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Laser-induced chemical transformation of graphene oxide–iron oxide nanoparticles composites deposited on polymer substrates

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ABSTRACT

Ultraviolet laser irradiation of films composed of graphene oxide (GO) and GO–magnetite (Fe_3O_4) nanoparticles deposited on polydimethylsiloxane substrates is carried out. The irradiations are performed in vacuum and ammonia-rich gas environments. Electron and scanning probe microscopies reveal a rippling process in GO sheets as the accumulation of laser pulses proceeds, being the effect more pronounced with the increase of laser fluence. X-ray photoelectron spectroscopy analyses point to laser-induced chemical reaction pathways in GO completely different depending on the environment and the presence or absence of Fe_3O_4 nanoparticles. It is demonstrated that GO-based films with diverse type of oxygen- and nitrogen-containing chemical groups can be obtained by means of laser irradiation processes. The sheet resistance of these materials is also correlated to their structure and composition.

1. Introduction

Graphene oxide (GO) has become a material of great value due to its fascinating physicochemical properties [1–3] and to its ability to be transformed into a graphene-like material, called reduced graphene oxide (rGO). This deoxygenating process can be obtained in large-scale and in an exceptionally cost-effective manner. Besides, composite materials based on graphene/rGO and metal oxide nanostructures have emerged as a subject of enormous scientific interest due to their high potential impact in diverse technological areas [4–6]. Particularly, graphene- and rGO–Fe_3O_4 nanohybrids are very promising to be used as active materials in strong electromagnetic interference attenuation systems [7,8], chemical sensors [9,10] as well as in energy storage devices such as lithium ion batteries and supercapacitors [11,12], among others. It is worth noting that most of these high performance devices are preferred to be lightweight and conformable in

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order to be used in diverse types of systems [12,13]. Thus, the support of rGO–Fe_3O_4 composites on polymer substrates is desirable. Recent works point to the improvement of rGO and rGO–Fe_3O_4 materials' functional properties, such as oxygen reduction reaction yield and supercapacitor performance, after the nitrogen doping of the graphene structure [14–16] due to the modulation of optical and electronic properties [17]. Particularly, doping of graphene structure by graphitic (substitutional) nitrogen provokes a n-type behavior, whereas pyridinic and pyrrolic N may lead to a p-type performance, instead. Thus, an easy and versatile method for synthesizing N-doped graphene-based materials is driving great research interest.

The fabrication of rGO–Fe_3O_4 hybrid materials is typically achieved by complex chemical methods many of them involving high temperature processes [18,19] which cannot be compatible with polymer substrates. Moreover, most of the synthesis procedures usually use toxic and/or hazardous agents. Thus, it is necessary to develop environment-friendly methods for the preparation of these types of materials. Conversely, laser irradiation techniques have recently emerged as versatile, scalable, eco-friendly and easy ways for fabricating thin films composed of rGO–metal oxide nanostructures either by direct irradiation [20] or laser deposition [21,22] methods. Remarkably, the nature of ultraviolet pulsed laser radiation could lead to the attainment of new chemical pathways for the development of graphene-based nanocomposites with improved functionalities to be used in future devices. To the best of our knowledge, no works regarding the laser treatment of GO–Fe_3O_4 hybrids exist in the scientific literature.

We present the easy fabrication and characterization of rGO and rGO–Fe_3O_4 nanoparticles (NPs) composite films on polydimethylsiloxane (PDMS) substrates from their oxidized form (i.e., GO and GO–Fe_3O_4 composite films) by means of nanosecond pulsed UV laser irradiation. Though, in principle, any polymer can be used as substrate PDMS has been chosen due to its optical transparency, ease of functionalization as well as inert, non-toxic, and heat stability properties [23]. The experiments are done in vacuum and under ammonia-rich atmosphere conditions, which enables the reduction and nitrogen doping of the generated GO structures. Comparative studies of the morphology, chemical composition and sheet resistance of the irradiated GO/PDMS and GO–Fe_3O_4/PDMS composite films are shown, indicating a rich chemical phenomenology which depends on laser parameters and the chemical environment.

