RSC Advances

Tribology Study of Lanthanum-treated Graphene Oxide Thin Film on Silicon Substrate

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Low friction coefficient and wear rate of components are crucial for nano-electromechanical-systems (NMES). Herein, we prepared carboxylated graphene oxide(GO) complexs with lanthanum on silicon substrate so as to form a two-dimensional self-assembled monolayer using 3-aminopropyltriethoxysilane (APTES) silane coupling agent (marked as APTES-GO-La). The chemical compositions, microstructures and surface morphologies of samples were analysed by X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The tribology behavior of the as-prepared thin films was tested by UMT-2 tribometer. Results show that GO sheets were successfully grafted on silicon substrate and lanthanum was attached to GO sheet by coordination reaction. The obtained APTES-GO-La film has low friction coefficient and good wear-resistant properties. Its remarkable tribological properties are attributed to the strong bond of the film to the substrate and the special characteristics of the RE element and GO sheet. This film has potential applications in NMES.

1. Introduction

A lot of progress has been made in nano-electromechanical-systems(NMES) technology in the past few years, and many scientists and researchers have plunged into this regime for its potential applications in areas such as biological research and medical instruments, environmental energy converters, radio frequency and optical/IFR communication, etc[1-3]. Compared with macroscopic engineering world, the microscopic length scale and high surface-area-to-volume ratio, characteristic of micro-electromechanical-systems, result in very high surface force such as friction and adhesion, which seriously undermine the lifetime, reliability and performance of NMES devices[4,5]. To improve the friction and wear behaviours of NMES has become an urgent issue to tackle. Breakthroughs in tribology performance of NMES were brought about by preparation of self-assembled monolayer (SAM), which could tremendously reduce friction coefficient and increase wear-resistance because of its strong head group-substrate binding, dense packing of hydrocarbon chains and low surface free energy[6,7]. It should be noted that both molecular properties and the crosslinking interactions between molecular chains have a significant effect on friction and wear performance of SAMs films[8]. Based on this, we prepared GO self-assembled composite thin films aiming to further improve the friction and wear behaviors of silicon substrate.

Graphene, a two-dimensional (2D) honeycomb lattice, has led to much excitement since it was first reported in 2004[9] because of its interesting characteristics, such as extraordinary thermal, mechanical, and electrical properties etc[10-16]. Potential applications of graphene in NMES have been actively pursued since the theoretical thickness of single-layered graphene is only 0.34nm, which is exactly suitable for NMES. Filleter et al.[17] found that graphene films exhibit frictional properties rather similar to those of bulk graphite and could be used as lowfriction antiwear coatings on silicon carbide surfaces. Jiangnan Zhang et al.[18] studied nanoscale frictional characteristics of three types of chemically treated graphene nanoribbons and found that the measured friction differences are attributed to the surface reactivity and hydrophilicity difference induced by different chemical functionalization schemes. However, a stable graphene film on silicon substrate is difficult to be prepared by common solution process for lack of active functional groups on its surface. The existence of hydroxyl groups, carboxyl groups and epoxy groups on GO sheets makes this possible[19], although these active oxygenous groups can cause negative impact showing as decrease of friction and wear performances. J.Ou has studied the reduced graphene oxide (RGO) film and self-assembled graphene oxide octadecyltrichlorosilane (APTES-GO-OTS) trilayer film which can seriously impair the influence of these active groups on friction and wear properties[20, 21]. The downside of these two methods is that the preparation of RGO film requires relatively complex experimental conditions, and the preparation of APTES-GO-OTS film to some extent increases the thickness of thin film. It's well known that the small clearances associated with NMES is only on the order of a few molecules thick[22]. Furthermore, the top-level of the APTES-GO-OTS film may affect the graphene to give full play to friction reduction and wear resistance properties since OTS covers the graphene sheets. Given above reasons, we attempt to take use of rare earths (REs) to improve the ability of APTES-GO composite thin film.

Rare earths (REs) have widely been applied in many fields such as optics, medicine, chemistry and magnetic for their special 4f electron shell structure[23-28]. It is little known that REs can improve tribology behaviors for its superior friction-reducing and wear-resistant abilities. In our previous research, we prepared REs-silane SAM films on silicon wafers surface. Results showed that the application of REs on those SAM films greatly improved their tribology performances[29,30].

