Self-assembly of multilayer films containing gold nanoparticles via hydrogen bonding

Yan Jiang, Yi Shen, Peiyi Wu *

The Key Laboratory of Molecular Engineering of Polymers (Ministry of Education), Department of Macromolecular Science, Fudan University, Shanghai 200433, People's Republic of China

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Abstract

Polymer/Au nanoparticle multilayer ultrathin films are fabricated via hydrogen-bonding interaction by a layer-by-layer technique. The Au nanoparticles surface-modified with pyridine groups of poly(4-vinylpyridine) (PVP) are prepared in dimethyl formamide (DMF). Transmission electron microscopy (TEM) image shows that uniform nanoparticles are dispersed in the PVP chains. Poly(3-thiophene acetic acid) (PTAA) and poly(acrylic acid) (PAA) are utilized to form hydrogen bonds with PVP, respectively. Considering the pH-sensitive dissociation behavior of PTAA and PAA, we investigate the release behavior of the Au-containing multilayers at different pH values in this work. UV–vis spectroscopy and atomic force microscopy (AFM) are employed to monitor the buildup and the release of the multilayers. The results indicate that in the films assembled with gold nanoparticles, the polymers are difficult to be removed from the substrate. The interaction between the gold particles and the neighboring PVP chains is responsible for the phenomenon. Gold particles act as physical cross-link points in the multilayers. Due to the additional interaction caused by the gold nanoparticles in the films except the hydrogen-bonding interaction between PTAA (or PAA) and PVP, the stability of the Au-containing multilayer film is ensured even though the changes in pH values may result in the break of the hydrogen bonds.

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1. Introduction

Metallic and semiconductor nanoparticles represent an advanced materials dimension and offer prospects of novel and even size-dependent chemical, electronic, and physical properties [1,2]. Extensive studies have been carried out to assemble nanoparticles into thin films, mainly by Langmuir–Blodgett (LB) techniques and self-assembly methods [3–5]. There remain great interests in fabricating thin films with nanoparticles for advanced electronic and photonic applications [6–10]. Layer-by-layer (LBL) assembly technique as an effective, simple, and versatile method of preparing ultrathin films has received much attention in recent years [3,11–18]. Electrostatic attraction, the most common driving force, is usually employed to fabricate the LBL films in many published work [13–19]. Since 1997, studies on LBL assembly based on the hydrogen bonding, the weak interaction between the neighboring components, were reported [20–23].

Recently, some erasable films have been prepared mainly depending on the pH-sensitivity of the hydrogen-bonding-directed multilayers [24–33]. Hydrogen-bonded LBL films were first demonstrated by Rubner et al. [24,25]. Granick et al. followed the destruction process of PMAA/PVPON polymer films using ATR-FTIR spectroscopy [26,27]. By prolonging the immersion time, Zhang et al. produced a microporous ultrathin film [28]. Furthermore, Hammond and Lynn et al. designed hydrolytically-degradable thin film by introducing the degradable polyelectrolytes [29]. Marks and co-workers prepared out-of-plane noncentrosymmetric microstructures by the layer-by-layer deposition from air phase [30,31]. Wang and co-workers proposed a new hydrogen-bonding-based LBL method that allows the fabrication of all conjugated polymer multilayer thin films in common organic solvents [32]. Xu, Chen and co-workers reported fabrication of composite LBL multilayer films fabricated from a spherical polymer brush with a
poly(methylsilsesquioxane) core and PAA hair chains through hydrogen bonding with poly(vinylpyrrolidone) as partner components [33]. The work has opened a way for the hydrogen-bonding-directed systems toward the development of functional delivery systems. However, as for our knowledge, few studies on the elimination process of the hydrogen-bonding-based multilayer film containing nanoparticles have been reported. In this article, we investigate the elimination process of the films with gold nanoparticles in alkaline and acidic aqueous solutions. Different from the Au-free system, films with gold nanoparticles are found to be stable at high and low pH values. Potential applications of this kind of films in advanced spectroscopy, chemical and biosensor technology, and micro-electronic devices have been greatly anticipated.

