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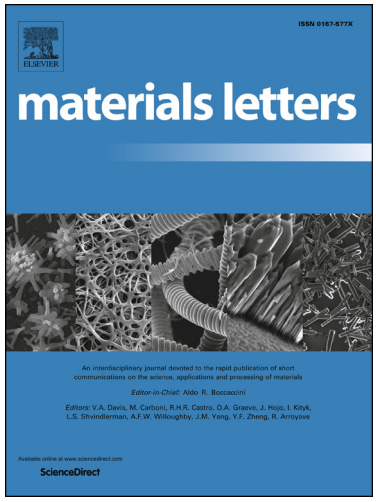

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Improving the macro-scale tribology of monolayer graphene oxide coating on stainless steel by a silane bonding layer

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Abstract

This work aimed at improving the macro-scale tribology of single-layer graphene oxide (GO) coating on metallic surfaces. To this end, stainless steel substrate was modified by a silane prior to the self-assembly of a GO coating. Tribological tests, Raman spectroscopy and elemental analysis were performed. The results show that the pre-deposited silane intermediate layer effectively enhanced the tribological performance of the top GO coating in terms of very low friction (~0.1), 10-fold reduction in wear and increased coating durability by 20 times. The improvement could be mainly attributed to the enhanced bonding via the silane layer.

Key words: Graphene; Thin film; Surface modification; Bonding; Tribology

1. Introduction

Recently there is an ever-increasing research interest in the tribology of graphene [1]. Nano- and microscopic studies have demonstrated that graphene can show extraordinary lubricity, even superior to bulk graphite [2]. Graphene has a thickness of merely 0.34 nm, rendering it probably the thinnest solid lubricant ever. However, in the literature there are just a limited number of reports on graphene-based surface coatings combating friction and wear at a macro scale [3]. This is partially due to the difficulty in obtaining such coatings continuously on a large area, but more likely due to the weak adhesion of graphene-based

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coatings to most engineering materials surfaces [4].

(3-Aminopropyl)triethoxysilane (APTES) is among the coupling agents [5] that have been reported to improve the bonding between silicon wafer and graphene [6] or graphene-based multi-layer [7]. It was also used to modify a titanium surface before a graphene coating for nano/micro tribological application and its advantageous simple processing demonstrated [8]. However, to our knowledge there is no report yet about such use on such common metallic materials as steel. In this study, graphene oxide (GO) coatings were fabricated on APTES modified steel surface by self-assembly. The tribological behaviour and durability of the GO coating were investigated and the effect of APTES treatment discussed.

2. Experimental

316L stainless steel specimens were polished before treatment in a 7:3 v/v mixture of concentrated H_2SO_4 and 30wt% H_2O_2 solution at 80 °C for 30 min. The specimens were then kept in a 3vol% APTES solution in ethanol-water (5:1 v/v) at room temperature for 30 min, and then rinsed and dried thoroughly, named 316L-A. The self-assembly of GO was done by keeping the APTES-treated steel substrate into a prepared GO suspension at 60 °C for 12 h. Excessive GO sheets were removed by ultrasonication and the sample was named 316L-A-GO. The same immersion process was applied to an untreated stainless steel (namely 316L-GO).

Samples were characterised by atomic force microscopy (AFM), Raman, scanning electron microscope (SEM) and Energy dispersive x-ray spectroscopy (EDS). Water contact angles (WCA) were measured using an OneAttension optical tensiometer. Reciprocating tribological tests were carried out in open air at room temperature using a ball-on-plate tribometer. A 316 stainless steel counter ball (ϕ8mm) and a normal load of 1 N were used (equivalent Hertz contact pressure ~530 MPa, contact area diameter 60 μm). The sliding distance, speed and frequency were set at 5 mm, 5 mm/s and 1 Hz, respectively.

