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Energy Applications of Graphene-Based Nanomaterials and Their Composites

by

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ABSTRACT

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Graphene-based nanomaterials, which contain two-dimensional graphene sheets that consist of sp²-C atoms arranged in a hexagonal lattice, have exceptional electrical conductivity and mechanical properties, thereby showing promise for use in energy-related devices. Two different types of graphene nanomaterials were studied: one-dimensional graphene nanoribbons and three-dimensional graphene foams. The graphene nanoribbons have both abundant edges for chemical functionalization that improves their dispersibility and interfacial interaction with other materials, and high aspect ratio that affords percolation on a specific area at a smaller mass loading. They have been demonstrated to be an excellent choice for making conductive films with deicing and anti-icing capabilities (Chapter 1) and as a conductive additive for dendrite-free Li metal anodes in Li metal batteries and red P anodes in high energy density Li-ion batteries (Chapter 2). It was found that red P was not only a good candidate for anode materials, but a surprisingly powerful tool to improve battery safety by in situ detection of Li dendrites in an ordinary two-electrode battery system. The other graphene nanomaterial, the three-dimensional graphene foams prepared from polyacrylonitrile using the powder metallurgy method,
exhibited high electrical conductivity and high mechanical strength that powdered graphene species cannot achieve, which enabled them to reinforce epoxy resin and enhance the electrical conductivity of the epoxy to an unprecedented level (Chapter 3).
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<tr>
<td>FDO-GNR</td>
<td>Perfluorododecylated graphene nanoribbon</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-walled carbon nanotube</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectra</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<td>FO-GNR</td>
<td>Perfluoroctylated graphene nanoribbon</td>
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<td>FD-GNR</td>
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<tr>
<td>HD-GNR</td>
<td>Hexadecylated graphene nanoribbon</td>
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<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>GNR</td>
<td>Graphene nanoribbon</td>
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<td>CNT</td>
<td>Carbon nanotube</td>
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<td>LIB</td>
<td>Li-ion batteries</td>
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<tr>
<td>Asp</td>
<td>Asphalt</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid-electrolyte interphase</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methly-2-pyrrolidone</td>
</tr>
<tr>
<td>Asp-GNR-Li</td>
<td>Asphalt-derived porous carbon-graphene nanoribbon supported Li</td>
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<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>LiFSI</td>
<td>Lithium bis(fluorosulfonylimide)</td>
</tr>
<tr>
<td>DME</td>
<td>1,2-Dimethoxyethane</td>
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<tr>
<td>PVDF</td>
<td>Polyvinylidene difluoride</td>
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RP       Red phosphorus
BP       Black phosphorus
NP       Nanoparticle
SDBS     Sodium dodecylbenzenesulfonate
CTAB     Cetyltrimethylammonium bromide
PEG      Polyethylene Glycol
PVA      Polyvinyl alcohol
EDS      Energy dispersive X-ray spectroscopy
TEM      Transmission electron microscopy
XRD      X-ray diffraction
CV       Cyclic voltammetry
RP-25-GNR Red phosphorus-graphene nanoribbon composite with 25 wt% of red phosphorus
RP-39-GNR Red phosphorus-graphene nanoribbon composite with 39 wt% of red phosphorus
RP-57-GNR Red phosphorus-graphene nanoribbon composite with 57 wt% of red phosphorus
RP-72-GNR Red phosphorus-graphene nanoribbon composite with 72 wt% of red phosphorus
EC       Ethylene carbonate
DEC      Diethylene carbonate
P-hc     Half cells with two regular separators and one RP-coated separator
ctrl-1   Control half cells with three regular separators
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<td>P-fc</td>
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<td>ctrl-3</td>
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<tr>
<td>ctrl-4</td>
<td>Control full cells with one regular separator only</td>
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<td>P-fc-2</td>
<td>Full cells with one regular separator and one RP-coated separator</td>
</tr>
<tr>
<td>Cu foil-Li</td>
<td>Cu foils with electrochemically deposited Li metal</td>
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<tr>
<td>GNP</td>
<td>Graphene nanoplatelet</td>
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<tr>
<td>uGF</td>
<td>Ultrastiff graphene foam</td>
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<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>GF</td>
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<td>ouGF</td>
<td>Oxidized ultrastiff graphene foam</td>
</tr>
<tr>
<td>nuGF</td>
<td>N-doped ultrastiff graphene foam</td>
</tr>
<tr>
<td>ruGF</td>
<td>Rebar ultrastiff graphene foam</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethylformamide</td>
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Chapter 1

Functionalized Graphene Nanoribbons for Deicing and Anti-Icing Applications

This Chapter is copied from reference 1.

Anti-icing and deicing are the two major pathways for suppressing adhesion of ice on surfaces, yet materials with dual capabilities are rare. In this chapter, we have designed a perfluorododecylated graphene nanoribbon (FDO-GNR) film that takes advantage of both the low polarizability of perfluorinated carbons and the intrinsic conductive nature of graphene nanoribbons. The FDO-GNR films are superhydrophobic with a sheet resistance below 8 kΩ·sq⁻¹ and then exhibit an anti-icing property that prevents freezing of incoming ice-cold water down to -14 °C. After that point, voltage can be applied to the films to resistively heat and deice the surface. Further a lubricating liquid can be employed to create a slippery surface to improve the film’s deicing performance. The FDO-GNR films can be easily switched between the superhydrophobic anti-icing mode and the
slippery deicing mode by applying the lubricant. A spray-coating method makes it suitable for large-scale applications. The anti-icing and deicing properties render the FDO-GNR films with promise for use in extreme environments.

1.1. Introduction

Icephobic surfaces that prevent formation of ice or snow are important for the reliable operation of equipment in extremely cold environments; these include radar domes, power lines, aircrafts and ships. Although the definition of “icephobic” is still under debate, the word indicates at least one of the following anti-icing capabilities: preventing the freezing of condensing water on the surface, preventing the freezing of incoming water, or weak adhesion forces of ice to a surface. Materials with anti-icing properties are being developed as passive systems to reduce the accumulation of ice on the surface of a structure or increase the time delay of ice nucleation. However, current anti-icing systems are not sufficient for complete and long-term protection from ice, and they are usually combined with active systems that have deicing capabilities requiring energy supplies. For example, electrical power has been applied to a graphite coating to create heat, electro-impulse through high-voltage capacitors have been used to rapidly propel ice off a surface, rubber boots inflated by engine bleed air have also been used to remove ice by expanding surfaces, pristine and functionalized graphene nanoribbons have been used as deicing coatings.

In recent publications, a number of materials have been reported to be superhydrophobic, including carbon-based materials, silica-based materials,
metal oxide nanostructures,\textsuperscript{18} slippery liquid-infused porous surfaces,\textsuperscript{19,20} textured metallic surfaces,\textsuperscript{21} and nanocomposites,\textsuperscript{22} some of which have shown excellent anti-icing performance. But materials with both passive anti-icing and active deicing functionalities have not been reported. In this chapter, we demonstrate a simple and large-area method (Figure 1.1) to generate superhydrophobic surfaces on different substrates that have both anti-icing and deicing capabilities. This is done by spray-coating perfluorododecylated graphene nanoribbons (FDO-GNRs) onto the surface of interest. The passive anti-icing property prevents freezing of incoming water without any power input, while the active deicing property provides an alternative function of removal of ice when the environmental conditions exceed anti-icing limits. We found that the continuous ice-cold water droplets would not adhere onto the superhydrophobic surface if the surface temperature was kept above -14 °C. On the other hand, a fluorinated lubricating liquid was applied to switching the anti-icing surface into the deicing mode in which ice quickly started to mobilize by gravity when the ice at the interface was melted by resistive heating.
1.2. Synthesis and Characterization of Functionalized Graphene Nanoribbons

Figure 1.1 (a) Schematic illustration of the synthesis of FDO-GNRs and (b) fabrication of FDO-GNR films.

Figure 1.2 XPS spectra of (a) C1s, (b) O1s, and (c) F1s for FDO-GNRs.
The synthesis of FDO-GNRs, schematically illustrated in Figure 1.1a, involves splitting multi-walled carbon nanotubes (MWCNTs) using Na/K alloy\textsuperscript{23-25} and functionalizing the edges with perfluorododecyl groups. Potassium intercalates between the walls of the MWCNTs and longitudinally splits the structure to form carboanion edges,\textsuperscript{23} which easily react with 1-iodo-perfluorododecane to be chemically bonded to the GNR edges. X-ray photoelectron spectra (XPS) show (Figure 1.2) a peak at ~284.5 eV which corresponds to C1s of the $sp^2$-C atoms on the basal planes of GNRs, while the peak at ~688.7 eV corresponds to F1s of the F atoms on the perfluorododecyl groups. Since the reaction is completed using reducing reagents under Ar, FDO-GNRs are formed where the oxygen content is only 3.6%, preserving the graphitic domains with low defect concentration and high conductivity. The atomic ratio of
C/O/F is 84.3:3.6:12.1. In Figure 1.3, the amount of functionalized groups was determined to be ~17% by thermogravimetric analysis (TGA) using pristine GNRs, synthesized by quenching the anions with methanol for proton edges, as the control.

The hydrophobicity of GNRs is largely improved by the modification of perfluoroalkyl groups compared to hexadecylated GNRs which are non-fluorinated, and the effect of the length of the perfluoroalkyl chains is studied by using different perfluoroalkanes for modification of GNRs.

### 1.3. Functionalized Graphene Nanoribbon Films with Deicing and Anti-icing Capabilities

![Graph](image)

**Figure 1.4** (a) Correlation between sheet resistance and static water contact angle of HD-GNRs, perfluorooctylated graphene nanoribbons (FO-GNRs), perfluorodecylated graphene nanoribbons (FD-GNRs), and FDO-GNRs. Values above 150° in contact angle are deemed superhydrophobic.²⁵ (b) Contact angles and sliding angles of FDO-GNR films with different sheet resistances.
To measure the water contact angle, functionalized GNRs were dispersed in chloroform and spray-coated on tape-coated substrates (polyimide films or glass slides) to make a uniform thin film. By changing the spray-coating time, we were able to tune the sheet resistance which was inversely related to the thickness of the films, and thereby measured the water contact angles for different sheet resistances. The thicknesses ranged from several hundred nanometers to several microns, depending on the sheet resistance. Figure 1.4a shows that the functionalized GNR films are superhydrophobic with a water contact angle above 150° when the sheet resistance is below 1,000 Ω·sq⁻¹. Lower sheet resistance indicates higher thickness, which means the water droplet and the substrate are further separated by thicker GNR layer in between. Therefore, water droplets are in better contact with the thicker GNR layers instead of the substrates underneath, resulting in higher water contact angles. Also, the sliding angles of FDO-GNR films decrease with lower sheet resistances (Figure 1.4b), which makes it harder for water to stick to the surfaces, though there is no significant change in contact angles. Additionally, the perfluoroalkylated GNRs are showing higher contact angles than the non-fluorinated hexadecylated graphene nanoribbon (HD-GNR) counterparts at the same sheet resistance. This verifies that the enhancement in hydrophobicity originates from the chemical properties of the perfluorinated chains. Perfluoroalkylated GNRs modified with longer perfluorinated chains exhibit a higher contact angle, suggesting that the length of the chains also has an impact on the hydrophobic properties.
The SEM image in Figure 1.5a shows that the percolating network of the spray-coated FDO-GNRs has a multi-layered structure with an $I_G/I_{2D}$ ratio $>1$ in the Raman spectrum (Figure 1.5b). The FDO-GNR bundles are disordered but interconnected which generates the surface roughness that further improves the hydrophobicity of the surface.
Figure 1.6 (a) Contact angle (161°) image of a water drop on an FDO-GNR film. Photographs of the FDO-GNR film fixed at a 45° tilt angle and maintained in a -14 °C environment (b) before and (c) after ice-cold water was dropped onto the film surface. (d) Contact angle (131°) image of a water drop on a HD-GNR film. Photographs of the HD-GNR film fixed at a 45° tilt angle and maintained at (e) -14 °C and (f) 4 °C environment after ice-cold water was applied onto the film surface. All the scale bars are 1 cm.

Hydrophobic surfaces have a low adhesion force for water molecules, but are not necessarily icephobic. If the contact angle could be increased to above 150° (superhydrophobic) rather than just above 90° (hydrophobic), the interfacial
interaction would be even lower, with a lower chance of freezing water on the surface. In order to test the anti-icing and deicing performance of the superhydrophobic FDO-GNR films, ice-cold water as the incoming water source was applied onto the test surfaces. As commonly done in studies on icephobicity, double-sided tape was used to improve robustness for the testing. The area covered by FDO-GNRs was 3 cm long and 1 cm wide with a sheet resistance of ~320 Ω·sq⁻¹ and a water contact angle of 161° was obtained (Figure 1.6a). Silver contacts were deposited on both ends of the film by applying colloidal silver paste to be connected to electrodes during deicing tests.

Results of anti-icing tests showed that the water droplets cannot stick to the film above -14 °C. The FDO-GNR film was clamped inside a Styrofoam box cooled to a series of temperatures using dry ice. The film was tilted at 45° as to clearly see the moving of water droplets falling from directly above. When the ambient temperature as well as the film temperature is 24 °C, 14 °C, 4 °C, -4 °C or -14 °C (Figure 1.6b,c), ice-cold water (<5 °C) can easily roll off the surface of the FDO-GNR film without any observed water remaining on the surface. There is no significant change of the surface compared to the original state, and it is still capable of propelling water when it is warmed to room temperature and again cooled to -14 °C. No energy input is applied in this case; it only takes advantage of the passive anti-icing capability. To further demonstrate the importance of superhydrophobicity, a non-superhydrophobic HD-GNR film with a contact angle of 131° (Figure 1.6d) prepared by the same procedure was tested for comparison. As shown in Figure 1.6e, water droplets stay on the film at -14 °C,
after which the water drops can freeze within less than 30 s. In Figure 1.6f, small water drops are still observed to be attached to the surface even at 4 °C. This suggests that superhydrophobicity is a key factor in preventing freezing of incoming water.

![Graph showing resistive heating intensity vs FDO-GNR film temperature (ambient temperature: -32 °C).](image)

**Figure 1.7** (a) Resistive heating intensity vs FDO-GNR film temperature (ambient temperature: -32 °C). (b) Photograph of the film kept at 30 °C by resistive heating after spraying ice-cold water on the surface for 10 min (ambient temperature: -32 °C). (c) Photograph of the film at -32 °C after spraying ice-cold water on the surface for 10 min (ambient temperature: -32 °C). All the scale bars are 1 cm.

Water droplets are not able to stay on the FDO-GNR surface. But this passive strategy is only effective within a certain temperature range of ≥-14 °C. Energy input is needed when the temperature is below -14 °C, as cold moisture can condense within the pores throughout the interconnected structure of FDO-GNRs, causing the surface to lose its superhydrophobic and icephobic properties. Figure 1.7a shows the increase of film temperature with increasing resistive heating intensity. We taped the thermocouple on the back side of the glass slide
to avoid damage to the FDO-GNR film on the front side. The temperature differential between the back and front side was measured to be only \( \sim 1.2 \, ^\circ\text{C} \) with the film temperature at \( \sim 80 \, ^\circ\text{C} \) and heat intensity at \( \sim 0.5 \, \text{W/cm}^2 \). As shown in Figure 1.7a, we applied \( \sim 12 \, \text{V} \) to keep the film at \(-14 \, ^\circ\text{C}\) when the ambient temperature was \(-32 \, ^\circ\text{C}\), and similar anti-icing behavior was observed as shown in Figure 1.6b,c. When using a higher voltage (\( \sim 40 \, \text{V} \)), the film temperature could be kept at \(30 \, ^\circ\text{C}\) even though the environmental temperature was \(-32 \, ^\circ\text{C}\). In Figure 1.7b, freezing of the sprayed water was prevented in most of the area covered by FDO-GNR, while water condensed and froze on the film without resistive heating (Figure 1.7c). These can be considered to be a combination of passive and active methods.

![Figure 1.8 Deicing test of the FDO-GNR films. Photographs of the film without lubricating liquid (a) before and (b) after active deicing by resistive heating. Photographs of the film with lubricating liquid (c) before and (d) after active deicing by resistive heat](image.png)
To test the deicing performance without involving the passive strategy, water droplets were allowed to stay on the FDO-GNR film and freeze at -32 °C (Figure 1.8a) and ~40 V was then applied to the film that gave it a power density of ~0.2 W·cm⁻². In Figure 1.8b, ice is melted after 90 s of resistive heating, which demonstrates the deicing capability even if ice is already formed.

