RICE UNIVERSITY

Nanomaterials for Hydrocarbon Exploration, Acid Gas Removal and Energy Devices

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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HOUSTON, TEXAS
May 2015
ABSTRACT

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This thesis discusses the synthesis and characterization of several different nanomaterials as well as their applications to oil and energy industries. The nanomaterials studied here include asphalt-derived high surface area activated porous carbon, commercial carbon black (CB), nanoporous metal compounds, graphene, and graphene nanoribbons (GNRs). Through proper design and functionalization, these nanomaterials exhibit interesting properties and their applications in hydrocarbon exploration, acid gas removal as well as energy devices are demonstrated.

Firstly, the research activities toward the development of new absorbents for carbon dioxide (CO₂) capture have been growing quickly. Despite the variety of existing materials with high surface areas and high CO₂ uptake performances, the cost of the materials remains a dominant factor in slowing their industrial applications. In the first chapter we study preparation and CO₂ uptake performance of highly porous carbon materials derived from a very inexpensive carbon source, asphalt. Carbonization of asphalt with potassium hydroxide (KOH) at high temperatures (600 - 750 ºC) yields asphalt-derived porous carbon materials (A-PC) with high surface areas of up to 2780 m² g⁻¹ and high CO₂ uptake performance of 21 mmol g⁻¹ or 93 wt% at 30 bar and 25 ºC. Furthermore, nitrogen doping and reduction with hydrogen yields active N-doped
materials (A-NPC and A-rNPC) containing up to 9.3% nitrogen, making them nucleophilic porous carbons with further increase in CO$_2$ uptake to 26 mmol g$^{-1}$ or 114 wt% at 30 bar and 25 °C for A-rNPC. This is the highest reported CO$_2$ uptake among the family of the activated porous carbonaceous materials. The CO$_2$ is released and the asphalt material is regenerated when the pressure is returned to 1 bar. Thus the porous carbon materials from asphalt have excellent properties for reversibly capturing CO$_2$ at the well-head during the extraction of natural gas, a naturally occurring high pressure source of CO$_2$. Through a pressure swing sorption process, the asphalt-derived material is a reversible capture medium that is highly efficient and very inexpensive.

Secondly, crude oil is called as “sour” crude oil when the total sulfur level is larger than 0.5 %. The sour crude oil is corrosive to the oil production and transportation facilities and toxic to human health. Among these sulfur species, H$_2$S is the one of main impurities in sour crude. Therefore it is important to develop a method to accurately measure the sulfur content which may help geologists evaluate the quality of the crude oil before large scale extraction. In the second chapter, we study polyvinyl alcohol functionalized carbon black (PVA-CB) nanoparticles which are stable under high temperature and high salinity conditions. After further being functionalized with H$_2$S-sensitive fluorescence probe, the probe molecule-PVA-CB (FB-PVA-CB) can be used to determine the H$_2$S content in H$_2$S-containing oil in porous rock based on the fluorescent enhancement of the H$_2$S-sensitive addends.

Thirdly, a flexible 3-dimensional (3-D) nanoporous NiF$_2$-dominant layer on poly(ethylene terephthalate) has been developed. The nanoporous layer itself can be freestanding without adding any supporting carbon materials or conducting polymers. By
assembling the nanoporous layer into two-electrode symmetric devices, the inorganic material delivers battery-like thin-film supercapacitive performance with a maximum capacitance of 66 mF cm\(^{-2}\) (733 F cm\(^{3}\) or 358 F g\(^{-1}\)), energy density of 384 Wh kg\(^{-1}\) and power density of 112 kW kg\(^{-1}\). Flexibility and cyclability tests show that the nanoporous layer maintains its high performance under long-term cycling and different bending conditions. The fabrication of the 3-D nanoporous NiF\(_2\) flexible electrode could be easily scaled.

Fourthly, in its monolayer form, graphene is a one-atom-thick two-dimensional material with excellent electrical, mechanical and thermal properties. Large-scale production of high-quality graphene is attracting an increasing amount of attention. Chemical vapor and solid deposition methods have been developed to grow graphene from organic gases or solid carbon sources. Most of the carbon sources used were purified chemicals that could be expensive for mass production. In this work, we have developed a less expensive approach using six easily obtained, low or negatively valued raw carbon-containing materials used without pre-purification (cookies, chocolate, grass, plastics, roaches, and dog feces) to grow graphene directly on the backside of a Cu foil at 1050 °C under H\(_2\)/Ar flow. The non-volatile pyrolyzed species were easily removed by etching away the frontside of the Cu. Analysis by Raman spectroscopy, X-ray photoelectron spectroscopy, ultraviolet-visible spectroscopy and transmission electron microscopy indicates that the monolayer graphene derived from these carbon sources is of high quality.

Fifthly, the preparation of polymer-functionalized graphene nanoribbons (PF-GNRs) in a one-pot synthesis is described. Multiwalled carbon nanotubes (MWCNTs)
were intercalated by potassium under vapor- or liquid-phase conditions, followed by addition of vinyl monomers, resulting in PF-GNRs. Scanning electron microscopy, thermogravimetric mass spectrometry and X-ray photoelectron spectroscopy were used to characterize the PF-GNRs. Also explored here is the correlation between the splitting of MWCNTs, the intrinsic properties of the intercalants and the degree of defects and graphitization of the starting MWCNTs. The PF-GNRs could have applications in conductive composites, transparent electrodes, heat circuits and supercapacitors.
Acknowledgments

Jesus says: “I am the vine; you are the branches. If you remain in me and I in you, you will bear much fruit; apart from me you can do nothing.” (John 15:5) I am thankful to God for his guidance, protection and blessings through my PhD studies at Rice University.

I would like to sincerely thank my advisor Dr. James M. Tour, for his great instruction in my research. As one of the top chemists in the world, Dr. Tour’s schedule is always busy. However, he still spends as much time as he can with students. Because of the group meetings and subgroup meetings, I can discuss my research with him every week. He always encourages me and other labmates with a saying, “You are sitting on a gold mine.” He also sets a great sample for me to follow in research as well as in daily and spiritual life. I am really grateful to have him as my PhD advisor in my life.

I also would like to thank my other two committee members, Dr. Paul S. Engel and Dr. Mason B. Tomson for their time and kind suggestions.

I would like to thank our lab managers, Dr. Dustin James and Dr. Paul Cherukuri, for correcting my manuscripts and assisting in my research. Thanks to all the group members in the Tour Research Group, especially Dr. Chih-Chau Hwang, Dr. Yang Yang, Dr. Jason Mann, Dr. Almaz S. Jalilov, Dr. Changsheng Xiang, Dr. Zhengzhong Sun, Dr. Yu Zhu, Dr. Jun Yao, Dr. Zheng Yan, Zhiwei Peng, Huilong Fei, Lei Li, Loic Samuel, Ruquan Ye, Andrew Metzger, etc. Due to their great help and thoughtful discussions, my research became more smooth and productive. Also, I would like to thank my Rice
collaborators in Dr. Mike Wong’s and Dr. Mason Tomson’s groups for their contributions and support in my research, especially Yinhong Cheng and Dr. Lu Wang.

Dear Lord, I would like to especially thank you for becoming your child three months after I arriving in the USA and giving me such a wonderful fellowship, the Rice Chinese Christian Fellowship (RCCF). I would like to thank Pastor Brian Lam, Lily Lam, Dr. Bo Chen, Dr. Yuanbo Li, Dr. Powei Feng, Yidan Wang, Chaoran Yang, Tianwu Zang, Mengcheng Wang for their prayers, care and support. I would also like to thank my girlfriend, Xinnan Lu, for her unconditional love. She shares my happiness when I make achievements in research, and she encourages me when I have difficulty in my research. I would also like to thank my parents, Mr. Yujun Ruan and Mrs. Xiujuan Shao, and my twin brother, Dr. Gechong Ruan. Though they are living in China and I could not be together with them quite often, I miss them every day and their love is always my support.

I would like to thank my Lord again for everything that you have done in my life. I will continue to honor your name.
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## Nomenclature

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<tr>
<th>Abbreviation</th>
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<tr>
<td>PC</td>
<td>Porous Carbon</td>
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<tr>
<td>A-PC</td>
<td>Asphalt-derived Porous Carbon</td>
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<tr>
<td>A-NPC</td>
<td>Asphalt-derived N-doped Porous Carbon</td>
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<td>A-rNPC</td>
<td>Asphalt-derived reduced N-doped Porous Carbon</td>
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<td>MOFs</td>
<td>Metal Organic Frameworks</td>
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<td>Nitrogen-doped Porous Carbon</td>
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<td>Activated Carbon</td>
</tr>
<tr>
<td>NP</td>
<td>Nanoparticle</td>
</tr>
<tr>
<td>CB</td>
<td>Carbon Black</td>
</tr>
<tr>
<td>ACPA</td>
<td>4,4’-Azobis(4-cyanopentanoic acid)</td>
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<tr>
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<tr>
<td>rGO</td>
<td>Reduced graphene Oxide</td>
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<td>CNT</td>
<td>Carbon Nanotube</td>
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<td>Description</td>
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<tr>
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<td>-------------</td>
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<tr>
<td>MWCNT</td>
<td>Multiwalled Carbon Nanotube</td>
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<tr>
<td>GNR</td>
<td>Graphene Nanoribbon</td>
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<tr>
<td>PF-GNR</td>
<td>Polymer-Functionalized Graphene Nanoribbon</td>
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<td>GIC</td>
<td>Graphite Intercalation Compound</td>
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<td>Portable electronic devices</td>
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<td>Nanoporous Layer</td>
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<tr>
<td>WPW</td>
<td>Wide Potential Window</td>
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<tr>
<td>BET</td>
<td>Brunauer, Emmett and Teller</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half-Maximum</td>
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<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
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<tr>
<td>FT-IR</td>
<td>Fourier Transformed Infrared Spectroscopy</td>
</tr>
<tr>
<td>DLS</td>
<td>Dynamic Light Scattering</td>
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<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
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<td>TG-MS</td>
<td>Thermogravimetric Mass Spectrometry</td>
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<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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Chapter 1

Asphalt-Derived High Surface Area Activated Porous Carbon for Carbon Dioxide Capture

This chapter was copied from reference 32.

1.1. Introduction

Global climate change is the main environmental concern that might be directly affected by anthropogenic carbon dioxide (CO₂) emission sources, which include industrial power plants, refineries and natural gas wells, the latter having CO₂ contents which can range from 1 to 70 mol% depending on the region of the world.¹ ² Therefore, efficient and reversible CO₂ capture from flue gas or from the higher pressure natural gas wells remains important in the use of carbon fuels if we are to maintain high standards of environmental stewardship, or the so-called “green carbon” approach.³ ⁶ In the sorption processes, in addition to the highly used aqueous amine solvents and membrane
technologies, solid sorbents such as activated carbon, zeolites and more recently metal organic frameworks (MOFs) are promising alternative materials for capturing CO₂.⁷⁻⁹ Despite the many new solid sorbents developed in past years, the cost remains a dominant factor when it comes to choosing the ultimate material.

Within CO₂ capture technologies, compression and separation of CO₂ at high pressures, high flow rates and low partial pressures of CO₂, remains a challenge for next generation solid sorbents. While aqueous amine solutions are among the most common industrial processes for CO₂ capture,¹⁰ the process is corrosive and energy intensive due to the high energy requirements for regeneration of the amines, and their large space requirements exclude off-shore use. Solid sorbents are promising alternative technologies for CO₂ capture,⁸ and they project several advantages over conventional separation technologies. These include lower energy regeneration requirements, higher capacity and selectivity, and easier handling of the non-corrosive solids.⁸ Generally, lower heat capacities, faster kinetics of sorption and desorption, and mechanical strength of solid sorbents are the primary advantages of solid sorbents for the use of pressure swing methods of CO₂ gas separation.¹¹,¹²

An advantage of the meso- and microporous activated carbon materials over the other solid sorbents are the low cost of raw materials. The availability of a wide variety of carbon sources (e.g. coals, polymeric materials, coke pitch, wood, biomass, and industrial by-products) makes activated carbons cost-effective at the industrial production stage. Recently we reported porous carbon materials synthesized from sulfur and nitrogen containing polymers. These afforded sulfur and nitrogen-containing porous carbons, SPC and NPC, respectively, which showed superior CO₂ uptake at higher pressures and
greater CO₂/CH₄ gas separation selectivity relative to the most common solid sorbents such as activated carbon, zeolites and MOFs.¹³

Here we report template free¹⁴,¹⁵ synthesis and characterization of activated porous carbons from asphalt, which serves as a very inexpensive carbon source, and the synthesis is done in one step. In general, the structure of asphalt is complex, which mainly consist of asphaltenes, the toluene or benzene soluble portion of crude asphalt.¹⁶,¹⁷ Asphaltenes contains nano-sized conjugated aromatic domains that are linked by small aliphatic side chains with heteroatom containing-polar functional groups, which induces van der Waals, hydrogen bonding and charge-transfer interactions to form porous asphaltene aggregates.¹⁸,¹⁹ Therefore, activation of crude asphalt formed micro- and mesoporous carbon materials have high surface areas, which could be further activated by nitrogen impregnation, to yield activated porous carbons with even higher CO₂ uptake performances than SPC and NPC.

1.2. Experimental Section

1.2.1. Materials

Versatrol HT, Versatrol M, Asphasol Supreme and Natural asphalt from Chile were kindly provided by MI SWACO, a Schlumberger Company. Untreated Gilsonite and Untreated Gilsonite Substitute are both provide by Prince Energy. Activated carbon Darco G-60 and KOH were used as received from Sigma-Aldrich.
1.2.2. Synthesis of asphalt derived porous carbon (A-PC)

0.50 g of asphalt (Versatrol HT) and 1.50 g (26.7 mmol) of KOH were mixed well in a mortar. The mixture was heated on a quartz boat inserted within a quartz tube furnace at 700 °C for 1 h with Ar flow at 500 sccm, 1 atm, before being permitted to cool to room temperature. Then the product was washed thoroughly with DI water and acetone until the filtrate attained pH 7. The A-PC powder was dried in an oven at 100 °C until a constant weight was achieved to afford 0.22 g of A-PC. Under comparable conditions different types of asphalt were screened: natural asphalt from Chile, Versatrol M, Asphasol Supreme, Untreated Gilsonite and Untreated Gilsonite Substitute; **Figure 1.1** shows the comparative CO₂ uptake data. Moreover, higher CO₂ uptake was reached by preliminary pretreatment of Versatrol M for 2 h at 400 °C and then activating at 800 °C for 1 h (**Figure 1.2**). Also, increasing the asphalt:KOH ratio to 1:5 and the temperature of the pretreatment to 750 °C for Natural asphalt, increased CO₂ uptake (**Figure 1.3**).
Figure 1.1. Volumetric CO$_2$ uptake of porous carbons derived from different asphalt sources over a pressure range from 0 to 30 bar at 23 °C. (a) Plotted in wt% and (b) in mmol g$^{-1}$. 
Figure 1.2. Volumetric CO$_2$ uptake of porous carbons derived from Versatrol M under different activation conditions over a pressure range from 0 to 30 bar at 23 °C. See Experimental Section for details.

Figure 1.3. Volumetric CO$_2$ uptake of porous carbons derived from natural asphalt under different activation conditions over a pressure range from 0 to 30 bar at 23 °C. See Experimental Section for details.
1.2.3. Synthesis of nitrogen doped asphalt derived porous carbon (A-NPC) and reduced nitrogen doped asphalt derived porous carbon (A-rNPC)

0.20 g of A-PC powder was placed in a quartz boat and transferred into to a quartz tube furnace. The powder was heated at 700 °C for 1 h with NH₃ flow at 100 sccm, 1 atm, before cooling to room temperature to afford 0.17 g of A-NPC. To synthesize A-rNPC, 0.20 g of A-NPC powder was heated at 700 °C for 1 h with H₂ flow at 100 sccm and Ar flow at 200 sccm at 1 atm to afford 0.18 g of A-rNPC.

1.2.4. Volumetric sorption

Volumetric sorption measurements of CO₂ or CH₄, or premixed gas were carried out in an automated Sievert instrument¹³ (Setaram PCTPro). Typically, ~120 mg of sorbent was placed in a stainless steel sample cell and pretreated at 150 °C for 2 h under vacuum (~20 mTorr). The sample volume was calibrated by helium before the sorption measurement.