2. Experimental

2.1. Materials

Ethyl 3-thiophene acetate (3TEA), anhydrous ferric chloride (FeCl3), poly(4-vinylpyridine) (PVP) (Mw = 6.0 × 104), poly(acrylic acid) (PAA) (Mw = 1800), polyethylenimine (PEI) (Mw = 7.5 × 105) were purchased from Aldrich and used as received. Chloroform (CHCl3) was dried over CaH2 for 24 h under the nitrogen atmosphere and distilled. Methanol and dimethyl formamide (DMF) were used as available. Deionized water (D.I. water) from a Milli-Q system was used throughout the experiments.

2.2. Polymerization of P3TAA

PTAA was synthesized via oxidative-coupling polymerization. The monomer, ethyl 3-thiophene acetate (3TEA), was polymerized in dry chloroform using anhydrous ferric chloride as oxidant. The molar ratio of the monomer to oxidant was 1:4 [34,35]. The blue-black mixture was stirred for about 24 h at 0 °C under nitrogen and the polymers were subsequently poured into a large excess of methanol. The poly(ethyl 3-thiophene acetate) (P3TEA) was thus precipitated, and turned into brown–red. After being washed repeatedly with methanol and D.I. water to remove the residual oxidant and the oligomers, P3TEA was obtained at a yield of 73.5%. The succeeding hydrolysis process was conducted by adding 0.3 g polymer in 30 ml of 2.0 M NaOH solution and heating to 100 °C for 24 h. After centrifugation to remove the insoluble part, the water-soluble part was neutralized and precipitated into the form of P3TAA by dilute HCl solution. The precipitated polymer was centrifuged, repeatedly washed with D.I. water and dried in a vacuum oven for 2 days, followed by the measurements of 1H NMR and FTIR.

2.3. Preparation of gold nanoparticles with pyridine group tailored surfaces (PVP-Au)

Au nanoparticles stabilized by PVP were synthesized in DMF solution using a modified procedure published by Hao and co-workers [21]. Briefly, 55.8 mg of PVP was dissolved in 150 ml of DMF. 70.8 mg of HAuCl4 in 10 ml of methanol was added under rapid stirring. The molar ratio of metal salts to pyridine units was about 1:3. 10 min later, 27 mg of NaBH4 in 10 ml of methanol was added quickly. A change of color from yellow to wine-red was immediately observed, indicating the formation of Au nanoparticles. In addition, the pH of the solution increased because of homogeneous reduction. After 60 min of further stirring, the image of the PVP-modified nanoparticles is offer by TEM.

2.4. Fabrication of multilayer films

Multilayer films were assembled on quartz substrates, which had been cleaned by first placing them in a H2SO4/H2O2 (7:3, v/v) solution at 80 °C for 1 h and then in a H2O/H2O2/NH3·H2O bath (5:1:1, v/v/v) at 40 °C for another hour. The plates were extensively rinsed with D.I. water after each cleaning step. These substrates were precoated with a single layer of polyethylenimine (PEI, 0.5 wt%).

The fabrication of the multilayer film was carried out at room temperature. The modified substrate was first immersed in a DMF solution of PTAA (0.25 g/L) for 15 min. After washing three times with pure DMF (each time for 1 min) and dried with mild nitrogen stream, it was subsequently transferred to a DMF solution of PVP-modified gold nanoparticles for another 15 min, followed by rinsing and drying as mentioned above. By repeating the steps, a layer-by-layer self-assembled multilayer film via hydrogen-bonding interaction between PTAA and PVP-Au was obtained and denoted as (PTAA/PVP-Au)n (n is the number of bilayer). A similar procedure is taken to fabricate another multilayer film composed of PAA and PVP-Au, which is denoted as (PAA/PVP-Au)n.

2.5. Elimination of multilayer films

All the studies on film elimination were performed in two different pH aqueous solutions: pH 11 and 3, which were adjusted by 0.1 M NaOH and 0.1 M HCl, respectively. The elimination of films was designed to be carried out for different periods of time. Rinsing and drying procedures were repeated after every immersion.

