

Facile in Situ Silver Nanoparticle Formation in Insulating Porous Polymer Matrices

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The in situ formation of well-dispersed silver nanoparticles in an insulating polymer matrix is reported. Poly(aryl ether)s (PAEs) incorporating an oxadiazole moiety were synthesized, and they demonstrated selective interaction with silver ions. Polymer–ion thin films were easily spin cast and exposed to hydrazine vapors in order to induce metal nucleation. Introducing a triptycene monomer into the polymer backbone resulted in a highly porous matrix and prevented nanoparticle aggregation. This provides a generalized approach to the facile preparation of well-dispersed metal nanoparticle embedded thin films.

Nanoparticle-dispersed polymer thin films offer several interesting applications in optics,¹ catalysis,² and electronics.³ The success of such high-performance nanomaterials relies on the controlled distribution of uniformly shaped and sized particles. Traditionally, metal–polymer nanocomposites are prepared via multistep techniques, including plasma deposition,^{3a,4} electrodeposition,⁵ self-assembly of functionalized nanoparticles,⁶ and other hybrid approaches.⁷ These methods are limited by the difficulty in controlling monodisperse nanoparticle formation over large areas, in addition to other drawbacks. For instance, the self-assembly example requires preformed nanoparticles (already having a size dispersity) to be isolated and then functionalized to ensure chemical compatibility with an appropriate polymer host. As a result, the in situ synthesis of metal nanoparticles in polymer matrices has attracted significant attention.⁸ The most common approaches involve either thermal annealing^{8a,f,h} or direct UV exposure^{8b,e} of a metal ion embedded polymer thin film. In both cases, the polymer acts as the reducing agent,

whereby an electron is extracted from the polymer and donated to the metal ion. This irreversible oxidation of the matrix leads to polymer degradation, which has detrimental effects on the system's thermal and mechanical durability. To date, there is considerable progress to be made in developing a facile route for the formation of robust metal nanoparticle–polymer composites. Here, we report on a simple preparation of well-dispersed silver nanoparticles in an insulating polymer matrix.

Our approach was to synthesize novel poly(aryl ether)s (PAEs) that incorporate a triptycene moiety. We are particularly interested in PAEs because they are an important class of high-performance engineering thermoplastics, known to have excellent thermal stability. In addition, our research group has previously shown that polymers incorporating rigid triptycene units have elevated glass transition temperatures (T_g), exhibit low dielectric constants, and are porous.⁹ Such a rigid framework has the potential to effectively suppress nanoparticle aggregation. Furthermore, the porosity affords an opportunity for the rapid diffusion of other small molecules into and out of the polymers, which is important for sensor and catalysis applications. By combining the attributes of the triptycene with a comonomer that could selectively interact with silver ions, PAE–ion thin films were easily spin cast and exposed to hydrazine vapors in order to induce relatively uniform silver nanoparticle formation.

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Scheme 1. PAE Synthesis

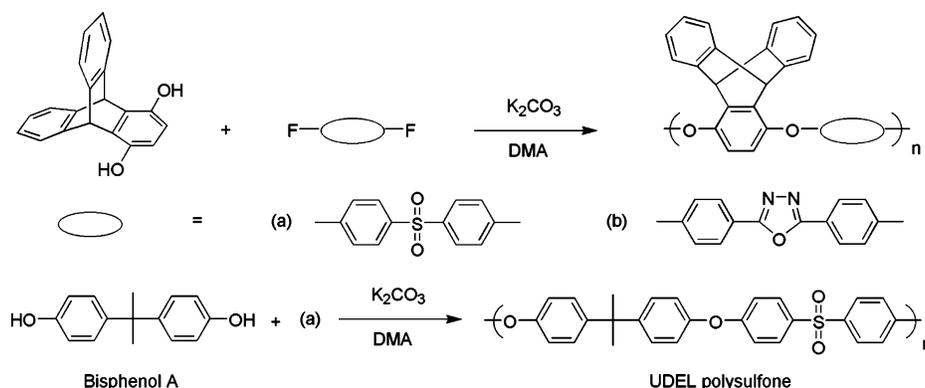


Table 1. PAE Characterization

PAE	M_n	M_w	PDI	T_g (°C)	T_d (°C) ^a
PAE-SO ₂	13 800	39 700	2.89	267	518
PAE-Oxa	13 800	35 700	2.58	284	478
UDEL polysulfone	37 100	91 656	1.69	190	512
PAE-Oxa-SO ₂	16 800	42 000	2.51	281	497

^a T_d = temperature at 5% mass loss.

