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Tribological behavior of ZnS-filled polyelectrolyte multilayers

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Abstract

The pristine polyelectrolyte multilayers (PEMs) were prepared by layer-by-layer deposition technique. The ZnS nanoparticles were in situ-synthesized in the pristine PEMs, and the composite was denoted as ZnS-filled PEMs. The friction and wear properties of ZnS-filled PEMs were investigated on a UMT-2 against stainless steel ball. The morphologies of the wear traces were observed by scanning electron microscope. It was found that ZnS-filled PEMs exhibit higher antiwear life than unfilled ones. This should be attributed to the ZnS nanoparticles formed in the PEMs enhancing the load-carrying capacity. Moreover, the PEMs with three reaction cycles have considerably lower friction coefficient and higher antiwear life than the PEMs with six reaction cycles, that is to say, an optimum amount of ZnS nanoparticles within PEMs can improve the tribological performance greatly.

Keywords: ZnS nanoparticles; Polyelectrolyte mulitilayers; Tribological behavior

1. Introduction

The layer-by-layer deposition technique is ideally suited to combat the tribological challenges in microelectromechanical systems (MEMS), because it is simple in preparation, easy to automate and friendly to the environment [1]. Especially, it can be deposited on a wide variety of substrates, and devices with complex architectures can be coated uniformly over large areas [2].

The attempts to improve the tribological properties of polyelectrolyte multilayers (PEMs) have been largely focused on transforming the structure of PEMs. For example, UV treatment [3,4], proper heat-treatment [5], biomimic method [6], the layer structure of liquid crystal materials [7] and so on were used to improve the antiwear life. Furthermore, the tribological behavior of PEMs as function of the number of layers, normal load [2], relative humidity [8], adhesion and scanning rate also have been investigated.

Zhang et al. [9,10] have systematically studied the tribological behavior of composite LB films consisted of organic molecule and inorganic nanoparticles, they found that the nanoparticles play a key role in increasing antiwear life of LB films, enhancing the load-carrying capacity of the films. In the present years, the organic–inorganic hybrid thin films have also attracted widespread attention because of their low friction coefficient and relatively long antiwear life [11].

In situ-synthesized nanoparticles in PEMs have been suggested by Rubner [12] and others [13]. Recently, friction and wear behavior of the nanoparticle PEMs via in situ synthesis has been studied. Pavoor et al. [14] reported the tribological behavior of silver-containing PEMs and found that silver-containing PEMs offer the advantage of a wear-preventing PEMs matrix and a low friction surface. In our previous work, we had studied the tribological behaviors of PEMs containing $Cu(OH)_2$ nanoparticles [15]. It has been reported that ZnS nanoparticles capped by diakyldithiophosphate were used as oil additive to enhance the friction-reduction and antiwear ability effectively [16]. In this paper, a novel approach toward the fabrication of dispersed ZnS nanoparticles is reported. Nucleation and growth of ZnS nanoparticles were achieved in a poly(diallyl dimethylammonium chloride) (PDDA)–poly(acrylic acid) (PAA) film prepared by the layer-by-layer deposition technique. We found that ZnS nanoparticles within PEMs possess load-carrying capacity and enhance antiwear life. Moreover, the PEMs with three reaction cycles show considerably lower friction coefficient and higher antiwear life than the PEMs with six reaction cycles.

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2. Experimental details

2.1. Materials

All materials were used without further purification. PDDA (20 wt.% in water, M_W = 100,000–200,000) was purchased from Aldrich. PAA was bought from chemical reagent factory. Other materials are all analytical pure reagents.

Deionized water (>18 MΩ cm, Millipore Milli-Q) was used for preparation of all aqueous solutions, and during rinsing procedures.

2.2. Preparation of pristine PEMs

Quartz slides used for ultraviolet–visible (UV–vis) analysis and silicon slides used for other tests were thoroughly cleaned by soaking in a piranha solution (H_2O_2:H_2SO_4 = 3:7, v/v) at 80 °C for 1 h. The piranha treatment allows removal of residues of organic and inorganic impurities from the substrates and makes the slides completely hydrophilic at the same time.

The polyionic solutions of PDDA and PAA were both prepared into 20 mM concentration. The former was directly dissolved in deionized water, while the latter was dissolved in deionized water and then adjusted to a pH of 5.5 with 0.1 M NaOH. All concentrations were calculated based on the monomer molecular weight.

