



Pencil sketch graphene films as solid lubricant on steel surface: Observation of transition to graphene/amorphous carbon

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ABSTRACT

During recent years, graphene as a solid lubrication material have been thoroughly studied under nano or micro scales, but rarely reported at industrial conditions. In present work, graphene films as solid lubricant were prepared on the surface of 201 stainless steel substrates by pencil sketch. And then the friction tests from 5 to 65 N were carried out via a homemade tribo-tester and used GCr15 balls ($\phi = 5$ mm) as friction pairs. Not surprisingly, graphene films cannot bear the loads beyond 5 N, but interestingly, via gradually increasing the loads, graphene films show prominent load performance and steady state of friction coefficients at about 0.12 while the loads varied from 5 to 65 N. Compared with bare steel, the coefficient of graphene films reduced by about 80%, and the wear volume reduced to 1/28 when variable load (from 5 N to 30 N) were applied. Raman spectra shown that the structure of graphene had been changing into diamond-like carbon films with graphene distributed inside, which was confirmed by HRTEM that graphenes were coming with amorphous carbon. Considering the roughness of steel wafers (170 nm), one can speculate that, with graphene films' protection, the steel has no abrasion but plastic deformation instead. It is concluded that the shearing force induced the film densification via sp^2 to sp^3 changing that enforced cross-linking. This cross-linking carbon matrix was responsible for high load bearing and the graphene exfoliated into graphene under shearing force contribute to low steady-state friction. Benefiting from sketch, one can get a lubrication film on any substrates with complex topography, our results shed light on the growth of graphene films for industrial use.

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1. Introduction

Precisely, friction and wear happen between surfaces and interfaces in relative motions. They are usually viewed as inevitable and irreversible process when the machines are running, which is regarded as one of three main forms (wear, corrosion and breakage) of the materials failure with energy dissipation (friction) and material deterioration (wear) [1]. This process is accompanying by the losses of material surface and change of parts size, which will finally affect the life of the machines directly. Thus, the friction and

wear properties of materials are crucial for their applications. Control friction, reduce wear and improve lubrication are urgent demands to solve scientific and engineering problems. In most cases, lubrication plays a significant role in reduce energy consumption and prolong the life span of machines [2].

Two-dimensional materials, like graphite, graphene, molybdenum disulfide and hexagonal boron nitride nanosheets are believed prominent lubricious materials due to its low shear force between layered structures [3–10]. Some of reports proved that these layer stacked films showed supelubricity properties sometimes, but most of reports showed that high friction coefficient in the scope of 0.01–0.2 [3–14]. Among them, graphene and multilayer-graphene are most prominent ones because of weak van der waals interaction which is 52 ± 5 meV per atom [15–19]. This unique property

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makes graphene layers can slide freely over another. Since using graphene as a solid lubrication has been studied for centuries. Usually, graphene shows high friction in vacuum due to mill into dust but low friction in oxygen, water vapor, and air environments, owing to the absorption of molecules which significantly lowers the cleavage energy [20,21]. Interestingly, Kumar showed that graphene friction properties strongly correlated with atmosphere [22]. In Ar atmosphere, super-low friction is observed. However, in oxygen or nitrogen, high friction is prominent due to presence of more dangling bonding [22]. Recent study proved that super-lubricity could be achieved due to the incommensurate contact in nanoscale [3–5,7,16,23]. But friction properties are more complicated in macroscale because the friction depends on the orientation of graphene between interface [23]. Friction coefficients, tested on parallel and perpendicular, show an opposite trend to the friction because that parallel graphene has lower dangling bonds than that of which perpendicular to substrates that holds a more high adhesive effects [24]. As a result, the super-lubricity property always refers to the phenomenon between two parallel graphene or graphite [3–5]. In the knowledge of the authors, graphene as a lubrication is used for years and some of articles have discussed the lubricity under appearance based on or at nanoscale, but it is obviously very different from industrial scales that high load might destroy layered stacks. Thus, how graphene reduces friction and wear remains uncertain under high loads. In this article, our goal is aiming to the possibility of graphene films using under industrial condition and to reveal the possible mechanism for lubrication and anti-wear under high contact pressure.

