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Preparation and nanotribological properties of polyelectrolyte multilayers with in situ Au nanoparticles

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ABSTRACT

Polyelectrolyte multilayers with in situ Au nanoparticles were prepared by alternate immersion of a substrate in poly(allylamine hydrochloride) (PAH)-$AuCl_4^-$ complexes solution and poly(acrylic acid) solution for layer-by-layer self assemble process followed by reduction of the metal cations Au^{3+} through immersion into a fresh $NaBH_4$ solution. UV–vis spectrum, atomic force microscopy (AFM), X-ray photoelectron spectra (XPS), and transmission electron microscope (TEM) were used to confirm the construction of multilayers and synthesis of the Au nanoparticles. The nanotribological behaviors also have been studied using AFM. The polyelectrolyte multilayers with in situ Au nanoparticles exhibited a lower surface adhesion and friction force than the pure polyelectrolyte multilayers due to the nanoparticles improved the mutilayers surface structure and possess a good load-carrying capacity in nanoscale.

1. Introduction

Ultrathin polyelectrolyte multilayers (PEMs) have been extensively studied over the previous decade [1]. The popularity of this film is due to its simplicity, versatility, and systematical control over the structure and thickness. The layer-by-layer (LBL) method is a thin film fabrication technique which has been invented by Decher and co-workers [2,3]. The film is formed by deposition of oppositely charged polyelectrolytes molecular or charged materials from dilute aqueous solutions with wash steps in between by way of the intermolecular electrostatic forces onto charged substrates. It is well known that the representation of the LBL technique as a multilayer construction based solely on electrostatic forces is simple and convenient which is a very effective method to construct polyelectrolyte multilayers. Moreover, the materials used in molecular deposition studies can be not only polyelectrolyte molecular but also various charged materials, including small organic molecular or inorganic compounds [4,5], nanoparticles or nanoplates [6–8], macromolecules [9], and biomacromolecules [10–12] such as proteins, DNA, mucin and so on.

The ultrathin films are ideally suited to combat the tribological challenges in the micro-electro-mechanical systems (MEMS) and micro/nano movement interface. In the previous research, the tribological properties of the polyelectrolyte multilayers had been studied, which indicated that the polyelectrolyte monolayer or multilayer could modify the friction surface, so as to reduce the surface adhesion and friction force [13]. Nevertheless, the polyelectrolyte molecular deposition layer is not of a well anti-wear property.

Nanoparticles as tribology and lubrication additions have attracted a wide spread attention increasingly because of their lower friction coefficient and high wear resistant [14,15]. Nanoparticles within polyelectrolyte multilayers could enhance the tribological properties of the polyelectrolyte multilayers. The commonly used steps are that the prepared nanoparticles which were preliminary treatment firstly, aiming to process of the nanoparticles surface charged. Then, the charged nanoparticles and opposite polyelctrolyte were deposited onto the substrates layer-by-layer. However, to prepare the good dispersibility nanoparticles solution was pivotal step which could influence the uniform of the multilayers. Since the control of the size and agglomeration of nanoparticles is difficult. With the novel approach and technology combining with the LBL method, various nanomaterials with desirable shape and composition can be synthesized by loading the reactants into the polyelectrolyte multilayers interior and then performing appropriate reactions which the nanoparticles in situ nucleation and growth in the polyelectrolyte multilayers [16–19].

In this study, poly(allylamine hydrochloride) and poly(acrylic acid) were used as polycation and polyanion, respectively. The metal cations of $AuCl_4^-$ were bound into the polycation layer. Then, post-binding chemistries of reduction by $NaBH_4$ solution cause the

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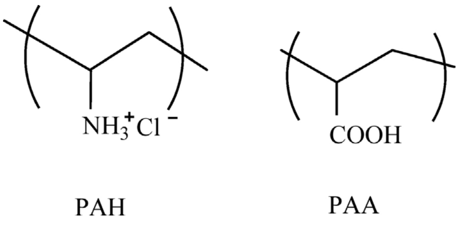

Fig. 1. Chemical structures of PAH and PAA polyelectrolytes.

metal cations Au^{3+} to be Au^0. Many means, such as atomic force microscopy (AFM), UV–vis spectroscopy, X-ray photoelectron spectra (XPS), and transmission electron microscope (TEM) were used to characterize the nanoparticles composite polyelectrolyte multilayers and the synthesis of in situ Au nanoparticles. Nanotribological properties of polyelectrolyte multilayers with in situ Au nanoparticles were investigated by AFM. The in situ Au nanoparticles doped polyelectrolyte multilayers exhibited a lower surface adhesion and friction force than that for the pure ones. It may be attributed to the in situ nanoparticles enhanced the uniform structure of multilayers and with a good load-carrying capacity.

