



Hydrogenation and exfoliation of graphene using polyamine reagents



Jeremy Kintigh^{a,*}, Bogdan Diaconescu^b, Yolanda Echegoyen^c, Ahmed Busnaina^c,
Karsten Pohl^b, Glen P. Miller^a

^a Department of Chemistry and Materials Science Program, University of New Hampshire, Durham, NH 03824, USA

^b Department of Physics and Materials Science Program, University of New Hampshire, Durham, NH 03824, USA

^c Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, USA

ARTICLE INFO

Article history:

Received 24 September 2015

Received in revised form 14 March 2016

Accepted 5 April 2016

Available online 9 April 2016

Keywords:

Graphene
Hydrogenation
Exfoliation
STM
Nanoribbons
Graphane

ABSTRACT

An efficient hydrogenation and exfoliation of graphene has been accomplished using polyamines as hydrogenation reagents. The source of graphene can be either chemical vapour deposition grown graphene, bulk graphite or highly ordered pyrolytic graphite (HOPG). Hydrogenation of graphite and HOPG is accompanied by exfoliation yielding suspensions of single-layer and few-layer hydrogenated graphene or graphane. Graphane nanoribbons with aspect ratios greater than ten are produced in abundance during the polyamine hydrogenation of pre-sonicated bulk graphite. Graphane samples have been characterized by transmission electron microscopy, scanning electron microscopy, scanning tunnelling microscopy, low-energy electron diffraction, Auger electron spectroscopy and Raman spectroscopy as well as elemental analysis.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Since the discovery of graphene in 2004 [1], several methods to hydrogenate this nanostructured carbon have been reported including treatment with a hydrogen plasma [2–4], e-beam lithography [5,6], AFM nanolithography [7] and catalytic hydrogenation [8–9]. Alternatively, single walled carbon nanotubes can be hydrogenated and unzipped at elevated temperatures to form graphane nanoribbons [10], and graphene oxide can be reduced to graphane in an aqueous suspension under ⁶⁰Co gamma ray irradiation [11]. While none of these methods is scalable due to cost, slow processing, low yield, or difficulty in either isolating product or recovering catalyst, they nonetheless represent methods to create small quantities of graphane, a new nanostructured hydrocarbon. In principle, the electronic properties of graphene can be tuned from semi-metal to semi-conductor to insulator through controlled, judicious hydrogenation [12]. Graphane also has potential as a reactive intermediate for the formation of additional new materials. For example, Baek and co-workers demonstrated edge-functionalized graphene using a Friedel-Crafts approach [13]. Since Friedel-Crafts

reactions involve electrophilic (E⁺) substitution for hydrogen (H⁺), these reactions should be facilitated by graphane. Likewise, Tour and co-workers functionalized graphane produced from atomic hydrogen using an electrophilic diazonium salt, 4-bromobenzenediazonium tetrafluoroborate [14].

Recently, scalable hydrogenations of fullerenes [15,16] and carbon nanotubes [17] were achieved using polyamines at elevated temperatures as both solvent and hydrogenation reagents (Fig. 1). These reactions proceed via electron transfer from polyamine to nanostructured carbon to produce radical anions of nanostructured carbon and amine radical cations in a polar organic matrix that can support both species as transient intermediates. Subsequent proton transfer from acidic amine radical cation to nanostructured carbon anion produces a new C–H sigma bond. Iteration of the reaction sequence (electron transfer-proton transfer) yields hydrogenated nanostructured carbon in excellent yield.

We now report that graphene from either chemical vapour deposition (CVD) grown graphene, HOPG or bulk graphite is rapidly and efficiently hydrogenated using polyamine reagents to produce hydrogenated graphene or graphane. Unlike all other hydrogenation methods reported for graphene, the polyamine hydrogenation is simple and inherently scalable. CVD grown single-layer graphene on Ru(0001)

* Corresponding author.

E-mail address: jeremy.kintigh@gmail.com (J. Kintigh).

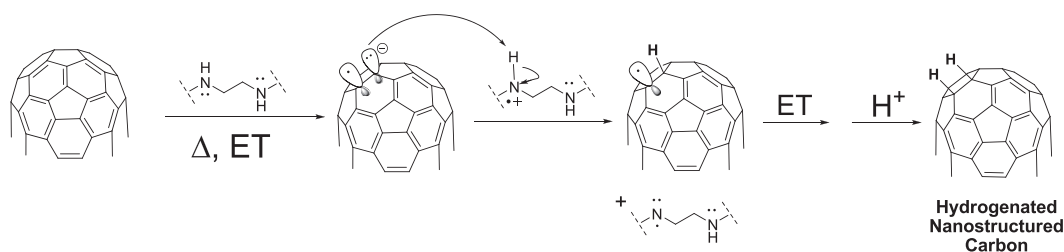


Fig. 1. Proposed mechanism for the polyamine hydrogenation of fullerenes and carbon nanotubes of references 15, 16 and 17.

is found to be quite reactive towards polyamines. It is readily and extensively hydrogenated using boiling diethylenetriamine (b.p. 204 °C). Bulk graphite and HOPG are both hydrogenated and exfoliated using boiling pentaethylenehexamine (b.p. 380 °C) leading to suspensions of single-layer and few-layer graphane.

2. Experimental

2.1. Materials

Diethylenetriamine (CAS: 111-40-0) and pentaethylenehexamine (CAS: 4067-16-7) were obtained from Sigma-Aldrich and used without further purification. HOPG disks were obtained from SPI Supplies. SEM stubs and TEM grids were obtained from Ted Pella, Inc.

