Advances in studies of the tribological behavior of molecular deposition films

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Abstract: An overview of the advances in studies on tribology of molecular deposition (MD) films is presented here to summarize the studies of nanofrictional properties, adhesion, wear and mechanical behavior, as well as the molecular dynamics simulation of nanotribological properties of the film in the last decade. Some key research topics which need to be investigate further are addressed.

Key words: Molecular deposition (MD) film, tribological behavior, adhesive property, wear characteristics, mechanical behavior

1 Introduction

The molecular deposition (MD) film, a type of ordered ultrathin film which is assembled from charged polyions and polycations (such as polyelectrolyte, also named polyelectrolyte multilayers (PEMs)) driven by intermolecular electrostatic forces, has been widely investigated in the last decade. MD film has the advantages of simple fabrication, a well-ordered structure, controllable film thickness and deposition on any type of material of any shape. In general, MD film is formed in aqueous solution. The pH value, ionic intensity, and the molecular weight of the polyelectrolyte influence the thickness of the film (Dubas and Schlenoff, 1999; Mermut and Barrett, 2003; Porcel et al, 2007; Sun et al, 2007). A few types of MD films can be fabricated in non-aqueous solutions (Tuo and Wang, 2006). Differing polyelectrolyte assembly can alter desired properties. The MD film can exhibit photoelectric (Fushimi et al, 2005), biologically-catalytic (Yu et al, 2005) and electrochemical performance (Li et al, 2005; Shen et al, 2003), and recently has been used as ion-selective nanofiltration membranes (Lu et al, 2008).

MD films, which can reduce friction and provide lubrication (Wang et al, 1999d), are expected to significantly improve the performance of micro-devices. Therefore, the aim of this work is to review the advances in the nanotribology of molecular deposition (MD) films.

2 Frictional and lubricating properties of MD films

The frictional and lubricating properties of MD films have been widely investigated in the last decade. The MD films deposited on substrates can reduce friction force, which is mainly influenced by the characteristics of MD films and

experimental conditions.

2.1 Effect of characteristics of MD film itself on the nanofrictional properties

The factors affecting the nanofrictional behavior of MD films include the characteristics of molecules assembling the films, characteristics of terminal group and surface charge, the interaction between layers, the hardness and morphology of the films.

2.1.1 Effects of the characteristics of molecules assembling films

The characteristics of the molecules forming the MD films have essential effects on the tribological behavior of the film. Polyallylamine hydrochloride (PAH)/graphite oxides (GO) (PDDA/GO for short MD films and PAH/polyacrylic acid (PAA) (TiO₂) composite MD films could reduce the coefficient of friction of the modified substrates when self-lubricating graphite oxides were embedded in the film (Feng et al, 2003a; 2004) and PAH incorporated with wearable TiO₂ were enwrapped by polyacrylic acid (PAA) (Feng et al, 2003b; Zhang et al, 2003), respectively.

Yang and his coworkers (2004) investigated the microtribological properties of PAMAMC (dendrimer molecules)/DR (diazo resin) and Pt-PAMAMC/DR multiplayer MD films which were formed from DR and PAMAMC with or without platinum nanoparticles. Experimental results showed that the film, containing Pt nanoparticles, exhibited stable frictional responses under the action of applied load. This can be attributed to the load-bearing capacity of the platinum nanoparticles and the flexible chains in the dendrimer.

The tribological behavior of three types of MD films were investigated by Pavor et al (2004b). The anchoring polystyrene-block-poly(acrylic acid)/PAH film enhanced the hardness and the load-bearing capacity, and hence substantial wear was prevented. The PAA/PAH film with in situ formed silver nanoparticles reduced the friction force at the optimum levels of silver clusters. And the PAH composite film with

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multi-wall carbon nanotubes exhibited a low value of friction.

Lanthanum-based MD films were investigated by Cheng et al (2006). The tribological experiment showed that the friction coefficient of glass substrates reduced from 0.85 to 0.13 after they were coated with lanthanum-based MD film, and the rare-earth MD film had a longer wear life (2,880 sliding passes).

The tribological behavior of poly(diallyldimethylammonium chloride) (PDDA) and poly(sodium 4-styrenesulfonate) (PSS) MD film and PDDA/PSS MD film containing copper hydroxide nanoparticles were compared and analyzed by Yang et al (2007). It was found that the friction coefficient of pristine MD film was smaller and was greatly affected

by normal load. However, the friction coefficient of the composite films reinforced by nanoparticles was little affected by the normal load, though the friction coefficient was higher than that of the pristine MD films (Fig. 1). It might be attributed to the enhanced load-carrying capacity of the inorganic nanoparticles in these MD films.