2.6. Characterizations

The structure of PTAA was determined by 1H NMR (DMX-500, Bruker). 1H NMR of the polymer (not shown here) was in agreement with its expected structure: P3TAA (DMSO) δ = 12.55 ppm (1H, –COOH), 7.35 and 7.28 ppm (1H, thiophene ring proton), 3.79 and 3.55 ppm (2H, –CH2–). FTIR spectrum was recorded on a Nexus 470 instrument equipped with a deuterated triglycine sulfate (DTGS) detector at a 4 cm–1 resolution (Nicolet). 64 scans were accumulated to obtain an acceptable S/N ratio. The morphology of the Au nanoparticles was examined using a JEOL JEM2010 electron microscopy operating at 200 kV accelerating voltage. The TEM sample was prepared by dripping a drop of the colloidal solution onto a carbon-film-coated copper grid and then naturally drying the
Fig. 1. TEM image of the PVP-modified gold nanoparticles.

Fig. 2. UV–vis absorption spectra of a (PTAA/PVP-Au)\text{\textsubscript{n}} multilayer film with different numbers of bilayers (n = 1–8) (the bottom line is the spectrum of PEI). The insets are plots of the absorbance at 256, 422, and 525 nm vs the number of PTAA/PVP-Au bilayers (n).

grid in air. Fig. 1 shows that the gold nanoparticles with a diameter of 2–3 nm are dispersed in PVP chains. UV–vis spectra of multilayer films on quartz plates during the fabrication and elimination processes were recorded by a UV–visible spectrophotometer (Lambda 35 spectrophotometer, Perkin–Elmer) and collected after each fabrication or elimination step. Atomic force microscopy (AFM) images were determined by using a tapping mode with a Nanoscope IV atomic force microscope (Digital Instruments, Veeco Metrology Group) under ambient conditions.

3. Results and discussion

3.1. PTAA/PVP-Au multilayer film

UV–vis spectroscopy has been proved to be a useful and facile technique for evaluating the growth process of multi-

Fig. 3. AFM image of a (PTAA/PVP-Au)\text{\textsubscript{6}} film.

Fig. 4. (a) FTIR spectra of a (PTAA/PVP-Au)\text{\textsubscript{6}} film (denoted by solid line), PTAA (denoted by dash line), and PVP (denoted by dot line) in the region from 1800 to 1350 cm\textsuperscript{-1}; (b) FTIR spectra of a (PTAA/PVP-Au)\text{\textsubscript{6}} film (denoted by solid line) and PTAA (denoted by dash line) in the region from 4000 to 2000 cm\textsuperscript{-1}. 

(a) (b)
Fig. 5. UV–vis spectra of the substrate originally coated with 8-bilayer PTAA/PVP-Au multilayers after immersion into the (a) pH 11 and (c) pH 3 aqueous solutions for different time intervals. The insets are plots of the absorbance at 256, 422, and 525 nm vs time. The corresponding UV–vis spectra of the (PTAA/PVP)_8 multilayers after immersion into the (b) pH 11 and (d) pH 3 aqueous solutions for different time intervals. The insets are plots of the absorbance at 256 and 422 nm vs time.

layer and is thus used in the present work to monitor the LBL assembly process of multilayer build-up. Fig. 2 gives the UV–vis absorption spectra of a (PTAA/PVP-Au)_n multilayer film (with n = 1–8) assembled on a modified quartz surface. The absorption bands appearing at 256, 422, and 525 nm are assigned to the π–π* transition of the pyridine ring of PVP [36], π–π* transition of the thiophene ring of PTAA [37] and surface plasmon resonance (SPR) peak of gold nanoparticles [38,39], respectively. A nearly linear increase of the intensities with the number of bilayers, n, is observed (inset of Fig. 2), suggesting that approximately the same amount of each component is adsorbed in each deposition cycle.

The AFM image provides more detailed information of the domain structure of the PTAA/PVP-Au multilayers. As shown in Fig. 3, the 6-bilayer PTAA/PVP-Au film exhibits a relatively uniform granular structure, indicating the high quality of the multilayers.

