Synthesis of graphene paper from pyrolyzed asphalt

I. Francis Cheng a,*, Yuqun Xie a, R. Allen Gonzales a, Przemyslaw R. Brejna a, Jency Pricilla Sundararajan b, B.A. Fouetio Kengne b, D. Eric Aston c, David N. McIlroy b, Jeremy D. Foutch a, Peter R. Griffiths a

a Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA
b Department of Physics, University of Idaho, Moscow, ID 83844-0903, USA
c Department of Chemical & Materials Engineering, University of Idaho, Moscow, ID 83844-1021, USA

ARTICLE INFO

Article history:
Received 14 October 2010
Accepted 2 March 2011
Available online 12 March 2011

ABSTRACT

A new technique for the synthesis of large sheets (>10 cm²) of multi-layered graphene is presented. The condensation onto a heated surface (≈650 °C) of fumes from the thermal decomposition of asphalt in a ceramic crucible produces carbon films with a metallic sheen. Heating was done by a Fisher burner (natural gas/air) flame and the crucible was covered but exposed to laboratory atmosphere. These films were determined to be multi-layered graphene by scanning electron microscopy, atomic force microscopy, X-ray photoelectron spectroscopy (XPS), Raman and infrared spectroscopy and X-ray diffraction. XPS indicates that the films are primarily sp² hybridized carbon with small amounts of sp³ C–H and C–O or C–N functionalities. Based on the D band shift (1593 cm⁻¹) and the ratio of D band to G band (1354 cm⁻¹) of 0.93, the Raman spectrum also indicates that the material is sp² C with some nanocrystalline features. The infrared spectrum exhibits A₁U (868 cm⁻¹) and E₁U (1599 cm⁻¹) stretching of the intralayer bonds of graphene. This form of chemical vapor deposition may be scalable to give much larger surface areas. Furthermore, the process does not require metal substrates. Deposition onto silica nanosprings and diatomites is demonstrated.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Graphene has attracted much interest based on its observed and calculated properties [1,2]. This two-dimensional material is an extended monolayer of graphite. In a multilayered form it is referred to as graphene paper. This material, along with graphene oxide paper, has also garnered much interest in terms of its mechanical and electrical properties and as a precursor to monolayer graphene [3–12]. Application for such material ranges from use in Li ion batteries, supercapacitors, optically transparent electrodes and as catalyst supports [5,6,8,11,12]. Furthermore, graphene paper has been demonstrated to have thermal stability, and strong mechanical properties [3]. However, to exploit such opportunities a spectrum of synthetic routes will be required. Present methods include chemical oxidation of graphite to exfoliated aqueous graphite oxide (GO) followed by reduction with hydrazine in the presence of surfactants [10,13–17]. This is followed by the assembly of graphene paper (GP) by filtration. Another GO dispersion and reduction technique enhances the stabilization of aqueous colloids without surfactants [11,18–20]. Such techniques are successful at creating large sheets of graphene paper; however, they may prove problematic at depositing GP onto templates, and producing nano- and micro-structures. We demonstrate an alternative to the filtration techniques. In the procedure that we report in this paper, tars are pyrolyzed, producing fumes that condense and rearrange into layers of graphene on heated surfaces. In this thermolyzed
asphalt reaction (TAR) no precautions were taken to exclude oxygen from the reaction and the temperatures required for deposition are estimated to be about 650 °C. This method offers the possibilities of depositing very large sheets of GP onto nano- and micro-scale structures and through fabrication masks.

2. Experimental

2.1. Chemicals

The graphene precursor was plastic roof cement (Ace Hardware), which consists primarily of asphalt but included mineral spirits, clay, cellulose and water. Diatomites, which are commonly used for the filtration of swimming pools, were also obtained from Ace Hardware. The silicon wafer was obtained from University Wafer (Boston, MA). It was of 111 orientations with a 300-nm layer of thermal oxide, and resistivity of 0.001–0.002 ohm cm. Silica nanosprings were synthesized as described by previous procedures [21].

2.2. Reaction vessel and conditions

The reaction vessel was a 60 mL (70 mm) Coors casserole crucible with an inner 5 mL crucible holding the starting material. The inner crucible was filled with 5 g of asphalt precursor and placed in the larger casserole crucible as illustrated in Fig. 1. A watch glass covered the top of the apparatus. For the TAR process, the system was heated for 12–15 min with a Fisher burner followed by cooling for 5–10 min. The yield of TAR graphene based on the initial mass of starting material was 0.11% (n = 3, r = 0.08%) on the flat crucible target. This yield is surface area dependant as it was found to increase to 0.93% (n = 3, r = 0.24%) when 5.0 g of diatomites were added to the apparatus. Various target substrates were placed on the bottom of the outer crucible, these include a silicon wafer fragments and diatomites. A silicon wafer acted as a flat substrate for XPS, AFM, Raman, SEM and optical microscopy studies.

