

Nanotribological behaviors of *in situ* nanoparticles doped molecular deposition films

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The molecular deposition films of poly (diallyl dimethylammonium chloride) (PDDA) and poly (acrylic acid) (PAA) with Cu²⁺ on quartz and glass substrates were prepared in laboratory first, then different bilayers films were dipped into fresh Na₂S aqueous solution. As a result, CuS nanoparticles were fabricated in multilayer molecular deposition films *in situ*. The structure and nanotribological properties of the composite films were analyzed by ultraviolet-visible (UV-visible) spectroscopy, XPS and atomic force microscope (AFM). It was found that the CuS nanoparticles were homogeneously distributed throughout the whole film. And these films had a much smaller friction force than their substrates and higher antiwear life than pristine PDDA/PAA molecular deposition films. The fluctuation and variation trend of the topography, hardness, and friction with the AFM indentation length were also investigated.

molecular deposition films, nanoparticles, *in situ*, nanotribology

As a new technique to prepare ultrathin films, molecular deposition (MD) method can be used to assemble a monolayer or multiplayer film with nanometer thickness by way of intermolecular electrostatic forces. This film is termed molecular deposition (MD) film. Comparing the MD film with Langmuir-Blodgett (LB) film and self-assembled (SA) film, it is simple in preparation, easy to automate and friendly to the environment. Especially, it can be deposited on a wide variety of substrates, and devices with complex architectures can be coated uniformly over large areas^[1,2].

With the high-speed development of microelectromechanical systems (MEMS) and the increasing demand for magnetic recording technology, this has to face the challenge of “physical limit”, that is, nano-space (1–100 nm) between friction pairs^[3,4]. The tribological problems will seriously affect the reliability of MEMS products because of the micro-structure, relatively larger surface area, surface enhancement effect and the nano-scale gap. Thus, the solution of the tribological problems is the key aspect to ensure their performance and improve their life. Over the past 20 years, the organized

molecular films lubrication technology was a response to this need, and has been expected to be an important means to solve the critical issue^[5]. The molecular deposition technique is ideally suited to combat the tribological challenges in microelectromechanical systems, it has been found that MD film is able to decrease the adhesive force on a surface; so as to modify the friction surface and reduce the friction force^[6,7]. However, MD film has poor anti-wear behavior owing to the weak intermolecular forces including electrostatic force. It was reported that the nanoparticles were used as oil additive to improve the property of antiwear and friction reduction of the base oil^[8], and the molecular films with nanoparticles also had better lubrication performance and high anti-wear life^[9]. To enhance the anti-wear life, Zhang et al.^[10] researched the tribological behaviors of

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poly(allylamine hydrochloride) (PAH)/graphite oxides (GO) ultrathin film and the multilayer film of PAH incorporated with TiO₂ enwrapped by poly(acrylic acid) (PAA).

In situ-synthesized nanoparticles in polyelectrolyte multilayers (PEMs) was suggested by Dante et al.^[11] and Joly et al.^[12]. This technology reduced the difficulty of preparing polymer with nanoparticles composite films and could effectively control the agglomeration of nanoparticles. In this paper, a novel approach toward the fabrication of dispersed CuS nanoparticles is reported. The molecular deposition films of poly(diallyl dimethylammonium chloride) (PDDA) and poly(acrylic acid) (PAA) with Cu²⁺ on quartz and glass substrates were prepared first, then the MD films were put into fresh Na₂S aqueous solution. Nucleation and growth of CuS nanoparticles were achieved in the MD films. We found that these films had a much smaller friction force than their substrates and higher anti-wear life than pristine PDDA/PAA molecular deposition films.

1 Experiments

1.1 Materials

All materials were used without further purification. Poly(diallyl dimethylammonium chloride) (PDDA, 20 wt% in water, $M_w = 100000 - 200000$) and poly(acrylic acid) (PAA, 45 wt% in water, $M_w \approx 30000$) were purchased from Aldrich. The chemical structures of PDDA and PAA are shown in Figure 1. All the other reagents are analytical reagents. Glass and quartz were used as the substrates.

