Coarsening of Silver Nanoparticles in Polyelectrolyte Multilayers

Jingjing Wei,† Liming Wang,† Xin Zhang,† Xiaojing Ma,‡ Hui Wang‡ and Zhaohui Su⁎†

†State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, and Graduate School of Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun, Jilin 130022, P. R. China
‡Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208, United States

ABSTRACT: In polyelectrolyte multilayer (PEM) films assembled from poly(diallyldimethylammonium chloride) and poly(styrene sulfonate) via the layer-by-layer deposition technique, the counterions were exchanged with silver ions, which were subsequently reduced in situ to produce silver (Ag) nanoparticles. The Ag nanoparticles embedded in the PEMs were found to undergo an interesting coarsening process over time, through which smaller Ag nanoparticles coalesce into larger ones until reaching an equilibrium. The process was investigated by monitoring the localized surface plasmon resonance of the Ag nanoparticles using UV–vis extinction spectroscopy, and the spectral evolution revealed an increase in nanoparticle size with time, a trend in qualitative agreement with theoretical calculation and further confirmed by transmission electron microscopy. The kinetics of the coarsening process and the size of Ag nanoparticles at equilibrium were found to be affected by the PEM structure as well as the temperature and relative humidity the PEM was exposed to, and coalescence was identified to be the mechanism.

INTRODUCTION

Noble metal nanoparticles have attracted extensive interest in recent years due to their remarkable properties and widespread applications in various fields such as catalysis, microelectronics, antibacterial agents, biosensors, and nonlinear optics.1−3 To take full advantage of nanoparticle functions, the nanoparticles are often embedded in polymer matrices to form nanocomposite films.4−6 Polyelectrolyte multilayer films (PEMs), assembled from oppositely charged polyelectrolytes via the layer-by-layer deposition technique, have been utilized extensively as nanoreactors and supporting matrices for the fabrication of such nanoparticle-containing nanocomposites.7−9 For example, Bruening and co-workers assembled polyethyleneimine/poly(acrylic acid) (PAA) PEMs with metal nanoparticles embedded through in situ reduction of the metal ions in the PEMs.10,11 Rubner and co-workers introduced various metal ions into PEMs composed of weak polyelectrolytes, in particular PAA and poly(allylamine hydrochloride) (PAH), by tuning pH in the polyelectrolyte solutions, which resulted in the subsequent formation of nanoparticle-loaded PEMs upon postassembly treatment.12 Recently, taking advantage of counterions universally present in PEMs, especially the ones constructed from strong polyelectrolytes such as poly-(diallyldimethylammonium chloride) (PDDA) and poly(styrene sulfonate) (PSS), we developed a general approach to PEM-based nanocomposites via ion exchange and in situ reduction process.13,14 The composition, size, and spatial distribution of the nanoparticles synthesized in the PEM matrix can be fine-controlled,13 and bimetallic nanoparticles with core−shell structures can be fabricated via the same strategy in PEMs as well.15 These PEM-supported nanoparticles exhibited superior catalytic,14 antimicrobial,16 and photonic properties.17 A number of studies have revealed that polyelectrolyte chains in the layer-by-layer assembled PEMs become mobile under certain conditions and the multilayer films may undergo interesting structural changes over time. For instance, PEM films composed of PAH and PAA exhibit significant swelling/deswelling hysteresis in humid air environments.18 Since PEMs are fabricated by alternating deposition of polyelectrolytes at solid/liquid interfaces, the salt content in polyelectrolyte solutions may have significant effects on the structural and compositional stability of the resulting PEMs.19,20 For example, PDDA/PSS multilayers have been observed to exhibit significant mass losses when treated with salt solutions at concentrations higher than 2 M.21 The evolution of the matrix structure is expected to have profound impact on the structures of the embedded nanoparticles as well.22 However, in contrast to the immense efforts devoted to the controlled synthesis of PEM-supported nanoparticles, little attention has been paid to structural stability of the nanoparticles in PEM matrices.23 Understanding how the structural changes of the PEM matrices affect the size and shape of the embedded metallic nanoparticles is of vital importance to the enhancement of our capabilities to selectively implement desired properties into metal−PEM nanocomposite materials for widespread applications due to the fact that the optical, electronic, and catalytic

Supporting Information

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properties of the metal nanoparticles are all sensitively dependent on size and shapes of the particles. In this paper, we investigate the evolution of the size of Ag nanoparticles embedded in typical PEMs assembled from PDDA and PSS and systematically study the influence of temperature, humidity, and salt content on the kinetics of the particle size evolution.