In general, the ordered building of the rigid structure in films can enhance the load-bearing property of the films, but lead to the defects that affect the surface roughness of films. However, the soft chain in the films can alleviate the building defects. The optimized deposition of the rigid and soft chains was presumed to show good tribological behavior.

Huang and his coworkers (2002a; 2002b; 2002c) studied

Fig. 1 Friction coefficient as a function of normal load with a sliding velocity of 100 mm/min

(a) 4.5 layer pairs and (b) 8.5 layer pairs. (■) Pristine MD films, (●) MD films containing Cu(OH)₂ nanoparticles (After Yang et al, 2007)

the microtribological property of the film assembled from diazo resin and C₆₀-containing polyelectrolyte. It was found that rigid chains containing C₆₀ molecules improved the load-bearing property and decreased the lubricating property of the film, and soft chains have the opposite effects of the rigid chains. The tribological properties of a C₆₀ carboxylic acid derivative/diazo resin film and a C₆₀ carboxylic acid derivative/diazo resin/poly(acrylic acid) film were compared by Cao et al (2002). The results showed that the polymer-bound C₆₀ film had not only good load-bearing properties but also low friction properties while the soft poly(acrylic acid) chain incorporated in the film increased the lubricating property of the film. Wang et al (2003b) examined the friction and wear behavior of liquid crystal aromatic polyamide self-assembled film. Experimental results showed that the film had good tribological properties because the liquid crystal aromatic polyamide molecules and the substrate could form hydrogen bonding to reinforce the connection between the film and the substrate. Moreover, heat treatment made the structure of the film more ordered, and more rigid. Ahn et al (2003) reported that the film which has long hydrocarbon chains with same functional group displayed a slightly higher coefficient of friction than that of the film with shorter hydrocarbon chains in the nanoscale contact, which was contributed to the higher rigidity because of stronger lateral cohesion among hydrocarbon chains.

Wang et al (2006) found that the tribological property of the PAH/PAA film was related to the molecular chain. The film fabricated with longer chains performed better in reducing the friction force when the layer number was small. The film with shorter chains performed better when the layer number was greater than a specific number.

2.1.2 Effects of characteristics of terminal groups and surface charge

Research on the influence of the characteristics of terminal groups and surface charge of the film was conducted quite early by the MD Film Research Group, China University of Petroleum (Beijing). It should be noted that the samples with the same terminal group would have similar nanofrictional characteristics, although their molecular chain-lengths and skeletons were different (Wang et al, 1999c). This phenomenon can be explained in two ways: 1) The dissipation of energy of the MD film during the friction process was completed only by the vibration and rotation of the molecular terminal on the sample surface, owing to the strong electrostatic attractive force between the layers of the molecules, which lead to the formation of dense layers on the substrate. 2) According to the Johnson-Kendall-Roberts (JKR) theory, the adhesive force is proportional to the square root of the radius of the tip. During the experiment, the adhesive forces of the anionized Au surface and the monolayer MD film were very low and equal to 8 nN and

5 nN, respectively. Therefore, it can be deduced that when the load and adhesive force are low, the contact between the atomic force microscopy (AFM) tip and the sample surface is atomic contact, and the nanofrictional characteristics of the samples are mainly determined by the terminals of the tip and the sample surface, which has nothing to do with the molecular chain-length and the skeleton. Later on, Zhang and his coworkers (Wang et al, 2003a; Zhang et al, 2005b) found that the coefficients of friction of the MD films with hydrocarbon chain as the terminal group were lower than those of the corresponding MD films with the same number of layers but without hydrocarbon chains. Moreover, MD films with different numbers of layers and the same terminal group were found to have similar nanofrictional behavior. But the films modified with alkyl terminal groups performed more stably than those modified with active terminal groups (Zhang et al, 2005b). They also analyzed the effects of the exposed terminal groups and surface charges on the nanofrictional properties of MD films on single crystal silicon substrate by using AFM (Gao et al, 2003c). The results showed that the friction was dependent on the exposed terminal groups under a relatively smaller load when the AFM tip slid on the film surface and was related to the surface net charge on Si_3N_4 tip to some extent. The surface positive charge had a larger effect than negative charge on the nanofrictional behavior of the MD film (Fig. 2) because of the adhesion caused by the surface charge. Adhesive force and friction force decreased due to the decrease in the surface charge in the MD film after being heated (Feng et al, 2004). The properties of the terminal group in the MD film can directly influence both the surface energy and the topography of the film and further affect the tribological behavior of the film.

The nano- and micro-scale tribological behavior of the films were compared and discussed in terms of the chemical structure such as terminal groups and chain length of the film molecules (Ahn et al, 2003). This investigation revealed that the tribological behavior of films was significantly affected by the molecular structure of the films both in nano- and micro-scales.

