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One- and Two-Dimensional sp²-Carbon Nanomaterials
Synthesis, Properties, and Applications

by

Abdul-Rahman O. Raji

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APPROVED, THESIS COMMITTEE

James M. Tour, Chair
T. T. and W. F. Chao Professor of Chemistry, Professor of Materials Science and NanoEngineering and of Computer Science

Pulickel M. Ajayan,
Benjamin M. and Mary Greenwood Anderson Professor of Engineering, Chair, Department of Materials Science and NanoEngineering

Angel A. Marti
Assistant Professor of Chemistry, Bioengineering, and Materials Science and NanoEngineering

HOUSTON, TEXAS
May 2015
ABSTRACT

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The unifying objective of this thesis is to synthesize, control, modify, hybridize, interface, understand, and apply one- and two-dimensional sp²-carbon nanomaterials. The materials include graphene (2D), carbon nanotubes (1D), and graphene nanoribbons (pseudo-1D); and their hybrids with each other. Other classes of materials such as molecules, polymers, and inorganic nanoparticles are also interfaced with the carbon materials. This thesis uncovers, demonstrates, and elucidates methods to (1) synthesize graphene with different number of layers; (2) to produce a full Li-ion battery based on a hybrid of graphene and carbon nanotubes; (3) to prepare a Li-ion battery electrode made from a composite of graphene nanoribbon (GNR) stacks and iron oxide nanoparticles; (4) to prepare an oxygen reduction reaction catalyst made from a composite of GNR stacks and silver nanoparticles; (5) to fabricate a conductive composite of GNR stacks and epoxy and employ it for Joule heating and deicing of surfaces; (6) to generate sprayable, electrically conductive, and radiofrequency transparent films made using functionalized GNR stacks for de-icing application; and (7) to produce conductive GNR films that are simultaneously radiofrequency and optically transparent. The various materials developed demonstrate the versatility of sp²-carbon in terms of synthesis, properties, and applications.
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Preface

The chapters are self-contained and they can be read independently of each other and in any order without loss of continuity.

First, a synthetic method to produce large area Bernal-stacked graphene films with precise thickness from 2 to 4 layers is developed. This makes controlled few-layer graphene more accessible to chemists, physicists, and materials scientists for exploring a variety of electronic applications. Bernal stacking order is of particular interests because of its unique tunable electronic structure. Large-area uniform Bernal-stacked bi-, tri-, and tetralayer graphene films were successfully synthesized on a Cu surface in selective growth windows, with a finely tuned total pressure and CH₄/H₂ gas ratio. A growth mechanism based on simultaneous-seeding and self-limiting process was observed, instead of an independent homoepitaxial layer-by-layer growth.

Second, high-performance Cu-graphene-CNT hybrid Li-ion electrode is demonstrated. The electrode exhibits a Li-ion capacity >1500 mAh/g, a cycle stability >350 cycles, and a rate performance >100 A/g in a half-cell configuration in conjunction with Li electrode; and a specific energy of ~200 Wh/kg in a full-cell configuration in conjunction with LiCoO₂-graphene nanoribbon (LiCoO₂-GNR) composite electrode.

Third, a facile and scalable synthesis method to obtain a composite of GNRs and iron oxide nanoparticles (GNRs/Fe₂O₃ NPs) was developed. The material was demonstrated as a viable electrode for LIBs. The large aspect ratio and electrically conductive GNRs and sub-20 nm size of Fe₂O₃ NPs lead to an excellent electrochemical
performance. The fabricated electrode shows a reversible capacity of 1190 mAh/g; and it retains 910 mAh/g after 134 cycles at a specific current of 100 mA/g. It also exhibits a high rate performance of 544 mAh/g at a specific current of 2 A/g.

Fourth, silver-GNRs (Ag-GNRs) were prepared from the chemical unzipping of multi-walled carbon nanotubes (MWCNTs) by reaction with Na/K alloy, Ag(O₂CCH₃) and then CH₃OH. Ag-GNRs exhibit improved electrocatalytic ability for the oxygen reduction reaction (ORR) in 0.1 M KOH as compared to the underlying GNR substrate alone and displayed an earlier onset and higher currents than a commercial Ag/Carbon (Ag/C) catalyst. The Ag-GNR hybrid demonstrates an outstanding tolerance to CH₃OH crossover which exceeds that of the commercial benchmark, 20% Pt/C.

Fifth, a conductive composite of GNR stacks and epoxy is fabricated. The epoxy is filled with the GNR stacks, which serve as a conductive additive. The GNR stacks are on average 30 nm thick, 250 nm wide and 30 μm long. The GNR-filled epoxy composite exhibit conductivity >100 S/m at 5 wt% GNR content. This permits application of the GNR-epoxy composite for deicing of surfaces through Joule (voltage-induced) heating generated by the electrical power though the composite. A high power density of 0.5 W/cm² (~5× higher than that typically applied in rear automobile windshield deicing system) was delivered to remove >1 cm and 14 g of ice from a helicopter rotor blade surface in 15 min at −20 °C.

Sixth, a de-icing heating layer composite made using GNRs is disclosed. De-icing heating layers are frequently used in covers of large radiofrequency (RF) equipment, such as radar, to remove ice that could damage the structures or make them unstable. Typically
the de-icers are made using a metal framework and inorganic insulator; commercial resistive heating materials are often non-transparent to RF waves. The preparation of sub-skin-depth thin film, whose thickness is very small relative to RF skin (or penetration) depth, is the key to minimizing RF absorption. The skin depth of typical metals is on the order of a micrometer at GHz frequency range. As a result, it is very difficult for conventional conductive materials (such as metals) to form large area sub-skin-depth films.

In this report, we demonstrate that the GNR film is thin enough to permit RF transmission. This metal-free, ultralight, robust, and scalable graphene-based RF-transparent conductive coating could significantly reduce the size and cost of de-icing coatings for RF equipment covers. This is important in many aviation and marine applications. This is a demonstration of the efficacy and applicability of GNRs to afford performances unattainable by conventional materials.

Seventh, conductive films made from hexadecylated GNRs (HD-GNRs) are demonstrated to be highly transparent to radiofrequency (RF) waves even at very high incident power density. Nanoscale-thick HD-GNR films with an area of several square centimeters were found to transmit up to 390 W (2 × 10^5 W/m^2) of RF power with negligible loss, at an RF transmittance of ~99%. The HD-GNR films conformed to electromagnetic skin depth theory, which effectively accounts for the RF transmission. The HD-GNR films also exhibit sufficient optical transparency for tinted glass applications, with efficient voltage-induced deicing of surfaces. The dispersion of the HD-GNRs afforded by their edge functionalization enables spray-, spin- or blade-coating on almost any substrate, thus facilitating flexible, conformal and large-scale film production. In addition to use in antennas and radomes where RF transparency is crucial, these capabilities
bode well for the use of the HD-GNR films in automotive and general glass applications where both optical and RF transparencies are desired.
# Nomenclature

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<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>GNR</td>
<td>Graphene nanoribbon</td>
</tr>
<tr>
<td>HD</td>
<td>Hexadecylated</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>Iron oxide</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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Chapter 1

Bernal-Stacked Graphene Layers

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Research contributions are included at the end of the chapter.

1.1. Introduction

Few-layer graphene, with Bernal stacking order, is of particular interests to the graphene community because of its unique tunable electronic structure. A synthetic method to produce such large area graphene films with precise thickness from 2 to 4 layers would be ideal for chemists and physicists to explore the promising electronic applications of these materials. Here, large-area uniform Bernal-stacked bi-, tri-, and tetralayer graphene films were successfully synthesized on a Cu surface in selective growth windows, with a finely tuned total pressure and CH₄/H₂ gas ratio. Based on the analyses obtained, the growth
mechanism is not an independent homoepitaxial layer-by-layer growth, but most likely a simultaneous-seeding and self-limiting process.

Parameters for the chemical vapor deposition (CVD) growth of graphene have been explored on different metal catalysts.\textsuperscript{1-3} Since the discovery of Cu-based graphene growth,\textsuperscript{1} the preparation of high-quality uniform large-area graphene monolayers becomes feasible. Multilayer graphene films with specific stacking orders have attracted enormous attention due to their tunable electronic structures.\textsuperscript{4-7} Until recently, most of these experiments were based on micron-sized multilayer exfoliated graphene flakes,\textsuperscript{4-7} requiring a tedious process that is difficult to scale. In order to solve this challenge, here we demonstrate consistent CVD growth windows for large-area Bernal-stacked bi-, tri-, or tetralayer graphene on Cu surfaces.

Parameters that could affect the thickness of graphene growth include the pressure in the system, gas flow rate, growth pressure (the partial pressure of both the growth gas and the carrier gas), growth temperature, and cooling rate.\textsuperscript{8-11} Based on previous CVD growth conditions for monolayer, bilayer, and multilayer graphene summarized in Table 1, we hypothesized that the partial pressure of both the carbon sources and the H\textsubscript{2} gas in the growth process, which is set by the total pressure and the mole fraction of the feedstock, could be the factor that controls the thickness of the graphene. A series of experiments with continual and precisely controlled total pressure and ratio of growth gases was performed to generate a coherent growth map, as shown in Table 2.
### 1.2. Synthesis of Mono-, Bi-, Tri-, Tetra- and Multilayer Graphene

<table>
<thead>
<tr>
<th>Entrya</th>
<th>Growth pressure (Torr)</th>
<th>Growth Temperature (°C)</th>
<th>H₂ pressure (Torr)</th>
<th>CH₄ pressure (Torr)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1⁶</td>
<td>760</td>
<td>1050</td>
<td>24.5</td>
<td>0.006</td>
<td>monolayer single crystal</td>
</tr>
<tr>
<td>2⁷</td>
<td>760</td>
<td>1000</td>
<td>76</td>
<td>0.068</td>
<td>monolayer no D peak</td>
</tr>
<tr>
<td>3⁷</td>
<td>760</td>
<td>1000</td>
<td>76</td>
<td>3</td>
<td>multilayer no D peak</td>
</tr>
<tr>
<td>4⁷</td>
<td>760</td>
<td>1000</td>
<td>707.25</td>
<td>62.75</td>
<td>multilayer with D peak</td>
</tr>
<tr>
<td>5⁸</td>
<td>0.2</td>
<td>1035</td>
<td>0.04</td>
<td>0.16</td>
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</tr>
<tr>
<td>6⁹</td>
<td>0.45</td>
<td>1000</td>
<td>0</td>
<td>0.45</td>
<td>bilayer with D peak</td>
</tr>
</tbody>
</table>

**Table 1.** Graphene growth summary from the literature.

aSome of the references reported the flow rates (sccm) of H₂ and CH₄ and the total growth pressure for the growth conditions; these have been converted into partial pressure.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth pressure (Torr)</th>
<th>Growth Temperature (°C)</th>
<th>H$_2$ pressure (Torr)</th>
<th>CH$_4$ pressure (Torr)</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.8</td>
<td>1000</td>
<td>5.6</td>
<td>0.2</td>
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</tr>
<tr>
<td>2</td>
<td>11.6</td>
<td>1000</td>
<td>11.2</td>
<td>0.4</td>
<td>monolayer</td>
</tr>
<tr>
<td>3</td>
<td>23.2</td>
<td>1000</td>
<td>22.4</td>
<td>0.8</td>
<td>monolayer</td>
</tr>
<tr>
<td>4</td>
<td>46.4</td>
<td>1000</td>
<td>44.8</td>
<td>1.6</td>
<td>1-2 layer</td>
</tr>
<tr>
<td>5</td>
<td>93.3</td>
<td>1000</td>
<td>89.5</td>
<td>3.6~3.8</td>
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<tr>
<td>6</td>
<td>139.2</td>
<td>1000</td>
<td>134.4</td>
<td>4.8</td>
<td>2-3 layer</td>
</tr>
<tr>
<td>7</td>
<td>152</td>
<td>1000</td>
<td>146.7</td>
<td>5.2</td>
<td>3 layer</td>
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<tr>
<td>8</td>
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<td>1000</td>
<td>179.2</td>
<td>6.4</td>
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<tr>
<td>9</td>
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<td>1000</td>
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<td>9.6</td>
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<td>1000</td>
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<tr>
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<td>555</td>
<td>1000</td>
<td>537.6</td>
<td>19.2</td>
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<td>740</td>
<td>1000</td>
<td>716.8</td>
<td>25.6</td>
<td>&gt;10 layer</td>
</tr>
</tbody>
</table>

*Table 2.* Growth conditions in the CVD system used here.
**Figure 1.** The growth chamber with a needle value to control the system pressure. (a) Scheme of the CVD growth chamber where a needle valve is placed downstream between the quartz tube and the vacuum pump to control the total pressure of CH\(_4\) and H\(_2\); the ratio of the two gases is controlled using mass flow controllers at the source of each gas. The growth chamber is placed in a furnace heated at 1000 °C. The inset is the partial pressure of CH\(_4\) correlated to the thickness of the graphene layers. The ratio between partial pressure of H\(_2\) (P\(_{H2}\)) and CH\(_4\) (P\(_{CH4}\)) in this system was set by fixing the flow rates.

As shown in Figure 1, a needle valve was installed between the CVD growth chamber (a quartz tube) and the vacuum pump to precisely control the gas flow rate and thus the total pressure of the CVD system. The total pressure was carefully monitored with a pressure gauge connected to the growth chamber. In Table 2, a monolayer graphene growth condition was set as the first data point in the series, Sample 1. The growth reaction
was maintained at 1000 °C for 15 min. The flow rates of H₂ and CH₄ were 300 sccm and 10 ± 1 sccm, respectively. The flow rates were kept the same throughout this series (Samples 1-12). The ratio between H₂ and CH₄ was thus fixed, while the total pressure was tuned from 5.8 Torr to 740 Torr, ranging from low pressure growth to near-atmospheric pressure growth. The partial pressures of H₂ and CH₄ were calculated from the total system pressure. The detailed growth parameter values are listed in Table 2. As the growth pressure increased, thicker graphene films grew on the Cu surfaces. Specifically, bi-, tri-, and tetralayer graphene films form when the PCH₄ was 3.6, 5.2, and 9.6 Torr, respectively (inset of Figure 1).

1.3. Optical Spectroscopy: Probing Graphene Thickness and Stacking Order

All of the graphene films were grown and transferred onto different substrates using the method previously described. Optical images of this series transferred onto quartz slides are shown in Figure 2. The graphene films became successively darker, suggesting that thicker films were grown with increasing PCH₄.

Figure 2. Optical photograph of graphene films transferred onto quartz substrates (~0.67 in²). The arrow begins at the monolayer graphene Sample 1 and ends at the multilayer
graphene Sample 10; the CH$_4$ partial pressure increases from 0.2 Torr to 12.8 Torr as shown in Table 2.

The thickness of the films was subsequently investigated using spectroscopic techniques. Raman spectroscopy was used to determine both the quality and thickness of the graphene film over a micron-sized area according to the laser spot-size. Based on the Raman spectra in Figure 1a, when the P$_{CH4}$ is below 1.6 Torr, only monolayer graphene films grow with an $I_G/I_{2D}$ ratio less than 0.5 (Samples 1-3). At 1.6 Torr, bilayer graphene starts to form on Cu surfaces as the average $I_G/I_{2D}$ increases to ~ 0.5, slightly higher than monolayer graphene $I_G/I_{2D}$ ratio. Sample 4 is a hybrid of mono- and bilayer graphene film as confirmed by optical absorption of ~3%. When P$_{CH4}$ was 3.6 ~ 3.8 Torr, Sample 5, the graphene film displays a dominant bilayer characteristic $I_G/I_{2D}$ ratio over a large area. Thicker graphene Raman signatures (3 to 10 layers) are also observed on the graphene films from Samples 6-10. Figure 3a displays the stacked Raman spectra as the P$_{CH4}$ increased; the G peak at ~1585 cm$^{-1}$ becomes more pronounced and the 2D peak at ~2700 cm$^{-1}$ broadens and blueshifts. In Figure 3b, the 2D peak-blueshift starts at 2690 cm$^{-1}$ for monolayer graphene and ends at ~2717 cm$^{-1}$ for >10-layer graphene, or graphite, which is consistent with the results obtained from mechanical exfoliated Bernal graphene.
Figure 3. (a) Raman evolution of graphene grown under increased CH$_4$ partial pressure (514 nm laser). (b) The 2D peak position of Raman spectra in (a).

Figure 4. Raman spectra of monolayer graphene and non-Bernal-stacked bi-, tri-, and tetralayer graphene with 514 nm excitation. In order to prepare the non-Bernal-stacked few-layer graphene, monolayer samples grown at CH$_4$ partial pressure of 0.2 Torr (Sample 1, Table 2) were transferred layer-by-layer onto a quartz surface (a PMMA-protected graphene layer was transferred onto the quartz surface and the PMMA was removed with
acetone and rinsed with isopropanol; this process was repeated for multiple layers). No annealing was performed before the Raman characterization.

The Raman spectra of non-Bernal-stacked graphene were also investigated by directly stacking monolayer CVD graphene films atop a SiO$_2$ surface without further annealing. As shown in Figure 4, both the $I_{2D}$ and $I_G$ increase as the thickness increases, while the relative ratio between the two peaks does not change, suggesting a relatively weak electronic interaction between graphene layers.$^{1,18}$ The deconvolution of the 2D peaks of bi-, tri-, and tetralayer graphene unveils more details, as shown in Figure 5.$^{16}$ The 2D peak of bilayer graphene can be fitted with 4 Lorentzian curves while the 2D peak in trilayer graphene can be fitted with 6 Lorentzian curves. The line shape of the peak shows little asymmetry with no obvious shoulder, which suggests that the graphene films are dominated by Bernal (ABA) stacking order rather than rhombohedral (ABC) stacking order.$^{19}$ The tetralayer graphene’s 2D peak can be fitted with 3 Lorentzian curves and its symmetrical line shape reveals its Bernal (ABAB) stacking signature. The full width at half maximum values (FWHMs) of the 2D peaks are 62, 71 and 72 cm$^{-1}$ in bi-, tri-, and tetralayer graphene, respectively, which are significantly broader than the FWHM of monolayer graphene at 30 cm$^{-1}$. All Raman spectra were acquired using a 514 nm laser at room temperature on SiO$_2$/Si substrates.
**Figure 5.** The fitted Raman 2D band of bi-, tri-, and tetralayer graphene with a FWHM of 69, 71 and 72 cm$^{-1}$, respectively.

The thickness of the graphene films was evaluated using visible spectroscopy in Figure 6a. At 550 nm, the bi-, tri-, and tetralayer graphene films on quartz substrates exhibit transmittances of 95.4%, 93.0%, and 90.4%, respectively, in good agreement with predicted and reported values. Figure 6b shows no difference in contrast across the trilayer graphene film, providing evidence for the uniformity of the film. Statistically, Raman mapping at the $100 \times 100 \ \mu$m$^2$ scale confirms the thickness and uniformity of graphene films. In a typical monolayer graphene film, more than 95% of the graphene area has an $I_G/I_{2D}$ ratio $< 0.5$ (Figure 7). In Figure 6c, no monolayer Raman signature ($I_G/I_{2D} < 0.5$) was observed at any pixel on the map and ~85% of the film had an $I_G/I_{2D}$ ratio of 0.7-1.1, suggesting uniform bilayer graphene. The Raman 2D band has been shown to be sensitive to graphene interlayer coupling, whereby ordered few-layer graphene exhibits 2D band-broadening in addition to a shift to higher frequency. In Figure 8, ~85% of the sample’s FWHM 2D peak falls within 42.5 cm$^{-1}$ and 62.5 cm$^{-1}$, characteristic of strongly coupled bilayer graphene. Substrate effects or incidental charging could contribute to the deviation in the ratio. In Figure 6d and e, the average $I_G/I_{2D}$ ratios were 1.29 (trilayer) and 1.44 (tetralayer), respectively. This result was similar to tri- and tetralayer Bernal-stacked exfoliated graphene (obtained from highly oriented pyrolytic graphite), while it is different than the previous values for CVD-grown graphene.
Figure 6. Spectroscopic characterization of Bernal bi-, tri-, and tetralayer graphene films.

(a) Transmittance of bi-, tri-, and tetralayer graphene films obtained with visible-absorption spectroscopy on quartz substrates. The transmittance of graphene was measured at 550 nm. \( n \) L signifies the number of graphene layers. (b) Optical image of a trilayer graphene on 2.5 × 2.5 cm\(^2\) quartz that indicates the uniformity of the film. \( I_G/I_{2D} \) Raman mapping of (c) bilayer, (d) trilayer and (e) tetralayer graphene.

Figure 7. Raman mapping of monolayer graphene (Sample 1).
Figure 8. FWHM of 2D band mapping (a) and histogram (b) of a bilayer graphene film.

1.4. Electron Microscopy and Diffraction: Atomic-Scale Thickness and Structure Determination

Selected area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM) images corroborate graphene’s stacking order and thickness. Bi-, tri-, and tetralayer graphene films were carefully transferred onto TEM grids (Ted Pella, Quantum foil).
Figure 9. SAED and TEM characterization of bi-, tri-, and tetralayer graphene.

(a-c) Representative SAED patterns from bi-, tri-, and tetralayer graphene samples, respectively. (d-f) The intensity profile from the SAED patterns in a-c, respectively. (g-i) High resolution TEM of randomly chosen representative edges of bi-, tri-, and tetralayer graphene that shows two, three, or four layers of carbon, respectively. Scale bar in g-i is 5 nm.
Figure 10. SAED (a and b) and HRTEM (c) edge characterization of monolayer graphene.