Figure 1.9 Deicing test of the FDO-GNR film supported by double-sided tapes in which lubricating liquid was added after ice formation. (a) Before deicing. (b) After deicing for 30 s with resistive heating intensity of ~0.2 W·cm⁻². All the scale bars are 1 cm.
Figure 1.10 Contact angle measurement and anti-icing test after the lubricant was removed from the film by electrical heating. (a) Contact angle (161°) image, photograph of the FDO-GNR film at -14 °C (b) before and (c) after ice-cold water dropped onto the surface.
Figure 1.11 Schematic illustration of the experimental setup for anti-icing and deicing tests.

The deicing mode is capable of melting ice but not removing water completely. This is due to the fact that the water molecules at the interface may be trapped in the pores formed by the interlinked FDO-GNR bundles. In order to have less liquid or solid residue after deicing, heptacosfluorotributylamine was added as a lubricant to wet the film (Figure 1.8c) which resulted in a slippery surface. The low melting point (-52 °C) of the lubricant allowed it to be employed without freezing in a cold environment. The sliding angle decreased from 12±2° to 3±1° after the addition of the lubricant, suggesting that the film became less sticky and more cleanable. In Figure 1.8d, ice started to fall off within 40 s under the same electrical power density as used in Figure 1.8b. The deicing process proceeded faster and it saved energy compared to the sample without the
lubricant, melting the ice at the interface so that the entire piece of ice could fall off by gravity. Ice repellency was also achieved even when lubricants were added after ice formation at -32 °C (Figure 1.9). When the film was electrically heated at a power density of 0.3 W·cm⁻² or kept above 50 °C on a hot plate for 10 min, the film became superhydrophobic and icephobic again (Figure 1.10). These enabled the film to be readily switched between the anti-icing and deicing modes no matter if the ice was formed on the surface or not. The apparatus for all anti-icing and deicing tests is shown in Figure 1.11.

In conclusion, we have prepared robust superhydrophobic films that are capable of both anti-icing and deicing. As for the passive anti-icing strategy, freezing of incoming water was prevented down to -14 °C on the surface. With a low power density of 0.2 W·cm⁻², the surface of the film remained at room temperature while the ambient temperature was -32 °C. Lubricating liquid further enhanced deicing capability and energy efficiency since removal of ice only required melting at the interface. The ease of the spray-coating method enables it to be used on a variety of substrates and devices, and anti-icing and deicing applications are expected to be practical in extreme environments.

1.4. Experimental Section

**Synthesis of FDO-GNRs.** MWCNTs (100 mg, 8.3 mmol) were added to a dry 100 mL round-bottom flask with a magnetic stir bar. The flask was transferred into a N₂ glovebox where 1,2-dimethoxyethane (35 mL) and liquid Na/K alloy (0.2 mL, molar ratio of Na:K=2:9) was added. The flask was sealed
and transferred out of the glovebox and ultrasonicated for 5 min before stirring at room temperature for 3 d. 1-Iodo-perfluorododecane or the corresponding iodoalkanes (5.0 mmol) were added to the reaction mixture through a syringe, and the reaction was allowed to stir at room temperature for 1 d. Methanol (20 mL) was used to quench and the mixture was stirred for 10 min. The reaction mixture was then filtered over a 0.45 μm pore size PTFE membrane and washed in the sequence of tetrahydrofuran (THF) (100 mL), i-PrOH (100 mL), H₂O (100 mL), i-PrOH (100 mL), THF (100 mL) and Et₂O (10 mL). The product was dried in vacuum (~10⁻² mbar) for 24 h. HD-GNRs, FO-GNRs and FD-GNRs were synthesized by using the same protocol.

**Fabrication of FDO-GNR films.** FDO-GNRs was dispersed in chloroform at a concentration of 0.5 mg·mL⁻¹ by bath ultrasonication (Cole Parmer EW-08849-00) for 30 min. Polyimide films (Kapton®, DuPont USA) and glass slides were cleaned with ethanol and dried. Using an Iwata airbrush connected to compressed nitrogen, the FDO-GNR solution was sprayed-coated on the polyimide film or glass slide heated to 90 °C on a hot plate. For more robust FDO-GNR films with double-sided tapes as an adhesive layer, the double-sided tape was placed on glass substrates before spray-coating FDO-GNR solutions. Colloidal silver paste (Pelco Colloidal Silver Liquid, Ted Pella) was applied on both ends of the film and dried at 70 °C for 15 min. HD-GNR films, FO-GNR films and FD-GNR films were prepared by using the same protocol.

**Characterization.** SEM images were recorded on a JEOL 6500 scanning electron microscope. Raman spectra were acquired using a Renishaw inVia Raman microscope with a 514 nm Ar ion laser. XPS spectra were taken on a PHI
Quantera SXM scanning X-ray microprobe with a base pressure of $5 \times 10^{-9}$ Torr. A pass energy of 26 eV with a 200 μm beam size was used for elemental spectra. TGA was performed on a Q-600 Simultaneous TGA/DSC (from TA instrument) under 100 mL·min$^{-1}$ Ar flow at a heating rate of 10 °C·min$^{-1}$.

**Measurement of sheet resistance.** A two-terminal method was used to determine the sheet resistance with a Cen-Tech digital multimeter, which was equivalent to four-terminal measurements which we performed using a Keithley 2010 multimeter and Alessi four-point probe without any deposited metal contacts. In the two-terminal method, silver contacts were deposited by applying colloidal silver paste (Pelco Colloidal Silver Liquid, Ted Pella) on both ends of the film to be connected with the probes. Sheet resistance was calculated using the following Equation 1.1,

$$R_s = R \cdot \frac{w}{l}$$

**Equation 1.1 Sheet resistance of functionalized GNR films.**

where $R_s$ is the measured resistance, and $w$ and $l$ are the width and length of the film, respectively.

**Measurement of static water contact angles and sliding angles.** Water was dropped onto the films placed on a flat sample stage and contact angles were measured with a Ramé-hart Model 500 Advanced Goniometer/Tensiometer. Sliding angle was the critical angle between the tilted film and the horizontal plane when water droplets started to slide.
Anti-icing test of FDO-GNR and HD-GNR films with double-sided tapes. The films were clamped in a Styrofoam box where dry ice was inserted to cool the boxed environment to the corresponding temperature. Ice-cold water (<5 °C) was dropped onto the film tilted at 45° while pictures and videos were recorded.

Resistive heating test of FDO-GNR films. The film was clamped in the same box as mentioned above. Dry ice was used to decrease the ambient boxed temperature to -32 °C. A thermocouple was taped to the back of the glass slide to measure the film temperature. Voltage was applied to heat the film while the film temperature was recorded. The film was then kept at 30 °C at a voltage of ~40 V when 25 mL ice cold water was sprayed onto the film using a spray gun over 10 min.

Deicing test of FDO-GNR films. Ice cold water was dropped onto the films without tilting at -32 °C to form ice. Specific voltages were applied to the film tilting at 45° to generate resistive heating while pictures and videos were recorded. To make a slippery surface, heptacosfluorotributylamine (0.1 mL) was dropped onto the film before or after ice formation followed by the same deicing procedure as above.

1.5. Contributions

Tuo Wang and Yonghao Zheng designed the experiments, synthesized functionalized GNRs, and completed the deicing and anti-icing tests. Tuo Wang prepared the GNR films, measured contact angles and sliding angles, and did all
the characterization. Abdul-Rahman O. Raji instructed on the synthesis of functionalized GNRs and the preparation of functionalized GNR films. Yilun Li performed SEM analysis. William Sikkema drew the scheme.
Chapter 2

Graphene Nanoribbons as Conductive additives for Li Metal Batteries and Li-Ion Batteries

This Chapter is copied from references 36, 75 and 108.

2.1. Advantages of Using GNRs as Battery Additives

Graphene nanoribbons (GNRs) are advantageous as conductive additives due to their high aspect ratio and high specific surface area. These advantages render GNRs good mechanical flexibility that results in good dispersion of GNRs in the matrix material. On the other hand, they can form a percolating network without any large aggregates at a small areal density which means the mass loading of conductive fillers is minimized. Over the past decade, people have developed multiple methods of synthesizing GNRs from carbon nanotubes (CNTs), especially the oxidative splitting and the reductive splitting methods,
which have made large-scale production of GNRs into reality. In this chapter, we discuss the use the GNRs in both Li metal anodes for Li metal batteries and red P anodes for conventional Li-ion batteries. It was also found that red P was not only a good candidate for Li storage, but a surprisingly powerful tool to improve battery safety by enabling in situ detection of Li dendrite formation in a two-electrode battery system.

2.2. Graphene Nanoribbon-Asphalt-Li metal Anodes for Full Li Metal Batteries

Li metal has been considered an outstanding candidate for anode materials in Li-ion batteries (LIBs) due to its exceedingly high specific capacity and extremely low electrochemical potential, but addressing the problem of Li dendrite formation has remained a challenge for its practical rechargeable applications. In this chapter, we used a porous carbon material made from asphalt (Asp), specifically untreated gilsonite, as an inexpensive host material for Li plating. The ultrahigh surface area of >3000 m²/g (by BET, N₂) of the porous carbon ensures that Li was deposited on the surface of the Asp particles, as determined by scanning electron microscopy (SEM), to form Asp-Li. Graphene nanoribbons (GNRs) were added to enhance the conductivity of the host material at high current densities, to produce Asp-GNR-Li. Asp-GNR-Li has demonstrated remarkable rate performance from 5 A/gₗ𝑖 (1.3C) to 40 A/gₗ𝑖 (10.4C) with coulombic efficiencies (CE) >96%. Stable cycling was achieved for more than 500 cycles at 5 A/gₗ𝑖, and the areal capacity reached up to 9.4 mAh/cm² at a highest
discharging/charging rate of 20 mA/cm² that was 10× faster than typical LIBs, suggesting use in ultrafast charging systems. Full batteries were also built combining the Asp-GNR-Li anodes with a sulfurized carbon cathode that possessed both high power density (1322 W/kg) and high energy density (943 Wh/kg).

2.2.1. Introduction

Li-ion batteries (LIBs) have played an important role in energy storage. The booming market for portable electronic devices and electric vehicles has resulted in a growing demand for high energy density and power density energy storage devices, and this is promoting the development of high-performance anode and cathode materials in LIBs. Of all the anode materials used in LIBs, Li metal itself has remained an excellent candidate, particularly due to its extremely high specific capacity (~3860 mAh/g) that is >10× commercial graphite anodes (~372 mAh/g). Moreover, its low operating potential (-3.04 V vs standard hydrogen electrode) and intrinsic conductivity also make it superior to most other practical anode materials. However, the formation of Li dendrites during the charging process can damage the cycling performance of the anode and increase the risk of fires, as the dendritic structures can easily penetrate separators to cause internal short circuits of batteries.

Two major strategies exist to suppress dendrite growth to make Li metal anodes safer: (i) constructing more stable and conductive solid-electrolyte interphase (SEI) layers, and (ii) developing a host material for Li plating/stripping. The stabilization of SEI layers could be achieved by using high-
concentration electrolyte, ionic liquid, solid electrolyte, and a variety of electrolyte additives including HF, LiNO$_3$-VC, LiF, LiNO$_3$-LiS$_x$, Cs$^+$, Cu(OAc)$_2$, H$_2$O, fluoroethylene carbonate, and fluoroethane. As for the host materials, they act as a substrate on which the deposition of Li metal is uniformly distributed, so that dendrite formation is unfavorable. Such host materials are usually conductive, which in recent publications include hexagonal unstacked graphene, sparked reduced graphene oxide, copper nanowire networks, carbon nanotubes, graphene-carbon nanotube seamless hybrids, and Li foils with mechanically modified surfaces. But the synthesis of these host materials often turned out to be complicated, time-consuming or expensive, which restricts the large-scale application of these materials.

In this subchapter, we describe a simple approach to improving the performance of Li anodes in Li-ion batteries by using an ultrahigh surface area porous carbon generated from asphalt (Asp). The Asp is a naturally occurring high carbon material called gilsonite. To improve the conductivity of the Asp, it is mixed with graphene nanoribbons (GNRs) and the composite is well-coated with Li metal through an electrochemical deposition process. The prevention of Li dendrite formation is demonstrated by SEM analysis and exceptional cycling stability was realized even at >500 cycles. A high current density of 20 mA/cm$^2$ shows the material’s promise for use in rapid charge and discharge devices with high power density. In addition, full batteries have been fabricated in combination with a sulfurized-carbon cathode that is compatible with the
concentrated electrolyte, which demonstrates the potential for practical applications, especially when ultrafast charging is desired.

**2.2.2. Graphene Nanoribbon-Asphalt-Li Metal Anodes**

![Diagram](image)

**Figure 2.1** (a) Preparation of porous carbon from untreated gilsonite. (b) Charge/discharge profile for preparation of Asp-GNR-Li anodes. (c) Schematic illustration of the typical lithium dendrites (left) vs the lithium-coated high surface area porous carbon from asphalt (right).
Figure 2.2  BET analysis of Asp. (a) Nitrogen adsorption/desorption isotherms at 77 K. (b) Fitting of nitrogen adsorption isotherm for BET surface area calculation.

An ultrahigh surface area porous carbon material was used as a host material for Li plating/stripping. The porous carbon Asp was activated with KOH after removing most of the oil from the Asp at 400 °C (Figure 2.1a). The simple activation process generated a large surface area of >3000 m$^2$/g by N$_2$ BET analysis (Figure 2.2). The conductive GNRs were added to a slurry of the KOH-activated Asp in N-methyl-2-pyrrolidone (NMP) that was then coated on Cu foil current collectors. The asphalt-derived porous carbon-graphene nanoribbon supported Li (Asp-GNR-Li) anode was prepared in coin cells by electrochemical deposition of Li (Figure 2.1b) while a concentrated electrolyte, 4 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME), was used. Instead of forming dendritic or nodule-like structures which would happen when no host material existed, the Li metal was deposited on the Asp-GNR particles to form a thin coating (Figure 2.1c).
Figure 2.3 Morphology of Asp-GNR electrodes on Cu foils investigated by SEM. (a) Top view. (b) Side view.

The mass loading of Asp-GNR on Cu foils is ~2.5 mg/cm², which is relatively high, thus providing a large carbon surface area for lithiation. The morphology of the Asp-GNR-Li electrode is shown by SEM images in Figure 2.3. The GNRs (~250 nm × ~10 µm) with high aspect ratio were well-mixed with Asp particles to a thickness of 60 µm when applied to the Cu foil current collectors.
Figure 2.4 (a) Coulombic efficiencies of Asp-GNR-Li anodes at different rates. (b) Discharge and charge profiles of Asp-GNR-Li anodes vs bare Cu foil-Li at 2.6C. (c) Discharge and charge profiles of Asp-GNR-Li anodes vs bare Cu foil-Li at 10.4C. (d) SEM image of bare Cu foil-Li electrodes after 30 cycles at 2.6C showing dendritic structures, as indicated by the yellow arrows. (e) SEM image of Asp-GNR-Li electrodes after 30 cycles at 2.6C. (f) SEM image of Asp-GNR electrodes (delithiated) after 30 cycles at 2.6C. Mass ratio of Li to C (Asp + GNR) is 1:5 and Asp to GNR is 1:2 for all the Asp-GNR-Li anodes here. Some of the GNR stacks and Li-coated GNRs are obvious.
The Asp-GNR-Li anode has a high coulombic efficiency in the half cell when assembled with Li foils. The Li:C ratio was set at 1:5 by controlling the Li plating time. The overall coulombic efficiency stayed above 95.4% with current densities from 1.3C (2.5 mA/cm²) to 10.4C (20 mA/cm²) as shown in Figure 2.4a. In particular, high areal current densities (>10 mA/cm²) have been rarely reported in the literature because they could lead to relatively low coulombic efficiency due to dendrite formation. However, stable efficiency above 96.0% were still observed in Figure 2.4a from cycle 31 to cycle 40 at 20 mA/cm².

Figure 2.5 (a) SEM image of bare Cu foil-Li electrodes after 30 cycles at 2.6C showing dendritic structures, as indicated by the yellow
arrows. (b) SEM image of Asp-GNR-Li electrodes after 30 cycles at 2.6C. (c) SEM image of Asp-GNR electrodes (delithiated) after 30 cycles at 2.6C. Mass ratio of Li to C (Asp + GNR) is 1:5 and Asp to GNR is 1:2 for all the Asp-GNR-Li anodes here. Some of the GNR stacks and Li-coated GNRs are obvious.