In this paper, we prepared APTES-GO-La thin film, and analyzed its structure by means of X-ray photoelectron spectroscopy (XPS), water contact angle (WCA), etc. In addition, tribological performances of samples were investigated and their friction and wear mechanisms were discussed. Owing to the self-lubricating and outstanding mechanical properties of GO and good tribological behaviors of REs, the prepared APTES-GO-La film has remarkable tribological performances. Many researchers have studied tribological properties of different SAMs. However, to our knowledge, the attempt of assembling APTES-GO-La thin film has not been performed. This study is helpful to the design and selection of appropriate thin films for NMES.

2. Experimental details

2.1 Materials

Expandable graphite purchased from Nanjing XFNANO Materials Tech Co., Ltd was used to prepare GO. 3-Aminopropyl triethoxysilane coupling agent(APTES, 99%,ρ＝0.942 g·ml^{-1}), lanthanum trichloride($LaCl_3$) and chloroacetic ($Cl\text{-}CH_2\text{-}COOH$) acid were acquired from Aldrich Chemical Co., Inc. Silicon wafer (100) obtained from Zhejiang Cubic Crystalline Silicon Materials Co., Ltd was cut into the size of 5mm×10mm used as substrate for the SAM film transfer. All other reagents were of analytical grade and used as received. Deionized water was used throughout the whole experiment.

2.2 Preparation of GO-COOH Solution

GO was prepared by a modified Hummers method[31-33]. Briefly, expandable graphite (1g) instead of graphite flakes to ensure more uniform oxidization, was soaked in concentrated H_2SO_4 (23mL) for 8 h to effect intercalation. After addition of $KMnO_4$ (3g) as oxidizing agent, the mixture was stirred at 40℃ for 30 min to get fully and uniformly oxidized graphite. Subsequently, distilled water (46mL) was slowly added and the mixture was kept at 100℃ for 30 min. Then the mixture was washed with distilled water (140mL) and 30% H_2O_2 solution (10mL). The as-obtained mixture was repeatedly centrifuged and filtrated until pH was approximately 7 and SO_4^{2-} anions could not be detected[34]. After the products were sonicated for 2 h, the resulting GO particles were mostly single-layered according to atomic force microscopy (AFM) characterization.

The obtained GO was treated with chloroacetic acid to allow the transformation of hydroxyl and epoxy groups to carboxyl groups. A scheme of the carboxylated GO preparation process is shown in Fig1 (a). The obtained GO was sonicated for 1h with NaOH alkaline solution to attain GO colloidal solution. The obtained GO colloidal solution was sonicated for another 1~3h and excess chloroacetic acid was added at the same time. Then the product was purified and thoroughly washed with water until the suspension reached approximately pH 7. Thus a homogeneous carboxylated graphene oxide suspension was obtained and marked as GO-COOH[26,34].

2.3 Fabrication of Multilayer Film

A scheme on the preparation of different kinds of films is shown in Fig.1 (b, c). Prior to the deposition of SAMs, silicon wafers were cleaned ultrasonically with absolute ethanol and deionized water in turn to remove other ions and molecules physically absorbed on the surface. Then the silicon wafers were immersed in Piranha solution (a mixture of 3:1 (v/v) 98% H_2SO_4 and 30% H_2O_2) at 90℃ for 30 min to make hydroxyl radicals on the surface, followed by a repeated washing with deionized water. After that the obtained silicon wafers were dipped into fresh APTES solution (0.5mM, the solvent is a mixture of acetone and water, with a volume ratio of 5:1) at ambient temperature for 30 minutes. Subsequently the wafers were rinsed with deionized water and dried for 1 h at 120℃ under nitrogen atmosphere. Until now APTES-SAM had been obtained, and on this basis GO was successfully grafted on the silicon substrate by keeping the APTES-SAM films in the surface modified GO-COOH aqueous solution (0.3mg·L^{-1}) at 80℃ for 12 h, then cleaned in deionized water and dried in nitrogen (see Fig.1 (b)). This film covered homogenously with carboxylated graphene oxide was coded APTES-GO. At last APTES-GO films were immersed into RE ethanol solution (2mM) at 90℃ for 12 h. The resulting products thoroughly rinsed with deionized water and dried under nitrogen atmosphere were marked as APTES-GO-La.

For comparison, we prepared APTES-RGO film by reducing APTES-GO at 200℃ for 2 h at a heating rate of 1℃ • min^{-1} under the protection of argon gas[35].

2.4 Experimental apparatus and measurements

Morphological properties of APTES-GO-La were investigated by NanoScope IIIa AFM in tapping mode (produced by Shimadzu Corporation, Japan), as it is crucial to study the morphology in the research of the self-assembly technique. SEM (Model Leica, Stereoscan 440) was employed to observe the surface microstructure of the samples after sputtered with a thin gold coating.

