



Preparation of surface coatings on a conductive substrate by controlled motion of graphene nanoflakes in a liquid medium



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ABSTRACT

Controlled motion of graphene and graphene oxide nanoflakes in a thin liquid film on metal surfaces was studied to unravel the significant variations of the electric field effects on the nanoparticles. It was found that graphene oxide flakes were negatively charged and migrated toward anode while the electrically neutral graphene flakes moved toward cathode. Therefore, thin layers of graphene as a protective coating were produced to inhibit corrosion of underlying metals and reduce friction and wear-related mechanical failures in moving mechanical systems. The method does not require an insulated substrate to confine the high electric field to the fluidic layer. The motion of the nano-particles under pulsed electric current was very efficient. The observed effects were interpreted in a possible mechanism associated to the effect of electric field on the mobility of different particles in different conductive media. This significant phenomenon, combined with unique properties of graphene and graphene oxides, represents an exciting platform for enabling diverse applications on the preparation of protective coatings on an arbitrary conductive substrate over large areas.

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1. Introduction

Reducing friction and wear-related mechanical failures in moving mechanical systems still remains a huge challenge due to friction's adverse impacts on efficiency, durability, and environmental compatibility [1–3]. Accordingly, increasing attention has been paid to develop new materials, coatings, and lubricants that can potentially provide low friction and wear even under severe operating conditions [1–3]. Graphene, a two-dimensional carbon material, was only very recently explored that it had unusual properties to reduce wear and friction in nano-scale to macro-scale systems due to the interplay of surface traction forces [4] and the effect of electron–phonon coupling [5]. Considering the fact that most of the previous studies have concentrated on the nano-scale friction [6,7], this is of particular interest in probing the tribological behaviours of graphene at a large scale for expanded practical applications. This requires a suitable deposition method that allows the production of graphene coatings over large areas. Although the chemical vapour deposition (CVD) process is widely used to prepare a thin film, this technique can not be used in the system with large size and complex structure. Furthermore, selective growth

of graphene coating on a substrate (e.g. Co, Pt, Ni, Cu) also greatly affected its application [8–10]. Additionally, CVD method can not be allowed to large-scale use in industry due to high cost of its production process. Therefore, it is critical to develop a simple and effective strategy to prepare a graphene coating on an arbitrary substrate over large areas.

Previously it has been reported that the friction decreases with increasing number of layers [5,11], so the coating of graphene will be produced with controlled thickness by the proposed technique. In this study, the coatings of graphene will be deposited on the steel surface by means of electrophoresis. The proposed method does not require an insulated substrate to confine the high electric field (at least 10 kV) [12,13] to the fluidic layer. This method can be applied to an arbitrary conductive substrate. A uniform coating with four to six layers can be fabricated in a few minutes. Except for reducing wear and friction, thin layers of graphene can also be as a protective coating that inhibits corrosion of underlying metals [14].

2. Experiment section

Here in the present work, pulsed electric current [15], has been implemented to drive the graphene nano-flakes in a thin ethanol film. 316L stainless steel is selected as the substrate for the thin ethanol film, which differs from the insulator substrate used in

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the early mentioned methods. This enables to reduce the electric potential from ~ 10 kV for insulator substrate to 24 V for conductor substrate. A commercially available ethanol solution containing graphene was obtained from Graphene Supermarket Inc. The solution was prepared by chemical exfoliation of the highly oriented pyrolytic graphite in ethanol [2]. The average diameter of graphene flakes is 550 nm (range: 150–3000 nm) and the average thickness is 0.35 nm. The weight concentration of graphene was 1 mg/L containing mostly single layer graphene. Small amount solution (0.1 mL of solution per 4 cm², that is, solution film in 0.25 mm thickness) was dropped on the highly polished surface of 316L stainless steel plates and the liquid ethanol part (70% ethyl alcohol + 30% water) was evaporated in air in a few minutes. The samples were divided into two groups, with each group containing three test pieces. Group 1 was processed without pulsed electric current. Group 2 underwent exactly the same experimental configuration as Group 1 but with the addition of pulsed electric current for 4 min. The ends of the steel plate were connected to the power supply via copper wires. The pulse is in square wave. Each pulse has a loading duration of 60 μ s, frequency of 1 Hz. The electric current density in steel is 1×10^7 A/m². The width between two electrodes is 20 mm (e.g. the width of the liquid film). The consumed electric power in pulse processing is 0.004 W, which is much less than the power of household fluorescent. Formation of graphene deposits on the steel surface has been confirmed by optical microscope. To determine the quality and location of formed graphene film, Raman spectroscopy was employed with 532 nm laser.

