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A photochemical approach for preparing graphene and fabrication of SU-8/graphene composite conductive micropatterns

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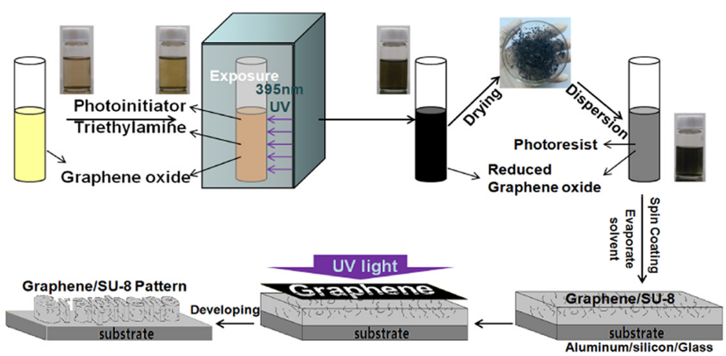
HIGHLIGHTS

- A metal-free photochemical reduction method towards graphene oxide is proposed.
- The mechanism relies on free-radical reduction and oxygen inhibition elimination.
- High electrical conductivity is obtained via removing oxygen containing groups.
- SU-8/graphene composite shows a facile processability on various substrates.

GRAPHICAL ABSTRACT



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ABSTRACT

We proposed herein a facile, fast and low cost metal-free photochemical method for preparing reduced graphene oxide (rGO) by ultraviolet (UV) irradiation of a solution containing mixture of a photoinitiator such as phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (GR-XBPO) and a triethylamine (TEA) in ethanol. Free radicals are generated via photoinitiator decomposition under UV irradiation. In this process, graphene oxide (GO) rapidly reduced to graphene via extensively removal of oxygen-containing functional groups (OFGs) by free radicals in the presence of anti-oxide inhibitor such as TEA exists. Furthermore, we prepared flexible conductive micropatterns over rGO/SU-8 composites deposited on several substrates (e.g., glass, polyethylene terephthalate (PET), aluminum, and silicon) by dispersing rGO into a photocurable SU-8 resin by means of a photolithography technique. The incorporation of rGO changed the properties of the composites. Thus, the behavior of SU-8 resin shifted from insulating to conductive/antistatic upon incorporation of rGO nanocomposites. This preliminary study provides us with the opportunity to not only develop an efficient metal-free photochemical reduction route towards GO but also obtain a processable conductive micropattern by optimizing the overall processing parameters, and maximizing the advantages of them for future carbon-based nanocomposites at large scale.

1. Introduction

The development of graphene-based materials has received a strong interest in recent years owing to the unique optical, electrical, thermal, and mechanical properties [1–4] and advanced and varied applications (e.g., energy storage, sensors, composites, semiconductors, and electrodes) of this material [5–11]. However, high-yield effective synthesis processes have to be developed before graphene-based materials can be successfully utilized in these fields [12]. Thus, graphene production has been intensively explored since its discovery [13]. Up to now, the main scalable and low cost route for graphene production is the two-

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step chemical/reduction approach [14]. This method offers potential scalability, impressive conversion efficiency, and superior processability, and several chemical methods have been performed under a variety of conditions [15]. Among them, a mild, high efficiency, low cost, simple and environmentally friendly method such as photochemical reduction has been used to prepare copper, silver, and gold nanoparticles [16–18]. The photochemical synthesis of metal nanoparticles allows controlling the rate of nanoparticle formation. Following the same idea, some works about GO reduction by this photochemical reaction with the assistance of a photocatalyst like TiO_2 [19–22], ZnO [23] and $BiVO_4$ [24] have been reported. However, the reduction with metal-free photocatalyst has been scarcely used, especially by a photoinitiator to prepare high conductive graphene materials.

Photolithography has been considered as a standard patterning method for decades owing to its well established procedures and particular characteristics (e.g., environmentally friendly, fast, and energy saving, among others) [25]. Furthermore, it is also a scalable and continuous micro/nanofabrication method of three-dimensional (3D) structures that has been proven to be an efficient approach for the development of micro- and nano-technologies [26,27]. Thus, under uniform illumination, a certain prepared pattern is transferred from a photomask to the light-sensitive photoresist material. Nanocomposite fillers allow providing the matrix with valuable properties such as electrostatic discharge, high mechanical performance, large operating temperature range, and chemical resistance, among others [28]. However, one of the most important factors influencing the properties of nanocomposites involves the uniform dispersion of the nanofiller into polymer matrix [8,9,29]. Recently, graphene has been proposed as filler, despite pristine graphene is prone to form irreversible agglomerates through van der Waals interactions [30–32]. Moreover, the structure of graphene is atomically smooth and lacks interfacial bonding [33]. In contrast, rGO nanoplates possess functional groups and are advantageous in that they can be added to the polymeric matrix [34].