Scheme 1 summarizes the condensation polymerization¹⁰ of triptycene-1,4-hydroquinone with two electron deficient comonomers, namely (a) bis(4-fluorophenyl)sulfone and (b) 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole. The polymers will be called PAE-SO₂ and PAE-Oxa, respectively. The former polymer is a triptycene homologue of the commercially based UDEL polysulfone, which is also depicted in Scheme 1. The characterization data of these polymers are presented in Table 1, as well as the results for another PAE having a 3:1 molar ratio of comonomers a and b. Monomer b was selected because it has already been demonstrated that conjugated polymers containing an oxadiazole unit interact with various metal ions.¹¹ The first part of this paper will explore this interaction through the preparation of colloidal silver nanoparticles. We will then extend our study to thin films in which we can exploit this interaction as well as the free volume provided by the triptycenes.

It is well-known that the preparation of polymer-stabilized nanoparticles in solution proceeds via two steps:¹² reduction of the metal ions and polymer “complexation”/stabilization of the metal. The order in which these processes occur is very important; the reduction can take place either before or after interaction between the metal ion and polymer. If the reduction precedes the interaction, the polymer may not properly control the nanoparticle growth, and hence, the latter case is more favorable. Our hypothesis is that the oxadiazole-containing PAE (PAE-Oxa) will interact with silver ions, and thus stabilize silver colloids more readily than the sulfonated PAE (PAE-SO₂). To test this theory, we performed the microwave-assisted synthesis of silver nanopar-

ticles in *N,N*-dimethylformamide (DMF). DMF was selected because it acts as both the solvent and the reducing agent.¹³

Solutions of PAE-SO₂ and PAE-Oxa were prepared in DMF with silver perchlorate (AgClO₄) as the silver ion source, having a PAE/Ag⁺ wt % ratio of 1.0. The process of nanoparticle formation under microwave irradiation was monitored with UV-visible spectroscopy; the surface plasmon resonance band of silver nanoparticles is a standard diagnostic generally found between 400 and 450 nm, depending on the particle size.^{8c} Figure 1 shows the time evolution of the absorption spectra for the oxadiazole-incorporated PAE, whereas the inset depicts the sulfonated PAE results. In the PAE-Oxa case, the absorption gradually becomes stronger (i.e., nanoparticle production increases) with longer exposure to microwave irradiation. The absorption maximum also red shifts with time, suggesting an increase in particle size.^{8c} However, once heating is maintained beyond 20 min, aggregation and adhesion of the silver colloids take place on the walls of the glass reaction vial.^{13d} This is clearly evident in the UV-visible spectra of the PAE-Oxa, whereby a dramatic drop and broadening of the plasmon absorption is observed. In contrast, the PAE-SO₂ exhibits minimal (if any) nanoparticle stabilization. In this case, there is no longer a controlled evolution of nanoparticle

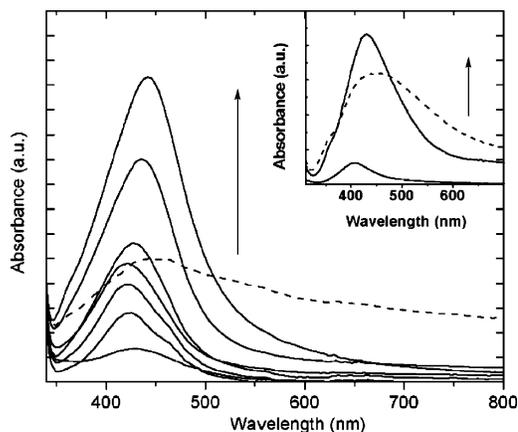


Figure 1. Time evolution of UV-visible spectra for the PAE-Oxa/silver DMF solution under microwave irradiation. The arrow represents the growth of the surface plasmon resonance band with increasing irradiation time (solid line; 1, 5, 6, 7, 14, 16, 18 min). The dashed line corresponds to aggregation and adhesion of the silver colloids onto the walls of the glass reaction vial, which occurs upon heating for more than 20 min. The inset plots the analogous absorption spectra of the PAE-SO₂/silver system. The solid absorption spectra are taken at 1 and 3 min. Within 5 min, the polymer-metal system precipitates out of DMF (dashed line).