Over ~2 mm², ~10 SAED patterns were acquired per sample and each area showed one set of diffraction pattern characteristic of Bernal stacking, other than at the grain boundaries. In the SAED patterns, the (1-210) intensity was 3.5~6.3 times stronger than the (1-100) in Figure 9a-f, suggesting these films are non-AA stacked. As a reference, the monolayer graphene diffraction pattern has a (1-210)/(1-100) intensity ratio of ~0.87 (Figure 10). The presence of the innermost diffraction spots (1-100) and the diffraction intensity ratio in Figure 9 is quite different from the ABC stacking order, which should have an intensity ratio larger than 14 according to theoretical calculations. However, experimental data does not always agree with theoretical diffraction data. The inner plane strain and small tilting angle from the imperfect wet-transfer method could affect the diffraction intensities. Using the SAED patterns, the graphene films are Bernal (AB) stacked polycrystalline graphene with an average domain size of 1 to 5 µm; this result has the potential to be optimized into a single crystal using newly developed methods. In Figure 9g-i, edges were
randomly chosen for imaging to confirm the thickness of the bi-, tri-, and tetralayer graphene samples.

1.5. Proposed Growth Mechanism

Additional control experiments were done to explore the growth mechanism for the Bernal stacked graphene films. Under bilayer growth conditions (Sample 5 in Table 2),

**Figure 11.** Same sample as used in Figure 6c. (a) SEM image of bilayer graphene grown for 15 min; the scale bar is 1 mm. (b) $I_G/I_{2D}$ Raman spectral map (Figure 6c) and (c) Raman spectrum of bilayer graphene grown for 15 min.
Figure 12. (a) SEM image of the bilayer graphene grown for 30 min; the scale bar is 1 mm. (b) $I_G/I_{2D}$ Raman spectral map and (c) Raman spectrum of bilayer graphene grown for 30 min. There was no change in thickness noted with the increased growth time.

Figure 13. (a) SEM image of graphene grown under monolayer conditions (15 min) followed by bilayers growth conditions (15 min); the scale bar is 1 mm. (b) $I_G/I_{2D}$ Raman spectral map and (c) Raman spectrum of graphene grown under monolayer conditions for
15 min, then bilayer conditions for another 15 min. There was no thickness change observed after the monolayer was obtained.

15-min-growth produces full coverage of a bilayer graphene film on the Cu surface (Figure 11). Extending the growth time to 30 min under the same conditions does not change the film’s thickness (Figure 12). In addition, monolayer graphene was grown to fully cover the Cu surface, after which the CVD system was changed to a higher pressure favorable for bilayer growth. However, no additional growth was observed (Figure 13). This confirmed that the graphene growth is not a layer-by-layer mechanism, in which an additional graphene film can grow directly atop or underneath existing graphene film. The polycrystalline nature indicates that the graphene is grown from multiple growth centers and that the crystals subsequently merge seamlessly. The growth of the Bernal stacked graphene suggests that a self-limiting mechanism is operating and that the thickness is inherent from its early seeding stage.

**Figure 14.** Proposed growth-mechanism. Graphene seeds form when the surface carbon in Cu is supersaturated. Higher CH₄ partial pressure deposits thicker graphene seeds. The
thickness of the graphene is pre-defined by these seeds, which grow epitaxially along the Cu surface (top). The graphene seeds grow independently and form graphene single-crystalline islands (middle) before they meet with each other. When graphene islands meet, they form domains and grain boundaries (bottom) and the growth stops. No additional graphene layer would be able to grow on the fully covered Cu surface.

Figure 15. (a) and (b) are different magnification SEM images of bilayer graphene seeds and islands after 2 min growth atop Cu. The Cu foil is pre-polished and annealed using the same method discussed reference 24. This additional treatment is necessary to remove excess of carbon contaminations on Cu surface. Without this treatment, the full coverage of graphene growth finished too quickly for the seeds to be arrested and captured. The red
arrow in (b) points to a graphene seed. This graphene seed is surrounded with graphene islands, which range from 100 nm to several micron meters in size. The scale bar in (a) and (b) is 1 µm. (c) Representative Raman spectrum of these bilayer graphene seeds and islands, which shows the same signature as its final bilayer film. Out of 10 random areas studied, 8 areas were bilayer while one area was monolayer and another was trilayer. This indicates that the seeds were mainly bilayer.

The proposed growth-mechanism scheme is illustrated in Figure 14. In a concentrated carbon species growth environment, multilayer graphene seeds form when C atoms are supersaturated in the surface layers of the Cu. In order to arrest the intermediate states, a short time-growth (2 min) on pre-treated Cu surface was performed. The Cu foil was pre-polished and annealed using the same method discussed in elsewhere.\(^{24}\) In Figure 15, the SEM and Raman spectra clearly confirmed that the graphene thickness was defined at the initial stage. Considering the top graphene layers have no direct lateral contact with the Cu underneath except for the edges, this two-dimensional growth is most likely catalyzed by the Cu catalyst-front close to the graphene edges (Figure 14). In this way, some of the seeds grow into graphene islands, forming and extending synchronously rather than layer-by-layer. The islands maintain their thickness and stacking order while the edges propagate laterally on the Cu surface. In analogy to the “tip-growth” mechanism of carbon nanotubes,\(^{25}\) the growth of Bernal graphene is most likely following an “edge-growth” mechanism. Cu “wave fronts” are pushed back into the surface by growing graphene crystals or they evaporate from this surface mobile state. As the graphene islands expand, the open Cu area shrinks. Finally, two graphene domains merge into one, with no Cu-front left in-between. As the growth temperature is close to copper’s melting point, the front of
the catalyst could be a highly mobile liquid phase. This mechanism is proposed for Bernal-stacked graphene growth. But it could be generalized for all 2D graphitic growth on Cu, including monolayer graphene and graphite (>10 layers) (Figure 16).

**Figure 16.** Graphite film with graphene thickness over 10 layers (Sample 11, Table 2). Scale bar is 5 nm.

### 1.6. Tunable Electronic Properties of Bernal-Stacked Graphene

Dual-gate field effect transistors (FETs) were built with a bilayer graphene film atop a SiO$_2$/Si wafer (Figure 17). The electrical measurements on the devices indicate that they have a tunable band structure with a biased electrical field perpendicular to the graphene basal plane.$^{1-4}$ The device hole mobility was as high as $\sim 2200$ cm$^2$V$^{-1}$s$^{-1}$ (Figure 18), which is considerably higher than the mobility for solution-exfoliated Bernal bilayer graphene.$^{23}$
Figure 17. Electrical measurement of Bernal-stacked bilayer graphene. (a) Overlaid SEM and optical microscopy top-view image of a dual-gate bilayer graphene FET device (TG = top gate; G = bottom gate; S = source; D = drain). Scale bar is 10 µm. (b) Cross-sectional view of the bilayer graphene device. (c) Graphene electrical conductance as a function of top gate voltage $V_t$ at different fixed bottom gate voltages $V_b$. The measurements were taken from -40 V to 40 V in $V_b$, with 20 V steps at 77 K.
Figure 18. Room temperature Bernal bilayer graphene device mobility.

1.7. Conclusion

With the same mechanism, Bernal-stacked graphite of more than 10 graphene layers could be produced from Cu substrates. Between 1 and 10 layers, the thickness could be tuned within selective growth windows, making Cu a more versatile catalyst for graphene synthesis. These Bernal-stacked graphene films are expected to show distinct electronic band structures, adding new building blocks to existing graphene catalogs and promoting physical and optoelectronic applications.26

1.8. Experimental Techniques

1.8.1. CVD Growth

In a 48-inch-long fused quartz tube (22-mm ID, 25-mm OD, Technical Glass Products) heated in a furnace, graphene films were grown on a ~ 1 in² copper foil mounted on a boat-shaped quartz holder with a magnet affixed at one end to facilitate insertion and removal (the magnet never enters to hot-zone of the oven). With the furnace heated to 1000 °C and tube under vacuum (<30 mTorr), filtered H₂ (ultra high purity grade, 99.999% from Matheson, this high purity cannot be substituted) was introduced at 300 sccm and the H₂ pressure was controlled with a needle valve (Figure 1a) to a specified value. The copper foil was then annealed for 10 min by sliding the holder containing the copper to the center of the furnace. In the presence of the pressure-controlled H₂, filtered methane (chemical purity grade, 99.0%, Matheson) was opened at 10 ± 1 sccm for a growth time of 15 min
after which the holder was removed from the furnace area of the tube to cool under H₂. The copper foil was 25 µm thick and 99.8 % grade, purchased from Alfa Aesar.

1.8.2. Graphene Transfer

Graphene was formed on both sides of the Cu foil. In order to protect the graphene film during Cu etching, a poly(methyl methacrylate) (PMMA) solution (950 PMMA A 4, MicroChem) was spin-coated (at 2500 rpm for 1 min) on the top of the graphene-coated copper foil twice and baked at 70 °C for ~30 min in a vacuum oven or on a hot plate. Marble’s reagent was used as an aqueous etchant solution, comprising 15.6 g CuSO₄.5H₂O (Aldrich), 45 mL deionized H₂O, and 50 mL conc. HCl (Aldrich). The PMMA-graphene-Cu assembly was etched for a few min after which the Cu foil was removed from the Marble’s reagent and dipped in water several times and wiped on a Kimwipe to completely remove the unprotected graphene on bottom of the Cu foil so that its residue did not merge with the top graphene. The remaining Cu was etched, leaving the PMMA-protected graphene that had been on top of the Cu foil floating on the etchant. The film was floated on deionized water and subsequently transferred onto a given substrate; the protective PMMA was removed using acetone after the transferred graphene layer completely dried. The graphene film was rinsed with 2-propanol, and gently blow-dried using N₂.

1.8.3. Structural Characterization

For Raman spectroscopy, scanning electron microscopy (SEM), and optical characterization, graphene films were transferred onto a 300 nm SiO₂/Si substrate. Raman spectra and 2D Raman maps were collected using a Renishaw inVia Raman microscope with a 514 nm Ar laser at ambient temperature. SEM images were obtained with a JEOL
6500F SEM at 15 KV. Optical images were taken with a Zeiss Axioplan Polarized Optical Microscope. On quartz slides, optical transmittance spectra were collected in a Shimadzu UV-3101PC UV-VIS-NIR Spectrophotometer. Transmission electron microscopy (TEM) images and electron diffraction patterns were acquired using a JEOL 2100F field emission gun TEM at 200 kV. The diffraction patterns were obtained at 80,000× with a zero degree tilt. For the TEM experiments, graphene films were transferred onto C-flat TEM grids (Electron Microscopy Sciences) in a method similar to the transfer method used for silicon oxide substrates.

1.8.4. Electrical Measurements

The bilayer graphene sheet was transferred to p-Si substrates with 300 nm thermal oxide and patterned into a strip (5 × 20 µm) using e-beam lithography and reactive ion etching (RIE). The source/drain electrodes (1 nm Ti/20 nm Au) were defined using e-beam lithography and e-beam evaporation. Then top gate dielectrics (alumina, 70 nm) and top gate electrode (1 nm Ti/20 nm Au) were defined in series using e-beam lithography and e-beam evaporation. The channel length was between 1 µm and 5 µm depending on the devices.

The dual-gate FET properties of the bilayer graphene devices were further characterized using a probe station (Desert Cryogenics TTPX-probe 6 system) under vacuum with chamber base pressure below 1 × 10⁻⁵ mm Hg. The I–V data were collected using an Agilent 4155C semiconductor parameter analyzer. The mobility was calculated using the following equation:

\[
\mu = \frac{L}{W C_{ox} V_{sd}} \left( \frac{\Delta I_{sd}}{\Delta V_g} \right)
\]
Equation 1. Mobility.

where $L$ and $W$ are the channel length and width, $C_{ox}$ the gate oxide capacitance, $V_{sd}$ the source drain voltage, $I_{sd}$ the source drain current and $V_g$ the gate voltage. The linear regime of the transfer characteristics was used to obtain $\Delta I_{sd}/\Delta V_g$. 
References


Research Contributions

Abdul-Rahman O. Raji optimized the growth experiments, worked out the detailed conditions, and performed Raman characterization; designed and performed the growth-mechanism experiments. Zhengzong Sun designed the growth experiments, performed TEM characterizations, and Raman analysis. Yu Zhu fabricated the FET device. Changsheng Xiang performed the UV-Vis experiments. James M. Tour and oversaw all aspects of the project.
Chapter 2

Graphene-Carbon Nanotube Hybrid Lithium-Ion Battery

Research contributions are included at the end of the chapter.

2.1. Introduction

Due to increased use of Li-ion batteries in mobile electronics, power tools, electric vehicles, and other mobile application areas, there is a motivation for high power density capability that will enable fast charge and/or discharge while maintaining the large energy density feature of contemporary Li-ion battery technology. Because supercapacitors are capable of high power density but have low energy density,\textsuperscript{1} realization of high power and energy densities in a Li-ion battery presents a unification of the existing capabilities of supercapacitors and Li-ion batteries. However, electronic and structural properties of current Li-ion battery electrodes have restricted the power capability due to limited electronic and ionic mobilities through the electrodes and across electrode interfaces. Faster electronic mobility in a Li-ion battery electrode would occur if the material is highly electrically conductive and if it maintains an exceptional contact with the current collector;
enhanced ionic mobility would take place if the electrode has a three-dimensional structure with a large surface area. Therefore, the use of electrically conductive electrodes with a seamless connection to the current collector and with a three-dimensional structure would facilitate electronic and ionic transport, respectively.

Carbon nanotubes (CNTs) have an exceedingly high intrinsic electrical conductivity, an enormous surface area, and when grown vertically from a substrate, a three-dimensional structure is rendered. Moreover, they have been demonstrated to possess reversible Li-storage capability. Li-ion battery electrodes made with single-, few-, and multi-walled CNTs can exhibit capacities >500 mAh/g with good cycle stability. For over three decades, the most ubiquitous anode material in Li-ion batteries has been graphite, which could reversibly store Li in its interlayers through intercalation, with a theoretical capacity of 372 mAh/g. Other forms of carbon, including graphene, have more than twice the Li-storage capacity of graphite. Theoretical calculations have shown that CNT-based Li-ion battery electrodes could have Li-storage capacity >1000 mAh/g through insertion within the triangular lattices of the CNT bundles. With chemical vapor deposition (CVD) growth of graphene film on Cu or Ni and subsequent deposition of iron and aluminum oxide atop as catalyst and catalyst support, respectively, we have previously demonstrated that the as-grown CNTs are covalently and seamlessly connected to the underlying graphene. The metal-graphene-CNT structure produced superior supercapacitor performance. The interfacial graphene played a significant role by enabling Ohmic conductance between the CNT and the Cu or Ni substrate. Without the interfacial graphene, a Schottky barrier exists between a CNT and a metal substrate, an effect that generates poor conductance across the interface, especially under high current.
The performance of Li-ion batteries can thus be enhanced by developing a three-dimensional CNT electrode that has the seamless electronic contact with the current collector and that is capable of large amounts of Li storage.

We hereby report the electrochemical properties of a hybrid Li-ion battery electrode made of seamlessly connected Cu current collector, graphene interfacial layer, and CNT active material. The CNTs are grown vertically from the graphene, which is pre-grown on the Cu substrate, with the aid of Fe nanoparticle catalyst and Al₂O₃ support. The purposes of this report are (1) to demonstrate that the graphene-CNTs can sustain high rate capability with prolonged cycle stability as a Li-ion electrode; (2) to lay the foundation for developing a graphene-CNT-based Li-ion battery that has large capacity, high voltage capability, high energy storage, and prolonged cycle stability. We found that the graphene-CNT electrode exhibits a Li-storage capacity ~1500 mAh/g, a cycle stability >350 cycles, a rate performance that reaches 100 A/g in a half-cell configuration; and a specific energy of ~200 Wh/kg in a full-cell configuration. We contend that a combination of the electrical conductivity, large specific surface area, and three-dimensional structure of the CNTs; and the seamless electrical connection of the graphene-CNTs to the Cu substrate are responsible for the observed performance.
2.2. Structural Properties of Graphene-CNTs

**Figure 19.** Schematic for the growth of graphene-CNTs and structural characterization of graphene-CNTs. (a) Schematic. (b–d) SEM images of graphene-CNT. Raman spectra of (e) Graphene as-grown on Cu, (f) CNTs grown on the Cu-graphene substrate, and (g) radial breathing (RBM) modes of the CNTs in expanded format.

In a Li-ion cell, copper often serves as a substrate that provides an electrical connection between the negative electrode (anode) and an external circuit, which is also connected to the positive electrode (cathode). However, direct growth of CNTs on the metal substrate could introduce Schottky barrier,\textsuperscript{11} which is known to hinder electrical transport across interfaces. This problem has been addressed through growth of graphene via chemical...
vapor deposition (CVD) on a Cu substrate (Chapter 1), followed by deposition of iron nanoparticles and aluminum oxide and subsequent CVD growth of CNT at 750 °C using acetylene as the carbon source (Figure 19a).\textsuperscript{9,10} E-beam deposited 1 nm iron nanoparticles were non-continuous and they served as the catalysts for the CNT growth while a 3 nm layer of aluminum oxide provided the support for a vertical growth.\textsuperscript{9,10} The graphene is chemically connected to its native Cu substrate on which it was grown and it requires chemical etching to remove the graphene from the Cu. The as-grown CNTs have been shown to be covalently connected to the graphene.\textsuperscript{9} Good electrical contact via Ohmic conductance between Cu and CNTs has also been demonstrated with the Schottky barrier eliminated.\textsuperscript{9}

The CNTs were grown vertically from the Cu-graphene substrate as a carpet and they exist in bundles (Figure 19b-d). Each bundle is a three-dimensional triangular superlattice held together by van der Waals interactions between the CNTs. In addition to graphite-like van der Waals (inter-tube) spacing of \(~3.4\ \text{Å}\), the CNT bundles have channels of \(6\ \text{Å}\) that might facilitate accommodation of Li ions on the surface of the CNTs.\textsuperscript{5,8} Prior to catalyst deposition and eventual CNT growth, the underlying graphene was confirmed by the characteristic Raman scattering with G band at \(1589\ \text{cm}^{-1}\), 2D band at \(2705\ \text{cm}^{-1}\), \(I_G/I_{2D}\) ratio >1, and a trace D band at \(~1360\ \text{cm}^{-1}\) (Figure 19e) – all signatures of a high quality multilayer graphene (Chapter 1).\textsuperscript{12} The CNTs were confirmed with the G band at \(1587\ \text{cm}^{-1}\), 2D band at \(2652\ \text{cm}^{-1}\), D band at \(1336\ \text{cm}^{-1}\,\), and radial breathing modes (RBM) at \(100-300\ \text{cm}^{-1}\) (Figure 19f). The RBMs indicate single- and/or double-walled CNTs (Figure 19g).\textsuperscript{13,14}
2.3. Electrochemical Properties of Graphene-CNT/Li Half-Cell

Figure 20. Electrochemical properties of graphene-CNT/Li half-cell. (a) Galvanostatic charge-discharge cycles at 100 mA/g. (b) Cyclic voltammogram at 0.5 mV/s. (c) Cycle stability at 500 mA/g. (d) Coulombic efficiency at 500 mA/g. (e) Rate performance from 100 mA/g to 100 A/g.
In a graphene-CNT/Li half-cell, the graphene-CNTs possess Li storage capacity of 1500 mAh/g, which surpasses the capacity of most known Li storage electrodes.\textsuperscript{15-17} The first discharge capacity is 4750 mAh/g, of which 1500 mAh/g is removable during the charge process (Figure 20a) and the remaining 3500 mAh/g constitutes an irreversible capacity. The first discharge is characterized by a plateau at \(-0.9\) V, followed by a downward slope below \(0.7\) V. The profile is similar to what has been observed for graphene\textsuperscript{18-20} and hard (non-graphitizable) carbons.\textsuperscript{21} This cycle encompasses formation of surface films on or into the CNT bundles and lithium insertion into the CNT bundles. It is uncertain whether the surface films are formed solely on the CNTs at the outer surface of the bundles or on the CNTs within the bundles as well. The 75\% irreversible capacity is due to formation of surface films on the graphene-CNTs and it is facilitated by the large surface area of the graphene-CNTs that reaches up to 2630 g/cm\(^2\).\textsuperscript{9} The SEI formation, with the resulting irreversible capacity, is observed in various Li-ion battery anode materials, including graphite,\textsuperscript{22} silicon,\textsuperscript{23} metals,\textsuperscript{24} and metal oxides.\textsuperscript{25} The surface films, called the solid-electrolyte interface (SEI), are known to be formed by precipitation of decomposed products of the organic carbonate-based electrolyte solution on electrode’s surface.\textsuperscript{26} In the graphene-CNT/Li cell, the graphene-CNT electrode is the cathode (reduction site) and a Li coin is the anode (oxidation site) during discharge. Thus, the SEI formation would occur through a reduction\textsuperscript{27} of the electrolyte solution mainly during the initial discharge (first lithiation) cycle. The absence of the plateau during the subsequent discharge suggests that the SEI formation predominantly occurs during the first cycle. The cyclic voltammogram during first discharge shows a pronounced cathodic feature that emerges at 0.6 V and peaks at 0.4 V (Figure 20b). This peak is also attributed to SEI formation, similar to the plateau
observed during first galvanostatic discharge cycle in Figure 20a. Like the plateau, it is also absent in subsequent cycles.

Graphene-CNTs have a Li storage capacity that is fourfold larger than graphite. The large capacity suggests an insertion process that is distinct from the well-defined graphitic-type intercalation. Charge storage via electric double-layer capacitance (EDLC) based on adsorption of electrolyte ions on graphene-CNTs would not account for the large capacity. EDLC has a value of 15-100 μF/cm². The capacitance of pristine carbon surface can reach up to 25 μF/cm² in aqueous electrolyte, where cm² denotes the material’s surface area. Even with the theoretical CNT specific surface area of 2630 m²/g, the specific capacitance is estimated to be no more than ~660 F/g, which is much larger than the best values obtained experimentally in CNT or carbon-based supercapacitors. In an organic electrolyte solution, the maximum specific capacitance is estimated to be ~265 F/g (based on a capacitance of 10 μF/cm²). This corresponds to a maximum specific capacity of 185 mAh/g, which is much less than that obtained in the Li-ion cell reported here. Moreover, the tail of the discharge curves below 0.5 V in (Figure 20a) is inconsistent with an EDLC mechanism. Though the mechanism is not well-understood, it is assumed to be due to Li insertion into the CNT bundles, in agreement with theoretical studies.

