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Contact Angle Hysteresis on Graphene Surfaces and Hysteresis-free Behavior on Oil-infused Graphite Surfaces

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ABSTRACT

Contact angle hysteresis (CAH) on graphitic surfaces, including chemical vapor deposition (CVD) graphene, reduced electrophoretic deposition (EPD) graphene, highly oriented pyrolytic graphite (HOPG), and polished graphite sheet, has been investigated. The hysteresis loops of water drops on the first three samples are similar but the receding contact angle is particularly small for the polished graphite sheet.The significant CAH observed on CVD graphene and HOPG associated with atom-scale roughness has to be attributed mainly to adhesion hysteresis (surface relaxation), instead of roughness or defects.The difference of the wetting behavior among those four graphitic samples has been further demonstrated by hexadecane drops. On the surface of HOPG or CVD graphene,the contact line expands continuously with time, indicating total wetting for which the contact angle does not exist and contact line pinning disappears. In contrast, on the surface of reduced EPD graphene, spontaneous spreading is halted by spikes on it and partial wetting with small contact angle ($\theta \approx 4^\circ$) is obtained. On the surface of polished graphite sheet, the superlipophilicity and porous structure are demonstrated by imbibition and capillary rise of hexadecane. Consequently, an oil-infused graphite surface can be fabricated and the ultralow CAH of water ($\Delta\theta \approx 2^\circ$) is achieved.

1. Introduction

Graphitic materials have been of paramount importance in industry with applications including biodevices [1], battery electrodes [2–4], catalysis and catalyst support [5], tribology [6], adsorption [7,8], and composites [9–11]. Recently, graphene as a planar nanosheet of carbon atoms arranged in a honeycomb lattice has attracted a great interest owing to its exceptional properties [12–14], such as extraordinary mechanical and thermal properties, excellent optical transparency, and high carrier mobility. The wettability of water on graphene and graphite surfaces is important implications for product design such as permeation, adhesion, conductivity, and electrochemical activity [15–17]. Moreover, the dispersion of graphene or graphite flakes in aqueous solutions or polymers depends strongly on their wetting properties.Although graphene and graphite have generally been recognized as hydrophobic materials, the water contact angles (CA) reported in the literature have been highly variable and their values are in the range of about 64°to 150° [18–26]. Besides limited understanding of their water CAs, the knowledge of the hysteresis behavior associated with CA is still scarce as well [24,26].

The wetting behavior depends generally on two factors of the solid surfaces: the chemical composition and geometrical microstructures. The wettability of a liquid drop on a solid surface is typically depicted by the CA between the gas-liquid and solid-liquid interfaces. On an ideal smooth surface, the CA relates to the interfacial tensions of solid-gas (γ_{sg}), solid-liquid (γ_{sl}), and liquid-gas (γ_{lg}) by the Young's equation [27], $\cos\theta = (\gamma_{sg} - \gamma_{sl})/\gamma_{lg}$. On a real solid surface, surface roughness is also important and has been considered in the Wenzel [28] and Cassie-Baxter theories [29]. Moreover, the CA can exist in a range of angles, $\theta_a \geq \theta \geq \theta_r$, where θ_a and θ_r denote the advancing and receding CAs, respectively. By continuous inflation and deflation of a sessile drop on a real surface, a hysteresis loop in the plot of CA versus drop volume can be observed. This behavior is called contact angle hysteresis (CAH) and it is generally represented by the difference between the advancing and receding CA ($\Delta q = \theta_a - \theta_r$).

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The occurrence of CAH on a real surface is generally ascribed to two mechanisms: (i) localized defects associated with hydrophilic blemishes or surface roughness [30–33], (ii)adhesion hysteresis associated with molecular rearrangement on a surface induced by wetting [34]. In the first mechanism, CAH comes from intrinsic defects which are more wettable than the rest of the surface. Thereby, the strength of CAH is a function of the area density, size, shape,and wettabilityof defects [31]. CAH can be shown by the variation of the apparent CA with the drop volume on a surface with periodical surface roughness. The contact line pinning appears as the sharp-edge of grooves is encountered by the liquid front [35,36]. In the second mechanism, CAH is originated from molecular relaxation on the surface in contact with the drop. As a liquid drop is deposited on a surface, the molecules of the solid surface below the liquid may rearrange their structure in order to lower the surface free energy. According to Young's equation, the reduced solid-liquid interfacial tension after surface relaxation will result in the decrement of the contact angle, corresponding to the receding contact angle.