2.3. Material characterization

All images (see Fig. 2C and D) were produced from a Zeiss Supra 35 scanning electron microscope (SEM) (Carl Zeiss, Germany). The samples were produced by depositing graphene onto a Si wafer followed by cleaving with a diamond glass cutter. Transmission electron microscopy (TEM) observations were conducted with a JEOL 1200 EX II TEM at 120 kV. For the micrograph (Fig. 2E) multilayered graphene samples were prepared by first washing the flakes in ethanol then embedding them into epoxy. The embedded sample was trimmed with a wire saw, smoothed with a glass blade, then microtomed with a diamond blade perpendicular to the plane of the graphene sample giving 100 nm sections.

The X-ray photoelectron spectroscopy apparatus was built in-house at the University of Idaho. X-ray photoelectron spectroscopy (XPS) was performed in a vacuum chamber with a base pressure of $1 \times 10^{-10}$ torr. Measurements were made with the Mg K$_\alpha$ emission line (1253 eV) and a hemispherical energy analyzer with a resolution of 0.025 eV. The samples were cleaved using cellophane tape prior to insertion into the vacuum chamber. During spectral acquisition the samples were grounded and exposed to a 500 eV electron beam to eliminate spurious charging. All spectra were acquired at room temperature.

The scanning confocal Raman microscope system was a WITec Alpha300 (WITec Instruments Corp., Ulm, Germany). The laser excitation wavelength was 532 nm and the optical magnification at the objective was 20×, producing a spot size of roughly 2.5 μm in diameter. Spectral scans were taken at 1-s integration times with 60 averaged accumulations with a pixel resolution of approximately 2.4 cm$^{-1}$ for the wide scans. Post-acquisition data processing provides better than 1 cm$^{-1}$ discrimination, or effective resolution. Various incident power settings up to roughly 25 mW were used with no instability or transient effects observed in the spectra of the sample. Multiple locations across multiple samples were analyzed. For IR analysis, a graphene film was deposited onto a 1.2 cm Ge disk (99.999%, 4 mm thick) (Lattice Materials LLC, Bozeman, MT) as above. Infrared (IR) spectra were taken in...
transmission with 4 cm\(^{-1}\) resolution and 128 scans on a Nicolet Magna-IR 760 (Nicolet Instrument Corp., Madison, WI, USA) spectrometer equipped with a deuterated triglycine sulfate detector.

The atomic scale structure of graphene was obtained using a Veeco di CP-II atomic force microscope (AFM) operating in contact mode in air at room temperature. The AFM was operated in low-voltage mode to minimize electronic noise with a contact force (between cantilever and sample) of approximately 10\(^{-9}\) N; a 5-\(\mu\)m scanner was used to obtain the images. The probes were made of non-conductive silicon nitride with a cantilever spring constant of 0.01 N/m, nominally. Before the AFM observation, the graphene samples were cleaved in air to obtain a fresh surface free of secondary contamination. The topography images were obtained in constant-height mode where the tip-to-sample spacing is not varied, as typical where molecular or atomic accuracy is desired and at a scan rate of 15 Hz. Use of this fast scan rate reduces the effects of thermal drift resulting in improved resolution. Micron scale AFM of graphene was obtained using a different cantilever of spring constant 0.03 N/m. A large area scanner (100-\(\mu\)m) was used to capture the layers of graphene. Before observation under AFM, the graphene sample was cleaned with IPA and was air dried to remove any possible contaminations. A scan rate of 0.1 Hz was used to get an optimal resolution of step edges.

![Image](image-url)

Fig. 2 – (A) A photograph of a 25 mm diameter graphene paper flake. (B) An optical micrograph (400-\(\times\)) of exfoliated graphene paper in water. The bar is 200 \(\mu\)m. (C) 9.45 K \(\times\) SEM of the cross-sections of folded graphene paper layers on Si. The distance bar is 1 \(\mu\)m. (D) 23.08 K \(\times\) SEM of the sample showing the layered characteristics. The bar is 200 nm. (E) A TEM showing the layered characteristics of the material on the nanometer scale.
X-ray diffraction (XRD) analyses were carried out by employing a Siemens D5000 Diffractometer (Germany) equipped with an FK 60-04 air insulated X-ray diffraction tube with Cu anode, the XRD spectrums were taken with Cu Kα radiation (1.5406 nm) at 40 kV and 30 mA in the range of 2θ = 2–60°. The graphite powder (300 mesh) samples were obtained from Johnson Matthey Inc. (Seabrook, New Hampshire).

