

Nanocomposite Hydrogen-Bonded Multilayer Ultrathin Films by Simultaneous Sexithiophene and Au Nanoparticle Formation

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Terthiophene-functionalized poly(4-vinylpyridine) (PVP3T) was incorporated successfully as a reductant to form Au nanoparticles within hydrogen-bonded complexed multilayer thin films. By employing polymer pendant terthiophene moieties, this eliminated the need for an external reducing agent. The redox reaction with HAuCl_4 yielded Au nanoparticles simultaneously with the formation of electrooptically active sexithiophene units. The nanocomposite films were characterized by TEM, XPS, UV–vis, photoluminescence, FT-IR, and ellipsometry measurements. The TEM images confirm unequivocally the formation of well-dispersed nanoparticles within the multilayer structure with a range of size distributions dependent on the preparation conditions. Interestingly, we observed the growth of dendritic nanostructures within the PVP3T/poly(acrylic acid) multilayers with modifications to the preparation procedure. On the basis of these results, this method yields a unique approach for the fabrication of nanocomposite multilayer heterostructures comprised of metallic nanoparticles and conjugated oligomers with interesting nanostructural and spectroscopic properties.

Introduction

Hybrid nanocomposite polymer materials combine the versatility of polymer processing with the interesting properties of inorganic materials such as those found in metal and semiconductor nanoparticles.¹ Because of their small size, metal and semiconductor nanoparticles often have electrooptical properties drastically different from those of the same bulk materials. The novel properties observed in materials with spatially confined dimensions on the nanometer scale may find applications in areas such as catalysis, optoelectronics, magnetism, and sensing. Although several methods for producing such nanostructured materials have recently been reported in the literature, those which focus on organic- or polymer-based thin film geometries are of particular interest. The thin film approach to nanoparticle composites provides a means to manipulate these otherwise difficult to handle particles for device applications. In addition, the ability of polymers to undergo nanoscale self-assembly, e.g., layer-by-layer methods, offers an added degree of control toward supramolecular structures of nanoparticle-containing thin films. For example, block copolymers have often been employed as “nanoreactors” for the fabrication of thin films with inorganic nanoparticles selectively incorporated into the various morphologies of the microseparated domains. Cohen and co-workers have published much of the work

on block copolymer templated synthesis of nanoparticles leading to a generalized nanoreactor scheme in which a wide variety of nanoparticles may be obtained.² Sohn et al. recently reported the fabrication of polymer thin film multilayer nanostructures of alternating polymeric lamellae resulting from the microphase separation of symmetric polystyrene-*block*-poly(4-vinylpyridine) block copolymers.³ Gold nanoparticles could then be selectively synthesized in the poly(4-vinylpyridine) lamellae to impart functionality for electronic and nonlinear optical applications. Similar results with multilayered thin films were also reported with symmetric block copolymers of polystyrene-*block*-poly(methyl methacrylate) and palladium nanoparticles.⁴

Another prevalent approach reported in the literature for the development of hybrid nanostructured thin films involves a simple layer-by-layer process. This method, first introduced by Decher, has proven to be a very useful technique to fabricate multilayer composites with a wide variety of architectures and properties. In this technique, the buildup of multilayers is based on the electrostatic interaction and spontaneous adsorption of oppositely charged polyelectrolytes.⁵ However, the formation of multilayer thin films need not be based on electrostatics. In recent years, a number of multilayer

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structures have been reported based on both strong and weak interactions such as coordination bonding, charge-transfer interactions,⁶ and specific recognition.⁷ Several groups have reported the preparation of alternating multilayer films via hydrogen bonding of complimentary partners.⁸ In general, the simplicity of the layer-by-layer process has led to the development of some complex nanostructured multilayer thin films comprised of materials such as electroactive and conducting polymers, biological molecules, and organic dyes.⁹ Although this method has been used extensively to fabricate multilayered thin films consisting of preformed nanoparticles,¹⁰ little work has been reported which combines the layer-by-layer deposition and the nanoreactor approach previously mentioned.

Rubner and co-workers have recently extended the nanoreactor concept to include the use of polyelectrolyte multilayer thin films to produce spatially confined nanoparticles within a supramolecular matrix.¹¹ This involved the use of multilayer heterostructures in which one polyelectrolyte has a strong affinity for inorganic ions and another polyelectrolyte layer is unable to bind any inorganic ions. Subsequent reduction of the inorganic ions yielded a multilayer thin film with spatial control over the growth of the nanoparticles. More recently, Nolte et al. have used this approach to create refractive index gradients within polyelectrolyte multilayers and demonstrated their function as rugate filters.¹² Using a similar approach, Dai and Bruening used poly(ethylenimine)-metal ion complexes and polyanions to fabricate multilayered polyelectrolyte films. External reduction of the metal ions after film deposition yielded a composite film containing catalytic nanoparticles.¹³ Bruening's group recently extended this work to include Pd nanoparticles embedded in polyelectrolyte multilayer coated colloidal particles which could then be used in selective hydrogenation reactions.¹⁴ Using a nanoreactor scheme with postdeposition reduc-

tion of the nanoparticle precursors has several distinct advantages over fabrication of multilayers using preformed nanoparticles. First, methods for the synthesis and isolation of uniform, stabilized nanoparticles in solution are not needed since nanoparticles can be formed after the polymer layers have been deposited. This should allow more control over the supramolecular structure of the resulting film. Second, the nanoparticles formed should be well stabilized by the surrounding polymer matrix, limiting the amount of particle aggregation that may occur otherwise. Finally, since the metal ions are well dispersed along the polymer backbone prior to reduction, the resulting particles are well distributed throughout the film, in a selective manner if so desired.

