



# Facile assembly of graphene and titania on micro-structured substrates for superhydrophobic surfaces

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## Abstract

Superhydrophobic surfaces based on chemically reduce graphene oxide (rGO) and titania (TiO<sub>2</sub>) nanoparticles on micro-structured K9 glass were facilely fabricated. Graphene oxide (GO) sheets were assembled on micro-structured K9 glass substrates by electrostatic self-assembly techniques. A positively charged rGO surface was achieved via reduction of GO by aniline vapors. Negative TiO<sub>2</sub> nanoparticles were assembled on rGO, and followed by surface modification with trichlorosilane. The resultant surfaces exhibited excellent superhydrophobic characteristics. A contact angle as high as 153.5° was achieved. The method is simple yet versatile, and the resultant structures are very useful because of the superhydrophobicity as well as light catalytic effects of rGO–TiO<sub>2</sub> hybrids, which make these as-tailored structures ideal candidates for self-cleaning applications.

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## 1. Introduction

Superhydrophobic surfaces have attracted increasing attentions [1,2]. Self-cleaning (anti-contamination) is the most important effect results from superhydrophobicity with water contact angle (CA) larger than 150°. Titania (TiO<sub>2</sub>) is a well-known widely used photocatalyst with long-term thermodynamic stability, low cost and non-toxicity [3–5]. TiO<sub>2</sub> can be used as a self-cleaning material and anti-pollution application. However, photocatalysis effect of TiO<sub>2</sub> is poor, because of its rapid recombination of electron–hole pairs and weak visible

light absorption [6]. Most recently, great interest has been focusing on compositing carbon nanomaterials [7], particularly graphene [8], hybridized with TiO<sub>2</sub> to improve their photocatalytic activities.

Graphene is a two-dimensional crystal with a single layer of carbon atoms [9]. It has excellent properties, such as ultrahigh mechanical stiffness [10], high conductivity, excellent electronic transport performance [11], and high thermal conductivity [12]. Intrinsically, the surface properties of graphene exhibits hydrophobicity because of its special structure and morphology [13,14]. The hydrophobic performance can be enhanced by modifications to get graphene with different micro-structures [15–17]. Chemical modifications were exploited to further increase hydrophobic performance. Graphene grown epitaxially on SiC showed slight hydrophobicity with CA of 92° [18]. The hydrophobicity of the chemically reduced

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graphene films could be enhanced by surface modifications [19]. Cheng's group presented 3D graphene foams fabricated by using a nickel skeleton upon which graphene was grown via CVD, the 3D graphene foam coated with Teflon exhibited superhydrophobicity, which has a CA of  $150.2^\circ$  [20]. Jin's group also demonstrated a porous composite composed of graphene and PVDF which exhibited a CA of  $153.0^\circ$  [21]. Zhang's group synthesized a free-standing superhydrophobic stiff composite films base on reduced graphene oxide/glassy carbon by the combination of in-situ polymerization and carbonization method [22]. Despite great advances have been made for superhydrophobic surfaces based on graphene materials, few work is reported focusing on graphene materials for superhydrophobic surfaces on devices. In this paper, we reported the superhydrophobicity of the surfaces based on the self-assembled hybrids of chemically reduce graphene oxide (rGO) and  $\text{TiO}_2$  nanoparticles. Graphene oxide (GO) sheets were assembled on micro-structured K9 glass substrates by electrostatic self-assembly techniques [23]. A positively charged rGO surface was achieved by aniline vapor. Negative  $\text{TiO}_2$  nanoparticles were assembled on rGO, and followed by surface modification with Trichloro (1H,1H,2H,2H-heptadecafluorodecyl) silane (THFS). A contact angle (CA) as high as  $153.5^\circ$  was achieved, which makes this structure an ideal candidate for self-cleaning applications in devices and other fields.

