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# Highly conductive free-standing reduced graphene oxide thin films for fast photoelectric devices

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ABSTRACT

Compared with mechanically exfoliated and chemical vapor deposited graphene, reduced graphene oxide (RGO) possesses unique advantages such as a wet process synthesis, high yield and the ability to assemble large-area thin films on various substrates. However, RGO is normally not recommended for advanced devices owing to its poor electrical conductivity. We report a new method to prepare highly conductive free-standing RGO thin films. The as-prepared RGO thin film possesses the highest conductivity of 87100 S $m^{-1}$, the second-lowest sheet resistance of 21.2 Ω $sq^{-1}$ and a medium-level mobility of 16.7 $cm^2$ $V^{-1}$ $s^{-1}$ among all of the reported RGO films. To demonstrate the application potential of the free-standing RGO thin films in photoelectric devices, a fully suspended RGO photodetector is constructed using the free-standing RGO thin film, which exhibits the fastest (*ca.*100 ms) and broadest (from the ultraviolet to terahertz spectral range) photoresponse among all of the RGO film photodetectors that have been reported. The response speed is even comparable with those of CVD-grown graphene photodetectors and mechanically exfoliated graphene photodetectors. These results pave the way towards high-conductivity RGO thin films by a wet process assembly, thus facilitating applications of RGO in advanced electronic, optoelectronic and sensing devices.



## 1. Introduction

Graphene is an appealing material for photonics and optoelectronics because it offers several advantages compared with other materials [1]. First, graphene is gapless, which enables charge carrier generation by light absorption over a very wide energy range, from the ultraviolet (UV) to terahertz (THz) spectral regimes. Second, graphene exhibits ultrahigh carrier mobility at room temperature, which enables ultrafast conversion of photons or plasmons to electrical currents or voltages [2,3]. Furthermore, graphene possesses low dissipation rates and the ability to confine electromagnetic energy within unprecedented small volumes, which result in strong light–graphene interactions [4,5].

However, good properties depend on good quality. Currently, there are several methods to prepare high quality graphene. Mechanical exfoliation of graphite is a method for the preparation of nearly defect-less high quality graphene but only with a very low yield and a very limited size on the micron scale. Epitaxial chemical vapor deposition (CVD) growth of graphene on silicon carbide is one of the most promising techniques to realize graphene-based electronics. The CVD route has recently been explored extensively to grow large-area and high quality graphene by using Ni films and Cu foils as the catalytic substrate [6,7]. However, the yields of graphene by these methods are generally low. Besides, a non-polluting transfer of the obtained graphene to the desired substrates is quite challenging. Alternatively, chemical exfoliation and reduction

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starting from graphite is a high-efficiency approach to produce reduced graphene oxide (RGO) sheets with high yield and low cost. The obtained RGO sheets, as building blocks, can be assembled into large-area RGO thin films on various substrates [8,9]. Unfortunately, RGO thin films obtained through the above method often exhibit poor electrical properties, such as a high sheet resistance of over 300 Ω $sq^{-1}$ [10–14], low conductivity usually below 36000 S $m^{-1}$ [15–18] and low carrier mobility of 0.01–1 $cm^2$ $V^{-1}$ $s^{-1}$ [19–21], which greatly restricts their application in electronic, photonic, optoelectronic and sensing devices.

Herein, we report a new approach to prepare a free-standing RGO thin film with exceptionally high conductivity, where GO sheets dispersed in ethanol were layer-by-layer assembled onto a pre-textured substrate by alternately drop-casting and drying, and then finally annealing at high temperature. The free-standing RGO thin film thus prepared possesses the highest conductivity of 87100 S $m^{-1}$, the second-lowest sheet resistance of 21.2 Ω $sq^{-1}$ and a medium-level mobility of 16.7 $cm^2$ $V^{-1}$ $s^{-1}$ compared with all of the reported RGO films. To demonstrate the application potential of the free-standing RGO thin films in photoelectric devices, a fully suspended RGO photodetector was easily fabricated on the basis of the as-prepared free-standing RGO thin film. The photodetector exhibits the broadest (ultraviolet to terahertz) and fastest (*ca.*100 ms) photoresponse among all the RGO film photodetectors reported so far. The photoresponse speed is comparable to those of CVD-grown graphene photodetectors and mechanically exfoliated graphene photodetectors.