3. Results

The TAR procedure outlined above led to the formation of films with a shiny metallic appearance at the bottom of the outer crucible shown in Fig. 1. This is consistent with visual observations regarding GP [2,9,11]. In some cases, the film was observed to be strongly adhered to the ceramic. However, if the cooling rate was rapid it was possible to exfoliate large flakes of GP from the crucible. Fig. 2A shows a photograph of an approximately 25 mm diameter GP flake. Much larger flakes are anticipated by simple scale-up of the apparatus. The visual features of the GP sheets in this work seem relatively flat when compared to GP produced by filtration methods. The optical micrograph (Fig. 2B) demonstrates the flat nature of the sample. The flakes were suspended in water to ease handling; this caused the GP to curl in the fashion noted in that photograph. Scanning electron micrographs of this material are shown in Fig. 2C and D. The SEMs
demonstrate the planar nature of the GP sample, with flatness down to approximately 10 nm or less. It appears much flatter than the SEM’s of other GP materials [2,9,11]. The material tends to fold back upon itself, hence the two layers with a thickness of approximately 1 μm each with the bottom one on a silicon substrate (Fig. 2C). The micron-level layered characteristics are noticeable under higher magnification in Fig. 2D. This layered characteristic is seen with other SEM of GP and graphene oxide papers samples in the literature [3,7,22–25]. Under the higher magnification of TEM (Fig. 2E) layered characteristics are apparent at the nanometer scale. It is also noteworthy to add that the GP of this work tended to cleave in flat planes as evident in the micrographs.

The temperature required for deposition was estimated based on the melting point of aluminum which is 660 °C. When aluminum foil is introduced into the apparatus of Fig. 1, it was observed to soften but not melt. We therefore estimate the temperature for graphene deposition to be about 650 °C.

### 3.1 Characterization by AFM

The most notable feature of the micron scale AFM of the graphene sample is its flatness (±0.01 μm) which was evident over several mm² (not shown). This is in agreement with the optical micrographs, TEM and SEM’s of Fig. 2. Visual observations indicate that this flat nature extends indefinitely. Fig. 3 demonstrates the step-like features that form when the material is cleaved. The TEM of Fig. 2E illustrates the same feature on the nano-scale. These steps are observed by AFM with materials such as highly ordered pyrolytic graphite (HOPG) which has graphene layers with low mosaic spread [26–28].

The atomic-scale AFM image shows the sample topography in 2D and 3D (Fig. 4) obtained in contact mode under ambient conditions. The image matches the expected hexagonal lattice and interatomic C–C distance (0.148 nm) of graphene and graphite [29–32]. That distance was from line analysis shown in Fig. 4 (bottom) for a scanning area of 2.2 nm × 2.2 nm and a scan speed of 15 Hz.

Care was taken to ensure that anomalous effects did not alter the atomic force micrographs [33,34]. These effects include repulsive force associated between the tip and the sample of approximately 1–5 nN. Generally, under ambient conditions the surface is covered by one or more layers of absorbed water and other low molecular weight airborne contaminants leading to substantial capillary forces pulling the probe towards the sample with pressures of the order of
1 GPa. Also, there is often an appearance of atomic structure without attaining true atomic resolution for materials of planar anisotropy such as HOPG and mica, where the molecular layers are known to translocate in a corrugated fashion moving in registry with the AFM tip. Imaging can further be complicated by the electrostatic forces between the tip and sample. Atomic repeat structures in the graphene layer were obtained by minimizing the tip force with a softer probe of high resonant frequency operating at a low setpoint. As the analysis was performed in air, the image is dominated by the topmost atomic layers.

3.2. Raman and IR analyses

TAR samples gave two observable and relatively broad bands in the Raman spectrum centered at 1593 and 1354 cm$^{-1}$ (Fig. 5, top). These two bands are located near to the typical G ($E_2g$) and D ($A_1g$) peaks, respectively. The G and D bands are associated with the ordered sp$^2$ carbon, and disordered defects and edge carbons, respectively [35]. The wavenumber positions and relative peak intensities of the D and G bands ($I(D)/I(G) = 0.93$) indicate that the carbon in this sample is nearly all sp$^2$ in hybridization and is graphitic with some nanocrystalline features (see Fig. 7 of Ref. [35]).

