PREPARATION, CHARACTERIZATION AND APPLICATIONS OF FUNCTIONALIZED CARBON NANO-ONIONS

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PREPARATION, CHARACTERIZATION AND APPLICATIONS OF FUNCTIONALIZED CARBON NANO-ONIONS

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Arts and Science at the University of Kentucky

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2013

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Carbon nano-onions (CNOs) discovered by Ugarte in 1992 are multi-layered fullerenes that are spherical analogs of multi-walled carbon nanotubes with diameters varying from 6 nm to 30 nm. Among the various methods of synthesis, CNOs prepared by graphitization of nanodiamonds (N-CNOs) and underwater electric arc of graphite rods (A-CNOs) are the subject of our research. N-CNOs are considered as more reactive than A-CNOs due to their smaller size, high curvature and surface defects.

This dissertation focuses on structural analysis and surface functionalization of N-CNOs with diameters ranging from 6—10 nm. Synthetic approaches such as oleum-assisted oxidation, Freidel-Crafts acylation and Billups reductive alkylation were used to functionalize N-CNOs to improve their dispersion properties in aqueous and organic solvents. Functionalized N-CNOs were characterized using various techniques such as TGA, TG-MS, Raman spectroscopy and pH-titrimetry. We designed an experimental method to isolate polycyclic aromatic adsorbates formed on the surface of oleum oxidized N-CNOs (ON-CNOs) and characterized them.

A-CNOs, on the other hand are bigger than N-CNOs with diameters ranging from 20—40 nm. In this dissertation, we discuss the preparation of graphene structures by unzipping of A-CNOs using KMnO₄ as oxidizing agent. These graphene structures were characterized using powder X-ray diffraction, TGA, BET nitrogen adsorption/desorption studies and compressed powder conductivity.

This dissertation also focuses on lithiation/delithiation studies of N-CNOs, A-CNOs and A-CNO-derived graphene structures to use them as negative electrode materials in lithium-ion batteries. The cycling performances of these materials at a charge/discharge rate of C/10 were discussed. The cycling performance of N-CNOs was tested at faster charge/discharge rate of C.

KEYWORDS: Nano-onions, oleum-assisted oxidation, Friedel-Crafts acylation, graphene, lithium ion batteries
PREPARATION, CHARACTERIZATION AND APPLICATIONS OF FUNCTIONALIZED CARBON NANO-ONIONS

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05/23/2013
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Dedicated to my grandmother, late Smt. Kanakamma Sreeramoju and my parents, Shri. Sambaiah Sreeramoju and Smt. Saroja Sreeramoju
ACKNOWLEDGEMENTS

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Chapter 1 Introduction

Carbon, one of the most abundant elements on the earth, plays an important role in our lives as it is the base element of all organic materials. Due to its unique ability to form allotropes, it exists in four different crystalline forms of diamond, graphite, fullerenes and nanotubes. It also exists in amorphous state in the form of charcoal, amorphous carbon, soot and glassy carbon. The hybridization of carbon in its allotropic form determines the physical and chemical properties. Diamond consist of three-dimensional networks of sp\(^3\) C atoms arranged in tetragonal manner[1] and graphite is the combination of several graphene planes held with weak van der Waals attractive forces with an interlayer distance of 3.35 Å.[2]

1.1 Fullerenes

Fullerenes (buckyballs) are the prominent spherical allotropes of carbon.[3] These were discovered by Kroto, Smalley _et al._ in 1985 while conducting experiments on vaporization of graphite by laser irradiation.[4] These closed convex cage molecules contain hexagonal and pentagonal faces with carbon atom located at vertices forming two single bonds and one double bond with neighboring carbon atoms with delocalized \(\pi\)-electrons throughout the molecule. According to a theorem of the mathematician Leonhard Euler, a spherical surface will be built up by 12 pentagons and \(V/2-10\) hexagons, where \(V\) is the number of vertices.\(^3\) Applying this theorem to fullerenes leads to a family of carbon molecules with 12 pentagonal faces and \(V/2-10\) hexagonal faces, of which \(C_{60}\), \(C_{240}\), and \(C_{540}\) are three prominent icosahedral members with 20, 110 and 260 hexagonal faces. With a radius of 0.71 nm, \(C_{60}\) is prominently used in making alkali-intercalated superconducting phases.[5]
1.2 Carbon nanotubes

Another crystalline allotrope of carbon, carbon nanotubes (CNTs) can be defined as one-dimensional nanostructures consisting of rolled, seamless cylindrical sheets of graphene with high aspect ratios (length/diameter) and fullerene endcaps.[6] CNTs were first prepared by Iijima in 1991 by arc-discharge evaporation of graphite rods.[7] The CNTs prepared by Iijima has cylindrical walls built of 2 to 50 graphitic layers.