Figure 2.6 Discharge and charge profiles of Asp-GNR-Li anodes at (a) 1.3C and (b) 5.2C showing more stable Li plating/stripping plateaus with lower overpotentials compared to the control (bare Cu foil-Li anodes).

The overpotential for Li plating and stripping in Asp-GNR-Li anodes are lower than in bare Cu-foil-Li anodes, as shown in the discharge and charge profiles in Figure 2.4b,c and 2.6a,b. This indicates a higher conductivity enabled by the host material. Although Li metal is conductive, the dendrite growth leads to non-uniform electrochemical deposition when Li metal is regenerated during the charge process, which is revealed by SEM analysis (Figure 2.5a). Further cycling of the anodes can cause fragmentation of Li metal that destroys its
intimate contact with the current collector and increases internal resistance, raising the overpotential.\textsuperscript{38} When Asp-GNR is present, the conductivity and high surface area allows Li to be coated on its surface, so that it forms a smooth surface of Li metal that gives a lower overpotential for both lithiation and delithiation. In order to demonstrate that Li metal was deposited on the surface of Asp-GNR without the formation of dendrites, SEM was used to study the morphology of the anode after cycling. Two anodes were lithiated then delithiated for 30 cycles at 2.6C (5 mA/cm\textsuperscript{2}), one of which was then lithiated again while the other was not. SEM was performed after the electrodes were taken out of the coin cells and washed with DME to remove the electrolyte on the surface. Unlike Figure 2.5a, the SEM image of the lithiated sample in Figure 2.5b shows that Li was uniformly coated on Asp-GNR composite while no mossy structure was detected. The delithiated sample in Figure 2.5c has a porous structure similar to the lithiated one, suggesting that morphology change was not significant after delithiation, helping to preserve the high surface area for plating of metallic Li.
Figure 2.7  (a) Cycling stability of the Asp-GNR-Li anode at 2.5 mA/cm² (1.3C) with a Li loading of 0.50 mg/cm². (b) Cycling stability of the Asp-GNR-Li anode at 5 mA/cm² (1.0C) with a Li loading of 1.25 mg/cm². (c) Cycling stability of the Asp-GNR-Li anode at 5 mA/cm² (0.52C) and 20 mA/cm² (2.1C) with a Li loading of 2.5 mg/cm².

Longer cycles were also tested in the half cell to study the cycling stability of the Asp-GNR-Li anode. An average coulombic efficiency of 99.0% was obtained with very small standard deviation of 1.5% for 505 cycles at 2.5 mA/cm² (Figure 2.7a). The efficiency became more consistent after ~150 cycles, which could be due to reactive species in Asp-GNR being consumed from the beginning and the SEI layers becoming more stable. The efficiency slightly above 100% were also observed in a handful of cycles, which could be beneficial for long-term use.
because the small amount of leftover Li after each Li stripping step was not completely unreactive, so that the coulombic efficiency would not keep declining.

The anode with higher areal capacity also maintains both high coulombic efficiency as well as good cycling stability. The areal capacity was increased by applying higher Li loading: the Li:C ratio was increased from 1:5 to 1:2 (Figure 2.7 b) and 1:1 (Figure 2.7c), and the anodes still showed average coulombic efficiencies of more than 97% with good cycling stability. Further enhancing the current density to 20 mA/cm² (Figure 2.7c) did not significantly reduce the average coulombic efficiency, although the stability was slightly impaired. The areal capacities for Li:C ratios of 1:5, 1:2 and 1:1 in Figure 2.7 were calculated to be 1.9, 4.7 and 9.4 mAh/cm², and the specific capacities were 643, 1287 and 1930 mAh/g.
2.2.3. The Role of Graphene Nanoribbons in the Anodes

Figure 2.8 Comparison between Asp-GNR-Li anodes and Asp-Li anodes by electrochemical tests. Nyquist plots in the (a) lithiated state and (b) delithiated state. Cycling stabilities at different rates: (c) 2.6C and (d) 5.2C.
Figure 2.9 Comparison between the Asp-GNR-Li anode and the Asp-Li anode by cycling performance test at (a) 0.65C and (b) 1.3C.

The high surface area of the host Asp material facilitates the good and stable coulombic efficiency. GNRs as the conductive filler were also essential for the stabilization of the electrochemical performance, and this was underscored when Asp-Li anodes were used as controls. The enhanced conductivity was first revealed by electrochemical impedance spectroscopy. When assembling with Li foils as the counter electrode, Asp-GNR-Li anodes have lower internal resistance than Asp-Li anodes, which did not contain GNRs or other conductive additives, in both the lithiated and delithiated states (Figure 2.8a and 2.8b). The conductivity might not make a difference at low current densities such as 0.65C and 1.3C (Figure 2.9), given that both Asp-GNR-Li anodes and Asp-Li anodes produced stable coulombic efficiency. However, the Asp-Li anodes started to show noticeable fluctuation after 40 cycles at 2.6C (Figure 2.7c); the efficiency dropped below 90% after only 15 cycles at 5.2C (Figure 2.8d).
Figure 2.10 Comparison of the Asp-GNR-Li anode and the Asp-Li anode (control) by SEM. (a) Asp-Li anodes (lithiated) after 30 cycles at 2.6C. (b) Asp-Li anodes (lithiated) after 30 cycles at 5.2C. (c) Asp-GNR-Li anodes (lithiated) after 30 cycles at 2.6C. (d) Asp-GNR-Li anodes (lithiated) after 30 cycles at 5.2C.

In the SEM images of Asp-Li anodes, mossy and nodule-like Li metal structures were seen in Figure 2.10a when tested at 2.6C, indicating non-uniform deposition of Li metal. When the current density was increased to 5.2C, Li dendrites started to form on top of the Asp layer in the Asp-Li anodes (Figure
In contrast, no obvious mossy or dendritic structures were found in Asp-GNR-Li anodes tested either at 2.6C (Figure 2.10c) or at 5.2C (Figure 2.10d), indicating that the GNRs provided the conductivity needed to prevent Li dendrite growth while preventing capacity or coulombic efficiency degradation, particularly at high current densities.

2.2.4. Building Full Li Metal Batteries Using Graphene Nanoribbon-Asphalt-Li Metal Anodes and Sulfurized Carbon Cathodes

Figure 2.11 TGA curve of sulfurized carbon under 100 mL/min Ar flow at a heating rate of 10 °C/min.
Figure 2.12 Performance of the full Asp-GNR-Li||sulfurized carbon batteries. (a) Rate performance test followed by cycling performance test at 0.5C for 100 cycles. (b) Discharge and charge profiles of the full batteries at different rates. (c) Ragone plots of the full batteries based on active materials or all electrode materials on both electrodes.

To provide further support for the use of the Asp-GNR-Li anode, we combined it with a sulfurized carbon cathode to produce a full battery using the same concentrated electrolyte. The sulfurized carbon was prepared by annealing a mixture of sulfur, polyacrylonitrile and GNRs with a mass ratio of 55:11:1. Unlike elemental sulfur, which usually evaporates at ~300 °C, the
sulfurized carbon did not show a significant weight loss until ~600 °C, according to the TGA analysis in Figure 2.11. It is presumed that this resulted from chemical bonding between sulfur and carbon atoms, which traps the sulfur species in the carbon matrix formed by decomposition of polyacrylonitrile.70-72 And this would also explain why the sulfurized carbon works with a concentrated electrolyte. The C-S bonds inhibit sulfur solubility.70-72 We deposited 20% more Li than was needed in the Asp-GNR-Li anodes to compensate for the loss of Li metal due to the formation of the SEI layer, and thus the C-rates (Figure 2.12a,b) were calculated based on the sulfur content in the cathode. Rate performances of the full batteries are shown in Figure 2.12a, where the specific capacity reaches 720, 690, 655, 613, and 559 mAh/g at 0.1C, 0.2C, 0.5C, 1C, and 2C. Stability was observed in the cycling test that gives a 92% capacity retention after 100 cycles at 0.5C (Figure 2.12a). In contrast, lower capacities at all rates and less stable cycling performance were seen in the control sample using the same cathode but bare Cu foils for Li plating in the anode. The single plateaus in both discharge and charge processes were observed at 1.6 to 2.3 V and 2.1 to 2.4 V respectively (Figure 2.12b), suggesting a different reaction mechanism than the two plateaus shown by elemental sulfur. The mechanism could be the solid-to-solid single-phase redox reaction of sulfur species.73,74 The full battery had a high power density of 1322 W/kg while achieving high energy density of 943 Wh/kg, considering all electrode materials including carbon matrix, binder and carbon black (Figure 2.12c).
In conclusion, we have developed an Asp-GNR composite material as a host material for Li plating that suppresses Li dendrite formation at current densities from 1.3C to 10.4C. The coulombic efficiency remained >96% and was stable for more than 500 cycles at 1.3C. An areal capacity of 9.4 mAh/cm² was obtained with a Li:C ratio of 1:1 at the highest current density of 20 mA/cm². This bodes well for very fast charging batteries, >10× faster than typically seen in present commercial systems. SEM images of Asp-GNR-Li anodes after cycling show that no obvious dendritic Li was formed, as opposed to Asp-Li anodes with the lack of the conductive additives. This high coulombic efficiency, areal capacity and high discharging/charging rate make Asp-GNR-Li suitable for applications in microscale and rapid-charge/discharge devices. The combination of the Asp-GNR-Li anodes with sulfurized carbon cathodes underscore the utility of an ultrahigh surface area carbon prepared from inexpensive asphalt.

2.2.5. Experimental Section

The GNRs were obtained from EMD-Merck. It is now available from MilliporeSigma.

Synthesis of Asp. Untreated gilsonite (Prince Energy) was pretreated at 400 °C under Ar for 3 h. The pretreated gilsonite was ground with KOH in a mortar. The mass ratio of KOH to pretreated gilsonite was 4:1. The mixture was then heated at 850 °C for 15 min, followed by filtration and washing with water until pH was ~7. The product was dried at 110 °C for 12 h. BET analysis with N₂ showed surface area of >3000 m²/g for multiple batches.
Preparation of Asp-GNR-Li anodes and electrochemical measurements. GNRs, Asp and polyvinylidene difluoroide (PVDF, Alfa Aesar) were mixed in a mortar with a mass ratio of 4.5:4.5:1. NMP (Sigma-Aldrich) was added to form a slurry which was then coated on a Cu foil substrate and dried in vacuum at 50 °C overnight. Control materials including GNR electrodes were prepared in the same way. Electrochemical tests were performed using CR2032 coin cells with Li metal foils as the counter electrode. The electrolyte was 4 M LiFSI in DME and the separator was a Celgard 2045 membrane. The capacity was calculated based on the mass of Li calculated from the time-control discharging lithiation process with \[ m_{\text{Li}} = I \times t \times M_{\text{Li}} / F, \] where \( m_{\text{Li}} \) is the mass of electrochemically deposited lithium metal, \( I \) is the discharging current, \( t \) is the discharging time, \( M_{\text{Li}} \) is the molecular weight of Li and \( F \) is the Faraday constant (96485 C/mol). Data were collected after 10 cycles of activation to form a stable SEI layer. EIS was performed on a CHI 608D workstation (CH Instruments).

Synthesis of sulfurized carbon. Polyacrylonitrile, GNR and sulfur with a mass ratio of 11:1:55 were mixed and heated in a quartz tube furnace to 450 °C at 5 °C/min and kept at 450 °C for 6 h in an Ar atmosphere.

Preparation of sulfurized carbon cathodes, full batteries, and electrochemical measurements. The sulfurized carbon was mixed with PVDF and carbon black in a mortar with a mass ratio of 8:1:1. NMP was added to form a slurry which was then coated on a stainless-steel foil substrate and dried under vacuum (~1 torr) at 50 °C overnight. Then the cathode was assembled in a CR2032 coin cell with lithiated Asp-GNR-Li anode (activated for 10 cycles at 2.6C)
to make a full battery. The electrolyte was 4 M LiFSI in DME and the separator was a Celgard 2045 membrane. The full batteries were tested between 1.0 V and 3.0 V at different rates. The energy densities (Wh/kg) were calculated by multiplying the specific capacities (Ah/kg) by the average voltages (V). The energy densities (W/kg) were calculated by multiplying the current densities (A/kg) by the average voltages (V). The average voltage values for 0.1C, 0.2C, 0.5C, 1C and 2C were 1.83 V, 1.83V, 1.80 V, 1.76 V and 1.70V.

**Characterization.** SEM images were recorded on a JEOL 6500 scanning electron microscope. TGA was performed on a Q-600 Simultaneous TGA/DSC (from TA instrument) under 100 mL/min Ar flow at a heating rate of 10 °C/min.

**2.2.6. Contributions**

Tuo Wang designed all the experiments, synthesized and characterized the materials, and performed electrochemical tests. Rodrigo V. Salvatierra instructed on Li plating and battery tests. Almaz S. Jaliolov and Tian Jian instructed on the synthesis of Asp.
2.3. Graphene Nanoribbon-Red P Composite Anodes for Li-Ion Batteries

Red phosphorus (RP) is considered a promising anode material for lithium-ion batteries (LIBs) due to its high energy density and low cost. While RP is electrically insulating, researchers have reduced its particle size and added conductive fillers to improve the electrochemical activity of RP. Here we report a method for making <1-µm-sized RP under ambient conditions by using tip-sonication. A specific surfactant solution was used to stabilize the dispersion of <1-µm-sized RP. Graphene nanoribbons (GNRs) were added to improve the conductivity. The RP-GNR composite achieved nearly maximum capacity at 0.1C and showed a capacity retention of 96% after 216 cycles at 0.4C in the half-cell. When combined with a LiCoO₂ cathode, the full cell delivered a total capacity of 86 mAh/g after 200 cycles at 0.4C. This study has demonstrated the fabrication of high-performance LIBs using RP in a safe, convenient, and cost-effective manner, and the method might be extended to the preparation of other battery or catalyst materials that are difficult to acquire through bottom-up or top-down approaches.

2.3.1. Introduction

The development of higher power and longer lasting rechargeable Li-ion batteries (LIB) is rapidly advancing because of the huge demand in portable electronics and electric vehicles.76,77 Tesla has planned to produce 70 GWh of batteries in 2020, which is double the amount of the Gigafactory’s designed
annual battery production announced in 2014. This is driven by the sustainability as well as the superior performance of LIBs compared to other energy storage devices. Thus, improving the energy density and power density of state-of-the-art LIBs has become important to the further development of several industries.

Phosphorus is a good candidate for anode materials in LIBs because it has a high theoretical capacity of 2596 mAh/g. It is the third highest among all the anode materials after Li (3860 mAh/g) and Si (3579 mAh/g). Over the past few years, researchers have studied the use of black phosphorus (BP) in anodes and achieved good cycling performance along with high capacity. However, the cost of BP (>1000/g) makes it cost prohibitive; additionally, it is sensitive to air and water, adding to the complexity of its use in large-scale applications. Alternately, red phosphorus (RP) is much less expensive and it is chemically inert. Although intrinsically non-conductive, it can be mixed with micro- or nanoscale conductive fillers to become an active material in electrochemical reactions.

Three primary strategies for preparing RP nanoparticles (NPs) mixed with conductive fillers are: wet-chemistry synthesis, vaporization-condensation, and ball-milling. Wet-chemistry is a newly developed method where PXn (X = halide) reacts with reducing agents to form a small size distribution of RP NPs. Current wet-chemistry methods involve the use of precursors such as PI3 and NaN3, and the yields are lower than afforded by other methods. The most commonly used method is vaporization-condensation where RP sublimes upon
heating and then condenses in the presence of fillers such as conductive carbon species. The RP NPs are generally evenly distributed in the fillers. But vaporization-condensation requires high temperature (>500 °C) and vacuum, and white phosphorus can be formed as a side-product. In comparison, the ball-milling method appears to be safer and less complicated, but it results in relatively larger RP particles with a wide size distribution.