The graphene-CNTs maintain a remarkable and steady specific capacity over several charge-discharge cycles. After 350 cycles, the discharge capacity is 1000 mAh/g, a 90% capacity retention compared to the second discharge (Figure 20c) and it does not show any signs of sharp decline. The graphene-CNTs also show a stable reversibility between charge and discharge that yield a coulombic efficiency of >99% (Figure 20d).
The rate performance of the graphene-CNTs is studied by measuring the specific capacity as a function of charge-discharge rates. The electrode is charged and discharged to a rate as high as 100 A/g producing a capacity over 100 mAh/g (Figure 20). At 15 A/g, graphite shows a minuscule capacity of 10 mAh/g; at 20 A/g, silicon exhibits 200 mAh/g. The high rate capacities and the corresponding stability of the graphene-CNT/Li half-cell supersede those of any other reported Li-ion electrode. After cycling at 100 A/g, subsequent cycling at 100 mA/g showed no loss in capacity compared to the initial cycles at the outset of the rate test at 100 mAh/g (Figure 20e). This demonstrates the material’s stability to high rate charge and discharge. Thus, the graphene-CNT Li-ion electrode combines the high capacity of a battery with the high rate capability and cycle stability of a supercapacitor.

The practical capacity of an electrochemical cell is largely determined by the various interfaces in the cell. Potential drops across the interfaces are a limiting factor to the actual capacity attainable, especially at moderate to high current density. The cell potential is the driving force for charge and discharge and interfacial losses (polarization) represent energetic costs to charge transport. With increased current density, there are lower input and out capacities due to the larger potential drop. Sources of interfacial resistances\textsuperscript{33} include current collector-electrode resistance, charge transfer resistance, and SEI impedance. Lowering the resistances would decrease polarization and increase the obtainable capacity. The excellent electrical conductivity of the CNTs is thought to have facilitated fast electron transport and direct electron transfer, unlike most lithium-ion battery electrodes that require conductive additives. The growth of CNTs on graphene that is directly connected to the underlying copper removes the electrode-current collector resistance. Unlike other materials that are subject to electrochemical etching\textsuperscript{34} to serve as
an independent electrode or as a scaffold for other materials to generate a nano-to-microporous three-dimensional feature that is crucial for cyclability and rate-performance,\(^{35}\) the graphene-CNTs are inherently a three dimensional structure with nanoporous and microporous features within a bundle and between bundles, respectively (Figure 19). The three-dimensional nature of the CNTs is expected to provide enhanced Li-ion diffusion, unlike the two-dimensional Li-ion diffusion in graphite\(^{36}\) and the solid-state Li-ion diffusion in nanoparticles,\(^{37}\) nanowires\(^{38}\) and thin films that often cause significant and unfavorable structural changes such as pulverization. Though there is significant SEI formation on the graphene-CNTs, Li-ion diffusion through the SEI is deemed a relatively fast process because of the relatively high ionic conductivity of SEI films.\(^{39}\)

Based on Figure 21, the graphene-CNT electrode does not show self-discharge characteristics of electrostatic energy storage in EDCL supercapacitors. After a discharge from 3 V to 0.01 V and recharge to 3 V, the electrode was rested for 24 h with no current flow. Then it was subject to another cycle of discharge, followed by charge. The initial potential had dropped to \(~2.5\) V (Figure 21a). There was no significant change in the starting potential for the same electrode rested for 54 h and 158 h. Upon discharge to 0.01 V, no loss in capacity was observed in all cases. Rather, there was a slight increase in capacity with rest time (Figure 21b). Since the drop to 2.5 V does not change appreciably with rest time, \(~2.5\) V is thus the open circuit potential (OCV) at the operating potential of 3.5 V. The difference can be ascribed to overpotential. Thus, it costs an additional 1.0 V to charge the electrode to remove the all of the stored capacity.
Figure 21. Self-discharge evaluation of graphene-CNT in a graphene-CNT/Li half-cell. (a) Galvanostatic charge-discharge cycles after resting cell for different amounts of time. (b) A bar graph showing the discharge capacity obtained after resting for different amounts of time. The potential window is 0.01–3.50 V at a rate of 200 mA/g in all cases.

2.4. Electrochemical Properties of Pre-Lithiated Graphene-CNTs

Figure 22. Electrochemical properties of pre-lithiated graphene-CNTs in a graphene-CNT/Li half-cell. (a) Galvanostatic charge-discharge cycles at 200 mA/g. (b) Cyclic
voltammogram at 0.5 mV/s. (c) Cycle stability at 200 mA/g. (d) Coulombic efficiency at 200 mA/g.

The irreversible capacity that occurred due to SEI formation as described above is hereby circumvented by pretreating the graphene-CNTs before device fabrication (Experimental Techniques). The pretreatment (an *ex situ* process) was carried out for 2 h after adding drops of the electrolyte solution on the graphene-CNT electrode and firmly pressing a Li coin onto it (Experimental techniques). The same potential difference during the electrochemical measurements (*in situ*) drives the Li insertion into the graphene-CNTs and the decomposition of the electrolyte solution when the process is performed *ex situ*. By forming the SEI *ex situ*, excessive consumption of Li from the Li-bearing electrode is thus prevented during cell operation (Figure 22a). Electrochemical properties of the pretreated graphene-CNTs are evaluated in a graphene-CNT/Li half-cell where the first cycle coulombic efficiency/reversibility is >70%, compared to 25% without pretreatment (Figure 22a). There is absence of the previously observed pronounced cathodic peak during the first discharge process in the CV in Figure 22b, indicating the effectiveness of the pre-lithiation treatment. Adding excessive amounts of the electrolyte solution during the pretreatment was found to yield ineffective pre-lithiation due to poor contact between the graphene-CNTs and the Li.
2.5. Electrochemical Properties of LiCoO$_2$/Li Half-Cell

![Graphs showing electrochemical properties](image)

**Figure 23.** Electrochemical properties of a LiCoO$_2$/Li half-cell. (a) Galvanostatic charge-discharge cycles at 10 mA/g at a potential window of 3.0-4.2 V. (b) Cycle stability at 200 mA/g at a potential window of 3.0–4.2 V. (c) Coulombic efficiency at 200 mA/g at a potential window of 3.0–4.2 V. Galvanostatic charge-discharge cycles at 10 mA/g with upper cut-off potential of (d) 4.2 V, (e) 4.5 V, (f) 4.6 V, (g) 4.7 V, and (h) 4.85 V. The lower cut-off potential is 3.6 V in all cases.

LiCoO$_2$ is a well-developed cathode material for Li-ion batteries with a theoretical specific capacity of 274 mAh/g.\textsuperscript{41} In this work, the cathode is characterized and
subsequently used as a complementary electrode to the graphene-CNT electrode to generate a complete battery cell. Because LiCoO$_2$ is not electrically conductive, an electrically conductive additive is typically mixed with it to improve electron transport. Here, graphene nanoribbon (GNR) stacks (Experimental Techniques) are used as the conductive filler because of their high conductivity, large surface area and large aspect ratio. The electrode is thus a LiCoO$_2$-GNR composite. In Figure 23a, at a rate of 20 mA/g, the specific charge capacity is 145 mAh/g; and a reversible discharge capacity of 129 mAh/g is obtained during the first cycle. At a rate of 200 mA/g, the first charge and discharge cycles are 143 mAh/g and 110 mA/g, respectively (Figure 23b). The electrode shows high cycle stability, with a discharge capacity of 107 mAh/g (and a discharge capacity retention of 97%) after 350 cycles (Figure 23b). Reversibility between the charge and discharge processes is >99% (Figure 23c).

The obtainable capacity increases with the charge potential cut-off (Figure 23d–f). The stored capacities removed during charging are 125 mAh/g, 206 mAh/g, 261 mAh/g, 269 mAh/g, and 309 mAh/g at cut-off potentials of 4.2 V, 4.5 V, 4.6 V, 4.7 V, and 4.85 V, respectively. Since it is impossible to produce more Li than theoretically available in the LiCoO$_2$, the extra capacity above the theoretical value at the 4.85 V cutoff comes from dissolution of Co ions.$^{42}$ Given that “y” represents moles of Li extracted per mole of LiCoO$_2$, Li$_{1-y}$CoO$_2$ describes the cathode material. At 4.2 V cut-off potential, the obtained charge capacity of 125 mAh/g corresponds to Li$_{0.54}$CoO$_2$. With further removal of Li$^+$, (1–y)<0.54 and the cathode potential increases. The cathode becomes less chemically stable as the electrode potential becomes larger. In the LiCoO$_2$ (y = 0 prior to Li extraction), the oxidation state of Co ions is 3+ and it increases to 4+ upon extraction of
Li\(^+\) (+ e\(^-\)) during the charging process. Since the LiCoO\(_2\)-GNR is anodic during charging, some of the extracted Li\(^+\) from LiCoO\(_2\)-GNR participates in irreversible oxidative decomposition of the electrolyte solution and dissolution of Co ions, which occurs increasingly at potential >4 V. In Figure 23d–h, with a discharge cut-off potential of 3.6 V, the discharge capacities are 102 mAh/g, 176 mAh/g, 209 mAh/g, 220 mAh/g, and 220 mAh/g, respectively. LiCoO\(_2\)/Li cells with charge cut-off voltages ≤4.6 V exhibit reversible charge-discharge cycles with high capacity retention (Figure 23d–f). The charge-discharge curves do not change significantly after the first cycles due to the stable electrode impedance. Charge voltages >4.6 V show lower discharge capacity during the first cycle and they undergo rapidly fading capacity upon cycling (Figure 23g, h). Upon cycling, overpotential increases due to increase in electrode impedance that arises from increased electrolyte decomposition and Co ion dissolution.\(^{43}\) Charge-discharge processes thus become more energetically costly. At 4.7 V charge cut-off, there is a large drop to 4.5 V, and at 4.85 V, there is an even larger drop to 4.3 V at the onset of discharge during the first cycle.
2.6. Electrochemical Properties of LiCoO$_2$-GNR/Graphene-CNT Full-Cell

**Figure 24.** Electrochemical properties of LiCoO$_2$-GNR/graphene-CNT full-cell. (a) Galvanostatic charge-discharge cycles for the first three cycles at 200 mA/g within a potential window of 3.0–4.2 V. (b) Enlarged version of “(a)” without the first charge. The Li-cell was assembled with pristine graphene-CNTs with no pre-lithiation.

A full-cell fabricated with a combination of LiCoO$_2$-GNR as the cathode and graphene-CNTs as the anode provided a reversible cell capacity of 1500 mAh/g (based on graphene-CNT mass) during the first discharge occurring at a high voltage (Figure 24a). Most of the capacity was discharged above 4 V in the first few cycles (Figure 24b). The capacity retention based on both anode and cathode masses decreases with cycling (Figure 25a, b). The combined cell capacity is 180 mAh/g during the first cycle (Figure 25c). During the first discharge, the combination of the capacity and voltage resulted in a specific energy of ~200 Wh/kg (based on the total electrode mass), comparable to the specific energies of commercially available batteries (200–300 Wh/kg, estimated based on total
electrode mass).\textsuperscript{44} After the first few cycles, the specific energy decreased to <20 Wh/kg, but the energy efficiency was still >90%.

\textbf{Figure 25.} Electrochemical properties of LiCoO\textsubscript{2}-GNR/graphene-CNT full-cell. Charge and discharge capacities over repeated cycles based on (a) anode mass, (b) cathode mass. (c) Combined cell charge and discharge capacities over repeated cycles. (d) Specific input and output energies over repeated cycles. Measurements were conducted over a potential window of 3.0–4.2 V.

The assembly of a cell made of a pre-lithiated graphene-CNT electrode and pristine graphene-CNT electrode produced a behavior that is characteristic of a supercapacitor (Figure 8). The pre-lithiated graphene-CNTs were used as the anode, with the pristine graphene-CNTs as the cathode. At different specific current, the curves slope downward, almost linearly with no plateau (Figure 26). No differences in the charge-discharge curves and specific capacity (as well as specific capacitance) were observed by reversing the polarity of the cell. The maximum attainable voltage is 2.5 V, a feature characteristic of supercapacitor made with organic electrolyte solution. Beyond 2.5 V, the curve significantly deviated from the almost linear shape and the additional capacity was irreversible. This is consistent with decomposition of the electrolyte solution. At 200 mA/g, the capacity is 22 mAh/g, corresponding to a capacitance of 40 F/g. The specific capacity is comparable to reported values for carbon-based supercapacitors but minuscule compared to that of graphene-CNT Li-ion battery electrode.
Figure 26. Electrochemical properties of Li$_x$graphene-CNT/graphene-CNT full-cell. LiPF$_6$ in EC:DEC:DME (1:1:1 by volume) was used as the electrolyte solution. The specific capacity was determined based on the anode (Li$_x$graphene-CNT) mass.

### 2.8. Conclusion

We have demonstrated high performance lithium ion batteries based on carbon nanotubes grown directly on Cu through an interfacial graphene. The graphene-CNT Li-ion electrode can sustain high rate capability with prolonged cycle stability. The capacity and rate capability are superior to those of most Li-ion electrodes. The Li-ion battery made with graphene-CNT and LiCoO$_2$ showed large capacity, high voltage, high energy but low cycle stability. The first couple of cycles have specific energy from 100–200 Wh/kg. The range of specific energies of Panasonic Li-ion battery series that are used in a variety of mobile and electronic applications is 220–300 Wh/kg (estimated based on total electrode mass for comparison with results obtained here). Although the specific energy range available
from these top commercial products is higher than the values reported here, there is plenty of room for improvement. The demonstrated high capacity and rate performance of the graphene-CNT electrodes offer a compelling evidence. A significant drawback of the system reported here is the sharp decline in specific energy to <20 Wh/kg upon cycling. This can be attributed to cathode instability since the graphene-CNT half-cell exhibited excellent stability. In order to increase the cathode potential to generate sufficient potential difference against the graphene-CNT anode, ~0.7 moles of Li\(^+\) per mole of LiCoO\(_2\) were extracted during the charging cycle, thus introducing instability in the cathode. Consequently, cycle stability of the full-cell may be enhanced by improved cathode performance. This work thus lays the foundation for development of high energy and power Li-ion batteries.

2.9. Experimental Techniques

2.9.1. Material Preparation

The graphene was grown on Cu by chemical vapor deposition (CVD) process in a quartz tube reactor at 1000 °C with a mixture of \(\text{H}_2\) (300 sccm) and \(\text{CH}_4\) (9 sccm) at ~360 Torr (\(\text{H}_2/\text{CH}_4\) pressure ratio is ~30:1). The detailed procedure was described in Chapter 1. The catalyst for growing CNT carpets was prepared by depositing 1 nm Fe catalyst and 3 nm \(\text{Al}_2\text{O}_3\) support layer sequentially on the Cu-graphene substrate by electron-beam evaporation. The CNT carpets were grown on the substrate in a quartz tube CVD reactor via water-assisted CNT growth technique. A mixture of \(\text{H}_2\) (210 sccm), \(\text{C}_2\text{H}_2\) (2 sccm), and \(\text{H}_2\) bubbled through in-house deionized \(\text{H}_2\text{O}\) (200 sccm) was flowed into the reactor at 750 °C at a pressure of 25 Torr. The \(\text{H}_2\) served as a carrier gas for the \(\text{H}_2\text{O}\). The mixture was
heated with a heating tape wrapped around the gas line before it passed through the flow controller. The role of the H$_2$O was to remove amorphous carbon formed on the catalyst surface during growth$^{45}$ and possibly in the sample being grown. The independently regulated gas lines were connected into a single pipeline that was connected to the quartz tube. The tube ran through a furnace that was heated to 750 °C. An independent tungsten filament at the hot zone was then heated with a current of ~9.5 A (power of ~30 W) to generate atomic hydrogen for quick reduction of the catalyst particles in order to initiate the CNT nucleation. The substrate was inserted into the hot zone and treated with the atomic hydrogen for 30 s. The pressure was then decreased immediately to 8.6 Torr (the limit of the pump) for the growth of the CNT carpets. All gases were purchased from Matheson and in-house filtered. The H$_2$ was 99.999% ultra-high purity grade. The CH$_4$ was 99.0% chemical purity grade.

2.9.2. Electrode Preparation and Characterization

All devices were assembled in an Ar-filled dry box. All device testing was carried out in the ambient laboratory environment. Galvanostatic measurements were conducted in a battery testing equipment (8 Channel Battery Analyzer, MTI) under constant current. Cyclic voltammetry experiments were carried out in a potentiostat (Electrochemical Analyzer, CH Instruments) at 0.5 mV/s.

2.9.2.1. Graphene-CNT/Li Half-Cell

In order to assemble a half-cell, the graphene-CNT electrode was placed in a 2032 Swagelok coin cell. A drop of electrolyte solution made of 1 M LiPF$_6$ in a solvent mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate (EC:DMC:DEC, 1:1:1 by
volume) was added on the graphene-CNT electrode. A separator was placed atop and 2 more drops of the electrolyte solution were added. A Li coin was placed atop. A steel plate was placed above and gently pressed with tweezers. After placing a spring washer, the lid was placed and the device was crimped with a pressure of ~900 psi using a hydraulic crimpling machine (MSK-110, MTI). The device was tested as described above within an hour. The graphene-CNT electrode was the positive electrode with respect to the Li reference and counter electrode. The first step, the Li insertion into the graphene-CNTs, was a discharge process with the assembled graphene-CNT/Li half-cell already in a charged state.

For pre-lithiation treatment, the graphene-CNT electrode was placed in a 2032 Swagelok coin cell (in an Ar-filled dry box) and a drop of the electrolyte solution was added for every 0.1 mg of graphene-CNTs. Li coin was placed atop with no separator. A steel plate was placed above and firmly pressed with tweezers in different directions for ~30 s. The cell was left untouched for 2 h after which the Li coin and steel plate were removed. The pre-treated graphene-CNT electrode was transferred to a new coin cell and a half-cell was fabricated as described for the non-treated material above.

2.9.2.2. LiCoO$_2$/Li Half-Cell

Using a spatula, 31 mg LiCoO$_2$ (Sigma-Aldrich) was mixed with 6 mg of pristine GNR stacks (H-GNRs, AZ Electronic Materials) and further mixed with 4 mg polyvinylidifluoride (PVdF, Sigma-Aldrich) in a watch glass. Two drops of N-methylpyrrolidone (NMP, Acros chemicals) were added and mixed with the powder mixture using a spatula. 2-4 mg of the resulting slurry was pasted on a 0.8 × 0.8 cm$^2$ Al
foil. The device was dried under vacuum at 70 °C for 6 h. A steel plate was placed above and slightly pressed by tweezers. A half-cell was assembled in a 2032 Swagelok cell as described above.

2.9.2.3. LiCoO₂/Graphene-CNT Full-Cell

After pretreatment of the graphene-CNT electrode as performed above in a 2032 Swagelok cell, the Li coin was removed and a drop of 1 M LiPF₆ in EC:DMC: DEC (1:1:1 by volume) electrolyte solution was added onto the graphene-CNTs. A separator was placed atop and 2 more drops of the electrolyte solution were added. The LiCoO₂-GNRs electrode was placed atop. A steel plate was placed above and slightly pressed by tweezers. After placing a spring washer, the lid was placed and the device was crimped with a pressure of ~900 psi.
References


**Research Contributions**

Abdul-Rahman O. Raji designed and performed all the experiments, device fabrication, and characterization. Xiujun Fan performed some of the CNT growth. Jian Lin and Nam Dong Kim deposited the catalyst and catalyst support for the CNT growth. James M. Tour and oversaw all aspects of the project.
Chapter 3

Graphene Nanoribbons and Iron Oxide Nanoparticle Composite as a Lithium-Ion Battery Electrode

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Research contributions are included at the end of the chapter.

3.1. Introduction

The advancement of environmentally acceptable anode materials for lithium-ion batteries (LIBs) with high energy and power density and a long life-time is a key step for the development of large-scale applications for portable electronics, renewable energy source and electrical vehicles.1, 2 To this end, iron oxide as an anode material for LIBs has drawn much attention because of its large reversible capacity (~1007 mAh/g), low cost, and non-toxicity.3-6 However, the poor intrinsic electrical conductivity and large capacity decay
caused by the large volume expansion of iron oxide during lithiation hinder its practical applications for LIBs. There are different approaches to overcome these problems; one solution is to fabricate iron oxide nanostructures such as nanoparticles (NPs),\(^3,^7\) nanoribbons\(^6\) and nanorods.\(^8\) Other solutions are to confine the iron oxide nanostructures with carbon\(^9-^{12}\) or to form a composite of the iron oxide with the carbon host matrix such that the carbon host acts as a mechanical buffer to release strain during cycling and to enhance lithium diffusion into the electrode.\(^4,^5,^{13}\) Thus, the electrochemical performance of iron oxide-based anode has been significantly improved.

