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Facile fabrication of transparent, broadband photoresponse, self-cleaning multifunctional graphene–TiO_2 hybrid films

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ABSTRACT

We reported a novel approach to fabricate graphene–TiO_2 hybrid films by combination of the layer-by-layer (LbL) assembly and the surface sol–gel (SSG) process. The reduced graphene oxide (RGO) nanosheets and films were characterized by means of transmission electron microscopy, Raman spectroscopy, UV–visible absorbance spectroscopy, contact angle/interface system, and four-point probe. It was found that the graphene–TiO_2 hybrid film showed enhanced photoresponse performance compared with RGO thin film and TiO_2 thin film. The photoresponse properties of hybrid films could be manipulated by variation of the cycle numbers of RGO LbL assembly and titanium precursor SSG process. Photoinduced superhydrophility of the hybrid film was shown under broadband light illumination. The obtained transparent, superhydrophilic and conductive graphene–TiO_2 hybrid film showed excellent photoresponse, antifogging, and antistatic behaviors.

1. Introduction

Directed self-assembly of nano or microsized materials as building blocks in an aqueous environment is a very exciting research topic to construct large-scale but still uniform architectures [1–3]. Graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms, exhibits excellent optical transparency, high electrical conductivity, and ultrahigh mechanical strength [4]. As a new star nanomaterial, graphene shows great potential as an advanced building block for fabricating varied graphene-based functional architectures [5–7]. Layer-by-layer (LbL) assembly of charged nanosized building blocks is a controllable and reproducible route for generating large-scale but still uniform nanostructured films, and is considered as a promising candidate for creating function-embedded thin films [8–11]. Recently, we reported a new approach to the fabrication of flexible transparent conductive thin films through LbL assembly of oppositely charged reduced graphene oxides (RGOs) and benign step-by-step post-treatment [12,13].

Moreover, the development of graphene-semiconductor hybrids provides an important way to improve the performance of semiconductor materials in varied fields, because the hybrids have versatile and tailor-made properties with super performance [14,15]. Titanium dioxide (TiO_2) is a well-known semiconductor, owing to its outstanding properties such as wide-band gap, nontoxicity, low cost, and long-term stability [16,17]. Graphene–TiO_2 hybrids present interesting possibilities in different areas; especially, in photo-catalysis and optoelectronic devices, combining graphene with TiO_2 creates a metallic-semiconductor interface, which is very important for dissociating electron–hole pairs into separate charges [18–20]. Strategies to fabricate such hybrids range from coating of TiO_2 nanoparticles on graphene nanosheets [20–24] to alternate LbL assembly of titania and graphene oxide (GO) nanosheets [25–30], which require pre-preparation of TiO_2 nanoparticles or nanosheets. It is known that the surface sol–gel process is a facile, controllable and reproducible solution-based route for preparing large but uniform metal oxide ultrathin films using metal alkoxides as the precursors source [31–33]. Thus, it is interesting to consider whether the graphene–TiO_2 hybrid films could be facilely fabricated using titania precursor by the surface sol–gel process. To the best of our knowledge, this approach has not yet been used so far to rationally design and facilely fabricate graphene–TiO_2 hybrid films.

Furthermore, broadband light absorption and self-cleaning properties are also important for the promising potential applications of graphene–TiO_2 hybrids as optoelectronic devices [34]. On one hand, it is known that TiO_2 is only photoactive to ultraviolet (UV) light, but transparent to visible-near infrared (Vis–NIR) light. Thus, to overcome the drawbacks, additional plasmonic nanostructures or quantum dots are usually used to effectively increase the photoresponse of graphene–TiO_2 hybrids in the visible region [22–24]. In fact, GO or RGO has been explored to achieve high

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photoresponse in the UV and Vis–NIR region, which could be considered to achieve broadband light absorption of graphene–TiO_2 hybrids [35–37]. On the other hand, the self-cleaning property is a mutual effect between surface superhydrophility and electroconductivity, favoring the long-term efficiency of optoelectronic devices [21,38–40]. Surface superhydrophility could prevent fogging by almost instantaneously spreading condensed water droplets to form a thin sheet-like water membrane, while electroconductivity could prevent adsorption of particulate contaminants by an antistatic effect [41–45]. Recently, flexible, transparent and conductive thin films reported by our group exhibited tunable wettability with change of oxidation degree [12,13]. However, few studies have focused on the self-cleaning property of graphene–TiO_2 hybrids. To the best of our knowledge, there has been no report yet about the fabrication and application of graphene–TiO_2 hybrids both with broadband light absorption and self-cleaning properties.

Herein, we report a new approach to fabricate graphene–TiO_2 hybrid films by combination of the LbL assembly and the surface sol–gel process. Mild heat-treatment in a mixture of Ar/H_2 (19:1, v/v) at 550 °C was used. Effects of varying the RGO LbL assembly and titanium tetrabutoxide ($Ti(O^nBu)_4$) SSG process cycles were studied on the photoresponse properties of hybrid films. The antifogging and antistatic behaviors of hybrid films were also investigated and discussed.

2. Experimental section

2.1. Materials

Titanium tetrabutoxide ($Ti(O^nBu)_4$, $\geqslant$98%) was obtained from Alfa Aesar. Poly (diallyldimethylammonium chloride) (PDDA, Mw = 200,000–350,000, 20 wt%) was purchased from Aldrich. Graphite powder ($\geqslant$98%), hydrogen peroxide (30%), concentrated sulfuric acid (98%), hydrochloric acid (38%), hydrazine solution (35%), aqueous ammonia (25%), potassium permanganate ($\geqslant$99.5%) and ethanol ($\geqslant$99.7%) were purchased from Beihua Fine Chemicals. Ultrapure water with a resistivity higher than 18.2 MΩ cm was used in all experiments, and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

2.2. Synthesis of RGO nanosheets

GO was prepared from natural graphite by using a modified Hummers method [46]. As reported by our previous work [12,13], 25 mL GO dispersion (1 mg/mL) was diluted with 55 mL of deionized water under sonication for 5 min. To the GO dispersion were then added 250 μL of hydrazine solution (35%) and 1700 μL of ammonia solution (25%). The mixture was stirred at 90 °C for 1 h. After cooling to room temperature, the black homogeneous dispersion was used for the following assembly.