The interaction between the neighboring polymers in the film is identified as hydrogen bonding by FTIR spectra. Fig. 4a shows the FTIR spectra of pure PTAA, PVP, and a 12-layer LBL film. The absorption around 1710 cm\(^{-1}\) appearing in the spectrum of pure PTAA indicates that the carboxyl group in pure PTAA is in a strong-associated state. The peak at 1597 cm\(^{-1}\) can be attributed to the ring vibration of pyridine of PVP [22]. On the other hand, in the spectrum of the 12-layer LBL film, the shift of the C=O stretching vibration (1710 → 1728 cm\(^{-1}\)) shows that in this case, carbonyl group is in a less associated state than that in pure PTAA [22]. Furthermore, in Fig. 4b, the broad O–H stretching vibration centering on 3400 cm\(^{-1}\) in the 12-layer film compared with that around 3440 cm\(^{-1}\) in pure PTAA means that the hydroxyl groups have formed stronger hydrogen bonds than those in pure PTAA. Both suggest that the hydrogen bonds are formed between PTAA and PVP in adjacent layers. The very slight shift of the ring
vibration of PVP ($1597 \rightarrow 1601 \text{ cm}^{-1}$) shown in Fig. 4a also supports the concept that the multilayer film is not assembled via electrostatic attraction but hydrogen bonding.

As mentioned above, the substrates coated with (PTAA/PVP-Au)$_n$ multilayers are immersed in the pH 11 aqueous solution to investigate the elimination of PTAA/PVP-Au multilayers. After each step of immersion in the alkaline aqueous solution for a period of time, a UV–vis spectrum is collected to record the information during the elimination process. The same experiment of a (PTAA/PVP)$_n$ multilayer film without gold nanoparticles is also conducted as a comparison. Figs. 5a and 5b present the UV–vis spectra of an 8-bilayer film with and without Au particles after immersion in the pH 11 aqueous solution for different time intervals, respectively. The line marked “0 min” is the spectrum recorded before immersion. The inset of Fig. 5a shows the trend of the decrease in the intensity at 256, 422, and 525 nm. The inset of Fig. 5b only gives the information at 256 and 422 nm. It is obvious that the intensities of those characteristic peaks of (PTAA/PVP)$_n$ multilayers decrease much more than that of the (PTAA/PVP-Au)$_n$ multilayers. It is implied that it is more difficult for the polymers inside the (PTAA/PVP-Au)$_n$ film to be removed from the substrate than the counterpart without gold particles under the same condition. The phenomenon at pH 3 is a little different (shown in Fig. 5c and 5d). Compared to the decrease in intensity at pH 11, the (PTAA/PVP)$_n$ film has a smaller decrease in intensity at pH 3 due to the remaining hydrogen bonds between adjacent PTAA. More details have been described in our previous study [40]. Even so, the extent of decrease of the film without gold particles is larger than that of the film containing nanoparticles. In a word, the introduction of the gold nanoparticles seems to hinder the elimination of the multilayers from the substrate no matter under the alkaline or the acidic condition.

3.2. PAA/PVP-Au multilayer film

As PTAA chains possess S atoms in the backbone, it is suspected that the interaction between S atoms and the gold nanoparticles is responsible for the small degree of elimination of the gold-containing multilayers. To confirm the suspicion, PTAA is substituted with poly(acrylic acid) (PAA), which has no special interaction with the gold nanoparticles.

The UV–vis spectra obtained during the fabrication of the (PAA/PVP-Au)$_n$ multilayers (Fig. 6) are similar as those in Fig. 2. The characteristic peaks at 256 and 540, which are corresponding to PVP and gold nanoparticles respectively, show nearly linear increment in intensity as well.

Fig. 7 shows the FTIR spectrum of the multilayer film on a CaF$_2$ window in the case of PAA, and the spectra of pure PAA and pure PVP film are exhibited as comparison. The C=O stretching vibration shifts from 1709 cm$^{-1}$, an associated state of carbonyl group in pure PAA [23], to 1715 cm$^{-1}$, a less associated state of that in multilayers. The shift of ring vibration of PVP from 1597 to 1605 cm$^{-1}$ is also observed. Moreover, O–H stretching vibrations appear around 2473 and 1948 cm$^{-1}$ (inset of Fig. 7), indicating strong hydrogen bonding between the carboxyl groups of PAA and pyridine groups of PVP [13,21,41,42]. The results are the proofs that the PAA/PVP-Au multilayer film is assembled via hydrogen-bonding interaction, the same as the PTAA/PVP-Au film.

