The tunable wettability in multistimuli-responsive smart graphene surfaces

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Abstract
The tunable wettability of smart graphene films onto stainless steel substrates with a multi-response to different environmental stimuli has been investigated including light irradiation, pH, electric field, and annealing temperature. Conductive graphene film exhibited the controllable transition from water-repellent to water-loving characteristic in response to different environment fields, which primarily resulted from the morpho-chemically synergistic effect as well as the restoration of electronic stucture. Based on the fundamental theories of wettability, mechanisms in switching from hydrophobicity to hydrophilicity for smart graphene surface including thermal chemistry, electrostatic, photo-induced surface chemistry, solvent, and pH methods were presented.

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The tunable wettability of smart graphene films onto stainless steel substrates with a multi-response to different environmental stimuli has been investigated including light irradiation, pH, electric field, and annealing temperature. Conductive graphene film exhibited the controllable transition from water-repellent to water-loving characteristic in response to different environment fields, which primarily resulted from the morpho-chemically synergistic effect as well as the restoration of electronic stucture. Based on the fundamental theories of wettability, mechanisms in switching from hydrophobicity to hydrophilicity for smart graphene surface including thermal chemistry, electrostatic, photo-induced surface chemistry, solvent, and pH methods were presented. © *2013 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4775360]

Smart surfaces with tunable wetting behavior in different stimuli-responsive environments have attracted considerable attention for their profound applications in self-cleaning surfaces, anti-adhesive coatings, biosensors, microfluidics, etc.[1–3] Based on the regulation of the micro/nano architecture and chemical compositions for various materials, many elegant methods have been used to controllably switch this wetting capability in response to different environmental stimuli, such as thermal treatment, pH control, solvent treatment, and light irradiation.[4–7] Graphene has attracted much attention because of its superior characteristics, such as its extraordinary electronic transport character, high mechanial strength, and high thermal conductivity as well as high surface-area volume ratio of special microstructure and morphology.[8,9] Understanding the surface property of graphene is fundamentally significant to large-area graphene for electronic applications because contact deposition often fails as a result of the hydrophobic nature of graphene.[10] Shin[11] and Zong[12] experimentally confirmed that graphene films exhibiting hydrophobicity strongly depend on the disorder level and the number of layers. However, only a few studies exist on the modulation of the wetting ability of graphene itself exposed to multi-stimuli-responsive environments. For example, Rafiee *et al.*[13] easily obtained graphene films from superhydrophobicity to superhydrophilicity by regulating the specfic concentration of acetone-water solutions. Zhang[14] and Bittolo Bon[15] demonstrated that graphene oxide film exhibited switchable wettability under photoinduced conditions, and the reversible wetting capability of graphene films was obtained by light irradiation. Therefore, the exploration of stimuli-reponsive graphene surfaces would open promising opportunities for the architecture of adaptive and responsive smart graphene films.

Our previous report showed that the obtained hierarchical micro-/nano-textured graphene film displays excellent hydrophobic character with high adhesion, showing a contact angle (CA) of approximately 140°. Although the surface electrical resistance of the sprayed $\sim 2\,\mu$m thick graphene film of approximately $7.2 \times 10^3\ \Omega\ \square^{-1}$ was above the theoretically calculated electrical resistance of graphene film ($\sim 31\ \Omega\ \square^{-1}$), this value enabled the engineering of a highly conductive film with "lotus effect" in optoelectronics.[16] However, whether conductive graphene nanosheets can be hydrophilic or hydrophobic in response to different stimulus-driven conditions remains an intriguing issue. In this letter, the inherent tunable wetting capability of graphene films was explored under different stimulus-driven conditions, including light irradiation, electric fields, high-temperature treatment, and pH values. Graphene samples from graphene-ethanol suspension and graphene-isopropanol suspension were examined to evaluate their photo-responsive wetting behavior, whereas graphene films from graphene-ethanol suspension were applied to investigate wettability when exposed to pH, electric field, and thermal treatment. Furthermore, the feasible stimuli-responsive wetting model of graphene film itself is presented.

