



Homogeneous transfer of graphene oxide into photoresist: Fabrication of high surface area three-dimensional micro-arrays by modified photolithography

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ABSTRACT

Herein, we studied the homogeneous transfer of graphene oxide (GO) into photocurable SU-8 photoresist for fabricating GO/SU-8 three-dimensional (3D) composite micropillar arrays by modified photolithography. SU-8 is a negative toned epoxy based photoresist, which includes 8 epoxy groups in each SU-8 monomer. The effects of the concentration of GO flakes on the thermal, mechanical and specific surface area (SSA) properties of the resultant composites were investigated. The large amount of oxygen functional groups on the GO plane and at the edges allowed uniform distribution of GO sheets within the SU-8 resin. The GO/SU-8 micropillar arrays were fabricated by a versatile ultraviolet (UV) photolithography technique that allowed the synthesis of various 3D micro–nano integrated carbon microelectrode arrays. The integrated GO flakes were bonded to the surface or embedded within the primary structure of SU-8 micro-pillars. These SU-8 micropillars having surface-bonded or embedded GO flakes showed superior thermal stability, strength, and SSA characteristics than bare SU-8 micropillars. Thus, this new synthesis approach provides a novel route for developing high performance catalysts, sensors, and adsorbents, among other materials.

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1. Introduction

Carbon composite materials based on graphite, carbon fibers, fullerene, carbon nanotubes (CNTs), graphene oxide (GO), and graphene nanosheets have been widely studied in recent decades owing to their superior specific surface area (SSA), electrical/thermal conductivity, and mechanical properties [1–8]. The utilization of carbon materials provides these composites with optical, electrical, magnetic, mechanical, and thermal properties that may otherwise be difficult to achieve using organic polymers alone [1,4,9–11].

Up to date, extensive research efforts have been devoted to explore the effect of incorporating carbon nanotubes (CNTs) into different matrices [12–14]. Since CNT/polymer nanocomposites were first synthesized in 1994, numerous researchers have attempted to develop a new class of reinforced materials by incorporating of CNTs into a variety of polymers [12–19].

Unlike CNTs, GO is composed by a single graphene layer of

carbon atoms which are oxidized to form various surface oxygen functional groups (e.g., hydroxyl, epoxide, carbonyl, and carboxyl) [20,21]. GO sheets present higher surface-to-volume ratios than single wall nanotubes (SWNTs) whose inner surface is inaccessible to polymer molecules. Thus, GO sheets are potentially more suitable for altering the properties (e.g., mechanical, permeability, and degradation stability) of polymer matrices [5,21–23]. Graphene has attracted both academic and industrial interest since it dramatically improves the properties (e.g., mechanical strength, thermal and electrical conductivities) of polymer matrices at very low filler contents. However, pristine graphene disperses poorly in the most common solvents, making it non-compatible with organic polymers. Additionally, bulk graphene does not form homogeneous composites because of its pronounced tendency to aggregate when forming polymer composites, especially at higher loadings. In contrast, GO sheets are comprised of heavily oxygenated graphene layers that can significantly enhance the compatibility with polymer matrix [20]. Moreover, GO can be prepared with high yields, which facilitates its wide application. Hence, GO has attracted considerable attention as a nanofiller for polymer nanocomposites since it was first synthesized by Brodie [22–24]. GO is an excellent

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carbon material with high SSA and rich in surface groups. Thus, GO has been incorporated into a wide range of polymer matrices including epoxy, polystyrene, and nylon with the aim to improve the properties of the resultant composite materials [5,25,26].

As recently demonstrated, the exfoliation behavior of GO can be altered by modifying the surface properties of its sheets via chemical functionalization [27]. Thus, routes involving covalent modification by amidation of the oxygenated groups [28], diazonium salts coupling [29], and grafting of polyvinyl alcohol (PVA) on the carboxyl groups placed at the edges of the GO planes have been developed [30]. All these works were aimed at achieving fillers uniformly distributed within the matrix, thereby significantly facilitating the practical use of these materials. While both covalent functionalization and non-covalent dispersion of GO in polymers have been explored, the former approach is not suitable for most applications especially because it may alter the intrinsic properties of GO [31]. In contrast, non-covalent dispersion is considered to have less impact on the structure and properties of GO [32].

In the present work, we successfully dispersed GO sheets into SU-8 photoresist to form a homogeneous composite by using cyclopentanone (CP) as a transfer solvent.