Herein we propose a new facile method for obtaining graphene via photochemical reduction of GO using a photoinitiator. This graphene product was successfully added to a photoresist to form conductive flexible patterns on various substrates (e.g., glass, aluminum, silicon, and PET, among others), thereby rendering the substrate with new characteristics and potential applications in surface coating, smart window, and simple conductive devices, among others [35]. GR-XBPO is a free radical type photoinitiator commonly used in photoresists, while also showing high efficiency and weather fastness characteristics. We also demonstrated that photoinitiator alone can hardly reduce GO. Thus, TEA is an essential part in this process, serving as an anti-oxide inhibitor, and the reduction mechanism was explored. Furthermore, the final graphene product was used as a filler to prepare flexible patterns on various substrates via a photolithography technique, which is a critical step in bring these excellent materials to practical applications. The SU-8 epoxy-based resin is extensively employed in microfluidic and micro-optics devices because of its good mechanical, thermo-mechanical, chemical resistance and biocompatibility properties [36–38]. In addition to carbon-based nanofillers such as carbon-nanotubes(CNTs), graphene can largely improve the electrical and thermal conductivities of polymer composites owing to its unique nanostructure and superior properties [39,40]. The planar structure of graphene can provide a 2 D path for phonon transport, which in favor of the fabrication of graphene nanodevices, nanoscale graphene transistors and single electron transistors [41,42]. Additionally, the presence of residual epoxy reactive groups on the platelets of rGO allows proper binding between the conductive filler and the polymeric matrix, and the high surface area can enhance the electrical conductivity [27,31,33,34]. This article provides a paradigm for the photochemical production of graphene while also developing graphene-based materials by using this as a filler. We anticipate that this work can pay the way for the development of new electrical products while also allowing the development of carbon-based devices at large scale.

2. Experimental

2.1. Starting materials

Graphite powder (325 mesh) was purchased from Qingdao HuaTai Co, Ltd. SU-8 2050 photoresist and developer (Propylene Glycol Monomethyl Ether Acetate, PGMEA) were purchased from MicroChem, USA. Sodium nitrate (99.5%), potassium permanganate (99%), concentrated sulphuric acid (98%), concentrated hydrochloric acid (A.R.), ethanol (A.R.) and 30% H_2O_2 aqueous solutions were analytical-grade and obtained from Beijing Chemical Reagents Company. All chemical reagents were used without any further purification, and all the experiments were completed in our lab.

2.2. Preparation of GO and rGO

GO was prepared according to the procedure described by Hummers and Offeman [43]. In the case of rGO, a reactive solution was prepared by mixing GO (4 mg), photoinitiator GR-XBPO (60 mg), TEA (4 mL) and ethanol (20 mL) in a transparent test tube. The suspension was irradiated with a 395 nm UV light source placed at a distance of 10 cm, for 10 min at ambient temperature in a dark environment. The radiation intensity of the 395 nm UV light source is 100 mW/cm^2. The radiation intensity was measured with an actinometer built by the Photoelectric Instrument Factory of Beijing Normal University. The final rGO was obtained by centrifugation of the black precipitate, washed with ethanol three times, dried at 65 °C for 5 h, and finally characterized.

2.3. Fabrication of rGO/SU-8 pattern

The as-obtained rGO was dispersed in ethanol and ultrasonicated for 10 min. The resultant suspension was subsequently added to the SU-8 photoresist. After 20 min of stirring in a beaker at 50 °C, a rGO sheet was uniformly dispersed in the SU-8 photoresist. SU-8 is a negative tone photoresist, and the patterned structures were prepared by the following process. First, the substrate (e.g., polyethylene terephthalate (PET), glass, aluminum, and silicon) was ultrasonically cleaned with isopropyl alcohol and dried with a purified nitrogen stream. The substrate was subsequently pre-baked at 95 °C for 10 min in a convection oven to remove potential moisture and contaminant traces. A typical spinning process for preparing SU-8 photoresist films on substrate was carried out (800 rpm for 10 s, then 1200 rpm for 60 s) on a SC-1B spin coater, followed by 65 °C (10 min) and 95 °C (30 min) soft bake processes. Next, the photoresist bearing a patterning mask was UV exposed on an Oriel exposure tool (light intensity: 360 mJ/cm^2) for ca. 6 min. The exposed photoresist samples were subsequently subjected to a post-exposure bake (PEB) for 30 min at 95 °C. The development process was carried out on an SU-8 developer from MicroChem (SU-8 Developer) to get rid of the unwanted SU-8 coverage.

2.4. Characterizations

The structure of the samples was analyzed on a Shimadzu X-ray diffraction (XRD) device model XRD-6000 (Cu Kα radiation, 1.5406 Å). The quality and structure of the GO and rGO layers were further characterized by Fourier transform infrared spectroscopy (FTIR) on an IRAffinity-1/Shimadzu spectrometer) in the 400–4000 cm^{-1} range, operating in the transmission mode. The samples were further characterized by X-ray photoelectron spectroscopy (XPS, ESCSLAB 250Xi/ThermoFisher) and by Raman spectroscopy (LabRAM Aramis/Horiba Jobin Yvon). The UV–Vis spectra were acquired on a PerkinElmer-LS55 instrument in the 200–700 nm range.

The morphologies of the GO and rGO films were characterized by scanning electron microscopy (SEM, S-4800/Hitachi) without any pretreatment. Transmission electron microscopy (TEM) imaging and electron diffraction were conducted on a TF 20 microscope. The TEM