The as-obtained graphene film exhibited excellent reversible photo-responsive wettability,[17] almost resembling that of a carbon nanotube (CNT).[18] Furthermore, a multi-stimulus-responsive graphene surface with switchable wetting character was especially sensitive to solvent pretreatment and photo-irradiation energy density, as shown in Fig. 1. After exposure to ultraviolet (UV) light irradiation (254 nm, 2 mW/cm²) for 12 h, the CA of the graphene film from the graphene–isopropanol suspension showed almost no change with the increase in duration of air storage. On the other hand, graphene film from the graphene-ethanol suspension displayed a clear transition from hydrophobicity to hydrophilicity. Interestingly, when both samples were restored to UV light irradiation (254 nm, 20 mW/cm²) for 12 h, the CA of the graphene film from the graphene-isopropanol suspension clearly decreased from 140° to approximately 85°, whereas the CA of the graphene film from the graphene-ethanol suspension decreased from 140° to 40°, showing good switchable wettability. Notably, the switchable wettability of the graphene film originates from the adsorption–desorption process of oxygen molecules on the graphene surface, following that of transition metal oxides and CNTs.[16–21] Moreover, the experimental results
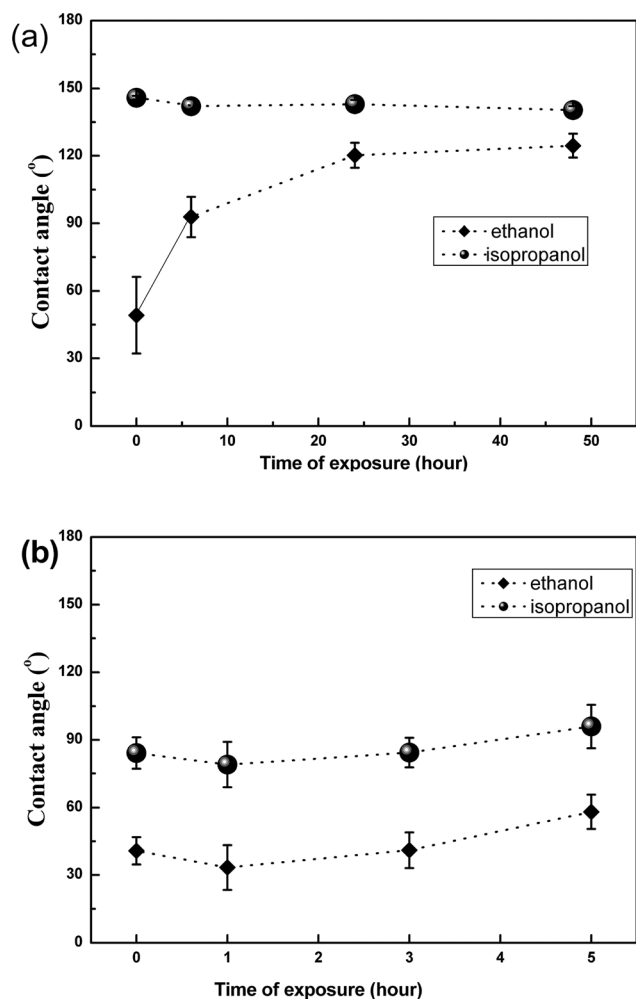
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FIG. 1. Plot of the contact angle with time of exposure for irradiated graphene–ethanol film and graphene-isopropanol film with different light irradiation energies: (a) 254 nm, 2 mW/cm^2; (b) 254 nm, 20 mW/cm^2.
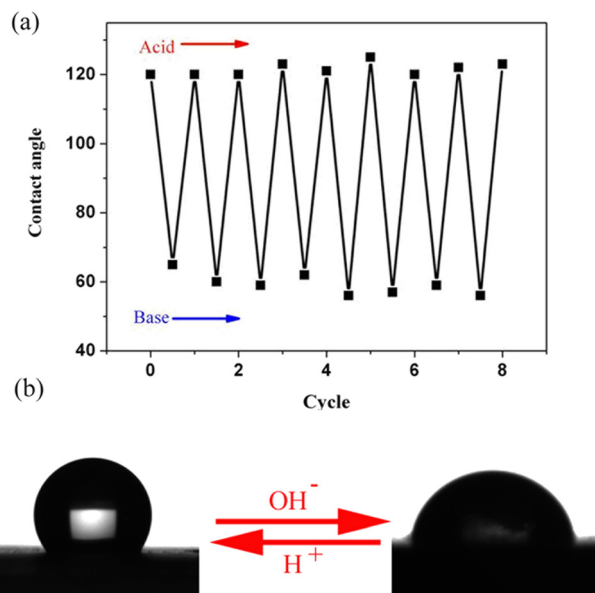

FIG. 2. (a) The reversible hydrophobic and hydrophilic transition of graphene films by alternating pH values from 12 to 2; (b) the shapes of water droplet on corresponding surface under a tilt angle of 0° and 180°, respectively.

