



Simple approach for large-scale production of reduced graphene oxide films



Ming Zhang^a, Bin Gao^{a,*}, Diana C. Vanegas^{a,b}, Eric S. McLamore^a, June Fang^a, Lin Liu^{a,c}, Lei Wu^a, Hao Chen^a

^a Department of Agricultural and Biological Engineering, University of Florida, Gainesville, FL 32611, USA

^b Department of Food Engineering, Universidad del Valle, Edif. 338, Ciudad Universitaria Meléndez, Cali, Colombia

^c College of Environmental Science and Engineering, Donghua University, Shanghai 201620, China

HIGHLIGHTS

- Ionic solutions can reduce GO at low temperatures to form films.
- The Re-GO films can directly be prepared onto target substrates.
- Re-GO film based sensor electrodes have better performance.

ARTICLE INFO

Article history:

Received 1 October 2013

Received in revised form 5 December 2013

Accepted 7 January 2014

Available online 17 January 2014

Keywords:

Graphene oxide
Reduction
Ionic solution
Low temperature
Graphene film
Sensor

ABSTRACT

The commercialization of graphene requires a new route for its industrial scale production that does not involve high costs, hazardous raw materials, and complex production techniques. Here, we report a simple and cost effective approach for producing highly conductive graphene films by reducing graphene oxide (GO) sheets without high-temperature annealing or any toxic solvent. At 90 °C, ionic solutions, such as MgCl₂, NaCl, AgNO₃, FeSO₄, CuCl₂, and AlCl₃, not only reduce GO but also cross-link adjacent graphene sheets to form reduced GO (Re-GO) films on various substrates. All of the GO-based films show color change from brown to grey and improved electro-conductivities. The as-prepared Re-GO films can directly be prepared onto target substrates without any transfer processes, which keeps the integrity of the films. Electrodes modified by Re-GO–metal nanocomposite films present extremely large electro-active surface area and fast amperometric response, which is promising for sensor development.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Graphene is an ultra-thin and ultra-light carbon material with high mechanical strength, super conductivity, and high surface area. Because of its unique mechanical, electronic, and optical properties, graphene is being utilized for various applications, including field effect transistors, sensors, transparent electrodes, batteries, supercapacitors, and composited materials [1–8]. Graphene is often prepared either through mechanical cleavage or chemical methods [9,10]. Chemical oxidation of graphite to exfoliated graphite oxide (GO) sheets, followed by reduction, has recently been suggested to be the most cost-effective way for large-scale production of graphene flakes/films (i.e., reduced GO (Re-GO)) [9,11,12]. In order to recover the unique properties of graphene from GO, various reduction approaches have been explored. These

techniques can be classified as ‘thermal annealing processes (high temperature annealing in vacuum) [13,14] or thermal wet processes (chemical reduction by strong agents in solution) [11,15]. These processes, however, either are expensive because of the requirement of heat resistant air-tight equipment or involve highly toxic reducing agents, such as hydrazine, N-Methyl-2-pyrrolidone, or dimethylformamide.

Nevertheless, the one-pot reduction approach has attracted tremendous attention in the past because of its relatively low cost and high potential for bulk production of Re-GO [12,16,17]. For example, GO can be reduced in a single reactor (one-pot) by using a formic acid [16] or a sodium-ammonia solution [12], or through hydrothermal reaction [17]. However, some of the reduction techniques may not be suitable for large-scale industrial production of Re-GO due to the risk of explosions (e.g., metallic sodium, liquid ammonia, inner pressure), environmental exposures of toxic chemicals and cost of hazardous material disposal (e.g., dimethylformamide, hydrazine, liquid ammonia), or requirement of multiple

* Corresponding author. Tel.: +1 352 392 1864x285; fax: +1 3523924092
E-mail address: bg55@ufl.edu (B. Gao).

starting materials (typically more than 3) and/or long reaction time (12 h–2 days). Furthermore, large size Re-GO films are easily fractured during the transfer of graphene films onto a target substrate via lift-off techniques. There are still critical needs for simple, environmentally friendly, and cost-effective approaches that are scalable for preparation of bulk quantities of high fidelity Re-GO films. Ideally, such techniques would not only simplify the production of graphene films for many applications with lower costs but also achieve direct deposition of the films onto target substrates without transfer.

Recent advances in ion solution mediated graphene-gel materials (e.g., hydrogel and aerogel) provide a great opportunity to develop a simple and environmental friendly method to produce highly Re-GO films on various substrates. Several previous studies have shown that highly conductive graphene-gel materials with large surface area can easily be fabricated by ion linkage, ion coordination, and redox reaction between the GO sheets and ions through hydrothermal treatment [18–22]. After some of these experimental processes were repeated in our lab, graphene/Re-GO films were observed along the inside of glass vials after hydrothermal treatment of 10 mL of 2 mg/mL GO and 0.5 mmol MgCl_2 solution at 90 °C (Fig. S1, supporting information). This interesting phenomenon was further investigated by directly dropping GO-ion (e.g., Mg^{2+} , Fe^{2+} , Cu^{2+} , Al^3 , Na^+ , or Ag^+) solution directly onto various substrates (e.g., glass, mica, metal, or plastic) without the hydrothermal treatment. We found that single to few-layer Re-GO films can be successfully prepared by heating the GO-ion solutions on target substrates at a low temperature (e.g., 90 °C) in air. Most importantly, the cations, particularly the divalent ones, in the GO-ion solution acted as an electrical “glue” (i.e., “cation bridge”), soldering (cross-linking) adjacent graphene sheets to form continuous films, such that electric contacts between the sheets can be dramatically improved. To demonstrate its potential multifunctional applications, this method was applied to create Re-GO-metal hybrid nanocomposite films on electrodes and showed attractive electrocatalytic activity because of graphene’s high electroactive surface, excellent sensitivity and selectivity, low Johnson noise, and fast response time.