1.2.5. Gravimetric sorption

Gravimetric sorption measurements of CO₂ were carried out in a Rubotherm magnetic suspension balance³¹ (Rubotherm, Germany). A blank test without sample was used to measure the weight and volume of the empty sample holder. For a typical measurement, ~120 mg of sorbent was placed in the sample holder and pretreated at 150 °C for 2 h under vacuum (~20 mTorr). A buoyancy test with helium was then used to measure the sample weight and sample volume before the sorption measurement.
1.2.6. Characterization

The XPS were obtained on a PHI Quantera SXM scanning X-ray microprobe system using a 100 µm X-ray beam of which the take-off angle was 45° and pass energy was 140 eV for the survey and 26 eV for the high resolution elemental analysis. The surface areas, pore volumes and pore size distributions (Barrett, Joyner, and Halenda – BJH) of different samples were obtained using an automated BET surface analyzer (Quantachrome Autosorb-3b). The samples were heated at 150 °C for 15 h under vacuum (20 mTorr) before each measurement. Scanning electron microscope (SEM) images were taken at 20 KeV in a FEI Quanta 400 high resolution field emission scanning electron microscope. High-resolution transmission electron microscope (TEM) images were obtained in a 2100F field emission gun transmission electron microscope. The porous carbon samples were transferred to a C-flat TEM grid (Protochips).

1.2.7. Conversion of excess uptake to absolute uptake

Total uptake includes all gas molecules in the adsorbed state, which is the sum of the experimentally measured excess uptake and the bulk gas molecules within the pore volume. For microporous materials with negligible external surface area, the total uptake is often used as an approximation for absolute uptake and could be represented in the following equation:

\[ N_{\text{total}} \approx N_{\text{abs.}} = N_{\text{ex.}} + V_p \bullet \rho_{\text{bulk}} (P,T) \]

where \( V_p \) is the pore volume of porous material and \( \rho_{\text{bulk}} \) is the density of gas in the bulk phase at given pressure and temperature. In the case of A-PC and A-rNPC, the
pore volume was determined to be 1.17 cm$^3$ g$^{-1}$ and 1.09 cm$^3$ g$^{-1}$, respectively, by N$_2$
adsorption isotherm at 77 K (BET analysis). The CO$_2$ density changes from 0.00180 to
0.06537 g cm$^{-3}$ in the pressure range between 1 and 30 bar at 22 ºC and 0.00164 to
0.05603 g cm$^{-3}$ at 50 ºC.

1.3. Results and Discussion

1.3.1. Synthesis and characterization of porous materials

Porous carbons were prepared by carbonization of mixtures of asphalt and
potassium hydroxide (KOH) at elevated temperatures under inert atmosphere (Ar). The
treatment of asphalt with KOH was performed at various temperatures (200-800 ºC) and
different asphalt:KOH weight ratios (varied from 1:1 to 1:4). The CO$_2$ uptake
performance of the final porous carbon materials (Figures 1.5 and 1.6) was evaluated
based upon the parameter changes in the synthesis. The asphalt-derived porous carbon is
designated as A-PC. The highest surface area A-PC was synthesized at 700 ºC (Figure
1.4) with a weight ratio of asphalt:KOH = 1:4 (Figure 1.5).

Asphalt
(Versatrol HT)  1. KOH, 700 ºC
   2. Water wash
   3. Filter, dry

Asphalt-derived porous carbon (A-PC)

Figure 1.4. The synthetic scheme of asphalt-derived porous carbon.
Figure 1.5. Optimization of the asphalt:KOH ratio during the carbonization process. Asphalt:KOH ratio varied from 1:1 to 1:4 at 700 °C. CO₂ uptake plotted in (a) wt% and (b) mmol g⁻¹. CO₂ uptake measurements were done at 23 °C.
As shown in Figure 1.6, A-PC has a steep nitrogen uptake at low pressures (0-0.3 P/P₀), and has a typical type IV sorption isotherm, indicating meso-porosity of the
material (Figure 1.8, inset). The Brunauer–Emmett–Teller (BET) surface area (2780 m$^2$ g$^{-1}$) and the pore volume (1.17 cm$^3$ g$^{-1}$) were calculated from the nitrogen isotherms (Table 1.1). X-ray photoelectron spectroscopy (XPS) of the A-PC showed C 1s and O 1s signals, with ~ 10% oxygen content, assigned to C-O and C=O functional groups (Figure 1.8).

![Nitrogen sorption isotherms for A-PC at 77 K. Nitrogen sorption isotherms for A-PC at 77 K. Absorption (filled symbols) and desorption (empty symbols). Inset: Differential nonlocal density functional theory (NLDFT) pore size distributions curve.](image)

Figure 1.7. Nitrogen sorption isotherms for A-PC at 77 K. Nitrogen sorption isotherms for A-PC at 77 K. Absorption (filled symbols) and desorption (empty symbols). Inset: Differential nonlocal density functional theory (NLDFT) pore size distributions curve.
Figure 1.8. XPS of A-PC. (a) Survey scan and (b) high resolution C1s signal.
SEM images of the **A-PC** shows porous material with a uniform distribution of the pores as shown in **Figure 1.9**. Uniform distribution of the pores is further indicated by the TEM images (**Figure 1.9b**) with pore diameters > 2 nm. This is close to the values determined from the nitrogen absorption isotherms.

Figure 1.9. (a) SEM and (b) TEM images of the A-PC.

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<tr>
<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)$^a$</th>
<th>Pore volume (cm$^3$ g$^{-1}$)$^a$</th>
<th>Density (g cm$^{-3}$)</th>
<th>CO$_2$ uptake capacity at 30 bar$^b$ (mmol g$^{-1}$)</th>
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**Table 1.1. Properties and CO<sub>2</sub> uptake performances of activated porous carbons.**<sup>a</sup><br>

Estimated from N<sub>2</sub> absorption isotherms at 77 K; samples dried at 200 °C for 20 h prior to the measurements.<sup>b</sup> CO<sub>2</sub> uptake at 23 °C. Prepared by H<sub>2</sub> reduction of NPC at 600 °C.<sup>c</sup>

Treatment of A-PCs with NH<sub>3</sub> at elevated temperatures resulted in asphalt derived N-impregnated porous carbon materials (A-NPC). The nitrogen content (3-9 % from 0%) and the surface area 2860 m<sup>2</sup> g<sup>-1</sup> increased after treatment of A-PCs with NH<sub>3</sub> at higher temperatures (Figure 1.10), as shown in Tables 1 and 2. This leads to the modified porous material of up to 9.3% N concentration obtained at 800 °C. At lower NH<sub>3</sub> treatment temperatures, the content of nitrogen decreased proportionally, reaching 2.7% at 500 °C (Table 1.2).
Figure 1.10. Optimization of the NH$_3$ treatment temperature during N-impregnation of A-PC. A-PC formed using 1:3 ratio of asphalt:KOH was used to optimize the temperature of the NH$_3$ treatment, which varied from 100 °C to 800 °C. CO$_2$ uptake of the N-impregnated A-NPC at various temperatures plotted in (a) wt% and (b) mmol g$^{-1}$. CO$_2$ uptake measurements were done at 23 °C.
Figure 1.11. High-resolution XPS N1s spectra of the (a) A-NPC formed at various
NH3 treatment temperatures, and (b) A-rNPC formed after reduction with H2 at
700 ºC. Experimental data are the open circles and the fitted curves are the solid
lines.

The surface N-bonding configurations reveal three main nitrogen functional
groups in the surface of the carbon framework. As shown in Figure 1.11, the XPS N 1s
spectra at variable doping temperatures deconvoluted into three peaks with binding
energies at 399.0, 400.7 and 401.7 eV. These are in the range of typical binding energies
corresponding to pyridinic N, pyrollic N and graphitic N, respectively. While lower
temperature (500 ºC) NH3 treatment primarily leads to pyrollic type functional groups,
treatment at higher temperatures (800 ºC) results in pyridinic and graphitic nitrogens.20
The new peak at binding energy of 396.0 was observed at 800ºC, which is assigned to the
N-Si binding energy. It is likely that at higher pyrolysis temperatures, silica-doping from
the quartz tube occurs, which also results in lower CO2 uptake (Table 2). Further H2
treatment of A-NPC at 700 ºC with the intent of reducing the amines resulted in the
reduced porous carbon material (A-rNPC). The elemental composition and the surface
area of the A-rNPC were investigated using XPS (Figure 1.11b and Table 1.2). There is noticeable change in the graphitic nitrogen signal after the H₂ reduction of A-NPC, which decreased from 5.4 % to 4.6 % and an increase in the concentration of the pyridinic nitrogen signal from 53.2 % to 55.1 % (Table 1.2). This suggests the H₂-induced transformation of graphitic nitrogen to the pyridinic nitrogen (Figure 1.12). The proposed mechanistic pathway for H₂ reductive N-C bond cleavage is shown in Figure 1.13a. An increase in the basic character of the nitrogen functional groups would be anticipated due to the H₂ reduction of the pyridinic nitrogens to aliphatic nitrogens (Figure 1.13b); however, we were not able to detect an increase in the pyrrolic nitrogen content during the H₂ reduction. Instead, the H₂ reduction could be contributing to the changes in the pore structures, which leads to the decrease in the BET surface area. Since the nitrogen sorption isotherms did change considerably during both the N-impregnation and reduction processes (Figure 1.14), we conclude that such activation has substantial effect on the morphological parameters of the porous carbons. Similar behavior was observed during the activation of porous carbons with NH₃, where the authors of that study explained the observed increase in the surface area by the reaction between the carbon lattice and NH₃ to afford an evolution of methane. The gaseous evolution can increase the surface area.²¹ Schematic representation of the synthetic route for the A-rNPC is shown in Figure 1.15.
Figure 1.12. Conversion of graphitic nitrogen into pyridinic nitrogen during the reduction with H$_2$.

![Conversion diagram](image)

Figure 1.13. Proposed mechanisms for high temperature H$_2$ reduction of A-NPC.

![Mechanism diagrams](image)
Figure 1.14. Nitrogen sorption isotherms for A-PC, A-NPC and A-rNPC.

Figure 1.15. Schematic illustration of the preparation of A-NPC and A-rNPC.
<table>
<thead>
<tr>
<th>Samples a</th>
<th>C%</th>
<th>O%</th>
<th>N%</th>
<th>Pyridinic N%</th>
<th>Pyrrolic N%</th>
<th>Graphitic N%</th>
<th>CO₂ uptake capacity at 30 bar b</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-NPC(500)</td>
<td>91.1</td>
<td>6.1</td>
<td>2.7</td>
<td>29.7</td>
<td>63.3</td>
<td>7.0</td>
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<td>33.1</td>
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<tr>
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<td>4.7</td>
<td>53.2</td>
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<td>5.4</td>
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<tr>
<td>A-NPC(800)</td>
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<td>9.7</td>
<td>9.3</td>
<td>52.3</td>
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<td>2.3</td>
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<tr>
<td>A-rNPC</td>
<td>88.0</td>
<td>7.5</td>
<td>4.5</td>
<td>55.1</td>
<td>40.3</td>
<td>4.6</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Table 1.2. Elemental composition and CO₂ uptake performances of activated porous carbons that were aminated with NH₃ at 500 - 800 °C. aThe temperature of amination is shown in parentheses. bCO₂ uptake at 23 °C.

1.3.2. CO₂ uptake

Activated carbons with a wide variety of surface parameters including surface area, pore structure and active sites on the surface, have been widely used as gas sorbents. SPC and NPC were prepared from the carbonization of poly[(2-hydroxymethyl)thiophene] and poly(acrylonitrile), respectively.¹³ SPC and NPC showed high CO₂ uptake 18.4 mmol g⁻¹ (82 wt%) and 14.7 mmol g⁻¹ (65 wt%) (Table 1.1), respectively; comparable or better than conventional solid sorbents such as activated carbons, zeolites and MOFs.¹³ Shown in Figure 1.16 are the CO₂ uptake of the activated porous carbons from asphalt (A-PC, A-NPC, and A-rNPC) along with the SPC, NPC and commercial activated carbon (AC), measured by the volumetric method at room temperature over the pressure range 0 to 30 bar. 30 bar was chosen as the upper pressure limit from the approximation that a 300 bar natural gas well-head pressure containing ~
10% CO$_2$ has 30 bar partial pressure of CO$_2$. Volumetric CO$_2$ uptake shows little hysteresis, which suggests the reversible nature of CO$_2$ uptake of the materials. No degradation of the porous carbons is observed during the CO$_2$ sorption-desorption process from 0 to 30 bar (Figure 1.17) or over 8 cycles (Figure 1.18). CO$_2$ uptake at a pressure of 30 bar were given in Tables 1 and 2, and the uptake capacities are up to 26 mmol g$^{-1}$ (114 wt%), which are not only the highest reported among the activated carbons$^{22-24}$ but also comparable with MOFs used under similar conditions.$^{25-28}$ Unlike MOFs, these can be prepared at a much lower cost and in one or two thermalization steps from asphalt.

![Figure 1.16. Comparison of volumetric and gravimetric CO$_2$ uptake of A-PC, A-NPC and A-rNPC with the other porous carbon sorbents at 23 °C.](image-url)
Figure 1.17. CO$_2$ sorption–desorption cycle on the A-NPC over a pressure range from 0 to 30 bar at 23 °C. (a) Plotted in wt% and (b) in mmol g$^{-1}$. 
Figure 1.18. Eight consecutive CO$_2$ sorption–desorption cycle on the A-NPC over a pressure range from 0 to 30 bar at 23 °C. (a) Plotted in wt% and (b) in mmol g$^{-1}$.

A-rNPC has the highest CO$_2$ uptake performance at 30 bar although the highest surface area is obtained for A-NPC. The volumetric uptake measurements correlate with the gravimetric uptake measurements (Figures 1.16, 1.19-1.21). As we increase the N-
impregnation temperature (from 100 °C to 800 °C, Figure 1.10) the nitrogen content starts to increase gradually, which affects the CO₂ uptake performance of the A-NPCs (Table 1.2). Thus we conclude that the basic nitrogen functional groups (pyridinic and pyrrolic) are essential for the enhanced CO₂ uptake performance of the porous carbon material. At lower NH₃ treatment temperatures, the concentration of the pyrrolic nitrogens increases while pyridinic nitrogens decrease (Table 1.2). These results indicated that the pyrolysis temperature during the NH₃ treatment is one of the critical factors in determining the CO₂ uptake performance.
Figure 1.19. Gravimetric CO$_2$ uptake on A-PC. Comparison of absolute uptake and excess uptake at 25 °C. (a) Plotted in wt% and (b) in mmol g$^{-1}$. 
Figure 1.20. Comparison of the volumetric and gravimetric CO$_2$ uptake for A-PC at 23 °C and 25 °C, respectively.
Figure 1.21. Gravimetric CO$_2$ uptake on the A-rNPC. Comparison of absolute uptake and excess uptake at 25 °C. (a) Plotted in wt% and (b) in mmol g$^{-1}$. 
Figure 1.22 shows the high and low pressure CO$_2$ uptake of A-rNPC as the temperature increases. As in other solid sorbents such as activated carbons, zeolites and MOFs, the capacity decreases with increasing temperature. However, when compared with commercial activated carbon and SPC, the A-rNPC has a greater CO$_2$ uptake at higher temperatures.

Figure 1.22. Volumetric uptake of CO$_2$ on A-rNPC as a function of temperature. (a) Higher pressure range of 0 to 30 bar; (b) lower pressure range of 0 to 1 bar.

