Reversible Formation of Silver Nanoparticles in Poly(vinyl alcohol)-Based Thin Films via Electrochemical Switching.

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ABSTRACT

Ag particles with nanometer dimensions were generated reversibly in the presence of air within micrometer-thick polymer films using electrochemical techniques. Crosslinked blend films of poly(vinyl alcohol) and poly(acrylic acid) swollen with a methanolic electrolyte served as matrices for the electrochemical processes. These optically transparent films enabled the use of spectroelectrochemistry as a means to follow and control the particle formation process. Particle evolution during electrochemical cycling was monitored via optical detection of the characteristic surface plasmon signal exhibited by spherical Ag crystallites. Transmission electron microscopy (TEM) analysis of microtomed films samples provided further characterization of the electrogenerated metallic products. Silver ions bound to carboxylate groups of the polyacid were reduced producing metal nanoparticles, which were then oxidized, reforming the initial Ag(I) species. Cyclic voltammetry experiments yielded Ag nanoparticles as well as large metallic aggregates. However, the Ag aggregates were not susceptible to oxidation, limiting the reversibility of the metal formation process to a few reduction/oxidation cycles. Reversible formation of small Ag crystallites through at least 20 redox cycles was accomplished employing a galvanostatic method, which subjected the films to alternating pulses at a fixed current. Varying the amplitude of the applied current resulting in formation of crystallites with different sizes. Large currents yielded high voltages as well as small particles. On the other hand, small currents produced larger particles and low voltages. Optical and TEM measurements showed that the reversibility of the process was maintained only under conditions that generated Ag crystallites with average diameter less or equal than 5 nm. Interestingly, N,N,N',N'-tetramethylbenzidine was found to oxidize silver particles in solution. Hence, attempts were made to improve the particle oxidation process employing the benzidine as a redox mediator. Data obtained from films including benzidine as an electron relay will also be presented.

Keywords: Spectroelectro chemistry, Silver Nanoparticle.

1 INTRODUCTION

Numerous strategies have been employed in attempts to realize electrochromic systems that are stable and efficient.[1] Ideal electrochromic devices (ECD’s) are systems based on robust, yet flexible polymeric matrices that can operate effectively in the presence of air and H₂O. However, ECD’s with these properties have not been achieved. Such devices are anticipated to find numerous applications, and are relevant to the Army’s Flexible Display Initiative. Recent advances in this area includes the preparation of poly(imide-benzidine) films electropolymerized onto indium-tin oxide windows that function as reversible, high coloration displays.[2,3] Reversible electrochemical coloration of these materials proceeds over 10⁵ cycles, even in the presence of air and moderate amounts of water. Presented here are results from a study aimed at inducing reversible formation of Ag particles with nanometer dimensions within thin, optically transparent polymer films employing electrochemical methods. Silver particles of such dimensions are known to exhibit optical properties that vary to some extent with size.[4] In addition, several colored Ag clusters are generated as intermediates during the particle formation process.[5] If such clusters are formed and stabilized in the films, they would provide for additional color-forming species accessible electrochemically. Recent studies have shown that Ag nanoparticles can be generated by photoreduction of Ag⁺ ions present within optically transparent, crosslinked films consisting of poly(vinyl alcohol), PVA, and poly(acrylic acid), PAA.[6] These polymer systems appeared to be interesting materials for ECD’s since stable Ag particles were photogenerated inside the films in the presence of air and water. An addition advantage is that metal generation is induced only at high photon intensities, but not under ambient light.

2 EXPERIMENTAL

PVA/PAA solutions were prepared as described before.[6] Casting of films took place within a glass-well created by stacking microscope slides and affixing them to a larger piece of glass. Optically transparent and conducting films of Indium Tin Oxide (ITO) deposited on glass, which served as electrodes and substrates, were placed inside the well. Then, the PVA/PAA solution was poured into the well until the ITO substrates were covered with a thin polymer film (average thickness = 60 µm). Crosslinking of PVA proceeded at 55 °C for 3.5-4 h;
separation of the polymer-coated ITO windows from the well was followed by an overnight immersion in methanol to extract excess crosslinking agent. Doping with Ag⁺ ions occurred by soaking PVA/PAA films in a 1 x 10⁻⁵ M methanolic solution of AgClO₄ for 24 h. The films were then rinsed with CH₃OH and dried under vacuum.

Electrochemical experiments with the polymer-covered ITO windows used a custom built spectroelectrochemical cell incorporating an Ocean Optics LS1 source and a Pine AFRDE5 Bi-Potentiatstat. The cell comprised the ITO substrate and a glass slide as optical windows, which were secured on both ends of a hollow Teflon sub-cell using Teflon seals and clamps. This arrangement allowed for the placement of optics fibers orthogonal to the ITO window; electrodes and electrolyte (NaClO₄ in methanol) were introduced through openings on the top of the cell. The Bi-potentiatstat was integrated to a computer using a NI DAQ board. Preparation of tertamethylbenzidine dication (TMB⁺³) proceeded according to published methods.[7] Transmission electron microscopy (TEM) measurements were carried out on a Zeiss EM10CR electron microscope using microtomed sections of the polymer films.