XPS is an ideal diagnostic tool to assess the chemical state of elements. In this paper, XPS analysis was conducted on a PHI-5702 XPS system (hν=1253.6eV) at a pass energy of 29.4eV, using a monochromatic AlKα irradiation. The resolution of C1s binding energy is about ±0.3eV with the binding energy of contaminated carbon (C1s:284.6eV) as the reference.

The static WCA of the samples was measured on the OCA-20 measurement apparatus (Data Physics Instruments GmbH) at ambient condition (23℃) with relative humidity 40%. Typically 10 μL droplets of deionized water were used to make contact angle measurements. Contact angle was measured on five different spots on the samples, and all the results on each sample were averaged.

The tribological properties of different thin films were tested on a UMT-2 tribometer in a ball-on-plate contact mode under an ambient condition (relative humidity 40%).The matching part was a GCr15 steel ball of diameter 3 mm with surface roughness(Ra) 0.02μm. The sliding velocity and stroke were 5mm/s and 5 mm. The normal load was set at 0.1N and 0.2N. The friction coefficient and running time were recorded automatically. The friction coefficient remained relative stable with slight fluctuation during the whole testing process. Once the friction coefficients suddenly increased to a high value (>0.5), it indicated that the film had failed. The corresponding sliding times were equivalent to the wear life of samples. Replicate tests were performed at least three times at different spots for each sample, and the friction coefficient and wear life were the average of the three results.