A common theme in the nanoreactor schemes reported thus far is the required use of an external reducing agent, e.g., NaBH₄ or hydrazine, to form the metal nanoparticles. In another case, an interesting approach would be to use polymers having pendant reducing agents for the reduction of the nanoparticles within thin films. It has previously been shown by Hempenius et al.¹⁵ that gold nanoparticles may be prepared inside well-defined polystyrene (PS)-oligothiophene (OT)-polystyrene triblock copolymer micelles without the use of an additional reducing agent. While a toluene solution of HAuCl₄ and the PS-OT-PS copolymer was stirred, it was observed to undergo a rapid color change from red to blue, which the authors attributed to the transfer of the gold salt to the oligothiophene core, followed by an electron transfer from the oligothiophene to the gold salt and the formation of gold nanoparticles within the core of the copolymer. Likewise, we have shown it is possible to synthesize gold nanoparticles within a terthiophene-based polyelectrolyte complex.¹⁶ Youk et al. demonstrated the oxidative coupling of terthiophene to form sexithiophene with the simultaneous formation of the gold nanoparticles. Interestingly, oligothiophenes and thiophene-containing compounds have attracted a great deal of attention as materials with potential applications in electronic devices such as light-emitting diodes, transistors, and photovoltaic devices.¹⁷ Thus, by incorporating conjugated organic materials into nanostructured multilayer thin films in conjunction with metallic nanoparticles, novel optical and electronic properties can be obtained.¹⁸ For example, Park et al. have shown an enhancement in the luminescent lifetime of polymer light-emitting devices by doping the emissive layer of the device with small gold nanoparticles.¹⁹ Likewise, such combinations of gold nanoparticles and conjugated dendrimers have proven useful as chemiresistor sensor devices.²⁰

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In the present work, we demonstrate for the first time that inorganic nanoparticles may be synthesized within hydrogen-bonded layer-by-layer multilayer films using polymers containing pendant terthiophene oligomers as reducing agents. The advantage of this approach to nanocomposite film formation is the elimination of the additional step of introducing an external reducing agent while incorporating simultaneously the optical and electrical properties of oligothiophenes. By modifying the type and architecture of the pendant organic reducing agent, these films could find application in the area of organic electronic and sensor devices. Additionally, we show that this method may provide a unique approach for the preparation of dendritic metal nanostructures within the confined dimensions of a layer-by-layer multilayer thin film.

Experimental Section

Chemicals. The polymers poly(4-vinylpyridine) (P4VP; MW ca. 60000) and poly(acrylic acid) (PAA; MW ca. 10000) were purchased from Aldrich and used as received. All other chemicals were used as received unless otherwise stated. All the essential chemicals and reagents were purchased from Aldrich except for Fisherbrand ultrasonic cleaning solution, which was purchased from Fisher. 5-(6-Bromohexyl)-2,2':5',2''-terthiophene (BHBT) was synthesized according to our previous studies.²¹ Terthiophene-functionalized P4VP (PVP3T) was obtained by quaternization of the pyridine moiety along the P4VP backbone with BHBT. In particular, P4VP was dissolved in dimethylformamide (DMF) under constant stirring. A prescribed amount of BHBT was then added to the reaction flask, and the reaction was carried out at 85 °C for 2 days. The progress of the reaction was monitored by TLC. At the completion of the reaction, the mixture was cooled to room temperature and precipitated in hexane at 0 °C under rigorous agitation. The polymer was purified by repeated precipitation (three times) in hexane. The resulting product was characterized by NMR, elemental analysis, and UV-vis. The degree of quaternization and thus the amount of BHBT incorporated into the P4VP were estimated using elemental analysis based on the amount of the bromide counterion present in the material. It was found that 20% of the pyridine units were successfully quaternized with BHBT. This was also confirmed by UV-vis spectroscopy using the molar extinction coefficient of BHBT to estimate the concentration of BHBT incorporated into the polymer.

Substrate Preparation. Multilayer films were fabricated on a variety of substrates including silicon (ellipsometry) and glass and quartz slides (UV-vis and fluorescence). Deionized water used in all cleaning steps was purified by an ion-exchange and filtration unit (Milli-Q Academic system, Millipore Corp.) equipped with a 0.22 µm Millistack filter at the outlet. The resistivity was 18.2 M·cm. Silicon wafers and glass microscope slides were cut into squares of 2.5 × 3.0 cm². The substrates were rigorously sonicated with ultrasonic cleaning solution, Millipore water, 2-propanol, and acetone consecutively for 15–20 min each. The substrates were then soaked in piranha solution [H₂O₂/H₂SO₄, 30/70 (v/v)] for 30 min and subsequently rinsed by sonication in Millipore water. The substrates were then immersed in 0.5% (w/w) poly(ethylenimine) (PEI), resulting in a NH₂-modified surface. For the freshly cleaned silicon wafers, the SiO₂ layer thickness was measured by ellipsometry and found to be 19.0 Å. By the same procedure, the PEI layer thickness was found to be 7.6 Å.