also indicated that the transition was strongly dependent on the level of light irradiation energy and the special chemical composition of the graphene surface. The diversity of wettability on the graphene surface was closely related to the stability of absorbed solvent molecules during ultrasonication. For instance, the functional –COOC$_2$H$_5$ and –COOC$_3$H$_8$ groups would anchor onto graphene edges following the esterification reaction of the –COOH group of chemically reduced graphene oxide film, which effectively modified the special composition of the graphene surface leading to the CA difference. The desorption rate of the –COOC$_2$H$_5$ and –COOC$_3$H$_8$ groups exposed to light irradiation greatly influenced the discrepancy in switchable wetting performance.

Indeed, such carbonyl, hydroxyl, or epoxy groups bonded on chemically reduced graphene surface not only provided the possibility of the esterification reaction during ultrasonication but also contributed to the high pH-responsive sensivity of the graphene surface, as shown in Fig. 2. Reversible wetting of the graphene film when exposed to pH 2 and 12 was also observed. When exposed to pH 2, the CA of the graphene film was approximately 130°. After being rinsed with distilled water and dried under a N$_2$ stream, the base-exposed graphene film showed a CA of approximately 60°, indicating the transition from hydrophobicity to hydrophilicity of the graphene surface. This reversible pH-responsive property of the

graphene film was repeatable. Furthermore, the dependence of the pH variation on the wetting performance of graphene film was investigated, as shown in Fig. 3. In acidic and neutral water conditions, graphene film apparently exhibit hydrophobicity. The CA of the graphene film increased linearly with the increase in pH value up to pH 6.0, and the maximum CA of 135° was reached at pH 6.0. On the other hand, a decrease in the CA of the graphene surface was observed in the alkaline media, indicating hydrophilicity of the graphene surface. These findings show that graphene film demonstrated tunable wettability by altering the pH values. All samples exhibited the presence of carbonyl, hydroxyl, or epoxy groups that inevitably bonded on the graphene surface prepared through chemical redox processing.[22–24] Such presence was observed from the Fourier tranform infrared spectra of the graphene films after CA testing, as shown in Fig. 3. No obvious characteristics in the microstructural evolution of graphene film was detected. Even so, the protonation-deprotonation of the surface carbonyl, hydroxyl, or epoxy groups among the solid/lqiuid interface induced by pH mainly was responsible for the high pH-responsive behavior of the graphene film. The feasible schematic diagram of the graphene films in different pH environments is proposed in Fig. 3(c).[25] In addition, the three-dimensional capillary effect of the fractal-like structured graphene surface on the wetting performance should be considered.[26]

Further efforts on investigating the electro-wetting performance of the graphene film from the graphene-ethannol suspension were conducted, which showed potential applications in capacitive deionization.[27] As shown in Fig. 4, the zero-voltage CA on the graphene film was approximately 130°, which can be described by the Wenzel model. Then, a rapid decrease in CA with respect to an increase in applied potential occurred, showing a remarkable tuning characteristic of the surface properties of the graphene film regardless of the applied positive or negative potential. Simultaneously,
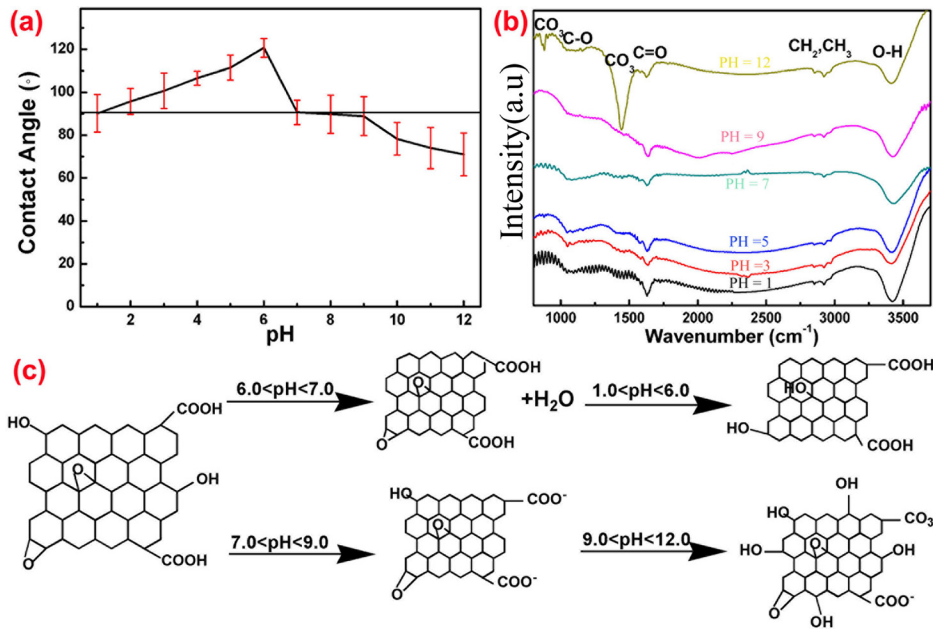
FIG. 3. (a) The CAs of graphene films as a function of pH values; (b) Fourier transform infrared spectra of graphene films exposed to different pH conditions; (c) mechanism of switchable wetting performance in graphene films at different pH conditions.