Herein, inspired by pencil sketch which is employed by many other artists, for example, portrait of Adolph von Menzel, we

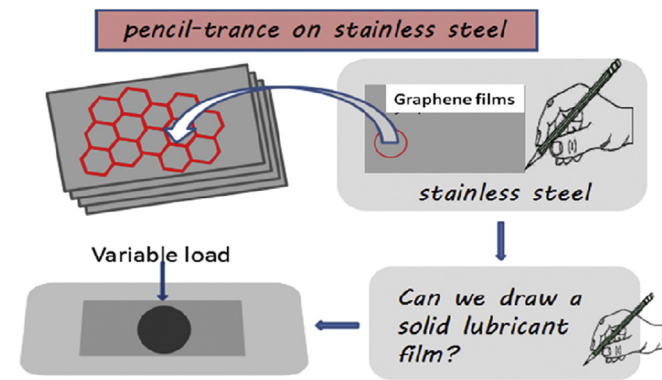


Fig. 1. A schematic representation of the pencil sketch process on stainless steel substrate.

successfully prepared graphene films on the surfaces of stainless steel substrates using a 2B pencil. The preparation process is shown in Fig. 1, which is a way with flexible, environment friendly, efficient and economy. Then, the tribological performances and the structural evolution of the resulted films were investigated by using the variable load process, Raman spectroscopy and high-resolution transmission electron microscopy (HRTEM), etc. The results indicate that the as-fabricated films possess excellent anti-friction and wear-resistance performances. In addition, based on the characterization results, possible mechanism for the enhanced anti-friction and wear-resistance properties is also proposed. The shearing force induced the film densification by promoting sp^2 to sp^3 changing which enforced cross-linking. This cross-linking carbon matrix was responsible for high load bearing. Moreover, the graphene exfoliated under shearing force contributes to the low steady-state friction.

2. Experimental section

Prior to preparation, all stainless steel wafers were cleaned by sonication for more than 30 min in ethanol solution in an ultrasonic bath to remove contaminants left from the sample preparation steps, and subsequently blown dry with N_2 . After that, graphene films were obtained by pencil (2B) sketch on stainless steel wafers along the perpendicular to the direction of the texture of the wafer, parallel to the direction of reciprocation.

The tribological experiments of the graphene films were conducted on a multifunctional material surface performance tester with a ball on disk contact geometry at room temperature (25–28 °C) and relative humidity (RH) of 42–45% in ambient air. During this course we chosen GCr15 balls ($\phi = 5$ mm) as the stationary upper counterparts. The friction tests were carried out along the sketch direction, namely, perpendicular to the direction of the texture of the wafer. Considering the binding force of the sketched films with the substrate is relatively weak. At the beginning applied a high load, as a result the films will be worn out soon. To avoid the films being worn out instantaneously, which requires an ever-increasing load applied to form transfer films in the process of friction. In this research, we chosen 5 N as initial normal load for 15 min for the densification of the films, then increased the load to 10 N in every 10 min, until increased the load to 65 N. Other test parameters include sliding velocity (240 mm/min) and slide stroke (5 mm). The COF was calculated by the formula as $COF = F/L$, where F is the frictional force in N, L is the applied normal load in N. In order to avoid the randomness of experiment results and make it more convinced. All friction experiments were repeatedly performed for more than three times under the same conditions.