Measurements. The UV-vis spectra were obtained on a Perkin-Elmer spectrophotometer (Lambda 20). Photolumines-

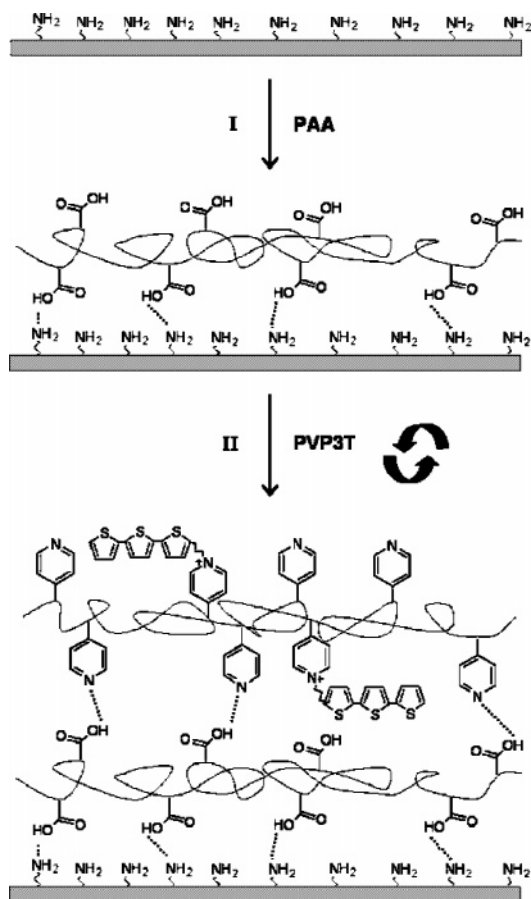


Figure 1. Schematic representation of the layer-by-layer deposition of PVP3T and PAA on an amine-functionalized substrate.

cence spectra were recorded on a Perkin-Elmer spectrofluorometer (LS50B) equipped with a Xe lamp and a front-face mirror configuration. All optical measurements were performed at room temperature under ambient conditions. The layer thickness was measured by ellipsometry (Si wafer) after drying. Three measurements were taken for every layer, and an average thickness was calculated. Ellipsometric thickness measurements were performed on a Multiskop (Optrel GbR) with a 632.8 nm He-Ne laser beam as the light source. Both δ and ψ value thickness data were measured and calculated by integrated specialized software. TEM was performed on a JEOL 2000 FX microscope operating at 200 kV. Films for TEM were prepared by depositing three bilayers on Formvar-coated gold grids followed by treatment as described in the sections below.

Multilayer Deposition. The fabrication of the multilayer thin films is shown schematically in Figure 1. Substrates were modified with PEI by submersion in a 0.5% (w/w) aqueous solution for 1 h. The poly(ethylenimine)-modified substrates were immersed in a methanol solution of PAA (0.236 mg/mL) for 15 min. This resulted in the deposition of a PAA layer through the interaction of the carboxyl groups with the NH₂ groups of the PEI prelayer. After being rinsed with copious amounts of methanol, the substrate was transferred into a methanol solution of PVP3T (0.236 mg/mL) for 60 min, thus adding a PVP3T layer through the interaction of the free pyridine groups with the carboxyl groups of the underlying PAA layer. Multilayers were obtained by repeating the above procedure in a cyclic fashion.

Nanoparticle Formation. After deposition of the PVP3T/PAA multilayers, the thin films were immersed into a 1 wt % methanol solution of HAuCl₄ for up to 3 h. The films were then removed and rinsed with copious amounts of methanol to remove the excess HAuCl₄. The thin films loaded with HAuCl₄ were then placed in an oven for a prescribed amount of time

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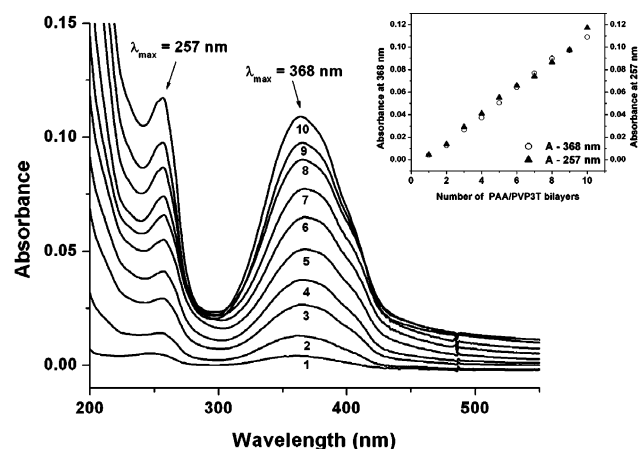


Figure 2. UV-vis absorption spectra of the PVP3T/PAA multilayer thin film with increasing number of bilayers. Inset: Absorbance at 257 and 368 nm vs the number of PVP3T/PAA bilayers showing the linear film growth.

at 60 °C and 95% humidity. The formation of the gold nanoparticles was followed by UV-vis spectroscopy. It should be noted that the reaction on the PAA/PVP3T multilayers was also carried out under various conditions (room temperature, ~70% humidity) with similar results. The differences lie in the kinetics of the reaction as it took ~8 days for the nanoparticles to form at room temperature. A temperature of 60 °C and 95% humidity were the optimal conditions for the experiments described herein.