2. Experimental

2.1. Materials

The polyelectrolytes used in the studies were the poly(allylamine hydrochloride) (35 wt.% in water, Mw 100,000–200,000), and poly(acrylic acid) (Mw 30,000) supplied from Aldrich Company and used as received. Hereafter the two polyelectrolytes were referred to as PAH and PAA, respectively. The chemical structures of PAH and PAA were shown in Fig. 1. Hydrogen tetrachloroaurate hydrate ($HAuCl_4{\cdot}3H_2O$) and sodium tetrahydridoborate ($NaBH_4$) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the other reagents contain rinsing processes were of analytical grade. The de-ionized water (≥18 MΩ cm, Millipore Milli-Q) was used to prepare all aqueous solutions and in the rinsing process.

The polycation solution of PAH and polyanion solution of PAA were prepared for 1×10^{-4} mol/L by directly dissolving in de-ionized water, respectively (in which the concentration was based on the molecular weight per repeat unit). Then, 0.1 mM $HAuCl_4{\cdot}3H_2O$ was added into PAH solution of 1 L. The complex compound formation schematic diagram was shown in Fig. 2. The polyelectrolyte PAH within water solution ionized polycation (PAH^+) and counter ion (Cl^-), PAA ionized for polyanion (PAA^-) and counter ion (H^+). Then, the $HAuCl_4{\cdot}3H_2O$ was added into the PAH solution. That the chloroauric acid radical completed with the polycation PAH^+ which shown in Fig. 2.

Glass and quartz plates were used for the substrates. All the substrates were processed according with the steps below [20]. Firstly, the substrates were ultrasonic treated in acetone, chloroform, and anhydrous ethanol (volume ratio = 3:3:1) bath for 30 min and rinsed to eliminate the residues on substrates surface using de-ionized water flushing. Secondly, the cleaned substrates were immersed in fresh piranha solution (98% H_2SO_4:30% H_2O_2 = 7:3 in volume) at 80 °C for 1 h. The piranha solution treatment allows the removal of residues of organic and inorganic impurities from the substrates and makes the plates completely hydrophilic at the same time, through making the substrates to be hydroxylated. Finally, the substrates were rinsed with plenty of de-ionized water and dried with nitrogen stream.

2.2. Preparation of polyelectrolyte multilayer with in situ Au nanoparticles

The glass and quartz substrates cleaned and processed by above steps were dipped into PAH and PAA polyelectrolyte solutions for 20 min alternately. Between the alternate processes, ultrapure water and nitrogen were used for rinsing and drying after each immersion, respectively. In this study, one monolayer of PAH and PAA constituted one bilayer polyelectrolyte which can be expressed as PAH/PAA. Furthermore, different bilayer films could be prepared by repeating the above process.

Polyelectrolyte multilayer containing in situ Au nanoparticles was prepared with similarity process which using PAH-$AuCl_4$

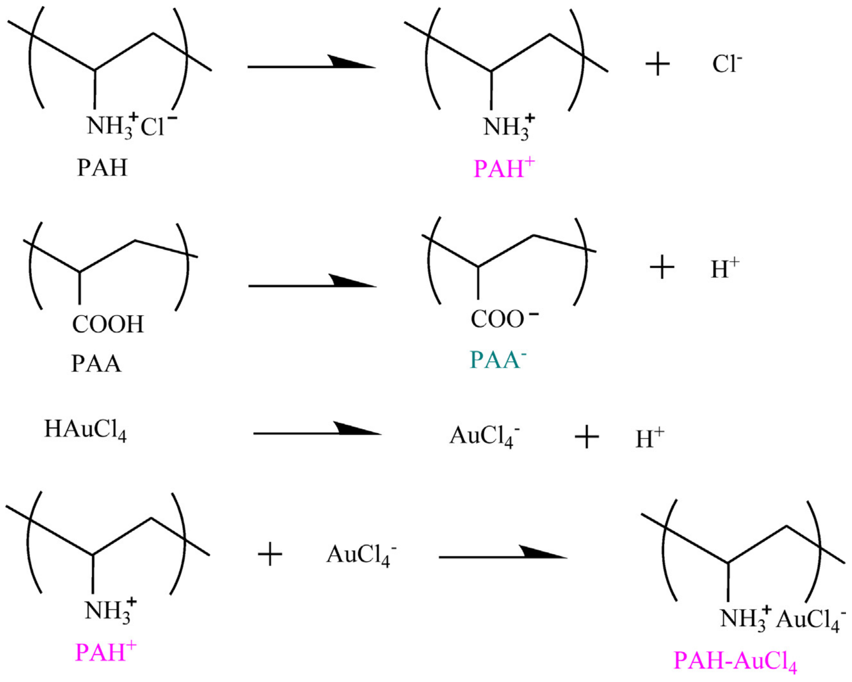

Fig. 2. Electrolytic formulas of reagents: structures of PAH, PAA and PAH-$AuCl_4^-$ complexes.