Although most of the real surfaces exhibit the characteristic of CAH, surfaces without CAH are found in nature.For example, when insects with the oils on their feet step on the pitcher plant surface, they slide from the rim into the digestive juices at the bottom. This is attributed to the vanishing capillary forces associated with the CAH-free surface which contains an aqueous film in contact with oils [37]. According to this inspiration, a slippery liquid-infused porous surface (SLIPS) that comprises a thin film of lubricating liquid locked in submicron/nano-sized porous structureis fabricated [38]. SLIPS possesses a intrinsically smooth, defectless liquid surface (e.g. lubricating liquid Krytox).Due to the immiscible liquid interface, contact line pinning of a liquid drop (e.g. water) on such a surface is essentially eliminated. It has been used in anti-ice [39] and anti-bacteria [40] applications.In addition, SLIPS can have some advantages such as transparency,self-repairing property, high pressure endurance,and thermal stability [41]. The fabrication of SLIPS involves three criterions: (i) the substrate must be able to imbibe the lubricating liquid readily, (ii) the lubricating liquid must be immiscible to the impinging test liquids, (iii) the substrate prefers the lubricating liquid rather than the impinging test liquids [38,42].

In this study, four kinds of graphitic surfaces, including chemical vapor deposition (CVD) graphene, reduced electrophoretic deposition (EPD) graphene, highly oriented pyrolytic graphite (HOPG), and polished graphite sheet, are fabricated to explore their wetting behavior. The mechanisms of CAH of water drops on these four samples are investigated. Since the CVD graphene with single-layered structure is smooth and defect-free, CAH observed on this nearly ideal surface is suitable for understanding the contribution of adhesion hysteresis.The influence of nano-scale roughness on CAH is studied by reduced EPD graphene and HOPG. Moreover, the effect of submicron-scale grooves on CAH is considered by polished graphite sheet. The differences of the wetting behavior(partial/total wetting) among those four graphitic samples can be further demonstrated by hexadecane drops. Because graphite is well-known as a lipophilic material, the oil-infused surface of a graphite sheet is produced by imbibition of hexadecane into its porous structure. The hysteresis-free property for water drops on such a surface is examined and quantitatively explained.

2. Experimental

2.1. Materials

High purity graphite sheets (IGS-743) are purchased from Nippon Techno-Carbon Co. (Japan).Highly oriented pyrolytic graphite (HOPG, 466HP-AB, SPI-2 grade) is bought from SPI Supplies Division Structure Probe Inc. (USA). In the fabrication of the reduced EPD graphene, the electrodes made of stainless steels (grade 304) are the products of Kow-Yi Co. (Taiwan). Potassium hydroxide (KOH, 85%) and hexadecane ($C_{16}H_{34}$, 98%) are bought from Showa Co. (Japan). All chemicals in this work are analytical grade and used as received without further purification.

2.2. Synthesis of CVD graphene

The single-layered graphene is grown on Cu foil (25 μm) by using a CVD method. Under the vacuum of 10 mTorr at 1000 °C, H_2 is introduced (2 sccm) for 40 min, followed by methane (35 sccm) for 15 min. Afterward, a quick cooling process (300 °C/min) are conducted in the H_2 and methane environment. The graphene film is then transferred into silicon wafer via polymethyl methacrylate (PMMA) coating and iron (III) nitrate etching [43–45].

2.3. Fabrication of reduced EPD graphene

Two graphite sheets are used as electrodes and placed in an electrolysis cell filled with the 0.16 wt% KOH aqueous solution. The electrochemical exfoliation is proceeded under a constant current mode at 300 mA. After a few hours, the graphene oxide (GO) nanoparticles are formed and the large precipitates are removed by centrifugation at 6000 rpm for 30 min.The suspension of GO nanoparticles is then filtered by 0.22 μm syringe filter to exclude the oversized particles [46]. Two stainless steel are employed as electrodes and immersed in the as-prepared GO suspension. The electrophoretic deposition is conducted under a constant current mode at 20 mA. After 10 minutes, the GO nanoparticles are deposited on the surface of steel at anode. Afterward, the thin film formed by GO is reduced in vacuum (0.67 Pa) at 110 °C for about 12 hrs to obtain the reduced EPD graphene.

2.4. Preparation of HOPG surface

The HOPG surface is prepared by the simple micromechanical exfoliation method [13]. The scotch-tape is used to peel multi-layers of graphene from HOPG.

2.5. Fabrication of oil-infused graphite sheet

The porous structure in the polished graphite sheet is filled with hexadecane via sonication until the mass of the samples no longer increase.Then, the infusion of the hexadecane into the graphene molecular structure has occurred.

2.6. Experimental methods and characterization

The wetting behaviors on graphitic samples are observed at room temperature by a Dataphysics OCA-15EC contact angle measurement system. A water droplet of about 3 μl is released by an automatic micro-syringe on the graphitic surfaces. The shapes of droplets are recorded by charge coupled device (CCD) camera and transformed into an enlarged image.The advancing and receding CAs are determined by the inflation/deflation method. The rate of inflation and deflation are about 0.01 μl/sec. The determination of CA adopts the tangent-1 method as provided by the Krüss software and the data does not depend on the rate of inflation/deflation. Our experiments are conducted under the condition of constant relative humidity (about 60%) and they are finished soon enough so that the effect of evaporation is negligible. The height of capillary rise is measured by the built-in scale of Multicam Easy 2007. The evolutions of the top-view shape of a liquid droplet on graphitic surfaces are also recorded by CCD-camera and the variation of the