## 2. Experiments

### 2.1. Preparation of graphene oxide (GO)

Graphene oxide was fabricated from natural flake graphite by modified Hummers method [24]. A mixture containing 2 g of graphite and 50 ml of concentrated sulfuric acid was added into a 250 ml flask and stirred for 30 min. Then 1 g of  $\text{NaNO}_3$  was added and stirred for 2 h in an ice bath. Afterwards, 7.3 g of  $\text{KMnO}_4$  was slowly added in small amount batches during 1 h. Followed by stirring for 2 h after heating from the ice bath to  $35^\circ\text{C}$ . Then, 90 ml of distilled water and 55 ml of  $\text{H}_2\text{O}_2$  (4%) were added to the mixture, which was kept in water bath for 30 min at  $70^\circ\text{C}$ . The GO suspension was filtered, and washed with plenty of HCl (3%) and distilled water, and dried for 24 h at  $45^\circ\text{C}$  to obtain GO.

### 2.2. Self-assembly of GO nanosheets on K9 glass substrate

GO nanosheets were ultrasonically separated in deionized water to form homogeneous GO suspensions solution. K9 glass substrate was immersed in mixture solution of sulfuric acid and hydrogen peroxide ( $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=3:1$ ) in  $80^\circ\text{C}$  water bath for 30 min to achieve hydrophilicity. The substrate surface was decorated with a high concentration of hydroxyl groups. Then, the substrate was washed with distilled water and immersed in a 1 mM 3-Aminopropyltrimethoxysilane (APS) aqueous solution for 3 h. Thermal treatment in a vacuum oven at  $120^\circ\text{C}$  for 1.5 h was used to enhance binding force between APS and the substrate by  $-\text{NH}_2$  groups. The

positively charged substrate were immersed in GO aqueous solution for 16 h, followed by washing with deionized water and drying at  $120^\circ\text{C}$  for 2 h. Finally, GO nanosheets were self-assembled onto the K9 glass substrate.

### 2.3. Preparation of superhydrophobic graphene surfaces

The substrate with GO nanosheets was put into the reaction kettle with 1 mL of aniline as reductant for 12 h at  $120^\circ\text{C}$ . After cooling down to room temperature, the black surface films were washed with dimethylformamide (DMF) and deionized water for three times. The rGO films formed. The rGO surface were then modified with  $\text{TiO}_2$  and THFS to enhance the hydrophobicity: (1)  $\text{TiO}_2$  powder was dispersed in ethanol via sonication for 1 h, and then the substrate with rGO nanosheets was immersed in  $\text{TiO}_2$  ethanol solution for 12 h. Negative  $\text{TiO}_2$  particles were electrostatically self-assembled onto the positive rGO surface to form rGO- $\text{TiO}_2$ ; (2) 1 drop of THFS were added in 10 mL DMF in a vessel, and the substrate with rGO- $\text{TiO}_2$  films was immersed in mixture solution for 5 h, followed by washing with DMF and ethanol for three times; (3) The superhydrophobic modified rGO- $\text{TiO}_2$  (M-rGO- $\text{TiO}_2$ ) was formed by drying in the vacuum oven for 3 h at  $120^\circ\text{C}$ .

### 2.4. Characterizations

Atomic force microscopy (AFM) with tapping mode was used to evaluate the structure of the surface. The morphology characterization of the rGO/ $\text{TiO}_2$  on the micro-structures of the substrate was observed by using a Hitachi S-4800 scanning electron microscopy (SEM). Raman scattering was performed on a Jobin-Yvon HR-800 Raman spectrometer using a 633 nm laser source. Ultraviolet–visible (UV–vis) spectroscopy was measured from 200 to 800 nm by using UV-3600 (Shimadzu). The CA measurements were performed at room temperature with water droplets (3  $\mu\text{L}$ ) using an optical goniometer, the average contact angle was obtained by measuring at five different positions of the sample surface.

## 3. Results and discussion

AFM image of graphene oxide (Fig. 1) shows two-dimensional, irregular ultrathin sheet with size of micrometers and thicknesses of  $\sim 1$  nm. Most of the sheets were single-layer with an average thickness of about 1.2 nm. The results clearly showed successful exfoliation of graphite to form the individual graphene oxide platelets.

The few-layered GO nanosheets were successfully assembled on the K9 glass by self-assembly method and rGO was obtained by using aniline as reductant. Then, rGO was modified using a  $\text{TiO}_2$  and THFS to enhance the superhydrophobicity. In order to further enhance the hydrophobicity of rGO, K9 glass substrate with micro-structured surface were designed and fabricated. Fig. 2a shows rGO prepared on the micro-structured substrate. SEM images of chemically modified rGO are shown in Fig. 2b. The rGO surface became

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