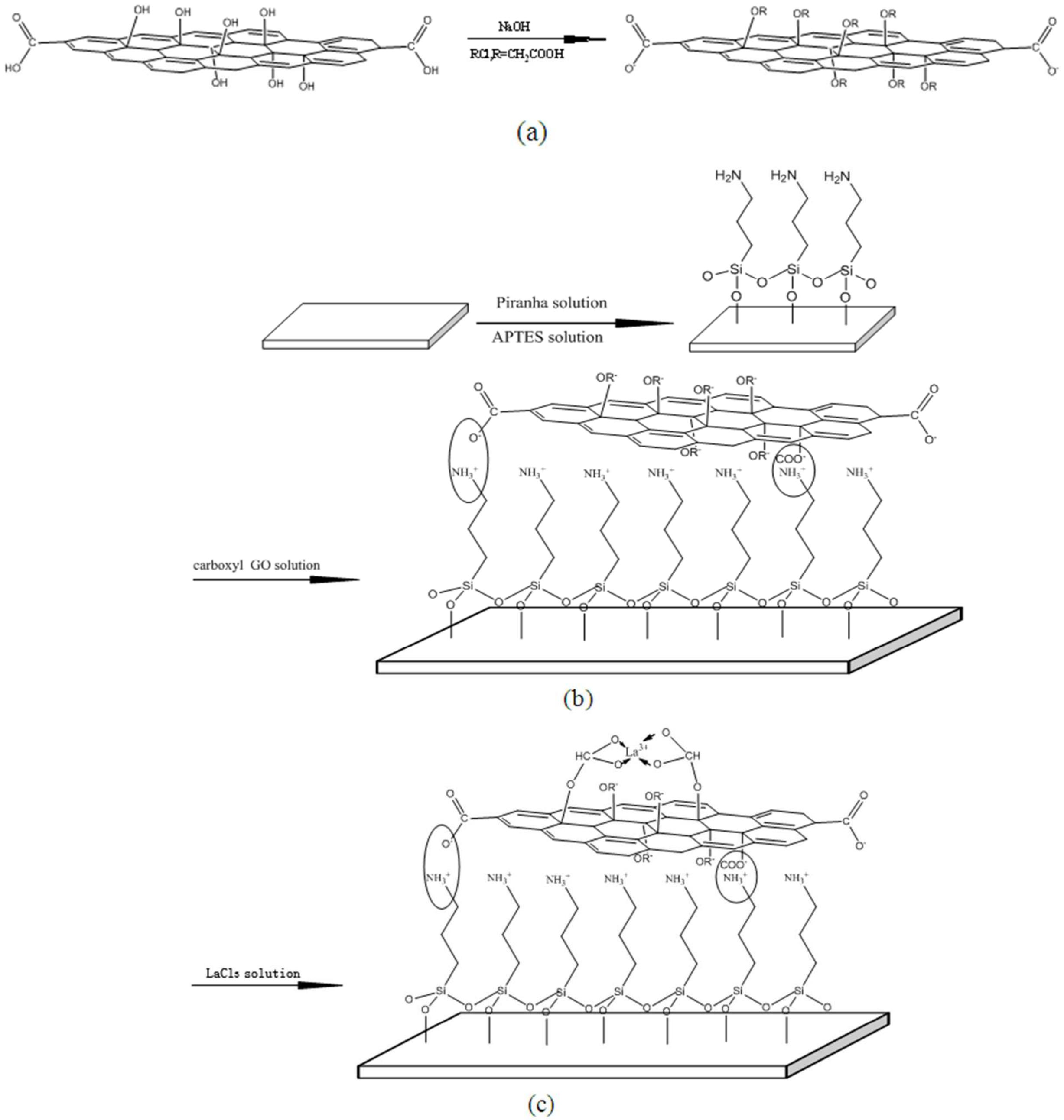


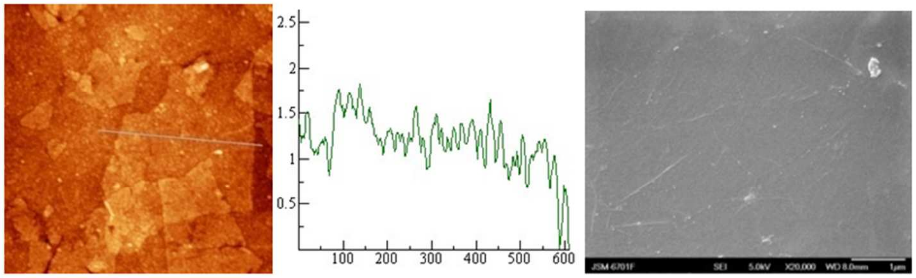
Fig.1. Schematic diagram illustrates the preparation of samples. (a) carboxy functionalized GO sheet (GO-COOH), (b) APTES-SAM film and APTES-GO film, (c) APTES-GO-La film.

3. Results and Discussion

3.1 SEM and AFM Analysis

Fig.1 illustrates the assembling mechanism of APTES-GO film. The existence of abundant polar oxygenous groups (such as carboxyl functionalized groups) enables GO to well dissolve in aqueous solution and react with amino groups of APTES molecules[34, 37]. By means of this amidation reaction, GO sheets are chemically combined to APTES in the form of covalently binding, hence assembled on the surface of silicon wafers[20].

The single-sheet nature of Graphene oxide obtained is confirmed by atomic force microscopy(AFM, Fig.2 (a, b)). As shown in Fig.2 (a), single layer GO sheet and overlapped sheet can be observed on the surface of silicon substrate. The thickness of GO sheet obtained is about 1.3 nm, which is little greater than the theoretical thickness of the exfoliated graphene oxide (about 1.2 nm). This can be attributed to the intrinsic out-of-plane deformation of graphene[38,39] as well as to the instrumental offset arising from different interaction forces between the AFM probe, the graphene oxide sheet, and the substrate[40]. Generally, this thickness value is consistent with others reported in previous studies[41-43]. From the SEM images of APTES-GO film(Fig2 (c)), we can observe that the graphene oxide uniformly distributed on the substrate surface. This is ascribed to the fact that the carboxylated GO with abundant carboxy groups can well dissolve in water.