2.2. Ball milling of bulk graphite

A sample of bulk graphite (300 mg, Sigma-Aldrich) was milled using a Retsch Mixer Mill 200 for either 99 min or 24 h at 30 Hz. A dilute suspension was prepared by placing 1 mg of milled graphite in 80 mL of denatured ethanol followed by brief sonication (2–5 s). Small volumes of the suspension were then applied to a 200 mesh lacey carbon grid for TEM imaging and an aluminum stub for SEM imaging.

2.3. Sonication of bulk graphite

A modified version of the method developed by Hamilton and co-workers [24] was utilized. Thus, a sample of bulk graphite (300 mg, Sigma-Aldrich) was suspended in 20 mL of absolute ethanol and sonicated for 24 h (VWR Model 150HT sonicator). A dilute suspension was prepared by placing 1 mg of milled graphite in 80 mL of denatured ethanol followed by brief sonication (2–5 s). Small volumes of the suspension were then applied to a 200 mesh lacey carbon grid for TEM imaging and an aluminum stub for SEM imaging.

2.4. Hydrogenation of bulk graphite and HOPG

In a typical experiment, 100 mg of either milled or sonicated graphite or an HOPG disk (1 mm, SPI Supplies) was added to 10 mL of pentaethylenehexamine in a 25 mL round bottom flask and heated to boiling (380 °C) under N₂ for 36 h. Denatured ethanol was added and the mixture was centrifuged at 5000 rpm for 30 min followed by solvent decanting. The process was repeated three times using fresh ethanol at each iteration. Excess ethanol was removed by rotary evaporation. For TEM and Raman characterization, a 1 mg sample was suspended in 80 mL of denatured ethanol and sonicated for 1–2 s. A small drop of the suspension was placed on a 200 mesh lacey carbon grid.

Alternatively, the hydrogenation of HOPG can also be conducted under high-pressure/high-temperature conditions. Thus, a 1 mm HOPG disk was placed in a high pressure reactor with an internal volume of 15 mL along with 3 mL of pentaethylenehexamine. The vessel was sealed and heated to 500 °C for 24 h. After cooling the vessel to room temperature, it was carefully opened in a fume hood. Caution: The amine containing gas produced by this reaction can cause nausea

and dizziness if inhaled. After proper venting, the reaction mixture was washed with ethanol three times allowing for the graphitic materials to settle for 30 min between each rinse. For TEM and Raman characterization, samples were prepared as described above.

2.5. CVD grown single-layer graphene grown on Ru substrate

Single layer graphene was grown and investigated in an ultra-high vacuum system with base pressure below 10⁻¹⁰ Torr [18]. Graphene was grown onto the clean Ru(0001) single crystal surface via bulk carbon segregation to the surface. The process is driven by a decreasing C solubility with increasing Ru bulk temperature, as described by Sutter and co-workers [23]. Due to the close lattice match of Ru(0001) and graphene, large micron-sized single domain graphene samples were grown.

3. Results and discussion

3.1. Graphane from CVD grown graphene and HOPG

In order to test whether or not the polyamine reagents were capable of hydrogenating graphene, we performed initial experiments on samples prepared from CVD grown graphene and HOPG. In the first case, we started with a well-defined, single-layer graphene grown in ultra-high vacuum (UHV) on the compact (0001) surface of a single crystal ruthenium sample. Single-layer graphene prepared in this manner was investigated by scanning tunnelling microscopy (STM) (Fig. 2a), low-energy electron diffraction (LEED) spectroscopy (Fig. 2c), and Auger electron spectroscopy (AES) (Fig. 2e). STM reveals the moiré pattern of graphene (Fig. 2a) with a triangular unit cell of approximately 3 nm [19]. The LEED pattern shows the six-fold symmetric diffraction spots of the underlying hexagonal Ru(0001) lattice surrounded by six-fold symmetric diffraction spots (or satellites) due to the graphene moiré overlayer structure (Fig. 2c); see Ref. 19. The AES spectrum shows only the corresponding signals for ruthenium and carbon (Fig. 2e, dotted line), as expected.

After the single layer graphene sample on the Ru(0001) substrate was prepared and characterized in UHV, it was moved to a preparation chamber, backfilled with an atmosphere of dry nitrogen, and subsequently vented to air. A few drops of diethylenetriamine (b.p. 205 °C at 1 atm.) were placed on its surface followed by fast annealing to about 200 °C for one hour while pumping the evacuated chamber back down to 10⁻⁸ Torr. In this way, the single-layer graphene sample was in contact with hot diethylenetriamine for less than 30 min. The sample was then moved back into the UHV chamber and outgassed for several hours at 200 °C. After cooling to room temperature, the sample was once again investigated by STM, LEED, and AES. The STM image of the polyamine treated sample (Fig. 2b) reveals a new, corrugated surface that lacks a moiré pattern. This surface roughening is consistent with a change in carbon hybridization from *sp*² to *sp*³, as expected to occur during hydrogenation. It is striking that the entire surface appears to have been modified, suggestive of extensive if not complete conversion of *sp*² hybridized carbon to *sp*³ hybridized carbon under polyamine conditions. The new LEED pattern (Fig. 2d) shows the presence of two

Download English Version:

<https://daneshyari.com/en/article/701768>

Download Persian Version:

<https://daneshyari.com/article/701768>

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