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Random occurrence of macroscale superlubricity of graphite enabled by tribo-transfer of multilayer graphene nanoflakes

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ABSTRACT

Superlubricity of layered materials, such as graphite, boron nitride, and molybdenum disulfide, is easy to achieve at the nano- or microscale by the formation of ideal incommensurate contact, but it has never been observed at the macroscale due to the size limitations of the contact zone. In the present study, the instantaneous superlubricity of graphite against steel was achieved at the macroscale, through the formation of many tribo-transferred multilayer graphene nanoflakes (MGNFs) on the steel contact zone after the initial sliding. The friction coefficient could reduce to a minimum of 0.001, which randomly appeared as the test progressed, with a maximal sliding distance of 131 μm. The macroscale superlubricity was derived from the statistical frictional forces of multiple transferred MGNFs (in the contact zone) sliding on the graphite with atomic steps. This finding provides a possible approach to achieving the macroscale superlubricity of layered materials by the discretization of a large contact area into multiple, dispersed nanoflake contacts.

1. Introduction

Graphite, consisting of layers of graphene sheets separated by 0.3 nm, has extremely high strength, stiffness, and thermal conductivity along the basal plane [1], which is widely used in batteries, sensors, and semiconductor devices [2–6]. During the recent years, it has also attracted attentions for application to the machine lubrication, such as being used for anti-friction additives [7,8], coatings [9], and atomically smooth surfaces for nanotribology [10,11]. Its lamellar structure, bonded by weak van der Waals (vdW) forces [12], allows the easy sliding of parallel planes. The friction in some special sliding directions can fall to near-zero when the lattices are in the incommensurate contact, owing to the extremely low shear strength [11,13]. Direct evidence for this can be seen in the micro-size island of graphite self-retracting back to its initial position after displacement from the equilibrium configuration, which originates from the ultralow friction between the incommensurate graphite interfaces [14]. This phenomenon is called “superlubricity” [15,16], and has also been observed between multiwall carbon nanotubes [17], graphene nanosheets [18], and other layered materials [19]. Moreover, the superlow friction of graphite can also be attained with the common non-layered materials at the nanoscale by the formation of transferred graphite or graphene nanoflakes [11,20,21]. For example, it was reported that the friction coefficient of graphite sliding against silica was reduced to 0.0003 by the transfer of multiple graphene nanoflakes onto the silica [21]. Obviously, the excellent lubricating properties of these graphite-based systems will be conducive to the design of high-performance mechanical sliding systems by enabling the fabrication of frictionless and wear-free sliding components.

However, the above superlubricity of graphite has only been achieved on a very small scale (e.g. 1 nm–10 μm) [22,23], because of the strict requirements for atomically smooth contact. Although some efforts have been made to reduce the friction of graphite at the macroscale (i.e., on the traditional tribometer with a large contact area), the friction coefficient of graphite or graphite-based composites at the macroscale was usually in the level of 0.1 [24–27], which is two orders higher than that measured at the nanoscale or microscale. At present, only diamond-like carbon (DLC) films and graphene nano-scrolls surrounding the nanodiamond particles are able to attain superlubricity at the macroscale [28,29]. However, this superlubricity system limits to DLC, graphene, and nanodiamond particles, and the achievement of superlubricity of graphite or other layered materials at the macroscale remains a challenge. In the present work, the macroscale friction behavior of highly oriented pyrolytic graphite (HOPG)

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sliding against steel was studied, in an attempt to determine the superlubricity conditions of graphite at the macroscale. The similar tribo-transfer process of graphene nanoflakes, in the same way as occurs at the nano- or microscale was observed, but the friction behavior was completely different. Therefore, the mechanism dominating the macroscale friction behavior of graphite was revealed and the relationship between nanoscale and macroscale superlubricity of graphite was also identified.

2. Materials and methods

Friction measurements were performed at the macroscale by using the Universal Macro-Tribotester (UMT-3, Bruker, USA) with a rotation mode of ball-on-disk. The ball was made of GCr15 bearing steel with a diameter of 4 mm, while a HOPG substrate (0.4° mosaic spread) glued onto a glass slide was used as the disk. Before each friction test, the ball was cleaned by ethanol and dried with nitrogen, and the HOPG was freshly cleaved by using the adhesive tape to give a clean, flat surface immediately before each friction test (Fig. 1a). The load applied on the HOPG varied from 0.5 to 2 N, and the diameter of the contact zone (D) could be estimated using the Hertz contact theory, as given by Equation (1) [30].

$$D = 2\left(\frac{3RF_n}{4E'}\right)^{1/3} \tag{1}$$

where F_n is the applied load, R is the radius of the steel ball, E' is the reduced Young's modulus of the two contacting solids, defined by $E' = 1/[(1-\nu_1^2)/E_1 + (1-\nu_2^2)/E_2]$ [30], where ν_i is the Poisson's ratio of material i, and E_i is the elasticity modulus of material i. When the applied load was set to 0.5 N, the diameter of the contact zone was obtained as D = 70 μm, and the average contact pressure was $P = 4F_n/\pi D^2 = 132\ MPa$. The rotational speed of the HOPG varied from 0.1 to 5 rpm with a track radius of 2 mm, corresponding to a sliding speed range of 10–524 μm/s. All the friction tests were performed at a temperature of 25 °C and a relative humidity of 15–30%.