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3. Results and discussion

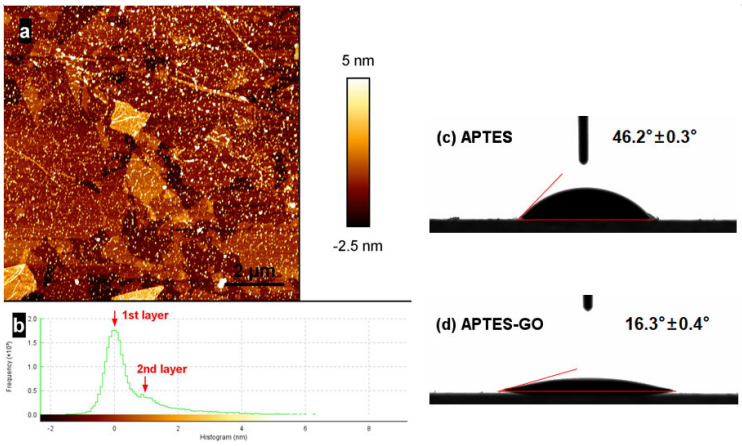

Figure 1a is an AFM image of the obtained APTES-GO coating featuring a high GO coverage rate of more than 90% and a relatively uniform coating thickness. The widespread white dots are likely short-range agglomerations of APTES molecules [9]. Figure 1b is the height histogram across the AFM examined area. The substrate level is assigned as -2.5 nm with most of the surface heights falling at 0 nm, indicating that the APTES-GO coating has an average thickness of 2 to 2.5 nm. Considering that the thickness of an APTES layer usually measures 1-1.5 nm [9], the GO top coat here likely has a thickness of ~1 nm, which corresponds to one single layer GO. Likewise, the shoulder peak around 1 nm indicates the second GO layer stacking on the top, in a small fraction. During self-assembly APTES molecules and GO sheets assemble themselves in succession via condensation reactions between the hydroxyl groups (-OH) on steel surface and the alkoxy groups (-O-R) on APTES, then between the amino heads ($-NH_2$) of APTES and the oxygen groups of GO. The assembly stops when the amino sites are fully occupied, much like paving a floor with mosaic tiles. Compared to the WCA of ~46° for the APTES layer (Figure 1c), the WCA decreased to ~16° with an additional self-assembled GO layer (Figure 1d), due to the hydrophilic oxygen groups in GO.

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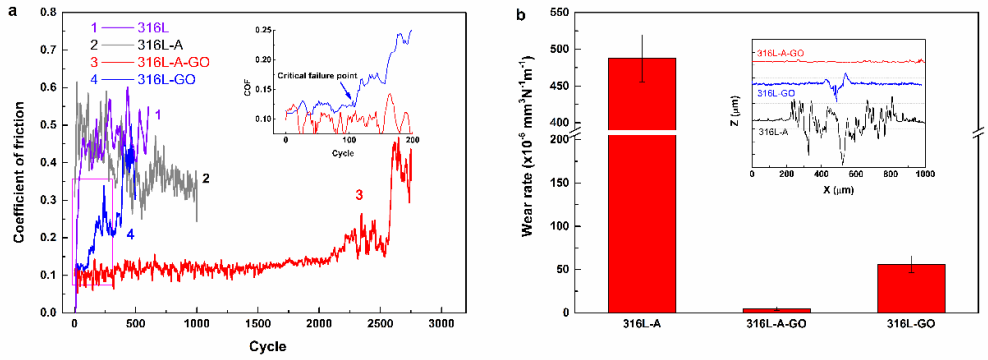

Reciprocating sliding wear tests were performed on four types of samples, namely: bare 316L steel, 316L-A, 316L-A-GO and 316L-GO. As shown in Figure 2a, the coefficient of friction (COF) for 316L-A fluctuated wildly in the running-in period and levelled off at 0.35 after 500 cycles, which is slightly below that (~0.45) of bare 316L. Clearly, the APTES layer alone offered little lubrication. 316L-GO initially benefited from graphene's lubricity as evidenced by the very low initial COF of 0.12 for the first 100 cycles. The friction then rose suddenly and eventually increased all the way to 0.4, which is very close to that of bare steel, implying that the GO coating might have been removed completely away from the contact. In contrast, with an additional APTES layer, 316L-A-GO exhibited substantially improved wear life. No sudden increase of friction but a slight rise to 0.12-0.13 took place, and the low-friction regime was extended remarkably from 100 to some 2000 cycles. While in other studies on self-assembled coatings micro-scale loads (100-200 mN) were used and COFs around 0.2 reported [7], in this study an even lower COF for such a nano structure on steel under a heavier load of 1 N was observed, suggesting its effectiveness for a wide range of engineering applications.

