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Incorporation of Metal Nanoparticles in Photopolymerized Organic Conducting Polymers: A Mechanistic Insight

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ABSTRACT

Electrically conducting polymers were prepared through a systematic photopolymerization of polypyrrole with the incorporation of Group 1B metal particles. The structural and morphological properties of incorporated metal nanoparticles were examined with respect to the role of the metals ions, nature of substrates, exposure time, and monomer counterion ratios. Elemental analysis confirmed the identities of the particles with sizes on the order of hundreds of nanometers in diameter. A mechanism is proposed for the formation of metal nanostructure during photopolymerization.

The deposition of metal nanoparticles in electrically conducting polymers (ECPs) have attracted considerable attention due to the possibilities of creating suitable materials for electrocatalysis, chemical sensors, and microelectronic devices.[1−6] ECPs can be patterned by inexpensive methods such as chemical and electrochemical techniques, hot embossing, and imprinting and therefore making attractive materials. Imprint methods that allow submicrometer patterning with dimensions smaller than 100 nm has been demonstrated with hard imprint materials.[7−9] Electrochemical methods enable the preparation of thin films on electrodes, inert metals, and carbon as well as on semiconductor surfaces. However, they are limited to the use of conducting substrates employed during deposition. Photopolymerization provides a means by which insulating substrates may be employed. Therefore, several metals and alloys can be deposited from an electrolyte onto a nonconducting surface.

Photochemical preparation of ECP films uses mixtures of monomer, electron acceptor, and photoactive species exposed to UV/visible light.[4−6] Oxidation of π-conjugated CEP's with gold trichloride following oxidative film generation in ferric chloride yields conducting films in conjunction with the incorporated gold nanoparticles.[7,8] Incorporating metal clusters into ECPs is known to enhance their conductivity[9,10] and the use of these composites as novel catalysts has been reported.[11−13] There is, however, little or no information on the role and fate of the incorporated metals in these films. This information is critical for controlling the reaction stoichiometry and enhancing conductivity, especially when the metal center serves as specific binding sites. It is also nesessary to understand the role of the metals in the reaction mechanism and their contribution to the structure and properties of the films.

In this work, the role and fate of metal nanoparticles incorporated into photochemically produced polypyrrole films is investigated. The preparations involve polymerization and concurrent oxidation to the conducting state in the presence of group IB metal ions. The resulting films were characterized by electrochemical, conductivity measurements, UV/vis spectroscopy, FTIR, SEM, TGA, and energy-dispersive elemental analysis. The rate of film formation was found to be dependent upon the metal salt utilized. Subsequent analysis of the ECP films show the incorporation of zerovalent metal particles, and the resulting film is conductive and electroactive. By varying the metal salt-to-monomer ratios, stoichiometric relationships were determined. Addition of anionic dopant sources, such as sodium dodecyl sulfate, are shown to alter the reaction stoichiometry, indicating that competition between the metal salt anion and surfactant ion for inclusion in the p-doped film may be a crucial factor in the mechanism of photonic polymerization.

Film preparations typically consist of aliquots of freshly distilled 0.5 M pyrrole in water mixed with one of three metal salt solutions; silver nitrate, copper sulfate, or gold trichloride, all 0.5 M in water. To this, quantities of counterion source, such as sodium dodecyl sulfate (SDS) or polystyrenesulfonate, were added, in a 1:3 counterion to monomer mole ratio. The solutions were photopolymerized within vials, or surfaces were coated with the solution. The preparations were placed under a UV/vis lamp set at 254 nm until a dark solid

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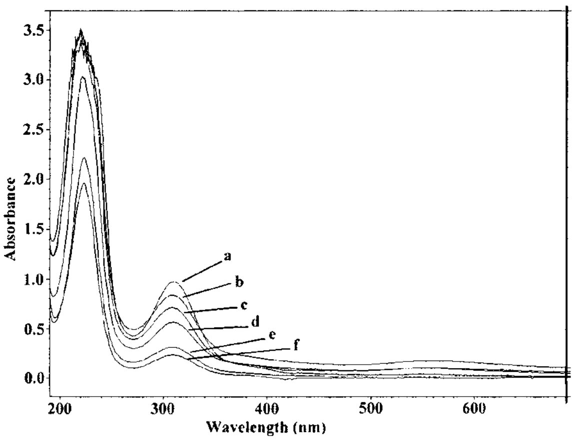

Figure 1. UV/vis spectra of diluted photopolymerization preparations with varying mole fractions of $AuCl_3$ to pyrrole following irradiation in UV light for 1 h and removal of film particulate. Mole fractions of $AuCl_3$ to pyrrole to gold trichloride are (a) 4, (b) 3.75, (c) 3.5, (d) 3.25, (e) 2.66, (f) 2.5.

material is formed. Numerous substrates have been used, including polystyrene sheets, acrylics, ceramics, glass, fiberglass printed wire board, and nalgene tubing. The photopolymerization time depends also on the volume of the solution used. Solutions of 1 mL volume containing gold trichloride typically show immediate darkening and formation of black precipitate upon addition of the gold to the monomer solution. This precipitate settles within a few minutes. The copper sulfate containing solutions will generate a black to dark gray deposition on vial walls within an hour whereas the silver nitrate containing preparations show a black deposition after a few hours. Control reactions in which the solutions were prepared and stored with the exclusion of light were performed. The $CuSO_4$ and $AgNO_3$ preparations did generate films but only after 48 h. The $AuCl_3$-containing preparations yielded a dark precipitate upon mixture of the gold solution to the monomer even with exclusion of light.