2. Experimental

2.1. Preparation of graphene films

Sodium chloride (NaCl), silver nitrate (AgNO_3), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), ferric sulfate hexahydrate ($\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$), cupric chloride dehydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), aluminum chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), and lead acetate 30% w/v were purchased from Fisher Scientific. Graphene oxide (GO) with size of 1–5 μm was obtained from ACS Material. Chloroplatinic acid 8 wt.% was procured from Sigma–Aldrich; hydrogen peroxide 35 wt.%, and potassium nitrate (KNO_3) were acquired from Acros organics; potassium ferrocyanide trihydrate ($\text{K}_3\text{Fe}(\text{CN})_6$) was purchased from EMD chemicals. Phosphate buffer saline (PBS) was procured from Mediatech, Inc. All the chemicals are analytical grade and their solutions were prepared using deionized water (18.2 M Ω) (Nanopure water, Barnstead), which was also used to rinse and clean the samples.

Graphene/Re-GO films were prepared by adding 0.5 mmol of a chemical reduction reagent (NaCl , AgNO_3 , MgCl_2 , FeSO_4 , CuCl_2 or AlCl_3) to 10 mL of 2 mg mL^{-1} GO aqueous suspension in a 25 mL cylindrical sampler vial. The solution was stirred by a vortex genie for 30 s and then directly used to prepare graphene films. Prepared GO-based solutions are referred to as GO-Xy, where GO represents graphene oxide and Xy is a two-letter abbreviation for the added

chemical reagent. After reduction, the prepared GO-based films are referred to as Re-GO-Xy.

Although we found Re-GO films could be prepared on various substrates (e.g., glass, mica, metal, and plastic) with the reduction reagent at a low temperature (50–100 °C), this work mainly used glass substrate and 90 °C heating. Thus most of the Re-GO films were prepared from the corresponding GO-Xy solution by drop-casting the solutions on borosilicate glass slides. After drop-casting, films were baked at 90 °C in an oven for 6 h (in air). Film properties were characterized after the surface cooled to room temperature.

2.2. Film characterizations

The microscopic features of GO/Re-GO film samples were characterized by field emission gun scanning electron microscopy (FEG-SEM, JEOL 6335F), atomic force microscopy (SPM/AFM Dimension 3100) and transmission electron microscopy (JEOL 200CX TEM). X-ray photoelectron spectra (XPS) of the samples were obtained with a Perkin Elmer 5100 XPS System. X-ray diffraction (XRD) analysis was carried out to identify crystallographic structures in the sample using a computer-controlled X-ray diffractometer (Philips Electronic Instruments) equipped with a stepping motor and graphite crystal monochromator. Raman spectra were recorded using a Renishaw Invia Bio Raman using a 785 nm diode laser for excitation.

2.3. Sensor application

To evaluate their potential sensor applications, the Re-GO films were also prepared on the tips of the platinum/iridium working electrodes (BASI MF-2013, 1.6 mm diameter, 7.5 cm length, 6 mm shaft diameter, CTFE plastic body). Amorphous platinum nanoclusters were deposited on graphene films by electrodeposition in a solution of 0.728% chloroplatinic acid and 0.002% lead acetate, which is a common practice for sensors using carbon-based materials, such as carbon nanotube [23,24] and reduced graphene oxide [25–27]. The electrode was connected to the cathode of a DC power supply (Electro Industries), and a bare platinum wire (0.3 mm diameter; Alfa Aesar, Ward Hill, MA) was connected to the anode. A 10 V potential was applied to the solution for 90 s while stirring at 500 rpm [24,28,29]. Electrochemical characterization was performed using a 3 electrode electrochemical cell stand (C-3, BASI, West Lafayette, IN). Cyclic voltammetry (CV) was carried out in a 4 mM $\text{Fe}(\text{CN})_6/1\text{M KNO}_3$ solution at a working potential of 800 mV, versus a Ag/AgCl reference electrode with 10 s of quiet time, and 50, 100, 150, and 200 mV/s scan rates. DC potential amperometry was conducted at a working potential of +500 mV versus Ag/AgCl reference electrode with a sampling rate of 1 kHz. The electroactive surface area of the probes was determined using the Randles–Sevcik equation [30]. Amperometric sensitivity towards hydrogen peroxide was determined using DC potential amperometry (DCPA) while successively injecting hydrogen peroxide into a stirred PBS solution (450 rpm). Since there is a linear relationship between the concentration of hydrogen peroxide and the current output, the sensitivity values ($\mu\text{A}/\text{mM}$) were estimated directly from the slopes of the calibration curves. The lower limit of detection (LOD) was calculated using the 3σ method [29]. Response time (t_{95}) was calculated by calculating the time required to reach 95% of the measured steady state response for each successive step change. Average sensor performance characteristics were determined by calculating the arithmetic mean of three replicate tests.

Download English Version:

<https://daneshyari.com/en/article/147915>

Download Persian Version:

<https://daneshyari.com/article/147915>

[Daneshyari.com](https://daneshyari.com)