2.1.3 Effects of interaction between layers, hardness and

Fig. 2 Friction force vs. loading force on an ionized Au surface (After Gao et al, 2003c)

morphology

The electrostatic force between the layered structure of the MD film would convert to covalent bonding after heat-treatment (Feng et al, 2003b; 2004) or under ultraviolet irradiation (Cao et al, 2002; Huang et al, 2002a; 2002b; 2002c; Yang et al, 2004). As a result, the stability and nanofrictional property of the film were improved because the bonding strength between the layers became stronger.

Feng et al (2003b; 2004) observed that after the MD films were heated, the growth of the GO and TiO_2 nanoparticles resulted in a decrease in topography and an increase in hardness of the films. They also found that there existed a difference in the variation trend of morphology, hardness, and friction force of the PAH/GO film with AFM indentation length, namely, the fluctuation of friction force lagged behind both morphology and hardness as shown in Fig. 3. Moreover, the variation trend of friction force was similar to that of morphology but was sensitive to hardness fluctuation (Zhang et al, 2005a). The fluctuation in friction force of the PAH/GO film was attributed not only to the morphology but to the uneven hardness of the film as well. It was presumed that, as the AFM tip slid along the surface of the PAH/GO film, the AFM tip was adhered by adhesive forces, which made the fluctuation of friction force lag behind that of hardness and morphology. On the other hand, as the AFM tip slid on the surface with non-uniform hardness (non-uniform plasticity), the friction force would have a larger fluctuation.

Moreover, the same type of MD film showed different

Fig. 3 Variations in the topography, hardness, and friction force of the seven-layer PAH/GO film with AFM indentation length (After Zhang et al, 2005a)

tribological behavior when sliding against different coatings, which was related to the different relaxation behavior of the MD films and the different interactions among the films and the metallic coatings as the counterparts (Zhang et al, 2004).

2.2 Effects of experimental conditions

2.2.1 Effects of load

The friction coefficient of the PDDA/GO MD composite film was found to decrease with increasing load. However, the decrease in friction coefficient reduced noticeably and

stopped when the load was beyond a specific value (Feng et al, 2003a).

The effect of load on nanofrictional properties of different silicon surfaces modified by different MD films, whose terminal groups were $\text{N}(\text{CH}_3)_2\text{H}^+$ and SO_3^- , respectively was investigated by Gao et al (2004). Experimental results showed that the friction force increased linearly with load for different silicon surfaces under a lower load. However, the silicon surface deposited with monolayer copper phthalocyaninetetrasulfonic acid, tetrasodium salt (CuTsPc) MD film did not show a reduction in nanofrictional properties, which might be attributed to the existence of its stable terminal groups.

2.2.2 Effects of scan rate

All the gold substrates deposited with MD film were found to have a lower friction force than the clean gold substrate at different scan rates, which was result from the molecular brush effects (Wang et al, 1999d; 2000). Moreover, all the samples with the same terminal group after being decorated with alkyl-terminal molecule had the same nanofrictional properties.

Silicon substrates modified with different MD films were investigated in order to reveal the effect of scan rate on friction force of MD films (Gao et al, 2003b). The friction force of the aminopropylalkylated silicon substrate first decreased and later increased with increasing scan rate, while the friction force of clean and hydroxylated silicon substrates increased continuously. A possible explanation for this phenomenon is that the amorphous structure of the film transformed into liquid crystal state due to the frictional heat generated during the increase of the scan rate. But for silicon surface deposited with monolayer CuTsPc MD film, the nanofriction force decreased with increasing scan rate, which might be attributed to its poor thermal conductivity and the plastic deformation of the surface during scanning.

2.2.3 Effects of relative humidity and controlled atmosphere

The influence of relative humidity on the tribological property of MD film was remarkable. It was found that friction force decreased with the increase in humidity owing to increasing condensed water and decreasing shear-strength at the interface (Gao and Yu, 2002; Wang et al, 2000). For positively charged Au surfaces and negatively charged Au surfaces, the higher the relative humidity, the lower the friction force and friction coefficient. This was resulted from the decrease in adhesive force which was attributed to the condensed water between the probe tip and the MD film (Gao et al, 2004). Additionally, the nanofrictional properties of MD films in controlled atmosphere, such as pure nitrogen, were different from those in ambient environment.

Qian et al (2003) examined the effects of relative humidity from 5% to 98% on the tribological properties of monolayer MD films. Relative humidity only had influence on the friction force of the film over a range of relative humidity when the terminal group was hydrophobic. Yang et al (2006b) also found that the friction force of MD films was almost independent of relative humidity when the surface of MD film was highly hydrophobic.

3 Adhesive property of MD film

Friction force is very closely related to adhesive force. The results of molecular dynamics simulation on tribological properties of MD film indicated that the friction phenomenon at the interface between the probe tip of the atomic force microscope and the MD film was attributed to adhesive action when the tip slid on the MD film (Lan et al, 2002; 2003a; 2003b; 2004).