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

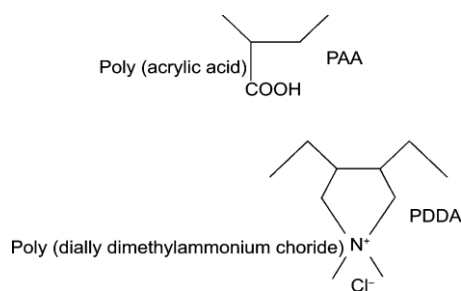


Figure 1 Chemical structures of poly (acrylic acid) (PAA) and poly (diallyl dimethylammonium chloride) (PDDA).

1.2 Instruments

UV-visible absorption spectrum was recorded on a Uni-

co UV-2102 ultraviolet-visible light spectroscope. X-ray photoelectron spectroscopy (XPS) was performed on PHI-5300 spectroscope. The tribological properties of the films were investigated on a Topometrix Explorer 2000 atomic force microscope (AFM) with standard silicon nitride tips (force constant 0.032 N/m) in contact mode.

1.3 Preparation of PDDA/PAA with CuS film

Quartz slides used for UV-visible absorption spectrum analysis and glass slides used for other tests were cleaned according to the following procedures. The substrates were ultrasonic cleaned in acetone/ chloroform/ anhydrous ethanol (3:3:1 v/v/v) bath for 30 min and treated in an 80°C piranha solution (H₂SO₄/H₂O₂ 70:30 v/v) bath for 60 min and rinsed in water. 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 prepared into 2 g/L and 1 g/L concentrations. The CuCl₂ was prepared into 1 mmol/L concentration.

The MD films with Cu²⁺ 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. Negatively charged PAA layer was subsequently deposited onto the positively charged substrates and washed three times by dipping in water, then dipped into CuCl₂ aqueous solution for 2 min, the carbonyl of PAA on the substrate adsorbed Cu²⁺^[13]. Repeating experimental process described above could fabricate multilayer film. Deposition always ended with the first half of a layer pair in order to terminate the film with a PDDA layer.

Nucleation of CuS nanoparticles within the MD film occurred by putting the polymer-coated substrates in fresh Na₂S aqueous solutions. The MD films with Cu²⁺ were dipped into the 1 mmol/L Na₂S aqueous solutions for 30 min. Finally the films were rinsed again and dried with nitrogen stream. The representation for the prepared process of CuS nanoparticles within the MD films is shown in Figure 2. The *in situ* nanoparticles doped molecular deposition films can be expressed as ((PDDA/PAA)- CuS)_n/PDDA, where *n* is the number of bilayer.

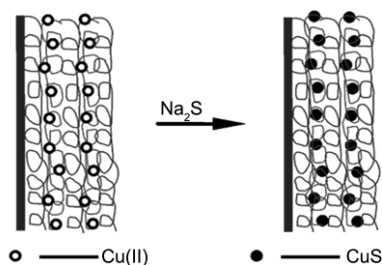


Figure 2 Representation for the prepared process of CuS nanoparticles within the MD films.

2 Results and discussion

2.1 UV-visible spectrum analysis

The UV-visible spectrum of ((PDDA/PAA)-CuS)_n/PDDA MD films with different layer numbers on quartz substrate is shown in Figure 3(a). The variation in the UV absorbance at 242 nm of these MD films are shown in Figure 3(b), which shows that the absorbance of the films increases with the increasing layer number *n* (1–5), and the absorbance versus the cycle *n* resulted in nearly straight lines. This may be caused by the increase of size or quantity of nanoparticles.

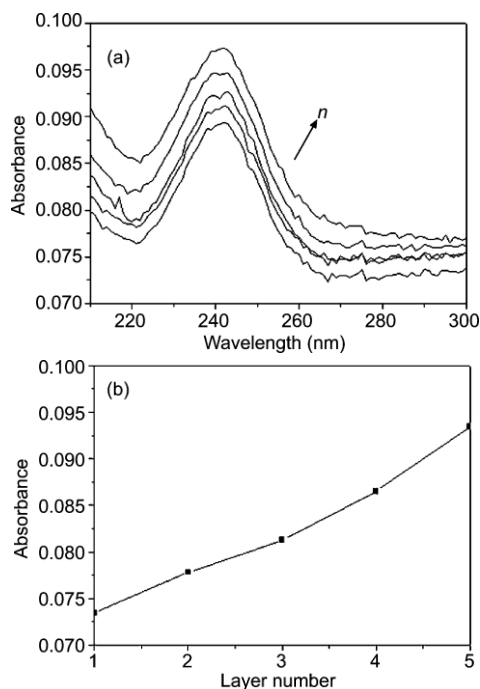


Figure 3 (a) UV-visible spectrum of ((PDDA/PAA)-CuS)_n/PDDA MD films with different layer numbers on quartz substrate; (b) variation in the UV absorbance at 242 nm of ((PDDA/PAA)-CuS)_n/PDDA MD films with increasing layer number.

