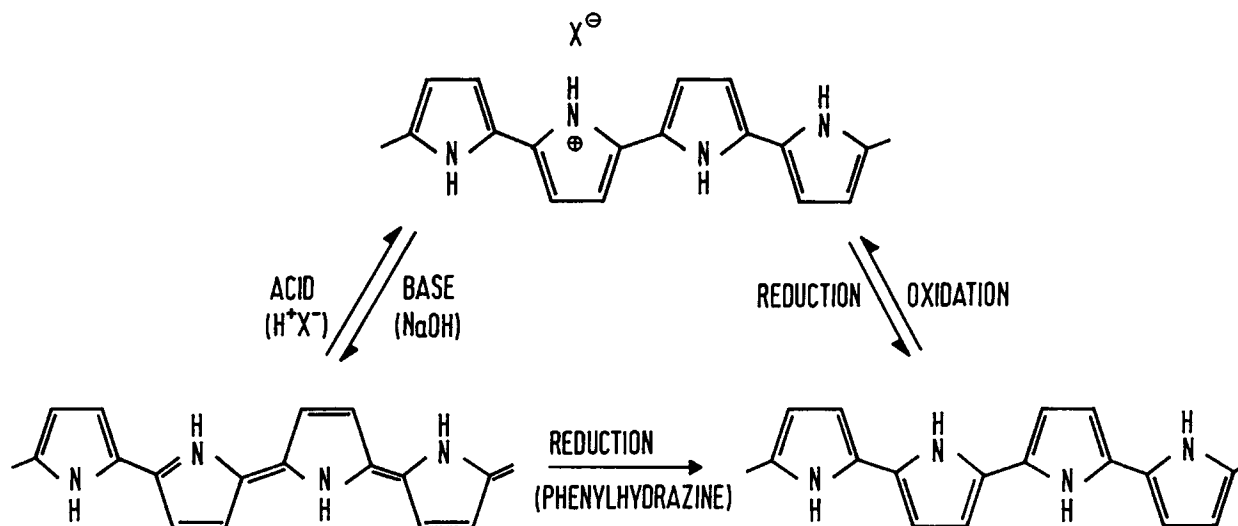Polypyrrole (PPY) powders were first prepared in their protonated salt form via the oxidative chemical

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**Figure 1** Interconversions between various oxidation states in PPY.

polymerization of pyrrole (Merck) by ferric chloride hexahydrate (FeCl$_3$·6H$_2$O) according to the method reported in the literature.[14] They were then converted to the 25% deprotonated neutral base form, DP-PPY, by treatment with excess 0.5M NaOH.[13] Some of the DP-PPY powders were subsequently converted to the fully reduced polymer.[13] The PPY films with a thickness of about 7 μm were obtained in their oxidized salt form by electrochemical polymerization[15] of pyrrole in aqueous toluene-4-sulfonic acid solution. They were then deprotonated by treatment with excess 0.5M NaOH to obtain the 25% intrinsically oxidized form. In each Au reduction experiment, a film size of about 3 × 3 cm (total surface area of about 18 cm^2, both sides) was used. The weight of each film was about 7 mg.

Solutions with different gold concentrations were prepared by diluting chloroauric acid solution containing 1000 mg dm^{-3} of Au in 0.5M HCl (supplied by BDH Chemicals). Gold concentration in each solution before and during reduction was determined by UV-visible absorption spectroscopy (Shimadzu Model UV-160A spectrophotometer) and by atomic absorption spectroscopy (Shimadzu AA-680 atomic absorption/flame emission spectrophotometer). Particle-size analyses of the polymer powders were carried out on a laser particle sizer (Malvern Instruments, Model 3600E). X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons) at a constant retard ratio of 40. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). To compensate for surface charging effects, all binding energies were referenced to the Cls neutral carbon peak at 284.6 eV. In peak synthesis, the line width (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 ±10%. The core-level spectra reported were obtained at photoelectron take-off angles (measured with respect to the sample surface) of 75° and 20° for the film samples and 75° for the powder samples.