In this sub-chapter, we introduce a top-down approach for making RP NPs under ambient conditions without the use of hazardous chemicals. The process involves tip-sonication and centrifugation in a specific surfactant solution that stabilizes RP NPs. High-power (~100 W) tip-sonication produces <1-µm-sized RP particles with uniform size distribution. They are isolated through centrifugation and co-filtered with graphene nanoribbons (GNRs) to form a RP-GNR composite. The RP-GNRs yield nearly maximum capacity at 0.1C with a C:P ratio of 3:1. This process of synthesizing RP anodes appears to be safe, convenient, and cost-effective.
2.3.2. Graphene Nanoribbon-Red P Composite Anodes

![Diagram of graphene nanoribbon-red P composite anodes preparation](image)

**Figure 2.13** Schematic illustration of the preparation of RP-GNR composites by tip-sonication and co-filtration.

The preparation scheme for the RP-GNR composites is shown in Figure 2.13. RP NPs were obtained through double tip-sonication treatment (~100 W, 2 h, Misonix Sonicator 3000) followed by centrifuge or decanting. The sediment was recycled by simply adding more surfactant solution, since it still contained RP NPs that can be redispersed by vigorously shaking the tube for 30 s. The concentration of RP in supernatant-2 was estimated to be ~0.1 mg/mL. A certain amount of GNR dispersion was added and co-filtered with RP in the final step to produce a RP-GNR composite with the desired P content.
Figure 2.14 Optical images and SEM images of RP dispersions. (a) Optical images of the RP dispersion before centrifugation and the sediment and supernatant-1 after centrifugation. (b,c) SEM images of RP particles in the RP dispersion after the first tip-sonication and before centrifugation. (d,e) SEM images of RP particles in the supernatant-1 after the first tip-sonication and centrifugation. The circles area regions showed the large RP particles. (f,g) SEM images of RP particles in the supernatant-2 (see Figure 2.13) after the second tip-sonication.

We started with bulk-phase RP and used 1 M sodium dodecylbenzenesulfonate (SDBS) in water/ethanol (v/v = 1/1) as the dispersion medium (Figure 2.13). This typical surfactant solution forms a stable dispersion
of RP NPs after tip-sonication and centrifugation. In this case, SDBS worked better than positively charged surfactants such as cetyltrimethylammonium bromide (CTAB) and neutral ones including polyethylene glycol (PEG), polyvinyl alcohol (PVA), and pluronic F-127 in terms of the physical stability of the dispersion. SDBS is also a low molecular weight surfactant that did not clog the filter membrane as did the polymer surfactants. There was a noticeable change in the color of the RP dispersion after centrifugation as shown in Figure 2.14a where an orange supernatant-1 was obtained while the sediment remained red. The orange color indicates a smaller particle size as a result of centrifugation that removed most of the large particles. This was confirmed by scanning electron microscopy (SEM) images before (Figure 2.14b,c) and after (Figure 2.14d,e) centrifugation. We tip-sonicated the supernatant again, allowed it to sit undisturbed overnight, and transferred ~90 vol% of the top dispersion, so that the remaining large particles (>1 µm) were almost completely removed and the resulting dispersion had only <1-µm-sized RP NPs observable with a small size distribution (Figure 2.14f,g). Instead of having to apply heat and vacuum or inert atmosphere as in the vaporization-condensation method, this entire procedure was performed at room temperature and ambient pressure while being exposed to air at all times.
Figure 2.15 TGA profiles of RP-GNR composites with different P content.

GNRs were added by co-filtration after tip-sonication (Figure 2.13) in an aqueous CTAB solution (1 wt%) to improve the conductivity. GNRs are known as a good conductive filler for electrode materials.\textsuperscript{80,71,100,101} Although other conductive fillers, such as carbon black, can also be used, high aspect-ratio fillers such as GNRs are preferred since they can afford higher percolation at a lower loading.\textsuperscript{102-106} Since the GNRs were synthesized via reductive splitting of multi-walled carbon nanotubes (MWCNTs) using Na/K alloy and the reaction proceeded under Ar atmosphere, the amount of O defects was limited and the high D to G ratio is attributed to the edge effects of GNRs where the MWCNTs were unzipped.\textsuperscript{23} The GNRs are also commercially available through MilliporeSigma. By tuning the amount of GNRs added, we obtained RP-GNR
composites with different P content from 25 wt% to 72 wt%, as measured by TGA (Figure 2.15).

Figure 2.16 Characterization of the RP-GNR composites: (a,b) SEM images; (c) XRD spectrum; (d) Raman spectrum; (e) TGA profile.
Figure 2.17 SEM images of (a,b) RP-25-GNR, (c,d) RP-39-GNR, (e,f) RP-57-GNR, and (g,h) RP-72-GNR. The numbers 25, 39, 57 and 72 represent the RP content in wt%.
Figure 2.18 EDS mapping for RP-25-GNR. (a) SEM image. (b) EDS mapping of carbon. (c) EDS mapping of phosphorus. (d) EDS mapping of carbon and phosphorus (overlap of (c) and (d)).

Figure 2.19 TEM images of RP-25-GNR.
SEM images of the RP-GNR (Figure 2.16a,b) revealed the percolating network of GNR with RP NPs attached to the ribbons. The morphology of RP-GNR samples with different RP contents were shown in Figure 2.17. Energy-dispersive X-ray spectroscopy (EDS) mapping of an SEM image under higher magnification (Figure 2.18) further identified the observed NPs and GNRs. Transmission electron microscopy (TEM) images of the RP-GNR are shown in Figure 2.19. X-ray diffraction (XRD) and Raman analyses were also performed: the peaks at ~15°, 33°, and 54° in the XRD spectrum of RP-GNR (Figure 2.16c) and the Raman peak at 300-500 cm\(^{-1}\) (Figure 2.16d) provide evidence for the presence of RP; the sharp peak at 26° in the XRD spectrum and the intense 2D peak in the Raman spectrum demonstrated the high graphene crystallinity. The P content in the composite was determined by the weight loss at ~400 °C in the thermogravimetric analysis (TGA) profile that corresponded to the sublimation of RP (Figure 2.16e), which was used to evaluate the contribution of RP to the electrochemical performance of the composite.\(^{91}\)
Figure 2.20 Electrochemical performance of RP-GNR composites in half-cells. (a) CV profile of RP-25-GNR between 0.01 V and 3 V. (b) Charge/discharge profile of RP-25-GNR between 0.01 V and 2.5 V. (c) Rate performance of the RP in RP-GNR with different phosphorus contents based on the mass of RP. (d) Rate performance and (e) cycling performance of the RP-GNR composites with different phosphorus contents based on the mass of the RP-GNR composite.
Figure 2.21 Charge and discharge profile of GNRs between 0.01 V and 2.5 V.

<table>
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<tr>
<th>C-rate for RP</th>
<th>0.1C</th>
<th>0.2C</th>
<th>0.4C</th>
<th>0.8C</th>
<th>1C</th>
<th>2C</th>
<th>4C</th>
</tr>
</thead>
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<tr>
<td>Current density for RP (A/g&lt;sub&gt;RP&lt;/sub&gt;)</td>
<td>0.26</td>
<td>0.52</td>
<td>1.04</td>
<td>2.08</td>
<td>2.6</td>
<td>5.2</td>
<td>10.4</td>
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<tr>
<td>Current density for GNR (A/g&lt;sub&gt;GNR&lt;/sub&gt;)</td>
<td>0.087</td>
<td>0.17</td>
<td>0.35</td>
<td>0.69</td>
<td>0.87</td>
<td>1.73</td>
<td>3.47</td>
</tr>
<tr>
<td>Specific capacity of GNR (mAh/g&lt;sub&gt;GNR&lt;/sub&gt;)</td>
<td>231</td>
<td>202</td>
<td>172</td>
<td>149</td>
<td>110</td>
<td>89</td>
<td>73</td>
</tr>
</tbody>
</table>

Table 2.1 Capacities of GNRs in RP-25-GNR at different rates.

The cyclic voltammetry (CV) analysis of RP-GNR carried out between 0.01 V and 3 V (Figure 2.20a) showed the charge/discharge mechanism of the active
materials in the composite and was consistent with what the charge/discharge profiles displayed (Figure 2.20b). RP-25-GNR (25 represents a RP content of 25 wt%) was selected as an example. The cathodic peaks at 0.8-0.6 V in the Figure 2.20a scan correspond to the continuous lithiation of RP to form Li_xP (1 < x < 3), and the cathodic peak at ~0.1 V in Figure 2.20a corresponds to both the intercalation of Li ions between graphene layers in the GNRs and the final lithiation step of RP that forms Li_3P. The voltage range of the peaks were very close to that of two discharge plateaus in Figure 2.20b, one at 0.7-0.5 V and the other at <0.4 V. In the anodic scan, the two peaks at 1.1-1.4 V in Figure 2.20a are assigned to continuous delithiation of Li_3P, which also matches the charge plateau in Figure 2.20b that begins from 1.0 V.

The rate performance from 0.1C to 2C of RP-GNR samples with different RP contents based on the mass of RP was shown in Figure 2.20c. The specific capacity was calculated using the method described in the Figure 2.21 and Table 2.1 using RP-25-GNR as an example. The specific capacity of GNRs was tested at the corresponding rates and deducted from the total capacity using the P content measured by TGA. The current densities of RP were converted to those of GNRs based on the mass ratio between C and P (3:1). The capacities of GNRs were then measured in half-cells from 0.01 V to 2.5 V. The capacity of RP in RP-25-GNR is calculated as such: At 0.2C, the total capacity of RP-25-GNR is 2790 mAh/g_{RP}. Given the specific capacity of GNRs at the corresponding rate (0.17 A/g_{GNR}) being 202 mAh/g_{GNR} and the mass ratio of GNR (assumed all C) to P being 3:1, the
capacity of RP in RP-25-GNR is $2790 - 3 \times 202 = 2184$ (mAh/g$_{RP}$). All values of capacity in Figure 4c are calculated in the same way.

![Graph showing rate performance of RP-25-GNR prepared by single and double tip-sonication.](image)

**Figure 2.22** Rate performance of RP-25-GNR prepared by single and double tip-sonication. double tip-sonication.

The RP-25-GNR exhibited the highest rate performance of RP (regardless of the capacity of GNRs) due to the high conductivity enabled by the high GNR content. The specific capacity of RP reached 2566 mAh/g in the second cycle at 0.1C, which is very close to the maximum value (2596 mAh/g). The RP in RP-25-GNR delivered 2211, 1974, 1675, 1321, and 969 mAh/g at 0.2C, 0.4C, 0.8C, 1C, and 2C, respectively. When the current density was reset back to 0.4C, a discharge capacity of 1742 mAh/g was recovered. The first cycle at 0.1C had a low Coulombic efficiency of 70%, which is commonly seen for high-capacity anode materials including P and Si.$^{81,91-94}$ After the first cycle, the Coulombic efficiency stays at nearly 100% from 0.1C to 2C. The rate performance decreases
progressively when the P content becomes higher, which underscores the importance of having sufficient GNRs to ensure high conductivity. Especially at 0.1C when RP became fully lithiated in the discharge step that delivered >1800 mAh/g, it presumably suffered from severe pulverization upon extraction of Li ions in the following charge step. When there are insufficient GNRs present (P content 57 wt% or 72 wt%), the pulverized RP NPs might lose intimate contact with the GNRs, causing capacity degradation at 0.1C as shown in Figure 2.20c. The effect of particle size was studied by comparing the rate performance of RP treated with single (supernatant-1) and double (supernatant-2) tip-sonication. The RP-25-GNR prepared from double tip-sonication (supernatant-2) showed higher capacity at all different rates (Figure 2.22), indicating that the <1 μm sized RP NPs were electrochemically more reactive than the larger ones.

The specific capacities of RP-GNR samples based on the mass of the RP-GNR composite are compared in Figure 2.20d. High RP content (RP-57-GNR and RP-72-GNR) resulted in higher capacity at low rate such as 0.1C and 0.2C. At higher rate (>0.2C), low P content yielded higher total capacity due to higher conductivity that benefited rapid charge and discharge. The cycling performance of different RP-GNR at 0.4C based on the mass of the composite was compared in Figure 2.20e. At 0.4C, which is closer to the rate normally used for charging commercial LIBs, the RP-25-GNR showed a high capacity retention of 98% after 225 cycles, which is equivalent to only 0.011% capacity loss per cycle. RP-39-GNR also exhibited stable cycling performance with a capacity retention of 96% after 216 cycles. Considering both rate performance and cyclin stability, RP-39-GNR
was used in building full cells with LiCoO$_2$ cathodes. The RP-GNR composite with lower P content (<25 wt%) was not investigated because the specific capacity of the composite would be too low.

### 2.3.3. Building Full Li-Ion Batteries Using Graphene Nanoribbon-Red P Composite Anodes and LiCoO$_2$ Cathodes

Figure 2.23 Rate and cycling performance of the RP-39-GNR||LiCoO$_2$ full cell. (a) Charge/discharge profile of the LiCoO$_2$ cathodes between 2.8 V and 4.2 V. (b) Charge/discharge profiles of the full cells between 0.5 V and 4.2 V. (c) Rate and cycling performance of the full cells.
Due to the voltage hysteresis and the high charging plateau of RP, a high-voltage cathode is needed to build a full cell that holds a complementary output voltage. Therefore, LiCoO$_2$ was selected as the cathode material because of its high operating voltage and small voltage hysteresis. The charge/discharge profile of LiCoO$_2$ cathodes at 0.2C between 2.8 V and 4.2 V is shown in Figure 2.23a, where discharge and charge plateaus were both at ~3.9 V. The mass loading of RP-39-GNR was ~1.3 mg/cm$^2$, and to match it with the total capacity of the cathode, the mass loading of LiCoO$_2$ was set at ~8 mg/cm$^2$. The full cell was tested between 0.5 V and 4.2 V, and the charge/discharge profile is shown in Figure 2.23b.

The full cell delivered a specific discharge capacity of 122 mAh/g at 0.2C, corresponding to 890 mAh/g for the RP-39-GNR anode (based on the mass of the RP-39-GNR composite). The complete rate and cycling performance of the full cell is shown in Figure 2.23c, where the full cell capacity at 0.1C, 0.4C and 2C are 139, 107, and 52 mAh/g, respectively. The full cell capacity is limited by the cathode at low rates (0.1C-0.4C) and by the anode (RP-39-GNR) at high rates (0.8C-2C), because LiCoO$_2$ delivered a slightly lower capacity at low rates and higher capacity at high rates. In the following test of cycling stability at 0.4C, the full cell showed a total discharge capacity of 86 mAh/g after 200 cycles with a capacity retention of 81%.

In conclusion, we have demonstrated that RP NPs with uniform size distribution can be prepared by a tip-sonication/centrifugation method with the assistance of SDBS to stabilize the NPs in a water/ethanol (v/v = 1/1) mixture.
GNRs were introduced by co-filtration to form a composite and to improve the electrical conductivity. The GNR addition afforded a higher rate performance of RP at a higher GNR content. The entire synthesis procedure was carried out at room temperature without vacuum or inert atmosphere and free of hazardous chemicals. We have shown stable cycling of the RP-GNR anodes with a capacity of 706 mAh/g based on the mass of the RP-GNR composite after 216 cycles at 0.4C in the half-cell, as well as a full cell capacity of 86 mAh/g after 200 cycles at 0.4C when combined with LiCoO₂ cathodes. The tip-sonicated RP-GNR composite is a good candidate for making energy storage devices with high energy density and high power density, and the tip-sonication method might be extended to the preparation of other battery or catalyst materials at the micro- or nanoscale, especially for those that are difficult to acquire through bottom-top synthesis.

2.3.4. Experimental Procedures

Preparation of RP NP dispersions. RP (≥99.99% trace metals basis) was purchased from MilliporeSigma. Sodium dodecylbenzenesulfonate (SDBS, from MilliporeSigma) solutions (0.1 wt% in water/ethanol (v/v = 1:1)) were used to disperse RP. RP (300 mg) was added to an SDBS solution (30 mL) and tip-sonicated at ~100 W for 2 h using the Misonix Sonicator 3000. The dispersion was centrifuged at 3200 rpm for 6 min and the supernatant was collected in a 500 mL round-bottom flask. More SDBS solution (40 mL) was added to re-disperse the sediment by shaking vigorously for 30 s, and the dispersion was centrifuged again. The re-dispersing and centrifugation was repeated until ~200
mL of RP dispersion was collected. The RP dispersion was tip-sonicated at ~100 W for another 2 h and transferred it into 5 × 50 mL centrifuge tubes. The centrifuge tubes were left to sit undisturbed overnight and then the supernatant was transferred (some RP aggregates on the bottom were left in ~5 mL of dispersion in the tube) to a 500 mL round-bottom flask.

**Preparation of GNR dispersions and RP-GNR composites.** GNRs were from MilliporeSigma. Cetyltrimethylammonium bromide (CTAB, ≥99%, from MilliporeSigma) aq. solutions (1 wt%) were used to disperse GNRs. GNRs were added to a CTAB solution (20 mL) and tip-sonicated at ~100 W for 30 min. The GNR dispersion (20 mL) was added to the RP dispersion (~200 mL) and stirred at 300 rpm for 5 min. The mixture was then filtered through a 0.45 µm pore size PTFE membrane (Sartorius) and washed with water (20 mL × 3), ethanol (20 mL × 3), and acetone (20 mL × 3). The product was dried under vacuum (~1 Torr) at 60 °C overnight.