2.2 XPS analysis

To provide further evidence for the formation of CuS nanoparticles, the sample was characterized by X-ray

photoelectron spectroscopy (XPS). XPS was performed on PHI-5300 spectroscope with Al K α ($h\nu=1486.6$ eV) X-ray source. The vacuum inside the analysis chamber was 1.333×10^{-6} Pa during the analysis. The binding energy was corrected using the benchmark C1s = 284.8 eV. Figure 4 shows the typical high resolution XPS spectra of Cu2p and S2p. In Figure 4(a) the peak of Cu2p has been fitted by peaks at 932.5 eV and 933 eV using XPS peak processing software. The peak of S2p at 162 eV is shown in Figure 4(b). This indicates that the CuS nanoparticles have been fabricated in MD films *in situ*. The peak at 933 eV may be caused by some Cu(OH)₂ nanoparticles which appeared in the films by the hydrolyzation.

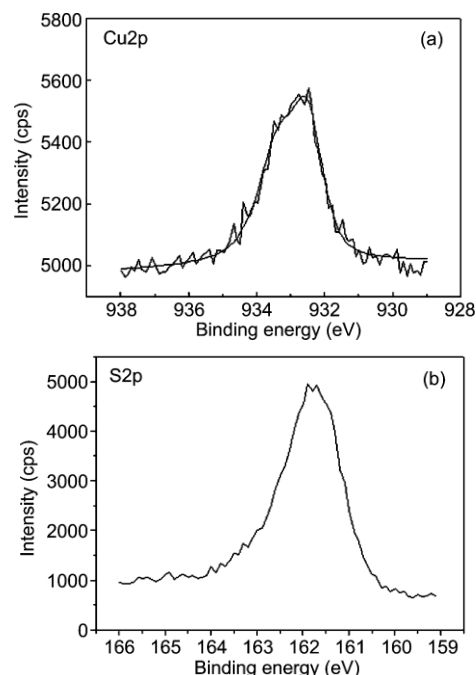


Figure 4 XPS spectrum of Cu2p (a) and S2p (b).

2.3 AFM analysis

(i) Topographic analysis. The surface morphologies of the composite multilayers MD films were investigated by contacting mode AFM. Figure 5 shows the surface morphologies of (PDDA/PAA)₂/PDDA, ((PDDA/PAA)-CuS)₂/PDDA and ((PDDA/PAA)-CuS)₃/PDDA, respectively. The images show the adsorption of polyelectrolyte molecule on the substrates. It is obvious that the surface of the thin film containing CuS nanoparticles is rougher than that of the PDDA/PAA pristine film. From Figure 5(b), (c), it is clearly shown that the spherical particles with size between 10 nm and 35 nm are well dispersed on the surface. As the amplification effect of

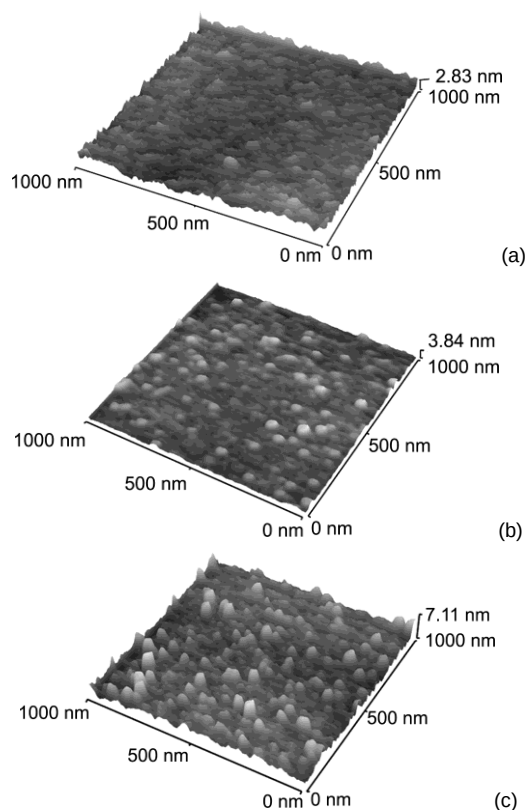


Figure 5 AFM images of MD films.

the probe, the size is smaller actually^[14].