![Figure 1.1. Images of (a) C\textsubscript{60} fullerene, (b) C\textsubscript{70} fullerene, (c) single-walled carbon nanotube and (d) multi-walled carbon nanotube (Ref [34]).](image)

CNTs exist in several different forms, of which the most prominent are single walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs),
whose aspect ratios are controlled by the method of their synthesis. With a diameter between 2 to 20 nm, CNTs grow up to 1 μm in length and ends up with half fullerenes. Depending on the diameter and helicity, the electronic properties of these nanotubes change periodically between metallic and semiconductor.[8] Due to their unique hardness, mechanical strength, metallic/semiconducting properties and hallow character, they are attractive to scientists.

### 1.3 Carbon nano-onions

A recently discovered family of carbon allotropes, known as carbon nano-onions, is largely unexploited.[9] Carbon nano-onions (CNOs), discovered by Ugarte in 1992, are multi-layered fullerenes that are spherical analogs of multi-walled carbon nanotubes with diameters ranging from 6 nm to 47 nm.[10] Basically the diameter depends upon the method of synthesis. For the first time in 1980, Iijima observed onion-like structured carbon with a diameter between 8–15 nm in amorphous carbon films prepared by vacuum evaporation method at 10⁻⁶ Torr and 4000 K.[11] He stated that this curved pattern in this material is due to the tetrahedral bonding in the structure of graphitized carbon black. In 1992, Ugarte synthesized carbon nano-onions by irradiating carbon soot with high energy electron beam in high resolution electron microscope for 20 min.[10, 12] With this method, it is possible to produce CNOs with a diameter of ~ 45 nm, but not in bulk quantities. In 1994, Kuznetsov prepared CNOs by graphitization of nanodiamonds at 1650 °C under inert atmosphere, and these are called N-CNOs.[13] This is a very useful method to prepare CNOs with a diameter between 6 – 8 nm in bulk quantities. Sano and group came up with a bench top method of arcing of graphite rods in water to synthesize CNOs with a diameter between 4–36 nm.[14] The apparatus consists of two submerged
graphite electrodes, and the arc discharge was initiated by contacting them with the discharge voltage and current of 16–17 V and 30 A. This is another good method to synthesize CNOs in larger quantities. The CNOs obtained through this method also contain other carbon materials such as carbon nanotubes and graphitic particles. The purity can be controlled up to some extent by optimizing the discharge voltage and power. More recently in 2011, Bai and group reported a method to synthesize CNOs in bulk quantities by reacting calcium carbide with copper chloride dihydrate at 600 °C.[15] They emphasized that the crystal water in CuCl₂·2H₂O plays an important role in the formation of CNOs. CNOs obtained by this method exhibit high capacity and good cycling performance as anode materials for lithium-ion batteries.

**Figure 1.2.** A model of carbon nano-onion (CNO) with several concentric graphitic layers.
The CNOs synthesized from nanodiamonds (N-CNOs) and arc-discharge of graphite rods in water (A-CNOs) comprise the subject of our research. I started my research with functionalization of N-CNOs to improve their solubility/dispersion properties using various synthetic approaches that I will discuss in chapter 3. As previously said, nanodiamonds are the precursors for N-CNOs. It is worth discussing more fundamental concepts regarding nanodiamonds before going in detail into N-CNOs.