The polymerization times were much shorter for solution coatings on substrates, with 2 h being sufficient to generate films on most surfaces. Fourier transform IR spectroscopy of KBr pellets of ground films confirmed the identity as polypyrrole, with strong absorbances at 1541, 1456, 1384, 1294, 1176, 1040, 964, 912, 869, and 794 cm^{-1}. These bands coincided with those obtained for electrochemically generated polypyrrole/dodecyl sulfate films. The conductivities of films deposited on fiberglass printed wire boards ranged from 1.0×10^{-2} to 1.1×10^{-6} S cm^{-1}, and the resistances were shown to vary upon exposure to organic vapors.

To determine the reaction stoichiometry of the photopolymerizations in the presence of gold trichloride, a series of solutions were prepared in shell vials that were 1.25×10^{-2} M in pyrrole and contained concentrations of $AuCl_3$ ranging from 6.25×10^{-3} to 6.25×10^{-2} M. The solutions were photopolymerized for 1 h and centrifuged. A portion of the clear supernatant was diluted in deionized water and analyzed using a Hewlett-Packard 8453 diode array spectrometer. Absorbances (Figure 1) were observed at 222 and 311 nm. Higher concentrations of $AuCl_3$ showed a broad band at 542 nm. The absorbance at 311 nm, which corresponded to a ligand field transition in $AuCl_3$, was observed to be proportional to the concentration of $AuCl_3$ remaining in the solution. Linear regression analysis of the intensity of the absorbance at 311 nm vs the mole fraction of $AuCl_3$ to pyrrole (Figure 2) showed the concentration at which there was no gold trichloride in the solution (absorbance is zero). At this point, the concentration of gold trichloride and pyrrole are in stoichiometric equivalence and all $AuCl_3$ has been consumed in the reaction. For a series of solutions containing only monomer and gold chloride (Figure 2b), the equivalence was found to be at 2.0 mol of $AuCl_3$ to 1 mol of pyrrole. When sodium dodecyl sulfate was added in a 1:3 molar ratio to the monomer with $AuCl_3$ (Figure 2a), the equivalence was found to be 1.35 mol of gold trichloride to 1 mol of monomer. Solutions where SDS was added in excess showed a deep purple coloration and a broad absorbance at 542 nm. For these solutions, centrifugation for 24 h was not adequate to remove the particles.

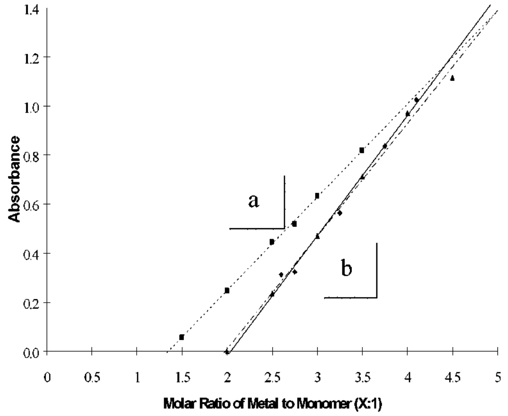

Figure 2. Plots of absorbance at 311 nm vs the mole ratio of $AuCl_3$ to pyrrole for photopolymerization solutions following 1 h UV light exposure and removal of film particulate: (a) solutions including 2.5×10^{-3} M sodium dodecyl sulfate (SDS) and (b) no (SDS).

Environmental scanning electron microscopy and electron dispersive elemental analysis of films were performed to determine the fate of metal ions consumed during the photopolymerization process. The films appeared to be typical of amorphous polypyrrole. In each of the films analyzed, it was found that there were bright particles on the surfaces. Elemental analysis confirmed that the identity of the particles corresponded with the metal employed in the solution preparation. For the silver-containing solutions, for example (Figure 3), small particles of somewhat consistent size with diameters on the order of hundreds of nanometers were observed among larger irregular particles. Similar particles were observed in polymerizations performed with each of the metals. Thermogravimetric analysis of reaction products was performed and confirmed the loss of polypyrrole at ~200 °C and retention of the metals.