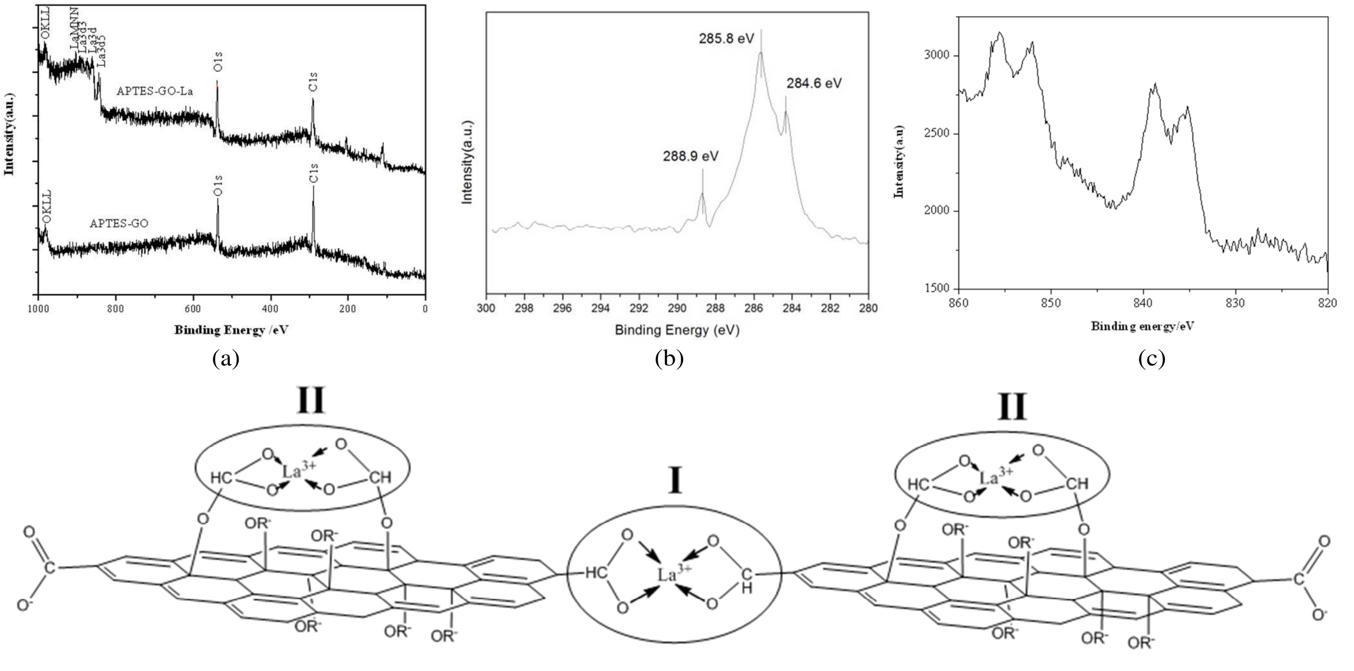


(a) (b) (c)

Fig.2. (a) AFM image of Si-GO, (b) The thickness value of GO (Corresponding to the mark of (a)), (c) SEM image of APTES-GO film.

3.2 XPS analysis

The presence of APTES-GO-La film on silicon substrate was substantiated by XPS measurement. As shown in Fig.3(b), the signal at 289.9 eV corresponds to O−C=O bond, indicating that GO has been successfully assembled on the APTES-SAM film while the signals at 285.8 eV and 284.6 eV correspond to C−O bond and C−C bond respectively[20] . Compared to APTES-GO film, there are some new peaks appearing 800eV to 1000eV in APTES-GO-La film, suggesting that La elements has been introduced in the APTES-GO film. The high resolution spectra of La 3d signal seen in Fig.3(b) shows four peaks, whose binding energies are 835.25 eV, 838.75 eV, 852.125 eV and 855.625 eV respectively. Compared with our early test data, the characteristic peak values of $LaCl_3$ is 853.0eV and 856.7eV. Thus, a rational inference can be made that the La element really reacts with carboxylate ions. Fig.3(c) is a schematic diagram of the probable coordination reaction. After the APTES-GO film dipps into RE solution, a large number of anion(COO^-) generated from COOH on the surface of GO become the active sites for La^{3+}, then coordination reactions occurs between COO^- anions and La^{3+} ions[26]. It is worth mentioning that the coordination reaction may occurs at the edge of different GO sheets (as Fig.3(c)-I shows), which can enhance the bonding force of lateral combination. Also, it may occurs on the GO sheets surface (as Fig.3(c)-II shows), which can reduce the surface free energy.



(a) (b) (c)

(d)

Fig.3. (a) XPS spectra of APTES-GO-La thin film. (b) High-resolution XPS spectra of C 1s on APTES-GO-La thin film. (c) High-resolution XPS spectra of La 3d on APTES-GO-La thin film. (d) probable coordination reaction.

