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Electrocoagulation driven fabrication of graphene oxide films

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ABSTRACT

A unique electrocoagulation based method enabling the deposition of graphene oxide (GO) films on copper was developed. This method involves two distinct steps, (i) electrocoagulation of GO particles dispersed in aqueous media, induced by copper ions produced at the anode and (ii) deposition of the particles onto the copper anode. Under acidic conditions, GO films with tailorable thicknesses (3–130 μm) were readily deposited on the anode by varying applied voltage and deposition time in a controllable manner. The GO particles exhibited negative zeta-potentials, facilitating deposition on the positive anode. The copper oxidation state in the GO film was confirmed using X-ray photoelectron spectroscopy to be 2+, while its concentration within the GO film was strongly dependent on the applied voltages and deposition time. This new approach can be extended to other metal substrates, opening up new avenues for employing GO in a wide variety of energy and membrane applications.

1. Introduction

Graphene oxide (GO), the oxidized counterpart of graphene, has found considerable applications as important constituents in electrodes [1–3] as well as in optoelectronic and photonic devices [4,5]. In addition, it has been shown to act as a strong barrier for oxidizing molecules, enabling anti-corrosion applications [6,7]. Further, reduction of GO has been a reliable route for obtaining chemically modified graphene platelets in large scale and low cost [8–13]. Recently, there has been significant interest in the utilization of GO thin films as filtration membranes underlined by their exceptional stability in water [14]. Their stability in water appears to be driven by the presence of multivalent metal ions within their matrix, that serve as strong cross-linkers [14]. While the focus of the above mentioned work was on examining the effect of the metal cations on the stability of the GO matrix in water, the underlying procedure for the cation integration within the GO film was accomplished in an uncontrolled and sometimes unintentional fashion.

In contrast, this work demonstrates, for the first time, the controlled and rapid formation of metal-ion-containing GO films from GO dispersions. Specifically, the method employed in this work is based on copper-ion-assisted electrocoagulation (EC) and deposition of GO particles on copper electrodes. Importantly, the thickness and the rate of deposition are controlled by varying the applied voltage and the concentration of GO particles under acidic conditions in the suspension. The EC-based method developed in this work has far-reaching technological implications and it provides a new avenue for obtaining stable metal-ion-containing GO films.

Electrocoagulation has been traditionally used as a method to separate ions and colloidal particles from wastewater [15]. In the classic EC process, metal cations are produced by electrochemical oxidation of a soluble anode. The multivalent metal ions can induce coagulation of particles in the suspension either by neutralizing the surface charge of the colloidal particles (if they are negatively charged) or by simply reducing the double layer thickness around the particles [16–18]. Much of the EC literature deals with coagulation of particles in the bulk of the dispersion. For the formation of films via the EC process, it is critical to selectively induce the coagulation very near the electrode surface.

In aqueous dispersions containing positively charged particles, film deposition at a cathode utilizing a combination of coagulation via cathodically generated hydroxide ions and electrophoretic (EP) migration has been reported [19,20]. The hydroxide ions, by their univalent state, are highly unlikely to be as effective as higher-valent cations in their coagulation power [21,22]. In the technique reported in this paper, bivalent copper ions with a high degree of coagulating power are generated near a copper anode to drive the anodic deposition of GO films from GO dispersions. On a related note, while previous work [23] has demonstrated that copper ions

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adsorb onto negatively surface-charged GO particles at acidic pHs, the ability to exploit and utilize EC-driven deposition of GO has not been demonstrated before. Additionally, in comparison to previous EP based deposition of GO films on conductive substrates [2,24,25], the developed method naturally allows for incorporation of metal ions, which is essential to ensuring the mechanical and chemical stability of GO films [14]. Further, the implemented procedure represents a readily scalable technique for the formation of GO films, which can be carried out at ambient pressure and temperature conditions.

2. Experimental

2.1. Preparation of graphene oxide

Graphene oxide (GO) was synthesized from natural graphite flakes (99.35% purity, 325 mesh, Asbury Carbons) based on a modified Hummers'method [26]. The graphite flakes (3 g, average diameter size 44 μm) and concentrated H_2SO_4 (69 mL, Honeywell, 96%, VLSI) were mixed in a beaker under magnetic stirring. Potassium permanganate ($KMnO_4$, 9 g, E.S.P. Chemicals, A.C.S reagent, Crystal) was then added to the graphite dispersion slowly over 30 min, while the beaker was in an ice bath. The dispersion was then kept at 40 °C for 30 min while being stirred vigorously. Deionized (DI) water (150 mL) was then added and the dispersion was stirred for 15 min at 95 °C. After being brought down to room temperature, more DI water (450 mL) was added, followed by a drop-wise addition of H_2O_2 (15 mL, Sigma-Aldrich, 30 wt % in H_2O, ACS reagent) to remove excess $KMnO_4$. Afterward, the dispersion was centrifuged at 6000 r.p.m. for 1 h. The settled solids were sonicated with 2 mL dilute HCl (2 mL of HCl purchased from Sigma-Aldrich as 37%, ACS reagent) in 250 mL of DI water. The resulting dispersion was centrifuged under the previously stated conditions. The settled solids were dispersed in water and centrifuged under the same conditions a final time. The resulting supernatant liquid was kept, while the settled solids were discarded. The supernatant liquid was ultrasonicated for 90 min. The primary suspension had a concentration of 13.5 mg/mL, a pH of 2, and a conductivity of 8.2 mS/cm. Other suspensions with varying concentration of GO and conductivity were also examined to discern the effect of dispersion properties on the ensuing quality of GO films deposited on the copper anode. For clarity, the GO dispersions from the primary medium will be referred to as Suspension A.