The IR analyses were conducted by depositing graphene onto germanium and measuring the transmission spectrum.

Fig. 5 – (Top) Raman spectrum for the graphene material acquired in ambient air using 532 nm excitation; G mode peak at 1593 cm$^{-1}$ and D mode peak at 1354 cm$^{-1}$ at maximum intensity. (Bottom) IR spectrum of graphene on a germanium disk. The 861 and 1576 cm$^{-1}$ bands correspond to the $A_{1u}$ and $E_{1u}$ intralayer graphene stretches.

Fig. 6 – (Top) A wide XPS scan of cleaved graphene. (Bottom) XPS spectrum of the C 1s core level state of graphene. The peaks at 284.24, 285.15 and 286.15 eV are assigned to sp$^2$ C–C, C–N sp$^2$ and sp$^3$ C–O or sp$^2$ C–N, respectively.

Table 1 – XPS peak assignments.

<table>
<thead>
<tr>
<th>XPS peak</th>
<th>Possible assignment</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>284.24 eV</td>
<td>C=C, sp$^2$</td>
<td>[45–49]</td>
</tr>
<tr>
<td>285.15 eV</td>
<td>C=N sp$^2$</td>
<td>[45,46,49]</td>
</tr>
<tr>
<td>286.15 eV</td>
<td>C=OH, C–O–C, or C=N sp$^2$</td>
<td>[45–49]</td>
</tr>
</tbody>
</table>

The spectrum appears in Fig. 5. Two bands appear at 868 and 1599 cm$^{-1}$. The position of these bands, respectively, matches those of the $A_{1u}$ out of plane and $E_{1u}$ stretch of the intralayer bonds of graphene [36–39]. There are no peaks that match the expected positions for C–O or C=O stretches (1715–1740 and 1050 cm$^{-1}$, respectively) [40,41] nor between 3100 and 2800 cm$^{-1}$, which would have indicated the presence of C–H bonds. Thus the Raman and IR spectra both indicate that...
the GP is mostly carbon in the sp² form, and that oxides are not the predominant form of this specimen.

3.3. XPS analysis

Wide XPS scan (Fig. 6) reveals peaks that correspond to C 1s (284.2 eV), O 1s (533.3 eV), Si 2p (103.7 eV), Si 2s (155.6 eV) and N 1s (401.2 eV). Given that the samples were cleaved in air prior to insertion into the vacuum chamber, it is difficult to ascertain if the O 1s peak is due to adsorbed H₂O, CO, or CO₂. In order to resolve the origin of O, i.e., in situ incorporation, or ex situ adsorption, the sample was annealed to 800 °C in vacuum. No change in the binding energy or intensity of the O 1s core level state was observed, indicating that O is due to in situ incorporation into the graphene films. The presence of broad features between 5 and 20 eV in the valence band spectrum is attributed to semi-metallic graphite, as opposed to diamond for which these features are much more pronounced [42]. However, in the case of graphene XPS of the valence band alone is not sufficient for evaluating the metallic nature of the samples. The large peak at 25.5 eV is unassigned. However, Schafer et al. have suggested that the appearance of O on the surface of graphene the O 2p state mixes with the graphene valence band resulting in a feature around a binding energy of 26 eV [43]. This assignment appears to be consistent with the present study when taken in conjunction with the observation of O incorporated into the graphene film.

Curve-fitting of the XPS spectrum (Fig. 6, bottom) demonstrates the presence of bands at 284.24, 285.15 and 286.15 eV. The 284.24 eV band agrees well with literature regarding the sp² hybridized carbon–carbon bond. These include carbon nanotubes (CNT), graphite, graphene and...
reduced graphene oxide [44–49]. The peak at 285.15 eV holds two possibilities, C–H sp³, as has been noted with graphite, or C≡N sp², as has been suggested for nitrogen doped graphene and CNT [45,46,49]. The latter is worthy of consideration based on the appearance of the N 1s peak (401.2 eV) in the wide scan XPS of Fig. 6 and the lack of C–H stretches in the IR spectrum. The 286.15 eV peak is associated with C–O sp³, or other forms of C≡N sp² [45–49]. These assignments are summarized in Table 1.