**Characterizations: TGA, XRD, SEM, EDS, and TEM.** TGA profiles of RP-GNR composites were acquired on a Q-600 Simultaneous TGA/DSC (TA instrument) under 100 mL/min argon flow from room temperature to 700 °C at a heating rate of 10 °C/min. XRD spectra were acquired on a Rigaku D/Max Ultima II X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). SEM and EDS were performed using a JEOL 6500 scanning electron microscope. TEM was performed on a JEOL 2100 field emission gun transmission electron microscope.

**Electrochemical test of half-cells.** RP-GNR anodes were prepared on Cu foils using a slurry that contained RP-GNRs and polyvinylidene difluoride
(PVDF) as the binder with a mass ratio of 90:10. The slurry was dried under vacuum (~1 Torr) at 60 °C overnight. Ethylene carbonate (EC) and diethylene carbonate (DEC) were obtained from MilliporeSigma. Half-cells were assembled in CR2032 coin cells using Li foils as the counter electrode. LiPF₆ (1 M in EC/DEC (v/v = 1:1)) was used as the electrolyte. Celgard 2500 membranes were used as the separator. Cyclic voltammetry (CV) test was performed between 0.01 V and 3 V on a CHI 608D workstation (CH Instruments). Rate performance and cycling performance were tested between 0.01 V and 2.5 V.

**Electrochemical test of full cells.** LiCoO₂ cathodes were prepared on carbon-coated Al foils using a slurry that contained LiCoO₂, carbon black, and PVDF with a mass ratio of 80:10:10. The slurry was dried under vacuum (~1 Torr) at 60 °C overnight. The mass loading of LiCoO₂ was ~8 mg/cm². The mass loading of RP in the RP-39-GNR anodes was ~0.5 mg/cm². The full cells were assembled in CR2032 coin cells using LiCoO₂ cathodes and RP-GNR anodes. LiPF₆ (1 M in EC/DEC (v/v = 1:1)) was used as the electrolyte. The amount of GNR depends on the desired C:P ratio. Celgard 2500 membranes were used as the separator. Rate performance and cycling performance were tested between 0.5 V and 4.2 V.

**2.3.5. Contributions**

Tuo Wang proposed the idea of using tip-sonication, synthesized RP-GNR composites, characterized all materials involved, and tested the electrochemical performance of RP-GNR in both half cells and full cells. Shiyuan Wei participated in the synthesis and characterization of RP-GNR composite. Rodrigo V.
Salvatierra performed TEM analysis of RP-GNR. Xiao Han drew the scheme in Figure 2.13. Zhe Wang helped with running CV scans of RP-GNR anodes in half cells.
2.4. Red P-Coated Separators for Li Dendrite Detection in a Two-Electrode Battery System

Li metal is considered the optimal choice for the anode material in high-energy density batteries due to its intrinsic electrical conductivity, exceedingly high specific capacity and low operating voltage. But the use of Li metal in rechargeable batteries has been prohibited because of the safety concern associated with dendrite formation that could potentially cause internal short circuits, resulting in a battery fire. Although so-called dendrite-free Li metal anodes have been reported in many recent publications, they do not change the fact that Li dendrite growth is still kinetically favorable and it remains a severe safety concern upon mass production. When it comes to the mass production of batteries on the industrial level, even a remote chance of dendrite penetration to the cathode becomes a safety concern. We report here a detection system that is capable of alerting for Li dendrite formation in a two-electrode battery with no additional electrodes required. When dendrites contact a red phosphorous (RP)-coated separator between the anode and the cathode, dendrite growth is revealed by a significant voltage change. We have demonstrated the feasibility of this detection system in both half cells and full cells. This detection system would act as a sensor and detect Li dendrite formation when the battery is being charged, such that a signal is sent to the battery management system, warning of the presence of Li dendrites and leading to shutdown of the battery before the dendrites become dangerous to its operation.
2.4.1. Introduction

Li metal batteries are thought to be the next-generation technology because of their amazingly high energy density and power density.\textsuperscript{109,110} Li metal has a theoretical capacity of \(\sim 3860\) mAh/g that is 10 times higher than commercial graphite anodes, and it can be combined with high-capacity cathodes including S and O\(_2\) that afford much higher capacity than conventional cathode materials such as LiCoO\(_2\) and LiFePO\(_4\).\textsuperscript{110,111} But commercially, Li metal has only been employed in primary batteries that cannot be recharged due to the safety issues associated with dendrite growth.\textsuperscript{110-112} When Li metal is regenerated in the charging step, it tends to form sharp, needle-like dendritic structures. These dendrites can penetrate separators and eventually short the batteries, which could lead to runaways, fires and explosions.\textsuperscript{113,114}

There have been very few studies on Li dendrite detection, and the only known method is to impregnate a thin Cu film in the middle of the separator and have it connected to a third electrode to directly detect short circuits.\textsuperscript{121,122} The added manufacturing complexity of three-electrode batteries retard such a consideration for large-scale use.

Tremendous efforts have been made to develop dendrite-free Li metal anodes by adding host materials, constructing supplemental solid-electrolyte interphase (SEI) layers, and using high-concentration or solid electrolytes to suppress dendrite growth.\textsuperscript{110,115-119} These studies were conducted on the bench scale, limiting the number of batteries tested in each case. The mass production of batteries on the industrial level could reach billions or more; it is nearly
impossible to ensure that all would operate dendrite-free. Even though certain types of separators react with Li and slow the growth of dendrites, the operating lifetime of those separators is unknown. However, if a detection system could be deployed in combination with so-called dendrite-free Li metal anodes where the chance of growing dendrites is already low, then the large-scale production of rechargeable and safe Li metal batteries can become a reality. The sensor system would detect Li dendrite formation when the battery is in use, such that a signal is sent to the battery management system, warning of the presence of Li dendrites and leading to its shutdown before an internal short circuit could result. We describe here the use of a separator coated by red phosphorus (RP) particles for Li dendrite detection in an ordinary two-electrode battery system. No additional electrode is needed, and the presence of Li dendrites can be detected simply based on the voltage profile during the charging step of a full battery. RP is inexpensive, and the preparation of the RP-coated separators is facile and scalable. The use of RP as an alert layer makes it convenient to produce Li metal batteries that mitigate the chances of a dendrite-induced short circuit and resulting thermal runaway.
2.4.2. Demonstration of Li Dendrite Detection in Half Cells

Figure 2.24 SEM image of cross section of the RP-coated Celgard 2500 separator. The yellow arrow and the black arrow show the thickness of the RP layer (~20 μm) and the Celgard 2500 separator (~20 μm). Scale bar: 10 μm.

A RP-coated separator was used for dendrite detection and was prepared by the slurry method using N-methyl-2-pyrrolidone (NMP) as the solvent and poly(vinylidene difluoride) (PVDF) as the binder. The RP layer has a thickness of ~20 μm with a mass loading of ~2 mg/cm² (Figure 2.24). Although RP was coated only on the side of the middle separator facing the Cu foil, some RP particles would diffuse to the other side through the edge when the slurry was being dried. Thus, the RP layer was physically isolated from the anode and the cathode by another two separators (Figure 2.25a), which prevents RP from
reacting with the cathode or the anode or being directly lithiated upon connection to the current collectors. However, the separator between the cathode and RP-coated separator could be removed if RP was only present on one side of the separator. When Li dendrites extend from the anode to the RP coating, there is a noticeable and dramatic electrochemical response in the voltage profile (voltage vs capacity or time). The voltage decreases in half cells or increases in full cells when Li dendrites contacted the RP; these voltage changes can activate a signal of Li dendrite formation through the battery management system that is installed on all battery-powered devices.

Figure 2.25 H Half-cell tests with RP coating on the middle separator. (a) Configuration of the half cell with RP coating (P-hc). RP was coated on one side of the middle separator and facing the Cu foil. Celgard 2500 made from polypropylene was used as the separator in
all layers and isolated RP from both the anode and the cathode. (b) Testing protocol showing the current density vs time. The discharge steps were time-control (20/10/5/2/1 min in the green region with an areal capacities of $\sim 0.083 \text{mAh/cm}^2$ and 12 min in the yellow region with an areal capacity of $\sim 1 \text{mAh/cm}^2$); the charge steps were voltage-control (2 V) and are thus shown as dashed lines because the areal capacity varied and were $< 0.083 \text{mAh/cm}^2$. (c) Voltage profile at low areal capacity ($\sim 0.083 \text{mAh/cm}^2$). (d) Voltage profile at 5 mA/cm$^2$ and high areal capacity ($\sim 1 \text{mAh/cm}^2$). The voltage decrease indicated by the arrow region is the electrochemical response generated when the Li dendrites contact the RP coating.

Half-cell tests were performed to demonstrate the epuration of the RP-coated separator. Li foils were used as the anode and Cu foils were used as the current collector for the cathode where Li metal was electrochemically deposited in the discharge process. The configuration of the phosphorus-containing half cell (P-hc) is shown in Figure 2.25a. The Celgard 2500 separators were 20-μm-thick microporous monolayer membranes made from polypropylene although we later show that 12-μm-thick polyethylene membranes work equally well. These separators were not electrical conductors and they do not react with Li metal. LiPF$_6$ was selected as the electrolyte since it is known to produce dendrites faster than other electrolytes such as LiClO$_4$ and lithium bis(fluorosulfonyl)imide (LiFSI).$^{123}$

In order to have dendrites growing on the Cu foils and reaching the RP-coated separator in a reliable manner, a special testing protocol was developed (Figure 2.25) to induce dendrite growth and demonstrate the response after dendrites touched the RP coating. The half-cell was first cycled at 0.25 mA/cm$^2$ under a low areal capacity of $\sim 0.083 \text{mAh/cm}^2$ for 30 cycles until the coulombic
efficiency (CE) stabilized. This generates a relatively stable solid-electrolyte interface (SEI) layer that is necessary in testing Li metal anodes to minimize the effects of irreversible side reactions.\textsuperscript{36,66} The discharge rate, for Li plating on the Cu foils, was increased progressively to 0.50, 1.0, 2.5, and 5.0 mA/cm\textsuperscript{2}. The entire cycling procedure at a low capacity of \( \sim 0.083 \) mAh/cm\textsuperscript{2} accelerates the aging of the Cu foil-Li cathode that benefits SEI formation and dendrite growth. The charge rate remained at 0.25 mA/cm\textsuperscript{2} to ensure (i) complete removal of Li from the Cu foil cathode after each cycle and (ii) negligible dendrite growth on the Li foil anode. This not only helps to assess the CE of the aging process at low capacity, but simplifies the analysis since it can focus on the electrochemical process in the Cu foil-Li cathode while the Li foil anode was merely a counter-electrode. At this stage, higher charging rates led to lower CE and hence more SEI and dendrite formation, but the low areal capacity ensured that the dendrites did not extend to the RP-coated separator (Figure 2.26a and 2.27). The voltage profile (Figure 2.25c) verifies that the half-cell was functioning normally at low areal capacity regardless of the applied current density because stable discharge and charge plateaus were always present. This will be compared to the electrochemical signals acquired later from high areal capacity cycles.
Figure 2.26 Characterization of the RP-coated separator at different stages. Photographs of the RP-coated separator showing (a) no silver-colored Li metal and (b,c) Li metal on the RP. (d) XRD spectrum of the silver-colored spots in b showing Li metal and Li₂O from reaction with air during transfer. (e-j) SEM images of the silver-colored spots in c. (f) and (g) show the dendritic morphology of Li in c; (h) and (i) show the RP particles around the Li dendrites in c; (j) shows the same aggregate of dendrites in the center of e. (k-m) EDS mapping of P, O and F for j. Scale bars: (a-c) 5 mm; (e) 100 µm; (f,h) 20 µm; (g,i) 2 µm; (j-m) 50 µm.
Figure 2.27 (a) Scanning electron microscopy (SEM) image of the RP-coated separator in Figure 2a (after the last discharge step at ~0.083 mAh/cm²). (b-d) Energy-dispersive X-ray spectroscopy (EDS) mapping of P, O and F for (a). Scale bars: 200 µm.
Figure 2.28 Half-cell tests without the RP coating on the middle separator. Celgard 2500 made from polypropylene was used as the separator in all layers. (a) Configuration of ctrl-1. (b) Voltage profile of ctrl-1 at low areal capacity (~0.083 mAh/cm²). (c) Voltage profile of ctrl-1 at 5 mA/cm² and high areal capacity (~1 mAh/cm²). (d) Configuration of ctrl-2. (e) Voltage profile of ctrl-2 at low areal capacity (~0.083 mAh/cm²). (f) Voltage profile of ctrl-2 at 5 mA/cm² and high areal capacity (~1 mAh/cm²).

The dendrite-detection alert signal was observed when the areal capacity in the discharge step was raised from ~0.083 mAh/cm² to 1 mAh/cm² while maintaining the high discharge rate (5 mA/cm²). The charge rate stayed at 0.25 mA/cm² to ensure complete removal of Li from the Cu foil and much slower dendrite growth on the Li foil. The high areal capacity was intended to increase the thickness of the dendrite layer so that the dendrites would extend to the RP coating on the middle separator. A striking decrease of voltage (|ΔV| > 2 V) was observed within 6 min of discharge (Figure 2.25d) in the first discharge step at high areal capacity (~1 mAh/cm²). In most cases, the voltage drop was
reproducible for ~5 cycles, while in some cases, it lasted for >10 cycles. In some discharge steps, the voltage returned to ~-1 V within 12 min, while in other steps, the voltage did not show the tendency to return to its normal position. The dramatic voltage decrease was readily distinguished from noise; the voltage was at least 2 V lower than normal for the first time the voltage decrease occurred. Two control samples, ctrl-1 and ctrl-2, were tested using the same protocol, and the voltage change was not present in either sample when being discharged at 5 mA/cm² under ~1 mAh/cm² (Figure 2.28).
Figure 2.29 (a-b) SEM images of the silver-colored spots on the RP-coated separator in Figure 2b (after the first discharge step at \( \sim 1 \) mAh/cm\(^2\)). (c-d) EDS mapping of P and O for b. (e-f) SEM images of Li metal deposited on the Cu foil at the same stage as in Figure 2b. Scale bars
The RP-coated separator at different stages of discharge was characterized to confirm the correlation between dendrite formation and the unusual electrochemical behavior. When the half cell was discharged at 5 mA/cm² to ~0.083 mAh/cm², the RP-coated separator remained red and clean with no visible impurities, and only RP particles were observed under scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) mapping (Figure 2.26a and 2.27). Once the areal capacity was enhanced to ~1 mAh/cm², silver-colored spots with metallic appearance were apparent on the RP coated separator (Figure 2.26b). After another 9 cycles, those spots grew larger (Figure 2.26c). The presence of Li metal in Figure 2.26b was confirmed by the X-ray diffraction (XRD) spectrum (Figure 2.26d). Under SEM we observed dendritic structures on the separator in Figure 2.26c (Figure 2.26e-g), while a sponge-like morphology was discovered instead on the separator in Figure 2.26b (Figure S2.29a-d), which might be the early form of Li metal deposition, given that the
same morphology was present on Li metal deposited on Cu foils as well (Figure S2.29e,f). For the aforementioned energy-dispersive X-ray spectroscopy (EDS) results, although Li is not active in EDS, we found large amounts of oxygen (Figure 2l, S2c, and S4d) distributed in the area suspected to be Li metal, likely resulting from Li₂O that formed when the sample was exposed to air during the transfer from an Ar-filled box to the SEM chamber. The surrounding particles were confirmed to be RP (Figure 2.26h,i,k, 2.27b and 2.29c). The control cell ctrl-1 was also opened after discharging at 5 mA/cm² to ~1 mAg/cm² for 10 cycles, and Li dendrite formation was revealed by the appearance and the SEM images (Figure 2.30), meaning that dendrite growth reached the same level without the RP coating, but no significant voltage change was detected. This indicates that the RP coating was indeed responsible for the dramatic voltage change in Figure 2.25d.
Figure 2.31 Periodic dendrite detection at early stage for P-hc. (a) Testing protocol where the times of inducing and detecting dendrite formation at ~1 mAh/cm² and 5 mA/cm² are marked by orange arrows. (b-f) Voltage profiles of the dendrite detection cycles indicated in a.
Figure 2.32 Visualization of dendrite growth while the cell voltage was being monitored. (a) Configuration of the transparent half cell with a RP-coated separator. (b) Voltage and current profiles of transparent half cells with and without the RP-coated separator when discharging the Li metal wrapped by the separator. The numbers 1 to 6 represent different stages of dendrite growth when (c) photographs (top view) of the Li metal surface wrapped by the RP-coated separator were taken. The areas indicated by the yellow arrows show signs of dendrite growth. (d) The enlarged image of the area indicated by the yellow frame in c5 where blue arrows show the path of dendrite growth. Scale bars: (c) 1 mm; (d) 0.2 mm.
Figure 2.33 Photographs (top view) showing dendrite growth at different stages in the transparent half cell without the RP-coated separator. The areas indicated by yellow arrows show signs of dendrite formation. The numbers 1-7 represent different stages of dendrite growth.
The high areal capacity was also applied to the P-hc periodically in the initial 70 cycles, and the voltage profiles showed that the initial 70 cycles at low areal capacity had facilitated dendrite growth such that they extended to the RP coating, presumably by increasing the thickness of the dendrite layer (Figure 2.31). The dendrite growth was visualized under an optical microscope using a homemade transparent cell (Figure 2.32a) and the voltage and the morphology of Li metal were monitored simultaneously to confirm the correlation between voltage change and contact between dendrites and RP.\textsuperscript{124-126} The transparent half cell was built by assembling Li foils, a RP-coated separator and electrolyte solution between two glass slides and sealing with epoxy. Cu foils were used to connect electrodes to the battery test equipment. When Li dendrites contacted the RP-coated separator at 5 mA/cm\textsuperscript{2} and started growing along the RP, a voltage drop to -6 V was observed in the voltage profile (Figure 2.32b). The photographs of dendrite growth are displayed in Figure 2.32c. In the control sample where an ordinary separator was used instead, no voltage change was observed when dendrites had contacted and penetrated the separator (Figure 2.33).
2.4.3. Demonstration of Li Dendrite Detection in Full Cells

Figure 2.34 Full-cell tests with and without the RP layer. (a) Configuration of the full cell with a RP coating (P-fc). (b) Voltage profile of P-fc at 5 mA/cm$^2$ and $\sim 1$ mAh/cm$^2$. The voltage increase indicated by the arrow is the electrochemical response generated when the Li dendrites contact the RP coating. (c) Configuration of ctrl-3 without a RP coating. (d) Voltage profile of ctrl-3 at 5 mA/cm$^2$ and $\sim 1$ mAh/cm$^2$.