After friction tests, Raman spectroscopy (LABRAM HR 800 at a

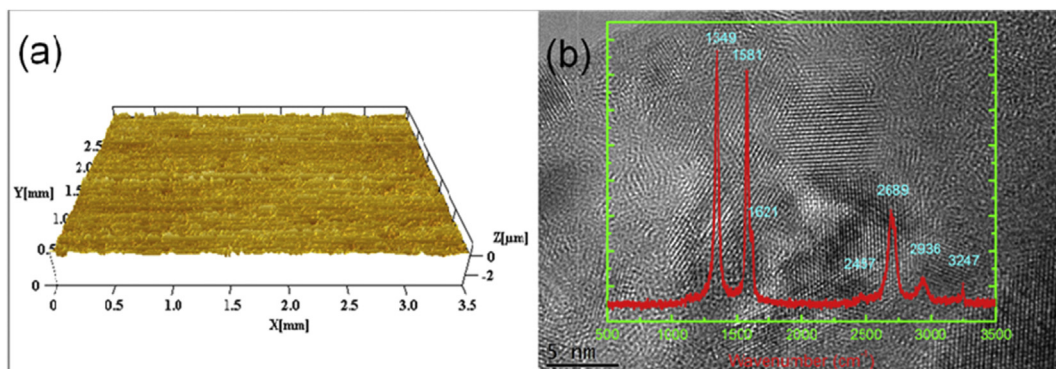


Fig. 2. (a) AFM image of 201 stainless steel and (b) HRTEM image of as-prepared films and corresponding Raman spectra (as inset in).

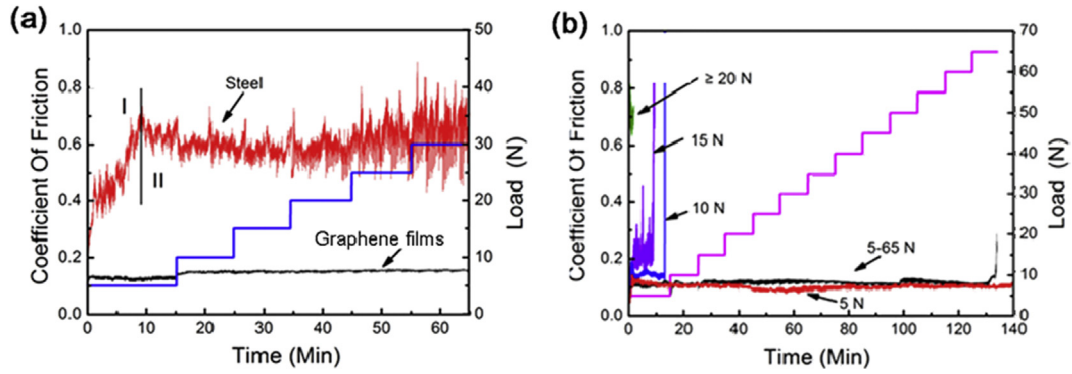


Fig. 3. Friction coefficients of graphene films: (a) under variation loads from 5 to 30N and (b) under loads of 5, 10, 15, 20 N and variation loads 5–65 N.

wavelength of 532 nm (2.3eV) was applied to reveal the microstructure of the wear surface. The topographies of debris were observed by HRTEM. The friction-load curves were recorded on a multifunctional material surface performance tester (MFT-4000, China), and the wear volumes were obtained by three-dimensional surface profiler (MicroXAM-3D).

3. Results and discussion

The 201 stainless wafers (20 mm × 20 mm) are firstly undergo a wiredrawing processing, and the roughness about 170 nm confirmed by atomic force acoustic microscope (AFM) (Fig. 2a). Then a 2B pencil was reciprocating sliding on steel surface in a direction perpendicular to the wiredrawing grain that easier to

grow graphene films. The debris of graphene after rubbing, tested under HRTEM and Raman spectroscopy, are shown in Fig. 2b. The graphene films show a fine crystal structure under HRTEM, and which is proved again by Raman spectra that an obvious G peak at 1581 cm⁻¹ and a D band at 1349 cm⁻¹ can be seen, of which are attributed to in-plane bond stretching of aromatic carbons in the graphitic structure (vibration modes E_{2g}) and breathing mode with A_{1g} symmetry [25–29]. Besides the main peaks, there are five satellite peaks at 1621, 2457, 2689, 2936, and 3247 cm⁻¹. The 1621 cm⁻¹ peak, usually referred as D' peak, can be observed from defect graphite or graphene, originates from the LO phonons near the Γ point [28–32]. 2457 cm⁻¹ band are assigned the band as “q = 0” branch of double resonance Raman scattering [33,34], 2689 cm⁻¹ band arises from 2D vibration, 2936 cm⁻¹ comes from