Results and Discussion

Multilayer Film Formation. To determine an appropriate deposition time for the PVP3T polymer, the adsorption of a single layer was monitored by UV-vis spectroscopy. The adsorption process was monitored using the maximum absorbance at 366 nm, which is assigned as the π - π^* transition for the terthiophene moiety. Prior to the deposition of PVP3T, a prelayer of PEI and poly(acrylic acid) was deposited on the glass substrate, allowing for the adsorption of the PVP3T layer to occur. This was shown by the growth in absorbance at 366 nm as a function of time when deposited from a 0.236 mg/mL PVP3T methanol solution (see Figure S1 of the Supporting Information). In this case, the absorbance initially increased in a rapid manner. After a period of 60 min, significant increases in the absorbance were no longer observed, indicating a point of saturation in the deposition process. Thus, the immersion time in the PVP3T solution was set at 60 min. A deposition time of 15 min was used for the PAA layer in accordance with the literature.⁸

Likewise, UV-vis spectroscopy was used to monitor the deposition and sequential growth of PVP3T and PAA multilayer thin films. Figure 2 shows the UV-vis absorption of a PAA/PVP3 film on a quartz substrate with increasing number of bilayers. The maximum absorbance, λ_{max} , at ~257 nm is due to the π - π^* transition of the pyridine ring of P4VP. As previously stated, the λ_{max} at ~368 nm is attributed to the π - π^* transition of the terthiophene oligomer. Figure 2 (inset) also shows that the absorbance at both λ_{max} values increases in a linear fashion with respect to the number of bilayers, indicating regular growth of the PAA/PVP3T multilayer thin film.

The thickness also increases linearly with layer formation for the thin films as measured by ellipsometry

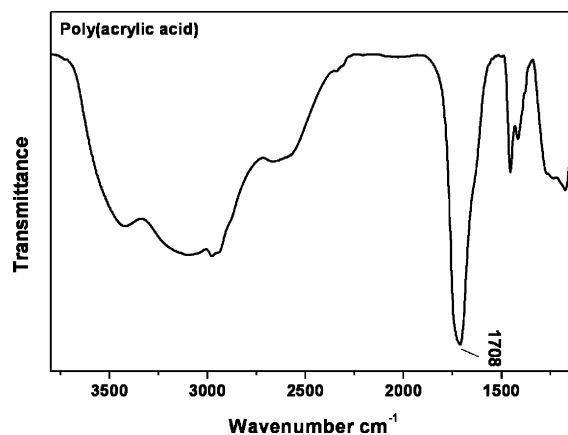


Figure 3. FTIR spectrum of pure PAA prepared as a KBr pellet.

(Figure S2 of the Supporting Information). The optical thickness data for the PAA/PVP3T combination reveal a linear trend in the deposition process consistent with the linearity shown by UV-vis. The average thickness for each PAA/PVP3T bilayer was 3.54 nm.

Driving Force for Adsorption. Although it has previously been shown that PVP and PAA are excellent hydrogen-bonding partners,⁸ the driving force for the adsorption process in our system was subjected to further investigation. This is due to the structure of the PVP3T polymer. PVP3T consists of a poly(4-vinylpyridine) backbone which is partially quaternized with a bromoalkylterthiophene derivative. The degree of quaternization was determined by elemental analysis of bromine present in the material as a counterion for the positively charged pyridinium units. Using this method, it was found that ~20 mol % of the pyridine units were quaternized. It is this partial quaternization that imparts a positive charge along the PVP backbone. Thus, it is necessary to determine whether the driving force for adsorption of PVP3T is based on hydrogen bonding or electrostatics. For this reason, FTIR spectroscopy was used to investigate the interactions responsible for multilayer formation. Figure 3 shows the FTIR spectrum for pure poly(acrylic acid) prepared in a KBr pellet. The spectrum of pure PAA has a broad absorption band in the 3000–3500 cm^{-1} region attributed to the -OH stretch and a strong absorption peak at 1708 cm^{-1} (-C=O). In the case of pure PAA, the majority of the carboxylic acid groups exist as intermolecular hydrogen-bonded cyclic acid dimers (self-association) as indicated by the position of the carbonyl stretch at 1708 cm^{-1} .²² This peak is observed at a significantly lower frequency than a peak due to unassociated carbonyl groups otherwise referred to as “free acid” groups. The free acid group in PAA is typically observed at ~1732 cm^{-1} . In the PAA/PVP3T film (Figure 5), the carbonyl stretch is observed at 1718 cm^{-1} . This intermediate band at 1718 cm^{-1} is attributed to neither a carbonyl present as a free acid group nor a self-associated acid dimer, but rather a carbonyl that has formed a stronger hydrogen bond as a result of the association with the nitrogen atom of the pyridine groups.²³ Additionally, changes in

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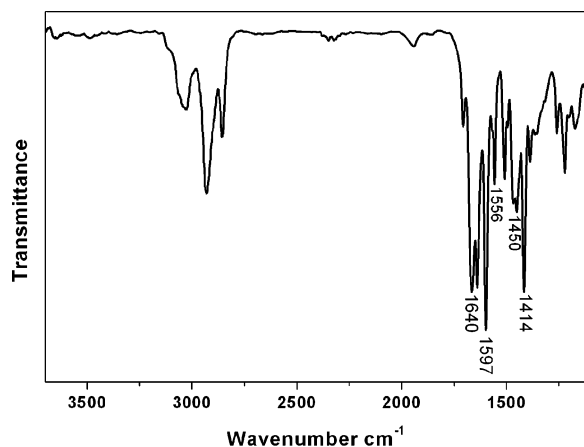


Figure 4. FTIR spectrum of pure P4VP prepared as a KBr pellet.