**EXPERIMENTAL SECTION**

**Materials.** PDDA (30 wt % in water, MW 200 000–350 000) and PSS (MW 70 000) were purchased from Sigma-Aldrich. Silver nitrate, sodium chloride, and sodium borohydride, all of analytical grade, were purchased from Beijing Chemical Reagents Company. All chemicals were used as received. Water (18.2 MΩ-cm) used for all the experiments was purified with a Pgeneral GWA-UN4 system.

**Substrate Treatment.** Quartz slides (Jingke Optical Instrument Co., Ltd.) and glass slides (Yancheng Medical Equipment Corporation) were used as substrates. They were cleaned in a boiling piranha solution (98% H2SO4/30% H2O2; 70:30 v/v) at 80 °C for 2 h and then washed with copious amounts of water and dried under a N2 stream. (Caution: piranha solution reacts violently with organic materials and should be handled with great care.)

**Fabrication of PEMs with Ag Nanoparticles.** PEMs (all capped with a PSS outmost layer) were assembled by sequential dipping of a substrate in PDDA (1.0 mg/mL, with NaCl present) and PSS (1.0 mg/mL, with NaCl present) aqueous solutions for 30 min each at room temperature, with water rinsing after each dipping step.26 The cycle was repeated 5 times to yield a (PDDA/PSS)5 film. The (PDDA/PSS)5 films are denoted as PEM-1 and PEM-2 for the PEM assembled at a NaCl concentration of 1.0 and 1.5 M, respectively. The PEM was immersed in a AgNO3 aqueous solution (0.01 M) for 10 min to exchange the Na+ in the PEM for Ag+, followed by rinsing with a copious amount of water. Then the film loaded with Ag+ was immersed in a freshly prepared NaBH4 aqueous solution (0.01 M) for 5 min to reduce Ag+ into Ag nanoparticles. The composite PEMs thus prepared were transferred immediately into an incubator (constant temperature and humidity incubator LHS-100CL, Hengke Co., Ltd., Shanghai, China) maintained at a specific temperature and relative humidity. Ag nanoparticles at various stages of the coarsening process were examined by UV–vis spectroscopy.

**Characterization.** UV–vis spectra were acquired on a PerkinElmer Lambda 750 spectrometer with a 0.2 nm slit width. Two replicates were analyzed for each sample, and the average numbers are reported with error bars. Transmission electron microscopy (TEM) characterizations were carried out on a JEOL JEM-2010 microscope operating with a 0.2 nm slit width. Two replicates were analyzed for each sample, and the average numbers are reported with error bars. In this study, the extinction spectra were measured at 25 °C as a function of time after fabrication. The LSPR peak of the Ag nanoparticles progressively shifted to longer wavelength from ∼412 to ∼424 nm over a time period of 27 h, indicating continuous growth in nanoparticle size over time, even in the dry PEMs.29 It is known that larger Ag or Au nanoparticles have larger optical extinction cross sections than the smaller particles; however, the extinction peak intensity was observed to progressively decrease as the size of the embedded Ag nanoparticles increased, essentially due to the decrease in total number of Ag particles embedded in the PEMs. Since the total amount of Ag embedded in the PEMs is fixed for a given

![Figure 1. UV–vis spectra of PEM-2 film as assembled, with Ag ions introduced as counterions, and after reduction of the Ag+ to yield Ag nanoparticles in situ.](image1)

![Figure 2. UV–vis absorption spectra of a PEM-2 film containing Ag nanoparticles acquired at varying time intervals after the Ag nanoparticles were synthesized.](image2)
nanocomposite sample, the total number of Ag nanoparticles would decrease when the smaller particles undergo a coarsening process to form bigger particles.