3.3 Water contact angle analysis

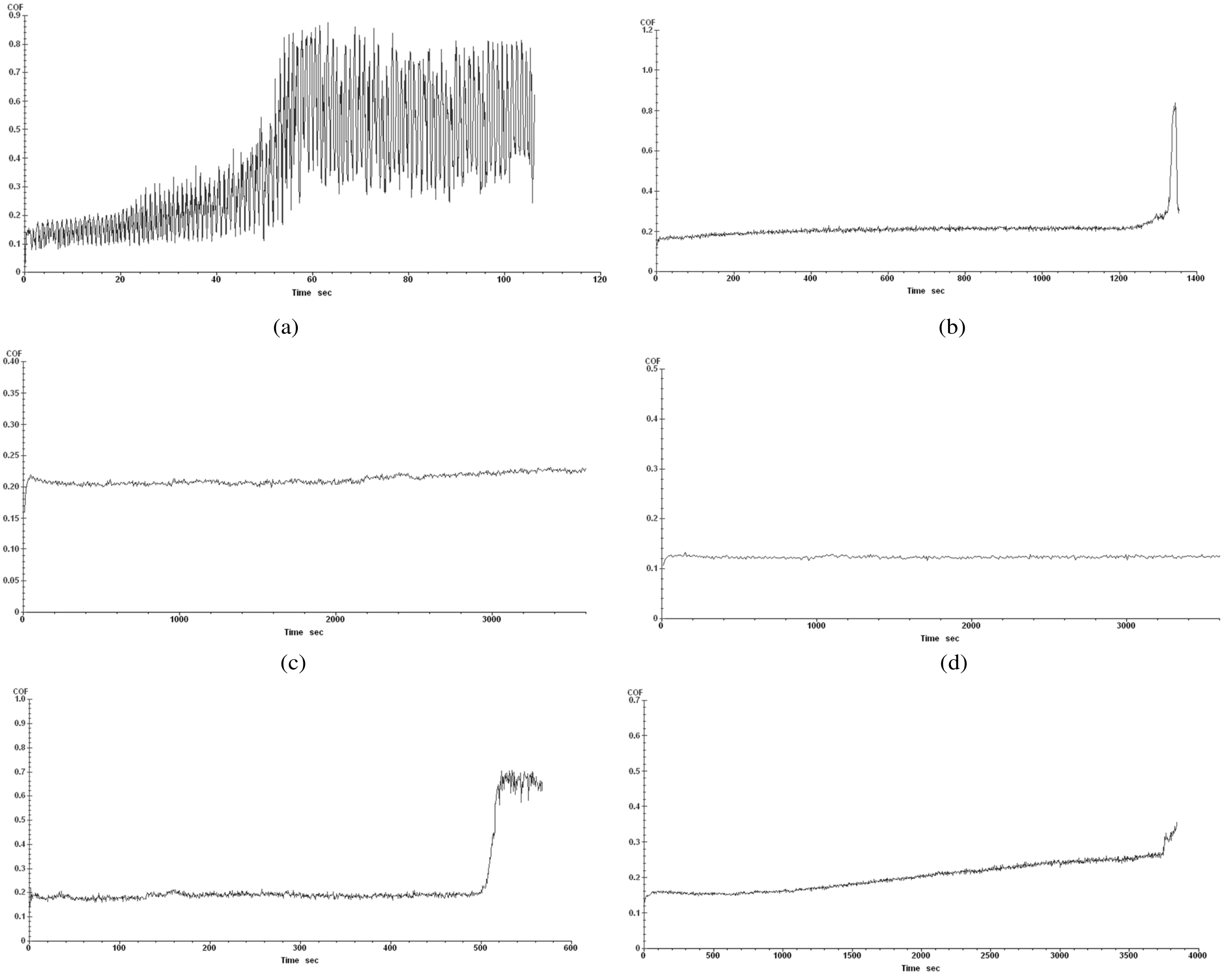
It's a facile and effective way to characterize the properties of a given surface including surface free energy, the hydrophobicity and hydrophilicity by water contact angle (WCA)[44]. We performed the WCA measurement of hydroxylated Si, APTES-SAM, APTES-GO, APTES-RGO and APTES-GO-La films. As Table1 shows, the hydroxylated silicon substrate with contact angle less than 10° is hydrophilic, indicating that the silicon substrate was thoroughly hydroxylated after treated in "Piranha solution", which increased the surface free energy. By contrast, the contact angles of APTES-SAM film and APTES-GO film increased to 51.0° and 53.8° respectively. It may be concluded that the silicon substrate had been successfully coated with APTES-SAM films and APTES-GO films whose moderately polar groups such as oxygenous and amine groups led to the reduction of surface energy[45, 46]. Table1 also gives the contact angle of APTES-RGO (80.5°). The sharp increase of contact angle is due to the disappearance of oxygenous functional groups on GO sheets caused by thermal reduction. The contact angle of APTES-GO-La film is 78.3°, fairly close to the contact angle of APTES-RGO film, demonstrating that lanthanum ions had successfully deposited on the APTES-GO films. It can be explained taking into account the fact that lanthanum ions can form ionic bond with several nearby COO^- anions on GO or ligand bond with oxygen on APTES, making the hydrophilic group COO^- immobile on the surface and arranged in a way that they are not exposed outward, which will reduce the number per unit area of hydrogen bonds formation. It should be kept in mind that for APTES-GO film the high surface free energy results from hydrogen bonds formation, where the electron-donor sites come from the $-COO$ groups and the electron-acceptor interaction originates from the polar probe liquid molecules, water. So it is reasonable to conclude that APTES-GO-La film has a lower surface free energy than APTES-GO film when its density of hydrogen bonds is smaller. There could be several other reasons for this, such as changes in the nanoscale roughness due to surface functionalization[47], flexibility and rotational mobility of functional groups[48], and conformational changes in the functional groups[49]. To find an clear explanation further studies are needed.