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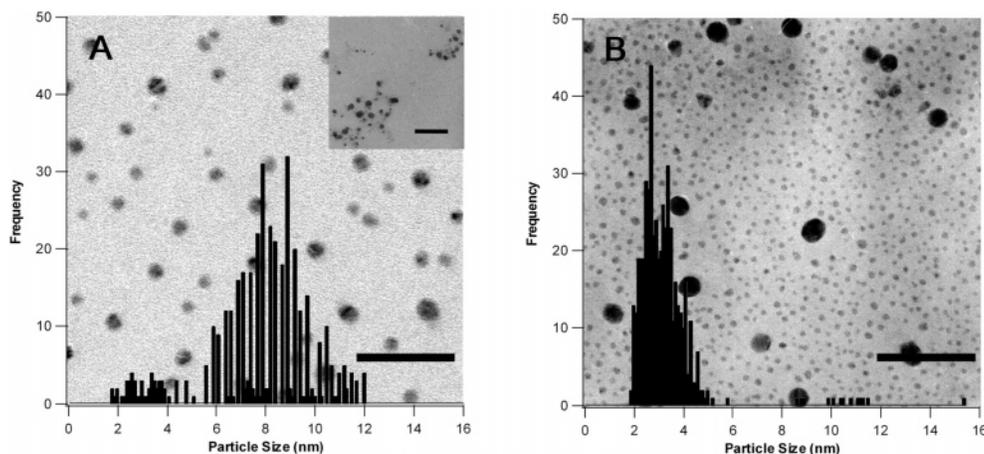


Figure 2. TEM images of silver nanoparticles stabilized in DMF by (A) PAE-SO₂ and (B) PAE-Oxa (scale bar = 50 nm), with their respective size distributions. Inset of (A) depicts the aggregation that occurs within the PAE-SO₂ sample (scale bar = 100 nm).

growth; instead, a single microwave pulse results in significant nanoparticle formation (Figure 1 inset). The silver nanoparticles then quickly aggregate and precipitate out of the DMF solution within 5 min. As a result, there is more reproducibility in the nanoparticle growth (i.e., evolution of the surface plasmon resonance band) when stabilized by the PAE-Oxa system.

Transmission electron microscopy (TEM) images of the nanoparticles are shown in Figure 2. To maintain consistency, the images were taken on the samples immediately prior to precipitation. A TEM image of the PAE-SO₂ sample, along with its corresponding histogram, is presented in Figure 2A. Although there were regions of isolated nanoparticles, many areas revealed the presence of large silver aggregates (Figure 2A inset). Overall, the size distribution of the isolated nanoparticles in the PAE-SO₂ sample gives a particle diameter of 8.2 ± 1.8 nm. Figure 2B is a representative TEM image of the PAE-Oxa sample. It is noted that there is a uniform distribution of fine particles (along with some larger particles), with an average particle size on the order of 3.0 ± 1.0 nm. Stopping the reduction well before the precipitation point would eliminate the large particles and, in turn, improve the dispersity of the PAE-Oxa-stabilized nanoparticles. This is not the case for the PAE-SO₂, as the majority of particle growth occurs in a single microwave pulse.

Having established that the oxadiazole-containing PAE interacts with silver ions, we proceeded to explore these systems in thin films. Our targeted approach was to use conventional spin-coating methods to cast uniform polymer-ion thin films, followed by in situ silver-nanoparticle formation via chemical reduction. The PAEs presented in Table 1 are all soluble in tetrahydrofuran (THF), a common organic solvent used for spin casting because of its volatility (i.e., low boiling point). As a result, silver triflate (AgOSO₂CF₃) was used as the silver ion source, because it is also soluble in THF.

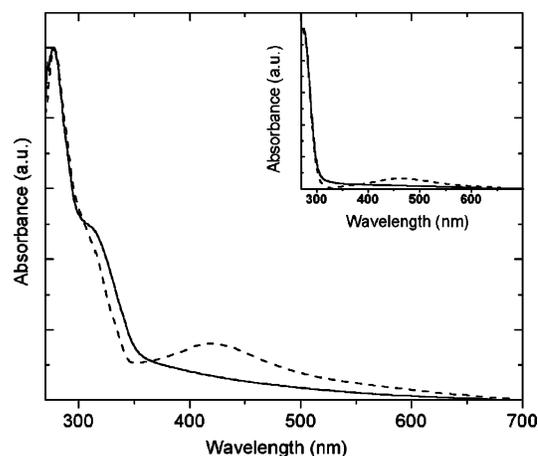


Figure 3. Absorption spectra of the PAE-Oxa-SO₂/silver film before (solid line) and after (dashed line) exposure to an aqueous solution of hydrazine. The inset plots the analogous absorption spectra of the PAE-SO₂/silver system.