3. Results and discussion

The distributions of graphene nanoparticles on the steel surface are as follows before applying the electric current. The coverage of the deposited flakes (by area) does not exceed 20% of the total surface area. For the deposited area (Fig. 1a), the population density is relative low, which will reduce the protective properties of the coating. The chemical composition of these particle deposits was confirmed by the characteristic Raman bands (Fig. 1b). In general, the Raman spectrum of single layer graphene is characterized by the sharp and large 2D band (~ 2700 cm⁻¹), which is the second order of the D band (~ 1350 cm⁻¹). The D peak is absent in a perfect graphene sheet because of symmetry, and grows as defects or disorders in the honeycomb structure increases [16]. The D band is the breathing mode of A_{1g} symmetry, while the G band (~ 1580 cm⁻¹) is generally assigned to the E_{2g} phonon of sp² bonds of carbon atoms [17]. Hence, the outstanding characteristics of 2D, G, and D bands in Raman spectrum can be used to quantify and compare the degree of defects and disorders. Here, the defect peak D is slightly strong, suggesting that partial oxidation of graphene might have occurred during evaporation of ethanol in air. In addition, the sizes of the deposited graphene flakes are varied, but do not extend 3 μ m in diameter. This is in consistent with the technical parameters of the investigated particles mentioned earlier.

Interestingly, after the application of the electric current the distribution of nanoparticles exhibits an apparent tendency, that is, most of graphene nanoparticles migrate toward the cathode (Fig. 2). Optical micrographs showed the formation of the deposits on the anode (Fig. 2a) and the cathode (Fig. 2b), respectively. An endless belt region with high density population was observed on the cathode, while a very low density area was presented on the anode. The width of the belt region on the cathode was approximately 1.5 mm. Apart from the areas near the two electrodes, the particle aggregation cannot be observed in other regions. To analyse the spatial distribution of the deposits, two-dimensional maps of the characteristic Raman peaks were measured. Two rectangular areas with the dimensions of 70 μ m \times 70 μ m were selected for the Raman

tests to confirm the characteristics of the deposits. The scanned results of rectangle E and F are shown in the two-dimensional maps of Fig. 2c and d, respectively. In the same scanned area, around 30 particles (e.g. 6122/mm²) were on the cathode while only one particle (e.g. 204/mm²) was on the anode. The size of the deposited particles was in the range of 3–12.2 μ m on the cathode, while the size is 4.8 μ m on the anode. All the sizes of the deposited particles with electric field extended 3 μ m in diameter. The locomotion under electric current causes aggregation of nanoparticles, thereby increasing the particle size.

To analyse the number of the deposit and its defects, the intensity ratios I_D/I_G and I_{2D}/I_G were calculated according to the Raman spectra. The band intensity ratio of I_D/I_G is proportional to the number of defects, and I_{2D}/I_G is inversely proportional to the number of graphene layers [18,19]. The I_D/I_G ratios collected at the anode (Fig. 3a) collected from Fig. 2c) and cathode (Fig. 3b) collected from Fig. 2d) were around 1.06 and 0.57 respectively, indicating that the defect peak D was much stronger at the anode. It suggests that graphene at the anode might be converted to a graphene oxide structure due to modifications during evaporation of ethanol in air. The different I_D/I_G ratios also indicate that graphene oxides migrated toward the anode while graphene particles migrated toward the cathode. This provides a method for the separation of graphene and graphene oxide with less energy consumption. Furthermore, the I_{2D}/I_G ratios collected at the cathode (Fig. 3b), anode (Fig. 3a), and the sample without electric field (Fig. 1b) were 0.40, 0.44 and 0.69, respectively. According to previous studies by Raman spectroscopy and atomic force microscopy [18,19], the number of graphene layers at cathode is determined as six layers (2.1 nm), and graphene oxide at anode consists of four layers (1.4 nm). Statistical analysis of I_{2D}/I_G ratio demonstrates that the average number of layers was affected by the locomotion of particles driven by the electric field. The smaller the I_{2D}/I_G ratio value, the more the number of layers, i.e. majority of graphene was driven toward the cathode and thereby resulting in an increase in the number of layers. Based on the above data, we can conclude that graphene oxides formed during evaporation of ethanol migrated toward the anode, but graphene nanoparticles with much more number of layers moved to the cathode. Therefore, this technique is valuable for fabrication of graphene or graphene oxide coatings with controlled thickness. Meanwhile, in order to obtain 100% coverage, the anode position can be fixed, and the cathode at a rate of 1.5 mm per 4 min moves to the anode. For a coating of size 20 mm \times 20 mm, it can be obtained in 14 min with ~ 2.1 nm thickness by the electric current. But the coverage of the deposited flakes does not exceed 20% of the total surface area without the application of the electric current. Additionally, we may turn to the question: how to keep the nanoflakes going in a steady direction and to steer and navigate them towards their destination by temporal and spatial regulation of the speed? The answer appears to be simple because we just need to adjust pulsed current density (or voltage) and the position of the electrode. Furthermore, the particle deposition rate can also be controlled. Here, it must be noted that the graphene oxide nanosheets (e.g. the defects near the anode) can also be a good corrosion-inhibiting coating with a superfine abrasion performance, as reported in the previous studies [1–4,20].

In general, it requires at least 10 kV high voltage to drive the large-sized particles (>200 μ m) to move on an insulator substrate [12,13]. In this study, the voltage is only 24 V, but it can drive the particles (<3 μ m) on the conductor surface. It demonstrates that the conductor substrate can reduce required electric field value (at least reduced by more than 400 times) greatly and has a huge contribution to the movement of small particles. Moreover, if the objects are very small (typically in the micron or nanoscale), viscosity effects will become very important and therefore momentum-based propulsion (e.g. bubble propulsion

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