One of the key properties of the solid sorbents is their CO$_2$/CH$_4$ selectivity. CO$_2$/CH$_4$ selectivity in this paper is defined as the molar ratios of sorbed CO$_2$ and CH$_4$ ($\nu_{\text{CO}_2}/\nu_{\text{CH}_4}$). In order to evaluate the CO$_2$/CH$_4$ selectivity of A-PC, A-NPC and A-rNPCs, we compared CH$_4$ uptake performances with SPC, activated carbon and ZIF-8 sorbents at 23 °C. Figure 1.23 shows the comparison of the CO$_2$ and CH$_4$ sorption capacities of A-rNPC and SPC. A-rNPC has higher CH$_4$ (8.6 mmol g$^{-1}$) uptake relative to SPC (7.7
mmol g\(^{-1}\)) at 30 bar, although both A-rNPC and SPC have similar apparent surface areas 2580 m\(^2\) g\(^{-1}\) and 2500 m\(^2\) g\(^{-1}\), respectively. The molar ratios of sorbed CO\(_2\) and CH\(_4\) \((v_{\text{CO}_2}/v_{\text{CH}_4})\) were estimated by the ratios of the amount of the absorbed gases at 30 bar, which was highest for A-rNPC (3.0), as compared to values for SPC (2.6), activated carbon (1.5) and ZIF-8 (1.9).\(^{13}\)

![Figure 1.23. Volumetric CO\(_2\) (filled symbols) and CH\(_4\) (empty symbols) uptake of A-rNPC (red) and SPC (blue) at 23 ºC.](image)

The isosteric heat of absorption (Q\(_{\text{st}}\)) of CO\(_2\) and CH\(_4\) on the surfaces of A-PC, A-NPC and A-rNPC were calculated using low pressure CO\(_2\) sorption isotherms at 0 ºC and 23 ºC as shown in Figure 1.24. The values for absorption of CH\(_4\) were found to be
comparable for A-PC, A-NPC and A-rNPC at 17 to 20 kJ mol\(^{-1}\) (Figure 1.24a) and they have relatively constant values during the filling of the pores. This points to the nucleophilic sites that can interact with CO\(_2\) but that do not have strong interactions with sorbed CH\(_4\) molecules.\(^{13}\) The observed values of 17 to 20 kJ mol\(^{-1}\) are close to the reported values for the absorption of methane on MOFs (MIL-53, 17.0 kJ mol\(^{-1}\))\(^{29}\) and zeolites (NaY, 17-17.8 kJ mol\(^{-1}\))\(^{30}\) and are all above the liquefaction enthalpy of methane (8.2 kJ mol\(^{-1}\)). Contrarily, the absorption energies of CO\(_2\) changes considerably between A-PC (20 kJ mol\(^{-1}\)) and A-rNPC (29 kJ mol\(^{-1}\)) as seen in Figure 1.24b, which is indicative of the stronger interactions between nitrogen containing nucleophilic sites of the pores in A-rNPC with the CO\(_2\) molecules. During the increase in the filling of the pores, the CO\(_2\) absorption enthalpy of A-PC starts to decrease and eventually reaches the enthalpy of liquefaction of CO\(_2\) (17.2 kJ mol\(^{-1}\)) (Figure 1.24a), while A-rNPC reaches its lowest value at 24 kJ mol\(^{-1}\) (Figure 1.24b). Relatively weak enthalpy for A-PC in contrast to the previously reported SPC (57 kJ mol\(^{-1}\)) suggest a better reversible CO\(_2\) uptake performance of undoped A-PC for the more efficient removal of CO\(_2\) at low pressures, in comparison to the nitrogen doped A-rNPC and sulfur containing SPC. Higher sorption enthalpy for the sulfur containing SPC than A-rNPC points to the stronger interactions of nucleophilic sulfur-containing sites of the pores with CO\(_2\) molecules. It is also worthy to mention that the SPC and A-rNPC have smaller CH\(_4\) sorption selectivity in comparison to the CO\(_2\) sorption selectivity (Figure 1.23). This points to a weak interaction of CH\(_4\) with the sulfur and nitrogen functional groups in the pores. CO\(_2\) has a larger quadrupole moment (13.4 C m\(^{2}\)) than does the CH\(_4\) (nonpolar).
Figure 1.24. Isostreric heat of absorption (Qst) using (a) CH$_4$ and (b) CO$_2$ on A-PC and A-rNPC at 0 ºC and 23 ºC.

1.4. Conclusion

In summary, we have demonstrated the successful synthesis of microporous active carbon from asphalt with uniform distribution of pores sizes and the subsequent activation with nitrogen functional groups. Changing the preparation conditions, the porous materials possess variable surface areas and nitrogen contents. Activated porous carbons from asphalt have been shown to have CO$_2$ uptake of 26 mmol g$^{-1}$ (114 wt%), which is the highest for any porous carbons and also one of the highest among all the porous materials. Additionally, nitrogen functionalized microporous carbon materials exhibit greater CO$_2$:CH$_4$ than the nucleophilic porous materials prepared from the heteroatom-containing organic polymers. These observations indicate the porous
materials from asphalt are promising and very inexpensive sorbents for industrial applications where CO\textsubscript{2} is removed from natural gas streams.

1.5. Reference


\textbf{1.6. Experimental Contributions}

Gedeng Ruan and Almaz Jalilov designed the project. Gedeng Ruan synthesized the A-PC, A-NPC, A-rNPC, took the CO\textsubscript{2} and CH\textsubscript{4} uptake measurements and and SEM
pictures. Almaz Jalilov took the BET measurements. Huilong Fei took the TEM images. Chih-Chau Hwang helped the N-doping process. Josiah Tour helped with the CO$_2$ uptake measurements.
Chapter 2

Carbon-Based Nanoreporters Designed for Subsurface Hydrogen Sulfide Detection

This chapter was copied from reference 29.

2.1. Introduction

Hydrogen sulfide is considered a broad spectrum poison that can adversely affect several different systems in the human body.\textsuperscript{1} The toxicity of H\textsubscript{2}S is even stronger than that of hydrogen cyanide in terms of the half maximal inhibitory concentration (IC\textsubscript{50}).\textsuperscript{2} It is worth noticing that the human nose quickly becomes desensitized to H\textsubscript{2}S, leading to an inability to detect higher concentrations of H\textsubscript{2}S that could cause rapid death. After exposure to nonlethal levels of H\textsubscript{2}S, humans may suffer sore throats, shortness of breath, and dizziness.\textsuperscript{3} Recent studies also observed that H\textsubscript{2}S is a biologically important signaling molecule in various tissues and processes including pain and inflammation;\textsuperscript{4}
therefore, chemists have synthesized a series of fluorescent probes for H$_2$S detection. We capitalize upon those probes here for downhole detection of H$_2$S in oilfields.

The presence of H$_2$S has a significant impact on the quality of crude oil in which it is found. Decayed organic material (kerogen) that is found in sedimentary rock formations can have high sulfur content. During thermal decomposition of the kerogen into crude oil or natural gas, H$_2$S can be one of the products.$^5$ As a result, crude oil and natural gas inherently contain varying amounts of H$_2$S depending on the original sulfur content of the kerogen.$^5$ Crude oil is classified as “sour” when it contains a total sulfur content greater than 0.5%.$^6$ Among these sulfur species, H$_2$S is the one of main impurities in sour crude. The sour crude is toxic and corrosive to the materials of construction in pipelines and other holding and transportation vessels. The sulfur impurities must be reduced to varying levels by additional refining steps. The reduction levels depend upon regulations and the targeted product slate before being refined into distilled products. These extra steps normally result in higher-priced fuel products than those made from “sweet”, or low-sulfur content, crude oil.$^7$ Today’s oil refineries are facing a problem as they have limited capacities to process the increasing amounts of sour crude being produced, especially regarding the processing of the heavier sour grades of crude oil.$^7$ The amount of sulfur in a sample of crude depends on where it was found. If the concentration of the sulfur species in the subsurface could be accurately monitored, then geologists might be able to evaluate the quality of the crude before large scale extraction ensues.

Recently, nanomaterials have been studied for transport through porous media$^{8-15}$ and they are expected to have significantly different transport behaviors than traditional
polymers. For instance, injecting nanoparticles (NPs) through simulated downhole porous media provides an innovative approach for subsurface oil detection and enhanced oil recovery.\textsuperscript{11-12, 16-17} Among these techniques, however, the design of a NP with an acceptable terrestrial transport efficiency is considered a formidable challenge because the NPs are prone to aggregation in the downhole environment of high temperature and high salinity, which could greatly restrain NP transport, decreasing the breakthrough efficiency.

In recent work, we developed a carbon black (CB)-based NP with high mobility and thermal stability that survives high temperature and high salinity conditions so that it could efficiently transport the cargo molecules through simulated downhole formations, effectively conducting subsurface exploration as a nanoreporter.\textsuperscript{17} These results have implications in downhole oil detection, enhanced oil recovery and environmental remediation of contaminated land.

Here, we synthesized a newly designed nanoreporter by attaching H\textsubscript{2}S-sensitive probe molecules onto the NPs; these functionalized NPs have the potential to detect H\textsubscript{2}S downhole with assessment immediately upon return to the surface. Based on prior work, the functionalized NPs should have high mobility and stability in the downhole environment. \textbf{Figure 2.1} is a scheme that outlines the use of a nanoreporter to detect subsurface H\textsubscript{2}S. When the nanoreporter is pumped downhole, the H\textsubscript{2}S-responsive nanoreporter would react with H\textsubscript{2}S trapped in the water and oil deposits. The fluorescent properties of the functionalized NP would change, based on the concentration of the H\textsubscript{2}S and the degree of functionalization. By interrogation of the nanoreporter in the effluent at
the production well, analysis of the fluorescence emission could give quantitative information regarding the downhole H₂S content.

![Diagram of subsurface H₂S detection by nanoreporters bearing fluorescent probe molecules](image)

**Figure 2.1.** Schematic diagram of subsurface H₂S detection by nanoreporters bearing fluorescent probe molecules that are transported through rocks in the subsurface by pumping. The fluorescent properties of the functionalized NP would change based on the concentration of H₂S and the degree of functionalization of the NP. By the interrogation of the nanoreporter in the effluent at the production well, analysis of the fluorescence emission could give quantitative information regarding the H₂S content.
2.2. Experimental Section

2.2.1. Synthesis of carboxyl-functionalized CB.

3 g of 15 nm carbon black (Cabot Monarch Lot # 1278105) was added to 100 mL of THF in a 250 mL round-bottom flask fixed with a stir bar and a rubber septum. The mixture was bath-sonicated (Cole-Parmer, 12 W, Model: 08849-00) for 3 h. 4,4’-Azobis(4-cyanopentanoic acid) (ACPA) (2.0 g, 7.0 mmol) was added to the flask and the reaction mixture was stirred at 65 to 70 °C for 24 h. At that point, a second portion of ACPA (2.0 g, 7.0 mmol) was added and the mixture stirred for another 24 h. Finally, a third portion of ACPA (2.0 g, 7.0 mmol) was added with continued stirring for 24 h. After cooling to room temperature, the mixture was filtered through a 0.45 µm PTFE membrane and the black solid was washed with THF (3 ×), ethanol (3 ×) and acetone (3 ×). The solid was dried at 60 °C under vacuum (100 Torr).

2.2.2. Synthesis of PVA-grafted carboxyl-functionalized CB (PVA-CB).

25 mg of carboxyl-functionalized CB and 1 g of PVA (PVA(2k), PVA(10k), PVA(50k) or PVA(100k)) were added to 25 mL of anhydrous DMSO in a 50 mL round-bottom flask. The mixture was sonicated for 3 h until carboxyl-functionalized CB and PVA were well-dispersed (for PVA(50k) and PVA(100k), the mixture was heated at 90 °C to dissolve the PVA and then cooled to room temperature and sonicated (Cole-Parmer ultrasonic cleaner) for 1 h). Then 0.2 g (0.97 mmol) of N,N’-dicyclohexylcarbodiimide (DCC) and 0.02 g (0.16 mmol) of 4-dimethylaminopyridine (DMAP) were added. The reaction mixture was stirred at room temperature for 24 h, transferred to a dialysis bag (MWCO = 300 k) and dialyzed in running DI water for 1 week. The product was filtered
through a 0.22 µm Millipore Express PES membrane filter to obtain the PVA-CB solution (approximate 200 mL, 120 ppm).

2.2.3. Preparation of the Probe Molecule 6-(5-(hydroxyamino)-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic Acid, Compound 3.

![Chemical Reaction Diagram]

3-Nitro-1,8-naphthalic anhydride (1) (1.08 g, 4.44 mmol) and 6-aminocaproic acid (1.165 g, 8.88 mmol) were added to 50 mL anhydrous DMF and the mixture was heated to 120 °C for 5 h. Then the DMF was evaporated at 90 °C under vacuum using a rotary evaporator equipped with a mechanical pump. The product was purified by silica gel chromatography (CH₂Cl₂:CH₃OH = 100:2) to give compound 2, 1.265 g, 80% yield of the intermediate, 6-(5-nitro-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic acid. FTIR (neat): 1530, 1598, 1625, 1658, 1700, 2620, 2867, 2947, 3075 cm⁻¹. ¹H NMR (500 MHz, DMSO-d₆, 293 K): δ 12.01 (br, 1H), 9.48 (d, J = 2.3 Hz, 1 H), 8.96 (d, J = 2.3 Hz, 1 H), 8.78 (dddd, J = 8.3, 1.2, 0.4 Hz, 1 H), 8.68 (dd, J = 7.3, 1.2 Hz, 1 H), 8.06 (dd, J = 8.2, 7.3 Hz, 1 H), 4.05 (t, J = 7.4 Hz, 2 H), 2.21 (t, J = 7.3 Hz, 2 H), 1.65 (quin, J = 7.5 Hz, 2 H), 1.55 (quin, J = 7.5 Hz, 2 H), 1.36 (m, 2 H). MS (ESI) m/z calcd for [M - H]⁻ C₁₈H₁₅N₂O₆ 355.10, found 355.10. Compound 2 (300 mg, 0.84 mmol) and Rh/C (5%, 50 mg) were mixed in 50 mL THF at 0 °C, followed by the addition of hydrazine hydrate solution (80%, 60 µL, 62 mg, 1.93 mmol) to the mixture with vigorous stirring for
another 5 h at 0 °C. The THF was evaporated and the product, 6-(5-(hydroxyamino)-1,3-
dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)hexanoic acid, was purified by silica
chromatography (CH$_2$Cl$_2$ : CH$_3$OH = 10 : 1). The yield of 3 was 109 mg, 38%. FTIR
(neat): 1592, 1625, 1660, 1695, 2647, 2869, 2889, 2981, 3074, 3270 cm$^{-1}$. $^1$H NMR (500
MHz, DMSO-$d_6$, 293 K): δ = 1.34 (m, 2 H), 1.54 (quin, $J$ = 7.5 Hz, 2 H), 1.62 (quin, $J$
= 7.5 Hz, 2 H), 2.19 (t, $J$ = 7.3 Hz, 2 H), 4.01 (t, $J$ = 7.5 Hz, 2 H), 7.68 (d, $J$ = 2.1 Hz, 1 H),
7.72 (dd, $J$ = 8.2, 7.3, 1 H), 8.02 (d, $J$ = 2.3, 1 H), 8.20 (dd, $J$ = 7.3, 1.2 Hz, 1 H), 8.24
(dddd, $J$ = 8.3, 1.2, 0.4 Hz, 1 H), 8.87 (s, 1H), 9.07 (s, 1 H), 12.01 (br s, 1 H). MS (ESI)
m/z calcd for [M - H]$^{-}$ C$_{18}$H$_{17}$N$_2$O$_5$ 341.12, found 341.12.

![IR spectra](image)

**Figure 2.2.** ATR-IR spectra for (a) the starting material 1, (b) intermediate 2, and (c)
product 3.
Figure 2.3. Electrospray ionization mass spectrometry (ESI-MS) was used to characterize (a) compound 2 and (b) compound 3. Analyses in negative ion mode showed two dominant peaks of the mass-to-charge ratio (m/z) at 355.10 and 341.12 that could be exactly matched to the parent ions of 2 and 3 after deprotonation.
Figure 2.4. $^1$H NMR (500 MHz, DMSO-d$_6$, 293 K) of compound 2.

Figure 2.5. $^1$H NMR (500 MHz, DMSO-d$_6$, 293 K) of compound 3.
2.2.4. Preparation of the Probe Molecule-PVA-CB (FP-PVA-CB).

25 mg of carboxyl-functionalized CB and 1 g of PVA(50k) were added to 25 mL anhydrous DMSO in a 50 mL round-bottom flask. The mixture was bath-sonicated for 3 h and heated at 90 °C for 5 min until the CB and PVA were well dispersed. After it was cooled to room temperature, 0.20 g of DCC (1.00 mmol) and 20 mg of DMAP (0.16 mmol) were subsequently added to the flask and then the mixture was stirred at room temperature for another 24 h. Compound 3 (100 mg, 0.29 mmol) was added to the flask and the mixtures was stirred for 24 h. Then the reaction mixture was transferred to a dialysis bag (MWCO = 50 k) and dialyzed in DMSO (500 mL) for 1 day (DMSO was changed every 8 h) and against running DI water (MWCO = 300 k) for one week, followed by filtering through a 0.22 µm Millipore Express PES membrane filter (approximately 200 mL, 120 ppm).

2.2.5. Preparation of Seawater.

The synthetic seawater was prepared by mixing the following in DI water: NaCl (28.311 g/L), Na$_2$SO$_4$ (0.072 g/L), NaHCO$_3$ (0.181 g/L), KCl (1.478 g/L), CaCl$_2$ (0.386 g/L) and MgCl$_2$ (0.523 g/L).

2.3. Results and Discussion

To prepare the thermally stable and mobile CB-based NPs, 15-nm CB (Cabot) was first functionalized with carboxylic groups by using the radical initiator 4,4’-azobis(4-cyanopentanoic acid) (ACPA) that produces a carboxyl group-functionalized CB.$^{17-18}$ 3 g of 15 nm carbon black (Cabot Monarch Lot # 1278105) was added to 100
mL of THF in a 250 mL round-bottom flask fixed with a stir bar and a rubber septum. The mixture was bath-sonicated (Cole-Parmer, 12 W, Model: 08849-00) for 3 h. 4,4’-Azobis(4-cyanopentanoic acid) (ACPA) (2.0 g, 7.0 mmol) was added to the flask and the reaction mixture was stirred at 65 to 70 °C for 24 h. At that point, a second portion of ACPA (2.0 g, 7.0 mmol) was added and the mixture stirred for another 24 h. Finally, a third portion of ACPA (2.0 g, 7.0 mmol) was added with continued stirring for 24 h. After cooling to room temperature, the mixture was filtered through a 0.45 µm PTFE membrane and the black solid was washed with THF (3 ×), ethanol (3 ×) and acetone (3 ×). The solid was dried at 60 °C under vacuum (100 Torr). 2,000 molecular weight polyvinyl alcohol (PVA(2k)) was subsequently grafted onto the carboxyl-functionalized CB core by condensation of the hydroxyl groups of the PVA with the carboxyl groups through a N,N’-dicyclohexylcarbodiimide (DCC) coupling reaction. Unbound PVA was removed by dialysis of the reaction product against running DI water. The PVA(2k) grafted-CB (PVA(2k)-CB) was finally obtained.
Figure 2.6. (A) ATR-IR spectra of the PVA(2k)-CB NPs, including an inset that is the high resolution C1s XPS of the NPs. (B) TGA of the PVA(2k)-CB NPs and the PVA(2k) as a control group. Samples were pretreated at 120 °C for dehydration prior to being heated to 900 °C at a rate of 3 °C/min in argon.