SU-8 is an epoxy-based negative resist with cyclopentanone as the solvent, which is commonly used as a photoresist material for the fabrication of high-aspect-ratio three-dimensional (3D) microelectrode arrays *via* lithography [14,33,34]. SU-8 consists of monomer, organic solvent and a photo acid generator (PAG). Upon UV irradiation, the PAG, which is sensitive to ultra-violet (UV) light, will generate acid to trigger the opening of the epoxy rings and their crosslinking [35]. The crosslinked structure is transparent and processes high thermal stability and good chemical resistance [36]. It was chosen as the matrix material because it has good compatibility with conventional microfabrication techniques, and it is easy to process, especially in the fabrication of microfluidic devices [37], AFM probes [36], biochemical sensors [38] and cantilevers [39, 40].

Actually, photoresists composites with carbon as filler had been studied for several years [35,41,42]. In this work, with the aim to confirm the uniform distribution of GO flakes within the SU-8 matrix, comprehensive morphologic and spectroscopic analyses were carried out. Additionally, the effect of the loading of GO flakes on the mechanical strength and thermal properties of the composites was investigated. The obtained results suggested that the GO flakes can significantly alter the GO–polymer interface, resulting in polymer matrices with enhanced mechanical and thermal properties.

In addition, 3D micropillar arrays with different GO loadings were fabricated (see Scheme 1). The high SSA of the GO sheets distributed within the GO/SU-8 micropillar resulted in surface effects governing the behavior of the composites. The method developed herein allowed wide utilization of GO while

constructing arbitrary structures. In particular, the 3D architectures exhibit many interesting advantages such as high surface to volume ratio, enhanced mass transport characteristics, and high reactive site density over a specific device area [43–45]. The increase in the surface area of the composites can improve related properties such as the catalytic activity or surface adsorption and reaction processes [45].

In summary, the designed route allowed hybridization of polymer materials, modifying the mechanical strength, thermal stability, and SSA characteristics of the resultant 3D composites. Thus, this route allowed easy fabrication of high-performance materials to be used as sensors, catalyst carriers, and adsorbents. We believe that this work can contribute to facilitate the preparation of GO-polymer composites and to the development of a broad class of GO-based hybrid materials.

2. Experimental section

2.1. 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. Cyclopentanone (CP) (99%) was purchased from Thermo Fisher Scientific, China. Sodium nitrate (99.5%), potassium permanganate (99%), concentrated sulphuric acid (98%), concentrated hydrochloric acid (A.R.), ethanol (A.R.) and 30% H₂O₂ aqueous solutions were analytical-grade and obtained from Beijing Chemical Reagents Company. All chemical reagents were used without any further purification.

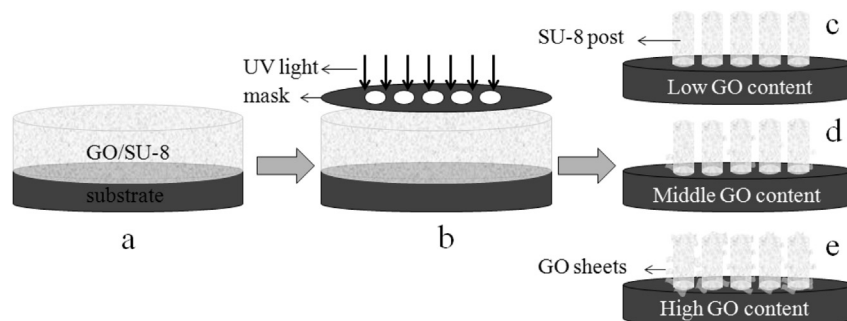
2.2. Preparation of GO and GO-dispersed SU-8 photoresists

GO flakes were synthesized from natural graphite powder by using the typical modified Hummers method (see Supporting Information).

GO-dispersed SU-8 photoresists were typically prepared by ultrasonication with PGMEA and CP as solvents. First, the as-prepared GO samples were ultrasonically dispersed in PGMEA and CP to prepare uniform slurry. The resulting slurry was subsequently mixed with SU-8 photoresist and stirred for ca. 40 min. Finally, after ca. 30 min of ultrasonication, and subsequently put into an oven at 80 °C for 3 h to evaporate most of the solvent, GO-dispersed SU-8 photoresists with different GO concentrations (i.e., 0.05, 0.1, 0.2, 0.4, 0.8, and 1.6 wt%) were obtained.

2.3. Photolithography process

The typical process flow of our photolithography method is



Scheme 1. Process flow for the fabrication of GO/SU-8 micropillar arrays. (a) Spin-coating, (b) UV exposure, (c) development at low GO concentration, and (d) – (e) development at middle and high concentrations of GO flakes.

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