Wang et al (1999a) studied quartzite modified by MD film with AFM. The analyses of force-displacement curve, surface topography, modulation force image and friction force image indicated that the reduction in friction force of MD film was due to the decrease in the adhesion between the probe tip of the atomic force microscope and the MD film. Moreover, Wang and his coworkers (1999b) deduced a formula for calculating the adhesive force according to the measured force-displacement curve. The adhesion of the quartzite modified by MD film was apparently smaller than that of the clean one.

Adhesion has a great effect on the nano-friction properties of MD film, which not only changed the nano-friction properties of the film surface, but also increased the normal force. This resulted in the enhancement of friction force. Moreover, experimental results proved that an unloading experiment was another method to verify the adhesive force (Gao et al, 2003a). The friction reduction effect of MD films was attributed to the surface micro-modification and the resulting decrease in the surface adhesion.

Richert et al (2004) reported that the adhesive properties of chondrosarcoma cells with poly(L-lysine/poly(L-glutamic) (PGA/PLL) multilayer MD films, could be tuned depending on the deposition pH value of the polyelectrolyte solutions. The high or low adhesion observed on the films built at pH 4.4 or pH 10.4 may rather be related to the secondary structure of the film and to its relatively low or high swellability in water. These fundamental studies will enhance the potential of MD films for future biomedical applications, for example drug release and cytoskeletal organization.

4 Wear characteristics of MD film

Substrates modified by MD film have some wear resistance under certain experimental conditions. Pavoort et al (2004a) found that the MD film deposited with poly(allylamine hydrochloride) and poly (acrylic acid) (PAH/PAA) could prevent wear of steel substrates in the dry state, and also in the presence of water and bovine calf serum, used to simulate synovial fluid in human joints. As indicated in Fig. 4, the PAH/PAA MD film protected the glass substrate. The wear track was observed on the glass coated with a (PAH 3.5/PAA3.5) 70 nm film at the end of 2,000 cycles and no steel deposition from the pin of the pin-on-disk tester was observed. For a clean glass substrate, conversely, steel deposition onto the wear track was observed within the first few cycles.

The wear-resistant property of MD film is closely related to the characteristics of structure units, the interaction between layers, the number of layers and the properties of the materials in the wear coupled parts.

Gao and Zhang (2002) investigated the wear-life of the

Fig. 4 Optical micrograph and cross-sectional surface profiles of wear tracks after macroscale pin-on-disk tests (2000 cycles)
(After Pavoor et al, 2004a)

poly(sodium 4-styrenesulfonate) (PSS)/PAH MD film. It was found that the higher the number of deposited layers the longer the wear-life. Moreover, the wear-life increased considerably after proper heat-treatment, but the mechanism requires further study.

They also found that the poly(ethylenimine)/poly(sodium 4-styrenesulfonate) MD film showed good friction-reducing and anti-wear behavior at a relatively low load. Scanning electron microscopic observation of the wear track of the film indicated that the composite film was characterized by adhesive wear in sliding against the steel counter-face (Gao and Zhang, 2002). The films assembled from acid red 18 as anion and poly(ethylenimine) (PEI) as well as PA exhibited good friction-reducing and anti-wear behavior in sliding against the steel counter-face at a relatively low load, which was attributed to the ordered “liquid crystal” state of the films (Gao and Yu, 2003).

In the study of the tribological behavior of PSS/poly (diallyldimethylammonium chloride) (PDDA) MD film, the surface charge, hydrophilicity and hydrophobicity of the surface greatly affected the tribological behavior of the films, and the surface with negative charge and high hydrophilicity had long antiwear life (Yang et al, 2006a). They also found that the anti-wear life of the film with fewer layers was longer than that of the film with more layers when the interaction force between the film and the substrate was electrostatic force, because the electrostatic force would be weakened with the increase in the number of layers. And the anti-wear life of the film with more layers was longer than that of the film with fewer layers when the interaction force between the film and the substrate was covalent bonding. The anti-wear life of the MD film with a hydrophilic group was lengthened with increasing relative humidity because condensed water was

formed to reduce the shear-strength at the interface. For the film with a hydrophobic terminal group, the relative humidity had little effect on the anti-wear life of the film, and the number of layers became an important factor.