To gain further insights into the extinction spectral evolution of the embedded Ag nanoparticles, we theoretically calculated scattering, absorption, and extinction spectra of the nanoparticles using the Mie scattering theory.37 In these calculations, we assumed perfectly spherical particle geometry and a homogeneous dielectric medium surrounding the nanoparticles with a dielectric constant of 2.25. The wavelength-dependent empirical dielectric functions of bulk Ag38 were used. The calculated extinction was expressed as optical extinction (scattering + absorption) efficiency ($E_{\text{ext}}$), which was the ratio of the total energy scattered and absorbed by the particle to the energy incident on the physical cross section of the particle. As shown in Figure 3a, the extinction peak of a Ag nanoparticle progressively red-shifted, accompanied by an increase in the extinction efficiency, as the particle became bigger. The extinction cross section of a Ag nanoparticle is dramatically amplified as the particle size increases due to the increase in both the physical cross section and the extinction efficiency of the particle. If we assume there are initially $10^6$ Ag nanoparticles (2 nm diameter) in the PEM film and the total amount of metallic Ag embedded in the PEM is fixed at this amount during the nanoparticle growth, the total observed extinction cross section ($\sigma_{\text{obs}}$) can be calculated using the equation

$$\sigma_{\text{obs}} = \pi E_{\text{ext}}/r \ (\mu m^2)$$

where $r$ is the radius of the Ag nanospheres. As shown in Figure 3b, $\sigma_{\text{obs}}$ decreased as the particle size increased simply due to the decrease in total number of particles embedded in the PEM film. The calculated results, both the LSPR shift and the $\sigma_{\text{obs}}$ evolution upon changes of the particle size, are in qualitative agreement with the experimental observations. The experimental LSPR bands turned out to be broader than the calculated ones largely due to the size distributions and structural nonideality of the experimentally fabricated particles. The structural heterogeneity inside the PEM films may also provide an inhomogeneous local dielectric environment surrounding each Ag nanoparticle. The effects of surface electron scattering39 and plasmon quantum confinement,40 which become increasingly significant when Ag nanoparticles are in the sub-10 nm size regime, may further introduce modifications to the Ag dielectric functions. Gaining more detailed and quantitative insights into the relationship between particle geometry and LSPR properties of Ag nanoparticles requires correlated single-particle spectroscopic measurements and electrodynamic simulations, which were not further pursued in this work.

A classical mechanism for nanoparticle growth in solutions is through monomer addition to the nuclei formed in a preceding nucleation period.41 Whereas, recent studies have shown that clusters composed of several atoms, such as Ag$_{13}$ or Au$_{13}$ clusters, play an important role as elementary species that guide the growth of Ag or Au nanoparticles,41,42 and alternative pathways involved in the size evolution and growth of metal nanoparticles can also be found in other reports.43,44 However, all these proposed mechanisms are for nanoparticle growth in the solution phase where intermediate species are present to facilitate mass transfer from one (smaller) particle to another (bigger). Knowledge about the growth of nanoparticles embedded in solid state matrices has been very limited so far, yet a better understanding of the growth mechanisms of metal nanoparticles in PEMs is crucial to further manipulation of the properties of the nanocomposite films.

We systematically studied the coarsening process of the Ag nanoparticles embedded in the PEM films at various temperatures and relative humidity. The LSPR peak wavelength ($\lambda$)
was used to represent average size of the nanoparticles, and the 
λ as a function of incubation time at different temperatures is
plotted in Figure 4. It can be seen that a spectral red-shift over
time occurred in each sample. All samples prepared under the
same conditions exhibited the same initial extinction peak (λ₀)
after fresh preparation but showed various final extinction peak
wavelengths (λ∞) after staying at different temperatures for
several hours. The plots clearly show that the size of the Ag
nanoparticles increased quickly in the initial stage and then
approached a plateau value with time until equilibrium was
reached, and temperature has significant effects on the kinetics
of the nanoparticle growth.