## 2. Experimental

### 2.1. Preparation of GO sheets

GO was synthesized from natural graphite by a modified Hummers method. In a typical preparation, 0.9 g of graphite, 1.5 g of $K_2S_2O_8$ and 1.5 g of white phosphorus were mixed with 7.2 mL of concentrated sulfuric acid (98%) in a 250 mL round-bottomed flask. The mixture was heated and stirred for 4.5 h in an oil bath at 80 °C. Subsequently, the mixture was washed with water and dried at 60 °C, and then mixed with 1 g of sodium nitrate and 23 mL of concentrated sulfuric acid (98%) in a 500 mL round-bottomed flask. After 1 h of stirring in an ice bath, 3 g of $KMnO_4$ was added into the suspension under vigorous stirring. The addition rate was carefully controlled to keep the mixture temperature below 20 °C. After removal of the ice bath, the mixture was further stirred at 35 °C for 2 h. Then, 46 mL of deionized water was added slowly, and the diluted suspension was stirred for another 2 h. Subsequently, 40 mL of deionized water and 5 mL of $H_2O_2$ (30%) were added to the mixture, which was then washed with 5% HCl and deionized water, and dried at 60 °C to obtain GO sheets.

### 2.2. Preparation of free-standing RGO thin films

The overall fabrication process for the free-standing RGO thin film is schematically presented in Fig. S1. Typically, a silicon nanowire (SiNW) array was prepared by chemical etching of a silicon wafer [22]. A certain volume of the GO/ethanol suspension (0.1–1 mg/mL) was drop-casted (75 μL/~1 $cm^2$) on the top surface of the nanowire array. The GO/ethanol suspension rapidly spread out and completely covered the top surface of the nanowire array. The obtained nanowire array was then dried at 60 °C in an oven for three minutes prior to the next drop-casting. After multiple cycles of drop-casting and drying overnight in air, reduction of the GO was achieved by annealing at 1000 °C for 3 h in an Ar (95%)-$H_2$ (5%) atmosphere.

### 2.3. Characterization

The size and thickness of the GO sheets were investigated using atomic force microscopy (AFM) (MM8-SYS scanning probe microscope, Bruker AXR) on a mica substrate. To evaluate the wettability of the SiNW array, static contact angles of water and ethanol on top of the SiNW array were respectively measured under ambient conditions on a Kino SL200B3 automatic contact angle meter. The contact angles were calculated using the Young–Laplace equation simulation software provided with the equipment. The morphology and structure of the as-prepared SiNW array and RGO film were characterized using a field emission scanning electron microscope (Hitachi S-4800) operating at 5 kV. Raman spectra of the GO film and RGO film were obtained on a Raman spectrometer (inVia-Reflex, Renishaw, U.K.) with the incident laser light of 532 nm. The Fourier transform infrared spectroscopy (FTIR) spectra (800–4000 $cm^{-1}$) of the GO film and RGO film were measured on a Varian 3100 FTIR spectrometer with KBr pellets. Transmission and total reflection spectra of the RGO thin film in the wavelength range of 350–2500 nm were recorded using an integrating-sphere attachment on the UV/Vis-NIR spectrophotometer (Varian Cary 5000). The sheet resistance, conductivity, Hall coefficient and carrier mobility of the RGO thin film were determined by Van de Pauw's method on HMS-5000 (Ecopia) under ambient conditions. The measurements were performed for both the forward and the reverse directions of the magnetic field with $B = 0.556$ T and the electric current $I = 3$ mA. All parameters were means of five measurements.

### 2.4. Photoresponse measurements

UV, VIS, NIR, MIR and THz irradiations were achieved using a 375 nm laser with spot diameter of ~2 mm (MDL-III-375-100 mW, Changchun New Industries Optoelectronics Tech. Co., Ltd), a 532 nm semiconductor laser with a spot diameter of ~2 mm (MGL-III-532-200 mW, Changchun New Industries Optoelectronics Tech. Co., Ltd), a 1064 nm laser with a spot diameter of ~3 mm (MIL-III-1064-500 mW, Changchun New Industries Optoelectronics Tech. Co., Ltd), a 10.6 μm $CO_2$ laser with a spot diameter of ~3 mm (CCL-II $CO_2$ COSMETIC LASER, Tsinghua University) and a 2.52 THz gas laser with a spot diameter of ~3 mm (FIRL 100, Edinburgh Instruments Ltd.), respectively. For the $CO_2$ laser and THz gas laser, various powers for illumination of the sample could be achieved by adjusting the output powers of the lasers. For the other lasers, the powers for illumination of the sample could be tuned by using neutral density filters. Turn-on and turn-off of the illumination were achieved by an electromagnetic shutter (SSH-C2B, Opto-Sigma). All the photoresponse measurements were conducted with the laser spot positioned in the middle of the fully suspended RGO thin films and recorded using a Keithley 2400 Source Meter.

## 3. Results and discussion

### 3.1. Formation mechanism of free-standing RGO thin films

The line scan of the height profile of the GO sheet by AFM (Fig. S2) shows an average topographic height of approximately 1.15 nm, confirming that the as-prepared GO sheet consisted of 1–2 layers [23].

In the current approach, it is crucial for achieving free-standing appearance that makes the interaction between GO sheet and substrate significantly weaker than that between GO sheets. We propose that the design of the surface structure of the substrate can decrease the contact area between the GO sheet and substrate, and thus decrease the interaction between the GO sheet and substrate.