More recently, Yang and co-workers (2006b; 2006c) investigated the tribological properties of MD films. Some conclusions were presented. The friction coefficient of $\text{Cu}(\text{OH})_2$ -doped PDDA/PSS MD film was higher and changed slightly with increasing normal load compared with pristine PDDA/PSS MD film. The $\text{Cu}(\text{OH})_2$ -doped MD film exhibited higher durability because the inorganic nanoparticles in the film enhanced the load-carrying capacity. The main wear-mechanism was adhesive wear, and the $\text{Cu}(\text{OH})_2$ nanoparticles mitigated plastic deformation and slowed down adhesive wear (Yang et al, 2006c). In the example of the friction and wear behavior of PDDA/PSS MD film sliding against stainless steel, brass, Si_3N_4 and WC balls, the shearing stress was higher and anti-wear life was shorter as the film was sliding against the hard counterparts, such as Si_3N_4 and WC balls. Under the same conditions, it possessed longer anti-wear life when sliding against stainless steel and brass (Yang et al, 2006b).

Wang et al (2004) investigated that the frictional behavior of two MD films of liquid crystal polymer PPTA (polymer aromatic polyamine), fabricated respectively on glass from lyotropic liquid crystal solution and isotropic solution. The juncture between the PPTA transfer film and counter-face was so strong that the sliding cycles could be prolonged beyond 1,000 times; furthermore, friction occurred actually between the deposited film and the transfer film, which was a balanceable course. When the transfer film eventually escaped from the counter-face, the deposited film would be worn out quickly.

Pavoor's recent work (Pavoor et al, 2006) explored the use of PAH/PAA MD film as coatings for wear reduction of orthopedic bearing surfaces. These films with easily tunable architectures provided excellent adhesion to a wide variety of metallic, plastic, and ceramic substrates. The wear-reducing capacity of these coatings in the presence of bovine calf serum-lubricant solution was established for metal/metal systems at the meso/microscale over 30 cycles of reciprocating motion, as well as for the commonly used metal/ultra-high molecular weight polyethylene (UHMWPE) system over 500,000 cycles of bi-directional motion in a macroscale pin-on-disk test. In the latter case, the use of the films reduced UHMWPE wear by up to 33% when compared with the uncoated control. This is the first clinically relevant laboratory demonstration of the wear-reducing ability of these films.

5 Molecular dynamic simulation of MD film

Molecular dynamic simulation is an important theoretical interpretation for the research on tribological properties, especially for the study of the origin of friction and the analysis of the interaction of molecules and energy dissipation during sliding.

In the work of the MD Film Research Group of China University of Petroleum (Lan et al, 2002) molecular

dynamics simulation was used to study the nanotribological properties of a gold surface decorated by hexadecanethiol self-assembled film during the scanning process with an Au tip. The simulation results showed that an obvious jump to contact occurred during the approach of the pure Au tip on to the surface of MD film. Furthermore, the tilt angle and load of the molecules under the tip experienced the same tendency of hysteresis, which might be attributed to the adhesive force between the tip and the MD film (Lan et al, 2003a).

Lan and Zhang (2004) examined the nanotribological properties of the MD film deposited on the Au (111) substrate during the scanning process with an Au tip by using molecular dynamics simulation. The results showed that the tilt angle and potential energy of the molecules near the tip both increased with decreasing distance between tip and monolayer. Continuous slip also occurred during the slip stage. Moreover, regular stick-slip was in agreement with the spatial structure. Fig. 5 showed that a continuous slip occurred under the action of Au tip, and afterwards a periodic stick-slip was produced. This phenomenon was in agreement with the planar structure, as shown in Fig. 5a. Its periodicity (8.64 ps) was equal to the nearest neighbor spacing of triangular lattice formed by the head groups of the absorbed molecules (Fig. 5b).

Molecular simulations of multilayer formation of polyelectrolyte and nanoparticles composite MD film

Fig. 5 Results of molecular dynamics simulation (a) Changes of the tilt angle θ and friction force F_f with scanning time; (b) Distribution of Au atoms on the substrate and sulfur atoms of MD film (Empty circles are Au atoms, shadow circles are sulfur atoms, dash-dot lines are the lattice directions of MD film) (After Lan and Zhang, 2004)

provided useful information about multilayer assembly processes and the factors governing the film buildup, some of which are particularly important to the structures, furthermore the properties of MD films (Panchagnula et al, 2005; Patel et al, 2006; Jeon et al, 2006). Abu-Sharkh (2006) presented that the assembly process of polyelectrolytes and nanoparticles was electrostatically driven with alternating charge reversal and an overcompensation mechanism.

6 Mechanical behavior of MD film

The mechanical behavior of MD film deposited on Au substrate was studied by using a nano-indenter (Lan, et al, 2003b; 2005). The results showed that after the film was deposited on the Au substrate, both modulus of elasticity and hardness decreased, moreover, elastic deformation increased but plastic deformation decreased. Obviously, the MD film can improve the nano mechanical properties of the Au substrate. The nano-indentation curves of both pure gold substrates and MD film deposited on the gold substrates (Fig. 6) illustrated that the film actively improved the properties of

the samples decorated by MD film.