Quasi one-dimensional graphene nanoribbons (GNRs) with good electrical conductivity\(^14\) and high aspect-ratio offer a suitable conductive matrix and provide mechanical flexibility for the iron oxide to accommodate volume changes during cycling. We demonstrate here a facile route to prepare a nanocomposite from GNRs and Fe\(_2\)O\(_3\) NPs. GNRs were intimately coated with \(~10\) nm Fe\(_2\)O\(_3\) NPs. The as-prepared Fe\(_2\)O\(_3\) NPs were predominately the maghemite phase (\(\gamma\)-Fe\(_2\)O\(_3\)). Fabricated electrodes made from the as-prepared nanocomposite exhibit an enhanced reversible capacity of > 1100 mAh/g in the first 20 cycles and maintain > 910 mAh/g after 134 cycles at a current density of 200 mA/g. The electrodes also have a high capacity performance of > 540 mAh/g at a charging rate of 2 A/g, still much larger than the capacity of graphite (372 mAh/g). The superior electrochemical performance of the as-prepared nanocomposite can be attributed to the unique structure of the Fe\(_2\)O\(_3\) NPs conformally coated with conductive GNRs.
3.2. Synthesis and Structural Characterization of the GNR/Fe$_2$O$_3$ Composites

3.2.1. Preparation and Morphology of GNR/Fe$_2$O$_3$

**Figure 27.** (a) Scheme of the synthesis of the GNRs/Fe$_2$O$_3$ composites. (b) Low magnification SEM image of the GNRs/Fe$_2$O$_3$-P composites. (c) High magnification SEM image of the GNRs/Fe$_2$O$_3$-P composites.
Figure 27a illustrates the synthesis procedure of the GNRs/Fe$_2$O$_3$ NPs composite. The GNRs were produced from unzipping multiwall carbon nanotubes (MWCNTs) that were treated with K/Na alloy, producing K-intercalated MWCNTs.\textsuperscript{14-16} FeCl$_3$ was added and reduced by the K/Na to form Fe. This process partially splitted MWCNTs on which Fe NPs were coated. The Na/K alloy was quenched with CH$_3$OH, generating H$_2$ that induced efficient unzipping of the MWCNTs into GNRs. In the above procedures some generated impurities such as KCl, NaCl, CH$_3$OK and CH$_3$ONa are water-soluble and were easily removed during washing. Next, the obtained GNRs/Fe composite was washed with deionized water, oxidizing the Fe NPs to iron oxide NPs, or GNRs/Fe$_2$O$_3$-P where “P” stands for pre-annealing (For the details, see the Supporting Information). Subsequently, the composite was annealed in air at 250 or 300 °C for 14 h. The samples were denoted as GNRs/Fe$_2$O$_3$-250 and GNRs/Fe$_2$O$_3$-300, respectively. The morphology of the GNRs/Fe$_2$O$_3$-P is shown in Figure 27b, in which the well dispersed GNRs, with widths of ~ 200 nm and lengths up to a 100 μm, form an interconnected web as observed with field emission scanning electron microscopy (SEM). The enlarged SEM image in Figure 27c shows that the GNRs are well covered by Fe$_2$O$_3$ NPs. This structure facilitates charge transfer between the Fe$_2$O$_3$ NPs and the current collectors.

3.2.2. X-ray Diffraction Studies of GNR/Fe$_2$O$_3$

To analyze the crystal structure of the GNRs/Fe$_2$O$_3$-P, GNRs/Fe$_2$O$_3$-250 and GNRs/Fe$_2$O$_3$-300, X-ray diffraction (XRD) measurements were performed (Figure 28). The characteristic peak at 2θ = 26.3° confirms the existence of graphene layers in all of the composites. Furthermore, the as-prepared composite shows a predominance of the maghemite phase of iron oxide (γ-Fe$_2$O$_3$). From XRD analyses, when annealed at 250 °C
for 14 h, the more stable hematite iron oxide ($\alpha$-Fe$_2$O$_3$) begins to appear in the GNRs/Fe$_2$O$_3$-250. As the annealing temperature was increased to 300 °C, the stronger characteristic peaks of hematite phase appeared, indicating the higher concentration of $\alpha$-Fe$_2$O$_3$ in the GNRs/Fe$_2$O$_3$-300. The different phases of the composites greatly impact the electrochemical performance.

![Figure 28. XRD spectrum of GNRs/Fe$_2$O$_3$ composite at different annealing temperatures.](image)

(bottom) The sample GNRs/Fe$_2$O$_3$-P shows a predominance of the maghemite phase of iron oxide ($\gamma$-Fe$_2$O$_3$). (middle) Annealed at 250 °C, hematite iron oxide ($\alpha$-Fe$_2$O$_3$) appears in the GNRs/Fe$_2$O$_3$-250. (top) As the annealing temperature increased to 300 °C, the stronger characteristic peaks of hematite phase indicate the higher concentration of $\alpha$-Fe$_2$O$_3$ in the GNRs/Fe$_2$O$_3$-300.
3.2.2. Microscopic Characterization of GNR/Fe$_2$O$_3$

**Figure 29.** TEM characterizations of GNRs/Fe$_2$O$_3$ composite. (a) TEM image of synthesized GNRs/Fe$_2$O$_3$ composite showing uniformly distributed Fe$_2$O$_3$ NPs on GNRs. (b) HRTEM image showing graphite structure of GNRs. (c) HRTEM image of a representative γ-Fe$_2$O$_3$ NP. The well-defined diffraction pattern indicates the highly crystallinity of γ-Fe$_2$O$_3$ NPs. (d) HRTEM image of a representative α-Fe$_2$O$_3$ NP. (e) An
STEM image of the GNRs/Fe$_2$O$_3$ composite and the corresponding elemental mapping of (f) carbon, (g) oxygen and (h) iron, suggesting the homogeneous dispersion of C, O and Fe in the composites.

The morphology and crystal structure of the composite were also investigated by transmission electron microscopy (TEM, Figure 29). Figure 29a, taken from GNRs/Fe$_2$O$_3$-P, shows well-distributed Fe$_2$O$_3$ NPs along the GNRs. Figure 29b shows that the sizes of the NPs are ~10 nm and the lattice spacing between graphene layers is 0.34 nm. Further inspection of the γ-Fe$_2$O$_3$ by high resolution TEM (HRTEM) shows different domains with clearly observed lattice fringes in each domain (Figure 29c), indicative of the polycrystalline nature of the as-prepared γ-Fe$_2$O$_3$ NPs. The uniform distance between the lattice fringes is 0.25 nm, in good agreement with the spacing between (311) planes of γ-Fe$_2$O$_3$. Normally, the synthesis of γ-Fe$_2$O$_3$ involves an aqueous pathway that results in metal cation vacancies induced by the water being incorporated into the material.[17, 18]

When annealed at 250 °C or higher, some of the γ-Fe$_2$O$_3$ NPs are converted to more thermodynamically stable α-Fe$_2$O$_3$,[19] as shown in Figure 2d taken from GNRs/Fe$_2$O$_3$-250. The distance of 0.47 nm between the uniform lattice fringe is the spacing of plane Fe$_2$O$_3$ (012). To confirm the composition of GNRs/Fe$_2$O$_3$, a TEM elemental mapping by was performed. As shown in Figure 29e-h, carbon, oxygen and iron were homogeneously distributed in the GNRs.
3.2.3. Spectroscopic Characterization of GNR/Fe₂O₃

Figure 30. XPS spectrum of a representative GNRs/Fe₂O₃-P composite. The weight percent is around 36.6 wt% for carbon and 63.4 wt% for iron oxide. a) whole spectrum; b) spectrum for carbon; c) spectrum for oxygen; d) spectrum for iron.

To gain further insight into the composite, X-ray photoelectron spectroscopy (XPS, Figure 30) was done on GNRs/Fe₂O₃-P. Carbon, oxygen and iron were detected in the XPS spectrum, (Figure 30), consistent with the result from the elemental mapping. The XPS atomic percentage of 54.8% for carbon corresponds to 36.6 wt% carbon. This result is
consistent with the thermogravimetric analysis data (TGA, Figure 31). The Raman spectrum of the GNRs/Fe₂O₃-P reveals strong peaks at 223 (A₁g), 290 (E₉), 408 (E₉), and 1321 cm⁻¹, a weaker peak at 607 (E₉) cm⁻¹, and very weak peaks at 242 (E₉) and 497 (A₁g) cm⁻¹ (Figure 32). These vibrational modes are in good agreement with the characteristic peaks of α-Fe₂O₃. The broad peak at 660 cm⁻¹ could be attributed to the maghemite residues in the sample. The reason for this major α-phase result by Raman when the XRD pattern of the GNRs/Fe₂O₃-P showed a predominance of the γ-phase (Figure 28), could be because α-Fe₂O₃ has a larger Raman cross-section than γ-Fe₂O₃ as previously suggested. Another reason could be the induced irreversible transformation to the α-phase by laser power.

![Figure 31. TGA spectrum of a representative GNRs/Fe₂O₃-P composite. Weight percentage is 67.6 wt% for iron oxide and is ~32.4 wt% for carbon.](image)
Figure 32. Raman spectrum of GNRs/Fe₂O₃-P. Raman spectrum was obtained using low-power 514 nm laser (0.714mW). The Raman spectrum revealed strong peaks at 223 (A₁g), 290 (E₂g), 408 (E_g), and 1321 cm⁻¹, a less strong peak at 607 (E_g) cm⁻¹, and weak peaks at 242 (E_g) and 497 (A₁g) cm⁻¹. These vibrational modes observed are in good agreement with the characteristic peaks of hematite. The Raman spectrum measured is however contradictory to the XRD pattern obtained for the GNRs/Fe₂O₃-P which showed predominance of the maghemite phase of iron oxide. This is because iron oxide absorbs virtually of the visible wavelength of the Raman even at reduced power. The laser power absorption could induce heating, thus transforming the iron oxide to the more stable phase, hematite. The strong signals at 1354, 1584, and 2706 cm⁻¹ are the characteristic D, G and 2D peaks of graphene nanoribbons, respectively.
3.3. Electrochemical Properties of GNRs/Fe$_2$O$_3$ Composite Anode Electrodes

**Figure 33.** Electrochemical properties of GNRs/Fe$_2$O$_3$ composite anode electrodes. All of the capacities shown here are based on the weight of iron oxide NPs. (a) Cyclic voltammetry of the GNRs/Fe$_2$O$_3$-P composite anode. (b) The first and second charge-discharge curves of the composite GNRs/Fe$_2$O$_3$-P anode. (c) Comparison of the cyclability of GNRs/Fe$_2$O$_3$-P, GNRs/Fe$_2$O$_3$-250 and GNRs/Fe$_2$O$_3$-300 at a rate of 0.2 A/g. (d) Comparison of rate performance of GNRs/Fe$_2$O$_3$-P, GNRs/Fe$_2$O$_3$-250 and GNRs/Fe$_2$O$_3$-300.
The electrochemical lithium storage properties of the GNRs/Fe$_2$O$_3$ composites as anode materials for LIBs were investigated by cyclic voltammetry (CV) measurements, galvanostatic charge/discharge measurements and electrochemical impedance spectroscopy measurements. Figure 33a shows the CV curves of an electrode made from GNRs/Fe$_2$O$_3$-P. The CV curves of the initial three cycles were obtained from 0.01 V to 3 V at a scan rate of 0.5 mV/s. In the first cycle, unlike the ordinary α-Fe$_2$O$_3$ electrode, there are no peaks at 1.0 V and only a minuscule peak at 1.5 V, both of which correspond to the formation of hexagonal α-Li$_x$Fe$_2$O$_3$ and phase change from α-Li$_x$Fe$_2$O$_3$ to cubic Li$_x$Fe$_2$O$_3$. This result agrees with the XRD result, suggesting that the predominant phase of the iron oxide NPs is maghemite (γ-Fe$_2$O$_3$). The profound cathodic peak at 0.5 V corresponds to the formation of a solid electrolyte interface (SEI) and the complete reduction to Fe(0). This peak disappears in subsequent cycles and evolves into a peak at 0.73 V, which is thought to be the reversible lithium insertion and complete reduction of Fe$_2$O$_3$ to Fe(0). The broad anodic peak at ~1.8 V corresponds to the reversible oxidization of Fe(0) to Fe(III). The reproducible cathodic and anodic peaks at 0.73 V and 1.8 V, respectively, in the second and third cycles agree well with the plateau voltages in the galvanostatic charge-discharge curves at a current density of 100 mA/g, with a cut-off potential window of 0.01 V-3.0 V (Figure 33b). The composite electrodes deliver an initial discharge capacity of 1586 mAh/g, with a reversible charge capacity of 1117 mAh/g. The relatively low 29% irreversibility can be attributed to the formation of SEI or the decomposition of electrolyte, which is quite common in lithium-ion battery electrodes. In the second cycle, the discharge and charge capacities of 1224 mAh/g and 1110 mAh/g indicate the high reversibility. The lithium storage capacity is more than the theoretical value of iron oxide.
(~1007 mAh/g). This enhanced storage capability occurs in some metal oxide nanostructures.\textsuperscript{13,25,26}

![Graph showing cycling performance of GNRs.]

**Figure 34.** Cycling performance of GNRs.

![Graph showing capacity retention of Fe\textsubscript{2}O\textsubscript{3} NPs without GNRs.]

**Figure 35.** Capacity retention of Fe\textsubscript{2}O\textsubscript{3} NPs without GNRs.

To further characterize the lithium storage properties of the composite electrodes with various annealing conditions, capacity retention tests were performed at a current density of 0.2 A/g (Figure 33c). The as-prepared GNRs/Fe\textsubscript{2}O\textsubscript{3}-P electrodes exhibited an
initial discharge capacity of 1190 mAh/g that increased to 1259 mAh/g after 26 cycles. Such capacity rise could be due to transformation of the crystalline structure to an amorphous-like structure during cycling, thus enhancing the lithium insertion kinetics. In the following cycles the capacity was slowly decreased then stabilized at ~ 850 mAh/g after ~ 90 cycles. This stabilization can be attributed to the stably transformed phase and structure of the host materials. Finally, the capacity remained ~ 910 mAh/g after 134 cycles. However, when annealed at elevated temperature, the initial capacity is not only less than that in the as-prepared sample, but the capacity retention decays much faster. In the case of GNRs/Fe$_2$O$_3$-250, the initial capacity was ~1003 mAh/g and was at ~ 745 mAh/g after 128 cycles. The electrodes prepared with GNRs/Fe$_2$O$_3$-300 had an initial capacity of 1291 mAh/g. However, the capacity quickly decayed to ~ 400 mAh/g after 50 cycles. The decreased capacity could be due to a number of reasons. The polycrystalline structure of the as-prepared Fe$_2$O$_3$ NPs ($\gamma$-Fe$_2$O$_3$), containing cationic vacancies, could enhance lithium storage kinetics. In addition, the $\gamma$-Fe$_2$O$_3$ phase of iron oxide does not possess the phase transition that $\alpha$-Fe$_2$O$_3$ has during lithium insertion; this phase transition induces irreversible lithium storage. As the annealing temperature increased, the concentration of $\alpha$-Fe$_2$O$_3$ in the composite increased, leading to irreversible lithium storage. In addition, when annealed at 300 °C, GNR layers start to oxidize, thus losing electrical conductivity. To investigate the major contribution of the lithium storage capacity, control experiments were performed. Figure 34 shows the capacity retention of bare GNRs at a rate of 0.2 A/g. The low reversible capacity of ~ 245 mAh/g from bare GNRs suggests that the major contribution of lithium storage capacity is from iron oxide NPs. To demonstrate the superior performance of the GNRs/Fe$_2$O$_3$ composite, the cycling performance of Fe$_2$O$_3$
NPs without GNRs at a current density of 0.2 A/g was investigated (Figure 35). The capacity quickly degraded to ~ 180 mAh/g after 50 cycles, indicative of the important role of GNRs in the cycling performance of the electrodes.

**Figure 36.** Comparison rate performance of GNRs/Fe$_2$O$_3$-P (a), GNRs/Fe$_2$O$_3$-250 (b) and GNRs/Fe$_2$O$_3$-300 (c) at various current densities.

The rate capability is an important parameter in evaluating the lithium storage performance of the electrodes. Here, the GNRs/Fe$_2$O$_3$ composites prepared using different annealing conditions were investigated. Figure 33d compares the capacity performance when applying current densities from 0.1 A to 2 A. The representative cycling data at different current densities are shown in Figure 36. The rate capacity strongly depends on
the annealing temperature. The GNRs/Fe$_2$O$_3$-P shows high reversible capacity of 1201, 1123, 930, 740 and 544 mAh/g at current densities of 0.1, 0.2, 0.5, 1 and 2 A/g, respectively. And the GNRs/Fe$_2$O$_3$-250 exhibits only slightly smaller capacities at the same current densities, with a capacity of 520 mAh/g at a current density of 2 A/g. Furthermore, the reversible capacity for both GNRs/Fe$_2$O$_3$-P and GNRs/Fe$_2$O$_3$-250 can be recovered to the value close to the original value when the current density was returned to 0.1 A/g (Figure 36), indicative of the good rate performance. However, when the annealing temperature was increased to 300 °C, the rate performance was significantly degraded. The sample of GNRs/Fe$_2$O$_3$-300 shows a capacity of only 68 mAh/g at the current density of 2 A/g.

3.4. Summary

In summary, a facile and scalable synthesis route to GNRs/Fe$_2$O$_3$ composite was developed. The as-prepared composite anode material for LIBs had a reversible capacity as high as 1190 mAh/g and retained ~ 910 mAh/g after 134 cycles at a rate of 0.2 A/g. In addition, the anode exhibited good rate performance of 544 mAh/g at a rate of 2 A/g. The unique structures of GNRs with high electrical conductivity and the enhanced vacancy of iron oxide NPs leads to excellent electrochemical performance. It is also noteworthy that the annealing conditions of the composite greatly impact the lithium storage performance. As the annealing temperature increased to 300 °C, both the cycling retention and rate capacity were significantly degraded. This straightforward, accessible method for preparation of anode materials for LIBs could pave the way to a new route for achieving high-performance energy storage devices.
References


Research Contributions

Abdul-Rahman O. Raji designed, synthesized, and characterized the materials. Jian Lin designed, fabricated and characterized the devices. Kewang Nan performed some of the Raman characterization. James M. Tour oversaw all aspects of the project.
Chapter 4

Silver-Graphene Nanoribbon Composite Catalyst for the Oxygen Reduction Reaction in Alkaline Electrolyte

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Silver-Graphene Nanoribbon Composite Catalyst for the Oxygen Reduction Reaction in Alkaline Electrolyte. *contributed equally

Research contributions are included at the end of the chapter.

4.1. Introduction

Graphene, a two-dimensional network of sp²-hybridized carbon widely recognized for its outstanding thermal, mechanical, and electronic properties, holds much promise for applications in energy storage and conversion. One such application garnering significant attention is in the electrocatalysis for the oxygen reduction reaction (ORR). Effective catalysts are needed for fuel cells and next generation metal/air batteries. While
Pt and/or Pt-based alloys have consistently demonstrated excellent catalytic activities, the prohibitive cost of Pt and its low abundance ultimately prevents their widespread utilization. Therefore, highly active, stable, cost-effective and abundant alternative materials are needed.\(^4\)

Functional graphene-based composite materials, obtained by either manual blending techniques or \textit{in situ} syntheses, are often studied for their ORR activity because of the possible synergistic effects that can further enhance the catalytic properties. Graphene is commonly employed as a support material onto which metal nanoparticles or other functional nanomaterials can be anchored or grown \textit{in situ}.\(^6\) While undoped graphene catalyzes the ORR via the less favorable two-electron reduction (forming peroxide species) graphene-composite materials often promote the favored four-electron process and can have improved kinetic rate constants relative to either component, therein illustrating the synergistic benefits of the two components in the hybrid.\(^6,8\) Graphene composites can also provide for catalysts with higher long-term stability that is less susceptible to oxidative degradation (e.g. from peroxide).

Numerous studies have demonstrated Ag and Ag-containing composites to be active ORR catalysts.\(^9\)\textendash\(^14\) In addition to being a more cost-effective and abundant metal as compared to Pt, the majority of reports conclude that Ag catalyzes the ORR via the ideal four-electron reduction process with very little peroxide formation.\(^4,10,11\) Ag-containing composites have achieved mass activities on the same order of magnitude as Pt/C catalysts.\(^13\) Ag/C commercial cathodes have been shown to achieve power densities comparable to a Pt/C electrode when employed in alkaline anion-exchange membrane fuel cells,\(^15\) providing compelling evidence that Ag composites should be considered highly
active electrocatalysts. Furthermore, when one considers the benefits of graphene along with the ~ 65 times lower cost of Ag as compared to Pt, composite Ag-graphene-based catalysts are of great interest due to the synergistic behavior that can be achieved.

A recent report details a Ag-reduced graphene oxide (RGO) composite catalyst that demonstrated activity superior to that of a commercial Ag/Vulcan XC-72 Carbon (termed Ag/C here) catalyst with a comparable Ag loading.\textsuperscript{16} This increase in activity was attributed to the more disperse and smaller Ag nanoparticles (i.e. higher electro-active surface area) that were prepared on the RGO than what was achieved with the commercial Vulcan carbon. The graphene component acted as a better dispersant and provided for better nucleation of Ag-nanoparticles. Ag-multi-walled carbon nanotubes (Ag-MWCNTs) have also been shown to operate via an efficient four-electron reduction process in the ORR.\textsuperscript{14,17} RGO sheets possess a strong capacity for absorption of the metal ions, enabling the initial nucleation while promoting the growth of smaller nanoparticles, which are consistently shown to be more catalytically active than their bulk counterparts.\textsuperscript{6} Graphene sheet defects have also been hypothesized to lower the activation energy for O\textsubscript{2} dissociation, thereby decreasing the energy barrier for the rate-determining step by destabilizing the intermediate species through accelerated charge transfer from metal to O\textsubscript{2}.\textsuperscript{6,18}

Composite materials based on graphene studied to date for the ORR most often include various chemically modified graphenes (CMGs), including those with heteroatom doping, often available from graphite/graphite oxide (such as RGO), or those prepared via thermal or chemical vapor deposition (CVD) methods. Carbon nanotubes (CNTs), MCWNTs and carbon nanofibers\textsuperscript{2} have also been studied; however, the catalytic behaviors
of graphene nanoribbon (GNR) composites, as synthesized here by the chemical unzipping of MWCNTs, have yet to be explored.

It is reported that the nanoribbon edge is uniquely reactive from both a chemical and electronic perspective.\textsuperscript{19-21} In addition, density functional calculations have suggested that because graphene edge structures are reactive by nature, ORR activity is promoted due to the significant decrease in the barriers posed to oxygen adsorption and the first electron transfer.\textsuperscript{22} Therefore, it follows that these edge effects could be increasingly important for a GNR-containing catalyst due to the high aspect ratio of these elongated strips of graphene.

In the present work, Ag-GNRs were examined for their ability to serve as a catalyst for the ORR in alkaline electrolyte. Ag-GNRs were prepared from the chemical unzipping of MWCNTs with Na/K alloy, reaction with Ag(O\textsubscript{2}CCH\textsubscript{3}) and then CH\textsubscript{3}OH. This hybrid material exhibited improved electrochemical behavior as compared to the underlying GNR substrate alone and a commercial Ag/C catalyst. In addition, the Ag-GNR hybrid demonstrates an outstanding tolerance to CH\textsubscript{3}OH crossover which exceeds that of the commercial benchmark, 20% Pt/C under the given conditions.