To quantitatively analyze the data for Ag nanoparticles
coarsening under different conditions, the peak position data
were fitted to the following single exponential decay function
$$\frac{\lambda_\infty - \lambda}{\lambda_\infty - \lambda_0} = e^{-kt}$$
where k is a constant for λ evolution with time and thus can
represent the particle growth rate constant. The experimental
data were fitted through a least-squares curve-fitting process
using this first-order kinetics equation.

The curve-fitting results for Figure 4 are summarized in
Table 1. We found that the kinetics of the particle coarsening
process and the final particle size at equilibrium were mainly
determined by three factors: ambient temperature, air relative
humidity, and salt concentration in the depositing solutions for
the PEMs.

It is obvious from both the plots in Figure 4 and the numbers
in Table 1 that the λ∞ increases with temperature, indicating
the increase of the final size of the Ag nanoparticles with
temperature. This was further confirmed by TEM measure-
ments as shown in Figure 5. In PEM-2 the average particle
radius grew from 2.1 nm into 4.1, 8.1, 13.4, and 25.6 nm after
equilibration at 10, 25, 60, and 90 °C, respectively. While the
formation of small particles is kinetically favored, the coarsening
process is essentially driven by thermodynamics. During the
reduction process it is easier to nucleate so as to form many
small particles in the early stage. However, smaller particles
have higher specific surface areas than large particles, and the
total surface energy would be much higher if only very small Ag
nanoparticles were formed in the PEMs compared with large
Ag nanoparticles. Thus, the coarsening of small particles into
large ones can distinctly lower the surface energy of the system,
making the larger particles more stable. There are two possible
mechanisms for the increase in average size of the Ag
nanoparticles: coalescence of the particles and Ostwald ripening.45 Ag does not spontaneously dissolve in PEM or
water, and there is no plausible intermediate species in the
system (Supporting Information) to assist the dissolution and
transport of Ag from one particle to another. Therefore, we
conclude that the Ag nanoparticles in the PEM grow via
coalescence. In fact, in Figure 5d, some big particles appear to
be aggregates of smaller ones, providing direct evidence for this
mechanism.

It is interesting to find that step heating leads to similar result
as direct heating. A PEM-2 film containing Ag particles was first
maintained at 10 °C until the average particle size
(characterized by λ) reached a plateau value, and then the
temperature was further increased to 90 °C, under which the
particles continued to grow and eventually reached a new
plateau value. As seen in Figure 6, λ∞ hence the particle size at
equilibrium, obtained through this stepwise heating process was
the same as that for the particles maintained at 90 °C all the
way through. The fact that the equilibrium particle size value is
a function of temperature while independent of the path
leading to the final temperature further suggests that the final
particle size is determined by thermodynamics.

From Figure 4 it is also clear that the time needed for the
particles to reach their equilibrium sizes is shorter at higher
temperature. Generally, temperature can significantly affect the
rate of a chemical/physical process, and the influence of
temperature on a chemical reaction may be quantitatively
described by the Arrhenius equation. For a first-order reaction
with a rate constant k, a plot of ln k versus 1/T should give a
straight line, the slope of which is related to the activation
energy of the reaction. In our case, k determined by curve-
fitting discussed above represents the rate constant for the
particle size increase. As seen in Table 1, the apparent rate
constant has strong dependence on temperature. Figure 7 plots
ln k versus 1/T, and a linear relationship is observed, which
indicates that Arrhenius equation is a simple but still
remarkably accurate formula for describing the temperature
dependence of the particle growth process in the PEM matrix.