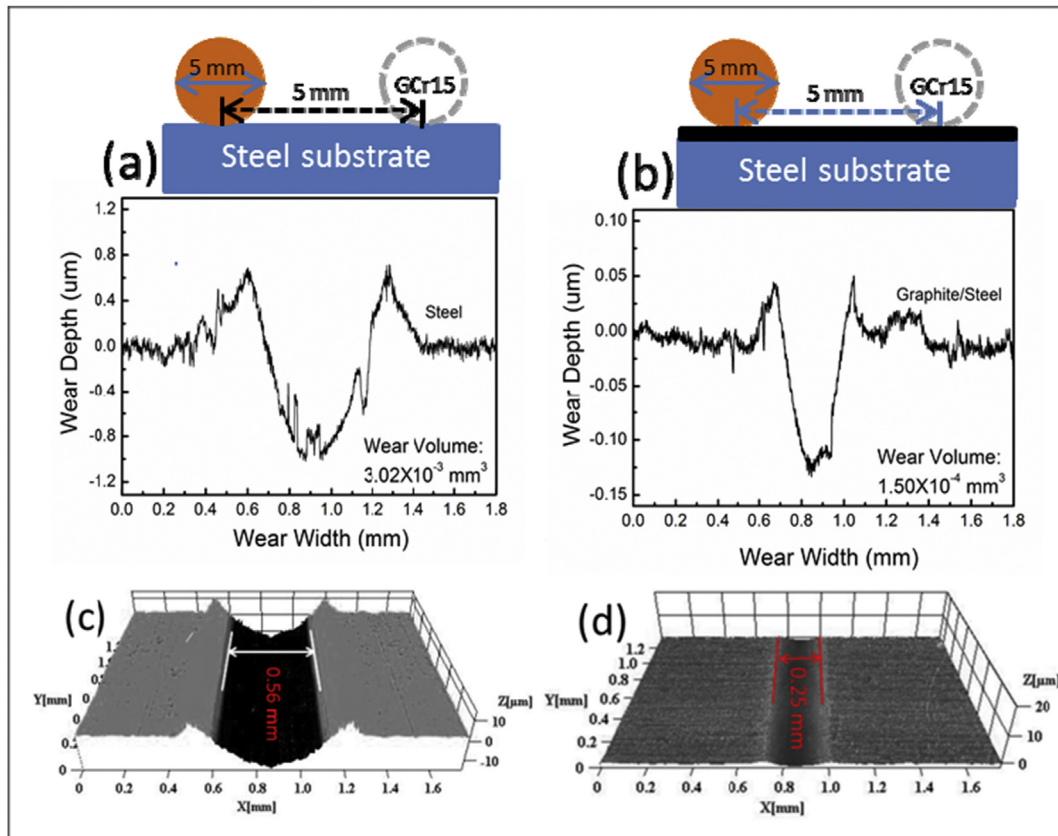


Fig. 4. The 2D cross-section surface profile (top row) and 3D scanning morphologies (bottom) of wear tracks under variable load 5–30 N condition.

D + G(S) vibration which is induced by two TO phonons around the K point and 3247 cm^{-1} peak arises from $2D'$ [25–34]. At this time we believe that polycrystal are grown on 201 stainless wafers.

Then the films were employed to do friction test under a reciprocating friction testing machine. All the friction tests were proceeding in a direction perpendicular to the wire drawing grain because that the graphene was easier push out of the contact interface in parallel directions. In order to more detailed study of the lubrication mechanism of the CNTs film, here, GCr15 balls ($\Phi = 5\text{ mm}$) were employed as the friction pairs. Some of the results are displayed in Fig. 3a. Not surprisingly, graphene films cannot bear the loads beyond 5 N (Fig. 3b). It is easy to see that pencil sketch is limited to dense films, and this will result in the compaction degree of that the films is poor. In this case, if applying a high initial load, the films will wear out soon, and the wear out time is inversely proportional to the initial load (see olive, red, and purple line of Fig. 3b). As we all know, when building a new road, a road roller is usually used to compaction and flattened the road. Inspired by a road roller, thus, in order to obtain the friction data under high loads, and aiming to prolong the life and improve the bearing capacity of the pencil sketch graphene films. Firstly, the graphene films were hardening under 5 N loads due to squeezed effects, and then increasing loads step by step to high load under a loading speed of 5 N in every 10 min (see the step line in Fig. 3a and b). In this variable loading process, the friction life of the films has greatly improved, and the ultimate bearing capacity is up to 65 N. In order to survey the effect of load on structure of these films when the load less than 65 N, 0 N, 5 N, 5–15 N, 5–25 N, 5–35 N, 5–45 N and 5–55 N experiments have been done separately. Then, wear traces and debris were observed via Raman and HRTEM, respectively (discussion later).