4.2. Synthesis and Structural Characterization of Ag-GNR

Graphene-based scaffolds are often examined for their ability to stabilize or limit nanoparticle growth, and to provide for good dispersions. We conjectured that reacting the intermediate K intercalated MWCNT, obtained in the unzipping reaction used to prepare GNRs, with Ag\textsuperscript{+} could lead to Ag-GNR whereby the GNR serves as a dispersant and
scaffold leading to small and stable \textit{in situ} prepared nanoparticles, ideally useful for catalysis applications. The reaction schematic for the one-pot synthesis of the Ag-GNR composite is depicted in Figure 37. The details of this procedure are described in the Experimental section. Based on previous reports\textsuperscript{24-28}, K intercalates between the layers of MWCNTs, which longitudinally splits to form GNRs upon quenching with CH\textsubscript{3}OH. Here, treatment with a Lewis acid, Ag(O\textsubscript{2}CCH\textsubscript{3}), before CH\textsubscript{3}OH quenching induces partial splitting. At this stage, Ag nanocrystals formed on the partially split tubes, which served as a scaffold for reduction of Ag(O\textsubscript{2}CCH\textsubscript{3}) by Na/K. The partially split tubes become fully unzipped after quenching the reaction with CH\textsubscript{3}OH by reacting with the intercalated K to generate H\textsubscript{2}.

\textbf{Figure 37.} Reaction schematic for preparation of Ag-GNR

TEM images in Figure 38 demonstrate the complete unzipping of the MWCNT (Figure 38a) into Ag-decorated GNR (Figure 38b). Figure 1c shows the edge of the GNR with Ag nanocrystals ranging in size from 5 to 25 nm. Figure 38d clearly depicts the crystalline structure of the Ag in the (111) crystallographic planes with lattice spacing of 0.24 nm. Though with a lower resolution than TEM, SEM images revealed more general microscopic information about the MWCNTs and the Ag-GNR, showing a consistent transformation from tubes into ribbons (Figure 38e, f). The interspersed particles on the
SEM image of the MWCNTs (Figure 38e) are due to remnant catalysts, such as iron, and amorphous carbon from the tube growth.

Figure 38. TEM images of a) MWCNT, b) Ag-GNR; HRTEM images of c) Ag-GNR, d) Ag nanocrystal along one of its crystallographic planes; SEM images of e) MWCNTs, f) Ag-GNR.

This post-growth residue has been well documented in the literature. The starting MWCNTs showed some trace iron residues that are too minute in amount to detect by XRD and amorphous carbon (Figure 38e). While such Fe impurities (e.g. iron oxide) could potentially influence the ORR catalysis, the observed activity (vide infra) with Ag-GNR >> GNR would indicate that their impact on ORR in the case of Ag-GNR here is not
significant. The majority of the *in situ* grown Ag is nanocrystalline, as verified in Figure 38b. XPS data given in Figure 39a and b confirmed the presence of GNRs showing the C 1s peak (see Figure 40 for the de-convoluted peak) and Ag with the 3d peaks at 368.5 eV and 374.6 eV for Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub>, respectively.\textsuperscript{30}

**Figure 39.** XPS spectrum of a) Ag-GNR, b) Ag 3d peak; c) XRD pattern of Ag-GNR; d) TGA of Ag-GNR in air.
The excellent crystallinity of the Ag nanocrystals demonstrated by high resolution TEM was supported by the XRD pattern (Figure 39c), which shows precise matching with known Bragg diffractions from highly crystalline Ag. Even after being heated to 900 °C, the Ag nanocrystals were stable in air, as expected, as shown in Figure 41. The structure of GNR was also intact along the c-axis, as shown by the 002 peak at 26.3°, corresponding to a d-spacing of 3.34 Å. The TGA in Figure 39d showed the weight loss of the Ag-GNR in air, with Ag nanocrystals as the remaining material, having a concentration of 70 wt% (corrected for the residual material from burning of GNR given in Figure 42). The weight loss from ~200 °C to 550 °C corresponds to the GNR loss.

Figure 40. C 1s peak of Ag-GNR; The C=C bond is the graphitic sp² carbon of the GNR. The C-C peak could arise from the edges or the basal plane.
Figure 41. XRD Pattern of residue of Ag$^0$-GNR from Fig. 2d (main text) after TGA. The peaks match the Ag$^0$ peaks from Fig. 2c (main text), indicating that there is no oxidation of the Ag$^0$ nanoparticles after TGA.
Figure 42. TGA of GNR as performed in air.
4.2. Electrochemical Characterization of Ag-GNR

**Figure 43.** Representative LSV in O\(_2\) saturated 0.1 M KOH for GNR with increasing negative current for 500, 900, 1600, 2500, 3600 rpm.

A RDE apparatus was used to analyze the catalytic properties of the GNR and Ag-GNR, as compared to Vulcan carbon, and the commercial catalysts, Ag/C, 20% Pt/C and averaged data is summarized in Table 3. Select electrocatalytic properties. RDE studies negate problems of mass-transfer and provide a method for kinetically controlled processes to be studied. Representative LSVs for GNRs are given in Figure 43 while its comparison to Vulcan at 2500 rpm is shown in Figure 44a. The increase in current with faster rotation rates, as shown in Figure 43, is expected, as faster rotation rates correlate with faster O\(_2\) flux to the catalyst surface.
Table 3. Select electrocatalytic properties. [a] The average of at least three independent catalyst films/LSV experiments is reported; [b] rate constants are [value shown x 10^{-2} cm/s]; [c] A value as high as 3.84 was obtained from one LSV data set.
**Figure 44.** LSV data in O\(_2\) saturated 0.1 M KOH for a) comparison of GNR (filled squares) and Vulcan carbon (filled circles) at 2500 rpm, b) Ag-GNR with increasing negative current for 500, 900, 1600, 2500, 3600 rpm; c) comparison of GNR (filled squares), Ag/C (filled diamonds), Ag-GNR (filled triangles) and 20% Pt/C (crossed squares) at 2500 rpm. d) Koutecky-Levich plots for Ag-GNR (filled triangles) and Pt/C (crossed squares); idealized slopes for n = 2 (short dash) or 4 (long dash) are also shown.

**Figure 45.** RRDE Data (@ 2500 rpm) for Vulcan (filled circles), GNR (filled squares), Ag/C (filled diamonds), Ag-GNR (filled triangles) and 20%Pt/C (crossed squares), with
expanded view b) of Ag-GNR and 20%Pt/C. All potentials vs. Hg/HgO reference. c) $i$-$t$ Chronoamperometric data for: Ag-GNR (filled triangles) and 20% Pt/C (crossed squares) at -350 mV at 1000 rpm in 0.1 M KOH solution. d) Percent chronoamperometric response upon 2 wt. % CH$_3$OH injection at t=250 s.

The GNR and Vulcan carbon have similar onset values (~ -322 mV vs. Ag/AgCl), with $n$ values (GNR = 1.97 vs. Vulcan = 1.6) that indicate that the 2-electron pathway reduction to peroxide is the dominant mechanism for both these materials, consistent with typical observations for carbon materials, including un-doped graphenes.[8,12-14] The production of significant peroxide with Vulcan (78-89%), and less so with GNR (~ 61-69%), was observed with RRDE studies, Figure 45a and Figure 46. In general, higher surface area carbons are often used in an attempt to increase both the specific current density and improve the onset potential of nanoparticle/carbon catalyst-composites [8]; however, despite the fact that the GNRs prepared here have surface areas only in the 30 to 50 m$^2$/g range (we estimate stacks of ~ 30 to 40 sheets), the GNR themselves are able to sustain more current at more negative potentials than the Vulcan carbon (230-250 m$^2$/g). On average, the GNRs exhibited a slightly lower charge transfer resistance (7998 Ω) than the Vulcan (9068 Ω), and exhibit the same or higher current at any given potential. Vulcan carbon is commonly used in commercial electro-catalysts due to its good electronic conductivity and reasonably high surface area, e.g. it finds application in our commercial Ag/C and 20% Pt/C benchmark electrocatalysts.
Figure 46. $\chi (\text{H}_2\text{O}_2)$ (@ 2500 rpm) for Vulcan (filled circles), GNR (filled squares), Ag/C (filled diamonds) Ag-GNR (filled triangles) and 20%Pt/C (crossed squares), with expanded view (on right) of Ag-GNR and 20%Pt/C. All potentials vs. Hg/HgO (0.1M KOH) reference. Percent peroxide was determined from RRDE data using $100\% \times \chi (\text{H}_2\text{O}_2)$, where $\chi (\text{H}_2\text{O}_2) = [2I_r/N]/[I_d + I_r/N]$. 
**Figure 47.** K-L Data for: GNR (filled squares), Ag-GNR (filled triangles) and 20% Pt/C (open squares). Idealized slopes for $n = 2$ (small dash) and $n = 4$ (large dash) are also shown.

Representative LSVs shown in Figure 44c demonstrate a 189 mV improvement in onset value (-0.133 V) for the Ag-GNR, as compared to GNR alone, which is attributed to the small and dispersed Ag nanoparticles. The Ag-GNR also displayed a ~ 150 mV more positive onset with more current than the commercial Ag/C. The Koutecky-Levich (K-L) equation was applied to the data in order to determine the number of electrons ($n$) involved in the ORR process. The obtained plots ($i^{-1}$ vs. $\omega^{-1/2}$) for Ag-decorated GNR are shown in the Figure 44d and Figure 47. The average $n$ value from Koutecky-Levich analysis for the Ag-GNR was found to be $n = 3.51$, while the best film gave a value of $n = 3.84$, similar to Pt/C. In contrast, ORR with the Ag/C was less efficient with $n = 3.09$ and ~ 2x slower rate constant, Table 3. Select electrocatalytic properties. RRDE studies (Figure 45a and b) for Ag-GNR were conducted (along with those for Pt/C, Ag/C, GNR and Vulcan) and less than ~ 1-5% peroxide was observed for the Ag-GNR, from -0.350 mV to -0.5 mV; Figure 46. This is slightly higher than the low amount observed for 20%Pt/C (< 1-3%) and better than that for Ag/C (< 10-25%). For both catalysts, more peroxide is produced at more negative potentials. Taken together, the results indicate the operation of a 4-electron reduction as the major pathway for oxygen reduction for Ag-GNR, similar to what was recently observed with Ag-RGO composites.
Figure 48. i-t Chronoamperometric data for: Ag-GNR (filled triangles) and 20% Pt/C (crossed squares) at -0.350 V. Additional data for Pt/C at -0.225 V (open circles) is also shown. Potentials vs. Ag/Ag\textsuperscript{+} at 1000 rpm in 0.1M KOH solution.

Pt/C is known to be susceptible to CH\textsubscript{3}OH crossover effects and poisoning (e.g. from carbon monoxide) which can impact its performance and limit its utility. To examine potential crossover effects in alkaline fuel cells, the electrocatalytic selectivity of Ag-GNR and 20% Pt/C for ORR vs. the electro-oxidation of CH\textsubscript{3}OH were examined at a potential value of –0.350 V vs. Ag/AgCl. Figure 45d and Figure 48 show the chronoamperometric percent response for the Ag-GNR hybrid material, as compared to 20% Pt/C. The 20% Pt/C suffers ~ 50% decrease in negative current upon addition of 2 wt. % CH\textsubscript{3}OH. In contrast, the Ag-GNR shows a fairly stable amperometric response with < 5% decrease in negative current, as illustrated in Figure 45c and d. In fact, after exposure to CH\textsubscript{3}OH, the Ag-GNR is producing approximately the same amount of current as the benchmark catalyst, if not slightly more. The exposure of 20% Pt/C to CH\textsubscript{3}OH at a lower potential (–
0.225 V vs. Ag/Ag⁺) also led to a large decrease (60%) in current, Figure 48. These results are encouraging for further development of Ag-GNR for alkaline fuel cells.

### 4.3. Summary

The *in situ* synthesis of Ag-GNRs was achieved via a chemical unzipping of K-intercalated MWCNTs with Ag(O₂CCH₃) and then CH₃OH, resulting in 5 to 25 nm Ag nanoparticles on the GNR surface. Ag-GNRs outperforms the commercial Ag/C for the ORR, operating by a 4-electron reduction with < 5% hydrogen peroxide produced in 0.1 M KOH. Ag-GNRs exhibited better electrocatalytic selectivity for the ORR in the presence of 2 wt.% CH₃OH, than the commercial benchmark, 20% Pt/C.

### 4.4. Experimental Techniques

#### 4.4.1. Materials Characterization

*Powder X-ray Diffraction (PXRD).* X-ray diffractograms were obtained from a Rigaku D/Max Ultima II Cu Kα (λ = 1.5418 Å) diffractometer and analyzed with Jade 9 software, equipped with the ICDD PDF-4+ database. Powder samples were mounted on a zero background holder.

*Scanning Electron Microscopy (SEM).* Images were taken using JEOL 6500F field emission microscope at 15 kV. Dry powder samples were placed on a double-sided carbon tape and mounted on a holder, without any conductive coating.
X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera spectrometer.

Transmission Electron Microscopy (TEM). Images were acquired from JEM 2100F field emission microscope, equipped with Gatan Digital Micrograph software. TEM samples were prepared by dispersing a small amount in 1,2-dichlorobenzene in a vial by bath sonication in an ultrasonic cleaner (Cole-Parmer, 08849-00) for 15 min to make a dilute dispersion. Several drops were pipetted onto a lacey carbon-coated TEM grid (Ted Pella) and dried on a hot plate at 70 °C for at least 3 h.

Thermogravimetric Analysis (TGA). Thermogravimetric data were obtained from Q-600 TGA (TA instruments) under dynamic air flow (compressed air, Matheson) at 60 mL/min. Samples were run at a rate of 10 °C/min from room temperature to 900 °C, using an alumina crucible.

4.4.2. Electrochemistry Calculations

Charge transfer resistances were calculated from the slope of the linear portion of the current-potential curve at low overpotential (c. ± 10 mV), recorded at 2500 rpm. Similar values were obtained using the 500 rpm data. Onset Potentials were calculated from the intersection of approximated tangent lines from; 0 V (base region before activation), and the half-wave potential ($E_{1/2}$), recorded at 2500 rpm. The resulting data was processed using Kaleidagraph software for presentation purposes.
References


**Research Contributions**

Abdul-Rahman O. Raji designed, synthesized, and characterized the materials. Danae Davis designed and performed the device characterization. Timothy Lambert oversaw the device fabrication, characterization, and analysis. James M. Tour and oversaw all aspects of the project.
Chapter 5

Composites of Graphene Nanoribbon Stacks and Epoxy for Joule Heating and Deicing of Surfaces

Research contributions are included at the end of the chapter.

5.1. Introduction

Deicing of surfaces such as on helicopter rotor blades, aircraft wings and tails, wind turbines, and transmission lines is a prevalent problem that degrades structural performance upon snow/ice accumulation.\textsuperscript{1,2} For instance, helicopter rotor blades are precisely designed and machined to generate airflow that supports buoyancy, but the presence or accumulation of snow and ice on the blade can cause surface roughness or shape modification that can compromise aerodynamic performance by perturbing airflow around the blade.\textsuperscript{3,4} Methods of ice removal include sprayed chemicals or hot fluid,\textsuperscript{5} mechanical force, infrared radiation,\textsuperscript{6} and Joule heating.\textsuperscript{7-9} Joule or resistive heating is an electrothermal technique that results from dissipation of electrical power generated in an electrically conductive material upon applied voltage, and it is an effective, energy-efficient, and versatile method
of ice removal that is also capable of real-time deicing. During Joule heating, a thin layer of ice near the interface between the ice and a heated surface can melt to generate a layer of water beneath the ice, thereby weakening the ice adhesion to facilitate removal by gravity, wind, or inflated pneumatic wrap. Lightweight, flexible, robust, and stable polymers could serve as an alternative to rigid, heavier metals or metal alloys as Joule heating elements if they were electrically conductive. However, such robust and stable polymers, for example epoxy, polyimide, and polyurethane, are insulating. Inclusion of additives, such as carbon black, carbon nanotubes, graphene, and silver nanowires, in the polymers generates an electrical network through the polymers to create a conductive polymer composite. Because the conductivity depends on interconnection of the additives to form an electrical pathway, large aspect ratio conductive additives are desirable for conductive polymer composites.

Graphene nanoribbon (GNR), a one-dimensional sp²-carbon nanostructure and an analogue of graphene, has excellent electrical conductivity. GNRs embedded in an epoxy-based polymer matrix could provide tunable electrical conductivity for the otherwise insulating polymer. GNRs are desirable conductive additives because of their good electrical and thermal conductivities. If long enough, GNRs need only be a relatively small fraction of a polymer composite to provide significant conductivity enhancement of the composite.

Here, we demonstrate that GNR-filled epoxy composites have sufficient electrical conductivity at relatively low GNR content (≤5 wt%) to perform voltage-induced heating. The GNRs were successfully applied as a stable additive for Joule heating and deicing of helicopter rotor blade surfaces. This was demonstrated in a helicopter rotor blade system
which consists of a rotor blade and a protective metal sleeve bonded with epoxy composite. By adding GNRs to the interlayer epoxy composite, the composite was made conductive; and it generated thermal energy upon applied voltage for deicing of the blade surface. This development will likely translate to other composite aircraft components and surfaces. It can yield immediate translation for formation of deicing coatings that can also mitigate lightening-induced charging of composite aircraft skins.

5.2. Structural Characterization of GNR Stacks

![Figure 49](image)

**Figure 49.** Structural characterization of GNR stacks. (a) Schematic of GNR stack (the actual GNR stack in this report contains more layers than shown in the schematic). (b) TEM and (c) SEM images of GNR stacks. (d) XRD pattern, (e) Raman spectrum of GNR stacks. (f) TGA curve of GNR stacks under air atmosphere.
In Figure 49a-c, the GNR stacks are shown to have up to 60 layers. There are up to 30 nm thick, 350 nm wide, and 50 μm long.\textsuperscript{20} The length-to-width aspect ratio is ~140. The (002) diffraction peak at 26.3° reveals a d-spacing of ~3.34 Å for the GNR stacks (Figure 49d). The Raman spectrum exhibits characteristic well-defined G and 2D bands at ~1587 cm\textsuperscript{-1} and ~2688 cm\textsuperscript{-1}, respectively (Figure 49e). They signify complete basal plane π-conjugated sp\textsuperscript{2}-carbon structure and absence of any significant surface defects. The pronounced intensity of the symmetry-forbidden D band in the Raman spectrum of the GNR stacks arises from the presence of edges. The GNR stacks are stable in air at room temperature; and oxidative decomposition only commences above 400 °C (Figure 49f). The material’s structural and chemical stability make it suitable for Joule heating and deicing applications.
5.3. Electrical Conductivity of GNR-Epoxy Composites

**Figure 50.** Electrical conductivity of GNR-epoxy composites. (a) A bar-shaped GNR-epoxy composite. (b) SEM image of cross-section of GNR-epoxy composite in “a”. (c) Surface resistance of the GNR-epoxy composite in “a”. (c) Electrical conductivity as a function of GNR mass fraction. Inset: electrical conductivity as a function of GNR volume fraction.
The fabricated composites is used in conductivity measurements by applying voltage across the bar from the contacts at the ends (Figure 50a). The GNRs form a network of percolating electrical channels inside the crosslinked epoxy matrix to generate an electrically conducting composite material (Figure 50b). The dark regions represent the interconnected GNRs. The bright regions signify charge accumulation by the insulating epoxy under electron beam of the SEM. The composite produces resistance that reaches as low as 1 Ω/□ at 5 wt% GNR content (Figure 50c). The GNR-epoxy composite produces conductivity of $10^{-4}$ S/m at 0.1 wt% GNR content; and the conductivity is >100 S/m at 5 wt% (2.5 vol%) (Figure 50d).
5.4. Joule Heating of GNR-Epoxy Composite

![Diagram of Joule Heating of GNR-Epoxy Composite](image)

**Figure 51.** Joule heating of GNR-epoxy composite. (a) Schematics of Joule-heated GNR-epoxy composite device. (b) Photograph of Joule-heated GNR-epoxy composite device. Scale: cm (c–e) Heating profile of the GNR-epoxy composite in “b”. The top surface temperature was measured with an infrared thermometer with a probe size of ~2 cm diameter. The ambient temperature was room temperature and the experiment was conducted in a well-ventilated laboratory hood.
The GNR-epoxy composite was divided into segments with silver contacts deposited at the ends of the sample and internal of segments for resistance measurement (Figure 51a,b). Voltage is applied across the entire sample from the two ends and the temperature of each segment is measured to evaluate the temperature across the composite during Joule heating (Figure 51c–e). Each segment of the device has a different resistance value due to a slight variation in average thickness. Since the current through the entire composite is the same, the higher resistance segment is expected to exhibit higher temperature due to higher power \((P = I^2R)\). The heating profiles of the composite segments are shown in the time-dependent in Figure 51b. Each profile shows that the right end has higher temperature than the left end because of higher resistance. Though the left segment has a higher resistance (and thus higher power) than the middle segment, its temperature is comparable to that of the middle segment because of greater heat dissipation. The temperatures increase with applied voltage for all segments (Figure 51c–e). As the voltage increases, the power delivered through the composite increases according to \(P = \frac{V^2}{R}\), generating higher surface temperature. However, since there is higher heat dissipation with increased power, increase in the surface temperature is less than increase in power. For the first segment at 20 V, the temperature plateaus at 45 °C with a applied voltage of 20 V (Figure 51c). When the voltage is increased to 40 V, the power increases 4× but the temperature rises 2.5×. Similar behavior is demonstrated in all three segments. This shows that more heat is dissipated at higher power (Figure 51c–e). This bodes well for removing ice accumulated on a surface heated with the GNR-epoxy composite. If the surface is covered with ice, the dissipated heat would go into melting the interfacial ice.
In the TGA in Figure 52, the onset of decomposition of the GNR-epoxy composite is at ~300 °C in air. This is due to decomposition of the epoxy composite. The TGA curve for the GNR-epoxy composite coincides with that of neat epoxy composite below 400 °C. After 400 °C, decomposition of the GNR stacks contribute to the GNR-epoxy weight loss. Because the GNR additive is more stable toward oxidative decomposition than the epoxy used here, it gives room for use of more thermally stable epoxy in an oxygen-containing environment.