the immobile droplet was distorted and finally detached from the top electrode. Indeed, the graphene film showed a transformed wetting state from the Wenzel state to the Cassie state, which is closely related to the electro-induced capillary effects along with water spreading through the roughened graphene. Although theories such as zero interfacial tension

and charge trapping have been proposed, the exact mechanism controlling this electro-wetting phenomenon has not yet been defined. The classical Lippmann's electro-wetting model is described as follows:[28,29]

$$\cos(\theta)_V = \cos(\theta)_o + CV_A^2/2r_L, \qquad (1)$$

where the interfacial capacitance C is a representative parameter of the electro-wetting characteristic for materials, and it was substantially appropriate for illustrating dielectric electro-wetting.[28,30] However, in the current case, graphene films were directly fabricated onto conductive steel substrate without a dielectric interlayer. A rapid drop in the good sensitivity of the CA in response to applied voltages indicated the existence of comparatively high interfacial capacitance. To further investigate the thermodynamically tunable wetting performance of the graphene film, two fitting curves for the transition from hydrophobic to hydrophilic state were created based on the Arrhenius equation and classical Lippmann equation, respectively, which are expressed as follows:

$$y = 0.39397 - 0.49328 \exp\left(\frac{V}{5.15959}\right), \qquad (2)$$

$$y = 0.11603 + 0.0197\,V - 4.49745 \times 10^{-4}\,V^2, \qquad (3)$$

where V is the applied potential. Equation (2) was used for the applied negative potential from -30 V to 0 V, and Eq. (3) was appropriate for the applied positive potential from 0 V to 30 V. The fitted analysis indicated that the electro-wetting behavior on the sprayed graphene film did not follow the Young–Lippmann quadratic relationship regardless of the positive or negative potential. When the applied voltage was negative, the wetting performance was strongly related to the carrier velocity of water electrolysis that was strongly dependent on the applied voltage. When the applied voltage was positive, the interfacial capacitance C on the quadratic voltage term was -4.49745×10^{-4}. Negative capacitance was related to the electronic structure of the sprayed graphene film, and the coefficient of the first-order voltage term of
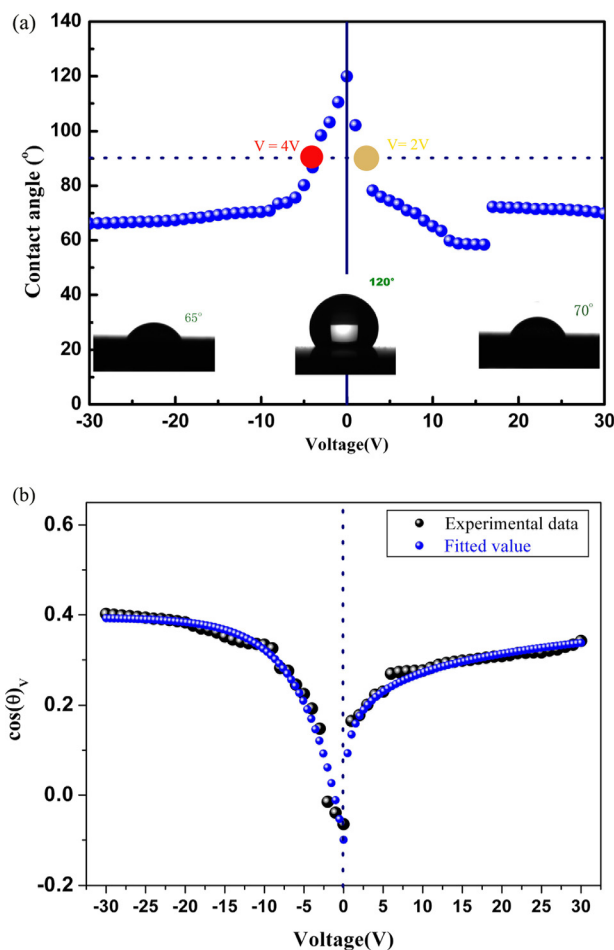

FIG. 4. The CA and the corresponding $\cos(\theta)_V$ switchably changed when the applied electric field was varied.