Figure 2.6A shows the attenuated total reflectance infrared (ATR-IR) spectra of the CB after the PVA(2k) modification. The PVA(2k)-CB spectrum was observed to have two broad peaks centered at 3320 and 2920 cm\(^{-1}\) that correspond to the stretching modes of the O-H and C-H, respectively, on the PVA\(^{19}\). The peak at 1735 cm\(^{-1}\) was assigned to carbonyl vibrations of the ester groups on the PVA(2k)-CB NPs, which confirmed that the PVA was grafted through chemical functionalization to the CB surface instead of only being physisorbed\(^{17}\). Extended dialysis treatment (7 days) was assumed to have removed all non-covalently bound PVA. The adsorption band from 1000 to 1300 cm\(^{-1}\) was attributed to C-O-C and C-OH stretching due to ester, ether and alcohol
moieties. High resolution X-ray photoelectron spectroscopy (XPS) was further used to analyze the surface chemical structures on the PVA(2k)-CB so as to corroborate the ATR-IR analysis. The C1s XPS spectrum of the PVA(2k)-CB (Figure. 2.6A, inset) showed two apparent peaks at 284.8 and 286.2 eV, which can be attributed to the sp²-carbon on the carboxyl-functionalized CB and the carbon attached to the OH group, respectively. Also, a weak band ~289.0 eV can be assigned to the carbon in the ester moieties, further evidence that the PVA polymers were covalently attached to the CB surface. Since the polymer brushes are assumed to surround the CB core via the ester linkages and therefore create a thick protective shell, the corresponding XPS signal from the ester group was weakened. Thermogravimetric analysis (TGA) also provides evidence for the amount of the PVA on the CB cores (Figure. 2.6B). The PVA(2k)-CB showed 87 wt% loss from 250 to 500 °C, which is reasonably attributed to the decomposition of the PVA(2k)-CB as compared to the profile of the starting polymer PVA(2k).

![Figure 2.7. SEM images taken from the PVA(2k)-CB. The NPs originally dispersed in aqueous solution were concentrated, followed by being precipitated through the addition of acetone.](image)

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Figure 2.7 shows scanning electron microscopy (SEM) images of the PVA(2K)-CB. These NPs samples were prepared by precipitating the concentrated PVA(2k)-CB in 500 mL acetone followed by filtration and drying of the filter cake under vacuum (~100 Torr) overnight at ambient temperature. Even though these NPs showed agglomeration due to the bridging effect between the polymers in the acetone, they still retained the spherical shape characteristic of carbon black.

Figure 2.8. Photographs taken from (A) the carboxyl-functionalized CB dispersed in DI-water after sonication. (B) After 6 h without sonication, the carboxyl-functionalized CB NPs precipitated from the suspension. (C) In spite of sonication, the carboxyl-functionalized CB NPs could not be dispersed in synthetic seawater. (D) After functionalization with the PVA(2k) polymer brushes, the PVA(2k)-CB NPs were stable in synthetic seawater without precipitation at room temperature. (E) When the temperature was elevated to 70 °C, the colloidal system became cloudy as the temperature reached the cloud point of the PVA(2k) and the particles precipitated. Both (F) PVA(50k)-CB and (G) PVA(100k)-CB were stable colloidal systems in synthetic seawater at 100 °C.
A colloidal system can be stable if the repulsive forces that exist between the particles prevail over the attractive forces as the particles approach one another. The CB bearing carboxyl groups could be expected to have negative surface charges under neutral pH; therefore, the electrostatic repulsion between those charged NPs provides a stabilizing mechanism in the colloidal system. It is therefore possible for the carboxyl-functionalized CB to be dispersed in deionized water after sonication (Figure 2.8A). After 6 h without sonication, the carboxyl-functionalized CB particles precipitated as a result of insufficient electrostatic stabilization (Figure 2.8B). This assumption could be indirectly supported by dispersing the carboxyl-functionalized CB into a synthetic seawater solution because these charge-stabilized NPs are sensitive to addition of salt, in particular high valency counter ions. When the electrolyte concentration increases, the corresponding Debye length of the colloidal system lessens, and the decay of the electrostatic stabilization rapidly causes the NPs to agglomerate (Figure 2.8C). When the carboxyl-functionalized CB was further functionalized with PVA(2k), the colloidal system was stabilized via the steric repulsive force between the polymer brushes (Figure 2.8D). Unfortunately, the PVA(2k)-FCB did not remain well-dispersed and the solution became turbid as the temperature was elevated to 70 °C, the cloud point of the PVA(2k), above which aggregations of the NPs could be expected (Figure 2.8E). Functionalization with longer chain stabilizing polymers, such as PVA(50k) and PVA(100k) with cloud points that are higher than that of the PVA(2k), the CB colloidal system remained stable in synthetic seawater at high temperature (100 °C, Figure 2.8F,G).
Figure 2.9. Temperature-dependent DLS measurements for the CB NPs after being modified with a variety of PVA molecular weights. All of the PVA-CB NPs were purified by filtration through a 0.22 μm membrane filter, followed by dispersion in seawater before the DLS measurement. The system temperature was elevated from 25 to 70 °C at a heating rate of ~ 5 °C/min.

To quantify particle size at different temperatures, dynamic light scattering (DLS) was applied to observe the changes in particle sizes of the PVA-CB over a temperature range from 25 to 70 °C. All NPs were purified by filtration through a 0.22 μm Millipore Express PES membrane filter, followed by dispersion in the synthetic seawater prior to the light scattering measurements. The PVA-CB, hydrodynamic radii were all similar at 25 °C. However, the particle size of the PVA(2k)-CB and the PVA(10k)-CB drastically increased with elevated temperature as expected by the Stokes-Einstein equation; their particle sizes increased to 530 and 500 nm, respectively, at 70 °C. Compared to PVA(2k) and PVA(10k), PVA(50k) and PVA(100k) provided CB with sufficient steric repulsion
so that the functionalized CB NPs were stable with no apparent agglomeration. The instability at lower molecular can be attributed to the thermal-induced loss of the water molecules surrounding the smaller PVA polymer chain, resulting in aggregation.

![Graph](https://via.placeholder.com/150)

Figure 2.10. Breakthrough studies for PVA-CB NPs in sandstone-packed columns. Synthetic seawater prepared to be equivalent to seawater was chosen as the carrier solution for the NPs. The temperature remained at 70 °C during the injection process and transport, with a flow rate of 8 mL/h and a linear velocity of 9.3 m/d. The percentage of PVA-CB NPs in the effluent \(C\) relative to the influent \(C_0\) was determined by UV spectroscopy. The arrows indicate when the flow was switched from the PVA-CB NPs to pure synthetic seawater.
In order to evaluate the PVA-CB NPs under more challenging conditions, the NPs were pumped through sandstone, a natural rock that is commonly found in oil fields, to mimic an oilfield environment. The ground sandstone (89-251 μm) was packed into a glass column. The corresponding pore volume (PV) of the sandstone-packed column could be calculated by saturating the column with liquid. The concentration of the PVA-CB NPs in the effluent (C) relative to the initial concentration in the influent (C₀) was measured by its UV absorbance at 232 nm and the C/C₀ ratio was then used to evaluate the transport efficiency for the PVA-CB NPs. Figure 2.10 shows the relative breakthrough performances of the PVA-CB modified by different molecular weight PVA, while they were pumped through the sandstone-packed column at 70 °C. The PVA(50k)-CB and the PVA(100k)-CB yielded asymmetrical breakthrough curves that reached ~ 80% in 7 PV; PVA(2k)-CB and PVA(10k)-CB did not smoothly flow through but blocked the column, finally resulting in limited breakthrough efficiencies. These outcomes were in agreement with the DLS results. According to the data, the PVA(50k)-CB and the PVA(100k)-CB NPs would be the better transporter candidates for nanoreporter downhole exploration because of their thermal stabilities and efficient mobilities under critical environmental conditions.

The PVA-CB NPs were next functionalized to monitor H₂S concentration downhole. This was done using molecules designed for selective imaging of H₂S in living cells, a probe reported to afford highly sensitive and selective monitoring of H₂S by a turn-on fluorescence signal enhancement. Inspired by the structure of the new probe, a naphthalimide-based molecule was selected as a model compound to functionalize the
PVA(50k)-CB. The combination was anticipated to have the potential for monitoring H$_2$S in the subsurface.

![Figure 2.11](image)

**Figure 2.11.** (A) Synthetic route to the H2S-responsive fluorescent probe 3. (B) The fluorescent probes were condensed with PVA-CB to produce a nanoreporter (FP-PVA-CB) that was purified by dialysis. The picture only shows the FP at the end of the polymer chains; however, they are functionalized throughout many of the repeat units.

Commercially available 3-nitro-1,8-naphthalic anhydride (1, **Figure 2.11A**) was chosen as the starting material. It could be converted to a naphthalimide by the addition of 6-aminocaproic acid. The extended aliphatic moiety in 2 was designed to covalently bond to the PVA chains of the PVA-CB via ester bond linkages. The naphthalimide bearing a 3-nitro electron-withdrawing group (EWG) was non-fluorescent because of the EWGs from the imide and the 3-nitro resulting in a “pull-pull” configuration, making the
intramolecular charge transfer (ICT) process forbidden. Upon conversion of the nitro group to a nitroamine by catalytic reduction, an electron-donating group (EDG), the ICT process would be restored, leading to a large fluorescent enhancement through the push-pull configuration. The nitro group was converted to a hydroxylamine 3, a relatively stable intermediate that is easily reduced by H₂S. Scheme 1A shows the synthesis of the probe molecule 3 and how the PVA-CB was functionalized with the fluorescent probe (FP) to produce the nanoreporter FP-PVA-CB (Figure 2.1B).

Figure 2.12. Configuration of the apparatus for the laboratory detection and quantitative analysis of hydrogen sulfide content in simulated downhole rocks. The nanoreporter FP-PVA(50k)-CB and the Na₂S (H₂S precursor at these concentrations) were diluted into seawater before simultaneous injection into a sandstone-packed column at a pump rate = 0.6 mL/h. The concentration of the nanoreporter was measured by the UV-vis absorbance at 412 nm (ε = 33,832 M⁻¹ cm⁻¹). 50 µM of the FP-PVA(50k)-CB and various concentrations of Na₂S(aq) (from 0
to 170 μM) were recovered and the amount of H$_2$S monitored through fluorescence spectroscopy.

The nanoreporter FP-PVA(50k)-CB and a series of given concentrations of Na$_2$S$_{\text{(aq)}}$ (commonly used as H$_2$S precursor at these concentrations) were separately dissolved in seawater before the solutions were simultaneously injected into a sandstone-packed column by an automatic injection system (Figure 2.12). The pump rate was controlled at 0.6 mL/h for each syringe pump, for the reduction reaction to occur in the column. The recovered solution was subsequently monitored by fluorescence spectroscopy, and the change in the fluorescence after each breakthrough study was recorded in Figure 2.13.

**Figure 2.13.** (A) Fluorescence spectra of the 50 μM FP-PVA(50k)-CB nanoreporter after pumping through the sandstone-packed columns containing different
concentrations of $\text{H}_2\text{S}_{(aq)}$. The fluorescence experiment was conducted at 25 °C with an excitation $\lambda_{ex} = 420$ nm. (B) correlation of the $\text{H}_2\text{S}$ concentration vs. the fluorescence intensity taken at $\lambda_{em} = 550$ nm.

**Figure 2.14.** The change of the functional groups on the nanoreporter during the $\text{H}_2\text{S}$ detection process.

**Figure 2.13** illustrates that the fluorescence change when 50 μM of the FP-PVA(50k)-CB was reacted with a series of concentrations of $\text{H}_2\text{S}_{(aq)}$ from 0 to 170 μM in the sandstone-packed column. $\text{Na}_2\text{S}$ is commonly used as a replacement for the $\text{H}_2\text{S}$ since both form $\text{HS}^-$ in solution. Indeed, fluorescence enhancement was observed when treating the nanoreporter with the $\text{H}_2\text{S}_{(aq)}$. The change in fluorescence intensity was found to be in direct proportion to the introduced concentration of the $\text{H}_2\text{S}_{(aq)}$, reaching an 11-fold enhancement at ~70 μM of the $\text{H}_2\text{S}$ concentration, which is close to the higher-end $\text{H}_2\text{S}$ concentration in sour oilfields. While the higher concentration of the $\text{H}_2\text{S}$ (170 μM) was added to react with the nanoreporter, the enhancement of the fluorescence intensity plateaued. This suggests that the probe molecules on the nanoreporters were fully
reduced by the H₂S. The overall reduction of the hydroxyl amine to the amine moiety is summarized in Figure 2.14.

Figure 2.15. Breakthrough study for the FP-PVA(50k)-CB nanoreporter. The column was packed with dolomite from a Kuwaiti oil field and Berea sandstone in order to simulate the oilfield environment. Prior to the breakthrough study, all the rock samples were ground and sieved to obtain 89~251 μm rock grains. The rock grains were further washed by 1 mM acetic acid (Fisher Scientific, USA) 5 × and with deionized water to remove fine particles and impurities. The dolomite had crude oil trapped on the surface; the total organic carbon content of the dolomite was 4.97%, analyzed by Galbraith Laboratories Inc. The crude oil-containing dolomite is termed “oil-dolomite”. The FP-PVA(50k)-CB and 65 μM Na₂S in the synthetic seawater were simultaneous injected into the oil-dolomite column.

Finally, a new column that was packed with Kuwaiti oilfield dolomite and Berea sandstone was used to replace the original sandstone-packed column in order to better
simulate the actual oilfield environment. As Figure 2.15A shows, the FP-PVA(50k)-CB not only had > 95% breakthrough efficiency in 6 PVs, but also exhibited good response to the H\textsubscript{2}S (Figure 2.15B). The fluorescent enhancement was comparable to that from the nanoreporter in the sandstone-backed column containing the same H\textsubscript{2}S concentration, suggesting that the PVA-coated nanoreporter is not trapped by crude oil. Additionally, the change in fluorescence enhancement depends upon the concentration of H\textsubscript{2}S in the column and not the type of rock formation.

### 2.4. Conclusion

In conclusion, PVA-CB NPs were synthesized and they exhibited efficient mobility as well as thermal stability under simulated downhole environments. The PVA-CB NP was subsequently functionalized with a H\textsubscript{2}S-sensitive probe molecule to show H\textsubscript{2}S detection in a simulated subsurface system. By taking advantage of the reducing efficiency of H\textsubscript{2}S, the ICT of π-conjugate push-pull properties of the probe molecule resulted in fluorescence enhancement. The FP-PVA-CB nanoreporter gave quantitative information of the H\textsubscript{2}S content based upon fluorescence enhancement.

### 2.5. Reference


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### 2.6. Experimental Contributions

Gedeng Ruan and Chih-Chau Hwang are the concept inventors. Gedeng Ruan developed the synthesis and purification procedure of the fluorescent probe, performed XPS, DLS, and SEM characterizations and scaled up the H\textsubscript{2}S-sensitive nanoreporter. Chih-Chau Hwang did the TGA and FT-IR measurement. Lu Wang did the breakthrough studies. Changsheng Xiang took photos of the nanoparticles. Errol L.G. Samuel ran the \textsuperscript{1}H-NMR experiment and analyzed the results. Kewei Huang helped with the fluorescent experiments.
Chapter 3

Flexible 3-Dimensional Nanoporous Metal-Based Energy Devices

This chapter was copied from reference 25.