Figure 52. TGA studies of thermal stability of GNR-epoxy composite.
5.5. Joule Heating and Deicing of Helicopter Rotor Blade Segment

A deicing experiment conducted in a Styrofoam box held at −20 °C showed complete ice removal of 14 g ice in <15 mins. GNR-epoxy composite is hereby demonstrated as a deicing heating layer that holds together a rotor blade and its nickel sleeve while delivering heat for deicing of the nickel surface (Figure 53). Since nickel is thermally conductive, heat can be transferred from the GNR-epoxy heater to the nickel surface for deicing. The only thermal barrier is a layer of bare epoxy coated under the nickel to prevent electrical shorting.
Figure 53. Joule heating and deicing of helicopter rotor blade segment. (a),(b) Schematics of the GNR-epoxy composite adhesive fabrication on a helicopter rotor blade. (c)–(e) Photographic image of deicing through Joule heating. Resistance across composite: 34 Ω; Applied voltage: 45 V; Current: 1.3 A; Power: 44 W; Heated area: ~100 cm². Box held at
−20 °C. The ice was formed on the rotor blade surface by first adding dry ice to the Styrofoam box until it reached −20 °C and stabilized, followed by spraying of cold de-ionized water from a wash bottle.

5.6. Conclusion

The tunable conductivity of the GNR-epoxy composites and low GNR content required to generate lower resistance facilitates deicing of structures by sub-surface GNR-epoxy coating. We can envision an embodiment whereby the GNR stacks can be used as a component of paints for ice removal and prevention of ice accumulation on surfaces.

5.7. Experimental Techniques

5.7.1. GNR-Epoxy Composite Fabrication

Pristine GNR stacks were obtained from AZ Electronic Materials Corp (H-GNRs, Batch no: 2699-119) and were used without any further treatments. To prepare a GNR-epoxy composite, 12–290 mg GNRs were added and blended in 3.9 mL epoxy (Loctite) matrix with a spatula. 1.1 mL hardener (Loctite) was added and further blended. GNR-epoxy composites containing GNRs of ~0.2–5 wt% (of total composite mass) were thus produced. Larger samples were prepared by scaling up according to the ratio of GNRs, epoxy and hardener weights above. The composites were heated on a hot plate at 70 °C for 3 h for curing.
5.7.2. Characterization

Transmission electron micrographs of samples prepared on an amorphous carbon-coated TEM grid were acquired with JEOL 2100F field emission gun transmission electron microscope (TEM). TEM samples were prepared by placing a tiny amount of the sample in ortho-dichlorobenzene (ODCB) (Sigma-Aldrich), sonicating to form a dispersion and drop casting on the grid. Scanning electron micrographs of powder samples placed on a double-sided carbon tape were acquired with JEOL 6500 field emission gun scanning electron microscope (SEM). Raman spectral plots of powder samples placed on a glass slide were acquired with Renishaw inVia Raman microscope equipped with 514 nm Ar ion laser and WiRe software. X-ray diffractograms of powder samples mounted on a grooved zero background holder were acquired with a Rigaku D/Max Ultima II Powder X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5418 Å) and JADE 2009 software.

5.7.3. Electrical Measurements of GNR-Epoxy Composites

~0.2–5 wt% samples were prepared as described above. The composites were cast in a silicone mold with a rectangular groove. The surfaces were smoothed with a spatula. The samples were then heated on a hot plate at 70 °C for 3 h. The molded rectangular bar of cured GNR-epoxy composite (dimensions, \( l \times w \times h: 2.5 \times 0.6 \times 0.5 \) cm\(^3\)) were used in all conductivity measurements. Colloidal silver paste (Pelco Colloidal Silver Liquid, Ted Pella) was applied on two ends of the sample to eliminate contact resistance between the composite and the probes during resistance measurement. The two probes of a Cen-Tech digital multimeter were placed on the silver-coated ends of the composite bar to measure
its resistance ($R$). Surface resistance ($R_s$), a dimensionless resistance, was calculated based on the measured resistance and composite geometry with $R_s = R \times \frac{w}{l}$ where $w$ and $l$ are the width and length of the composite bar, respectively. The DC conductivity, $\sigma_0$, was calculated with $\sigma_0 = \frac{1}{R_s \times h}$ where $h$ is the height of the composite bar.
References


Research Contributions

Abdul-Rahman O. Raji designed, synthesized, and characterized the materials; designed and performed the Joule heating and deicing experiments. Tanvi Varadhachary participated in the Joule heating experiments. Kewang Nan carried out some of the composite fabrication.
6.1. Introduction

De-icing heating layers are frequently used in covers of large radiofrequency (RF) equipment, such as radar, to remove ice that could damage the structures or make them unstable. Typically the de-icers are made using a metal framework and inorganic insulator; commercial resistive heating materials are often non-transparent to RF waves. The preparation of sub-skin-depth thin film, whose thickness is very small relative to RF skin
(or penetration) depth, is the key to minimizing RF absorption. The skin depth of typical metals is on the order of a micrometer at GHz frequency range. As a result, it is very difficult for conventional conductive materials (such as metals) to form large area sub-skin-depth films. In this report, we disclose a new de-icing heating layer composite made using graphene nanoribbons (GNRs). We demonstrate that the GNR film is thin enough to permit RF transmission. This metal-free, ultralight, robust, and scalable graphene-based RF-transparent conductive coating could significantly reduce the size and cost of de-icing coatings for RF equipment covers. This is important in many aviation and marine applications. This is a demonstration of the efficacy and applicability of GNRs to afford performances unattainable by conventional materials.

Ice-elimination systems are very common in large radio frequency (RF) structures. They can be classified as either passive anti-icing films (preventing the accumulation of ice) or active de-icing devices (removing ice after accumulation). A typical application of an icing protection system is in radomes. Radomes are protecting shells or covers for radar instruments in aviation and marine environments. The radomes are subject to hostile environments, such as high winds containing sand, rain, hailstones and saltwater, over wide temperature variations. Explosive pressure blasts can also take place nearby the radomes. Thus radome de-icing conductive films must be extremely tough with good adhesiveness to the heated surface. In addition, these de-icing structures must not compromise reliability of the original RF system, which, in case of radome applications, means that the de-icing film must be predominately transparent to the RF radiation at any polarization with minimal impact on the antenna scan performance. It is desirable that this film be light-weight and low-cost, with physical characteristics that allow it to cover large curved
surface areas. Currently, most radome systems are constructed using a metal wire framework with supporting ceramic materials.\textsuperscript{1-3} The metal wire framework serves as the conductive layer and the ceramic materials are the heat-transfer medium. Due to the strong RF absorbance of metals, they need to be installed far from the RF source to achieve minimal RF attenuation. Consequently, current radomes are large, heavy, and costly, complicating their use on aircraft and ships.

The RF signals propagating through a material can be attenuated by absorption, reflection or scattering.\textsuperscript{4} Randomly dispersed multilayer graphene nanoribbons (GNRs) form isotropic or very close to isotropic conductive films. Each multilayer GNR component of the film is made of several crystallographically stacked narrow graphene monolayers that are 0.3 nm thick.\textsuperscript{5-9} Since 1 nm = 10^{-6} \text{ mm}, a film of 100 nm thickness is a tiny fraction of wavelength even for RF signals up to 300 GHz (1 mm wavelength). As such, we can evaluate the propagation through such films using the classical skin effect concept\textsuperscript{10} where the electrical field strength $E$ (V/m) in the conductive layer decreases exponentially from its value at the surface as in Equation 2.

$$E \sim E_0 e^{-d/\Delta}$$

\textbf{Equation 2.} Electromagnetic field propagation.

where $d$ is the film thickness in m, $\Delta$ is the distance at which incident $E$ (i.e. $E_0$) diminishes to $1/e$ or $\sim 37\%$ of its original value. Based on this equation, the electrical field strength can be very small with an ultra-thin conductive film (where $d \ll \Delta$). Since the GNR film is ultrathin, the electrical field variation is small and the electromagnetic waves reflected from the front and back surfaces of the film cancel each other since they are practically equal in
magnitude and opposite in phase. Thus we can expect very low mismatch loss that is nearly insensitive to frequency. Then according to Equation 3, the film full transmission loss $L$ in dB is defined by the frequency, the physical thickness of the film, and the conductivity of the film.

$$L = -126d\sqrt{f\sigma}$$

**Equation 3.** Transmission loss as a function of frequency.

Here we disclose a new radome de-icing coating based on an ultrathin conductive GNR film. A high-throughput spray-coating technique was developed to prepare GNR films that can function as the conductive layer for de-icing coatings of large RF equipment such as bridge antenna towers and radome systems. In the new de-icing system, the ultrathin GNR layer is used to conduct DC or AC current. The resistance of the GNR film is adjustable and is enough to generate sufficient heat for de-icing the protected surface at voltages that are commonly used aboard ships and aircraft. The conductive GNR film is demonstrated to be thin enough to be transparent to RF signals. We have further demonstrated that ice formation on the protected surface can be prevented while the antenna array is operational.

### 6.2. Fabrication of Graphene Nanoribbon Films

The high aspect ratio, non-oxidized GNRs were synthesized by splitting multiwalled carbon nanotubes (MWCNTs) with potassium vapor or sodium-potassium alloy.\(^{11,12,13}\) The raw material, MWCNTs, are much less expensive than single walled carbon nanotubes. Over 500 tons per year of MWCNTs are produced. In one chemical step, MWCNTs are converted to GNRs, and the process is scalable.
Figure 54. The high-resolution TEM images of graphene nanoribbons used in this work. a) The TEM image of a GNR stack across a lacy carbon grid. b) High resolution TEM of a GNR edge. The graphitic structure of GNR is clear.

The produced GNRs (the TEM images of single GNRs used in this work are shown in Figure 54) are free of oxidation and relatively conductive. In addition, they are solution-processable and compatible with many thin film formation techniques such as spray-, spin-, or blade-coating. Compared to graphene oxide, the GNRs are more promising materials for thin conductive film coatings as they need no annealing to achieve the high conductivity state. The single GNRs exhibit conductivities over 60000 S/m.\textsuperscript{11,12} The electrical conduction mechanism through the GNRs is the same as through bulk graphite as we have described in our previous work,\textsuperscript{11,12} where detailed electrical measurements of the GNRs were performed. A significant difference between GNRs and bulk graphite is that it is much easier to attain electrically percolative network with GNRs because of their high aspect ratio, thus facilitating fabrication of conductive thin films. In comparison to other carbon
materials, conventional carbon black has much lower conductivity when compared to the
GNRs. As a result, it requires much higher voltage to deliver the same amount of heat for
the same size sample. It is thus not practical to use carbon black for resistive heating on
equipment such as radomes. Though MWCNTs have similar conductivity as GNRs, the
films produced from them would be thicker and would not meet the ultrathin film
requirement for RF transparency due to their tubular structure. Functionalizing the
sidewalls of nanotubes for dispersion in a solvent would make them less conductive
compared to the GNRs where only the edges are functionalized for enhanced dispersion.
We have developed GNR-based thin films that were produced using large area coating
techniques such as spray coating.\textsuperscript{14,15} Our previous work demonstrated that GNRs can be
dispersed in ODCB at concentrations up to \( \sim 1 \text{ mg/mL} \).\textsuperscript{11} Here, the GNRs were synthesized
based on the reported work, dispersed in ODCB, and the dispersion was used in a high-
throughput spray-coating procedure for preparing thin GNR films on polymer substrates.

GNR films with various thickness and sheet resistance were prepared (See
Experimental Methods for the details). Polyimide was used as the substrate in this work
because it is resistant to the ODCB solvent and stable to \( > 200 \text{ °C} \). In the initial test, it was
found that the GNR films did not adhere well to the polyimide substrate. Thus,
commercially available clear-coat Dupli-Color\textsuperscript{TM} automotive paint (pigment- and dye-free
polyurethane which adheres well to the substrate) was used as an adhesive layer in which
the GNRs could be embedded.
Figure 55. Characterization of ultrathin GNR films. a) The SEM cross-sectional image of the ultrathin GNRs film. The bottom layer is the polyimide substrate (25 µm thick). The middle is the clear-coat Dulpi-Color™ automotive paint (pigment- and dye-free polyurethane). The upper layer is the GNR film which is also embedded into the polyurethane layer. Scale bar = 100 µm. b) Top view SEM image of the GNR film that shows GNRs embedded in the polyurethane. Scale bar = 100 µm. c) High-resolution SEM image of the GNR film. The GNRs are entangled to form a conducting percolated network embedded in the polyurethane. The center dark rectangular region was formed while focusing the instrument due to the charging effect of the polymer substrate. Scale bar = 1 µm. d) Relationship of GNR film thickness and sheet resistance. The sheet resistance was determined by the four-point probe method. e) A 0.6 × 0.6 m² (2 × 2 ft²) GNR film on
polyimide. This sample was prepared in the lab using the spray-coating technique and a commercially available air-brush. The large film was heated using three heating plates covered with a 1.3 cm (0.5 in) thick panel of aluminum. A 30.5 cm (1 ft) ruler is in the lower left.

The polyurethane (~30 nm thick) was spray-coated on the polyimide and permitted to dry. Polyurethane was found to be a robust protective coating that works well in our experiments. The polyimide-polyurethane film was then placed on a 200 °C hot-plate in a fume hood. The ODCB suspension of the GNRs was then spray-coated atop the polyurethane whereupon the ODCB rapidly evaporated leaving the GNRs well-embedded in the polyurethane adhesion layer. Figure 55a-c show the SEM images of the ultrathin GNR films on the flexible polyimide substrates. The GNRs were embedded throughout the adhesive polyurethane layer to form a network that is conductive through percolation. This composite film is very robust and removal requires sandpaper treatment. The GNRs are not removable by touch or by pulling on the surface with adhesive tape. By controlling the spraying time or GNR solution concentrations, the thickness of the GNR films can be tuned to modulate the resistance of the films. The sheet resistance vs. GNR film thickness was studied and the results are shown in Figure 55d. Large samples, such as the GNR film panel measuring 0.6 × 0.6 m² (2 × 2 ft²) in Figure 55e were prepared in the lab.

6.3. Design of GNR Films for Radome De-icing Coatings

The DC conductivity was calculated through the measured resistance as shown in Equation 4:
\[ \sigma = \frac{l}{AR} \]

**Equation 4.** DC Conductivity.

where \( A = wt \), \( A \) is the GNR layer cross-sectional area in \( \text{nm}^2 \), \( w \) is the GNR layer width in \( \text{nm} \), \( t \) is GNR layer thickness in \( \text{nm} \), \( l \) is the GNR layer length in \( \text{nm} \), and \( R \) is the sheet resistance in k\( \Omega/\square \).

### 6.3.1. Graphene Nanoribbon Films on Polyimide Substrate

![Image](image_url)

**Figure 56.** The small samples of GNR film on polyurethane-coated polyimide substrates. The number noted in the picture is the volume of GNR solution (1 mg/mL in ODCB) used to make the corresponding films.
In order to melt ice on the surface, a heating power density of \(~0.386~\text{W/cm}^2~(2.5~\text{W/in}^2)\) is used because this is a common ship-board power delivery quantity. As for the test, small samples (Figure 56) were prepared. The two ends of the sample were sputter-coated with Pt as electrodes and the size of the active GNRs film was 25.4 mm by 76.2 mm (1 inch \(\times\) 3 inch) (Figure 57a and Table 4 entries 1-3). The parameters of the samples are presented in Table 4 (entries 1-3). The voltage and the current required to deliver the power were calculated based on Ohm’s law. The results show that the voltage and current are within the applicable range of a common ship or aircraft power supply.

<table>
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<th></th>
<th>Rs (kΩ/□)</th>
<th>R (kΩ)</th>
<th>DC Conductivity (kS/m)</th>
<th>Approximate GNR Film Thickness (nm)</th>
<th>Sample Size (width (\times) length, mm)</th>
<th>V (V)</th>
<th>I (mA)</th>
<th>Calculated Energy Delivered (W)</th>
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Table 4. Properties of GNR films on a polyimide substrate used for DC and RF measurements. Rs is the sheet resistance measured by four-point probe. R is the DC resistance of the active GNR film. The GNR film thickness was estimated based on Figure 57d. DC conductivity was calculated based on the sheet resistance and the thickness. V and I are the applied voltage and current, respectively. Entries 1-3 are films used for DC measurements and heat power test. Entries 4-5 are films used for DC measurement and RF measurements. Films 4 and 5 were smaller because they needed to fit into a waveguide. This is the reason for the opposite trend between sheet resistance and DC resistance between samples 1 and 4 and samples 3 and 5.

Figure 57. De-icing and transmittance tests. a) A polyimide/polyurethane/GNR sample with platinum coated at the two ends. The size of the active GNR film (the center black region) is 25.4 mm by 76.2 mm. b) The GNR film resistance change over a temperature range. c) A picture from the video of the de-icing demonstration at -20 ºC. The GNRs film
is connected to two flat copper clamps that are connected to the power source. The ice is pre-formed on the surface of the GNR film. The wire hanging above the GNR film is a thermocouple to monitor the environmental temperature which is maintained at -20 °C within the experiment observation box. With the current passing through the film, the ice is melted in minutes (See Supplementary Information for the full video). d) The block diagram of the RF test assembly. The sample is mounted between two waveguides and the RF wave was generated and analyzed by a network analyzer. The sample can be rotated in order to acquire the transmission coefficient at different angles. e) The WR-284 waveguide with the wired GNR film. f) Transmission loss in dB vs. frequency for a GNR coated polyimide film; comparison of HFSS simulated and experimental data. The red line is based on the HFSS simulation with a GNR film of 8 kS/m RF conductivity and 110 nm thickness. The blue line is the RF measurement of a 110-nm thick GNR polyimide film with 7.24 kS/m DC conductivity.

6.3.2. Temperature-Dependent Resistance of GNR Films

For practical applications, it is important to know how the GNR film responds to temperature variations. The results of thermal tests are shown in Figure 57b. The experimental set-up to determine the temperature-dependent resistance of GNR films is shown in Figure 58. According to the data, the GNR film has a negative temperature coefficient which affords a much narrower range of temperature dependence than found in typical metals such as copper, aluminum or silver. The variation of resistance is -10% from 20 °C to 100 °C, significantly smaller than those for metals (typically +30% from 20 °C to 100 °C). The smaller resistance change to temperature is very helpful for these applications.
Thus, the GNR film delivers more reliable power from a stabilized voltage supply across any temperature range.

**Figure 58.** The experimental setup for determining the temperature-dependent resistance of a GNR film. a) The overview of the setup. b) The end view of the tubular heater/cooler. The GNR sample can be seen in the middle, inside the Pyrex tube, with the alligator clip in the foreground. The glass wool plug has been removed from the Pyrex. c) This picture shows the inner Pyrex tube partially withdrawn from the home-made aluminum tube furnace. The surface thermocouple is taped to the backside of the GNR with heat-resistant tape to assure good thermal contact. Just to the right of the white thermal tape on the aluminum tube is the thermocouple inserted under the brown silicone rubber heater tape. The heavy wall aluminum tube and uniform wrapping of the heater tape gives uniform heating, which was checked to be within 1 °C variation at 50 °C temperature. Modified alligator clips by filing off the teeth, and soldering on thin copper sheets are used for the test. This is clipped onto the Pt electrode with a large contact area, but without puncturing it. These "gentle" clips are then connected to standard banana pins that also have very low
resistance. To start with the low temperature measurements, the Pyrex tube is completely withdrawn, the tube furnace is wrapped with bubble wrap (not shown in the photos) and dry ice is placed inside to chill the aluminum. The remaining dry ice is then evicted when the aluminum tube reaches ~ -35 °C. Then the Pyrex tube is quickly inserted. This way the apparatus is both heater and chiller. Glass wool is added on the ends to prevent moisture from condensing. Then the two temperatures were monitored: the Pyrex tube cools as the aluminum tube warms by heat transfer to the Pyrex. When the temperature of the GNR film and the aluminum become equal, ~ -20 ºC, the heating was turned and the experiment was started. When the aluminum tube reaches room temperature, the bubble wrap was removed and heating continued until the GNR film reached 100 ºC.

6.3.3. Deicing based on Joule Heating

To demonstrate that the GNR film can meet the heat power requirements, the GNR film on polyimide shown in Figure 57a was put at a 45° angle with 5 g of ice that was grown atop the film. The ice had been grown by placing the polyimide/polyurethane/GNR film on a block of dry ice and spraying it with water from a mist bottle until the film accumulated 5 g of ice. A fan blowing over dry ice provided a -20 ºC atmosphere in an insulated box to simulate freezing conditions, as recorded by the thermocouple above the film sample (Figure 57c). The DC-power supply was connected to film electrodes as shown in Figure 57c. After 3 min the ice was completely removed from the area around the center of GNR film; it took another 2.5 min to melt the ice close to the electrodes (Figure 59)
Figure 59. The Scheme of de-icing demonstration. The scheme of the experiment is outlined in Fig. S4. A -20 °C chamber was set up for the de-icing demonstration experiment (see video). Inside the chamber, a fan blowing over dry ice provided a chilling breeze for the sample. An insulated glass window was used to provide a frost-free view of experiment. The film was tilted at ~45° to horizon. During the de-icing process, most of the ice sloughed off when a thin layer of ice against the GNR liquefied. 