Schneider et al (2006) showed that the elastic modulus of the wet poly(L-lysine)/hyaluronan (PLL/HA) MD films, which was determined by using the AFM nano-indentation technique with a colloidal probe, would be modified by adjusting the cross-linker, a water-soluble carbodiimide (EDC) concentration (Fig. 7). The adhesion between the cell and (PLL/HA) MD films cross-linked by different EDC directly depended on the Young's modulus of the films.

7 Conclusions

Fig. 6 Nano-indentation curves of both the pure Au substrate and MD film deposited on the Au substrate (After Lan et al, 2003b)

Fig.7 Spreading cell area measured for cells grown on (PLL/HA)₁₂ films cross linked at various EDC concentrations (at least 70 cells were analyzed for each condition) after 3 days in culture. Error bars are standard deviations (After Schneider et al, 2006)

Very promising prospects for the tribological application of MD films has been opened up by recent research in China and overseas. The studies of MD films have been extended because of their unique properties. However, there is still a long way to go to put MD film into practical application. In order to prepare more varieties of MD films which have better tribological properties and promote the use of MD film in micro/nano-electro-mechanical systems (MEMS/NEMS), some key problems in the studies of MD film should be addressed, such as optimization of the preparation conditions, improvement of the wear-resistance, friction and wear mechanism, as well as clarifying the factors influencing

tribological behavior of the film.

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References

- Abu-Sharkh B. Structure and mechanism of the deposition of multilayers of polyelectrolytes and nanoparticles. *Langmuir*. 2006. 22(7): 3028-3034
- Ahn H S, Cuong P D, Park S, et al. Effect of molecular structure of self-assembled monolayers on their tribological behavior in nano- and microscales. *Wear*. 2003. 255: 819-825
- Cao T B, Wei F, Yang Y L, et al. Microtribological properties of a covalently attached nanostructured self-assembly film fabricated from fullerene carboxylic acid and diazo resin. *Langmuir*. 2002. 18(13): 5186-5189
- Cheng X H, Bai T, Wu J, et al. Characterization and tribological investigation of self-assembled lanthanum-based thin films on glass substrates. *Wear*. 2006. 260(7-8): 745-750
- Dubas S T and Schlenoff J B. Factors controlling the growth of polyelectrolyte multilayers. *Macromolecules*. 1999. 32(24): 8153-8160
- Feng D P, Wang D G and Zhang S W. The preparation of graphite oxide molecular deposition films and its study by atomic force microscopy. *Tribology*. 2003a. 23(1): 1-4 (in Chinese)
- Feng D P, Wang D G and Zhang S W. Preparation and nanotribological behavior of PAH/PAA(TiO₂) molecular deposition film. *Materials for Mechanical Engineering*. 2003b. 27(11): 13-14, 38 (in Chinese)
- Feng D P, Wang D G and Zhang S W. Preparation and nanotribological behavior of PAH/Graphite oxide molecular deposition film. *Science in China, Ser. E*. 2004. 47(4): 385-390 (in Chinese)
- Fushimi T, Oda A, Ohkita H, et al. Photocurrent generation in heterostructured ultrathin films fabricated by layer-by-layer deposition of polyelectrolytes bearing tris(2,2'-bipyridine) ruthenium(II) and ferrocene moieties. *Langmuir*. 2005. 21(4): 1584-1589
- Gao M L, Nie S C and Zhang S W. Effect of adhesion on nano-frictional properties of molecular deposition films. *China Surface Engineering*. 2003a. 16(4): 12-14 (in Chinese)
- Gao M L, Nie S C and Zhang S W. Effect of scan rate on nanofriction properties of monolayer deposition film on silicon. *Chemical Research and Application*. 2003b. 15(5): 734-736 (in Chinese)
- Gao M L, Nie S C and Zhang S W. Several factors influencing nanofrictional properties of molecular deposition films. *Tribology*. 2003c. 23(6): 472-476 (in Chinese)
- Gao M L, Nie S C and Zhang S W. Effect of load, relative humidity and controlled atmosphere on nanofrictional properties of silicon and Au surfaces. *Mechanical Science and Technology*. 2004. 23(1): 87-89 (in Chinese)
- Gao S Y and Yu L G. Molecular deposition polymeric nanocomposite films and their tribological properties in sliding against steel. *Chinese Journal of Chemical Physics*. 2002. 15(2): 132-136 (in Chinese)
- Gao S Y and Yu L G. Preparation and investigation of the tribological behavior of small molecular weight organic dye and polycation ultrathin films. *Acta Polymerica Sinica*. 2003. (1): 18-22 (in Chinese)