RESULTS AND DISCUSSION

Earlier XPS studies on polypyrrole[13,16,17] synthesized by different methods have demonstrated that the iminelike ($=$N$-$), aminelike ($-$NH$-$), and positively charged nitrogens corresponding to any particular intrinsic oxidation state and protonation level of the polymer can be quantitatively differentiated in the properly curved-fitted N1s core-level spectrum. They correspond to peak components with binding energies (BEs) at about 397.8, 399.7, and > 400.5 eV. Figure 2(a)–(d) show the N1s core-level spectra for a 50% deprotonated or intrinsically oxidized PPY, a 25% deprotonated PPY (DP-PPY), a 90% reduced PPY, and a 1M HCl protonated DP-PPY. Protonation of the 50% intrinsically oxidized PPY gives rise only to a 25% protonated polymer with a N1s spectrum not unlike that shown in Figure 2(d). The presence of various intrinsic redox states and the fact that protonation occurs preferentially
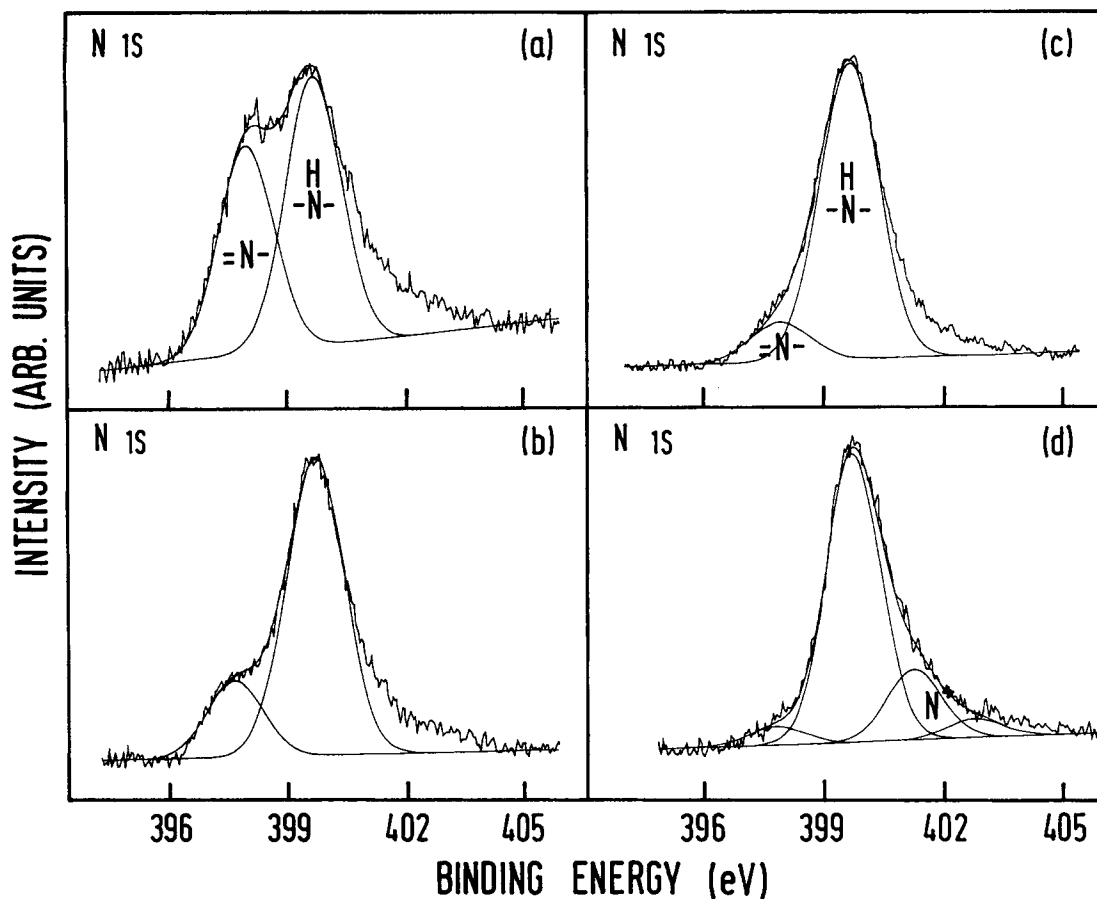
Figure 2 N1s core-level spectra of (a) a 50% deprotonated PPY, (b) a 25% deprotonated PPY (DP-PPY), (c) a 90% reduced PPY, and (d) a HCl protonated DP-PPY.

at the imine units readily confirm the chemical similarities between the nitrogens in PPY and polyaniline.[17] Thus, the conductive states of PPY and polyaniline correspond to those of the 25% protonated DP-PPY and the 50% protonated emeraldine, respectively.