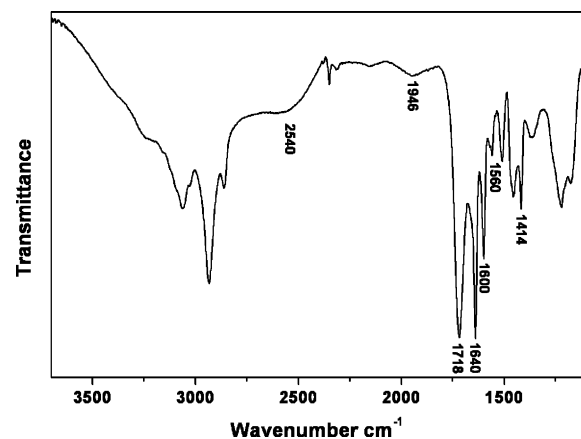


Figure 5. FTIR spectrum of a 10-bilayer PVP3T/PAA thin film as prepared on a polished silicon substrate.

the satellite bands for the -OH stretching mode indicate hydrogen bonding as the driving force for film formation. In pure PAA, a satellite band for the -OH group is observed at $\sim 2650\text{ cm}^{-1}$. The position of this band has been attributed to relatively strong hydrogen bonds such as those present between carboxylic acid dimers. When we compare this to the satellite stretching band (-OH) in the PAA/PVP3T film in which acid dimers have been disrupted by the interaction of the acid groups with pyridine, we see that the satellite band shifts to lower frequency and is observed at 2540 cm^{-1} (see Figure 5). This shift to lower frequency is indicative of the formation of stronger hydrogen bonds than those present in pure PAA. In addition, a new satellite band for the -OH group is observed at 1946 cm^{-1} in the PAA/PVP3T film, which has also been attributed to the formation of strong hydrogen bonds between the acid and pyridine groups.²⁴ The FTIR spectrum of pure PVP3T is shown in Figure 4. The strong absorption peak observed at 1597 cm^{-1} is attributed to the in-plane C–N skeletal vibration of the free pyridine unit. Absorption peaks at 1556 , 1450 , and 1414 cm^{-1} are also assigned to the ring vibration of the pyridine ring but are generally unaffected by the formation of hydrogen bonds.⁸ With regard to the peaks associated with the pyridine unit in P4VP, the strong absorption band at 1596 cm^{-1} observed in pure P4VP shifted to 1600 cm^{-1} , indicating the forma-

tion of hydrogen bonds.²⁵ These results provide sufficient evidence to support hydrogen bonding as the driving force for the adsorption of the PAA/PVP3T multilayers. The absorption band appearing at 1640 cm^{-1} is a result of the alkylation of the pyridine units with the bromoalkylterthiophene derivative BHTT.²⁶ In comparison with the FTIR spectrum of pure P4VP (not shown), a decrease in the intensity of the absorption band at 1414 cm^{-1} is also observed as a result of the quaternization of the pyridine unit.²⁷ The presences of skeletal ring vibrations of both pyridine (1600 and 1414 cm^{-1}) and pyridinium (1640 cm^{-1}) species in the PVP3T material further support the fact that only a partial number of the pyridine groups are quaternized with BHTT.

Gold Nanoparticle Formation. UV–vis spectroscopy was first employed to follow the formation of gold nanoparticles and simultaneous coupling of the terthiophene units within the multilayer films. UV data shown hereafter were obtained from a 10-bilayer PAA/PVP3T multilayer film prepared on a glass substrate. After the fabrication of the PAA/PVP3T multilayer thin films, the next step is “loading” the film with the gold precursor, HAuCl_4 . The thin PAA/PVP3T films were immersed into a methanol solution of HAuCl_4 so that gold precursors, AuCl_4^- , were coordinated to the free pyridine units within the PVP3T layers. Here, the term “free pyridine” is used to refer to those P4VP pyridine units which are neither quaternized with BHTT nor hydrogen-bonded to PAA. The films were exposed to the HAuCl_4 for 3 h to ensure a near-equilibrium condition between the free pyridine units and HAuCl_4 , i.e., one HAuCl_4 /free pyridine. It is important to note that the stoichiometry of the reactants (terthiophene and HAuCl_4) is difficult to determine within the multilayer thin film. While the ratio of 3T to free pyridine is initially 4:1 in bulk PVP3T, this ratio is not consistent once the PVP3T is deposited as a thin film in conjunction with PAA. After deposition, a number of pyridine units are involved in hydrogen bonding with PAA and are unavailable for the reaction with HAuCl_4 .²⁸ Thus, the exact concentration and corresponding ratio of the reactants are not quantitatively known for this system since the number of free pyridine units within the multilayer is not easily obtained. However, on the basis of the evidence presented herein, it is believed that the ratio of 3T to free pyridine (subsequently protonated with HAuCl_4) is sufficient for the reaction to occur to completeness. Protonation of the pyridine groups by HAuCl_4 is evident from the appearance of the metal–ligand charge transfer (MLCT) transition of the AuCl_4^- ions at 325 nm shown in Figure 6. This is typically observed for AuCl_4^- complexes.²⁹ The “loaded” PAA/PVP3T thin films were then placed in an oven at $60\text{ }^\circ\text{C}$ under 95% humidity. The progress of the reaction was monitored by taking

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(28) It is believed that the hydrogen-bonded 4VP units do not participate to a great extent in the protonation reaction with HAuCl_4 since this process would lead to film degradation due to the loss of hydrogen-bonding sites on PVP3T. UV–vis showed no degradation of the multilayer thin film upon exposure to a methanol solution of HAuCl_4 .