- Gao S Y and Zhang P Y. Preparation and investigation of the tribological behavior of poly(ethylenimine) and poly(sodium 4-styrenesulfonate) molecular deposition composite film. *Tribology*. 2002. 22(6): 421-425 (in Chinese)
- Huang L, Gu Q Y, He Y K, et al. Studies of microtribological property of the self-assembling films from diazoresin and C₆₀-containing polyelectrolyte. *Chemical Journal of Chinese Universities*. 2002a. 23(6): 1193-1197 (in Chinese)
- Huang L, Hou X R, He Y K, et al. Fabrication and AFM/FFM studies of C₆₀-containing polyelectrolyte self-assembled films. *Chinese Journal of Polymer Science*. 2002b. 20(3): 197-203
- Huang L, Huang F, He Y K, et al. The self-assembly of thin films from water-soluble C₆₀-containing polyelectrolytes: Synthesis, fabrication, AFM/FFM studies. *Acta Polymerica Sinica*. 2002c. (2): 192-197 (in Chinese)
- Jeon J, Panchagnula V, Pan J, et al. Molecular dynamics simulations of multilayer films of polyelectrolytes and nanoparticles. *Langmuir*. 2006. 22(10): 4629-4637
- Lan H Q, Li D C and Zhang S W. Computer simulation on mechanical properties of molecular deposition film. *Materials Science Forum*. 2005. 475-479: 3665-3668
- Lan H Q and Zhang S W. Molecular dynamics simulation on nanotribological properties of molecular deposition film during the scan process. *Tribology International*. 2004. 37(8): 661-665.
- Lan H Q, Zhang S W and Wang D G. Molecular dynamics simulation on nanotribological properties of self-assembly film. *Progress in Natural Science*. 2002. 12(6): 652-654 (in Chinese)
- Lan H Q, Zhang S W and Wang D G. Molecular dynamics simulation of molecular deposition film subject to nano-indentation test. *Tribology*. 2003a. 23(5): 398-401 (in Chinese)
- Lan H Q, Zhang S W, Li D C, et al. Nano-indentation of molecular deposition film. *Materials for Mechanical Engineering*. 2003b. 27(9): 40-42 (in Chinese)
- Li X F, Zhao S, Yang M, et al. Covalently attached multilayer assemblies of diazo-resins and binuclear cobalt phthalocyanines. *Thin Solid Films*. 2005. 478(1-2): 310- 317
- Lu O Y, Malaisamy R and Bruening M L. Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations. *Journal of Membrane Science*. 2008. 310(1-2): 76-84
- Mermut O and Barrett C J. Effects of charge density and counterions on the assembly of polyelectrolyte multilayers. *J. Phys. Chem. B*. 2003. 107(11): 2525-2530
- Panchagnula V, Jeon J, Rusling J F, et al. Molecular dynamics simulations of polyelectrolyte multilayering on a charged particle. *Langmuir*. 2005. 21(3): 1118-1125
- Patel P A, Jeon J, Mather P T, et al. Molecular dynamics simulations of multilayer polyelectrolyte films: Effect of electrostatic and short-range interactions. *Langmuir*. 2006. 22(24): 9994-10002
- Pavoor P V, Gearing B P, Bellare A, et al. Tribological characteristics of polyelectrolyte multilayers. *Wear*. 2004a. 256(11-12): 1196-1207.
- Pavoor P V, Gearing B P, Gorga R E, et al. Engineering the friction-and-wear behavior of polyelectrolyte multilayer nanoassemblies through block copolymer surface capping, metallic nanoparticles, and multiwall carbon nanotubes. *Journal of Applied Polymer Science*. 2004b. 92(1): 439- 448
- Pavoor P V, Gearing B P, Muratoglu O, et al. Wear reduction of orthopaedic bearing surfaces using polyelectrolyte multilayer nanocoatings. *Biomaterials*. 2006. 27: 1527-1533.
- Porcel C, Lavallo Ph, Decher G, Senger B, et al. Influence of the polyelectrolyte molecular weight on exponentially growing multilayer films in the linear regime. *Langmuir*. 2007. 23(4): 1898-1904
- Qian L M, Tian F and Xiao X D. Tribological properties of self-assembled monolayers and their substrates under various humid environments. *Tribology Letter*. 2003. 15(3): 169-176
- Richert L, Arntz Y, Schaaf P, et al. pH dependent growth of poly(L-lysine)/poly(L-glutamic) acid multilayer films and their cell adhesion properties. *Surface Science*. 2004. 570(1-2): 13-29
- Schneider A, Francius G, Obeid R, et al. Polyelectrolyte multilayers with a tunable Young's modulus: Influence of film stiffness on cell adhesion. *Langmuir*. 2006. 22(3): 1193-1200