Unfortunately, the interaction between the PAE-Oxa and silver triflate was such that the polymer-ion complex precipitated out of solution. To circumvent this solubility problem, we synthesized a PAE with reduced oxadiazole content and labeled it as PAE-Oxa-SO₂ in Table 1. Thin PAE-ion films were easily prepared from THF (10 mg PAE/mL), and were exposed to the vapors of an aqueous hydrazine solution for a few minutes to induce silver-ion nucleation. Silver nanoparticle formation was again confirmed with UV-visible spectroscopy and TEM.

The PAE-Oxa-SO₂ system has the additional benefit of a built-in oxadiazole-metal interaction. Therefore, any excess silver ions can be eliminated from the blend solution by first removing the THF through rotary evaporation. The residual composite material is then redissolved in chloroform (CHCl₃); any silver triflate not specifically interacting with an oxadiazole unit (i.e., excess silver ions) precipitates as AgCl, and is removed by centrifugation. Figure 3 shows the absorption spectra of the PAE-Oxa-SO₂/silver thin film (prepared from CHCl₃ and using the protocol mentioned above) before and after exposure to the hydrazine solution. The expected plasmon absorption of silver nanoparticles occurs at 420 nm in the thin film upon hydrazine exposure. In addition, a slight but noteworthy blue shift of the

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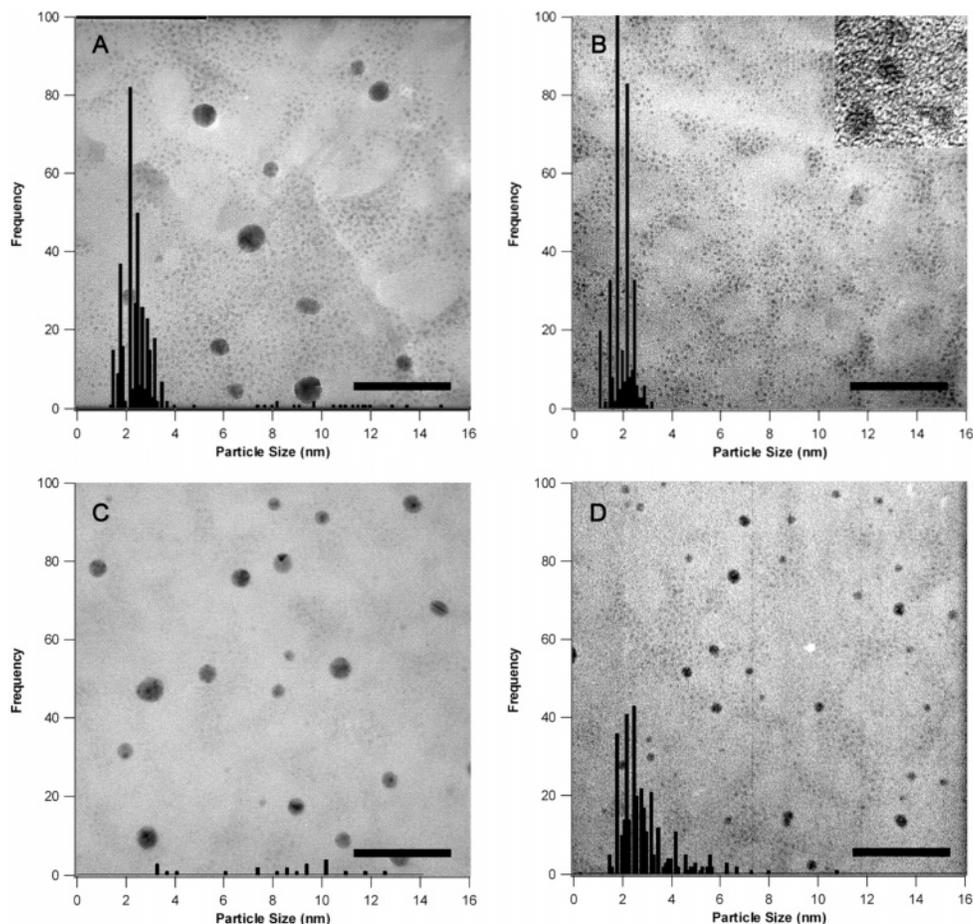