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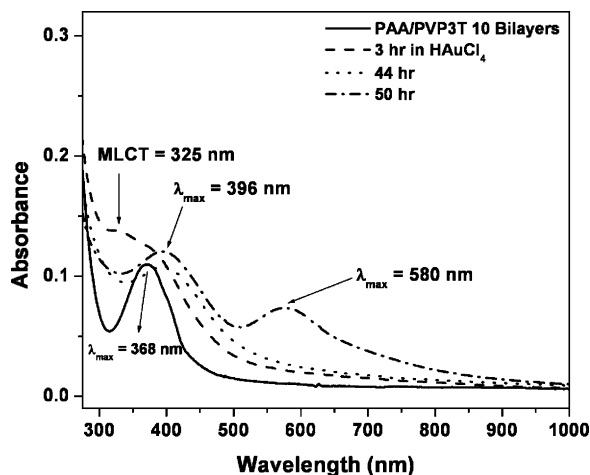


Figure 6. UV-vis spectra of a PVP3T/PAA multilayer thin film showing the progress toward Au nanoparticle formation: (solid line) 10-bilayer PVP3T/PAA as deposited; (dashed line) PVP3T/PAA film after exposure to HAuCl_4 ; (dotted line) PVP3T/PAA at 44 h under the reaction conditions; (dashed-dotted line) PVP3T/PAA at 50 h under the reaction conditions.

the UV-vis spectrum of the film as a function of time. Figure 6 shows the series of spectra for a 10-bilayer PAA/PVP3T thin film. The solid line represents the spectrum as taken from a freshly prepared 10-bilayer PAA/PVP3T thin film. The peak at 368 nm is an absorption feature attributed to the terthiophene moiety as previously discussed. Under exposure of the described conditions, the MLCT band at 325 nm observed in the loaded thin films can be seen to disappear over time. By 44 h, the MLCT band of the AuCl_4^- /pyridine complex is no longer observed. Simultaneously, the absorbance of the terthiophene moiety is red-shifted from 368 to 396 nm and is substantially broadened with respect to the original absorption peak of the PVP3T terthiophene derivative. The broad red-shifted absorption band at 396 nm can be attributed to coupling of the terthiophene moieties and the formation of sexithiophene via a radical cation mechanism (Figure 7).^{16,30} It can be assumed that not all of the terthiophene units participate in the redox reaction with the gold precursor, leading to a system with both terthiophene and sexithiophene present. If this is true, one would expect to see a convoluted absorption spectrum which spans the absorbing region of both species with a λ_{max} between those of terthiophene and sexithiophene. Such is the case in Figure 6. Although the absorption spectrum of sexithiophene derivatives strongly depends on the degree and type of substitution, in general they absorb around 420–435 nm.³¹ Clearly, the absorption spectra of the PAA/PVP3T thin film observed at 44 and 50 h show characteristics of a mixed system of terthiophene and sexithiophene

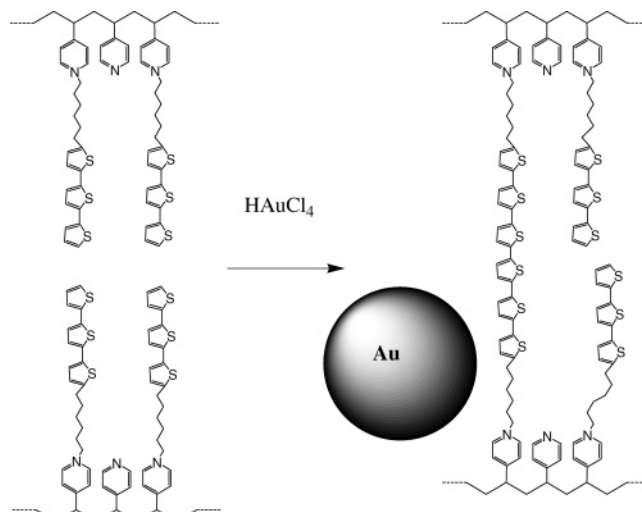


Figure 7. Diagram showing the simultaneous formation of Au nanoparticles and sexithiophene units via redox coupling: oxidation of terthiophene (radical cation mechanism) and reduction of AuCl_4^- to Au^0 .

derivatives indicated by the red-shifted broadened absorbance which tails off around 500 nm.

As a result of the redox reaction between the terthiophene derivative in PVP3T and the gold precursor (AuCl_4^-), we also expect the formation of gold nanoparticles to occur as Au^{III} is reduced to Au^0 . Selvan et al. have reported similar results in the preparation of gold-polypyrrole composites in which pyrrole can be polymerized in the core of a diblock copolymer micelle with simultaneous formation of gold nanoparticles.³² Similar results have also been shown using *o*-anisidine as a reductant in aqueous and organic systems.³³ In our system, the observation of a distinct gold surface plasmon (SP) band at 580 nm (shown in Figure 6) confirms the formation of gold nanoparticles. This peak indicates that electron transfer from the terthiophene to AuCl_4^- occurred, resulting in a slow reduction of AuCl_4^- to gold nanoparticles. Although the spectrum at 44 h shows evidence of the redox reaction, the absence of the surface plasmon band may be explained by the formation of tiny nanoparticles (<2 nm) for which the plasmon band is not observed.³⁴ The surface plasmon peak at 580 nm consistently appeared in the absorption spectrum of the PAA/PVP3T thin film at a time of 48–50 h when subjected to the described conditions. The appearance of the surface plasmon peak in the UV-vis absorption spectrum was accompanied by a change in color from yellow to red of the PAA/PVP3T multilayer film. A similar observation was reported on dendrimer/gold nanoparticle thin films.³⁵ The peak was observed to grow in intensity until such a time when a measurable change in the absorbance at 580 nm could no longer be recorded, usually ~ 72 h. To rule out the possibility of thermal reduction of the gold precursor, a 10-bilayer PAA/PVP film loaded with HAuCl_4 was subjected to the same conditions (60 °C, 95% humidity) as the PAA/PVP3T system. Unlike the PVP3T system, a surface