- Shen Y, Liu J Y, Wu A G, et al. Preparation of multilayer films containing Pt nanoparticles on a glassy carbon electrode and application as an electrocatalyst for dioxygen reduction. *Langmuir*. 2003. 19(13): 5397-5401
- Sun B, Jewell C M, Fredin N J, et al. Assembly of multilayered films using well-defined, end-labeled poly acrylic acid): Influence of molecular weight on exponential growth in a synthetic weak polyelectrolyte system. *Langmuir*. 2007. 23(16): 8452-8459
- Tuo X L and Wang X G. Construction of polyelectrolyte self-assembled multilayers in non-aqueous media. *Acta Polymerica Sinica*. 2006. (1): 156-159 (in Chinese)
- Wang D G, Gao M L and Zhang S W. A study on micro-friction properties of a molecular deposition film on silica rock. *Tribology*. 1999a. 19(1): 28-32 (in Chinese)
- Wang D G, Gao M L and Zhang S W. Silica surface by atomic force microscopy. *Journal of the University of Petroleum, China*. 1999b. 23(4): 53-55 (in Chinese)
- Wang D G, Zhang S W and Gao M L. Nano-scratch study of molecular deposition films on silicon wafers using nano-indentation. *Tribotest*. 2003a. 9(3): 231-237
- Wang D G, Zhang S W, Yu X X, et al. Effect of molecular chain-length on nanotribological behavior of the polymer molecular deposition films. *Proceedings of the Third Asia International Conference on Tribology*. Kanazawa, Japan, October 16-19, 2006. 121
- Wang H J, Wang Q H and Pei X Q. Friction and wear behavior of liquid crystal polymer aromatic polyamide self-assembled films. *Polymer Materials Science and Engineering*. 2003b. 19(6): 111-114 (in Chinese)
- Wang H J, Wang Q H and Pei X Q. Friction and wear behavior of lyotropic liquid crystal polymer aromatic polyamide self-assembled films. *Polymer Materials Science and Engineering*. 2004. 20(5): 125-128 (in Chinese)
- Wang Q B, Gao M L and Zhang S W. Tribological application of molecular deposition (MD) films. *Materials Science and Engineering. C, Biomimetic Materials, Sensors and Systems*. 1999c. 10(1-2): 127-129
- Wang Q B, Gao M L and Zhang S W. Study on nanofriction properties of molecular deposition (MD) films on the Au substrate by atomic force microscopy. *Progress in Natural Science*. 1999d. 9(10): 938-941
- Wang Q B, Gao M L and Zhang S W. Nanofriction properties of molecular deposition films. *Science in China, Series B*. 2000. 43(2): 138-142.
- Yang G B, Ma H X, Wu Z S, et al. The tribological behavior of PDDA/PSS molecular deposition films. *Lubrication Engineering*. 2006a. (2): 27-30 (in Chinese)
- Yang G B, Ma H X, Wu Z S, et al. Effect of counterparts on the friction and wear behavior of PDDA/PSS molecular deposition film. *Lubrication Engineering*. 2006b. (7): 61-63 (in Chinese)
- Yang G B, Wu Z S and Zhang P Y. Study on the tribological behavior of polyelectrolyte multilayers containing copper hydroxide nanoparticles. *Tribology Letters*. 2007. 25(1): 55-60
- Yang G B, Zhao Z, Wu Z S, et al. Investigation of friction and wear behavior of Cu(OH)₂-doped polyelectrolyte multilayers. *Tribology*. 2006c. 26(4): 300-305 (in Chinese)
- Yang L, Luo Y F, Jia X R, et al. Microtribological property of self-

- assembly multilayer films based on PAMAM dendrimers. *Acta Polymerica Sinica*. 2004. (5): 780-784 (in Chinese)
- Yu A M, Liang Z J and Caruso F. Enzyme multilayer-modified porous membranes as biocatalysts. *Chem. Mater*. 2005. 17(1): 171-175
- Zhang H C, Gao Y Z, Li Y B, et al. Effects of interfacial contact characteristics on the friction properties of octadecyltrichorosilane and 3-aminopropyltrimethoxysilane self-assembled monolayers. *Tribology*. 2004. 24(1): 6-10 (in Chinese)
- Zhang S W, Feng D P and Wang D G. Tribological behavior of composite molecular deposition films. *Tribology International*. 2005a. 38(11-12): 959-965.
- Zhang S W, Wang Q B, Gao M L. Characterisation and nano-friction behavior of molecular deposition films. *Lubrication Science*. 2005b. 17(2): 164-171
- Zhang S M, Zhang Z J, Dang H X, et al. Preparation, characterization and microtribological behavior study of PSS/TiO₂ orderly alternating nanocomposite multilayer films. *Journal of Henan University (Natural Science)*. 2003. 33(1): 38-40 (in Chinese)
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