It can be concluded from the AFM images, UV-visible spectrum analysis and XPS analysis that the multilayer films contain CuS nanoparticles have been successfully constructed by the present method.

(ii) Tribological behaviors. Table 1 lists the average surface roughness, hardness, and relative friction force of the 3 bilayer films with CuS nanoparticles determined by AFM analysis. The data of the 3 bilayer films without CuS nanoparticles and the fully cleaned glass substrate are also given in Table 1 for comparison, while the AFM images of the 3 bilayer MD films are shown in Figure 5(c). It is seen that the undefiled glass substrate has a small surface roughness than the MD films, while the surface roughness of MD film is increased after doping nanoparticles. The nanoparticles urge the protuberance of film to increase. It is also seen that the composite MD film has a high hardness than pristine MD film. A tentative explanation is that the nanoparticles play the role as bearing nogs, which makes the MD film have high load-carrying capacity^[15].

The wear properties of the films were studied by AFM at the contact pattern. The scanning speed was 10 $\mu\text{m/s}$, the load was 10 nA, and the scanning step pitch was 2 nm.

Table 1 The average surface roughness, hardness, and the relative friction force of the films

Specimens items	Glass substrate	PDDA/PAA	Nanoparticles doped PDDA/PAA
Hardness (nA)	17.34	7.9	9.8
Roughness (nm)	7.52	13.4	20.1
Relative friction force (nA)	9.2	4.9	3.6

Figure 6 shows the surface wearing capacity of the pristine PDDA/PAA MD films and *in situ* nanoparticles doped MD films. From Figure 6 we can find that the wearing capacity increases with the times of reciprocating scan. The pristine PDDA/PAA MD film's wearing capacity is bigger than that of the *in situ* nanoparticles doped MD film. The wearing capacity of pristine PDDA/PAA MD film does not show change basically at 90 to 100 times, possibly because the film has been destroyed. But the MD film with CuS nanoparticles has not been destroyed, and the wearing capacity increases with the times of reciprocating scan.

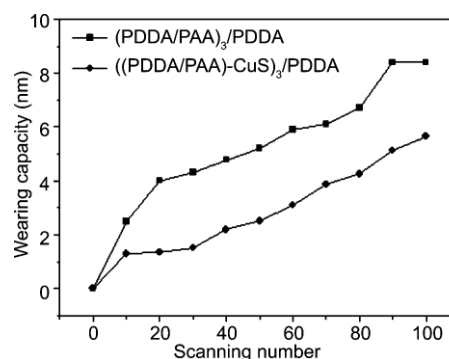


Figure 6 The surface wearing capacity of MD films.

The AFM image of the *in situ* nanoparticles doped MD film after the friction movement is shown in Figure 7. From the left figure, we can find that part of the nanoparticles accumulated in the film's attrition trace, which may be due to some nanoparticles fell off the matrix of polyelectrolyte and accumulated in the reciprocating friction movement. The left figure shows the fluctuation of surface correspondingly.

From the above analysis, we can find that the *in situ* nanoparticles doped MD films showed better wear properties than the pristine MD film. It is quite evident that the nanoparticles within the MD films can enhance anti-wear life of MD films. This may be attributed to the fact that nanoparticles possess load-carrying capacity^[15]. It indicates that the MD films matrix with nanoparticles could decrease the mobility of the polymer chain segments to undergo reversible shear deformation^[16].