4.3.4. RF Conductivity Measurements and Simulation

It well known that the bulk conductors such as silver, gold, or copper have similar DC and RF (in GHz frequency range) conductivity. Prior published work concerning graphene RF conductance was focused on measurements of few-layered graphene, where the RF conductance of few-layered graphene slightly increases with frequency; at 4 GHz, it is ~1.5 times higher than the DC conductance. Thus, classical skin depth theory does not hold. However, the GNR films of ~100 nm thickness that are made of electrically percolating,
long graphene nanoribbons are structurally distinct from a few-layered, continuous sheet of graphene. Therefore, it is necessary to explore the actual RF conductivity of the GNR thin film that is much thinner than the skin depth. It is also important to determine the correlation between DC and RF conductivity to assess the applicability of normal classical skin depth theory in order to verify the equations introduced earlier for this specific system.

In this work, an S-matrix measurement waveguide technique was used to experimentally determine the RF conductivity. A GNR film with 110 nm thickness was prepared and the DC conductivity was measured to be 7240 S/m. The film was fitted in the perpendicular position within a rectangular waveguide and was measured using a Vector Network Analyzer (Figure 57d). Figure 57e shows the GNR film mounted within the S-band WR-284 rectangular waveguide (to fit the size of the waveguide, the sample size was decreased to 25.4 × 50.8 mm). Since the WR-284 waveguide cutoff frequency of the dominant mode is 2.08 GHz and the first high mode starts propagation at 4.16 GHz, all the measurements were taken between 2.4 GHz (far enough from the dominant mode cutoff frequency to achieve low empty waveguide transmission loss) and 4 GHz (to be sure of a negligible level of high modes). The scattering parameters such as reflection (S11) and transmission (S21) of the waveguide section with and without GNR film samples were collected.
According to DC and waveguide test results and their analyses, it has been established that the electrical performance of the GNR films of 75 to 110nm thickness are very similar to classical conductive material. The commercially numerical software such HFSS are used to solve Maxwell equation. The top and bottom faces of the air box surrounding the GNR layer are defined as Floquet ports and used to represent incident and reflected plane waves with different propagation direction as a function of azimuth and elevation angles. The matching periodical boundary conditions are assigned for side surfaces extending the model periodically to infinity in both directions. So the results of such HFSS simulation are valid if the GNR surface is much larger than the wavelength of incident plane wave. It is customary to consider two polarization cases of plane waves obliquely incident on a planar surface: plane wave with electrical vector perpendicular to plane of incidence or TM00-mode and plane wave with electrical vector parallel to plane of incidence or TE00-mode. The plane of incidence is defined as a plane normal to the GNR layer and containing the direction of propagation of the incident wave.
Then, the measured data (blue line in Figure 57f) were compared with the simulated transmission loss from Ansoft's high frequency structure simulator (HFSS) to determine the RF conductivity. The details of the HFSS simulation are described in Figure 60. The exact HFSS model of the same GNR film on a substrate was simulated with several RF conductivity values close to the DC conductivity value of the film. It was found that the best match between the measured and simulated data took place if the HFSS model of the GNR film had a RF conductivity of 8000 S/m (red line in Figure 57f). The ~9% difference between DC and RF conductivity was expected and is predominantly related to mismatch loss. The measured reflection coefficient from the GNR film alone, with no electrodes, is below -20 dB. The reflection of electromagnetic waves from the GNR layer can be calculated as the superposition of all electromagnetic waves reflected at the front and back boundaries between areas of different dielectric properties. Because of the extremely small GNR film thickness in comparison to the wavelength at S-band frequencies, most of these reflected waves cancel each other. Additional GNR films were tested and the RF sheet resistance values are plotted with DC sheet resistance values in Figure 61. In all cases, very good correlation between DC and RF conductivity was demonstrated. A good match between HFSS simulations based on normal classical skin depth theory and the experimental waveguide tests shows that conventional conductive materials concepts hold for the GNR films.
Figure 61. DC sheet resistance vs. RF sheet resistance.

6.4. Radiofrequency Transmission Measurements

6.4.1. Radiofrequency Transmission through GNR Films

The real-time waveguide transmission test scheme is shown in Figure 62a. The setup is shown in Figure 62b-d. A two-port network analyzer was calibrated without a GNR film inside the waveguide between 2.4 GHz and 3.8 GHz, and it provides the measurement of the complex transmission and reflection coefficients $S_{ij}$ of the S-matrix in Equation 5:

$$S = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix}$$
Equation 5. S-matrix.

In Figure 62d, the two wide copper electrodes plated on the GNR layer are parallel to the vector of electrical field in the waveguide, which formed an inductance diaphragm and served as a source of additional reflections. Therefore, an additional test was carried out to determine the reflection from the diaphragm only. The transmission coefficient of the GNR layer was calculated as the difference between the transmission coefficient of the GNR layer plus electrodes and the transmission coefficient of the electrodes only. The results of these measurements are shown in Figure 62e-f.

During the real-time waveguide transmission test, the voltage was applied to the GNR films to simulate the de-icing working status. The RF transmission experiment was carried out simultaneously. As the current passes through the GNR films, the films become hot and the surface temperature of the film was recorded by a flat thermocouple. The transmission loss increases as the layer temperature increases (i.e. RF transmission decreases with temperature) (Figure 62e and f). Thus, the RF transmission has the same negative temperature coefficient as the DC resistance.
Figure 62. Real-time waveguide transmission test results. a) The scheme of the real-time waveguide transmission test. The current passes through the GNR film during the RF measurement. This is to simulate the RF signal transmission when the de-icing is progressing. b) The wired GNRs film. c) The overview of the waveguide with the wired GNR film installed. d) The WR-284 waveguide with the wired GNR film. The thermal sensor is under the white tape patch covering the sensor and it monitors the surface temperature of the GNR film. e) Real-time waveguide transmission coefficient of the GNR film with a thickness of 110 nm (entry 4 in Table 4). The legend on the right is the surface
temperature of the GNR layers. f) Real-time waveguide transmission coefficient of the GNR films with a thickness of 75 nm (entry 5 in Table 4). The legend on the right in 2e-f is the surface temperature of the GNR layer.

As expected, the GNR film behaves as a classical conductor with respect to electromagnetic wave despite its negative temperature coefficient of resistance. Even though it becomes slightly more lossy with temperature, the loss is still small because the material is much thinner than the skin depth. According to the results in Fig 3e-f, the transmission loss of a GNR film depends on the thickness and conductivity of the layer. For the GNR sample with a thickness ~110 nm, the transmission loss did not exceed 0.9 dB in the range of 2.4 GHz to 3.8 GHz. The sample of 75 nm thickness exhibited a better loss < 0.5 dB. The testing results convincingly suggest that the GNR films can replace the conventional de-icing heat circuits, thereby improving radome performance.

6.4.2. Antenna Range and High Power Measurements

The high-power tests were carried out in waveguide WR-284 with the GNR film located between two waveguide flanges as shown in Figure 63c. The typical dependence of average output power vs. average input power is shown in Figure 63d. The linear characteristic behavior of input power and output power is up to 25 W (power density about 20 kW/m²) which is quite good for most antenna applications. The non-linear behavior was observed when the power was further increased (in the sample shown in Figure 63d, > 25 W).
Figure 63. Antenna range test and high power test results. a) A $0.6 \times 0.6$ m$^2$ ($2 \times 2$ ft$^2$) GNRs film in front of an open waveguide for the antenna range test. b) HFSS simulated radiation pattern of an open waveguide with a GNR film in front. The angles are labeled in 30° clockwise increments from 0° at the top to 150°, -180° at the bottom, and from -150° to -30°. c) The GNR film window in a WR-284 waveguide for the high power test. d) The plot of average output power vs. input power. The linear region is up to 25 W in this specific case. The non-linear behavior after 25 W is probably due to the carbonization of the polymer substrate.
A possible explanation, based on this test, is that the RF transparent GNRs film did absorb a small amount of RF energy that heated the polyurethane and polyimide substrate of the film, leading to a change of film morphology or carbonization in the extreme case. However, it should be emphasized that the power density of ~ 20 kW/m$^2$ already meets most antenna application specifications and further improvement in the substrate materials could enhance the high power test performance. We conjecture that there are local regions of thicker GNR film thickness due to puddling during spray-coating of the GNRs onto the wavy polyimide film. New, more planar substrates are therefore being investigated to address this problem.

6.5. Conclusion

In this work, a robust GNR film was integrated on a flexible polymer substrate and its application as a radome de-icer was evaluated. Based on the RF transmission test (from 2.4 GHz to 3.8 GHz) and simulations, the transmission loss was ultra-low and did not exceed 0.5 dB for any frequency below 3.8 GHz for a GNR film with a thickness of 75 nm and did not exceed 1 dB for a film with a thickness of 110 nm. The antenna range tests showed that the measured transmission loss was in the range of 0.2 dB to 0.4 dB for any polarization in the angular sector ± 60°. No depolarization effect was detected. The de-icing capability of the GNR films were evaluated at -20 °C and the efficient removal of an ice coating under those cold conditions was demonstrated. To the best of our knowledge, there is no existing design of de-icing system that can provide such RF transparent performance combined with low-weight, low-cost materials. This underscores the efficacy of the GNR-based nanomaterial for performance unattained by conventional materials.
6.6. Experimental Techniques

6.6.1. Preparation of Graphene Nanoribbon Films

GNRs were synthesized based on previous reports.\textsuperscript{11,12} GNRs were suspended in ortho-dichlorobenzene (ODCB) at a concentration of 1 mg/mL and bath-sonicated (12 W model 08849-00, Cole-Parmer) immediately before use. The polyimide film (McMaster, 25 µm thickness) was cleaned with acetone and DI-water and dried. Polyurethane (clear-coat Dupli-Color\textsuperscript{TM} auto paint, O ’Reilly Auto Parts) was spray coated on the polyimide substrate and dried at room temperature for 24 h. The polyurethane-coated polyimide substrate was placed atop a hot plate at 220 °C and the GNR solution was spray-coated on the substrate using an Iwata airbrush connected to compressed nitrogen. The composite film was removed from the hot plate immediately after the spraying.

6.6.2. Structural Characterization

SEM images were taken using a JEOL 6500 SEM and a FEI Quanta 400 field emission gun SEM. TEM images were taken using a 200 KV JEM 2100F.

6.6.3. Radiofrequency Transmission Experiment and Simulation

Waveguide kit (WR-284) was first calibrated between 2.1 GHz and 4 GHz. The sample was then mounted into the waveguide and $S_{11}$ and $S_{21}$ were measured in series. The waveguide simulation was carried out by using Ansoft's High Frequency Structure Simulator (HFSS) 14.0.
Notes

Description of the de-icing video

3 × 1 in² film of GNRs on polyimide set at a 45° angle with 5 g of ice that was grown atop the film. A fan blowing over dry ice provided a -20°C atmosphere in an insulated box (insulated windows) for the freezing conditions, as recorded by the thermocouple above the sample. Operation parameters: Resistance of film: 4.2 kΩ, V = 177 V, I = 42 mA → 2.5 W/in². Ice removal time ~3 min with a part attached via a lip of ice on the upper edge requiring 2.5 min additional heating.
References


Research Contributions

Abdul-Rahman Raji synthesized the materials, fabricated films, and participated in the Joule heating and deicing experiments. Yu Zhu designed the film fabrication technique, designed and performed Joule heating and deicing experiments, and performed the
characterization. Vladimir Volman performed the RF transmittance experiments and performed the simulations. Carter Kittrell participated in the Joule heating and deicing experiments. Bostjan Genorio and Wei Lu synthesized some of the materials. James M. Tour oversaw all aspects of the project.
Appendix A

Superhydrophobic GNR Films

There are many known deicing technologies. Traditionally, deicing has been accomplished by mechanical, chemical, and thermal means. The simplest mechanical methods include the use of hammers, mallets, crow bars, and baseball bats to loosen ice from surfaces through impact, and shovels to throw the ice from surfaces. Such widely used approach for ice removal is very labor intensive and expensive and can damage underlying structures. Another mechanical method is based on rubber or other elastomeric bubble wraps placed on surface for protection from ice/snow. After a certain amount of ice/snow accumulation, the ice/snow breaks upon rapid inflation and is carried away by the relative wind or fall by gravity. Such pneumatic bubble wrap systems have low power consumption and operation cost and they can be completely autonomous. The main challenge with them have been residual ice/snow that is not fully removed when the bubble wrap inflates, and problems with ice bridging. Some chemical methods are based on wet or dry chemicals applied to reduce the freezing point temperature, break and melt ice, or reduce ice adhesion strength. The chemicals could reach water bodies in concentrations that are toxic to the ecosystems. The environmental control of chemical pollution and surface corrosion are significant problems. Another chemical method is based on icephobic coatings applied to the ice-
accreting surface to reduce the adhesion strength of ice, preventing or reducing icing. However, icephobic coatings typically do not completely prevent icing. Electric or infrared heating is the most common and most successful de-icing and anti-icing technique. Though costly in energy, heating is often the best and still the most cost-effective approach with regard to engineering.

The present report seeks to establish the basis for a sophisticated lightweight, RF-transparent GNR coating that combines the capabilities of superhydrophobic (potentially icephobic) surfaces and electrical heating into a single material with the potential of low power consumption, low operation cost, and potential large-scale production for de-icing and anti-icing in a wide range of applications. The contact angle for water adhesion on polyimide substrate was $60^\circ$ (Figure 64). Upon spray-coating with HD-GNR films, the contact angle reached $152^\circ$ (Figure 65) with a sheet resistance of $\sim 700 \ \Omega/\square$ (Figure 66). Thus, HD-GNR films are very promising for deicing and anti-icing applications.

Figure 64. Water droplet on polyimide.
Figure 65. Water droplets on HD-GNR films spray-coated from 1 mg/mL HD-GNRs with increasing thickness.

Figure 66. Sheet resistance of HD-GNR films in Figure 65.
Research Contributions

Abdul-Rahman Raji designed and synthesized the materials and oversaw the film fabrication. Tuo Wang and Chenhao Zhang fabricated the films. James M. Tour oversaw all aspects of the project.
Chapter 7

Graphene Nanoribbons as a Radiofrequency and Optically Transparent Material

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Research contributions are included at the end of the chapter.

7.1. Introduction

Electrically conductive films made from hexadecylated graphene nanoribbons (HD-GNRs) can have high transparency to radiofrequency (RF) waves even at very high incident power density. Nanoscale-thick HD-GNR films with an area of several square centimeters were found to transmit up to 390 W (2 × 10⁵ W/m²) of RF power with negligible loss, at an RF transmittance of ~99%. The HD-GNR films conformed to electromagnetic skin depth theory, which effectively accounts for the RF transmission. The HD-GNR films also
exhibited sufficient optical transparency for tinted glass applications, with efficient voltage-induced deicing of surfaces. The dispersion of the HD-GNRs afforded by their edge functionalization enables spray-, spin- or blade-coating on almost any substrate, thus facilitating flexible, conformal and large-scale film production. In addition to use in antennas and radomes where RF transparency is crucial, these capabilities bode well for the use of the HD-GNR films in automotive and general glass applications where both optical and RF transparencies are desired.

Radiofrequency (RF) transmissions are used in a wide range of communication applications such as antennas and radomes, mobile services and global positioning systems. We recently reported RF-transparent, electrically conductive hexadecylated graphene nanoribbon (HD-GNR) films for targeted voltage-induced deicing of RF equipment such as radar domes (radomes) and phased array antennas.\(^1\) A large-scale HD-GNR composite film fabrication was demonstrated by spray-coating HD-GNRs on a polymer substrate whereby the HD-GNRs were embedded in polyurethane atop a polyimide flexible substrate rendering a black and optically opaque film. The HD-GNR films were transparent to RF and they transmitted up to 20 W \((7 \times 10^3 \text{ W/m}^2)\) of average RF power without significant loss. However, at \(> 7 \times 10^3 \text{ W/m}^2\) of average RF power density, there was some RF absorbance localized at thicker spots on the HD-GNR film that caused local increases in temperature. Subsequent thermal breakdown and carbonization of the polyurethane coating and polyimide substrate significantly reduced the RF transmittance. Thus fabrication of highly uniform HD-GNR films would enhance RF transparency.

Though HD-GNRs films are not continuous films, they are composed of a percolating network of ribbons without any thick aggregates or random thick regions.
Strong optical and RF absorption can occur on film surfaces where there are thicker regions and contaminants.\textsuperscript{2-4} Although conductive carbon-based thin films have been heavily studied,\textsuperscript{5-8} there is a lack of reports on conductive carbon-based films that are highly transparent to RF. Previous studies have reported on the electromagnetic shielding properties of carbon-based\textsuperscript{9,10} and metal nanowire\textsuperscript{11,12} films and composites in the RF/microwave region where the materials absorb a significant amount of the electromagnetic radiation. The HD-GNR films are an interlinked network, but the ribbons and pores are uniformly distributed and lack thick regions. This, combined with ultrathin film dimensions while also possessing significant optical transparency, support excellent RF transparency that is consistent with theoretical values up to very high power density.

Production of RF-transparent films that are also optically transparent while still being useful for deicing would extend applications to automotive glass and specialized window coating materials.\textsuperscript{13,14}

Here we report HD-GNR thin films that are highly RF-transparent, namely, up to a RF power density of \( \sim 2 \times 10^5 \) W/m\(^2\) as permitted by the thermal capability of the underlying glass substrate. The HD-GNR films are also optically transparent enough for many tinted glass or plastics applications. Both the RF and optical transmittances vary with the sheet resistance of the HD-GNR films, which can be tuned based on the film thickness. We expand a model based on skin depth theory to explain the RF transmission through the HD-GNR films. The skin depth (or decay length) of the RF wave in HD-GNR films is hundreds of microns, allowing RF-transparency of sub-skin depth films. The quality and uniformity of the films is a contributing factor to the high RF-transparency due to mitigation of thick HD-GNR regions or spots on the films. A voltage-induced deicing is also demonstrated.
7.2. Synthesis of Functionalized Graphene Nanoribbons and Fabrication of Films

CAUTION: Na/K is a potent reductant and is highly reactive. All procedures involving Na/K alloy must be executed with extreme caution. The Na/K and the reaction mixture were prepared in a nitrogen-filled dry box, then sealed with a screw-cap and removed from the dry box, and the mixture was stirred with a magnetic stirrer in the hood. Piranha (used to clean the glass substrates) is a strong oxidant and must also be handled with care. Personal protective equipment including thick rubber gloves, flame-retardant lab coat, goggles and face shield should be worn at all times during the experiment.

Organic-soluble HD-GNRs were synthesized by splitting multiwalled carbon nanotubes (MWCNTs) using Na/K alloy in 1,2-dimethoxyethane and alkylationing the edges with 1-iodohexadecane (Figure 67a). Upon completion of the reaction, the Na/K alloy was slowly and carefully quenched with methanol and the product was washed sequentially with methanol, water, and diethyl ether. The sample was dried in vacuo for 24 h. (These HD-GNRs are now available commercially through AZ Electronic Materials Corp. and Sigma-Aldrich). The HD-GNRs were then suspended in ortho-dichlorobenzene (ODCB) at a concentration of 0.5 mg/mL and bath-sonicated for 15 min (12 W model 08849-00, Cole-Parmer) before use. The concentration of the HD-GNR solution was found to be optimal for spray-coating. Low concentrations required prolonged spraying to achieve the required film density. Concentrations that were too high made it difficult to finely control the film thickness to remain optically transparent. Non-functionalized GNR stacks were difficult to disperse in solvents to form a stable dispersion for spray-coating films without
thick spots. Functionalization with hexadecyl groups enabled dispersion in organic solvents, such as ortho-dichlorobenzene, as reported in our earlier work on HD-GNR synthesis where detailed solubility studies can be found. Microscope soda lime glass slides (McMaster, 1 mm thick) were cleaned with piranha (7:4 v/v solution of H₂SO₄ and 35% H₂O₂), rinsed with copious amounts of de-ionized water and blow-dried with a nitrogen stream. With an Iwata airbrush connected to compressed nitrogen, the HD-GNR solution was spray-coated on the glass slide that had been placed on a hot plate heated to 200 °C. At this temperature, the HD-GNRs formed a uniform film on the glass with rapid evaporation of the solvent. After cooling to room temperature, polyurethane (clear-coat Dupli-Color™ auto paint, O ’Reilly Auto Parts) was spray-coated over the HD-GNRs to provide a robust film. Since the HD-GNRs form a porous network on the glass, there is sufficient glass exposure for the adhesion of the polyurethane to the glass surface.

7.3. Morphology: Electron Microscopy and X-ray Diffraction Studies

The HD-GNR films consist of an isotropic array of HD-GNRs (Figure 67a). The films studied vary from 50 nm to 200 nm thickness. Individual HD-GNRs are, on average, a 30 nm thick multilayer stack of HD-GNR layers. They are 1 to 50 µm long (average ~ 10 µm) and 50 to 350 nm wide (average ~ 250 nm) (Figure 67b, c). Based on microscopic studies, the outer tubes are clearly split but whether the innermost tubes are split (Figure 67c) is uncertain. Based on the X-ray diffractogram in Figure 67d, the (002) peak of the HD-GNRs at 25.8° is close to that exhibited by a graphitic structure (26.3°) but with additional distinctive features. The pronounced asymmetry and shoulder of the (002) peak, coupled with the (001) peak at 12° is characteristic of intercalation with hexadecyl
groups. During the synthetic step at which the MWCNTs were treated with 1-iodohexadecane for edge functionalization, a significant amount of the moieties intercalated into the tube layers that were not split.