Figure 2b compares the wear rates and the corresponding wear tracks (inset). 316L-A exhibited the highest wear rate, with a broad track formed of deep furrows and build-ups. 316L-GO showed medium wear. A dramatic further reduction of one order of magnitude in wear was seen on 316L-A-GO. These improvements can be attributed to the strengthened bonding between the GO lubricant coating and the steel surface due to the covalent bonds via

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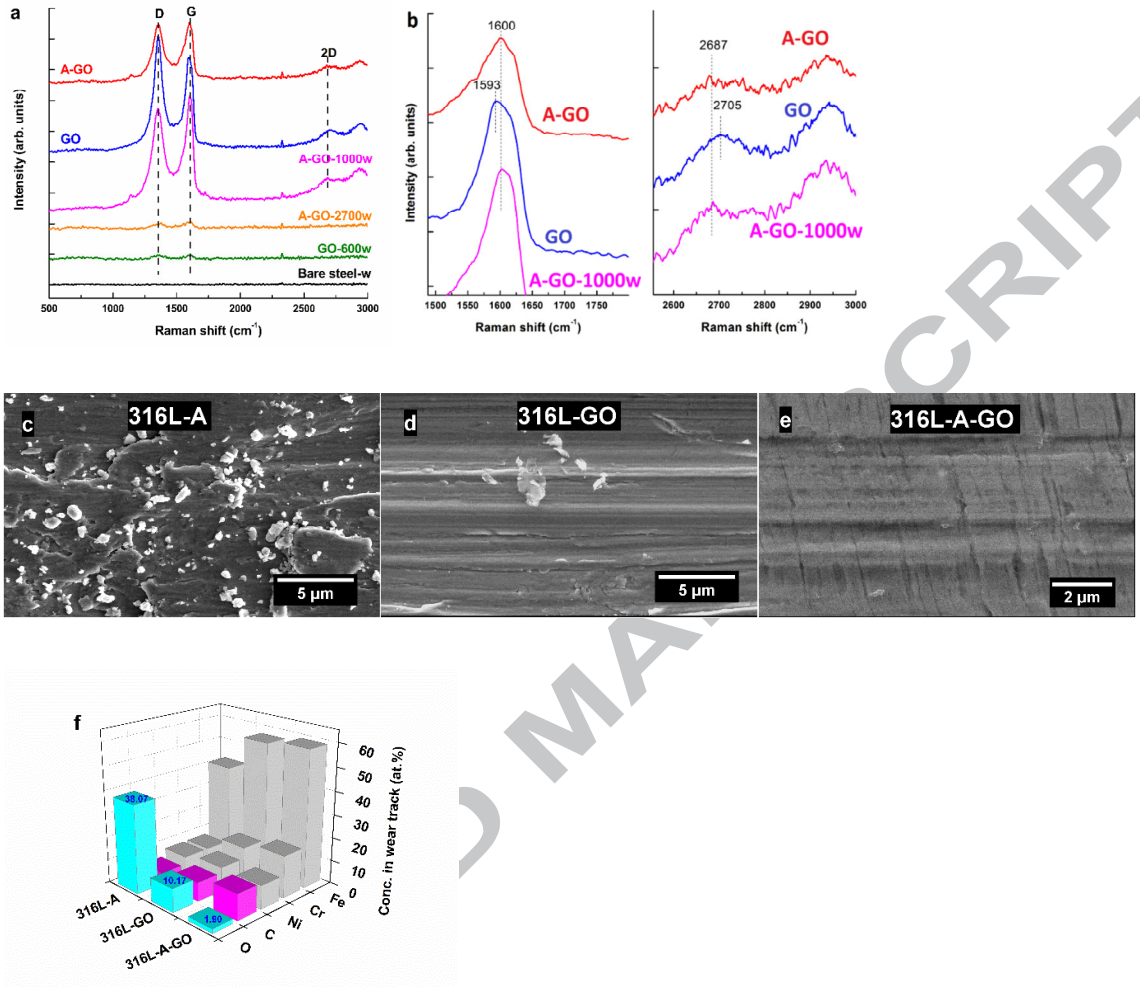
APTES.



Raman spectra of 316L-A-GO and 316L-GO, both before and after specific numbers of sliding cycles, were showed in Figure 3a-b. The intensity ratio of the D to G bands for 316L-A-GO is significantly smaller than that of 316L-GO (0.92:1.24), indicative of less disorder in the former. This could be attributed to the condensation reactions between APTES molecules and GO sheets, which led to a reduction of the oxygen group concentration in GO and thus a recovery of its sp^2 conjugated structure.

Note that the G band of 316L-GO downshifted by 7 cm^{-1} and the 2D band upshifted by 18 cm^{-1} compared to 316L-A-GO (Figure 3b), implying that the graphene layer number of 316L-GO is likely larger than the other [10]. However, the bands of 316L-GO shrank to

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minimum after 600 cycles due to severe destruction of the coating. In contrast, 316L-A-GO kept substantially the same Raman features even after 1000 cycles, suggesting an improved structure integrity. The Raman results are in line with the frictional tests, indicating that APTES is effective in enhancing the durability of the GO coating.