Pristine PEMs were obtained using the layer-by-layer deposition of opposite charge on substrates, which were built by dipping the substrates into an aqueous solution of PDDA for 20 min, washed three times by dipping in water for 2, 1, 1 min, respectively, followed by drying with nitrogen stream. Negatively charged PAA layers were subsequently deposited onto the positively charged substrates by using the same washing procedure as described above. Deposition always ended with the first half of a layer pair in order to terminate the film with a PDDA layer.

2.3. The in situ synthesis of ZnS nanoparticles within the pristine PEMs matrix

Nucleation of ZnS nanoparticles within the PEMs occurred by cycling the polymer-coated substrates in Zn^{2+} and Na_2S solutions. The polymer-coated substrates were dipped into the 5 mM or 20 mM Zn^{2+} solution for 2 min, removing excess Zn^{2+} by rinsing with purified water for about 20 s, then treating the slides with 10 mM or 0.1 M Na_2S for 5 min to initiate the formation of ZnS nanoparticles (5 mM Zn^{2+} and 10 mM Na_2S for TEM and UV–vis). Finally the film was rinsed again and dried with nitrogen stream before the same reaction cycle was repeated.

2.4. Characterization of the PEMs

Absorption spectra of the ZnS-filled films in the 200–900 nm range were recorded on a Heλios α UV–vis spectroscopy which was used to monitor the influence on the in situ synthesis ZnS within PEMs.

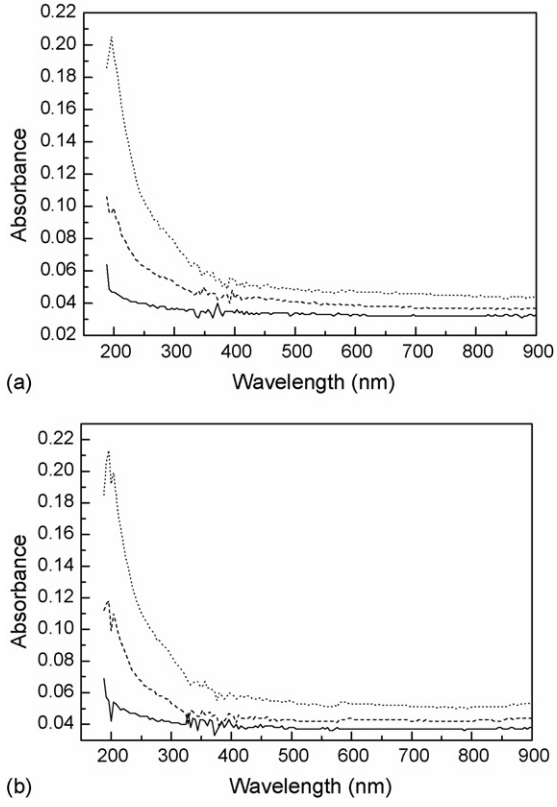

Fig. 1. The UV–vis absorption spectra of ZnS nanoparticles formed in: (a) 4.5 bilayer and (b) 8.5 bilayer thick PDDA–PAA polyelectrolyte multilayers exposed to three (dashed line) and six (dotted line) reaction cycles. The absorption spectra of the pristine PDDA–PAA films are also shown (solid line).

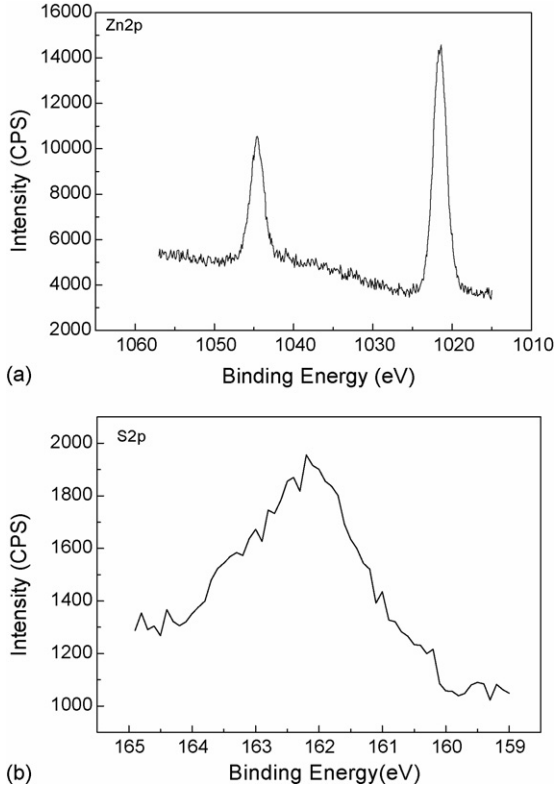

Fig. 2. XPS spectra of the 4.5 layer pairs with three reaction cycles on the Si substrate.