Fig. 3a shows the friction curves of steel before and after sketch graphene films under the variable loads (5–30 N) conditions. It is clear that the bare stainless steel friction curve have two regimes, running-in (I) and stable stage (II). In the running-in regime, friction coefficient tends to increase. The reasons may be that rough surface hinder the fully contact with the ball at beginning. However, in stable stage the friction coefficient of bare steel substrate against GCr15 ball as high as 0.65, and it remains unstable and fluctuate seriously, especially under the high load, due to the strong adhesion effects. In contrast, for the graphene/steel, due to the Van der Waals forces between the layers is low, a low and relatively stable friction coefficient (~ 0.12) could be obtained, and more importantly, the friction coefficient is immune to the change of load. Here, we call such a variable load (from 5 to 65 N) friction process as a steady process (Fig. 3b), and it is essential to mechanical equipment work under the changing-condition for reducing friction and extend the lifespan.

Wear resistance is another important manifestation of the performance of solid films. To better understanding that, both 2D cross-section surface profile (Fig. 4a and b) and 3D scanning morphologies (Fig. 4c and d) of wear tracks under variable loads 5–30 N conditions were measured. On bare steel substrates, the wear track for bare steel substrate up to 0.56 mm and 1.05 μm in width and depth, respectively (Fig. 4a and c), and the wear volume is $3.02 \times 10^{-3}\text{ mm}^3$. In contrast, however, the wear tracks for sketch graphene films is shallower and narrower, about 0.25 mm and 0.13 μm in width and depth, respectively (Fig. 4b and d), and the wear volume is $1.05 \times 10^{-4}\text{ mm}^3$, which only 1/28 of the values of the bare steel substrate. Considering the roughness of steel wafers (170 nm or 0.17 μm , comparable to the wear depth), one can speculate that, with graphene films' protection, the steel has no abrasion but plastic deformation instead. Namely, pencil sketch films could reduce wear of the steel substrate significantly.

Until now, one can confirm that pencil sketch is an effective

solid lubricating films preparation method. But we still do not know what happened in nanoscale. People can suppose that if the graphene can be easy exfoliated which afford to the low friction, it can not be sustaining for a long friction life at high load. To reveal that, wear trace and debris were observed via Raman and HRTEM, respectively.

Raman spectroscopy has historically played an important role in the structural characterization of graphitic materials, in particular providing valuable information about defects, stacking of the graphite [35]. Fig. 5 shows the Raman spectra of the as-prepared films as well as the wear traces after friction with different variable loads in the wavelength range of $200\text{--}4000\text{ cm}^{-1}$. Through comparing the Raman spectra under different variable loads, it is obvious of that as-prepared films (0N) there is a D' peak (1620 cm^{-1}), but disappeared after friction. To further investigate the effect of loads on defects of these films, we employed Gauss fitting to quantitative analysis the I_D/I_G (Fig. 6b) and peak shift move (Inset). After friction test, the relative intensity of the D and G peak weaken significantly due to the thinning of graphene films. The value of I_D/I_G decreases with red shift of G peak and blue shift of D peak which indicate that the size of graphene decrease. And the band between $3000\text{ and }3500\text{ cm}^{-1}$ comes wider and two peaks at $2457\text{ and }3247\text{ cm}^{-1}$ are overlapped or disappeared due to the reinforce of bands at $2689\text{ and }2936\text{ cm}^{-1}$ and new peak at 3200 cm^{-1} (Fig. 6). It seems that the bands at $2689\text{, }2936\text{ and }3200\text{ cm}^{-1}$ turn up a strong relationship with the size of graphene (Fig. 6). To further analysis, the bands between $3000\text{ and }3500\text{ cm}^{-1}$ is fitted