Salt in polyelectrolyte solutions is known to exhibit a strong
influence on the structure and properties of the layer-by-layer
assembled PEMs46 and thus is expected to impact the particle
coarsening process occurring in the PEM matrix. As shown in
Figure 4 and Table 1, at the same temperature, Ag
nanoparticles embedded in PEM-2 (assembled at a NaCl
concentration of 1.5 M) were bigger initially (a higher λ₀), grew
faster (a greater k), and reached a larger equilibrium size (a
higher λ∞) than their counterparts in PEM-1 (assembled at a
NaCl concentration of 1.0 M). In Figure 7, the slope of the ln k
versus 1/T plot was smaller for the particles in PEM-2 than in
PEM-1. The empirical activation energy derived from the slope
was 14.4 and 13.3 kJ/mol for particle coalescence in PEM-1
and PEM-2, respectively. In a PEM assembled at a higher salt
concentration, more of the polyelectrolyte units are compen-
sated by small counterions. The higher counterion content
results in bigger Ag nanoparticles as prepared,13 and the fewer
sated by small counterions. The higher counterion content
results in bigger Ag nanoparticles as prepared,13 and the fewer

<table>
<thead>
<tr>
<th>PEM</th>
<th>temperature (°C)</th>
<th>( \lambda_0 ) (nm)</th>
<th>( \lambda_\infty ) (nm)</th>
<th>k (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEM-1</td>
<td>10</td>
<td>410.5</td>
<td>412.5</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>412.5</td>
<td>425.0</td>
<td>0.56</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>412.5</td>
<td>425.0</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>412.5</td>
<td>425.0</td>
<td>1.50</td>
</tr>
<tr>
<td>PEM-2</td>
<td>10</td>
<td>422.7</td>
<td>424.0</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>424.0</td>
<td>425.9</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>425.0</td>
<td>431.4</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>429.5</td>
<td>431.4</td>
<td>1.70</td>
</tr>
</tbody>
</table>

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100% relative humidity. Figure 8 compares Ag particle growth at 0%, 30%, and 90% relative humidity, and the curve-fitting results are summarized in Table 2. It can be seen that the final size of Ag nanoparticles at equilibrium and the particle growth rate both increased with relative humidity. This is because water acts as a plasticizer for the PEM to increase the mobility of the polyelectrolyte segments in the matrix, resulting in faster mass transport that facilitates the particle growth process.

CONCLUSION

The polymer chains inside the PEMs are mobile rather than being fixed, and the PEMs may undergo structural changes under suitable conditions. The structural changes of the PEM matrices may give rise to interesting size and shape evolution of the nanoparticles embedded in the PEMs. Here, we have observed that Ag nanoparticles embedded in PDDA/PSS PEMs undergo an interesting coalescence process upon incubation under different ambient conditions. The Ag nanoparticles tend to grow into larger ones until equilibrium is reached and the coalescence process follows first-order kinetics. We have investigated three factors that significantly affect the coarsening processes: the temperature, relative humidity, and PEM structure as mediated by the salt concentration in the depositing solutions. Both the particle growth rate and the final particle size at equilibrium were found to increase with the temperature, relative humidity, and salt concentration. Our results demonstrate the coalescence of nanoparticles in PEM matrices and correlate the kinetics with chain dynamics in the PEM. On the basis of these findings, it is also conceivable that the nanoparticle coalescence process would significantly slow down or freeze when the polyelectrolyte chain motion is severely restricted, such as at much lower temperatures or in more glassy PEMs. These factors need to be considered when nanoparticle size control is important for designated applications.


Table 2. Summary of the Curve-Fitting Results for Different Relative Humidity

<table>
<thead>
<tr>
<th>PEM</th>
<th>λ0 (nm)</th>
<th>k (h⁻¹)</th>
<th>0%</th>
<th>30%</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEM-1</td>
<td>410.5</td>
<td>0.54</td>
<td>410.5</td>
<td>421.5</td>
<td>425.5</td>
</tr>
<tr>
<td></td>
<td>425.5</td>
<td>0.56</td>
<td>412.5</td>
<td>424.5</td>
<td>427.0</td>
</tr>
<tr>
<td>PEM-2</td>
<td>421.5</td>
<td>0.56</td>
<td>421.5</td>
<td>424.0</td>
<td>427.0</td>
</tr>
</tbody>
</table>

ASSOCIATED CONTENT

Supporting Information

UV–vis data showing in situ reduction kinetics and particle growth kinetics in the absence of Cl⁻, AFM images, and TEM images for PEM-1 containing Ag nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mail: zhsu@ciac.ac.cn.

Notes

The authors declare no competing financial interest.

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