3.4. X-ray diffraction

Fig. 7 shows the comparison of XRD diffraction patterns of natural graphite (top) and graphene paper (paper). The 002 XRD peak corresponds to 3.35 Å interspacing between the graphene layers. The sharp (0 0 2) peak at 26.5° is representative of graphite [50]. The broader diffraction (0 0 2) peak at 26.6° is typical of multilayered graphene indicating that the TAR process does indeed produce multilayered graphene [50–54].

4. Discussion

The various methods of physical characterization in this work all indicate that the deposited films by the TAR procedure of Fig. 1 are multilayered graphene (graphene paper). Visual observations (Fig. 2A and B) show a metallic appearance consistent with previous observations [2,3,11]. Figs. 2 and 3 show a layered and essentially an atomically flat surface. This layered characteristic is observable at both the nm (TEM of Fig. 2E) and the µ-scales (AFM, Fig. 3). The atomic-scale AFM image (Fig. 4) indicates an atomic structure consistent with the sp² hybridization of graphite/graphene [29–32]. This hybridization is verified by XPS (Fig. 5 and Table 1). Since the apparatus (Fig. 1) for vapor deposition is open to laboratory atmosphere, there is a possibility that the graphene is oxidized (to form graphene oxides). However, the elemental composition as indicated by XPS is nearly pure carbon (Fig. 6) with minor peaks to higher binding energy that can be visualized on curve fitting. Of these, the band at 286.15 eV is associated with C–O–C, however it is minor in comparison with reduced graphene oxide materials in the literature [45–49]. Furthermore, the expected binding energy for C=O in graphene oxide is 288.5 eV, which is absent in the XPS spectrum of Fig. 5. The IR (Fig. 4) spectrum indicates only an extremely weak C=O stretch and insignificant C–O stretch, confirming the XPS interpretation. The XRD of Fig. 7 is consistent with graphene [50–55]. Thus all these measurements strongly indicate a layered carbon material primarily of sp² hybridization, i.e., graphene paper (GP).

The estimated temperature for deposition of 650 °C compares well with contemporary techniques [55]. However, the TAR method does not require Fe patterned films as a substrate. Furthermore, other techniques require higher temperatures, typically 800–1000 °C. The TAR process also another interesting advantage over others, the ability to deposit graphene onto porous, textured and nanostructures. Fig. 8B–D illustrates the results of the deposition of graphene paper onto diatomites and silica nanosprings. Fig. 8A is the SEM of the untreated diatomites, which require a Au sputtered coating to prevent charging effects. On the other hand, graphene coated samples did not require this treatment. This gives the intriguing possibility of coating a variety structures and patterns with GP that cannot be done by present methods. Such applications may include composite materials, Li ion batteries, supercapacitors, RF shielding, thermal cooling and electronic devices.

5. Conclusion

The demonstrated (TAR) process is significant in several respects: (1) this is the lowest reported temperature for a chemical vapor deposition of graphene; (2) it is conducted under atmospheric pressures and in open containers without need to exclude oxygen; (3) no specialized apparatus is required and (4) no catalysts are required. Foremost, the simplicity of the technique will allow for the immediate implementation by other groups. Also, the large GP flakes produced by this pyrolysis method may provide an economical path to monolayer graphene through exfoliation. Further studies will be aimed at strategies for control of depth of layers, including monolayers, electrical conductivity studies and control of dopant concentrations through precursor purity.

Acknowledgements

The authors thank Dr. J. Franklin Bailey of the University of Idaho Center for Electron Microscopy and Microanalysis and to the internal Y-accounts of Drs. I.F. Cheng and D. McIlroy.

References

electrocatalytic oxygen reduction activity of graphene-
supported Pt₃Co and Pt₃Cr alloy nanoparticles. Carbon 

[51] Liu F, Zhang Y. Substrate-free synthesis of large area, 
continuous multi-layer graphene film. Carbon 
2010;48(9):2394–400.

[52] Wakeland S, Martinez R, Grey J, Luhrs C. Production of 
graphene from graphite oxide using urea as expansion–

[53] Pei S, Zhao J, Du J, Ren W, Cheng H. Direct reduction of 
graphene oxide films into highly conductive and flexible 
graphene films by hydrohalic acids. Carbon 

[54] Fan Z, Wang K, Wei T, Yan J, Song L, Shao B. An 
environmentally friendly and efficient route for the reduction 
of graphene oxide by aluminum powder. Carbon 

Nihei M, et al. Low-temperature synthesis of 
graphene and fabrication of top-gated field effect transistors 
without using transfer processes. Appl Phys Express 