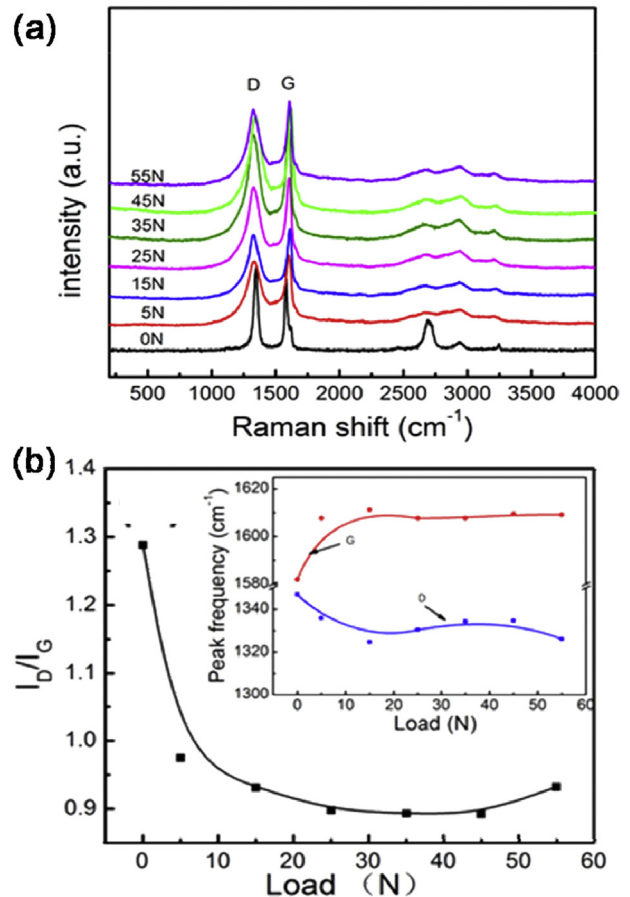


Fig. 5. (a) Raman spectra of graphene film (0N) and friction trace of the graphene films under different loads and (b) I_D/I_G values as a function of loads and the D and G peak position.

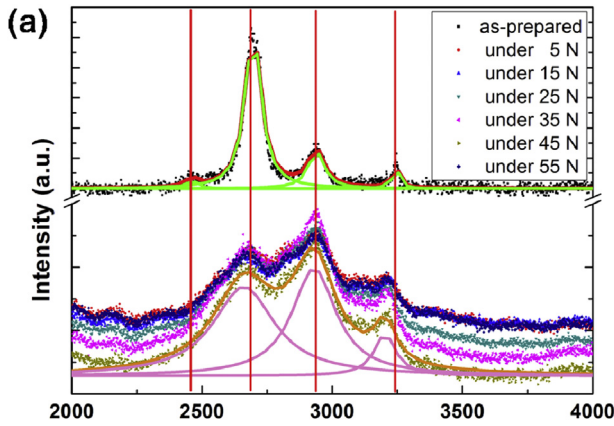


Fig. 6. Raman Spectra of as-prepared graphene films (un one) and of wear traces after friction (down one).

with Lorentzian function. The results show that the peaks relative intensity are unchanged with variation of loads. This result is in accordance with the variation of the I_D/I_G values and D and G peaks position. That is, the microstructure remains the same beyond the load of 5 N, i.e., after a load desiccation under 5 N, the graphene films' structure remains very stable under different load friction processes.

It is very interesting if one considers the change of friction coefficient that remains constant and steady, and has nothing to do with loads, which is a big difference from friction properties under micro-loads [3]. Kumar et al. reported that load-dependent nonlinear trends of friction coefficient were observed in graphene when tested under ambient atmospheric conditions with tens of mN load, and they stated that friction in graphene increases with increasing load due to lattice disordering [36], and hexagonal crystal transition to orthorhombic phase has been confirmed [36]. The increase of friction coefficient has also been reported on amorphous carbon films, and is a norm [37–39].