To demonstrate that the RP-coated separator would function in full Li metal batteries, it was tested in a full Li-S cell (Figure 2.34a) that contained a sulfurized carbon cathode. Sulfurized carbon was selected as the cathode material because of its high specific capacity and low charging voltage. 36,66 The high
specific capacity results in a relatively low mass loading compared to using conventional cathode materials such as LiCoO$_2$ or LiFePO$_4$. The low charging voltage means that we have a 3 V window for the voltage to increase, with the voltage limit of the battery test equipment being 5 V. If conventional cathode materials are used, the voltage would only be able to increase by 1-1.5 V before reaching the equipment limit.

The testing protocol for full cells was the same as used for half cells, except that the charge rate was tuned while the discharge rate was fixed, in that the Li dendrites we studied were grown from the cathode in half cells but from the anode in full cells. A dramatic voltage increase (|ΔV| > 2 V) was observed at 5 mA/cm$^2$ and ~0.8 mAh/cm$^2$ within 6 min of charging for the P-fc (Figure 2.34b), which is consistent with the voltage decrease in half cells, while the control sample, ctrl-3 (Figure 2.34c), had a normal charge plateau at ~3 V (Figure 2.34d). The fact that the voltage stayed >5 V for more than 6 min in the P-fc revealed another advantage of using an overpotential instead of detecting short circuits with a conductive interlayer. Voltage is monitored in both cases, and voltage fluctuation could happen occasionally. When a voltage change occurs, it is necessary to determine whether it is a valid dendrite-detection signal or merely noise. For the method involving a non-conductive interlayer, we can simply wait for 1 min and see if the voltage remains at that level. But for methods involving conductive interlayers, it is more difficult to further analyze the signal since the charging process cannot be allowed to continue, because if it is indeed a dendrite-
detection signal, there will be a short-circuit current that might cause a runaway within seconds.

Figure 2.35 (a-c) Photographs, (d-f,m,n) SEM images and EDS mapping of (g-i) P and (j-l) O for the RP-coated separators in full cells at different stages. (d,g,j), (e,h,k,m) and (f,i,l,n) correspond to (a), (b) and (c), respectively. Scale bars: (a-c) 5 mm; (d,g,j)
Figure 2.36 (a) Photograph and (b,c) SEM images of the middle separator on the bottom side (facing the Cu foil) from ctrl-3 after the 10th discharge step at ~1 mAh/cm². Scale bars: (a) 5 mm; (b) 20 µm; (c) 2 µm.

Figure 2.37 (a) Configuration of ctrl-4. (b-d) Normalized charge and discharge profiles of ctrl-4, ctrl-3 and P-fc at 0.4C, 0.7C and 1.3 C. The mass loading of sulfurized carbon was ~8 mg/cm².
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**Table 2.2** The specific capacity of the full cells (ctrl-4, ctrl-3 and P-fc) based on the mass of sulfurized carbon at 0.4C, 0.7C and 1.3C.

The voltage change in P-fc could be reproduced for at least 10 cycles, which lasted longer than in half cells probably due to the thicker and more ductile Li foil than the Cu foil-Li that resulted in smaller spacing between the current collector and the RP coating. This could also explain why the dendrites in full cells (Figure 2.35a-c) tended to concentrate in the center where the Li foil was pressed against the separators, rather than randomly distributed across the RP-coated separators as seen in half cells (Figure 2.26a-c). SEM analysis and EDS mapping were conducted at different stages of dendrite growth (Figure 2.35 and Figure 2.36), which displayed the dendritic structures of the Li metal attached to the RP-coated separators in both P-fc and ctrl-3.

Additionally, the charge and discharge profiles of P-fc at different rates (0.4C, 0.7C and 1.3C) were obtained and compared to ctrl-3 and another control sample (ctrl-4) that has only one separator (Figure 2.37). The RP did not lower the specific capacity of the sulfurized carbon (Table 2.2), and the normalized
charge/discharge profiles of all the above cells displayed similar charge/discharge plateaus, suggesting no significant overpotential resulted from the RP layer.

2.4.4. The Mechanism of Li Dendrite Detection

Figure 2.38 Study on electrolyte drying in half cells (P-hc). (a) Testing protocol where the times of electrolyte resistance measurement are marked by orange arrows. (b) Electrolyte resistance of P-hc. (c) Voltage profile at 1 mAh/cm² and 5 mA/cm² (the 71st cycle in a). (d) Voltage profile for the cycle at 1 mAh/cm² and 1 mA/cm² (after 71st cycle in a).
The mechanism was further studied in half cells since the half-cell battery system is much simpler and the impact of the sulfurized carbon cathode can be avoided. Large resistance is often a reason for having an overpotential in batteries. We first analyzed the electrolyte resistance of P-hc (Figure 2.25a), because we might have consumed a significant amount of electrolyte for SEI formation before the voltage drop was present as indicated by the low CE of <80% (Figure 2.25c). We performed electrochemical impedance spectroscopy (EIS) analysis to directly measure the electrolyte resistance,\textsuperscript{127,128} which only increased by ~3 Ω over cycling at low capacity (Figure 2.38a,b). This small increase would only change the voltage by 30 mV under a total current of 10 mA (5 mA/cm\textsuperscript{2} × 2 cm\textsuperscript{2}). In another test, the discharge rate of the half cell was reduced from 5 mA/cm\textsuperscript{2} to 1 mA/cm\textsuperscript{2} after the voltage drop occurred, and a stable discharge plateau was again observed (Figure 2.38c,d), suggesting that the voltage drop was not caused by electrolyte drying or large electrolyte resistance.
Figure 2.39 (a) Voltage profile of P-hc tested at 5 mA/cm² for which EIS analysis was conducted at the start of the test, three times during the test when the voltage dropped to -5 V, and at the end of the test. (b) Voltage profile of ctrl-1 tested at 5 mA/cm² for which EIS analysis was conducted at approximately the same points as in a. (c) Comparison of the charge transfer resistance of P-hc and ctrl-1 collected from the EIS spectra. (d) P-hc tested at different current densities (the unit of current density labelled in the figure is mA/cm²). (e) Mechanism of dendrite detection: schematic illustration of Li dendrite growth at 5 mA/cm² under low and high areal capacities in P-hc. The numbers I to III represent different stages of dendrite growth.

Large charge-transfer resistance is another possible reason for having an overpotential in batteries. We performed EIS analysis on P-hc (Figure 2.25a) and ctrl-1 (Figure 2.26a) before, during, and after the dendrite-detection step (Figure 2.39a,b). Based on the results, the RP coating did not significantly increase the charge transfer despite its connection to the cathode (Cu foil-Li) via the dendrites. With a total current of 10 mA, the extra resistance needed for an overpotential
of >4 V would be at least 400 Ω, which was far beyond the resistance difference between P-hc and ctrl-1 shown in Figure 2.39c.\textsuperscript{127,128} In fact, the small resistance difference was reasonable because the Li metal above the top separator (Figure 2.25a) was in contact with the electrolyte solution and not with the RP coating, where charge transfer could still take place.

If the resistance was not the answer, the high current might be the key to generating the voltage decrease. We tried discharging P-hc to \(-0.5\) mAh/cm\(^2\) with the current density alternating between 5 mA/cm\(^2\) and 0.50/1.0/2.5 mA/cm\(^2\) (Figure 2.39d), and only at 5 mA/cm\(^2\) could we observe the voltage decrease, indicating that the high current density was crucial for dendrite detection, and the minimum current density for sensing dendrites should fall between 2.5 and 5 mA/cm\(^2\) for the typical half-cell configuration. When the current density is switched from 5 mA/cm\(^2\) to 0.50/1.0/2.5 mA/cm\(^2\), there was an instant voltage recovery indicating that the low voltage was only stable at high current density. We also found that the insulating property of the dendrite-detection interlayer was essential. Graphene nanoplatelets (GNPs) were added in the coating with different P/GNP ratios. When the GNP content was low (10 wt% and 25 wt%), the voltage drop was still observed at 5 mA/cm\(^2\) and 1 mAh/cm\(^2\) (Figure 2.40a-f); when the GNP content was 50 wt%, 75 wt% or 100 wt% (pure GNPs), the voltage change was not observed (Figure 2.40g-o).
Figure 2.40 Half-cell tests with RP/GNP- and GNP-coated separators in place of RP-coated separators. (a,d,g,j,m) Voltage profiles. (b,c,e,f,h,i,k,l,n,o) SEM images showing dendrite growth. Scale bars: (b,e,h,k,n) 20 µm; (c,f,i,l,o) 1 µm.
Figure 2.41 Voltage profile of P-he discharged above (a) -1.5 V and (b) -5 V (lower voltage limit of the instrument) at 5 mA/cm² and charged at 0.25 mA/cm².

Another two conditions were investigated where the discharge voltage was limited to above -1.5 V and -5 V (Figure 2.41). The former condition yielded a higher CE than the latter one, suggesting that in the low voltage region, a large fraction of electrons resulted in either irreversible side-products, such as the SEI layer, or non-rechargeable Li such as the silver-colored spots on the RP coating in Figure 2.26b,c.

Based on these results, we propose the following mechanism for the voltage change observed when dendrites contact the RP. When a small areal capacity (~0.083 mAh/cm²) was applied, the dendrites did not grow long enough to reach the RP coating (Figure 2.39e, stage I). The ends of those dendrites were fully exposed to electrolyte solution and were accessible to Li⁺ for the charge transfer that resulted in Li plating during the discharge process in half cells. When the areal capacity was increased to ~1 mAh/cm², the dendrites penetrated the bottom
separator and reached the RP coating (Figure 2.39e, stage II). They developed electrical contact with RP by forming $\text{Li}_3\text{P}$ at the interface.\(^{129}\) Note that RP has a very low electronic conductivity of $\sim 10^{-14}$ S cm\(^{-1}\).\(^{130}\) Meanwhile, the local current density was exceedingly high on the dendrites, especially at high bulk current density.\(^{131}\) As a result, electrons were blocked at the interface between the dendrites and RP, and the reaction between $\text{Li}^+$ and electrons was substantially inhibited. The negative charges thus accumulated on the dendrite tips and lowered the voltage of the electrode, conditions which resemble a double-layer capacitance around the RP coating. Under these conditions, the reaction between $\text{Li}^+$ and electrons became the rate-determining step of the entire discharge process due to the limited access of $\text{Li}^+$ in the electrolyte solution to the dendrite tips and the electrons that had to inevitably flow through them. As dendrites continued to grow, albeit slower, they bypassed the RP particles or extended their surface underneath the RP particles to become exposed to the electrolyte again (Figure 2.39e, stage III). This explains why the voltage eventually returned to its near-original level (Figure 2.25d). As the dendrite growth repeated in additional cycles, Li was irreversibly transferred onto the RP interlayer in each discharge step. Those Li dendrites created additional electron pathways for Li plating through the RP interlayer; the RP was no longer an effective electron and $\text{Li}^+$ barrier after several cycles, and the voltage decrease eventually disappeared. It may therefore be important to stop charging and halt cell use at the first or second indication of significant voltage change ($|\Delta V| > 2$ V).
Figure 2.42 (a) Configuration and (b) voltage profile at 5 mA/cm² and 1 mAh/cm² of P-fc-2 (full cell) assembled using thinner separators (Targray SW312D, ~12 µm thick) with no separator present between the RP-coated separator and the cathode.

In practice, when dendrites formed and reached the RP-coated separator layer in full cells, the charging voltage reached the upper limit much sooner than expected, triggering another detection protocol to rule out the possibility of random voltage fluctuation. For instance, the charge mode will be switched from voltage-control constant-current (e.g. 5 mA/cm²) charging to voltage-control charging. If the voltage remains at the upper limit with a current density no higher than the constant one used just before it (5 mA/cm²) for a significant amount of time such as 1 min, it is likely that severe dendrite formation is present. Another option is to let the cell rest for a certain amount of time to have the accumulated electrons dissipated, so that the voltage might drop back to the normal range and rise to the upper limit rapidly again, which would confirm the presence of dendrite formation. When high charge rate (5 mA/cm²) is not always
applicable, it could be applied periodically (e.g. every 15 cycles) in the charge steps to reveal possible dendrite formation before it is too late. It is upon such algorithms that the battery management system can be programmed. Finally, some other fabrication designs were explored. For example, vacuum filtration was used in place of the slurry method to coat RP on the non-electrode side of one of the separators. The two separators were each only 12-µm-thick (Targray SW312D), thereby reducing the thickness of the entire separator/RP/separat or stack to ~45 µm. The configuration of the cell is shown in Figure 2.42a. The dendrite detection signals were still observed (Figure 2.42b) using the same testing protocol for P-fc in Figure 2.34b. Hence there are design modifications that can make the RP-layer dendrite detection system well-within present fabrication constraints for mass production, thereby ensuring safe use of Li metal rechargeable batteries.

In conclusion, we have developed a RP-coated separator for Li dendrite detection in an ordinary two-electrode system. When Li dendrites contact the RP interlayer while Li plating proceeds at 5 mA/cm², a significant voltage change (decrease in half cells and increase in full cells) of >2 V is observed. The correlation between the dendrite-detection signal and the contact between Li dendrites and RP is confirmed by optical images, SEM images, and visualization of dendrite growth in the presence of RP-coated separators. The dendrite-detection signal (voltage change) is caused by electrons that accumulate at the interface between the Li dendrites and RP when Li metal is regenerated. The RP insulating property and its capacity to react with Li are essential in yielding the
dendrite-detection signal. The only component for the dendrite alert system is a RP interlayer, and the only parameter that needs to be monitored is the cell voltage in the charging step. We will explore other methods such as vacuum filtration to achieve better uniformity of the RP coating. This facile, scalable method enables in situ detection of Li dendrites with no additional electrodes required.

2.4.5. Experimental Procedures

Preparation of RP-, GNP- and RP/GNP-coated separators. RP (32 mg, MilliporeSigma), GNP (32 mg, xGnP® C-300 from XG Sciences), or a mixture of RP and GNP (32 mg in total with ratios specified in Figure 2.40) was added in a mortar, and PVDF (3.5 mg, 10% of total mass, Alfa Aesar) was added as a binder. NMP (0.5-0.8 mL, MilliporeSigma) was then added, and the mixture was ground for 5 min to form a slurry which was then coated on 8 Celgard 2500 polypropylene separators (20 µm thick, ~2 cm² each) using a spatula. The separators were dried under vacuum (~1 Torr) at 60 °C overnight. The mass loading of RP, GNP or RP/GNP was ~2 mg/cm².