3.1. Introduction

Advances in soft portable electronic devices (PEDs), such as roll-up touch screen displays, artificial electronic skin, e-paper and wearable systems for both personal and military uses, require the development of flexible energy devices. Flexible supercapacitors or electrochemical capacitors (ECs) can be based on non-faradaic electrostatic adsorption such as in electric double-layer capacitors (EDLCs) on carbon materials. Or their behavior can be based upon faradaic redox reactions such as in pseudocapacitors made from transition metal oxides. These flexible EC devices are displaying an increasing role in portable energy storage devices due to their fast dynamic responses, long-term cyclability and integrated advantages over conventional capacitors.
(for high power) and batteries (for high energy).\textsuperscript{3,4} From a practical viewpoint, for use in PEDs, it is necessary to achieve high capacitance within a limited area or volume, since PEDs are small in size.\textsuperscript{5} Hence, areal capacitance ($C_A$) and volumetric capacitance ($C_V$), rather than the conventionally used gravimetric capacitance,\textsuperscript{6} are better indications of the performance. Conducting polymers such as polyaniline and various carbon-based materials, including carbon nanotubes (CNTs), reduced graphene oxide (rGO) and carbon fibers, deliver low $C_A$ and $C_V$ due to their low densities (less than 2 g cm\textsuperscript{-3}), although they have high flexibility.\textsuperscript{7,8}

The poor mechanical flexibility of inorganic metal compounds with high $C_A$ and $C_V$, having the general formula MX ($X = O$, N or F), have been improved by forming hybrid composites using conducting polymers or carbon-based materials as the matrix, or by manufacturing the materials into nanostructures.\textsuperscript{9-12} 3-Dimensional (3-D) nanoporous structures hold promise due to their good flexibility and high surface area. The nanopores lead to enhancement of the performance of the ECs by facilitating ion transport and creating more active reaction sites.\textsuperscript{13,14} Here we present a technique to fabricate 3-D nanoporous NiF$_2$-dominant flexible thin film energy storage devices. The fabricated thin film can be freestanding without support from other carbon materials and conducting polymers. The technique is scalable for possible mass production and could be extended to fabricate freestanding all-solid-state electrodes. The technique also has the potential to be applied to fabricate other 3D metal nanoporous materials. NiF$_2$ was used in this study due to the large operation potential window of metal fluorides and the possibility to convert NiF$_2$ to Ni(OH)$_2$ under certain electrochemical conditions, which would produce an extremely high theoretical capacitance of 2082 F g\textsuperscript{-1}.\textsuperscript{15}
3.2. Experimental Section

3.2.1. Fabrication

Poly(ethylene terephthalate) (PET, ~ 35 μm thick) was cleaned with 2-propanol (99.5%, Sigma-Aldrich, USA) followed by deionized water. A Fischione 1020 argon/oxygen plasma cleaner was then used to clean the substrates further by exposure for 2 min under 600 W power. After that, 10 nm Cr was sputtered on the substrates as the adhesion layer using a Denton Desk V Sputter System, followed by sputtering 40 nm of Au as the conductive layer. Electrochemical deposition was then carried out in an aqueous solution of 0.05 M NiSO₄ (99%, Sigma-Aldrich, USA) with 0.5 M H₃BO₃ (99.5%, Sigma-Aldrich, USA) to deposit nickel layers on the treated substrates. Further anodic treatments were conducted at 15 mA cm⁻² in a solution of 0.2 M NH₄F (98%, Sigma-Aldrich, USA) with 2 M deionized water in ethylene glycol (Fisher Scientific, USA) performed in a two-electrode set-up with platinum foil as a counter electrode. The samples were then rinsed with deionized water and dried by nitrogen gas flow.

3.2.2. Device assembly

In order to enable access to the practical supercapacitor device performance of the fabricated flexible electrode, all-solid-state two-electrode symmetric cells (see Figure 3.1a) were used instead of three-electrode testing in aqueous solution.¹ PVA/KOH (weight ratio ~ 1:1) membrane was prepared by dissolving 4.2 g KOH in 50 mL water at room temperature under the N₂ atmosphere. Then 4.2 g PVA (50,000 or 100,000 MW) was added to the KOH solution which was heated at 85 °C for 5 h under rapid stirring. After the PVA/KOH sol became clear, the sol was dried at room temperature in a fume
hood for 10 h to form the PVA/KOH membrane that was ~ 100 μm thick. For assembling into a two-electrode symmetric supercapacitor device, two pieces of the NPL electrodes sandwiched a piece of PVA/KOH membrane, the latter being both a solid electrolyte and separator. The entire sandwich including the PET outer layers was ~ 170 μm thick. The geometrical area of the electrode was 1 cm in diameter (~ 3.8 cm²) and the mass of the electrode was found to be ~ 0.7 mg for each piece. To avoid the decay of the dissolved KOH in the solid electrolyte, which can occur by forming carbonates through exposure to atmospheric moisture and CO₂ during ECs testing, the edges of the devices were sealed with PTFE tape.
Figure 3.1. Microscopy observation of the 3-D nanoporous layer (NPL). (a) Cross section SEM image in low magnification. (b) Cross section SEM image in high magnification. (c,d) TEM images of the NPL.

3.2.3. Activation process

The NPL based symmetric EC devices show only EDLC behavior tested within potential window from -0.8 to 0.8 V, without an activation process, to \textit{in situ} convert NiF$_2$ to Ni(OH)$_2$. An activation process was performed by CV (Figure 3.13) within a potential window from -1.4 to 1.4 V at scan rate of 1 V s$^{-1}$. Because the conversion from NiF$_2$ to Ni(OH)$_2$ is an irreversible reaction, the more Ni(OH)$_2$ formed the higher redox
reaction peaks in CVs emerging, while there is shifting away from of their initial
positions. After 400 cycles, the redox current peaks in CVs gradually become stable and
no further increase in peak intensity. That implies that the NiF$_2$ was fully converted to
Ni(OH)$_2$ and the EC devices started to behave as pseudocapacitors.

3.2.4. Characterization

A JEOL 6500F scanning electron microscope (SEM) was used to investigate the
morphology of the samples. A JEOL 2010 HRTEM was used to observe the
morphologies and lattice fringes of the samples. The pore distribution of the NPL was
investigated using Brunauer-Emmett-Teller (BET) analysis (Quantachrome Autosorb-3B
surface analyzer). The data was used to determine the Barrett-Joyner-Halenda (BJH) pore
size. The 20 mg sample was dried at 130 °C under vacuum for 17 h before the test. XPS
(PHI Quantera, Perkin Elmer, USA) was used to characterize the chemical composition
of the nanoporous layer.

3.2.5. Electrochemical measurement

The supercapacitor performance of the assembled flexible all-solid-state
supercapacitor devices including galvanostatic discharge/charge (GDC) tests, CVs and
EIS analyses were carried out with an electrochemical analyzer (CHI 608D, CH
Instruments, USA). Long-term GDC cycling tests were performed on a multichannel
battery analyzer (Land, CT2001A). The EIS were carried out on fresh cells at open circuit
potentials with a frequency range from $10^{-2}$ to $10^4$ Hz with an ac signal amplitude of 5
mV.
3.2.6. BET analysis of the NPL

Brunauer-Emmet-Teller (BET) analysis by adsorption/desorption of nitrogen gas was performed. The data was used to determine the Barrett-Joyner-Halenda (BJH) pore size (Figure 3.2). Nanopores distributed from 2 to 10 nm were observed. The pore distribution is consistent with SEM and TEM observations.

![Figure 3.2. BJH pore size distribution derived from the adsorption branch of the isotherm of the heterogeneous NPL.](image)

3.2.7. XPS analysis of the NPL

XPS full spectrum scan and fine scan were performed on the NPL to investigate its chemical composition before and after electrochemical testing (activation process). The chemical composition changes are clear from XPS F1s, O1s and Ni2p spectra as shown in Figure 3.3. Before EC testing (black curves), the XPS peaks at 684 eV in F1s, 530.9 and 532.4 eV in O1s, 856.9 eV in Ni2p3/2 are ascribed to fluoride in NiF2, oxygen...
in the surface adsorbed moisture\(^2\), and nickel in NiF\(_2\)\(^3\), respectively. While after EC testing (activation process, red curves), F1s peak disappears, the O1s peak shifts to 530.5 eV and Ni2p\(_{3/2}\) peak shifts to 855.0 eV, which corresponds to oxygen and nickel from Ni(OH)\(_2\) and NiOOH\(^4,5\). Based on the XPS analysis, a probable conversion reaction occurred during EC testing: NiF\(_2\) + 2KOH → Ni(OH)\(_2\) + 2KF. Then the formed Ni(OH)\(_2\) is responsible for the reversible redox reactions during discharge/charge testing.

![XPS analysis on the NPL before (black line) and after (red line) electrochemical capacitor (EC) performance testing.](image)

- **Figure 3.3.** XPS analysis on the NPL before (black line) and after (red line) electrochemical capacitor (EC) performance testing. (a) XPS full spectra. (b) F 1s spectra. (c) O 1s spectra. (d) Ni 2p spectra.
3.3. Results and Discussion

To fabricate flexible devices based on nanoporous NiF₂-dominant thin film electrodes for supercapacitor applications, nickel was electrodeposited on Au/Cr/polyethylene terephthalate (PET) substrates (Figure 3.4a). Anodization was then used to electrochemically etch the deposited nickel to form a 3-D nanoporous structure. The as-prepared 3-D nanoporous layer (NPL) on the substrate showed good flexibility (Figure 3.4b) due to the enhanced mechanical properties conveyed by the nanoporous structure. The NPL became freestanding after removal of the substrate (Figure 3.4c). The fabricated thin film with the NPL had a thickness of ~ 900 nm and an average pore size ~ 5 nm, as confirmed by scanning electron microscopy (SEM) observation from different viewing directions: cross sectional (Figure 3.4d and Figure 3.1a,b), top (Figure 3.4e) and bottom (Figure 3.4f). The NPL with an average pore size of ~ 5 nm was also observed by transmission electron microscopy (TEM, Figure 3.4g and Figure 3.1c,d). The identified d-spacing from high resolution TEM (HRTEM) was ~ 0.32 nm, which corresponds to the NiF₂ (110) plane, as indicated by the lattice fringes (Figure 3.4g). To investigate the porous structure of the NPL, Brunauer-Emmett-Teller (BET) analysis by adsorption/desorption of nitrogen gas was performed. The data was used to determine the Barrett-Joyner-Halenda (BJH) pore size. Nanoscale pores distributed mainly in a range from 2 to 10 nm were observed (Figure 3.2). Furthermore, X-ray photoelectron spectroscopy (XPS) analysis (Figure 3.3) also confirms that the as-prepared NPL is mainly composed of Ni and F. The Ni2p spectrum indicates Ni is mostly bound to F to form NiF₂. The detected O1s and C1s spectra are from the adsorbed moisture and CO₂ from the atmosphere.
Figure 3.4. Structure of the 3-D nanoporous layer (NPL) and electrode schematic. (a) Schematic of the flexible NPL on Au (~ 40 nm)/Cr (~ 10 nm)/PET substrate (~ 35 μm). The figure on the right is only half of the final embodiment. Atop the solid electrolyte layer is another nanoporous layer, then Au/Cr and finally PET to complete the sandwich structure. More specifically, there is one solid electrolyte layer separating two halves of nanoporous layer, Au/Cr, and PET. The entire
sandwich shown at left is ~ 170 nm thick. (b) Photograph of flexible electrode under bending. (c) The freestanding NPL after removing the substrate. (d-f) SEM images taken from different viewing directions: cross section, top and bottom, respectively. (g) HRTEM image of the NPL.

To discover reasonable EC testing conditions for the flexible NPL in the two-electrode symmetric devices, different potential windows (Figure 3.5) and compositions of solid electrolytes (Table 3.1 and Figures 3.6 - 3.10) were screened. The optimum solid electrolyte composition for the NPL was found to be KOH in poly(vinyl alcohol) (PVA, molecular weight of ~ 50,000) with weight ratio ~ 1:1. The operating potential windows were set within -0.8 to 0.8 V (narrow potential window, NPW) and -1.4 to 1.4 V (wide potential window, WPW).
Figure 3.5. Cyclic voltammograms (CVs) of the flexible devices operated in different potential windows before activation process (black curve is from -0.8 to 0.8 V, red curve is from -1 to 1 V, green curve is from -1.2 to 1.2 V, blue curve is from -1.4 to 1.4 V). (a-d) Scan rates of 50 mV s$^{-1}$, 1 V s$^{-1}$, 10 V s$^{-1}$, and 100 V s$^{-1}$, respectively.
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<td><strong>PVA (50 k): KOH = 1:1</strong></td>
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<tr>
<td>PVA (50 k): KOH = 5:3</td>
<td>0.51</td>
<td>133</td>
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Table 3.1. The variation in the ECs performance with different compositions of the solid electrolyte.
Figure 3.6. EC testing on the devices by using solid electrolyte composed of KOH in polyvinyl alcohol (PVA, molecular weight of ~ 100 k) with weight ratio ~ 2:3. (a,b) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -0.8 to 0.8 V. (c,d) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -1.4 to 1.4 V. (e,f) Galvanostatic discharge/charge (GDC) curves operated at 0.2 mA cm\(^{-2}\) and 1 mA cm\(^{-2}\), respectively. (g) Electrochemical impedance spectroscopy (EIS) measured within a frequency range of 10\(^{-2}\) to 10\(^{4}\) Hz.
Figure 3.7. EC testing on the devices by using solid electrolyte composed of KOH in PVA (molecular weight of ~ 100 k) with weight ratio ~ 1:1. (a,b) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -0.8 to 0.8 V. (c,d) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -1.4 to 1.4 V. (e,f) GDC curves operated at 0.2 mA cm\(^{-2}\) and 1 mA cm\(^{-2}\), respectively. (g) EIS measured within a frequency range of 10\(^{-2}\) to 10\(^{4}\) Hz.
Figure 3.8. EC testing on the devices by using solid electrolyte composed of KOH in PVA (molecular weight of ~ 50 k) with weight ratio ~ 2:3. (a,b) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -0.8 to 0.8 V. (c,d) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -1.4 to 1.4 V. (e,f) GDC curves operated at 0.2 mA cm\(^{-2}\) and 1 mA cm\(^{-2}\), respectively. (g) EIS measured within a frequency range of \(10^2\) to \(10^4\) Hz.
Figure 3.9. EC testing on the devices by using solid electrolyte composed of KOH in PVA (molecular weight of ~ 50 k) with weight ratio ~ 4:3. (a,b) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -0.8 to 0.8 V. (c,d) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -1.4 to 1.4 V. (e,f) GDC curves operated at 0.2 mA cm\(^{-2}\) and 1 mA cm\(^{-2}\), respectively. (g) EIS measured within a frequency range of 10\(^{-2}\) to 10\(^{4}\) Hz.
Figure 3.10. EC testing on the devices by using solid electrolyte composed of KOH in PVA (molecular weight of ~ 50 k) with weight ratio ~ 5:3. (a,b) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -0.8 to 0.8 V. (c,d) CVs recorded at different scan rates from 50 mV s\(^{-1}\) to 100 V s\(^{-1}\) within a potential window from -1.4 to 1.4 V. (e,f) GDC curves operated at 0.2 mA cm\(^{-2}\) and 1 mA cm\(^{-2}\), respectively. (g) EIS measured within a frequency range of 10\(^{-2}\) to 10\(^{4}\) Hz.