3 RESULTS AND DISCUSSION

Formation of nanometer-sized Ag particles in solution proceeds through a mechanism involving short-lived transient clusters consisting of a few metal atoms.⁵ A simplified version of this mechanism is:

\[
\begin{align*}
\text{Ag}^+ + e^- & \rightarrow \text{Ag} \quad (1) \\
\text{Ag} + \text{Ag}^+ & \rightarrow \text{Ag}_2^+ \quad (2) \\
\text{Ag}_2^+ + \text{Ag}^+ & \rightarrow \text{Ag}_4^{2+} \quad (3) \\
\text{nAg}^+ + \text{mAg}^{2+} & \rightarrow (m+n)\text{Ag}^{x+y} \quad (4)
\end{align*}
\]

The standard redox potential of step (1) is 0.8 V, but formation of an isolated Ag atom in solution is believed to involve a negative potential of about -1.8 V.⁵ Combinations of the charged clusters eventually form nanoparticles. In other words, the chemical potential of the intermediates decreases continuously as they grow. However, ligands able to bind to the clusters alter their reactivity and complexation of Ag₃⁺⁻ in solutions containing PAA yields stable species exhibiting a blue color. Formation of Ag crystallites in PVA/PAA films was anticipated to proceed differently given the restrictions in mobility of charged species imposed by the solid matrix. Photochemical experiments showed that particle generation was fast since no post-irradiation reaction was observed.⁶ Thus, the Ag crystallites were produced in a time scale shorter than one min (the time required to run an optical scan). Despite of the high concentration of PAA present in the films, blue species were not detected and Ag₃⁻ was proposed to be the chromophore responsible for a stable signal centered at 280 nm. The kinetics of particle photogeneration in dry films was consistent with a mechanism resembling somewhat the one proposed for solutions, in which Ag atoms acted as the mobile species.

In the electrochemical experiments Ag atoms are formed at the ITO-polymer interface, which then diffuse into the swollen films producing ionic and neutral clusters. Hence, particle growth involves mobile clusters as well as Ag atoms. Growing ionic or neutral clusters will become fixed nucleation sites due to interactions with the polymer matrix. This reasoning leads to the conclusion that oxidation of large Ag particles located away from the polymer-ITO interface would be severely limited by their lack mobility as well as by the need of performing a simultaneous oxidation of a large number of metal atoms. On the other hand, oxidation of small clusters/particles was expected to be easier since they are less stable thermodynamically. Figure 1 depicts a schematic representation of the oxidation processes. Thus, in order to achieve reversible formation of Ag particles, an important goal was to find experimental conditions enabling complete oxidation of the crystallites to occur. A simple way to test for reversibility is to use cyclic voltammetry (CV), since the spread of the anodic and cathodic peaks provide a measure of relative reversibility; shifting of the peaks is also an indication of the system becoming less reversible. As shown in Figure 2, ΔEp = 665 mV, hinting that formation of Ag particles in the films is an irreversible process.

![Figure 1](image.png)

Figure 1 shows a CV of a film exposed to Ag ions.

Small particles located within a few μm of the ITO/film interface are thermodynamically easier to oxidize than large particles present a few nanometers into the film. Formation of small particles deep into the film requires many nucleation sites to be present within the polymer matrix. In an electrochemical system species move according to mass transfer in Cartesian space.[8]

\[
J_x = -D_x \frac{DC_x}{v} - (Z_x F/R T) \frac{D_x C_x D\phi + C_x v}{v} \quad (5)
\]

Where J is the flux of a species, Dₓ is the diffusion coefficient, Zₓ is the charge, F is faradays constant, R is the gas constant, T is the temperature, Cₓ is the concentration, and v is the velocity. The first term on the right half of the equation gives the contribution of diffusion, the second relates to migration in an electric field and the third is the contribution of convection. Since convection is not important in the polymer matrices, the last term from the equation becomes negligible.
We will first discuss the role that diffusion plays on the particle formation process. Diffusion of particles takes place in the presence of concentration gradients. Since the working electrode is large, linear diffusion is assumed to occur perpendicular to the polymer/ITO interface. Previous studies have shown that ions may not follow a linear trajectory due to interactions with the surrounding matrix.[9] Since the polymer films are swollen, we still treat this system as if diffusion was linear. Exhaustive electrolysis was used to determine the diffusion coefficient of Ag	extsuperscript{+}, which can be extracted from the slope of plots of current versus t	extsubscript{1/2} by means of the Cottrell equation. The resulting value (2 x 10	extsuperscript{8} cm	extsuperscript{2}/s) agrees with those determined for diffusion of silver ions in polymers.[3] Once the diffusion coefficient is obtained one can use equations

\[ D_{Ag} = \frac{\kappa T}{6\pi \eta r} \]  

and

\[ X_{Ag} = \sqrt{2\pi D_{Ag}} \]

(6)

(7)

to get a relative viscosity and the maximum diffusion distance. Where \( \kappa \) is the Boltzman constant, \( \eta \) is the viscosity, \( r \) is the radius, \( X \) is the distance and \( D \) is the diffusion coefficient. The mobility of other species can be calculated after assessing the viscosity of the medium assuming that there is no significant change in size. For species such as Ag atoms diffusion seems to be the only possible source of mobility.