2.2. Deposition through electrocoagulation

GO films were deposited onto copper foils (0.127 mm thick, annealed, 99.9%). After pre-cleaning in 0.1 M HCl, copper substrates were electrochemically etched at 10 V in dilute sulfuric acid (pH ~2) to roughen the surface to promote film adhesion. In addition, the substrates were coated on the backside and the sides with epoxy (3 M, Scotch-Weld, DP 270 Clear) to eliminate deposition on the back of the substrate, as well as gas evolution on the sides. The copper sample was used as the anode, while a platinum cathode was used to perform EC in GO suspensions. Electrocoagulation was performed by applying the required potential across the electrodes using a Hewlett Packard 6334 A power supply. Deposition voltages ranged from 2 to 10 V and deposition times ranged from 2 to 60 s. The distance between the cathode and anode was fixed at 0.015 m. Acidic conditions were used in order to ensure the presence and stability of solubilized copper ions in the GO dispersion [27]. GO films on the anodes were removed from the deposition bath, rinsed immediately with DI water, and dried on a hot plate at 55 °C under a nitrogen purge (2 psi).

2.3. Characterization

The composition, morphology, and surface coverage of the GO coatings were characterized using a micro-Raman spectrometer (Jobin—Yvon Horiba Lab-Ram HR800), an X-ray photoelectron spectrometer (Kratos 165), and a single crystal X-ray diffractometer (Bruker Kappa APEX II Duo). Raman spectra were collected using an Argon ion laser (wavelength = 514.5 nm, 100 mW). Copper $K\alpha$ X-rays were used as the source for the XRD analysis. The XRD pattern was obtained at 2θ values ranging from 5° to 70°. The XPS analysis used a hybrid active lens mode and a charge neutralizer. The thickness of the films was measured with a profilometer (Dektak 6 M, Veeco) with a scan length of 2000 μm and a stylus force of 3 mg. The thickness was measured at 5 to 10 different locations on a given sample then averaged. Fracture surface cross-sections were

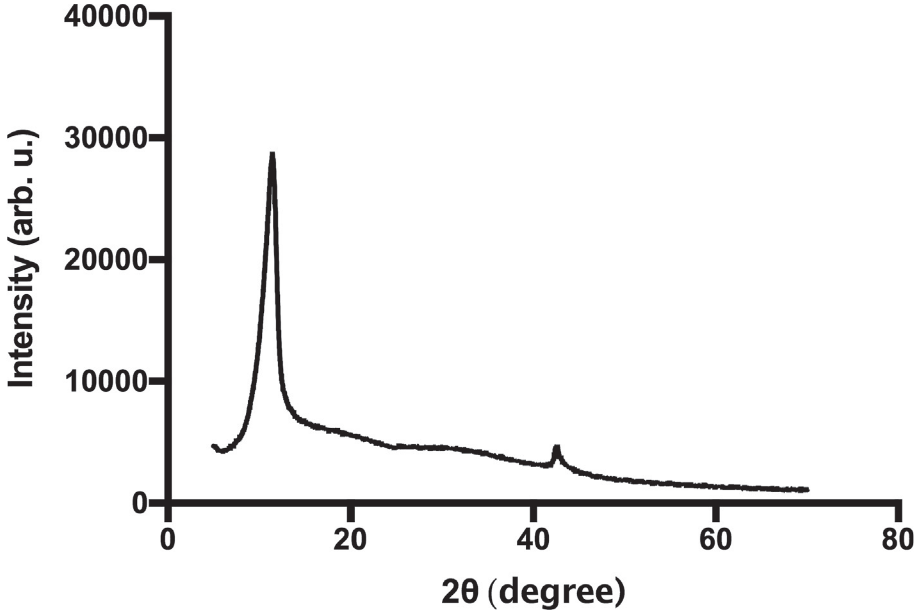

Fig. 1. Representative XRD spectrum of the graphene oxide produced using the modified Hummer's process prior to film deposition.