0.0197 was related to the roughening effect of the graphene film surface. Thus, two main factors might synergistically contribute to the controllable electro-wetting property of the graphene surface as follows: First, based on the reorientation of charges on the three-phase contact line under the applied potential, electro-induced capillary effects along with water spreading through the roughened graphene were responsible for the transition from the Wenzel state to the Cassie state; second, the water electrolysis induced by electrical potential and the reduction–oxidation reaction among the solid/liquid interface resulted in the chemical variation in the graphene surface, causing the tunable wetting transition to some extent, which also resulted in the discrepancy in the turning point under different polar potential values.

Finally, different from thermo-responsive functionalized graphene nanosheets at room temperature,[31] the good thermo-sensitive wetting property of the graphene film was studied as shown in Fig. 5. Surprisingly, the CA first increased up to 140° and abruptly decreased to 50° at 300 °C. Then, the CA values almost remained constant above 300 °C, which resembled the result of a previous report on pristine CNT film.[18] Graphene inherently displays negative thermal expansion in the range 0 K to 2500 K estimated using a first-principle calculation. However, Yoon *et al.*[32] and Bao *et al.*[33] experimentally estimated the negative thermal expansion within the range 200 K to 400 K using Raman spectra and ~350 K by monitoring the slight change in the sagging of the graphene piece suspended over a trench, respectively. These analyses at least allowed us to exclude that the wetting activity of the annealed graphene film resulted from the chemical composition change below 200 °C. The inherent negative thermal expansion property of graphene can trigger the contraction of the graphene membrane, causing high wrinkle intensity and the subsequent increase in the micro/nano structured surface, which explains the increase in CA values from 50 °C to 200 °C. However, the subtle change in morphology of the graphene membrane cannot be observed using field emission scanning electron microscopy. As the temperature further increased, the more the hydrophilic covalent attachments onto the graphene membrane appeared, such as epoxy and hydroxyl groups. Moreover, water molecules easily interacted with the defective sites of the graphene surface, which competitively undermined the hydrophobic properties. Generally, thermal treatment can
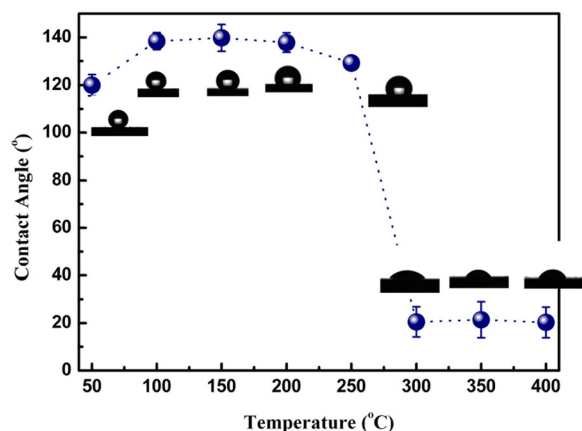
cause the accumulation of charge and transform the electronic structure of carbon-based nanomaterials from semiconducting to metallic,[33–36] which favored the improvement of graphene surface wettability. For example, the surface free energy at room temperature was derived as follows: graphite, 54.8 mJ/m^2; GO, 62.1 mJ/m^2; and graphene, 46.7 mJ/m^2.[37] It should be highlighted that the thermo-responsive property was a consequence of the morpho-chemical competition mechanism along with the restoration of electronic structure triggered by temperature.

In conclusion, stimulus-responsive smart graphene film possessing reversible switchable wettability was investigated using different external stimuli. The graphene film can be controllably switched from hydrophobicity to hydrophilicity. In essence, besides the fractal-like structured surface and the restoration of electronic structure for graphene, the transition from hydrophobic to hydrophilic state in the graphene film was mainly attributed to the solid/liquid interface reactions when exposed to different external stimuli. These stimuli include etherification reaction, protonation–deprotonation, water electrolysis, and thermo-oxidation. This smart graphene surface also holds great promise for the development of various engineered products.

FIG. 5. The CAs of graphene films varied with the thermal treatment.

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