Table 1 Water Contact Angle of Various Samples

Samples	Si(hydroxylated)	APTES-SAM	APTES-GO	APTES-RGO	APTES-GO-La
WCA(deg)	<10	51.0±2.6	53.8±1.4	80.5±1.3	78.3±2.5

3.4 Tribological Behaviours of samples

The friction coefficient and wear life of the prepared samples were obtained on UMT-2 friction tester. Fig.4 shows the variation of frictional coefficient of different SAMs as a function of sliding time. It can be seen from Fig.4 (a) that APTES-SAM recorded high friction coefficient around 0.36 and short wear life less than 60 s. While APTES-GO (Fig.4 (b)) film shows better tribological properties with friction coefficient 0.21 and wear life 1320s. This can be ascribed to the excellent mechanical and self-lubricating properties of GO, which improves the tribological performance of APTES-GO film[20,21]. The friction coefficient of APTES-RGO film (Fig.5 (c)) was 0.22, little changed from the APTES-GO film, while the wear life has a remarkable improvement (>3600s). This significant change is due to its lower surface free energy than APTES-GO film. Low surface free energy can reduce adhesive bonds of the solid contact surface, so that friction coefficient values of SAMs having lower surface energy are expected to be lower and wear life accordingly longer[20, 50]. The friction coefficient value of APTES-GO-La film shown in Fig.4 (d) is 0.13, which is the best among APTES-SAM, APTES-GO, APTES-RGO and APTES-GO-La films. What's more, the wear life is longer than 3600s, as much as that of APTES-RGO film. This mainly because lanthanum ions introduced in APTES-GO-La films not only greatly decrease the surface free energy but also enhance some mechanical properties, which determine the resistance to permanent plastic deformation of the materials and improve the tribological properties[51]. Lanthanum ions can form ionic bond with COO^- anions on GO or ligand bond with oxygen on APTES and acylamino. Both of them can increase the density of chemical bond, thereby increasing the shear strength and the hardness of the films[52]. It is found qualitatively that low friction coefficients are found for sliding materials with low surface energy/hardness ratios in the friction field. The hard films exhibit better mechanical and wear properties. No matter what kind of methods of formation, solid surface generally contain surface irregularities. The contact between two nominally flat surfaces occurs in fact at discrete contact points as a result of surface roughness. The sum of the areas of all the contact points constitutes the real area of contact and deformation often occurs at these points. This deformation is usually plastic for a softer material at heavy loads, which can cause plastic flow deformation and ploughing effect during friction and increase the actual contact area with the contact time growth, finally giving rise to the increase of adhesion. That is why APTES-GO-La films have a lower friction coefficient value, though having a smaller water contact angle than APTES-RGO films. Fig.4 (e-f) shows the tribological performance of APTES-RGO film and APTES-GO-La film under the normal load of 0.2N at sliding frequency 1Hz. It shows that APTES-GO-La film exhibits a close frictional coefficient with APTES-RGO films, but has a longer wear life (3750s). This peculiar phenomenon can also be ascribed to lanthanum ions. The lanthanum ions intruded in the defect of the APTES-GO-La films can form strong chemical affinity with carbon, oxygen, nitrogen or hydrogen on APTES and GO, or form ionic bond with COO^- anions. These interdigitations will greatly reinforce the bond force between APTES-GO-La films and silicon surface to withstand the big shear due to friction force under heavy loads in contrast with APTES-RGO films.



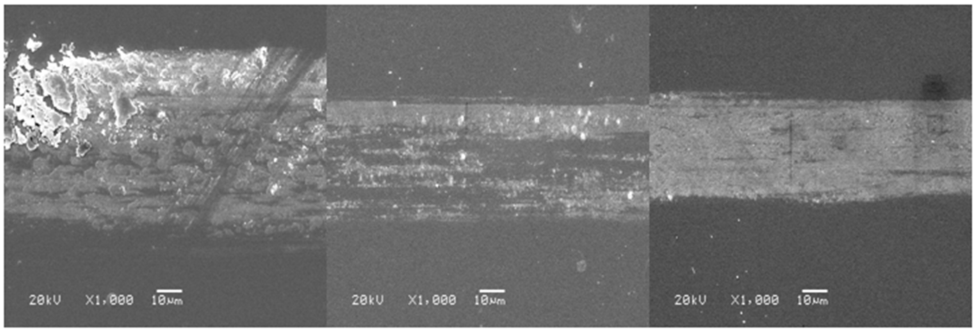
(a) (b)