Figures 3c-e display the worn surfaces. The worn 316L-A showed high roughness and galling due to adhesive wear at the steel-steel interface. The widespread debris in the track suggests that three-body abrasive wear may also have happened. 316L-GO exhibited a smoother wear track, but the grooves along the sliding direction are sign of limited protection by the GO coating. Some fragments of the GO coating are visible inside the wear track. In sharp contrast, 316L-A-GO exhibited negligible wear loss except for minor material deformation. EDS (Figure 3f) performed inside the wear tracks shows the chemical composition differences. The worn 316L-A-GO surface showed nearly 20 times less oxygen compared with 316L-A. The flash temperature resulted from frictional heat at real contacted asperities can be up to hundreds of degrees high [11]. In ambient environment, these hot-spots can readily result in oxidation. In this study, the well-bonded GO coating reduced the friction and energy dissipation so greatly that the transient heat generation was effectively inhibited; furthermore, the excellent thermal conductivity along the lamellar graphene structure could minimise heat accumulation. It is also possible that GO, a derivative of graphene which has been reported to be impermeable to even the smallest molecules [12], blocked external oxygen from diffusing inwards, thus inhibiting oxidation. However, this feature was degraded for 316L-GO due to lack of bonding.

4. Conclusions

In conclusion, a single-layer GO coating was fabricated on stainless steel by self-assembly, and the effect of pre-modification of the steel surface with APTES on the tribological behaviour was investigated. The results show that the APTES pre-treatment can

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effectively enhance the tribological performance and the durability of the GO coating. The improvement could be mainly attributed to the enhanced bonding of the GO coating to the steel surface via the APTES intermediate layer. The present study has shown by example that chemical surface modification could improve the service life of graphene-based coatings on metallic substrates.

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Figure captions

Figure 1. (a) AFM image of the self-assembled APTES-GO coating. (b) is histogram for the thickness distribution across the area. (c) and (d) are the snapshots of the water contact angle tests on APTES and APTES-GO, respectively.

Figure 2. (a) Coefficients of friction for samples vs. steel in air under 1 N load and (b) the corresponding wear rates measured after 1000 cycles.

Figure 3. (a) Raman spectra of as-coated (A-GO and GO) and worn (the rest) surfaces after a given number (*viz.* 1000, 2700, 600) of sliding cycles. (b) enlarged view of the G and 2D modes in the Raman spectra. (c-e) are SEM images of the worn surfaces after 1000 cycle frictional tests. (f) summarises the EDS analysis for the worn surfaces.

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Highlights of this manuscript

- Monolayer graphene oxide coating was self-assembled on pre-treated steel surface.
- The tribological performance of the coating was evaluated at a macro-scale.
- The intermediate silane bonding layer improved the coating durability effectively.

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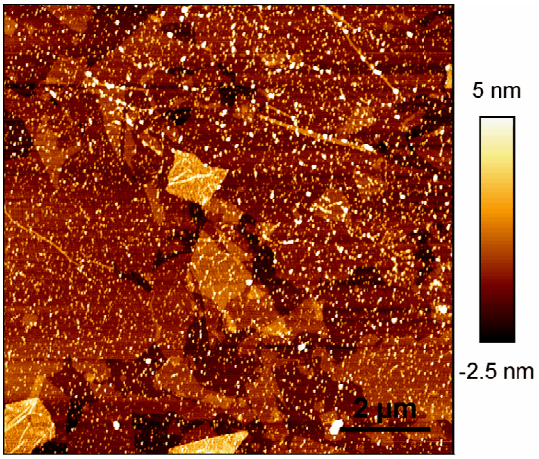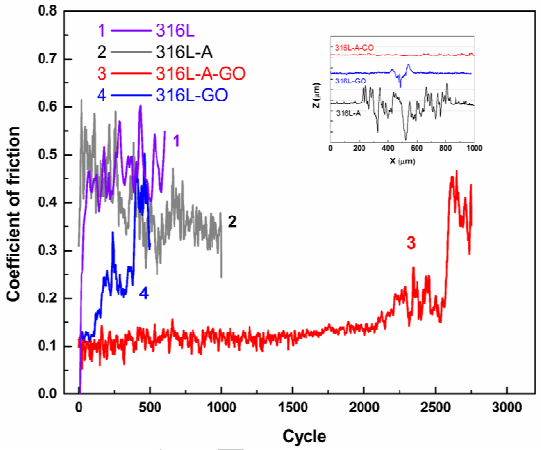
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