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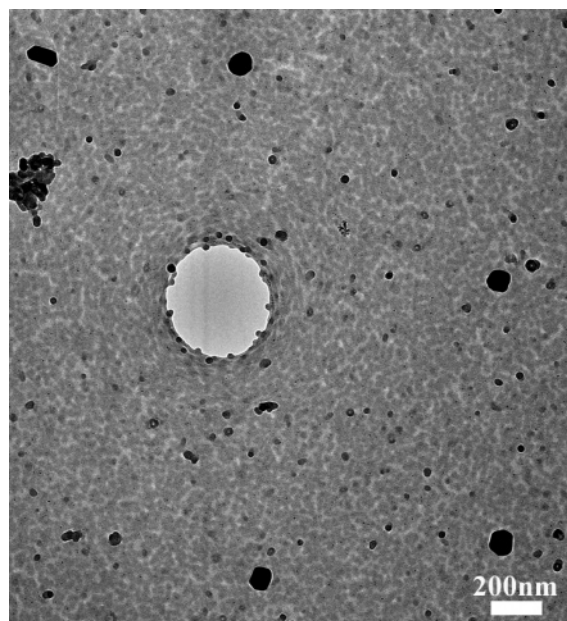


Figure 8. TEM image of a three-bilayer PVP3T/PAA film containing Au nanoparticles after ~50 h at 60 °C and 95% humidity. Scale bar = 200 nm. The bright feature in the center of the image is a hole in the Formvar film.

plasmon peak was not observed for the PAA/PVP in the absence of the terthiophene moiety (Figure S4 of the Supporting Information). X-ray photoelectron spectroscopy (XPS) was employed to investigate the valence of the Au nanoparticles as synthesized within the PAA/PVP3T multilayer films. The emission of the Au4f photoelectrons identified by two peaks at 88.3 and 84.8 eV in the XPS spectra were assigned to Au⁰ (Figure S3 of the Supporting Information).³⁶ The absence of gold in a higher oxidation state indicates that a complete reduction of the AuCl₄⁻ has occurred.

It should be noted that the position of the surface plasmon band in our system is somewhat red-shifted from what is predicted by Mie theory.³⁷ Typically, the surface plasmon band for gold nanoparticles appears around 520 nm, although several factors influence its position including particle size and shape³⁸ and the refractive index of the surrounding medium.^{39,40} In the present case, the observed red shift and broadening in the surface plasmon band can be attributed to a wide distribution of particle sizes ranging from 6 to 100 nm (average 33 nm) as shown by the TEM image in Figure 8. In general, the size of the nanoparticles obtained by the reduction of a gold species within a given matrix depends on several factors including the type of reducing agent and the loading of the gold precursor.⁴¹ The type of reducing agent generally determines the particle growth and the rate of nucleation: a slow reduction

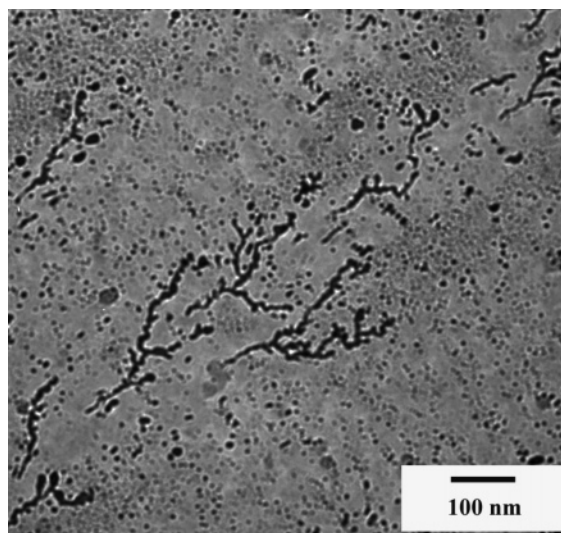


Figure 9. TEM image depicting dendritic nanostructures formed with the PVP3T/PAA thin film after a modification of the preparation conditions (see the text for a description).

yields large particles, while a fast reduction yields smaller particles. The latter factor determines the local concentration of metal species available for reduction, with a higher concentration giving larger nanoparticles. The large size of the nanoparticles in our system may be attributed to a combination of these two factors given the extended times needed for reduction to occur and the high concentration of HAuCl₄ at the time of loading. In addition, the spectrum observed after 50 h shows an absorption tail extending from ~650 to 800 nm, which is generally regarded as an indication of either particle elongation or particle aggregation.⁴² In our system, this absorption tail is most likely due to the presence of a small amount of particle aggregation. This would result in the coexistence of a number of smaller nanoparticles scattered within the multilayer thin film with a large agglomeration of individual particles (Figure 8). Note that the nanoparticle intensity (contrast) is variable for the scattered particles in the image, indicating their presence at different depths, consistent with their formation in a multilayer film.