2.3. Fabrication of graphene–TiO_2 hybrid films, RGO thin film, and TiO_2 thin film

Silicon or glass substrates were cleaned by Piranha solution (98 wt% H_2SO_4/30 wt% H_2O_2, 7/3, v/v) (Caution: the Piranha solution is highly dangerous and must be used with great care). To fabricate $(RGO)_{10}$–$(TiO_2)_n$ hybrid films, a $(PDDA/RGO)_{10}$ thin film was firstly fabricated by alternate dip-coating of the pretreated substrates in the PDDA dispersion and RGO dispersion according to our previous work [13]. Then, the $(PDDA/RGO)_{10}$ thin film was dipped into an ethanol solution of $Ti(O^nBu)_4$ (50 mg/mL) for 5 min, washed in pure ethanol for 5 s, washed in pure water for 1 min to promote hydrolysis of $Ti(O^nBu)_4$, and dried by a stream of nitrogen. This process was repeated 5, 10 and 15 times to prepare $(PDDA/RGO)_{10}$–(titania gel)$_5$, $(PDDA/RGO)_{10}$–(titania gel)$_{10}$, and $(PDDA/RGO)_{10}$–(titania gel)$_{15}$ hybrid films, respectively. The films were then dried in air at 60 °C, and were further subject to mild heat-treatment in a mixture of Ar/H_2 (19:1 v/v) at 550 °C for 3 h.

To fabricate $(RGO)_n$–$(TiO_2)_5$ hybrid films, $(PDDA/RGO)_5$, $(PDDA/RGO)_{10}$, and $(PDDA/RGO)_{15}$ thin films were firstly fabricated by alternate dip-coating of the pretreated substrates in the PDDA dispersion and RGO dispersion, respectively. Then, The $(PDDA/RGO)_n$ thin films were dipped into an ethanol solution of $Ti(O^nBu)_4$ (50 mg/mL) for 5 min, washed in pure ethanol for 5 s, washed in pure water for 1 min to promote hydrolysis of $Ti(O^nBu)_4$, and dried by a stream of nitrogen. This process was repeated 5 times to prepare $(PDDA/RGO)_5$–(titania gel)$_5$, $(PDDA/RGO)_{10}$–(titania gel)$_5$, and $(PDDA/RGO)_{15}$–(titania gel)$_5$ hybrid films, respectively. The films were then dried in air at 60 °C, and were further subject to mild heat-treatment in a mixture of Ar/H_2 (19:1 v/v) at 550 °C for 3 h.

For comparison, the RGO thin film and TiO_2 thin film were also fabricated as follows. To fabricate the RGO thin film, the pretreated substrate was alternately dipped into the PDDA dispersion and RGO dispersion. 10 cycles were repeated. The film was then dried in air at 60 °C, and was further subject to mild heat-treatment in a mixture of Ar/H_2 (19:1 v/v) at 550 °C for 3 h. To fabricate the TiO_2 thin film, the pretreated substrate was dipped into an ethanol solution of $Ti(O^nBu)_4$ (50 mg/mL) for 5 min, washed in pure ethanol for 5 s, washed in pure water for 1 min to promote hydrolysis of $Ti(O^nBu)_4$, and dried by a stream of nitrogen. This process was repeated 10 times. The film was then dried in air at 60 °C, and was further subject to mild heat-treatment in a mixture of Ar/H_2 (19:1 v/v) at 550 °C for 3 h.

2.4. Photoresponse tests of graphene–TiO_2 hybrid films, RGO thin film, and TiO_2 thin film

The photoresponse properties of the films were directly measured in a probe station under ambient conditions using a standard two probe method both in dark and under illumination. A Xe lamp (200–900 nm) was used as the simulated solar-light source for illumination. The light intensity was measured at the distance (ca. 15 cm) where the Xe lamp was placed from the sample using a Newport calibrated Si detector. The broadband light (200–900 nm) was directly supplied by the Xe lamp and the Vis–NIR light (420–900 nm) was supplied by the Xe lamp with UV filter ($\lambda \leqslant 420$ nm). All data were recorded using a SourceMeter (Keithley 4200). The currents in dark and under illumination are defined as dark current and light current, respectively. The photocurrent is calculated by subtracting dark current from light current.

2.5. Characterization

The morphologies of the films were characterized by scanning electron microscopy (SEM) on a Hitachi S-4800 scanning electron microscope operated at 10 kV. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were achieved on a JEOL JEM-2010 transmission electron microscope operated at an acceleration voltage of 150 kV. The crystaline phases of samples were characterized using powder X-ray diffraction (XRD) on a Bruker D8 Focus X-ray diffractometer by using Cu Kα radiation (λ = 1.5418 Å) at a step size of 0.1° per second. Raman spectra were obtained on a Raman spectrometer (inVia-Reflex, Renishaw) with 532 nm wavelength incident laser light. UV–visible absorbance spectra were obtained on a Varian Cary 5000 UV/Vis–NIR spectrophotometer. $BaSO_4$ was used as a reflectance standard in a UV–visible diffuse reflectance experiment. Fourier transform infrared spectra (FTIR) were recorded on a Varian Excalibur 3100 spectrometer using the attenuated