**Figure 67.** Fabrication and characterization of the HD-GNR film before coating with polyurethane. a) Schematic of the HD-GNR synthesis and film fabrication. b) SEM image of the HD-GNR film morphology. c) SEM image of the HD-GNR film that shows HD-GNRs connected to form a percolating network. d) X-ray diffractogram of the HD-GNR film. e) Raman spectrum of the HD-GNR film.
7.4. Raman Spectroscopic Characterization

Raman spectroscopy is a well-established technique for studying the stacking of graphene.\textsuperscript{18-22} A multilayer graphene stack is not inevitably AB-stacked or graphitic.\textsuperscript{19,23} Spectroscopic measurements are used here to determine the stacking order, or lack thereof, of the multilayer HD-GNRs. The strong characteristic Raman G and 2D bands at \( \sim 1587 \text{ cm}^{-1} \) and \( \sim 2688 \text{ cm}^{-1} \), respectively, indicate that the HD-GNRs maintain the basal plane \( \pi \)-conjugated sp\(^2\)-carbon structure.\textsuperscript{15,16,19,24} Though the HD-GNRs are not monolayer, their Raman spectra exhibit features of monolayer graphene films. The Raman spectrum shows an I\(_G\)/I\(_{2D}\) ratio of 0.29 (Figure 68a), a single Lorentzian 2D band and a 2D bandwidth of 40 cm\(^{-1}\) (Figure 68b). It is well-documented that monolayer graphene features an I\(_G\)/I\(_{2D}\) ratio of \( \leq 0.50 \), a single Lorentzian 2D, a bandwidth of \( \leq 33 \text{ cm}^{-1} \) and a 2D band position at 2680 cm\(^{-1}\).\textsuperscript{18-22,25,26} The I\(_G\)/I\(_{2D}\) \( \leq 0.50 \), upshifted 2D band position, and larger but single Lorentzian 2D bandwidth observed for the HD-GNRs compared to those for monolayer graphene have also been reported for non-oriented or non-AB-stacked multilayer graphene formed as-grown\textsuperscript{23} or by folding\textsuperscript{27,28} or \textit{ex situ} stacking\textsuperscript{18} of monolayer graphene films. The I\(_G\)/I\(_{2D}\) and lineshape for monolayer graphene, non-AB-stacked graphene and HD-GNRs are thus similar. These Raman features for multilayer graphene and HD-GNRs are due to non-graphitic stacking that exhibits weaker interlayer electronic interactions than the AB-stacked graphite.\textsuperscript{19,26,29} In contrast, AB-stacked graphite spectrum consists of a more intense G band, a strongly upshifted 2D band that has a larger bandwidth (\( > 60 \text{ cm}^{-1} \)) and that can be fitted with two Lorentzians.\textsuperscript{19,26,30} As such, AB-stacked GNRs with 2 to 40 layers\textsuperscript{24} were reported to feature Raman characteristics similar to those of graphite. The non-AB-stacked GNRs reported here can be called turbostratic graphene nanoribbons,
multilayer graphene nanoribbons, graphene nanoribbon stacks, or simply, graphene nanoribbons.

**Figure 68.** Raman spectroscopy of HD-GNRs. a) Raman spectra of HD-GNRs–as-prepared (red), heated to 900 °C (black). b) 2D bands of HD-GNRs–as-prepared (red), heated to 900 °C (black). Lorentzian fits of the 2D bands (cyan). c) Excitation laser power effect on Raman spectrum of HD-GNRs. Spectra were collected from the same spot of the HD-GNR powder sample in the order presented in the plot. 100% power = 25 mW. d) 2D bands of HD-GNR before and after measurement at 100% laser power.
The relative intensity of the D band with respect to the G band of HD-GNRs (I_D/I_G ratio ~ 3.7) is higher than that of defunctionalized HD-GNRs (I_D/I_G ratio ~ 0.23) (Figure 68a). The higher I_D/I_G ratio is attributed to the MWCNT splitting, hexadecylated edges, and intercalation of the HD-GNRs.\textsuperscript{15} It should be noted that HD-GNRs, due to their relatively higher edge content, always show a larger D band\textsuperscript{15,16} than their large graphene flake\textsuperscript{18,25,31} or unfunctionalized GNR counterparts.\textsuperscript{16,24} After heating the HD-GNRs to 900 °C under Ar at 20 °C/min, the I_D/I_G ratio is significantly reduced because of defunctionalization (Figure 68a).\textsuperscript{15} Though edge-functionalized and intercalated edges are removed,\textsuperscript{15} the non-AB stacking of the GNRs is retained as shown by Raman 2D band characteristics (Figure 68b).

During Raman measurements, a sufficiently low excitation laser power is critical in preserving the intrinsic Raman features.\textsuperscript{26} Changes in the Raman spectral features of HD-GNRs could appear in the form of a change in I_D/I_G\textsuperscript{32} or shifts of the Raman bands\textsuperscript{32-35} due to laser-induced temperature effects. Laser powers of 2.5 mW or lower do not induce changes in the spectral features (Figure 68c). However, Raman spectra obtained with laser power of 12.5 mW or higher show smaller I_D/I_G ratios (Figure 68c) that arise from defunctionalization due to the laser-induced temperature increase. Thus, the Raman spectra obtained at higher power alter the sample through defunctionalization, and the increase in temperature affects the analyses. Subsequent low power Raman analysis of the laser-heated sample shows that the 2D band is more upshifted than apparent during the relatively high power Raman measurement (Figure 68d). This result of low power measurement after laser-induced heating is consistent with the Raman spectrum of the thermally heated sample in Figure 68a.
7.5. Radiofrequency Transmission through Uniform Graphene Nanoribbon Films

Figure 69 shows the RF transmission measurements through HD-GNR films. For the highly uniform films produced in separate experiments on a glass substrate with sufficient thermal conductivity, the transmitted power increases linearly with the incident power. The RF transmittance was ~ 99% and ~ 98% for the two films of ~ 85 nm and ~ 110 nm thickness, respectively, and designated with red and blue dots, respectively, in Figure 69. Thus, there is a very small percentage of power loss during transmission up to 390 W (2 × 10^5 W/m^2) as permitted by the thermal capability of the substrate (Figure 69 inset). The linear relationship (slope = 1) between incident and transmitted RF indicates that the HD-GNR films are homogenous, consistent with the SEM images. According to our previous work,^1^ the transmitted power becomes non-linear as the incident power increases for the reported non-homogenous film. The transmitted power approached a plateau after 20 W (7 × 10^3 W/m^2) and subsequently dropped as the heating melted the polyurethane coating and further carbonized the polyurethane-coated polyimide substrate. This was attributed to the electromagnetic and the resulting thermal energy concentration in the thick regions generated by non-uniform dispersion of the HD-GNR films where HD-GNRs were spray-coated at 200 °C atop polyurethane pre-coated on polyimide; the resulting coating was black and optically opaque.
Figure 69. Transmitted vs incident RF power for two different films, designated with red and blue dots, sprayed to different thicknesses that had the designated sheet resistances of 14.8 kΩ/□ and 6.9 kΩ/□, respectively. Resistances were measured with a two point probe with silver electrodes at both ends of the film and sheet resistance was calculated based on the film geometry (Experimental Techniques and Figure 74 at the end of chapter for details). The transmitted powers are of the HD-GNR films only and those of the protective polyurethane coatings were subtracted. Inset: Transmission loss vs. incident RF power.

During the deposition, the nanoscale-thick polyurethane would be in a gel-like state and the underlying micron-scale-thick polyimide would buckle, yielding a non-uniform film with some thick regions. In the present work, however, the HD-GNR films were first
deposited on a glass surface and polyurethane was deposited atop as a protection layer. Thus, the HD-GNR films formed a homogenous percolating network on the glass without thick regions. Any GNR-thick regions would have been optically black, further resulting in significant RF absorbance since they are > 250 nm thick. The fabrication of the uniform dispersion was done by monitoring the visual optical transparency and ensuring the absence of black, thicker locations. Optical transmittance measurements (discussed later) obtained at several locations on the film after fabrication were reproducible to ±2% (standard deviation), verifying the visual observation of uniformity. This uniformity proves to be essential for the desired RF transparency without the thicker regions that can significantly increase absorption at higher RF powers.

7.6. Theoretical Description of Radiofrequency Transmission through Films

In describing wave propagation through the conductive HD-GNR film, the electric field component \( \vec{E} \) (in \( V/m \)) of a uniform plane wave traveling in a given direction, \( z \), perpendicular to the surface of the film, is given as Equation 6:\(^{36}\)

\[
\vec{E}(z,t) = \vec{E}_0 e^{i(\vec{k}z - \omega t)}
\]

**Equation 6.** Electromagnetic field propagation.

where \( \vec{E}_0 \) (in \( V/m \)) is the electric field vector parallel to the film surface and “\( \vec{k} \)” (in \( 1/m \)) is the complex wave number such that Equation 7 applies:

\[
\vec{k} = k + ik
\]
Equation 7. Complex wave number.

**Figure 70.** Predictions from electromagnetic skin depth theory. a) Dependence of the theoretical RF skin depth on the sheet resistance of the HD-GNR film. b) Dependence of the calculated RF transmittance on the sheet resistance of the HD-GNR. c) Transmitted RF power (experimental and theoretical) vs. incident RF power for a HD-GNR film with a resistance of 14.8 kΩ/□. d) Transmitted RF power (experimental and theoretical) vs. incident RF power for a HD-GNR film with a resistance of 6.9 kΩ/□.

$\vec{E}$ is expressed in terms of the real and the imaginary parts of $\vec{k}$ as in Equation 8:

$$\vec{E}(z,t) = \vec{E}_0 e^{-\kappa z} e^{i(kz - \omega t)}$$
**Equation 8.** Electromagnetic field propagation.

The imaginary part shows exponential attenuation of the amplitude $\tilde{E}_0$ with respect to the distance $z$ from the surface of the material. As a result, the distance through the material in which the field diminishes to $1/e$ or $\sim 37\%$ of its value from the surface satisfies Equation 9:

$$\kappa z = 1 \quad \text{or} \quad z = 1/\kappa$$

**Equation 9.** Skin depth from electromagnetic propagation.

This distance is referred to as the skin depth and will be denoted by $\Delta$ (in m) and Equation 10 applies:

$$\Delta = \frac{1}{\kappa} = \frac{1}{\sqrt{\pi \sigma \mu_0 f}}$$

**Equation 10.** Skin depth as a function of frequency.

where $\sigma$ is the material conductivity at frequency $f$, $\mu_0$ is the permeability of free space, all in the S.I. units. The skin depth characterizes the depth of electromagnetic wave propagation into a typical conductor. Since $e^2 \approx 10$, the electromagnetic wave loses 90% of its energy on its path at every skin depth. The application of this concept to describe RF transmission in HD-GNR thin films was previously suggested and proven through waveguide RF measurements at frequencies between 2 and 4 GHz.\(^1\) It was demonstrated that, similar to classical conductors, the RF conductivity was very close to the DC conductivity of HD-GNR thin films.
When a traveling free-space plane-wave is incident on the front boundary of an HD-GNR film, a portion of the wave energy is reflected from the film back to free space while the propagation continues inside the HD-GNR film.\textsuperscript{36,37} As this propagated wave reaches the back boundary, it is reflected again in the direction of the front boundary with the phase shift $\varphi = kz$; and the remaining energy is transmitted to the free space behind the HD-GNR film. Therefore, the total reflected wave from the front boundary and transmitted wave through the film are superpositions of multiple partial waves moving back and forth. The total transmission loss is the sum of reflection/mismatch loss and HD-GNR absorption loss of the wave defined by Equation 8. But the thickness of the HD-GNR film is such a small fraction of the wavelength that all the reflected waves at the front boundary are in almost opposite phase and cancel each other. In addition, since mismatch loss, from waveguide measurements, does not exceed 1\% of incident power,\textsuperscript{1} the main part of the loss is the HD-GNR absorption loss defined by the skin depth (Equation 10) that increases at higher sheet resistance (Figure 70a) due to lower conductivity at higher sheet resistance (Equation 10, Table 5). Thus, the RF transmittance for a film is related to its skin depth $\Delta$ and thickness $d$ by Equation 11:\textsuperscript{37}

$$T = \frac{P_T}{P_0} = \left(\frac{E_{0,T}}{E_{0,I}}\right)^2 = e^{-2d/\Delta}$$

\textbf{Equation 11.} RF Transmittance as a function of film thickness.

where $P_T$ and $P_0$ (in W) are transmitted and incident RF powers and $E_{0,T}$ and $E_{0,I}$ (in V/m) are transmitted and incident amplitudes, respectively, through the HD-GNR film. As with the skin depth, the RF transmittance increases with higher sheet resistance (Figure 70b). In order to validate this theory for HD-GNR films, the transmitted RF powers were compared with a series of incident RF powers for the two films measured in Figure 69. The results
demonstrate an excellent match between the theoretical calculations and the experimental measurements (Figure 70c, d) for the sample HD-GNR films, thus supporting the classical conductivity behavior at radio frequencies. Thus, for a thin HD-GNR film, the wave propagates with an amplitude very close to that of the incident wave. As a result, the HD-GNR film is transparent to the RF wave.

<table>
<thead>
<tr>
<th>$R_s$ (kΩ/□)</th>
<th>27.7</th>
<th>26.0</th>
<th>8.1</th>
<th>5.8</th>
<th>4.3</th>
<th>1.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$ (nm)</td>
<td>42.1</td>
<td>88.8</td>
<td>138.1</td>
<td>174.1</td>
<td>202.6</td>
<td>213.0</td>
</tr>
<tr>
<td>$\sigma$ (S/m)</td>
<td>857.2</td>
<td>432.5</td>
<td>1346.8</td>
<td>550.0</td>
<td>2878.4</td>
<td>3427.9</td>
</tr>
</tbody>
</table>

**Table 5.** Properties of HD-GNR films. $R_s$ is the sheet resistance of the HD-GNR film. $d$ is the thickness of the HD-GNR film. $\sigma$ is the DC conductivity calculated based on the sheet resistance and the thickness of the HD-GNR film. Conductivity is thickness-independent for a bulk material. However, the density of HD-GNR films is proportional to the thickness; thus, increase in the DC conductivity is related to the increase in film density.

**7.7. Optical Transmittance vs Sheet Resistance**

Sheet resistances and optical transmittances of the HD-GNR films can be tuned by varying the film thicknesses. In Figure 71a, the optical transmittance of the films increase with increasing sheet resistance. Images in Figure 71b show the decreasing optical transmittance of HD-GNR films from 75% to 50%. At > 65% optical transmittance, the sheet resistance of the HD-GNR film is $\sim$ 6 kΩ/□. With this amount of resistance, the film is suitable as a
thin film resistor where heating power \( P = \frac{V^2}{R} \) can be delivered through the film subject to an applied voltage.

**Figure 71.** a) Optical transmittance dependence on sheet resistance of HD-GNR films. The sheet resistances were measured using the two-terminal measurement technique as described in the Experimental Techniques at the end of the chapter (see Figure 74 for comparison to four-terminal measurements). Transmittance of HD-GNR films at 550 nm vs sheet resistance. The resistances are of the HD-GNR films without polyurethane coating. b) Photograph showing optical transparency through the HD-GNR films with transmittance from 75% (top) to 50% (bottom).
Figure 72. DC and optical conductivity of HD-GNR films. a) DC conductivity of HD-GNR films as a function of thickness. b) Optical conductivity of HD-GNR films as a function of thickness. c) DC conductivity/optical conductivity ratio of HD-GNR films as a function of thickness. The conductivities and thicknesses are of the HD-GNR films without polyurethane coating.

Though optical transparency is not essential in many applications of RF transparent conductive HD-GNR films, certain applications would require optical transparency in addition to RF transparency. The transmission properties of HD-GNR films in the visible region can be evaluated by studying the relationship between DC (i.e. zero frequency) and optical (i.e. frequency-dependent) conductivities. The DC conductivity \( \sigma_0 = \frac{1}{R_s \times d'} \) (Experimental Methods) of HD-GNR films is found to increase with the thickness (Figure 72a). The sheet resistance of a material depends on the thickness. However, the electrical conductivity of a uniform, homogenous material is thickness-independent provided that the uniformity is invariant with thickness. Thus, increase in the DC conductivity is due to increase in the film density rather than the film thickness. This behavior is similar to that observed for carbon nanotube\(^{38,39}\) and silver nanowire films.\(^{40}\) Unlike those films, however, the optical conductivity, \( \sigma_{\text{550nm}} \), of HD-GNR films decreases with the film thickness
(Figure 72b), producing optical conductivity/DC conductivity ratio greater than unity ($\frac{\sigma_{550\text{nm}}}{\sigma_0} > 1$) (Figure 72c). This behavior is similar to that observed in chemically exfoliated graphene films.\textsuperscript{41} Thus, the sheet resistance of the HD-GNR films is required to be high in order for the second term in Equation 12, below, to approach zero so as to produce an optical transmittance that approaches unity or 100%:\textsuperscript{38-40}

$$T = (1 + \frac{188\sigma_{550\text{nm}}}{\sigma_0 R_s})^{-2}$$

\textbf{Equation 12.} Optical transmittance as a function of sheet resistance.

Film density is an important parameter for obtaining a low $\frac{\sigma_{550\text{nm}}}{\sigma_0}$; however, the thickness and width of individual components of the film has to be small as well in order to reduce the overall film thickness. Carbon nanotube films and silver nanowire films were reported to exhibit $\frac{\sigma_{550\text{nm}}}{\sigma_0} < 1$. The thickness of an individual carbon nanotube\textsuperscript{39} was 2.4 nm and an individual silver nanowire\textsuperscript{40} was 85 nm. This enabled fabrication of sub-100-nm-thick, dense films with high optical transmittance and low sheet resistance.\textsuperscript{38-40} The foliated HD-GNRs (in stacks) reported here are ~ 30-nm-thick and ~ 250 nm wide, and the films made from them are 50 to 200 nm thick. Since the optical conductivity/DC conductivity ratio of HD-GNR films decreases with higher film density thick (Figure 72c), our results suggest that if the individual HD-GNRs were of much smaller width and thickness, the film density could be significantly increased but with film thicknesses being much lower than those obtained here.\textsuperscript{42} Thus, HD-GNR films with lower optical conductivity relative to the DC conductivity may be obtained, i.e. $\frac{\sigma_{550\text{nm}}}{\sigma_0} < 1$; a condition that would facilitate fabrication of HD-GNR films with high optical transmittance at low
sheet resistance. However, efficient exfoliation of the GNRs derived from MWCNTs has been, hitherto, unattainable.\textsuperscript{15-17}

\section*{7.8. Deicing Application}

In order to demonstrate deicing capability with the HD-GNR films, an HD-GNR film with a resistance of 3.8 kΩ was fabricated on a glass slide and mounted in a Styrofoam box cooled to -20 °C (Figure 73a). A voltage of 190 V was applied across the film through silver contacts on both ends providing \( \sim 1.3 \) W/cm\(^2\) to the film. The ice melted and then detached entirely in 3.7 min (Figure 73b), underscoring the deicing capability along with the RF and optical transparency discussed above.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig73.png}
\caption{Photographs of resistively heated HD-GNR films at -20 °C. a) During deicing. b) After deicing which took 3.7 min. The experiment was conducted in a Styrofoam box maintained at -20 °C. The sample was mounted at an angle of \( \sim 40^\circ \) so that the partially melted ice could slide off. The ice that melted off the surface can be seen rapidly refreezing once it hits the dish below. A surface thermocouple was taped to the bottom of the polyurethane-HD-GNR-coated glass slide. All heating was done through an applied...}
\end{figure}
voltage to the left and right ends of the film. The HD-GNR film has a resistance of 3.3 kΩ, a thickness of 140 nm and an optical transmittance (at 550 nm) of 70%.

7.9. Conclusion

In summary, we have demonstrated that conductive HD-GNR thin films can be produced with high uniformity. We verified 99% RF transmission at a power density up to $2 \times 10^5$ W/m$^2$ in an 85 nm thick HD-GNR film with an optical transmittance of 75%. The small HD-GNR film thickness relative to the large skin depth and propagation wavelength through the film permits the exceedingly high RF transmission at high RF power. The absence of thick spots and relatively high thermal conductivity of the substrate is crucial to transparency at high RF power. We also demonstrated the possibility of obtaining more optically transparent films with better exfoliated HD-GNRs. The optical transparency is important in controlling the quality of fabricated RF transparent films as optical transmittance could be easily measured at different regions of the film to assess uniformity and the presence of thick spots. Finally, the RF and optically transparent films permitted voltage-induced deicing.

7.10. Experimental Techniques: Structural and Electrical Characterization

SEM images were acquired on a JEOL 6500 SEM. Raman spectra of powdered samples placed on a glass slides were acquired using Renishaw inVia Raman microscope equipped with 514 nm Ar ion laser. X-ray diffractograms were obtained on a Rigaku D/Max Ultima
II Powder XRD with Cu Kα (λ = 1.5418 Å) diffractometer using a zero background holder. Optical transmittance was obtained using a Shimadzu UV-3101PC UV-vis-NIR spectrophotometer. In order to determine the sheet resistance, the film resistance was measured using a two-terminal method with a Cen-Tech digital multimeter. This was further shown to be equivalent to four-terminal measurements (Figure 74). To eliminate contact resistance between the probes and the film, silver electrodes were deposited by applying colloidal silver paste (Pelco Colloidal Silver Liquid, Ted Pella) on both ends of a 7.62 cm × 2.54 cm film; they were used for contact to the probes. Sheet resistance, $R_s$, was thus calculated based on the measured resistance and film geometry with $R_s = \text{measured resistance} \times \frac{w}{l}$ where $w$ and $l$ are the width and length of the film, respectively. The DC conductivity, $\sigma_0$, was calculated with $\sigma_0 = \frac{1}{R_s \times d}$ where $d$ is the film thickness.
Figure 74. Comparison between the two-terminal and four-terminal measurements. Both methods show excellent agreement with each other. The sheet resistance with the two-terminal measurement is described in the Experimental Methods. The four-terminal measurement was carried out using Alessi four-point probe and Keithley 2010 multimeter. The four-point probe was placed directly on the HD-GNR films without any deposited metal contacts, unlike the two-terminal method. The sheet resistance was determined by $R_s = \frac{\pi V}{ln2 I}$. The film size was 7.62 cm × 2.54 cm, large enough to prevent the need for any correction due to finite size and edge effects that could arise from the four-terminal measurement.
References


**Research Contributions**

Abdul-Rahman O. Raji designed, synthesized, and characterized the materials; fabricated the films; designed and performed the Joule heating and deicing experiments. Sydney Salters participated in the film fabrication and Joule heating experiments. Vladimir Volman conducted the RF transmission experiments. James M. Tour oversaw all aspects of the project.