Interestingly, we have observed the growth of some elegant dendritic nanostructures using an approach similar to the one described above by slightly altering the preparation conditions. The PVP3T/PAA multilayer thin films deposited on Formvar-coated gold TEM grids were loaded with HAuCl₄ as previously described. The film was then subjected to the same reaction conditions as above for ~44 h. The film was then removed from the reaction environment, exposed once again to a solution of HAuCl₄ for 1 h, and then returned to the reaction conditions for an additional 24–48 h. As shown in the micrograph in Figure 9, dendrite-like nanostructures were observed to grow among a multitude of small spherical nanoparticles. The average width of the fractal growths was ~5–6 nm with similar sizes observed for the spherical particles. Similar observations of metal dendrites have been reported by Wang and co-workers using tetrathiafulvalene as a reducing agent for silver

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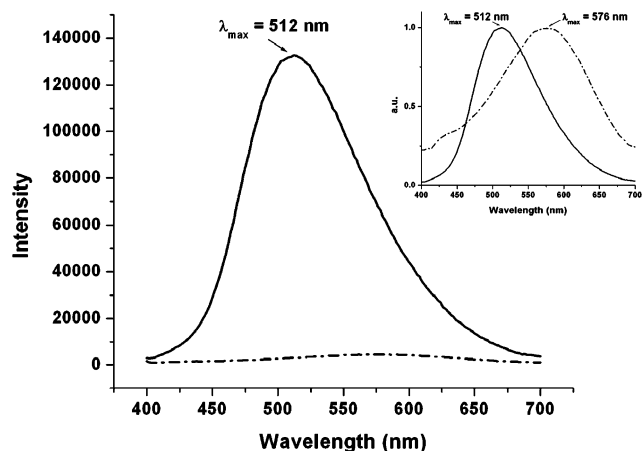


Figure 10. Photoluminescence (PL) spectra of a 10-bilayer PVP3T/PAA multilayer thin film before and after the incorporation of gold nanoparticles. The inset shows the same spectra normalized to illustrate the red shift in the PL spectra with the formation of sexithiophene within the film.

ions in acetonitrile.⁴³ Selvan et al. have also observed fractal growth in their gold–polypyrrole nanocomposites.³² It is generally accepted that dendritic fractals occur by a nonequilibrium growth phenomenon. These random supramolecular nanostructures are usually explained by a diffusion-limited monomer–cluster aggregation model.⁴⁴ The factors that influence the nucleation and growth mechanism for the dendritic nanostructures observed in the current work will be addressed in a future paper.

Photoluminescence Measurements. In addition to UV–vis spectroscopy, photoluminescence measurements were used to investigate the PAA/PVP3T multilayer thin films before and after nanoparticle formation. Figure 10 shows the photoluminescence spectra for a 10-bilayer PAA/PVP3T multilayer thin film before and after gold nanoparticles have been formed. The inset has been normalized to illustrate the red shift in the emission spectrum. Before gold nanoparticles are incorporated into the film, the emission spectrum ($\lambda_{\text{ex}} = 365$ nm) of the PAA/PVP3T film displays a broad band from 425 to ca. 650 nm, centered at 512 nm. After the redox reaction was carried out between AuCl_4^- and the terthiophene moieties, we observed a red shift in the emission spectrum ($\lambda_{\text{ex}} = 390$) of the PAA/PVP3T film. The spectrum then displayed a very broad band from 425 to ca. 700 nm, centered at 576 nm. The red shift observed in the emission spectrum results from the increase in conjugation length as terthiophene units are coupled into sexithiophene. These results are consistent with the red shift observed in the UV–vis data for these samples. As shown, by incorporating gold nanoparticles into the PAA/PVP3T multilayer thin films, the photoluminescence is effectively quenched as compared to that of the pure PAA/PVP3T sample. Fan et al. have obtained similar results in which the fluorescence of polyfluorene could be quenched by gold nanoparticles of sizes 5–20 nm.⁴⁵ This is explained by sufficient spectral overlap of the absorption of the gold nanopar-

ticles with the emission of the polyfluorene such that efficient energy transfer may occur. A similar mechanism for photoluminescence quenching may be used to explain this phenomenon in our system since we have good spectral overlap between the absorption of the incorporated nanoparticles and the emission of the sexithiophene units. A more detailed study would be necessary to fully understand this process. However, the observed photoluminescence data correlate well with the previous UV–vis data and support the result that the terthiophene units are coupled into sexithiophene with simultaneous formation of gold nanoparticles within the multilayer thin films. The quenching effect indicates the sensitivity of this combination toward energy-transfer mechanisms.

Conclusion

We have demonstrated that gold nanoparticles may be prepared within hydrogen-bonded multilayer thin films without the use of an additional reducing agent. Through the use of terthiophene-functionalized poly(4-vinylpyridine), it is possible to reduce metallic precursors to form metal nanoparticles while simultaneously cross-linking the terthiophene units to form sexithiophene. The cross-linking of the terthiophene units and the formation of the gold nanoparticles were confirmed through the use of UV–vis and photoluminescence spectroscopy. XPS data showed a complete reduction of the gold precursors in the redox reaction with the terthiophene functionalities. This method yields a unique approach for the fabrication of multilayer heterostructures comprised of metallic nanoparticles and conjugated oligomers with interesting spectroscopic properties. In addition, this method may provide a means for the preparation of uniquely shaped nanostructures as shown by the observation of dendritic fractal growths under certain conditions. Further research in this direction is needed to explore the factors that influence the growth of gold nanostructures, multilayer film integrity, and corresponding energy-transfer mechanisms.

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Supporting Information Available: Experimental details showing (a) the growth in the absorbance of PVP3T as a function of adsorption time, (b) the thickness increase of PVP3T/PAA multilayers with increasing layer number as determined by ellipsometry, (c) XPS spectra showing the characteristic peaks of metallic Au obtained from a PVP3T/PAA film, and (d) a P4VP/PAA (no terthiophene) multilayer thin film loaded with HAuCl_4 and exposed to the same reaction conditions as previously described for the control experiment (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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