Figure 3(a) shows the typical rates of Au removal and reduction by the 25% deprotonated DP-PPY films of similar size (see Experimental section) in 150 mL of chloroauric acid solutions of different initial concentrations. In each case, the initial rates of Au uptake by the polymer films exhibit a strong dependence on the concentration of the acid Au solution. However, upon increasing the surface coverage of the film by elemental Au (see below), the effect of surface area limitation on the charge-transfer interactions between the polymer film and the Au solution becomes predominant. As a consequence, the rate of Au reduction is gradually retarded, especially in the case of the solution with very high initial Au concentration (100 mg dm^{-3}). Nevertheless, the polymer film has accumulated

about its own weight of Au in the acid solution containing, initially, 50 mg dm^{-3} of Au under the present experimental condition.

The effect of surface area limitation on the present Au reduction process is best demonstrated by the 10-fold increase in the reduction rate for DP-PPY base powders (particle size, Sauter mean diameter about 40 μm) of comparable weight as the films. The corresponding rates of Au reduction by DP-PPY powders are shown in Figure 3(b). The increase in effective surface area of the powders also allows a substantially higher degree of Au loading. The polymer powders can readily accumulate two to three times its own weight of Au before encountering significant surface reaction limitations.

The intrinsic structure of the polymer after Au reduction and the fact that the $AuCl_4^-$ ion has been reduced to elemental gold or Au(0) by the polymer are readily revealed by the XPS results. Figure 4(a)–(c) show the respective N1s, Au4f, and Cl2p core-level spectra, obtained at a photoelectron take-off angle of 75°, for a DP-PPY base film after exposure
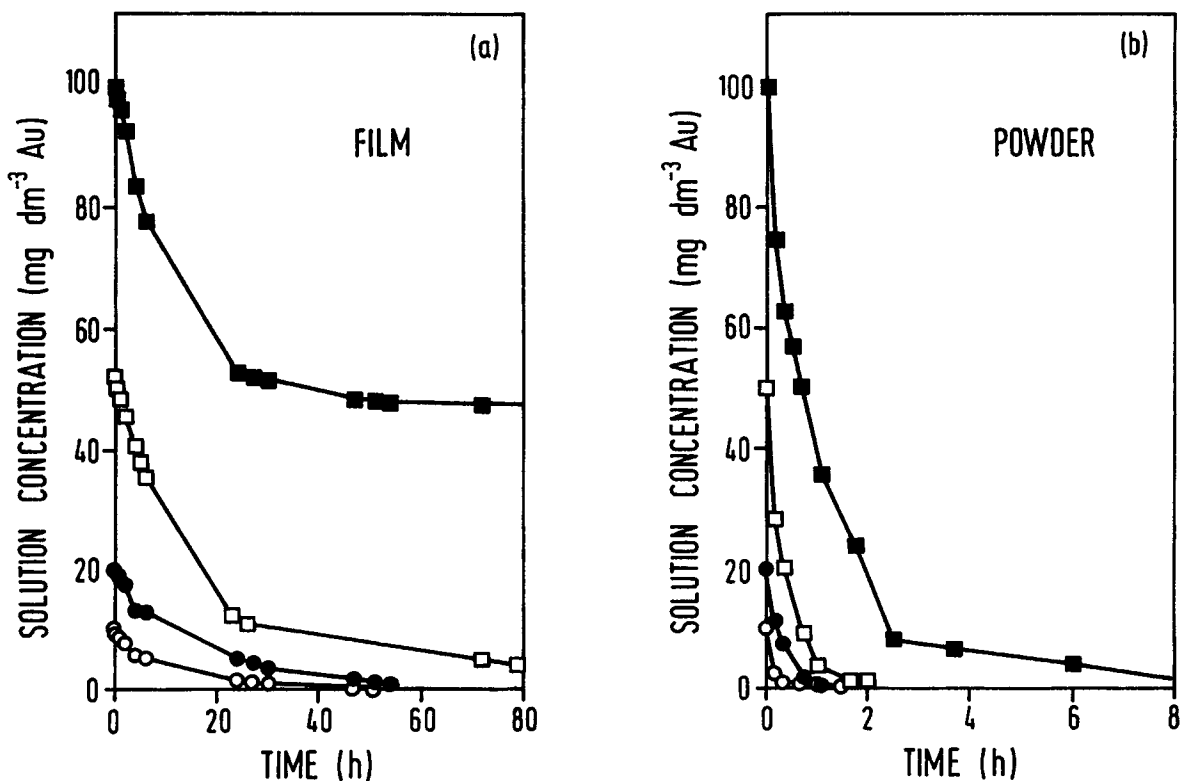
Figure 3 Rates of Au reduction in chloroauric acid solutions of different initial concentrations by (a) DP-PPY base films and (b) DP-PPY base powders. The initial concentrations of the chloroauric acids are (■) 100 mg dm^{-3}, (□) 50 mg dm^{-3}, (●) 20 mg dm^{-3}, and (○) 10 mg dm^{-3} Au.