When testing in a NPW, a NPL can only behave as an EDLC by electrostatic adsorption in the 3-D nanoporous structure. However, operating in a WPW, the window is sufficient to trigger an electrochemical conversion from NiF\(_2\) to Ni(OH)\(_2\) at ~ 1 to 1.2 V depending on the scan rate. It is interesting that the NPL shows a typical EDLC behavior that is a quasi-rectangular shape in the cyclic voltammograms (CVs) even at high scan rates of 100 V s\(^{-1}\) (Figure 3.11a and Figure 3.12a). The data establishes that the nanoporous structure of the NPL is responsible for the electrostatic adsorption effect during testing and the high electric conductivity of the devices mitigates the polarization effect during CV testing even at high scan rates up to 100 V s\(^{-1}\). By fitting a log (anodic peak current)-log (scan rate) plot (Figure 3.11b), a \(b\)-value of 0.85 was obtained, which indicates that a surface-controlled electrode process (for capacitive, \(b = 1\)) dominates in the device. The quasi-triangle shape in galvanostatic discharge/charge (GDC) curves (Figure 3.11c and Figure 3.12b) also indicates the EDLC behavior of the NPL. The \(C_A/C_V\) (based on the size of the NPL) calculated from CVs (Figure 3.12c) can reach up to 0.5 mF cm\(^{-2}\) (5.6 F cm\(^{-3}\) or 2.7 F g\(^{-1}\)) at a scan rate of 50 mV s\(^{-1}\). Whereas \(C_A/C_V\) calculated from the GDC curve (Figure 3.11c) is 0.29 mF cm\(^{-2}\) (3.2 F cm\(^{-3}\) or 1.57 F g\(^{-1}\))
at 0.1 mA cm\(^{-2}\) (0.54 A g\(^{-1}\)). To convert NiF\(_2\) to Ni(OH)\(_2\), an activation process is initiated by cyclic voltammetry within a WPW (Figure 3.13). It is clear from the CVs (Figure 2d and Figure 3.14a,b) that a pair of redox peaks at anodic (0.19 V) and cathodic (-0.19 V) sweeps appear after activation. The widening potential difference (\(\Delta V\)) between the anodic and cathodic peaks with increased scan rates indicates that a diffusion-controlled process dominates the electrode reactions. \(b = 0.64\), obtained after fitting (Figure 3.11e) also indicates that a diffusion-controlled process (\(b = 0.5\)) dominates the electrode reactions. Furthermore, a pair of battery-like plateaus at 0.2/-0.2 V were found from GDC curves (Figure 3.11f and Figure 3.14c), which originated from anion (OH\(^{-}\)) intercalation and the reversible reactions between Ni(II) and Ni(III), Ni(OH)\(_2\) + OH\(^{-}\) \(\rightleftharpoons\) NiOOH + H\(_2\)O + e\(^{-}\). The energy storage mechanism of the fabricated devices is similar to that of a Ni-Cd battery.\(^{18}\) The \(C_A/C_V\) calculated from the CVs (Figure 3.14d) and GDC curves are 75 mF cm\(^{-2}\) (833 F cm\(^{-3}\) or 407 F g\(^{-1}\)) at scan rate of 50 mV s\(^{-1}\) and 66 mF cm\(^{-2}\) (733 F cm\(^{-3}\) or 358 F g\(^{-1}\)) at 1 mA cm\(^{-2}\) (5.4 A g\(^{-1}\), Figure 3.11f), which is significantly higher than those found in flexible electrodes made with carbonaceous materials such as graphene/polyaniline composite (135 F cm\(^{-3}\) at 2 mV s\(^{-1}\), ref.19), carbon nanotubes (less than 16 F cm\(^{-3}\) at 1 mV s\(^{-1}\), ref. 20) and carbide-derived carbon materials (up to 90 F cm\(^{-3}\) at 1 mA cm\(^{-2}\)).\(^{21}\)
Figure 3.11. Electrochemical capacitor (EC) performances of the NPL in two-electrode symmetric devices within different potential windows; (a-c) NPW (-0.8 to 0.8 V) and (d-f) WPW (-1.4 to 1.4 V). (a) CVs of the NPL at different scan rates from 10 to 100 V s\(^{-1}\). (b) Log (anodic peak current) vs. log (scan rate) plot. (c) Galvanostatic discharge/charge (GDC) curves of the NPL at a current density of 0.1 mA cm\(^{-2}\). (d) CVs of the NPL at 10 (black line) and 20 (red line) mV s\(^{-1}\). (e) Log (anodic peak current) vs. log (scan rate) plot. (f) GDC curves of the NPL at current density of 1 mA cm\(^{-2}\).
Figure 3.12. EC testing on the devices within a potential window from -0.8 to 0.8 V by using solid electrolyte composed of KOH in PVA (molecular weight of ~ 50 k) with weight ratio ~ 1:1. (a) CVs recorded at different scan rates from 50 mV s$^{-1}$ to 5 V s$^{-1}$. (b) GDC curves recorded at 0.2 mA cm$^{-2}$, 0.5 and 1 mA cm$^{-2}$. (c) $C_A/C_V$ vs. scan rates measured from CVs.
Figure 3.13. Activation process by CVs at 1 V s$^{-1}$ for over 400 cycles. (a-d) CVs recorded from 1$^{\text{st}}$ to 100$^{\text{th}}$, 101$^{\text{th}}$ to 200$^{\text{th}}$, 201$^{\text{th}}$ to 300$^{\text{th}}$ and 301$^{\text{th}}$ to 400$^{\text{th}}$ cycles, respectively. The inset in (a) is the initial three CV cycles.
Figure 3.14. EC testing on the devices within the potential window from -1.4 to 1.4 V by using solid electrolyte composed of KOH in PVA (molecular weight of ~ 50 k) with weight ratio ~ 1:1. (a,b) CVs recorded at different scan rates from 50 mV s$^{-1}$ to 10 V s$^{-1}$. (c) GDC curves recorded at 2 mA cm$^{-2}$, 5 and 10 mA cm$^{-2}$. (d) $C_A/C_V$ vs. scan rates measured from CVs.

Furthermore, electrochemical impedance spectroscopy (EIS) was used to investigate the kinetic processes of the electrode reactions in the flexible devices. Nyquist plots (Figure 3.15a) for the NPL measured at the open circuit potential (OCP) illustrate an equivalent series resistance (ESR, the intersection with the real axis) of ~ 2.8 Ω, which indicates a high ionic conductivity of the solid electrode and low interface resistance between the NPL and solid electrolyte. The capacitance response frequency for the flexible device at a phase angle of -45° ($\phi_{45}$) was found to be 800 Hz from bode plot
which is equivalent to a relaxation time constant ($\tau_0$) $\sim$ 1.25 ms. This indicates that pseudocapacitive behavior and stored energy are accessible at frequencies below 800 Hz. At 2 Hz, the phase angle for the device is $\sim$ -82° which is close to ideal capacitive behavior (-90°). Moreover, $\tau_0$ calculated from the plot of frequency-dependent imaginary capacitance ($C''$) is consistent with that calculated from the bode plot, i.e. 1.25 ms (Figure 3.15c). It is appealing that the $\tau_0$ of 1.25 ms obtained in this work is much lower than those found in most recently published reports, for example graphene (33 ms), carbon-onions (26 ms) and MnO$_x$/Au multilayers (4.7 ms). For comparison, the Ragone plot (Figure 3.15d) was plotted in areal/volumetric power density ($P_A/P_V$) vs. areal/volumetric energy density ($E_A/E_V$) for the NPL tested in both the NPW (-0.8 to 0.8 V) and WPW (-1.4 to 1.4 V). The maximum $P_A$ and $E_A$ tested in the NPW are 8 kW kg$^{-1}$ and 0.6 Wh kg$^{-1}$, respectively. The values increase to 112 kW kg$^{-1}$ and 384 Wh kg$^{-1}$, respectively, when being tested in a WPW. Compared to flexible EC devices based on EDLCs such as carbon nanotubes, the NPL delivers better specific power and energy density in the NPW. Whereas the NPL shows much higher power supply performance in WPWs than that of pseudocapacitors recently published, for detailed EC performance comparison with some of the state-of-the-art thin film or flexible supercapacitors, see Table 3.2). From a practical view, the EC performance of a flexible device is better measured when it is connected both in tandem and in parallel. It is clear that doubled operation potential windows and GDC durations are obtained from the devices tested within both NPW (Figure 3.15e) and WPW (Figure 3.15f) in tandem and parallel connections, respectively. To characterize the cyclability of the devices, 10,000 GDC cycles (Figure 3.15g) were performed within both a NPW (at 1 mA cm$^{-2}$ or 5.4 A g$^{-1}$)
and WPW (at 2 mA cm$^{-2}$ or 10.8 A g$^{-1}$). It is interesting that the capacitance increased to 220% during the initial 900 cycles in a NPW, which probably indicates a gradual increase in electrochemically active surface area or surface passivation. After 900 cycles, the capacitance gradually decreased and finally stabilized at 150% after 10,000 cycles, which is still higher than the initial capacitance. Similarly, when being tested within the WPW, the devices increased to 105% for the initial 300 cycles and then decreased and stabilized at 76% retention after 10,000 cycles. This indicates that the delivered capacitance based on both EDLCs (NPW) and faradaic reactions (WPW) can maintain over 75% of the initial value over long-term testing, which is promising for practical applications. A more important feature is that after 10,000 cycles of testing, the NPL still maintained its nanoporous structure (Figure 3.16), and no decay of the layer was observed. Moreover, after cyclability testing, the ESR increased to only 3.8 $\Omega$ (Figure 3.17), which indicates that the EC testing did not significantly change the solid electrolyte/NPL interface.
Figure 3.15. EC performance of the NPL. (a) Nyquist plot of the device tested at the open circuit potential within frequency range from $10^2$ to $10^4$ Hz. The inset shows $\tau_0 = 1.25$ ms. 

(b) Impedance magnitude $|Z|$ and phase $\phi$ at 800 Hz. 

(c) Capacitance $C$ as a function of frequency with $C' = 0.20$ mF at $10^2$ Hz and $C'' = 0.10$ mF at $10^4$ Hz. 

(d) Power density $P$ and energy density $E$ at potentials of 0.8 to 0.8 V and -1.4 to 1.4 V. 

(e) Potential-time profiles for single device, two devices in tandem, and two devices in parallel. 

(f) Potential-time profiles for each configuration at different potential ranges. 

(g) Capacitance retention as a function of number of cycles for potentials of 0.8 to 0.8 V and -1.4 to 1.4 V.
the enlarged plot in the high frequency region. (b) Bode plot. (c) Real ($C'$) and imaginary ($C''$) portion of complex capacitance. (d) Ragone plot. (e) and (f) GDC curves of a single device and two devices connected in series and in parallel, tested in NPW and WPW, respectively. (g) 10,000 cycle GDC testing within both a NPW (black) and WPW (red).

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<th>$C_V$ (F cm$^{-3}$)</th>
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</thead>
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<td>NPL in this work</td>
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<td>733/833</td>
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<td>246</td>
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<td>MWCNTs$^{11}$</td>
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<td>132</td>
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</table>

Table 3.2. ECs performance of the NPL compared with state-of-the-art thin film or flexible electrodes for supercapacitors.
Figure 3.16. Microscopy observation of the NPL after 10,000 GDC cycles. (a,b) SEM cross sectional images with different magnifications. (c,d) TEM images.
Figure 3.17. Nyquist plot of the NPL after 10,000 GDC cycles. The inset shows enlarged high frequency region.

The effect of bending on the EC performance was also measured on the NPL-based devices (Figure 3.18a,b). The delivered capacitance is influenced by the bending angles in a non-linear fashion (Figure 3.18c and Figure 3.19). At bending angles of 90° and 120°, the capacitance increased to 125% and 117%, while the capacitance retention was 80% at the 180° bending angle. In addition, flexibility tests were carried out by bending a device to 180° 1000 times. The capacitance (Figure 3.18d) shows a quick drop after the initial few bending cycles and it was then maintained at 76% capacitance retention. Finally, complementary NPLs based on Fe and Co were prepared using the same fabrication technique (Figure 3.20). This underscores the generality of the anodization approach.
Figure 3.18. Flexibility tests on the NPL based EC devices. (a) Photograph of the flexible EC device while bent. (b) Schematic representation of the definition of bending angle. (c) Dependence of capacitance retention on bending angle. (d) Dependence of capacitance retention on bending cycles to 180° bending angle. The inset shows GDC curves recorded before and after bending for 500 and 1000 cycles.
Figure 3.19. Dependence of EC performance on the bending angle.
Figure 3.20. Microscopy observation of the NPL grown from different electrodeposited metals on PET substrates. (a, b) SEM images of the nanoporous layer grown on Fe/PET. (c, d) SEM images of the nanoporous layer grown on Co/PET.

3.4. Conclusion

In summary, 3-D nanoporous NiF$_2$-dominant thin film grown on PET shows good flexibility and can even be freestanding. The thin film NPL delivers exacting supercapacitive performance with a maximum capacitance of 0.29 mF cm$^{-2}$ (3.2 F cm$^{-3}$ or 1.57 F g$^{-1}$), energy density of 0.6 Wh kg$^{-1}$ and power density of 8 kW kg$^{-1}$ from
electrostatic adsorption; and a maximum capacitance of 66 mF cm\(^{-2}\) (733 F cm\(^{-3}\) or 358 F g\(^{-1}\)), energy density of 384 Wh kg\(^{-1}\) and power density of 112 kW kg\(^{-1}\) from faradaic reactions. Flexibility and cyclability tests show that the nanoporous layer maintains its high performance, which is an important advance in flexible devices. The designed approach has the potential of being applied to the fabrication of other metal NPLs.

3.5. Reference

77. Schaedler, T. A.; Jacobsen, A. J.; Carter, W. B. Science 2013, 341, 1181.
3.6. Experimental Contributions

Gedeng Ruan and Dr. Yang Yang designed the concept. Gedeng Ruan designed the solid electrolyte membrane and did the BET and XPS analysis. Dr. Yang Yang developed the procedure of preparing nanoporous NiF$_2$, did the device assembly and took the electrochemical measurements.
Chapter 4

Growth of Graphene from Food, Insects and Waste

This chapter was copied from reference 37.

4.1. Introduction

Graphene, in its monolayer form, is an attractive two-dimensional material with an atomically thick honeycomb structure.\textsuperscript{1-3} Due to its extraordinary electrical,\textsuperscript{4} mechanical,\textsuperscript{5} thermal\textsuperscript{6} and spintronic\textsuperscript{7} properties, graphene has the potential to be applied in nanoelectronic devices\textsuperscript{8,9} and in nanocomposites.\textsuperscript{10,11} In the past years, many methods for production of graphene, such as exfoliation, chemical methods, and chemical vapor deposition (CVD), have appeared in the literature. For the exfoliation methods, researchers originally used adhesive tape to mechanically peel away the graphite crystals into few-layer or monolayer graphene.\textsuperscript{1,4} Later, liquid exfoliation methods\textsuperscript{12-14} were reported, consisting of chemical oxidation and dispersion of graphite, reduction of
graphite oxide, and annealing in Ar/H$_2$. Although it could become an industrially important method to produce graphene, until now the quality of this liquid exfoliated graphene is still lower than mechanically exfoliated graphene due to the destruction of the basal plane structure during the oxidation and incomplete removal of the functional groups. Recently, many research groups have published several CVD methods for growing large-sized graphene on wafers. For the growth of epitaxial graphene on single-crystal silicon carbide (SiC), the cost of this graphene is high due to the price of the 4H-SiC substrate. Also, metals such as copper, nickel, iron, cobalt, and platinum have been used as catalytic substrates to grow mono-, bi- or multilayer graphene. The carbon source can be a gas, such as methane or acetylene, or solid carbon sources, such as poly(methyl methacrylate) (PMMA) or sucrose. However, all of these are purified chemicals.

Here we demonstrate that much less expensive carbon sources, such as food, insects and waste, can be used without purification to grow high-quality monolayer graphene directly on the backside of Cu foils under the H$_2$/Ar flow. For food, a Girl Scout cookie and chocolate were investigated. For waste with low or negative monetary value, we used bulk polystyrene plastic, a common solid waste, blades of grass and dog feces. For insects, another often negative value carbon source, a cockroach leg was used. Growing high-quality graphene from these carbon sources opens a new way to convert the waste carbon into a high-value-added product, as graphene is one of the most expensive materials in the world. We propose a possible purification and growth mechanism. The graphene forms as the solid carbon sources decompose and diffuse to the backside of the Cu foil, leaving the other elemental residues on the original side.
Using this procedure, only high quality pristine graphene with few defects and ~97% transparency was grown on the backside of the Cu foil, as confirmed by Raman and UV-Vis spectroscopy. No heteroatoms were detected in the monolayer graphene according by X-ray photoelectron spectroscopy (XPS), suggesting its pristine nature. Analysis by selected area diffraction pattern (SAED) in transmission electron microscopy (TEM) confirms the hexagonal lattice structure of the graphene.

4.2. Experimental Section

4.2.1. Growth and Transfer of Graphene Samples

Six different carbon sources were used: Girl Scout Cookie (the Girl Scouts of America Troop 25080 from Houston, Texas, provided the cookies, shortbread flavor), chocolate (Chocolate Kennedy Half Dollar Gold Coins), grass (Ophiopogon picked at Rice University), plastic (Fisherbrand polystyrene Petri dishes, catalog # 08-757-12), dog feces (Miniature Dachshund) and a cockroach leg (American cockroach caught in a house). The grass and the dog feces were dehydrated in a vacuum oven (102 Torr) at 65 °C for 10 h before being used in the growth process.

The CVD system was evacuated to 10 mTorr for 10 h before growth. For the growth of graphene, 10 mg of a carbon source was placed atop the Cu foil (99.8% purity). The Cu foil was slightly bent to better retain the solid sources without spilling. The foil was then supported by the steeper-curved quartz boat as shown in Figure 4.1. The sample was annealed at 1050 °C for 15 min with Ar flow at 500 cm³ STP min⁻¹ and H₂ flow at 100 cm³ STP min⁻¹. The pressure was 9.3 Torr during growth. When growing
graphene from different carbon sources, the quartz tube and boat were cleaned by annealing them at 1050 °C in air for 10 min between each growth to eliminate the cross contamination. The system was then fast cooled (moved to the cool zone using a magnetic transfer rod) to room temperature under the H₂/Ar flow. A 100 nm-thick PMMA film was deposited on the backside of the foil using a 4% PMMA anisole solution spin-coated at 3000 rmp for 40 s. The frontside of the Cu foil was etched away by floating the foil metal-down on an acidic CuSO₄ solution (made with CuSO₄·5H₂O (15.6 g), con. HCl (50 mL), H₂O (50 mL) and H₂SO₄ (2 mL)) for ~5 s, then dipping the foil in DI water; this process was repeated at least two times in order to wash away the residue left on the frontside of the Cu foil. If the water washes did not remove the residue from the frontside of the Cu foil, a Chemwipe was used to carefully brush the residue away before all of the Cu was removed. The PMMA-coated graphene was transferred to different substrates such as 100 nm SiO₂/Si wafers and quartz. After the film was completely dried in a vacuum oven at 65 °C for 2 h, the film was rinsed with acetone 3× before characterization.
Figure 4.1. Arrangement of the Cu foil within the quartz boat. The size of the Cu foil was ~2 cm × 1.5 cm and the boat was 40-cm-long and cut from a quartz tube with a 15 mm inside diameter.