Charged species can also migrate when placed in an electric field. This applies to silver ions and to some of the small charged clusters. As the electric field increases the speed in which the ions migrate increases. When the flux of silver ions is greater than the flux of silver atoms a concentration build up around the electrode would occur, increasing the speed of diffusion of silver atoms. If the Ag atoms diffuse fast into the polymer, they can form nucleation sites deep into the film and eventually producing small particles. When Ag atom diffusion is slow then reaction 4 occurs close to the electrode leading to growth of large particles. All these rationalizations neglect possible solvation effects induced by the electrolyte and water. For example, if the electrolyte forms ion pairs with Ag	extsuperscript{+} then the flux of silver would be drastically altered, potentially transforming the silver ions and clusters into neutral species.

Detection of the particles is accomplished by following the formation and decay of the surface plasmon signal typical of spherical Ag particles.[4] As small particles are formed a plasmon peak is observed at around 400 nm giving a visual yellow color to the film. Larger particles display plasmon signals that are red-shifted by as much as 100 nm. Figure 3 shows that production of silver particles was possible in the presence of air using CV, where the voltage is constant and the current may fluctuate freely. However, as was found in a earlier solution study, the reversibility of the silver crystallite formation process was limited to 5 reduction/oxidation cycles.[10]

Furthermore, the optical spectrum exhibited a plasmon peak located at 467 nm corresponding to large particles. When the film was removed from the electrode, a large number of Ag particles were found to remain on the surface of the electrode. As revealed in the TEM image shown in Figure 4a, very few particles were present inside the films and that they were located only a few nanometers deep. This means that formation of Ag particles via CV is a slow process in which most of the silver atoms remain localized at the polymer-electrode interface. The atoms transform fast into clusters, which then act as nucleation sites yielding large metal particles on the polymer surface.

Figure 2 is the resulting optical spectrum from figure 2 having \( \lambda_{max} = 467 \) nm implying large particle growth.

Figure 4 is TEM’s of microtomed polymers. a) Film exposed to CV cycling producing large particles located on film surface. b) Film exposed to 5 \( \mu \)A of cycling producing small particles within the film.

These findings mean that higher currents were required in order to achieve a larger concentration gradient and, therefore, a faster diffusion of Ag atoms into the polymer films. This was accomplished by means of a galvanostatic method producing large current pulses, where the voltage was allowed to fluctuate freely. Using higher current densities yielded an optical absorption centered near 400 nm (and the desired yellow coloration of the films) typical of small spherical Ag crystallites. Shown in Figure 4b is a TEM image demonstrating that Ag particles with an average diameter of 5 nm were formed deep inside the
PVA/PAA films. The results obtained from these experiments are summarized in Table 1. Ag particles produced at low current densities resembled those generated using the CV procedure. At the highest current density the reaction became irreversible in a short amount of time. A possible explanation for this observation is that the high flux of Ag atoms diffusing into the film yields crystallites far away from the polymer/ITO interface, which are hard to reoxidize. The best results were obtained when a current density of 2 uA was utilized, where the particle formation process remained reversible for about 20 reduction/oxidation cycles.

<table>
<thead>
<tr>
<th>Vmax</th>
<th>Intensity</th>
<th>λmax</th>
<th>Switching Speed</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 µA</td>
<td>0.125</td>
<td>462 nm</td>
<td>3 s</td>
<td>25-30 nm</td>
</tr>
<tr>
<td>1 µA</td>
<td>0.025</td>
<td>433 nm</td>
<td>2 s</td>
<td>n/a</td>
</tr>
<tr>
<td>2 µA</td>
<td>0.05</td>
<td>377 nm</td>
<td>1 s</td>
<td>4 nm</td>
</tr>
<tr>
<td>5 µA</td>
<td>0.07</td>
<td>367 nm</td>
<td>5 s</td>
<td>2-4 nm</td>
</tr>
</tbody>
</table>

To help achieve greater reversibility of the particle formation process, a redox mediator was considered. Such species were intended to act as electron relays that would help to oxidize the Ag crystallites. TMB$_2^+$ was selected as a redox mediator because initial experiments showed that immersion of films containing Ag nanoparticles into a solution of this cation resulted in complete bleaching of the plasmon signal. Electrochemical experiments with films containing TMB$_2^+$ showed that the mediator affected the redox processes.

4 REFERENCES

(2) Cammarata, V.; Zhu, W.; Liang, J. Polymer Preprints, 2005, 46, 537.