2. Experimental

Two types of dispersions were prepared for the synthesis of GO and GO–Fe_3O_4 nanocomposite films. The solutions respectively consisted of (i) 0.5 wt.% GO plates (sheets around 1 μm^2 area, provided by Nanoinnova Technologies), and (ii) 0.05 wt.% Fe_3O_4 NPs (about 50–100 nm in size, Sigma–Aldrich) and 0.5 wt.% GO plates, all of them dispersed in distilled water. The weight percentages used in this work ensure the mechanical stability and adhesion of the deposited films on PDMS, in addition to a moderate electrical conductivity provided the insulating nature of Fe_3O_4 NPs. The PDMS membrane used as substrate in our experiments was prepared pouring a mixture of PDMS oligomer and cross-linking agent (hardener) 10–1 in weight inside a plastic petri dish. The PDMS and the cross-linking agent were purchased from Dow Corning (SYLGARD® 184 Silicone elastomer kit). In order to ensure a flat and smooth PDMS substrate the mixture was cured at room temperature in a level surface during 24 h. After that, the cured PDMS substrate was peeled off from the plastic petri dish and cut with a razor blade in small pieces of $10 \times 10\ mm^2$ and about 1 mm in thickness. Next, in order to ensure a good film formation on top of the PDMS membrane, the PDMS pieces were plasma treated in air with a corona discharge during 2 min (Electro Technic Products, INC.) and subsequently placed under a pressurized chamber containing N-[3-(trimethoxysilyl)propyl]-ethylenediamine (TPEDA, Sigma–Aldrich, 97%) vapors. This treatment with TPEDA vapors was conducted during 12 h and facilitated the formation of amine groups on the PDMS substrate that favor a well spread film formation. The pressure was regulated to be around 0.5–0.8 bars during the treatment. Subsequently, 200 μL of the synthesized graphene oxide-based dispersions, previously sonicated during 1 h, were casted on functionalized PDMS substrates. GO/PDMS and GO–Fe_3O_4/PDMS samples were respectively heated at 100 and 50 °C until they dried. This methodology ensured a regular, unbroken and uniform film formation with thickness in the micron range.

The obtained samples were exposed to a laser irradiation process at room temperature inside a reaction chamber, which was previously evacuated down to a residual pressure of 10^{-4} Pa. Irradiation experiments were made using a Nd:YAG ($\lambda = 266$ nm, $\tau_{FWHM} = 3$ ns, $\nu = 10$ Hz) laser system (Brilliant model from Quantel), applying 10, 100 and 1000 subsequent laser pulses with an incident laser fluence of 40 and 100 mJ cm^{-2}. A squared laser spot, $1 \times 1\ mm^2$ in size, and highly homogeneous intensity distribution was used by means of a beam homogenizer and mask system. The irradiations were performed in vacuum (at residual pressure), or in ammonia (NH_3)-rich environment at nearby atmospheric pressure. In this last case, the NH_3-rich environment was obtained by flowing N_2 gas through an ammonia solution (30% v/v) and introducing the gas mixture in the reaction chamber. Non-irradiated reference drop-cast thin films (raw) were also prepared from initial dispersions for comparison to the laser treated ones.

Numerical simulations were carried out in order to obtain a general view of the laser-induced temperature evolution in simple GO and GO–Fe_3O_4 NPs systems (model described in Supporting Information). The calculations were done solving the two-dimensional heat equation in compact GO/PDMS films (0.1–1 μm GO film thickness deposited on PDMS substrate) and in 50 nm-sized Fe_3O_4 NP on GO/PDMS systems by means of COMSOL 5.0 software. For the sake of simplicity, and the lack of knowledge about the fine arrangement of the raw material and their real physical properties, the model only contemplated photothermal mechanisms in an idealized system, neglecting the effects of nanometric dimensions on optical properties and heat transport. The optical and thermophysical properties of GO and Fe_3O_4, summarized in