Figure 4. TEM images of silver-nanoparticle-embedded thin films (A) PAE-SO₂, (B) PAE-Oxa-SO₂, (C) UDEL, and (D) 50% triptycene (scale bar = 50 nm), with their respective size distributions. The inset of (B) presents a high-resolution image of the PAE-Oxa-SO₂/silver nanoparticle system.

oxadiazole absorption (from 315 to 310 nm) is observed, whereas the sulfone absorption remains unchanged (278 nm). This implies that the metal is selectively interacting with the oxadiazole moieties. The absence of any metal ion-polymer interaction in the sulfonated PAE system required spin casting directly from THF solution, and the analogous results are shown in the inset of Figure 3.

Characteristic TEM images of the PAE-SO₂ and PAE-Oxa-SO₂ nanoparticle-stabilized thin films are presented in panels A and B of Figure 4, respectively, with their corresponding size distribution histograms. Given the poor stabilization of nanoparticles by the PAE-SO₂ in solution, it is surprising to observe a much narrower distribution (2.3 ± 0.7 nm) of smaller particles in the corresponding thin film. In fact, the sulfonated PAE stabilizes silver nanoparticles almost as readily as the PAE-Oxa-SO₂ system. The obvious advantage of the latter PAE is that the excess silver triflate can be removed. The resulting nanoparticles are relatively uniformly dispersed (average particle diameter of 1.9 ± 0.7 nm), and do not display the larger silver particles that are present in the sulfonated PAE film.

We attributed the general improvement in the stabilization of nanoparticles by the sulfonated PAE film relative to that in solution to the free volume and porous polymer network that results from the presence of the triptycene monomer. To confirm this rationale, the same thin-film technique was

applied to the UDEL polysulfone. A TEM image of the commercial PAE is shown in Figure 4C. The nanoparticles are significantly larger (and more sparse) than those observed in panels A and B of Figure 4. This finding suggests that the triptycene unit readily isolates the silver ions, and prevents the nucleation of predominantly large nanoparticles. To further probe this effect, we synthesized a poly(aryl sulfone) ($M_n = 14\,100$; PDI = 2.90; $T_g = 234$ °C; $T_d = 489$ °C) with equimolar amounts of triptycene-1,4-hydroquinone and monomer bisphenol A (see Scheme 1). A TEM image of the corresponding nanoparticle-stabilized thin film is given in Figure 4D. Although the amount of triptycene was reduced by a factor of 2, the film readily stabilized small nanoparticles similar in size (2.3 ± 0.8 nm) to those present in the PAE-SO₂ film (Figure 4A). Our expectation was that the film would stabilize silver particles between the size distributions of Figure 4A (PAE-SO₂) and Figure 4C (commercial polysulfone). From the analysis in Figure 4D, it is apparent that the nanoparticle size trails into the 4–6 nm particle-size region, which further supports the importance of free volume in this in situ technique. Our group is currently conducting a thorough investigation of the threshold limit of triptycene required in the film in order to stabilize the smaller nanoparticles.

In summary, this study introduces a new convenient route to the in situ formation of well-dispersed silver nanoparticles

in an insulating polymer matrix. By appropriately engineering the PAE backbone structure to interact with metal ions, we were able to easily spin cast relatively uniform polymer-ion thin films. Subsequently, nanoparticle formation was induced by exposure of the polymer-ion film to the vapors of a chemical reducing agent. In contrast to traditional in situ methods,^{8a,b,e,f,h} our approach maintains the chemical integrity of the polymer matrix. Because PAEs are an important engineering thermoplastic, we expect that such metal-polymer composites will readily find applications in high-performance devices. Moreover, the present protocol provides an even broader platform, which offers great modularity and versatility in the design of the polymer host and the selection of the metal-ion source. One can easily

envision applying this system to the formation of other metal or metal alloy nanoparticles.

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Supporting Information Available: Details of the PAE synthesis and characterization, microwave nanoparticle synthesis, polymer-nanoparticle thin-film preparation, and TEM samples (pdf). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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