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Non-covalent functionalization of graphene with poly(diallyl dimethylammonium) chloride: Effect of a non-ionic surfactant

Prabhsharan Kaur^a, Mun-Sik Shin^b, Neha Sharma^a, Namarta Kaur^a,
Anjali Joshi^a, So-Ryong Chae^c, Jin-Soo Park^{b,*}, Moon-Sung Kang^b,
Satpal Singh Sekhon^{a,d,**}

^a Department of Physics, Guru Nanak Dev University, Amritsar 143005, India

^b Department of Environmental Engineering, College of Engineering, Sangmyung University, 31 Sangmyungdae-gil, Dongnam-gu, Cheonan, Chungnam Province 330-720, Republic of Korea

^c Department of Biomedical, Chemical, and Environmental Engineering, 701 Engineering Research Center, University of Cincinnati, Cincinnati, OH 45221-0012, USA

^d Department of Physics, The University of the West Indies, St. Augustine, Trinidad and Tobago

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ABSTRACT

Carbon based nanomaterials (carbon nanotubes, graphene etc) containing various hetero atoms are promising metal free catalysts for oxygen reduction reaction in fuel cells. We report the non-covalent functionalization of graphene with poly(diallyl dimethylammonium) chloride (PDDA), a polyelectrolyte containing nitrogen, using a very simple method. The addition of a non-ionic surfactant (Triton X-100) during functionalization has been observed to improve the interactions between graphene and PDDA. An up-shift in the position of G-peak in the Raman spectra, down-shift in the binding energy (B.E.) of N1s peak and an up-shift in the B.E. of C1s peak in XPS spectra have been observed due to an intermolecular charge-transfer from carbon in graphene to nitrogen in PDDA, which get enhanced in the presence of Triton X-100. Graphene functionalized with PDDA also show good thermal stability. The addition of a non-ionic surfactant enhances the non-covalent functionalization of graphene with PDDA, which is desirable from applications point of view. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The applications of graphene in diverse fields have recently generated much interest and are mainly due to its unique properties such as large surface area, high intrinsic mobility,

high thermal conductivity etc [1,2]. However, in pristine form graphene being chemically inert as well as insoluble in many organic and inorganic solvents, cannot be used in many applications. In addition, it is a zero band gap material. To render it suitable from application point of view, there is a

* Corresponding author. Tel.: +82 41 550 5315; fax: +82 41 550 5313.

** Corresponding author. Department of Physics, The University of the West Indies, St. Augustine, Trinidad and Tobago. Tel.: +1 (868) 662 2002x82591; fax: +1 (868) 662 9904.

E-mail addresses: energy@smu.ac.kr (J.-S. Park), sekhon_apd@yahoo.com (S.S. Sekhon).
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need for the modification of graphene either by functionalization (post-synthesis) or by doping (during in-situ synthesis). Out of the two main approaches used for functionalization (covalent and non-covalent), non-covalent functionalization is generally preferred as it can add various chemical moieties through van der Waals interactions without damaging or changing the atomic structure [3]. Doping of graphene with different hetero atoms in-situ during the synthesis is another route available for modifying its atomic and electronic structure. However, the post-synthesis functionalization is much easier than doping during in-situ synthesis. Nitrogen, which is next to carbon in the periodic table, is the most appropriate dopant in graphene due to their atomic size similarity. Recently, many studies have been reported on nitrogen doped graphene, which has potential applications in many devices like biosensors, fuel cells, and lithium ion batteries [4–6]. Graphene functionalized with a polyelectrolyte containing nitrogen, poly(diallyl dimethylammonium) chloride (PDDA), has been reported to have excellent activity as metal-free electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells [7]. As PDDA contains positively charged nitrogen (N^+) in its chemical structure, so it has strong electron-withdrawing ability which has been exploited for ORR. The adsorption of PDDA on graphene sheets results in charge-transfer from C (in graphene) to N^+ (in PDDA) and as a result it makes graphene electron deficient. The positively charged carbon atoms in graphene can then readily attract electrons from the anode of fuel cell and in turn enhances the ORR. Theoretical studies on interactions between graphene and a surfactant have been also reported [9–11].

During functionalization, many surfactants could be used as dispersing agents for carbon nanotubes (CNTs) and graphene [8]. In our earlier study on PDDA functionalized multi-wall carbon nanotubes [12], we have found that among the various surfactants used for dispersion of carbon nanotubes, Triton X-100 is not only the best dispersant but it also enhances the inter-molecular charge transfer from carbon in CNTs to nitrogen in PDDA. As the surfactant could also be used to disperse graphene, so it is reasonable to expect similar behavior in PDDA-functionalized graphene. This altogether set up the motivation for the present work.

In order to have efficient wrapping of PDDA on graphene, we have functionalized graphene with PDDA in the presence of a non-ionic surfactant (Triton X-100) by using a very simple method. The effect of addition of a non-ionic surfactant on the properties of graphene functionalized with PDDA has been studied by Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and thermogravimetric analysis (TGA).

Experimental

Materials

The graphene nanopowder (~8 nm in thickness; ~550 nm in average particle size) was supplied by Graphene Supermarket, Graphene Laboratories Inc., NY. All other chemicals used in

the present study are of analytical grade, and were purchased either from Sigma Aldrich or Merck.

Non-covalent functionalization of graphene with PDDA

The composition and codes of different samples studied in the present work are listed in Table 1. In the following text, these samples will be referred with their code names.

Preparation of G1

The sample G1 is pristine graphene and it has been used as received.

Preparation of G2

The sample G2 is graphene oxide (GO) and it was prepared by following the modified Hummer's method [13]. To prepare GO, 100 mg graphene nanopowder and 15 mL H_2SO_4 were taken in a round bottom flask and stirred over an ice-water bath for 180 min. After this, 600 mg $KMnO_4$ was added and the mixture was stirred for another 60 min while the temperature was increased from 0 to 30 °C. The sample was then diluted by adding 25 mL of de-ionized (DI) water, and refluxed in a hot oil-bath until its temperature reaches 90 °C. The solution was then allowed to cool to room temperature. After this, 60 mL DI water and 1.8 mL H_2O_2 were added to it slowly. A change in color of the sample from black to yellowish brown was observed, which indicates the oxidation of graphene.

Preparation of G3

The sample G3 is reduced graphene oxide functionalized with PDDA. This sample was prepared by adding 1.4 mL PDDA and 100 mL DI water to GO (G2) prepared above [14]. The solution was stirred for 7–8 h at room temperature, followed by ultra-sonication for 120 min. Further, 100 mg $NaBH_4$ was then added for the reduction of GO and it was again stirred for 30 min at room temperature. An oil-bath heat treatment was given to this sample at 130 °C for 180 min to ensure efficient reduction of GO.

Preparation of G4

The sample G4 is reduced graphene oxide functionalized with PDDA in the presence of Triton X-100. To prepare this sample, 1.4 mL Triton X-100 and 100 mL DI water were added to GO (G2) prepared above. The mixture was stirred for 7–8 h, followed by ultra-sonication for 120 min at room temperature. To this solution, 1.4 mL PDDA was added and it was again stirred for 7–8 h, followed by ultra-sonication for 120 min at room temperature. Then 100 mg $NaBH_4$ was added for the reduction of GO and it was again stirred at room temperature for 30 min.

Table 1 – The composition and codes of different samples.

Sample composition	Code
Pristine graphene	G1
Graphene oxide (GO)	G2
Reduced graphene oxide + PDDA	G3
Reduced graphene oxide + PDDA + Triton X-100	G4

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