to an acid Au solution containing 20 mg dm^{-3} of Au for about 48 h. The surface region analyzed has a [Au]/[N] mol ratio of about 1.7, as determined from the sensitivity factor-corrected Au4f and N1s core-level spectral areas. A [Au]/[N] mol ratio as high as 3.2 was obtained at the more glancing take-off angle of 20°. The Au4f core-level spectrum reveals, unambiguously, the presence of a predominantly single Au species with a Au4f$_{7/2}$ BE at about 83.8 eV, characteristic of Au(0).[18] The N1s core-level spectrum is characteristic of that of a partially HCl-protonated DP-PPY base, with protonation occurring preferentially at the imine units. Three nitrogen species, viz., the imine nitrogens, the amine nitrogens, and the positively charged nitrogens, are discernible from the curve-fitted N1s core-level spectrum. The Cl2p core-level spectrum is best curve-fitted with three spin-orbit split doublets (Cl2p$_{3/2}$ and Cl2p$_{1/2}$), with the BEs for the Cl2p$_{3/2}$ peaks lying at about 197.1, 198.6, and 200.2 eV.[13] The highest and the lowest BE components are attributable to the covalent and ionic chlorine species (— Cl and Cl$^-$), respectively. The chlorine species

with an intermediate BE, Cl* [dashed component in Fig. 4(c)], which has been widely observed[13] in HCl-protonated PPY and polyaniline, is probably associated with the chlorine anion in a more positive environment or chlorine charge transfer complexed with the conjugated polymer chain. Similar N1s, Au4f, and Cl2p core-level spectra were observed for the powder samples.