Half-cell tests. Cu foils (~2 cm²) were used as the current collector in the cathode. Li foils (~2 cm²) were used as the counter electrode (anode). The electrolyte was 1 M LiPF₆ in ethylene carbonate/diethylene carbonate (EC/DEC, v/v = 1/1). For P-hc, two Celgard 2500 separators were used with one layer of RP, GNP or RP/GNP-coated separators in between, with the coating facing the Cu foil.
Half cells were assembled using CR2032 coin cells. For ctrl-1, three Celgard 2500 separators were used. For ctrl-2, one Celgard 2500 separator was used.

**Full-cell tests.** The synthesis of sulfurized carbon and the preparation of sulfurized carbon cathodes were described previously. Carbon-coated Al foils were used as the current collector for sulfurized carbon cathodes, and 1 M LiPF$_6$ was used as the electrolyte. The mass loading of sulfurized carbon was ~8 mg/cm$^2$. For P-fc, two Celgard 2500 separators were used with one layer of RP-coated Celgard 2500 separator in between, and the RP coating was facing the Li foil. For ctrl-3, three Celgard 2500 separators were used. For ctrl-4, one Celgard 2500 separator was used. For P-hc-2, one Targray SW312D separator and one RP-coated Targray SW312D separator were used.

**Transparent half cells for visualization of dendrite growth.** The cell was constructed inside a glove box by attaching Li metal foil (300 µm) to glass slides (75 × 25 × 1 mm$^3$, Corning) according to Figure 2.32a. Epoxy (Extra fast setting, Hardman) was used to adhere the Li metal surface to the glass slides and prevent leakage. Copper (Alfa Aesar, 25 µm) ribbons were used to electrically connect the Li metal electrodes to the battery testing station. An adapted resistance pulse spot welder (Sunkko 788H) was used to connect Li metal and Cu foil. Epoxy was also used to cover Li metal and prevent oxidation in air. The separator was folded over the Li metal foil and fixed with epoxy. The cell was filled with electrolyte (~200 µL) and sealed with epoxy. The cell was put to rest for 1 h inside the glove box before the video test. The video was recorded using a portable microscope (Specwell 10 × 30) and a smartphone camera. The pictures
in Figure 2.32c,d and 2.33 were obtained from the videos recorded. The area and current density were calculated based on the exposed Li metal area filled with electrolyte. The working electrode was initially plated with Li at 1 mA/cm² for 10 min then the current density was increased to 5 mA/cm².

**Characterization.** EIS analysis was performed on a CHI 608D workstation (CH Instrument). XRD spectra were obtained using Rigaku D/Max Ultima II X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å), and Kapton tapes (Reterm, 20 mm wide) were used to seal the sample. SEM and EDS were performed on a JEOL 6500 scanning electron microscope.

**2.4.6. Contributions**

Tuo Wang designed all experiments for half-cell tests, full-cell tests and investigation of the mechanism. Rodrigo V. Salvatierra designed the transparent half cell and performed the relevant experiments. Ruquan Ye instructed on the electrochemistry associated with the mechanism of dendrite detection.
Chapter 3

Three-Dimensional Graphene Foams as Conductive Fillers for Epoxy Resin

This Chapter is copied from reference 132.

Conductive epoxy composites are of great interest due to their applications in electronics. They are usually made by mixing powdered conductive fillers with epoxy. But the conductivity of the composite is limited by the low filler content because increasing filler content causes processing difficulties and reduces the mechanical properties of the epoxy host. We describe here the use of ultrastiff graphene foams (uGFs) as three-dimensional (3D) continuous conductive fillers for epoxy resins. The powder metallurgy method was used to produce the dense uGFs that resulted in a very high filler content of 32 wt% in the uGF-epoxy composite, while the density of epoxy was only increased by 0.09 g/cm³. The composite had an electrical conductivity of $41.0 \pm 6.3$ S/cm, which is higher than all the polymer-based composites with non-conductive polymer matrices and
comparable to the conductive polymer matrices reported to date. The compressive modulus of the composite showed an improvement of 1732% compared to pure epoxy. We have demonstrated that the 3D uGF filler substantially improves the conductivity and reinforces the polymer matrix with a high filler content but retaining a density similar to that of the polymer alone.

3.1. Introduction

Epoxy resin is a thermosetting polymer with exceptional processability, and is commonly used in coatings, adhesives, electronics, industrial tooling, and structural composites because of its low cost, excellent mechanical properties, and chemical resistance.\textsuperscript{133} Due to its low density compared to inorganic conductors, although epoxy is intrinsically an insulator it has also been explored for applications where electrical conductivity is needed, especially electromagnetic interference shielding.\textsuperscript{134-139} Conductive fillers such as metals and carbon materials are often added to epoxy to produce a composite material that is both electrically conductive and mechanically robust.\textsuperscript{139-142} Normally, the increase in conductivity per wt% or vol% of fillers would be used to evaluate how efficient the fillers are in terms of improving the conductivity of epoxy, assuming that the filler content is easily adjusted. But in many cases, the total conductivity is limited by the low filler content (usually <10 wt%) because high mass loading of conductive fillers affects two of the composite properties: (i) increased viscosity of the raw mixture that results in processing difficulties and (ii) reduced mechanical strength due to insufficient dispersibility and poor host-guest
interfacial interactions.\textsuperscript{143-147} For some graphene species, the optimal content was reported to be only 0.1-0.5 wt\%.\textsuperscript{148-154}

Three-dimensional (3D) continuous conductive fillers were developed in recent years to achieve higher electrical conductivity while maintaining high mechanical performance,\textsuperscript{155-158} and they are becoming efficient substitutes for traditional powdered fillers. Owing to the porous, interconnected scaffold, the 3D filler does not need to be dispersed and is completely separate from the epoxy in the raw mixture, hence keeping the viscosity of the epoxy unchanged. Moreover, the mechanical properties of the epoxy may not be impaired if the 3D structure is sufficiently strong. 3D carbon fillers reported to date include graphene aerogels from hydrothermal reactions, carbon nanotube (CNT) sponges, graphene foams (GFs) from chemical vapor deposition (CVD) growth, and 3D graphene skeletons from freeze-drying and thermal reduction.\textsuperscript{137,138,156-158} Despite the highly porous structure, those 3D fillers displayed limited enhancement of the mechanical and electrical properties of epoxy because of the low bulk density resulting from low deposition thickness, large volume expansion, or high amounts of template compounds added.

We introduce here the use of an ultrastiff GF (uGF) as a 3D continuous conductive filler for making epoxy-matrix composites. The uGF was synthesized from polyacrylonitrile (PAN) that formed a highly graphitized structure at high temperatures. We used a powder metallurgy method where cold-pressing of the precursor mixture generated much higher bulk density than that of conventional GFs and afforded superior stiffness and conductivity with almost no metal
content after processing.\textsuperscript{159,160} The open pathways throughout the scaffold allowed for infiltration of epoxy, producing a uGF-epoxy composite that demonstrated significant improvement in both mechanical strength and electrical conductivity.

3.2. Pristine Graphene Foams for Epoxy-Matrix Composites

3.2.1. Synthesis and Characterization of Pristine Graphene Foams

![Diagram of graphene foam synthesis and characterization process]

Figure 3.1 Schematic illustration of the preparation of uGFs and uGF-epoxy composites.
Figure 3.2 Characterization of the uGF. (a) Photographs of the uGF disk. (b) TGA profile (in air); (c) XRD spectrum; (d) and Raman spectrum of the uGF.
The preparation scheme for uGFs and uGF-epoxy composites is shown in Figure 3.1. High-crystallinity uGFs were obtained by using PAN as the precursor for graphene growth because PAN is known to be well graphitized at high temperature.\(^{161-163}\) The mixture of PAN and Ni was cold-pressed at \(~740\) MPa to produce coupons with a high solid carbon source density. The coupons were then annealed under \(\text{Ar}/\text{H}_2\) at \(1000\) °C for graphene growth and the Ni was removed from the coupons by soaking them in 1 M aqueous \(\text{FeCl}_3\) solution. The resulting uGF monolith was black on the outside as shown in Figure 3.2a. The removal of Ni particles was confirmed by the TGA profile (air atmosphere) that showed only a residue of 0.12 wt% iron oxide (from the etchant) at 900 °C (Figure 3.2b). The
absence of nickel was described previously.\textsuperscript{159,160} The major weight loss in the TGA profile is between 500 °C and 750 °C, suggesting that most of the carbon was graphitized rather than remaining amorphous. The high quality of graphene was also verified by the X-ray diffraction (XRD) and Raman spectra (Figure 3.2c,d) where the graphite peak at \( \sim 26^\circ \), low ratio of D band to G band (0.45), and noticeable 2D peak were present. Also, the multi-layered graphene structure was observed in TEM images (Figure 3.3. As a result of the high density of the solid carbon source generated by cold-pressing, the uGF has a bulk density of 0.29 g/cm\(^3\), which is at least 4 times higher than typical graphene aerogels, GFs synthesized from gaseous carbon sources, or CNT sponges.\textsuperscript{138,155,157,158}
3.2.2. Electrical and Mechanical Properties of Pristine Graphene Foams

Figure 3.4 SEM images of the uGF. (a,b) Horizontal cross-section; (c-d) Vertical cross-section.
The die used in the cold-pressing step produced cylindrical coupons that were pressed along the axis. Consequently, the uGFs had anisotropic morphology with smaller pore size and denser packing of particles in the vertical cross-section than in the horizontal cross-section (Figure 3.4). This leads to anisotropic electrical conductivity as shown in Figure 3.5. Pt electrodes were deposited on the top surface of uGF and an Al foil was used as the bottom electrode (Figure 3.5).
3.5a,b). To ensure good contact between the foam and the bottom electrode, a thin layer of Ag paste was applied to the carbon. The vertical conductivity (25.4 ± 2.1 S/cm) was 2 orders of magnitude higher than the lateral conductivity (0.20 ± 0.02 S/cm).

3.2.3. Structure and Properties of Pristine Graphene Foam-Epoxy Composites

![Experimental setup for infiltration of epoxy into the uGF samples.](image)

Figure 3.6 Experimental setup for infiltration of epoxy into the uGF samples.
Figure 3.7 Characterization of the uGF-epoxy composite. (a) Photographs. (b,c) SEM images (horizontal cross-section). (d,e) I-V curves in the (d) vertical direction and (e) lateral direction.

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Table 3.1 Bulk density and porosity of uGFs and uGF-epoxy composites.
The uGF-epoxy composite was prepared by vacuum-assisted resin infiltration (Figure 3.1) and the apparatus is shown in Figure 3.6. Since the pore size of the uGF was only 3-5 µm, a low molecular-weight epoxy (D.E.R. 736) with low viscosity (30-60 mPa·s) was used for making uGF-epoxy to ensure successful infiltration of the uGF monolith. Figure 3.7a shows the photographs of the pure epoxy and the uGF-epoxy. The SEM images of uGF-epoxy (Figure 3.7b) display small graphene platelets and shells that build up the 3D graphene skeleton and constitute the pores. There are sections that have a smooth appearance similar to that of pure epoxy (Figure 3.8). The 3D filler did not add significant weight to the epoxy: the bulk density of uGF-epoxy (1.17 g/cm³) was very close to that of the pure epoxy (1.13 g/cm³), though a high filler content of 25 wt% was achieved, according to Table 3.1.

The conductivity of uGF-epoxy was measured in the same way as depicted in Figure 3.5a,b and the results are shown in Figure 3.7d,e. The vertical
conductivity was 14.4 ± 3.2 S/cm, which was slightly lower than that of uGF and two orders magnitude higher than the lateral conductivity of uGF-epoxy (0.05 ± 0.01 S/cm).

Figure 3.9 Mechanical performance of different uGF-epoxy composites. (a) Compressive modulus. (b) Compressive stress-strain curves with the segments I, II and III corresponding to the phases in section d of this figure. (c) Compressive stress at different strains. (d) Schematic illustration of the deformation behavior of individual cells in uGF-epoxy composites; “original” and the numbers I - III represent the stages of deformation of the cell. The dark edge represents the graphene and the yellow part represents the epoxy. (e,f) SEM images of uGF-epoxy (vertical cross-section) at 0 and 70% strain. (g,h) Nanoindentation tests: force-displacement curves and indentation moduli (using a spherico-conical diamond indenter tip, R = 200 µm, α = 90°). (i) Improved compressive modulus of uGF-epoxy upon oxidation and N-doping of uGF. (j) XPS N1s spectra of oxidized uGF (ouGF) and
N-doped uGF (nuGF). The black circles are the original plots; The blue and yellow curves correspond to pyridinic N and pyrrolic N, respectively.

Apart from high electrical conductivity, the uGF-epoxy also displayed much higher mechanical performance than pure epoxy (Figure 3.9). The uGF-epoxy composite had a compressive modulus of $165 \pm 7.2$ MPa, which was $\sim700\%$ higher than that of pure epoxy ($18.4 \pm 1.5$ MPa), whereas the compressive modulus of the control sample, graphene powder-epoxy (GP-epoxy, $23.5 \pm 1.6$ MPa), was only $28\%$ higher (Figure 3.9a). This indicates that 3D monolithic fillers are substantially more efficient than powdered fillers in reinforcing the polymer matrix. It was attributed to the high compressive strength of the 3D uGF ($32.9 \pm 1.5$ MPa) resulting from the high density (0.29 g/cm$^3$) that was rarely achieved by conventional 3D GFs, graphene aerogels or powdered materials. The typical compressive stress-strain curves of different samples are shown in Figure 3.9b, and the stress at certain strains (10%, 30%, and 60%) are shown in Figure 3.9c as an indicator of compressive strength because the stress kept increasing in the densification region and it was hard to determine the strains at which the materials failed.$^{164,165}$
Figure 3.10 Graphene powder (GP)-epoxy samples (control group). (a) Photograph of GP-epoxy composite with a graphene content of 25 wt%. (b) Stress-strain curves of GP-epoxy composites with graphene content from 0.1 wt% to 12.5 wt%. (c) Compressive moduli of GP-epoxy compared to those of pure epoxy and uGF-epoxy.

The control sample, GP-epoxy, was made by grinding the same uGFs into powder and mixing them with epoxy, such that the only difference between the fillers uGF and GP is that the former one had a 3D scaffold while the latter one did not. For the control sample, different filler content from 0.1 wt% to 25 wt% were studied and detailed mechanical performance is shown in Figure 3.10. When we used the same filler content of 25 wt% as it was in the uGF-epoxy composite, the viscosity of the raw mixture was very high and the coupons did not remain intact after being cured. For other filler contents at which a block of
composite could be made, the compressive moduli were all very close to that of pure epoxy, and 5 wt% was found to be the optimal value, which was selected as the GP-epoxy in Figure 3.9a-c.

The compressive stress-strain curve of the uGF-epoxy composite (Figure 3.9b) can be divided into three regions and explained by the deformation behavior of the cells illustrated in Figure 3.9d. The “original” in Figure 3.9d represents the original shape of the cells at 0 strain. From 0 to ~8% strain, it is the elastic region where the material deforms elastically and the slope refers to the compressive modulus.\textsuperscript{166,167} In the microstructure of the composite, the cell walls bend (stage I of Figure 3.9d) in response to the compressive loading and the shape of cells is able to recover once the load is removed.\textsuperscript{166,167} The second region is from ~8% to ~37% strain where the material behaves plastically and does not return to its original shape once the load is removed, because the cell walls have buckled or even fractured (stage II of Figure 3.9d).\textsuperscript{166,167} In the third region where strain is >37%, the cell walls become densified (stage III of Figure 3.9d) and the stress increases much faster.\textsuperscript{166,167} This is confirmed by the morphology change observed in the SEM images of uGF-epoxy at 0 strain (Figure 3.9e) and 70% strain (Figure 3.9f).
Figure 3.11 Penetration depth-time curve (red) and trapezoidal force-time curve (blue) for (a) epoxy and (b) uGF-epoxy.