As for the (PAA/PVP-Au)$_n$ film, the manipulations of elimination described in the experimental section are conducted as well. Fig. 8 gives the UV–vis spectra during the whole processes of elimination at pH 11 and 3. The extent of the decrease is close to that of the (PTAA/P4VP-Au)$_n$ multilayers. Zhang and co-workers [28] have reported that (PAA/PVP)$_n$ multilayer film can be changed into microporous film by the removal of PAA at high pH value and subsequently the reformation of PVP in alkaline aqueous solution. However, the Au-containing film is no longer the case. The AFM images shown in Fig. 9 depict the surface morphologies of a 6-bilayer film before and after the immersion in pH 11 or 3 aqueous solution.
Fig. 8. UV–vis spectra of the substrate originally coated with 8-bilayer PAA/PVP-Au multilayers after immersion into the (a) pH 11 and (b) pH 3 aqueous solutions for the different time intervals. The insets are plots of the absorbance at 256 and 540 nm vs time.

Fig. 9. AFM images of a (PAA/PVP-Au)$_6$ film (a) before and after immersion in the (b) pH 11 and (c) pH 3 aqueous solutions for 4 h.
solutions for 4 h. As can be seen, there are few differences between Figs. 9a and 9b or 9c. No microporous structure is observed.

3.3. Interactions between Au nanoparticles and PVP

The phenomenon observed in the UV–vis spectra of the (PAA/PVP-Au)ₙ multilayers has contradicted our suspicion that the interaction between S atom and the gold nanoparticles is the major factor of the small decrease in intensity of corresponding characteristic peaks. Indeed, it is only one of the factors in PTAA system. In addition, there may exist, actually, other interaction in the film except the hydrogen bonds, so that the film remains stable even if the hydrogen bonds may be broken at high or low pH value. It has already been reported that the gold nanoparticles modified with carboxylic acid groups are not pH-stable [43]. In this way, the interaction between the carboxylic acid groups and the gold nanoparticles may not be responsible for the pH stability. It is likely that the interaction between PVP and Au has made the major contribution.

A concept should be mentioned that there is no clear borderline in the LBL film, and actually, the polymer chains of neighboring layers penetrate and entangle each other [22,44–46]. According to our previous work [40], the flexible PVP chains will entangle the PTAA or PAA chains to form more hydrogen bonds in the fabrication process and thus the distance between each bilayer is greatly shortened. So it is possible for the PVP chains to interact with the gold nanoparticles in the neighboring layer and a new type of interaction between each bilayer is formed. The model is sketched in Fig. 10. As shown, the gold particles may be associated with the PVP chains not only within the layer (marked with dotted square) but also in adjacent layers (marked with dashed square). Thus, the gold nanoparticles act as physical cross-link points, which link the adjacent polymers as a network. Therefore, even in alkaline or acidic solution, the polymers are still associated together and difficult to be removed from the substrate. This may be a reasonable explanation of the small extent of elimination.

4. Conclusions

The present work has successfully assembled two kinds of multilayer ultrathin films containing gold nanoparticles, (PTAA/PVP-Au)ₙ and (PAA/PVP-Au)ₙ. In the elimination process of the films by controlling the pH values, it is found that the extent of the release of the polymers from the substrates is much smaller compared to the Au-free counterparts. Further comparison of (PTAA/PVP-Au)ₙ and (PAA/PVP-Au)ₙ films has confirmed that the interaction between S atom of PTAA and the gold particles is not the only excuse. The phenomenon is possibly related to the interaction between neighboring bilayers induced by the gold particles as physical cross-link points. The interaction will remain when the hydrogen-bonding interaction may be broken caused by the changes of the pH values. Thus, the gold-containing multilayer film is quite stable in acidic or alkaline aqueous solution.

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