4.2.2. Characterization.

Raman spectra were obtained by the single scan generated by the WiRE spectral acquisition wizard using a 514.5 nm laser in a Renishaw Raman RE02 microscope. UV-Vis spectroscopy was done using a 1-mm-thick quartz slide on which the sample was placed in a Shimadzu UV-3101 system. The XPS were obtained using a 100 µm X-ray beam of the 45° take-off angle and 26.00 eV pass energy in a PHI Quantera SXM scanning X-ray microprobe system. TEM imaging was obtained in a 2100F field emission gun transmission electron microscope. The graphene samples were transferred to a C-flat TEM grid (Protochips).

4.3. Results and Discussion
In a typical growth experiment, as shown in Figure 4.2A, 10 mg of the dry carbon source was placed atop a Cu foil, and the foil was introduced into a 1050 °C tube furnace. The sample was annealed for 15 min under low pressure with H$_2$ and Ar at a flow rate of 100 cm$^3$ STP min$^{-1}$ and 500 cm$^3$ STP min$^{-1}$, respectively. For the grass and dog feces, the samples were heated in a 65 °C vacuum (102 Torr) oven for 10 h to remove excess moisture. The experimental setup and procedures are similar to the method used to grow PMMA-derived graphene.$^{24}$ The main difference in this work is that the high quality monolayer graphene only forms on the backside of Cu foil, while the PMMA-derived graphene grows on both sides of the Cu foil.

![Diagram of the experimental apparatus for the growth of graphene from food, insects or waste in a tube furnace.](image)

Figure 4.2. (A) Diagram of the experimental apparatus for the growth of graphene from food, insects or waste in a tube furnace. On the left, the Cu foil with the carbon source contained in a quartz boat is placed at the hot zone of a tube furnace. The growth is performed at 1050 °C under low pressure with a H$_2$/Ar gas flow. On the right is a cross view that represents the formation of pristine graphene on the
backside of the Cu substrate. (B) Growth of graphene from a cockroach leg. (a) One roach leg on top of the Cu foil. (b) The roach leg under vacuum. (c) The residue from the roach leg after annealing at 1050 °C for 15 min. The pristine graphene grew on the bottom side of the Cu film (not shown).

Since the carbon sources contain non-carbon elements, non-volatile residue may remain on the Cu foil after annealing. Figure 4.3 shows SEM images of both sides of the Cu foil after a growth experiment. On the original frontside, many residual particles were found, as shown in Figure 4.3A, while almost no particles were observed on the backside of the Cu foil where the graphene is formed (Figure 4.3B). In Figure 4.2B, photographic images of different growth stages are shown and black residue is present after the growth in Figure 4.2Bc. Based on the experimental evidence during the growth, most of the carbon segments from the decomposition of the solids are carried away as gases by the H$_2$/Ar flow. However, since the quartz boat has a semicircular shape, the slightly bent Cu foil is supported by the quartz boat and a portion of the carbon source diffused to the backside of the Cu foil, forming a monolayer graphene film. It is not known whether the diffusion is through the Cu foil or via the edges. As a comparison experiment, if the solid carbon sources were placed 5 cm ahead of the Cu substrate (but still in the quartz boat) and both were introduced into the hot furnace at the same time, only amorphous carbon formed on both sides of the Cu foil; the representative Raman spectrum of the film displays a large D peak as shown in Figure 4.4.
Figure 4.3. SEM images of the Cu foil after growth of graphene from a Girl Scout cookie. (A) The original frontside of the Cu foil; there was a large quantity of particle residue after the pyrolysis of the cookie. (B) The backside of the Cu foil.

Figure 4.4. Representative Raman spectrum of amorphous carbon grown on the backside of Cu foil when the Girl Scout cookie fragments were placed 5 cm ahead of the Cu foil in the tube furnace.
After the monolayer graphene samples on the backside of the Cu foil were transferred onto a 100 nm SiO$_2$/Si wafer using standard protocols, the product was analyzed using Raman spectroscopy at 514 nm laser excitation. As shown in Figure 4.5, all of the graphene samples grown have small or no D peaks in their Raman spectra, an indication of few graphene defects. The large 2D/G ratio suggests that it is high quality monolayer graphene. The exact G and 2D peak positions and their full-width at half-maximum (FWHM) for each spectrum were measured and are summarized in Table 4.1; the results are similar to the reported data. The G and 2D peaks are located at 1585.5-1591.4 cm$^{-1}$ and 2682.6-2693.9 cm$^{-1}$, respectively. The FWHM of the G peak and 2D peak are 14.1-16.3 cm$^{-1}$ and 32.0-35.1 cm$^{-1}$, respectively. In order to investigate the uniformity of the graphene film, a Raman mapping over a 100×100 µm$^2$ area (graphene derived from dog feces) was acquired. Over 95% of the scanned area had a signature of $I_{2D}/I_G > 1.8$ and $I_D/I_G < 0.1$, which further demonstrated the high quality of the monolayer graphene, as shown in Figure 4.6.
Figure 4.5. Raman spectra of monolayer graphene from six different carbon sources. The Raman spectra graphene were derived from (A) Girl Scout cookie; (B) chocolate; (C) grass; (D) plastic (polystyrene Petri dish); (E) dog feces and (F) a
cockroach leg. There was only a trace D peak in some of the spectra, and the 2D to G peak intensity ratios were ~ 4, indicating monolayer graphene.

<table>
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<th>Carbon source</th>
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<th>2D peak (cm(^{-1}))</th>
<th>2D peak FWHM (cm(^{-1}))</th>
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</thead>
<tbody>
<tr>
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<td>14.1</td>
<td>2682.6</td>
<td>32.0</td>
</tr>
<tr>
<td>Chocolate</td>
<td>1591.4</td>
<td>15.9</td>
<td>2693.9</td>
<td>32.6</td>
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<tr>
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<td>1587.7</td>
<td>15.8</td>
<td>2685.7</td>
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<td>16.3</td>
<td>2689.7</td>
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</tr>
<tr>
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<td>1588.4</td>
<td>14.6</td>
<td>2687.4</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Table 4.1. The wavelength number of the G and 2D peak, and their FWHM for graphene samples derived from six different carbon sources.

Figure 4.6. Raman spectra mapping of graphene from dog feces. The scanning was performed at every 5 µm over an area of 100 µm × 100 µm. (A) Raman spectral
mapping of 2D/G ratio, over 95% of the scanning area has the signature of $I_{2D}/I_G > 1.8$. (B) Raman spectral mapping of D/G ratio; note that over 95% of the scanning area has the signature of $I_D/I_G < 0.1$. This is confirmation of high-quality monolayer graphene.

XPS analysis of the graphene films was performed to confirm the elemental composition and the chemical environment of the C atoms. In Figure 4.7, only a sharp peak at 284.5 eV with an asymmetric tailing towards high bonding energy is observed for C1s peak, suggesting a sp$^2$ graphitic peak.$^{28-30}$ The FWHM was $\sim 1.1$ eV for each C1s peak. Although the raw carbon sources contain other elements such as oxygen, nitrogen, iron, sulfur, or phosphorus, the obtained graphene consisted of carbon, with none of these other elements found in the XPS survey spectra, confirming the graphene’s pristine composition.
Figure 4.7. XPS spectra of graphene from six carbon sources. The C1s XPS spectra of the randomly selected detection spots on graphene derived from the various sources.

In the growth system, the $\text{H}_2$ gas might act as both a reducing reagent and a carrier gas. Since carbon is the most abundant element in these materials and graphene is the most thermodynamically stable form of carbon, only pristine graphene forms on the
Cu. According to the C-C bond length (0.142 nm) in the hexagonal lattice of graphene, \(^{32}\) the surface area of one side of a monolayer of graphene is about 1315 m\(^2\)/g. \(^{33}\) Theoretically, it only takes 228 ng of carbon to cover one side of a 2 cm \(\times\) 3 cm Cu foil with monolayer graphene. In our growth system, the size of the graphene is ultimately limited by the size of the tube furnace, which limits the size of the Cu substrate that can be used. With a larger furnace, larger-sized graphene could be produced with 10 mg of the carbon source. Therefore, the limiting reagent in this work is the Cu foil, though scrolled Cu foil could provide enhanced surface areas.

All the graphene films were transferred to a quartz slides before UV-Vis analysis. In the spectra, each graphene film exhibits a peak at 268 nm, a typical \(\pi\rightarrow\pi^*\) transition for the aromatic C-C bond in graphene,\(^ {34,35}\) and the typical (2.4\% ± 0.1\%) absorption at 550 nm corresponding to the monolayer nature of graphene,\(^ {24,36}\) as shown in Figure 4.8. In the photographic images, the graphene films on quartz slides are uniform and transparent. Also, the sheet resistance (\(R_s\)) of the graphene was in the range of 1.5 - 3.0 k\(\Omega\)/square by the four-probe method.
Figure 4.8. UV-Vis spectra of graphene derived from six carbon sources. The absorbance of each monolayer graphene film at 550 nm is approximately (2.4% ± 0.1%). On the right top of each spectrum is the photographic image of the
monolayer graphene film of \( \sim 1 \text{ cm} \times 1 \text{ cm} \) in size on a 1-mm-thick quartz slide, labeled with a dashed square.

TEM images and the selected area electron diffraction (SAED) pattern were taken to determine the crystal structure of a representative graphene sample derived from the cookie. The graphene was transferred to a c-flat TEM grid (Protochips), where most of the area of the graphene was determined to be crystalline by its hexagonal diffraction pattern (Figure 4.9A) and was continuous as shown in Figure 4.9B. A randomly chosen monolayer edge of the graphene was imaged in Figure 4.9C. The thickness of the graphene corresponds to monolayer graphene, corroborating the UV-Vis spectra and Raman data. The dark spots in the image in Figure 4.9C might arise from the PMMA residues introduced during the etching and transferring step.\(^{24}\)

![Figure 4.9](image.png)

**Figure 4.9.** Diffraction pattern and TEM images of the cookie-derived graphene. (A) SAED pattern, (B) suspended graphene film on a 1 \( \mu \text{m} \) diameter hole and (C) the edge of monolayer graphene.
4.4. Conclusion

We have demonstrated a general method to grow high-quality graphene from various raw carbon materials at 1050°C under vacuum and H₂/Ar flow. The carbon sources were foods (cookie and chocolate), waste (grass, plastic, dog feces) and insect-derived. With this technique, many kinds of solid materials that contain carbon can potentially be used without purification as the feedstocks to produce high-quality graphene without pre-purification. Furthermore, through this method, low-valued foods and negative-valued solid wastes are successfully transformed into high-valued graphene which brings new solutions for recycling of carbon from impure sources.

4.5. Reference


### 4.6. Experimental Contributions

Gedeng Ruan developed the procedure of growth of graphene from food, insects and waste and performed fundamental characterizations (XPS, Raman, and UV-VIS). Zhengzhong Sun took the SEM and TEM images. Zhiwei Peng helped the CVD process.
Chapter 5

Functionalized Graphene Nanoribbons via Anionic Polymerization Initiated by Alkali Metal-Intercalated Carbon Nanotubes

This chapter was copied from reference 23.

5.1. Introduction

Due to their interesting electronic and mechanical properties, graphene nanoribbons (GNRs) have attracted attention for use in the preparation of conductive composites, and several techniques have been explored to synthesize bulk quantities of functionalized GNRs.\(^1\) GNRs have been obtained through oxidative unzipping of multiwalled carbon nanotubes (MWCNTs) using potassium permanganate and sulfuric acid,\(^2\) by intercalating lithium into MWCNTs followed by thermal expansion\(^3\) and by longitudinal splitting of MWCNTs using transition metal clusters.\(^4\) GNRs have also been prepared via intercalation of potassium into MWCNTs\(^5,6\) or expansion of MWCNTs
using molecular nitrogen. In order to produce conductive and mechanically reinforced GNR composites, the GNRs must be well-dispersed in the polymer matrix, and to this end, functionalization of the GNRs is critical. However, the existing approaches do not generate bulk quantities of GNRs functionalized with addends that render the products well-dispersible in polymer matrices. Here, we demonstrate that, in analogy to the intercalation chemistry of graphite, potassium intercalation into MWCNTs followed by in situ reaction with vinyl monomers results in exfoliation of the MWCNTs and subsequent splitting with functionalization into polymer-functionalized GNRs (PF-GNRs) in a one-pot solution-based process. These polymer addends provide enhanced integration between the GNRs and polymer matrices. Furthermore, since polymerization is mainly initiated from GNR edges, the basal planes can remain sp²-hybridized. This stands in contrast to the covalent functionalization of carbon nanotubes where the functionalized nanotubes must contain sp³-hybridized carbons at all functionalization sites. We also correlate the exfoliation of MWCNTs with the structural characteristics of the starting materials and the intrinsic properties of the intercalants. This scalable and low-cost approach to functionalized GNRs produces materials that could be useful for transparent electrodes and heat circuits, electroactive polymer/graphene supercapacitors, and conductive nanocomposites.

5.2. Experimental Section

MWCNTs were obtained from Mitsui & Co. (lot no. 05072001K28), NanoTechLabs, Inc. (lot no. #5T10M10), or Bayer MaterialScience (lot no. C720P) and they were used as received. THF was treated with potassium hydroxide for several days,
degassed and freshly distilled over sodium/benzophenone under nitrogen atmosphere. Styrene was passed through a neutral alumina column and then degassed before use. Isoprene was distilled under a nitrogen atmosphere. All chemicals were purchased from Sigma-Aldrich unless otherwise specified.

TG-MS measurements were performed using a Netzsch449 F3 Jupiter® instrument under a dynamic Ar (99.999 %) flow with a flow rate of 60 mL/min in a temperature range from 25°C to 900 °C. A heating rate of 10 °C/min was used. About 5 mg of the sample was placed in an alumina (Al₂O₃) crucible. Simultaneous MS used a MS 403CAëolos® with a detector secondary electron multiplier Chenneltron at a system pressure of 2x10⁻⁵ mbar. Gasses evolved under TG heat treatment were transferred to a MS detector using a quartz transfer capillary with an inside diameter of 75 µm that was heated to 220 °C. The upper limit of the MS detector was 100 amu. Raman spectroscopy was done using a Renishaw Raman RE01 microscopy with a 514.5 nm laser. The PF-GNRs were dispersed in ortho-dichlorobenzene using mild bath sonication (Cole-Parmer, EW-08849–00); the suspension was drop-cast onto Si chips with a 500 nm-thick SiO₂ layer, then the solvent was evaporated upon heating, and the sample was imaged using a JEOL 6500 field-emission microscope and 2100F field emission gun transmission electron microscope.

To prepare PF-GNRs, 0.1 g of alkali metal (Li, Na, or K), 0.256 g of naphthalene and 50 mg of MWCNTs (Mitsui MWCNTs, NTL MWCNTs or Baytubes) were added to a 100 mL oven dried Schlenk flask. 50 mL of THF was added. The flask was capped and the suspension was subjected to three freeze-pump-thaw cycles to remove oxygen. The reaction mixture was stirred at room temperature for 3 d and 20 mL of monomer (styrene
or isoprene) was added dropwise while cooling in a dry ice/acetone bath. The mixture was stirred at room temperature for 1 d and then the reaction mixture was quenched by 20 mL of anhydrous ethanol. The gray precipitate was filtered through a polytetrafluoroethylene (PTFE) membrane (0.45 µm), followed by extraction with boiling chloroform in a Soxhlet extractor for 1 week to remove unbound polymer. The final product (55 mg of PF-GNRs) was collected on a PTFE membrane (0.45 µm), washed with THF (3 × 100 mL), ethanol (3 × 100 mL), DI water (3 × 100 mL), and acetone (50 mL), ether (50 mL), and dried in vacuum oven at 60 °C overnight.