We measured the electrical conductivity of photopolymerized polypyrrole with and without metal nanoparticles. The polymers were prepared on microscopic slides. Six microscope slides were washed in KOH/IPA (10 g of KOH in 100 mL of 2-propanol). They were incubated in this solution for 30 min. The slides were then rinsed with

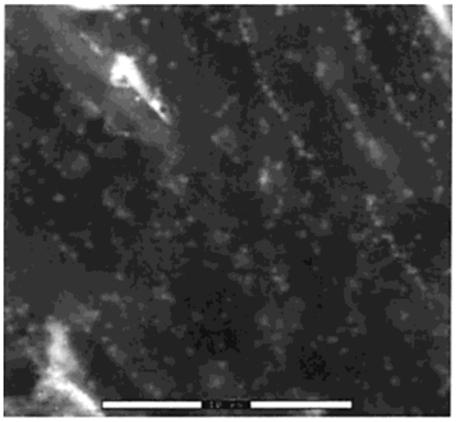

Figure 3. Environmental scanning electron micrograph of polypyrrole film on fiberglass. EDS confirms that bright spots are silver. Scale bar is 10 μm.

deionized water until no schlieren lines were observed. The slides were dried under a nitrogen stream and placed in a PDMS patterning template. A 50/50 mixture of silver nitrate and pyrrole was prepared by mixing equal quantities of 0.5 M pyrrole in deionized water and 0.5 M silver nitrate. All solutions were aqueous. Three control experiments were conducted, which included 0.5 M pyrrole only (control #1), solution containing only silver nitrate (control #2), and pyrrole mixed with potassium nitrate (control #3). The pyrrole/silver nitrate mixture and controls were then placed into the channels of the patterning templates using syringes. The patterning templates were illuminated under a UV pen lamp overnight for polymerization to occur. The slides were removed after polymerization and dried under a gentle nitrogen stream for 1 min. The resistances were measured using four-point probe techniques. The probes were placed approximately 2 cm apart. A support was used to keep the probes stable and the spacing consistent. All controls showed no conductivity. The conductivity determined for the metal-dispersed photopolymerized polymers was found to be 3×10^{-2} S/cm^2. We then compared this value with photopolymerized films available in the literature. Murphy et al. reported the conductivity of 9.7×10^{-3} S/cm^2,[4] Segawa et al. reported 3.0×10^{-4} S/cm^2, and Rodriguez et al. found their photopolymerized films was in the range 1×10^{-3} S/cm^2.[10] Therefore, the result obtained for our metal-dispersed photopolymerized films is consistent with the expected enhancement provided by the metals incorporated.

$$3\text{Py} + 6\text{AuCl}_4{}^- + h\nu \rightarrow [\text{Py}-\text{Py}-\text{Py}]^+\text{AuCl}_4{}^- + 3\text{HAuCl}_4 + 2\text{Au}^0 + 8\text{HCl} \quad (1)$$

$$3\text{Py} + 4\text{AuCl}_3 + \text{NaDS} + h\nu \rightarrow [\text{Py}-\text{Py}-\text{Py}]^+\text{DS}^- + \text{HAuCl}_4 + \text{NaCl} + 3\text{Au}^0 + 7\text{HCl} \quad (2)$$

The photopolymerized films were also characterized using UV/vis spectroscopy. The results of the UV/vis studies and evidence of zerovalent metal particles in the films generated using gold trichloride indicate that the photopolymerization reaction involves reduction of the gold. This appears to be consistent with other accounts of gold-oxidized conducting polymer preparations where a product of gold reduction is incorporated into a conducting polymer as $\text{AuCl}_4{}^-$.[8] The variation in the molar ratios of gold to pyrrole when a surfactant dopant source is added may indicate preferential doping with DS$^-$ and exclusion of $\text{AuCl}_4{}^-$. That AuCl_3 is still consumed in excess quantities of SDS and the reaction occurs rapidly, indicating that the gold trichloride is involved in the polymerization event. The reaction schemes in eqs 1 and 2 are offered to describe our findings for the photoreaction where gold trichloride is incorporated into the film as $\text{AuCl}_4{}^-$ (eq 1) and the condition where the additional anionic dopant, dodecyl sulfate (DS$^-$), excludes the $\text{AuCl}_4{}^-$ (eq 2).

The reaction starts with the absorption of a photon and spontaneous reduction of AuCl_3 salt from solution to form gold clusters. This leads to the oxidation of pyrrole and the formation of pyrrole radical cation through excitation of electrons in the π orbital. Next is the coupling of two radical cations to form a dimer and a deprotonation process where two protons are lost per coupling. Upon excitation of the monomer, the dimers or higher oligomers are also oxidized and this can further react with the radical cation of the monomer to build up the chain. Coupling of oxidized oligomers may also occur.

Equations 1 and 2 involve the loss of two electrons from each mole of pyrrole, resulting in the reduction of 2 mol of gold to the zero state (net total of six electrons). When each pyrrole monomer loses just two protons, the polymer is not conductive. The polymer becomes conductive when it is further oxidized by an anion in the electrolyte. For each proton lost, an anion must associate with the polymer for charge neutrality. A necessary condition for the reaction is that the polymerization steps should proceed with 100% efficiency. In this case, all electrons produced during the reduction of AuCl_3 ions must result in the oxidation of the pyrrole monomer. If, indeed, the metal ion is an active participant in the initiation step by facilitating pyrrole oxidation, then it is likely that the same effect will be observed using copper or silver solutions, given the similarities in electronic configuration and electron affinity.

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