Figure 4(d)–(f) show the corresponding N1s, Au4f, and Cl2p core-level spectra of the Au-deposited film after treatment with excess 0.5 M NaOH. The fact that the intrinsic structure of the polymer at the polymer–metal interface is not significantly altered by the Au reduction reaction is indicated by the reappearance of about 25% of the imine nitrogens and a [C]/[N] mol ratio deviated by less than 10% from its ideal value of 4. Nevertheless, it is noted that the C1s core-level spectrum of the sample is skewed slightly toward the high BE side, suggestive of the formation of surface oxidation products, such as the C — O species and the C — Cl species.[19] The presence of the latter is consistent with the persistence of a weak Cl2p core-level component at a
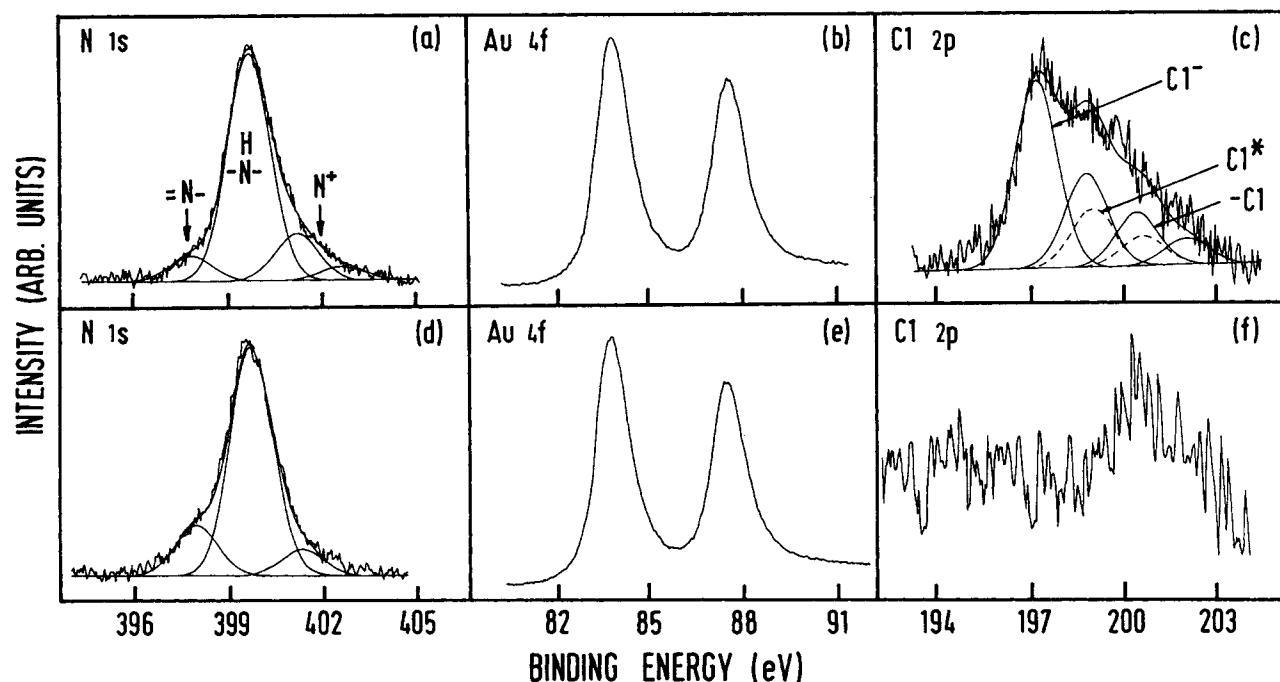
Figure 4   (a) N1s, (b) Au4f, and (c) Cl2p core-level spectra for a DP-PPY film recovered after 48 h from an acid Au solution with an initial Au concentration of 20 mg dm^{-3}; the corresponding core-level spectra after the film has been treated with 0.5 M NaOH are shown in (d), (e), and (f). The surface has an [Au]/[N] ratio of about 1.7 (take-off angle = 75°).
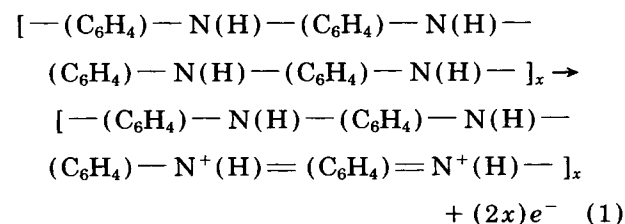
BE of about 200.2 eV in the deprotonated polymer [Fig. 4(f)]. Halogen addition during protonation of DP-PPY and polyaniline has been widely observed.[13]
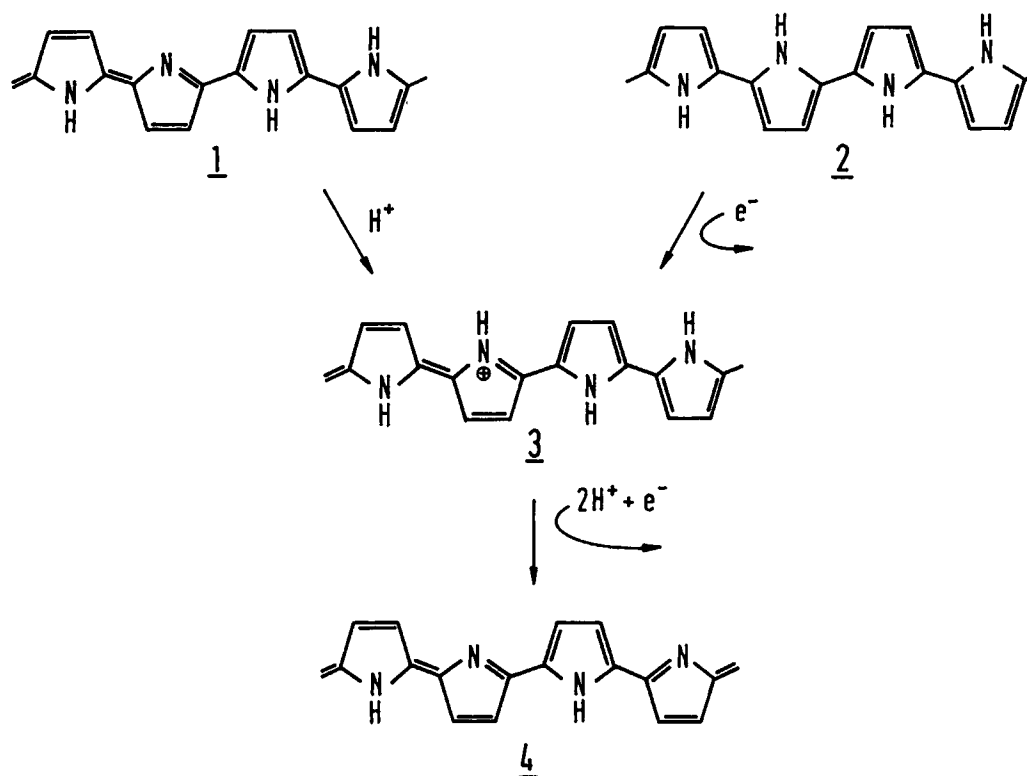
The simultaneous presence of the three nitrogen species, the chloride anion and the reduced Au at the polymer–metal interface during the Au reduction process, together with the fact that the Au-laden polymer surface readily returns to its 25% intrinsically oxidized DP-PPY state upon deprotonation, can be accounted for by the self-sustained redox and protonation reaction schemes shown in Figure 5. Thus, in an acid Au solution, such as chloroauric acid, the imine nitrogens of the DP-PPY base **1** are readily protonated to give rise to **3**. Structure **3** is also equivalent to that which results from the oxidation of the fully reduced PPY **2**. In the presence of Au(III) ions, spontaneous deprotonation of **3** will give rise to a more intrinsically oxidized polymer **4** and reduce Au(III) to a lower oxidation state. The highly oxidized polymer **4**, in turn, is readily reprotonated and reduced to **3** in an acid medium,[12] thus allowing the deprotonation and oxidation of **3** to **4** to be sustained. Although the highly oxidized polymer **4** cannot be isolated from the acid medium under the present experimental condition, the 50% in-