5.3. Results and Discussion

The synthetic strategy for the one-pot synthesis of PF-GNRs used in the present study is shown in Figure 5.1. MWCNTs were converted into edge-negatively charged polymerization macrorinitiators via intercalation and splitting. It is assumed, based on the proposed mechanism, that the edges of the split tubes are lined by aryl anions and their associated metal cations. Second, anionic polymerization of vinyl monomers starting at the negatively charged GNR edges results in PF-GNRs. An analogous alkylation with alkyl halides was recently disclosed with Na/K. While the vapor phase intercalation of MWCNTs was reported earlier, the potassium naphthalenide liquid-phase intercalation will be described here along with the subsequent polymerization methodology. Briefly, MWCNTs, potassium metal, naphthalene and THF were added to a Schlenk flask and subjected to three freeze-pump-thaw cycles to remove oxygen. As suggested by our previous work, the intercalation of solvent-stabilized potassium cations into MWCNTs may lead to expansion of the d-space between MWCNT layers, causing the MWCNTs to
partially or fully split. The fissures in the sidewalls of the MWCNTs serve as the starting points for vinyl monomers, such as styrene isoprene, or ethylene oxide in the present case, to anionically polymerize from the GNR edges. Due to polymerization probably proceeding between the GNR layers, only a small amount of olefin was needed to effect the exfoliation of the MWCNTs. The non-attached polymer was removed by extracting the raw product with boiling chloroform in a Soxhlet extractor.

Figure 5.1 Reaction scheme for the one-pot synthesis of functionalized GNRs. (a) The MWNTs are intercalated with potassium naphthalenide (blue dots). (b) A longitudinal fissure is formed in the walls of the MWCNTs due to expansion caused by intercalation of THF-stabilized potassium ions into the MWCNT host. The edge radicals would be immediately reduced to the corresponding anions under the
reducing conditions. (c) Polymerization of styrene (for instance) assists in exfoliation of MWCNTs. (d) PF-GNRs are formed upon quenching.

Scanning electron microscopy (SEM) was used to image the MWCNTs after intercalation and polymerization. PF-GNRs with widths in the range of several hundred nm are clearly shown in Figure 5.2 (See Figures 5.3 - 5.5 for additional images). These PF-GNRs are far more suspend-able (soluble) in THF than the regular GNRs due to the polymer addends (See Figure 5.4(c) for the photos).

Figure 5.2. Representative SEM image of MWCNTs treated with potassium naphthalenide followed by addition of styrene (See Figure 5.3 for SEM images of Mitsui MWCNTs treated with potassium naphthalenide followed by addition of isoprene). GNRs can be readily identified under SEM; their widths are in the range of several hundred nm. The amorphous material wrapping the GNRs or extending across neighboring GNRs is polystyrene.
Figure 5.3. SEM image of Mitsui MWCNTs: (a) low-magnification and (b) high-magnification. The spherical nanoparticles are amorphous carbon. According to previous work,\textsuperscript{2,3} thermal annealing at 2800 °C under argon atmosphere improved not only the structural integrity of those carbon nanotubes but also removed polyaromatic hydrocabons and a significant amount of iron nanoparticles. The mean diameter of those tubes is 81 ± 5 nm and the mean length is 8.19 ± 1.7 μm.
Figure 5.4. (a) Overview of a large area showing the conversion of MWCNTs to GNRs through liquid-phase intercalation of Mitsui MWCNTs followed by addition of styrene. (b) TEM image of the edge structure of 6-layer GNRs; the red arrow points to the edge. (c) Comparison of solubility of 10 mg PS-GNR and 10 mg GNR in 15 mL THF. After functionalization, PS-GNRs could be well dispersed in THF (Left), while the regular GNRs could not be dispersed in THF (Right).
Figure 5.5. SEM image of Mitsui MWCNTs treated with potassium naphthalenide followed by addition of isoprene. The ribbon-like structure can be easily identified, as indicated by the red dashed circles. The blue rectangle indicates an exfoliated MWCNT that is partially split. Since the sample was imaged before extraction with chloroform, the amorphous polymer domains are present.

Thermogravimetric mass spectrometry (TG-MS) was used to confirm the presence of the polystyrene chains, to estimate the quantity of the repeat units, and to determine the temperature window of degradation of the PF-GNRs. To exclude the influence of the surface physisorbed components, all of the PF-GNRs were extracted with chloroform in a Soxhlet extractor for 1 week and then dried at 60 °C overnight. The thermogravimetric analysis (TGA) thermogram (Figure 5.6a) indicates a one-step
weight-loss process with a total weight loss of 9% between 100 and 900 °C. Major decomposition occurs between 384 and 474 °C. According to MS analysis and a previous report, this is the range where depolymerization of the polystyrene occurs. Charged molecule fragments with mass to charge ratios (m/z) 78, 77, 51, and 50 were observed, with intensities that are distinct for the styrene monomer, one of the expected degradation products. A control experiment with starting MWCNTs was also performed where no weight loss was observed (blue curve in Figure 5.6a). Based on the weight loss between 384 and 474 °C, the weight ratio between the styrene monomer unit and carbon atoms of the graphene material was 1:136. If all of the edge carbons of the graphene nanoribbons were functionalized, this data would indicate that the average polymer chain length was only 9 units for a 3 µm × 150 nm ribbon, but it is unlikely that all sites had equal exposures to the monomer, so dramatically varied chain lengths are presumed. However, further definition of this point is not easily obtained, nor is it in the ultimate interest of our study.

Raman spectroscopy was also used to characterize the graphitic structure of the PF-GNRs. An increase in the intensity of the D band over the G band from 0.15 for MWCNTs to 0.35 for PF-GNRs was observed in Figure 5.6b. Upon splitting of MWCNTs, a prominent D peak is an indication of disorder in the graphene structure due to the high edge content. The disordered structure also results in a slight broadening of the G band and the 2D band, as well as the combination mode of D + G band at ~2700 cm⁻¹ in PF-GNRs. However, splitting of the G band, corresponding to an intercalated graphitic structure, is not observed in the Raman spectrum, implying that little residual intercalants, if any, or solvents were between the PF-GNRs. X-ray
photoelectron spectroscopy (XPS) was used to examine the PF-GNR surface functionalities. The survey spectrum in Figure 5.6c shows that no oxygen was detected in the PF-GNRs. This is further confirmed by the high-resolution XPS C1s spectrum in the inset of Figure 5.6c, as no peaks corresponding to 286 eV (C–O) or 287 eV (C=O) were observed.²
Figure 5.6. Characteristics of PF-GNRs. (a) 3D TG-MS spectra of the gas phase in the thermal degradation of PF-GNRs and MWCNTs. Different colors represent gas...
products with different $m/z$ in which $m$ is the mass of the gas products and $z$ is the charge. The black and blue curves correspond to the TGA profile of PF-GNRs and starting MWCNTs, respectively. (b) Raman spectra of PF-GNRs and MWCNTs. (c) XPS survey spectrum of PF-GNRs. The inset is high-resolution XPS C1s spectrum of PF-GNRs, indicating PF-GNRs are nearly free of oxidation.

To further explore polymerization initiated by reactive GNR anions, MWCNTs were potassium vapor-treated at 350 °C for 24 h. The product was transferred to a round-bottom flask in the glove box and styrene was added dropwise. The reaction mixture was kept at room temperature for 24 h and then at 60 °C overnight to complete the polymerization. The potassium intercalated MWCNTs were fluffy and randomly distributed inside the flask. Addition of styrene monomer led to plastic beads with black centers, indicating the growth of polystyrene on partially split GNRs, as shown in Figure 5.7a. Some ribbon-like structures were identified in Figure 5.7b (see Figure 5.8 for additional images). The TGA in Figure 5.7c shows that the weight loss was 22% (after extensive Soxhlet extraction with chloroform), four times higher than that of MWCNTs treated in the liquid-phase intercalation process.
Figure 5.7. Characteristics of potassium vapor treated MWCNTs quenched with styrene. (a) Photograph of the polymerization of styrene initiated by potassium-vapor-treated MWCNTs. (b) Representative SEM image of split MWCNTs. The majority of MWCNTs were split and ribbon-like structure could be identified in the image (see Figures 5.8 for SEM images of Mitsui MWCNTs treated with potassium vapor followed by addition of isoprene). (c) 3D plot of the TG-MS results of PF-GNRs and MWCNTs. Different colors represent gas products with different m/z.
The black and blue curves correspond to the TGA profile of PF-GNRs and MWCNTs, respectively.

Figure 5.8. (a) SEM image of Mitsui MWCNTs treated with potassium vapor followed by addition of isoprene. Most MWCNTs are split but they are not fully exfoliated to form GNRs. The ribbon-like structure and split MWCNTs bridged by polymer domains can be observed. Highlighted here (red dashed circle) is a partially exfoliated tube associated with GNRs. (b) TEM image of an isolated PF-GNR sitting atop of a lacy carbon grid. (c) TEM image of the edge structure of multi-stack PF-GNRs.
To explore the flexibility of the present protocol, ring opening polymerization using ethylene oxide was also performed and poly(ethylene oxide)-functionalized GNRs could be obtained. Two other sources of MWCNTs, NanoTechLabs MWCNTs (NTL MWCNTs) and Bayer MWCNTs (Baytubes), were subjected to the reaction to compare the results to those from the Mitsui MWCNTs used for the former two experiments. Upon liquid-phase intercalation followed by polymerization, NTL MWCNTs were split but not further flattened to form GNRs (Figure 5.9a). With the Baytubes MWCNTs, although some partially flattened GNRs could be identified, most of the MWCNTs remained intact (Figure 5.9b).

Figure 5.9. (a) SEM image of NTL MWCNTs treated with potassium naphthalenide in THF followed by addition of styrene. The majority of NTL MWCNTs are split but they are not completely flattened to form ribbon-like structure (see Figures 5.10 for SEM images of pristine NTL MWCNTs). (b) SEM image of Baytubes treated with potassium naphthalenide in THF followed by addition of styrene. Some of the MWCNTs are split due to intercalation followed by polymerization but many others
retain their tube-like structure (see Figure 5.11 for SEM image of pristine Baytubes).

Figure 5.10. SEM image of NTL MWCNTs: (a) low-magnification and (b) high-magnification.

Figure 5.11. SEM image of pristine Baytubes that are highly defective.
Generally, the charge transfer from naphthalene radical anions to the graphitic structure is governed by the electronic state of the host material. If the host materials are highly crystalline, overlap of the valence and conduction bands could lead to two carriers, electrons and holes, in the conjugated graphene plane. Therefore, the electrons, during intercalation, can be transferred from the potassium naphthalenide to the host to balance the concentration of holes, and then into the graphene conduction band. Consequently, well-defined graphite intercalation compounds (GICs) can be obtained from highly crystallized hosts. For materials with a low degree of crystallinity, unorganized intercalation structures are observed since there is no overlap between the conduction band and the valence band due to the disrupted graphitic structures. Previous work on exfoliation of GICs suggests that forming a well-defined intercalation structure could be a prerequisite for making exfoliated GNRs via polymerization-assisted exfoliation of MWCNTs. The important link between the structural characteristics of the MWCNTs host and splitting and exfoliation of MWCNTs has been less explored, despite the fact that Mordkovich et al. studied the scroll carbon nanotubes by intercalating potassium metal into carbon nanotubes. The degree of graphitization can be calculated from the interplanar \( d \) spacing between two graphitic layers, according to eq 1.\(^{18}\)

\[
g = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \quad (eq \ 1)
\]

where \( g \) is the degree of graphitization, 0.3440 (nm) is the interlayer spacing of the fully non-graphitized carbon; 0.3354 (nm) is the \( d \) spacing of the ideal graphite crystallite and \( d_{002} \) (nm) derived from X-ray diffraction (XRD) is the interlayer spacing corresponding to (002) planes of the graphitic material. For Mitsui MWCNTs and NTL
MWCNTs, \( g = 0.58 \), which is higher than that for Bayer MWCNTs, where \( g = 0.23 \) (Figure 5.12), indicating that more facile exfoliation of the carbon host would be possible with Mitsui and NTL nanotubes. Note that the presence of any disordered structures caused by \( \text{sp}^3 \)-hybridized carbons or defects that could terminate the splitting or exfoliation of MWCNTs cannot be determined from XRD patterns. Consequently, Raman spectroscopy was used to differentiate the degree of disordered structure in the host materials by calculating the ratio of the intensity of the D band to the G band.\(^{19}\) The relative intensity of disorder-induced D band to crystalline G band, \( I_D/I_G \), is 0.15 for Mitsui MWCNTs, 0.27 for NTL MWCNTs, and 0.92 for Baytubes, as shown in Figure 5.12b. Defect sites on graphite do not favor the formation of well-defined intercalation structure\(^{14}\) and thus the complete exfoliation of highly defective Baytubes by intercalation is likely more difficult (See Figure 5.13 for TEM images). This is corroborated by recent work on reductive alkylation of MWCNTs with potassium naphthalenide, in which the outer surface of highly defective MWCNTs (\( I_D/I_G > 1 \)) were functionalized with decanoic acid and no ribbon-like structure was observed in the SEM images.\(^{20}\) Although NTL MWCNTs have fewer defects, flattening ultra-long split tubes may require further treatment. Thus, most NTL MWCNTs remained split and stacked rather than completely flattened (See Figure 5.14 for TEM images). It is difficult to precisely establish the structural threshold (i.e. the critical value for \( g \) or \( I_D/I_G \)) that can be used to predict if the MWCNTs can be split and exfoliated; however, it is noteworthy that the higher the degree of graphitization of the carbon host, or the less defective the carbon host, the easier the exfoliation of the MWCNTs \textit{via} intercalation.
Figure 5.12. Spectral fingerprints from three different MWCNT sources. (a) XRD patterns of Mitsui MWCNTs, NTL MWCNTs and Baytubes. The $d_{002}$ was calculated according to Bragg’s equation $\lambda = 2d \sin \theta$, where $\lambda$ is 1.54 Å for Cu Kα. (b) Raman spectra of Mitsui MWCNTs, NTL MWCNTs and Baytubes. Baytubes have the highest $I_D/I_G$, indicating the most defective graphitic structure. Also present is the combination of $G+D$ band$^{12}$ induced by disorder structure, which is not observed in Mitsui MWCNTs or NTL MWCNTs.
Figure 5.13. (a) Overview of a large area showing Baytubes treated with potassium naphthalenide followed by addition of styrene. (b) An image of isolated treated Baytubes. The majority of Baytubes remain tube-like structure and they are not split to form GNRs.

Figure 5.14. Two representative TEM images of isolated NTL MWCNTs treated with potassium naphthalenide followed by addition of styrene. The majority of NTL MWCNTs are split but they are not completely flattened to form GNRs.
Similar to the degree of graphitization of the starting carbon nanotubes, the ionization potential and the atomic size of the alkali metals also play an active role in intercalation and subsequent exfoliating. Since sodium naphthalenide and lithium naphthalenide have been used to make GICs\textsuperscript{18,21} and they are also commonly used as initiators for anionic polymerization, the intercalation of solvent-stabilized sodium and lithium into MWCNTs for making functionalized GNRs was explored.

However, neither of the reaction products contained significant numbers of exfoliated MWCNTs; most of the MWCNTs remained intact, as shown by the SEM images in Figure 5.15. Both lithium and sodium failed to form significant fissures on MWCNTs for subsequent exfoliation assisted by polymerization, as discussed in our previous work.\textsuperscript{5}

![Figure 5.15. Representative SEM images of styrene treated alkali-metal intercalated MWCNTs. (a) SEM image of MWCNTs treated with sodium naphthalenide followed by styrene. (b) SEM image of MWCNTs treated with lithium naphthalenide followed by styrene. Clearly, most MWCNTs remained intact in](image)
these two cases, due to the fact that sodium naphthalenide or lithium naphthalenide failed to form fissure structures on MWCNTs for further splitting.

5.4. Conclusion

The wet chemical preparation of high-quality PF-GNRs was achieved by polymerization-assisted exfoliation of MWCNTs in a one-pot synthesis. The in situ functionalized GNRs were examined by TG/MS, SEM, TEM and Raman spectroscopy. Compared to MWCNTs treated with potassium vapor followed by addition of isoprene, liquid-phase intercalation of MWCNTs and subsequent polymerization was more efficient in exfoliating MWCNTs to form PF-GNRs, but with less polymer bound onto the edges. Also demonstrated was the correlation between the structural characteristics of the host (the degree of graphitization and the intensity of D band over G band) and the exfoliation efficiency. The PF-GNRs or split tubes could be used for reinforcing polymers, since the sword-in-sheath type failure of MWCNTs due to interlayer slip could be retarded owing to the entangled polymer chains anchored on the edges. Through the compatibilizing appended polymer chains, the load might be effectively transferred from the polymer matrix to the rigid PF-GNRs, thus making stronger composites. In addition, it has been shown that functionalized GNRs remain conductive, since the functionalization preferably occurs on the graphene edges. Systematic studies are underway to better understand the correlation between functionalization and conductivity of the PF-GNRs for use in making reinforced conductive composites and conductive transparent films.
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5.6. Experimental Contributions

Wei Lu and Gedeng Ruan developed the procedure of functionalizing graphene nanoribbons via anionic polymerization. Gedeng Ruan did the SEM and TGA measurements. Wei Lu did Raman and XPS measurements. Bostjan Genorio and Barbara Novosel helped with the TGA-MS measurements.