Nanoindentation was performed to investigate if the uGF also enhanced the mechanical properties of the epoxy at the microscale. In compliance with the bulk compressive tests, the uGF-epoxy composite showed notably enhanced indentation modulus and penetration resistance compared to the pure epoxy (Figure 3.9g). Figure 3.9h illustrates the typical load-displacement curves acquired from the indentations performed with a sphero-conical tip. As indicated by the lack of hysteresis coupled with the lack of permanent deformation, the pure epoxy exhibited almost perfectly elastic behavior. On the other hand, the
uGF-epoxy exhibited elastoplastic behavior, as verified by the significant plastic deformation during the indentation process. The average maximum depth for the composite was $1.6 \pm 0.2 \ \mu m$, 42% lower than that for the pure epoxy ($2.7 \pm 0.6 \ \mu m$). A typical penetration depth-time curve and trapezoidal force-time curve for both epoxy and p-GF-epoxy is shown in Figure 3.11. The complete reversal of the penetration depth upon unloading supports the perfectly elastic behavior of the control epoxy sample (Figure 3.11a), while the sudden change in slope at $\sim 12 \ s$ during the loading, coupled with the decreased penetration depth at the peak load verifies the enhanced micro-scale stiffness of uGF-epoxy (Figure 3.11b). The decrease in penetration depth achieved at the peak load shows the lower ductility of the graphene-based composite. Alternatively, the $\sim 500\%$ increase in the average elastic modulus confirms that the uGF significantly enhances the stiffness of epoxy at the microscale.

Figure 3.12 Nanoindentation test of uGF-epoxy composite using a Berkovich indenter. (a) Optical image where three spots tested on the surface of uGF-epoxy. Spot 1: low uGF content (mostly epoxy). Spot 2: medium uGF content (interface). Spot 3: high uGF content (mostly graphene). (b) Indentation modulus and surface hardness collected at the three spots shown in (a).
In addition, there might be a spatial variation in nanomechanical properties on the surface of the composite as indicated in Figure 3.12. At the extremely low applied force of 3 μN, the reduced elastic modulus and hardness varied significantly at those distinct points. As we switched from the bright region (assumed to be epoxy-rich) to the dark region (assumed to be uGF-rich), an 88% increase in elastic modulus and a 270% increase in hardness were observed. This implies that there might be a spatial variation in nanomechanical properties on the surface of the composite. Multiple indentations on different sites on the surface may further support this variation but it is outside the scope of this work.

3.3. Oxidized and Nitrogen-Doped Graphene Foams for Epoxy-Matrix Composites

![Figure 3.13 XPS elemental results of uGF-epoxy. (a) O1s spectrum. (b) N1s spectrum. The blue and yellow curves in section b correspond to pyridinic N and pyrrolic N, respectively.](image)
<table>
<thead>
<tr>
<th>Duration</th>
<th>O$_2$-Ar plasma treatment</th>
<th>UV-ozone treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C (at%)</td>
<td>N (at%)</td>
</tr>
<tr>
<td>45 min</td>
<td>93.0</td>
<td>2.1</td>
</tr>
<tr>
<td>1.5 h</td>
<td>92.5</td>
<td>2.2</td>
</tr>
<tr>
<td>3 h</td>
<td>93.3</td>
<td>2.5</td>
</tr>
<tr>
<td>6 h</td>
<td>91.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3.2 XPS elemental analysis of ouGF treated by O$_2$-Ar plasma and UV-ozone for different amounts of time.

<table>
<thead>
<tr>
<th></th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>O (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nuGF 550 °C</td>
<td>92.6</td>
<td>3.3</td>
<td>4.1</td>
</tr>
<tr>
<td>nuGF 650 °C</td>
<td>91.4</td>
<td>5.5</td>
<td>3.2</td>
</tr>
<tr>
<td>nuGF 750 °C</td>
<td>92.5</td>
<td>3.3</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 3.3 XPS elemental analysis of nuGF annealed under NH$_3$ after 6 h UV-ozone treatment.
Figure 3.14 Stress-strain curves of (a) ouGF-epoxy and (b) nuGF-epoxy.

The surface of the graphene framework is relatively nonpolar, according to the XPS result. The uGF only has 3.7 at% oxygen and 1.0 at% nitrogen (see Figure 3.13 for XPS O1s and N1s spectra). In order to have stronger interfacial interactions between uGF and epoxy and correspondingly higher mechanical performance of the composite, the uGFs were oxidized and N-doped before being infiltrated with epoxy (Figure 3.1). The corresponding composites, oxidized uGF-epoxy (ouGF-epoxy) and N-doped uGF-epoxy (nuGF-epoxy), showed increase in compressive modulus by 31 MPa (19%) and 42 MPa (25%) compared to uGF-epoxy, respectively (Figure 3.9i). The ouGF was prepared by treating the uGF in a UV-ozone reactor for 6 h and the oxygen content increased to 11.0 at% (Table 3.1). The high oxygen content in ouGF originates from the polar oxygen-containing groups on the surface of graphene, which was responsible for the improved mechanical performance. The nuGF was prepared by annealing the ouGF at 650 °C in ammonia (90 sccm) for 1 h, and the nitrogen content increased
to 5.5 at% while the oxygen content dropped to 3.2 at% (Table 3.2 and Table 3.3). XPS N1s spectra (Figure 3.9j) suggested that the N-doping process decreased the proportion of pyrrolic N (~400.6 eV) from 63% to 43% while increasing the proportion of pyridinic N (~398.6 eV) from 37% to 57%. The pyridinic N was nucleophilic and capable of reacting with epoxide groups such that the graphene would be covalently bonded to the epoxy. The stress-strain curves of ouGF and nuGF can be found in Figure 3.14.

3.4. Rebar Graphene Foams for Epoxy-Matrix Composites

![Figure 3.15 Characterization of the ruGF. (a,b) SEM images; (c) Stress-strain curve; (d) Compressive stress at different strains. (e) I-V curve in the vertical direction.](image)

Figure 3.15 Characterization of the ruGF. (a,b) SEM images; (c) Stress-strain curve; (d) Compressive stress at different strains. (e) I-V curve in the vertical direction.
The mechanical performance of the composite became even higher when using multi-walled carbon nanotube (MWCNT)-reinforced GFs, namely rebar uGFs (ruGFs), as the filler (Figure 3.1). The addition of carbon nanotubes was not to change the surface chemistry of the uGF, but to strengthen the uGF via covalent bonding between graphene sheets and CNTs.\textsuperscript{160,176} It also increased the density of the foam while slightly reducing the porosity (Table 3.1). The ruGF also had anisotropic structures as shown in the SEM images (Figure 3.15a,b). In the stress-strain curves, ruGF showed a noticeable increase of stress in the elastic region compared to uGF under the same strain (Figure 3.15c,d), and the compressive modulus increased from 32.9 ± 1.5 MPa to 50.2 ± 2.2 MPa. Moreover, the electrical conductivity of ruGFs reached 54.9 ± 9.7 S/cm (Figure 3.15e), which is 116\% higher than that of uGFs.
Figure 3.16 Characterization of ruGF-epoxy composite. (a) Stress-strain curves; (b) compressive stress at different strains. (c) I-V curve in the vertical direction. (d) Summary of compressive moduli. (e) Summary of electrical conductivities. (f) Improvement in compressive modulus compared to the best results reported in the literature.\cite{165,177-183} (h) Electrical conductivity compared to the best results reported in the literature.\cite{138,151,156-158,184,185}
Figure 3.17 Improved thermal conductivity to uGF and ruGF composites.

After the infiltration of epoxy, the ruGF-epoxy yielded a compressive modulus of $337 \pm 9.2$ MPa (104% higher than that of uGF-epoxy) and higher compressive stress than the uGF-epoxy within the entire range of strains (Figure 3.16a,b). It also afforded higher vertical electrical conductivity ($41.0 \pm 6.3$ S/cm) than the uGF-epoxy (Figure 3.16c). The compressive moduli and the electrical conductivities of all of the samples are summarized in Figure 3.16d,e. Compared to the pure epoxy, the ruGF-epoxy showed an improvement of 1732% in compressive modulus, which was higher than all the polymer-based composites (not including thin composite films) reported in the literature (Figure 3.16f). The electrical conductivity of ruGF was superior to all the polymer-based composites containing non-conductive polymer matrices (epoxy,
polydimethylsiloxane, polystyrene and polyethylene) reported so far (not including thin composite films), and was even comparable to polymer composites with conductive polymer matrixes such as poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), as shown in Figure 3.16. Additionally, the ruGF had a thermal conductivity of 0.92 ± 0.04 W·m⁻¹·K⁻¹ (Figure 3.17) that was 10.5 times higher than that of pure epoxy (0.08 ± 0.01 W·m⁻¹·K⁻¹).

In conclusion, uGF and ruGF were prepared using PAN as a solid carbon source through the powder metallurgy method. The uGFs displayed high crystallinity and anisotropic electrical conductivity associated with anisotropic morphology. The uGF and ruGF yielded high compressive modulus of 32.9 MPa and 50.2 MPa, respectively, with porosities of 87% and 82%, respectively. Upon infiltration of epoxy under vacuum, the resulting ruGF-epoxy composites showed an electrical conductivity of 41.0 ± 6.3 S/cm that is among the highest of all the 3D carbon-polymer composites with nonconductive polymer matrixes reported so far. The high filler content of 32 wt% has a large impact on the high conductivity, and more importantly, the compressive modulus was not impaired, but showed a 1732% improvement compared to pure epoxy. Further oxidation and N-doping of the uGFs presumably produced stronger interfacial interactions between uGF and epoxy and thereby enhanced the mechanical strength of the composites. These results have shown the robust 3D GF structure to be a remarkable filler material for epoxy that improves electrical conductivity and reinforces the polymer matrix at the same time due to the exceedingly high mass...
loading, which can rarely be achieved using conventional powdered filler materials.

3.5. Experimental Procedures

Preparation of uGF and ruGF.\textsuperscript{159,160} PAN (0.4 g) was dissolved in dimethylformamide (DMF, 20 mL) at \(\sim80\) °C on a hot plate and Ni powder (2.2-3 \(\mu\)m, Alfa Aesar, 3 g) was added after the solution was cooled to room temperature. DMF was removed by rotary evaporation at \(\sim90\) °C and the mixture was ground into powder by hand using a ceramic mortar and pestle. The powder were dried at 60 °C in vacuum (\(\sim1\) Torr) overnight and then pressed into coupons at \(\sim740\) MPa using a 13 mm cylindrical die (Tianjin Keqi High and New Technology Corporation, China) on a Carver Hydraulic Press (Model #3912). The pressure was held for 7 min when making the coupons. To make a 3 mm-thick foam, \(\sim1.8\) g of the powder was needed. The coupons were then placed in a CVD furnace under Ar/H\(_2\) atmosphere (Ar flow: 500 sccm; H\(_2\) flow: 200 sccm). The temperature was increased to 1000 °C at a heating rate of 10 °C/min and stayed at 1000 °C for 30 min for graphene growth. After the coupons were cooled to room temperature, they were soaked in 1 M \(\text{aq. FeCl}_3\) solutions for 3 d to etch away Ni. The resulting uGFs were transferred to DI water and soaked for 1 d to wash away the \(\text{FeCl}_3\). They were dried by a critical point drier. For the preparation of the ruGF, multi-walled carbon nanotubes (MWCNTs, NTL-M-grade, 0.05 g) were sonicated in DMF (20 mL) using a tip-sonicator (Misonix Sonicator 3000) at \(\sim100\) W for 20 min. The dispersion was added to the
PAN/DMF solution before adding Ni powder and the subsequent procedure was the same as above.

**Preparation of ouGF.** The uGF was treated in a UV-ozone cleaner (Boekel Model 135500) for 6 h. Other ouGF samples listed in Table 3.2 were treated for different amounts of time in either the UV-ozone cleaner or an O₂/Ar plasma cleaner (Fischione, Model 2010 Plasma Cleaner).

**Preparation of nuGF.** The ouGF that was treated in the UV-ozone cleaner for 6 h was placed in the CVD furnace under NH₃ atmosphere (NH₃ flow: 90 sccm). The temperature was increased to 650 °C at a heating rate of 10 °C/min and stayed at 650 °C for 1 h.

**Preparation of uGF-epoxy, ouGF-epoxy, nuGF-epoxy, and ruGF-epoxy.** The corresponding foam was placed in a Schlenk tube or a three-neck round-bottom flask connected to a vacuum pump. The system was evacuated (~1 Torr) for 30 min, after which the mixture of D.E.R. 736 (6 g, epoxy) and 1,5-diamino-2-methylpentane (0.9 g, curing agent) was added from a separatory funnel connected to the top of the tube/flask. When the entire foam was immersed in the epoxy, the tube/flask was exposed to the air and heated at 70 °C for 1 h to cure the epoxy. The composites were removed by removing the bottom of the tube or flask and were cut by a fiber laser using the Universal XLS10MWH platform to remove the extra epoxy and sanded by hand with sandpaper (grit size: 100, 400, and 1500) to obtain smooth surfaces and the desired thickness.
**Preparation of GP-epoxy.** The uGF was ground into powder using a mortar and pestle and mixed with D.E.R. 736 (6 g, epoxy) and 1,5-diamino-2-methylpentane (0.9 g, curing agent) in a 20 mL glass vial. Different amounts of powder was used depending on the filler content. The mixture was heated at 70 °C for 1 h to cure the epoxy. The removal from the vial, subsequent cutting and sanding processes were the same as for the uGF-epoxy.

**Characterization:** TGA profiles were acquired with a Q-600 Simultaneous TGA/DSC (TA Instruments) under 100 mL/min Ar flow from room temperature to 1000 °C at a heating rate of 10 °C/min. XRD spectra were obtained from a Rigaku D/Max Ultima II X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Raman spectroscopy was performed on a Renishaw Raman microscope. SEM images were taken using a FEI Quanta 400 field-emission scanning electron microscope. TEM was performed on a JEOL 2100 field emission gun transmission electron microscope. XPS was conducted using a PHI Quantera scanning X-ray microprobe.

**Electrical conductivity measurement.** Electrical conductivity was measured using an Agilent B1500A semiconductor parameter analyzer with a customized DC probe station by a two-probe configuration measurement method under ambient atmosphere and room temperature. Platinum contact pads with a size of 250 µm × 250 µm were deposited onto a 2 mm-thick sample using shadow mask evaporation, and the spacing between the contacts was 120 µm.

**Compressive tests.** Stress-strain curves were obtained through uniaxial compressive tests at room temperature with a standard tensile testing machine.
Samples (~3 mm thick) were held between two crossheads checked to avoid misalignment then compressed at a constant rate of 2 mm·s⁻¹, and 5 samples for each different type were tested in order to ensure consistency of the data.

**Nanoindentation tests.** Nanoindentation was performed using two distinct instruments, the Bioindentation Tester from Anton Paar equipped with a spher-conical diamond indenter tip (R = 200 µm/α = 90°) and the Hysitron TI 980 Triboindenter equipped with a Berkovich tip that had a pyramidal geometry. For the calculation of indentation modulus from using the spher-conical tip, 9 different indentations were performed for each sample with a constant applied force of 500 µN. We used a trapezoidal loading profile where the loading/unloading rate was fixed at 1 mN/min and the hold time at the peak load was maintained at 5 s. For the indentations using the Berkovich indenter tip, the applied force was 3 µN. Elastic modulus and hardness were calculated using the Oliver Pharr approach, which employs the following fundamental equations:

\[ E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A_p}} \]

**Equation 3.1 Calculation of the reduced elastic modulus.**

\[ \frac{1}{E_r} = \frac{1 - v^2}{E} + \frac{1 - v_i^2}{E_i} \]

**Equation 3.2 Calculation of the elastic modulus of the sample.**
\[ H = \frac{P}{A_p} \]

**Equation 3.3 Calculation of the hardness of the sample.**

where \( E_r \) is the reduced elastic modulus, \( S \) is the stiffness of the initial part of the unloading curve, \( A_p \) is the projected area of contact, \( E \) and \( v \) are elastic modulus and Poisson’s ratio of the sample, \( E_i \) and \( v_i \) are elastic modulus and Poisson’s ratio of the indenter, \( H \) is the hardness, and \( P \) is the applied load.

**3.6. Contributions**

Tuo Wang suggested the use of polyacrylonitrile as the carbon source to make graphene foams to achieve higher mechanical property and electrical property, prepared and characterized all GFs, completed infiltration of epoxy, and characterized all GF-epoxy composites. Xiao Han proposed the idea of making GF-epoxy composites using all GFs, characterized GFs and GF-epoxy composites, optimized the experimental conditions for making ouGF and nuGF, instructed on infiltration of epoxy, and drew the scheme in Figure 3.1. Peter S. Owuor performed elastic modulus tests. Sung H. Hwang performed nanoindentation tests. Junwei Sha advised on the preparation of uGF and ruGF. Lulu Shen and Chao Wang instructed on the failure mechanism of GF-epoxy under compressive loading and drew the scheme in Figure 3.9d. Jongwon Yoon performed electrical conductivity tests. Weipeng Wang performed thermal conductivity tests. Rodrigo V. Salvatierra performed TEM analysis.
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