The topography of the steel ball before and after one rotation in the friction test (load = 0.5 N, and sliding speed = 52 μm/s) was investigated using the field emission scanning electron microscope (FESEM, HITACHI SU8220) under a low voltage of 5 kV to protect the transferred nanoflakes from damage. The topography of the freshly cleaved HOPG was measured by the atomic force microscopy (AFM, Bruker ICON) with a scanning area of 30 × 30 μm^2 in a tapping model. The wear track on the HOPG was detected by both FESEM and a 3D white light interferometer. The Raman spectrum of the nanoflakes was obtained using a Raman spectrometer (Jobin Yvon HR800), with a laser wavelength of 532 nm.

The cross-sectional sample for the high-resolution transmission electron microscope (HRTEM) was prepared using the focused ion beam (FIB), picked out from the contact zone on the steel ball, with a length of 10 μm. A Cr film with a thickness of 20 nm was firstly sputtered onto the steel ball and a Pt film with a thickness of more than 100 nm was subsequently deposited as a protective layer before the FIB microprocess. The TEM images were obtained using a 200 kV high resolution transmission electron microscope (JEM-

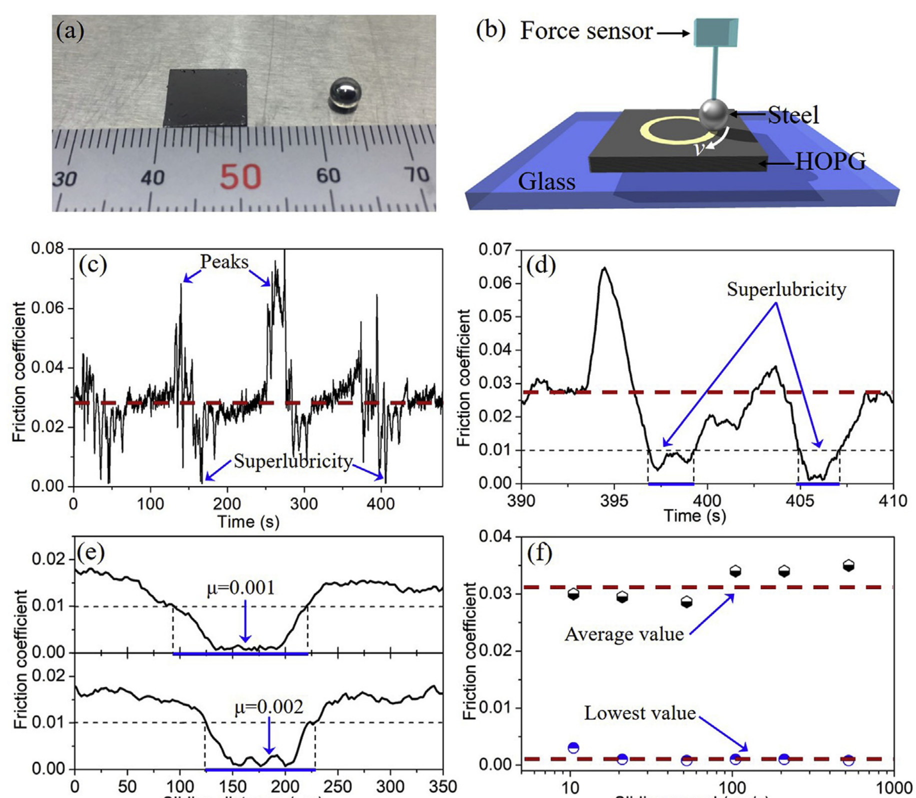

Fig. 1. Schematic illustration of the experiments and friction behavior of graphite sliding against steel at the macroscale. (a) Image and size of HOPG and steel ball. (b) Experimental setup of ball-on-disk friction test with a rotation radius of 1 mm under ambient conditions. (c) Evolution of friction coefficient with time under a constant load of 0.5 N and a sliding speed of 52 μm/s. (d) Enlarged view of friction coefficient curve in (c) when the test time was in the range of 390–410 s. The period in which the friction coefficient is less than 0.01 is defined as the superlubricity region (blue line). (e) Two partial friction coefficient curves measured with two different HOPG samples and steel balls. The test conditions were the same as those in (c). (f) Relationship between the average and lowest friction coefficient attained during the test period (480 s) and the sliding speed. (A colour version of this figure can be viewed online.)