(c) (d)

(e) (f)

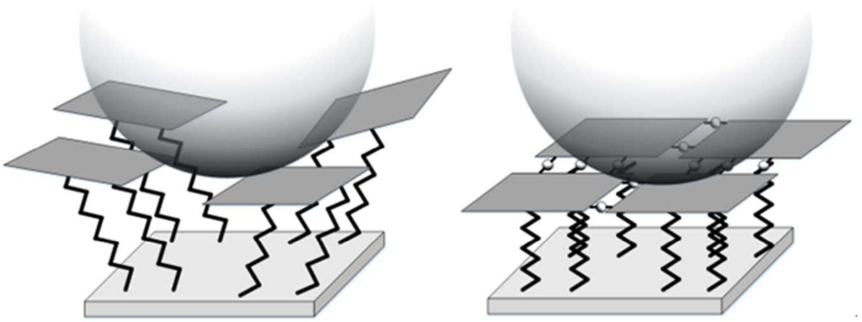
Fig.4. Friction coefficient of samples as a function of sliding time for various samples under different loads at sliding frequency of 1Hz: (a) APTES-SAM (0.1N), (b) APTES-GO (0.1N), (c) APTES-RGO (0.1N), (d) APTES-GO-La (0.1N), (e) APTES-RGO(0.2N), (f) APTES-GO-La(0.2N).

To further understand the influence of lanthanum ions on the microscale friction behaviour, we investigated the wear tracks of APTES-GO film, APTES-RGO film and APTES-GO-La film using SEM after the friction test under load 0.1N and at sliding frequency 1 Hz. Their wear tracks reveal why APTES-GO-La film has the best anti-wear properties. APTES-GO-La film has the most homogeneous wear scar(Fig.6 (c)) among the three SAM films within the same time frame. Having good shear resistance and hardness, this uniform and smooth film reduced the apparent areas of contact and the number of particles trapped at the interface, thus minimized the ‘ploughing’ contribution to the friction force. While APTES-RGO film has some shot-like particles around the wear spot, which would cause abrasive wear and exacerbate the wear. APTES-GO film even has large abrasive dust piling up in the wear scar caused by the exfoliation and agglomerate of GO sheets. Although the deoxygenation of GO decrease the surface activity of graphene sheets and the friction coefficient, the interface force between adjacent APTES-RGO film is also weakened. Thus some APTES-RGO films not firmly fixed on silicon substrate or boding loosely to neighbors become wear debris stacking on sliding area and aggravating the roughness, which in return produces more wear debris. By contrast, the bring-in of lanthanum element in APTES-GO-La film not only reduces the surface free energy, but also enhances the strength between each other. So it makes much more sense why APTES-GO-La film has the best tribological properties.



(a) (b) (c)

Fig.5. SEM images of wear track of (a) APTES-GO film, (b) APTES-RGO film and (c) APTES-GO-La film.



(a) (b)

Fig.6. The schematic diagram of (a) APTES-RGO film and (b) APTES-GO-La film.

The friction and wear mechanisms for APTES-RGO and APTES-GO-La film can be simulated by a simple schematic diagram (Fig.6 (a,b)). For APTES-RGO film, the silane molecules connected with GO sheets are divided into small discontinuous pieces under the normal load. So the steel ball needs to overcome the lateral Van der Waals force between alkyl chains during the course of friction. However, for APTES-GO-La film, these discontinuous pieces can cross link with each other by chemical bond to form a whole large film through La elements (see Fig.3(c)-I), just like “hand by hand” to be a cross linking net (Fig.6 (f)). The cross linkage can make lateral friction force uniformly dispersed on films, and thus enhance the wear resistance property of the APTES-GO-La film.

4. conclusions

In this work, graphene oxide was covalently assembled on silicon substrate via amidation reaction between carboxyl on carboxylated GO and amino groups of APTES molecules. APTES-GO films had a low friction coefficient(around 0.21),which is owing to excellent mechanical and self-lubricating properties of GO. With the introduction of lanthanum ions, APTES-GO-La films exhibited excellent friction reduction and wear resistance properties under relatively high applied load in comparison with APTES-RGO films. The superior tribology performances of APTES-GO-La films were attributed to the circumstance, that the coordination chemistry reaction between La elements and carboxyl groups decreased surface free energy and improved lateral cross linking binding force. The APTES-GO-La film prepared by this method can serve as a low-friction anti-wear coating in NMES. Although the proposed approach is based on silicon wafers, it has a potential application in many other substrates, such as glass, mica, and metal oxide and so on.

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