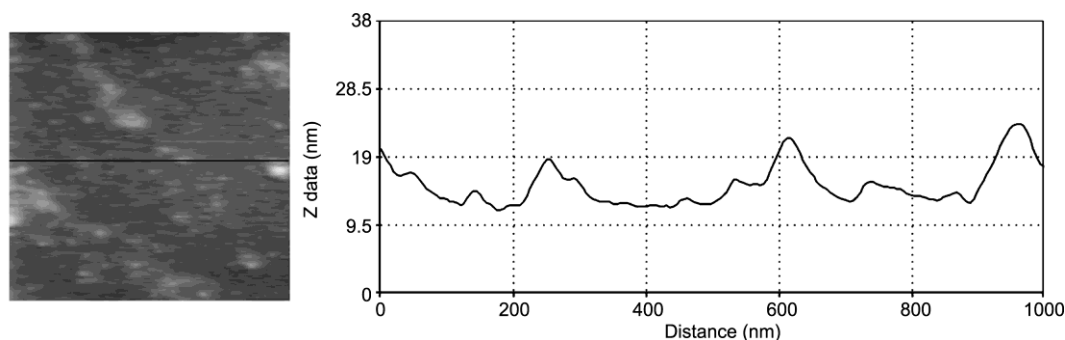


Figure 7 AFM image and fluctuation of *in situ* nanoparticles doped MD films after friction movement.

To confirm the fluctuation of the friction on the surface of the molecular deposition films, the variations in the topography, hardness, and friction of the pristine PDDA/PAA film (Figure 8(a)) and the *in situ* nanoparticles doped MD film (Figure 8(b)) with AFM indentation length were investigated. As shown in Figure 8(a), there exists difference in the variation trend of the hardness, topography, and friction of the pristine PDDA/PAA MD films with AFM indentation length, namely, the fluctuation of the friction lags behind both the morphology and the hardness of the film. Moreover, the variation trend of the friction is similar to that of morphology but sensitive to the hardness fluctuation, i.e. a small change in the hardness corresponds to a significant change in the friction force. In general, the fluctuation of friction is mainly influenced by the surface morphology during the AFM scratch test. However, in this experimental work, the fluctuation in the friction of the pristine PDDA/PAA MD film is attributed not only to the morphology but to the uneven hardness of the film as well. It can be explained as follows. On the one hand, as the AFM tip slid on the surface of the film, the AFM tip was adhered by the adhesive forces, which made the fluctuation of the friction lag behind that of the hardness and morphology. On the other hand, as the AFM tip slid on the surface with non-uniform hardness (non-uniform plasticity), the friction would have a larger fluctuation.

As shown in Figure 8(b), the fluctuation and variation trend of the friction of the *in situ* nanoparticles doped MD film is similar to that of morphology and hardness. The fluctuation of friction does not lag behind that of the hardness and morphology obviously as compared with Figure 8(a). It could be explained that the existence of CuS nanoparticles made the adhesive force of MD films reduce.

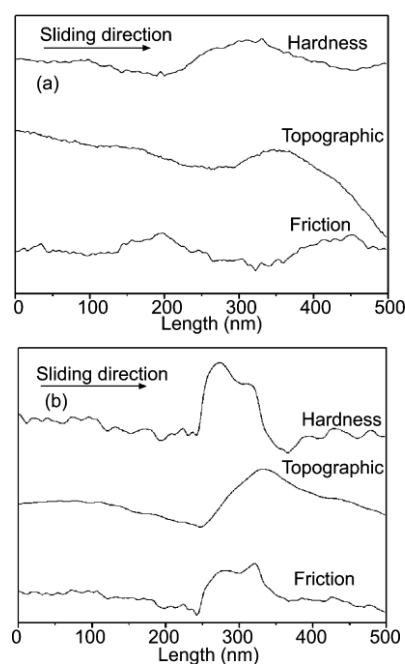


Figure 8 Variations in the topography, hardness, and friction of the PDDA/PAA film (a) and (PDDA/PAA)-CuS film (b) with AFM indentation length.

3 Conclusions

The *in situ* nanoparticles doped MD films were prepared on the glass and quartz substrate by molecular deposition method and *in situ* synthetic technology.

AFM studies showed that the *in situ* nanoparticles doped MD films had good tribological performance; the films had a protective effect to the substrate and higher anti-wear life. This may be attributed to the fact that nanoparticles possess load-carrying capacity and make the adhesive force of MD films reduce. The MD films matrix with nanoparticles would decrease the mobility of the polymer chain segments to undergo reversible shear deformation.

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