To further reveal the structural evolution during the friction process, HRTEM test was conducted for wear debris and the corresponding images (Fig. 7) show that after friction at 5 N,

amorphous structure appears with graphene (Fig. 7b), in contrast with as-prepared films that only hexagonal graphene was observed. Even at high load of 55 N, still graphene mixed with amorphous matrix can be seen (Fig. 7c), and the corresponding debris from GCr15 ball shows similar hybrid structure with the film of wear trace (Fig. 7d). These results are well agreed with the Raman results. When taken into account the structure influence, it is obvious to conclude that our results are closer to neither graphite under micro-load conditions nor amorphous carbon films under high loads because that multicrystal graphene films in present work undergo high loads distinct from the friction test to graphene and are very different from that amorphous carbon films which has a structure transition during friction, but not happened in our work. One can confirm that only a desiccation happens under 5 N in a short friction and there is no obvious change beyond that which can be concluded from both HRTEM and Raman results.

Until now, one can speculate that under short friction, the graphene film structure comes to a steady state which can tolerate 65 N reciprocating friction without further structure changing. Combined all results together, one can conclude that the shearing force induced the film densification via sp^2 to sp^3 changing that enforces cross-linking under 5 N short friction. This cross-linking carbon matrix was responsible for high load bearing and the graphene exfoliated into graphene under shearing force contributes to low steady-state friction. The reasons why the coefficients do not go down to lower or super-low friction are that, firstly, the roughness of the steel wafer is non-negligible though after friction it is smoother, and secondly, the presence of amorphous matrix hinders the slipping of graphite. On the other hand, the smooth surface cannot hinder the slippage which contributes to the failure of lubricant on steel surface under 65 N.

4. Conclusion

Graphene films for solid lubricating can be obtained by pencil sketch on a stainless steel wafer along the perpendicular to the direction of the texture of the wafer. When applied variable load to the pencil sketch graphene films, which presents low friction, low wear, and the wear tracks are shallow and narrow, the curves of

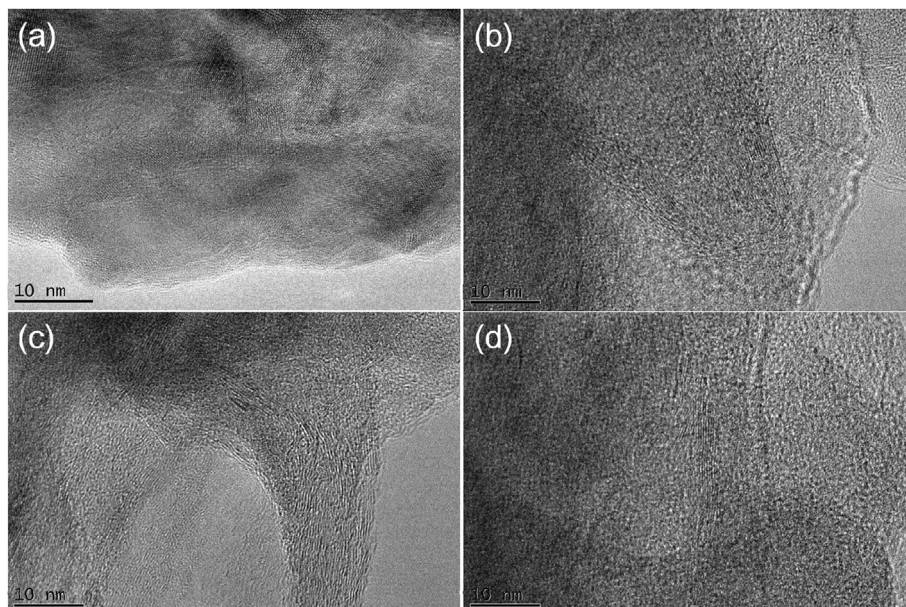


Fig. 7. The FESEM (a) and HRTEM images (a1) of CNTs and FESEM micrograph of CNTs film as-prepared (b).

friction remains stable, moreover, the lifespan and bearing capacity greatly have improved, and the ultimate bearing of graphene films is 65 N. It is commendable that the entire variable loads friction process was a steady-state process. Many of the above phenomena show that the pencil sketch graphene films have good lubricating properties when they used as solid lubricant. Moreover, frictional effect makes the orderliness of the graphene better. Namely, the variable load friction process is a ordering process of the disordered graphite. Benefit from sketch, one can get a lubrication film on any substrates with complex topography, our results shed light on the growth of graphene films for industrial use help understanding the tribology of graphene under high loads.

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