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

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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.

Keywords: Gold nanoparticle; Layer-by-layer; Hydrogen-bonding interaction

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-sensitiveness 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

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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 microelectronic devices have been greatly anticipated.

2. Experimental

2.1. Materials

Ethyl 3-thiophene acetate (3TEA), anhydrous ferric chloride ($FeCl_3$), poly(4-vinylpyridine) (PVP) ($M_w = 6.0 \times 10^4$), poly(acrylic acid) (PAA) ($M_w = 1800$), polyethylenimine (PEI) ($M_w = 7.5 \times 10^5$) were purchased from Aldrich and used as received. Chloroform ($CHCl_3$) was dried over CaH_2 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 $HAuCl_4$ 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 $NaBH_4$ 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 H_2SO_4/H_2O_2 (7:3, v/v) solution at 80 °C for 1 h and then in a $H_2O/H_2O_2/NH_3{\cdot}H_2O$ 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 $(\text{PTAA/PVP-Au})_n$ (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 $(\text{PAA/PVP-Au})_n$.

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) $\delta =$ 12.55 ppm (1H, –COOH), 7.35 and 7.28 ppm (1H, thiophene ring proton), 3.79 and 3.55 ppm (2H, $-CH_2-$). 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