trinsically oxidized PPY shown in Figure 2(a) was actually obtained in an organic solvent using a metal salt, Cu(ClO$_4$)$_2$, as the oxidant.[12]

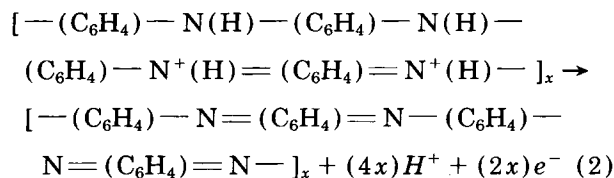Finally, the self-sustained reaction mechanism is further supported by the presence of [Au]/[N] or [Au]/[monomer] ratios in excess of 1 at the Au–polymer interfaces, despite the fact that only about one out of every four pyrrole nitrogens is protonated. In fact, the gradual decrease in the rate of Au reduction is attributable to the "activation polarization" of the polymer "anode." As Au accumulates on the film surface, the overall contact efficiency between the polymer film and the acid medium is significantly reduced.

The reaction scheme shown in Figure 5 also parallels the reactions that occur during the electrochemical oxidation and reduction[20] of polyaniline in aqueous HCl in the pH range of 1–4:

$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-$$
$$(C_6H_4)-N(H)-(C_6H_4)-N(H)-]_x \rightarrow$$
$$[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-$$
$$(C_6H_4)-N^+(H)=(C_6H_4)=N^+(H)-]_x$$
$$+ (2x)e^- \quad (1)$$

Figure 5   Plausible mechanisms for the spontaneous and self-sustained reduction of Au by PPY in acid Au solutions.

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

Reaction (1) is pH independent and has an oxidation potential of about 0.1V vs. SCE, whereas the oxidation potential for reaction (2) is about 0.7V vs. SCE. A recent study[21] has also suggested that treatment of the fully oxidized pernigraniline with HCl involves protonation and reduction to produce a 50% protonated emeraldine. Thus, by coupling the metal reduction process in acid solutions with the increase in the intrinsic oxidation state of the polymer, and the subsequent reprotonation and reduction of the intrinsically oxidized polymer in acid media, the feasibility of a spontaneous and sustained reduction of Au to its elemental form by polyaniline has been demonstrated recently.[10]

CONCLUSION

It was shown that spontaneous and self-substained reduction and accumulation of elemental Au from

acid solutions by polypyrrole, which is capable of assuming a number of intrinsic redox states arising from different imine/amine nitrogen ratios, can be readily achieved. The mechanism involves the initial oxidation of the polymer to a higher intrinsic oxidation state during metal reduction and the subsequent reprotonation and reduction of the highly oxidized state in an acid solution. The mechanism is similar to that observed during Au reduction by polyaniline in acid solutions. The latter polymer is well known for its various intrinsic redox states associated with the chain nitrogens.

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