1.4 Nanodiamonds

Nanocrystalline diamond particles (nanodiamonds) were first produced by detonation synthesis in the USSR in 1960,[16] but known to rest of the world only in 1980s.[17] These zero-dimensional nanoparticles have diameters of 4 to 8 nm. Nanodiamonds (ND) are obtained by detonation of powerful explosive mixtures such as RDX and TNT at higher temperature and pressure in an insulated steel chamber.[13] Being structurally analogous to natural diamond, ND inherits most of the bulk diamond properties such as superior Young’s modulus, biocompatibility, optical fluorescence, high thermal conductivity, high electrical resistivity and chemical stability with wide range of applications. ND used as additives for electrolytic metal plating, in chemical vapor deposition of diamond films,[18] in magnetic resonance imaging[19] and chromatography.[20] ND also used in tribology as additives to lubricants,[21] nanocomposites to make high-strength polymer composites,[22] drug delivery,[23] tissue scaffolds and surgical implants.[24]

The detonation synthesis of ND was achieved by Soviet military scientists by detonation of explosives such as RDX and TNT and their mixtures under highly insulated conditions in an inert atmosphere at 3500 °C and 2000 atm to give nanodiamond soot,
which is also called as diamond blend (DB).[13] This DB is purified using liquid oxidants (such as HNO₃, a mixture of H₂SO₄ and HNO₃, K₂Cr₂O₇ in H₂SO₄, KOH/KNO₃ and HNO₃/H₂O₂ under pressure)[25] to remove non-diamond carbon particles to give purified ultra-dispersed diamonds (UDD) with mean size ranging from 4 nm to 8 nm, agglomerating to 20 to 50 nm. The non-carbon impurities such as metal oxides were removed by treating UDD with dilute HCl. This oxidative purification with acids leads to the increase in the heteroatom/carbon ratio and these heteroatoms exist in the form of various oxygen-containing functional groups such as hydroxyl, carbonyl and carboxyl (Figure 1.3).[26] The increase in the degree of oxidation further increases the number of oxygen-containing functional groups on the surface of UDD. The elemental composition of a typical ultra-dispersed nanodiamond is:

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>88–92%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1–3%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1–2%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0–10%</td>
</tr>
</tbody>
</table>

corresponding to a typical molecular formula of C₇₅H₃₄N₈O₂₇.
Figure 1.3. Schematic model of ultra-dispersed nanodiamond with various functional groups on the surface.

Similar to the structure of natural diamond, the structure of nanodiamond contains three different types of crystal planes, (111), (110) and (001). During the graphitization of nanodiamonds, the preferential exfoliation and transformation of (111) and (110) crystal planes leads to the formation of (002) graphitic planes.[27, 28] This transformation proceeds from the surface to the center of nanodiamond. Consequently, carbon nanonions with almost the same size as nanodiamonds are formed. The transformation rate of the (111) diamond planes to the (002) graphitic planes is higher than that of (110) diamond planes.[28] The transformation or exfoliation of the (001) diamond planes is much more complicated than that of (111) and (110) planes because the (001) planes require more atomic rearrangement to form graphitic planes and their cleavage energy is very much higher than that of both (111) and (110) planes. Between (111) and (110)
planes, the former have lower cleavage energy than the later, hence (111) transform more rapidly than (110). The zipper-like transformation of three (111) diamond planes into two (002) graphitic planes is shown in Figure 1.4.

**Figure 1.4.** Exfoliation and transformation of (111) crystal planes of nanodiamond to (002) crystal planes of CNO (adapted from Ref [27])

During this graphitization, the edges of exfoliated graphite-like sheets merge with the upper untransformed diamond planes as shown in Figure 1.4. Like this three (111) planes of ND converts to two (002) planes of CNO with an interlayer spacing of 0.33 nm. As-obtained N-CNOs after graphitization contain impurities such as amorphous carbon. These amorphous impurities were removed by heating at 400 °C under airflow in a tube furnace.

To get a better model about the structure, N-CNOs were structurally analyzed using several characterization techniques and the results were discussed in Chapter 2. To
improve the dispersion properties and to understand the chemistry of N-CNOs, we used several synthetic approaches to functionalize the surface of N-CNOs. In Chapter 3, we discussed the preparation and characterization of functionalized N-CNOs. Chapter 4 deals with the preparation and characterization of graphene structures prepared by unzipping of arc-prepared CNOs (A-CNOs). We have tested some of our materials as negative electrode materials in lithium ion batteries (LIBs). In Chapter 5, we discussed some preliminary results of N-CNOs and A-CNO-derived graphene materials as negative electrode materials in LIBs. Chapter 6 outlines proposed future research activities.
Chapter 2 Structural Analysis of N-CNOs

It is desirable to understand the structural and surface properties of N-CNOs before chemical modification to improve solubility properties of these materials. To study the surface and structural properties of these materials, we used thermogravimetric analysis (TGA), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), Raman spectroscopy and BET nitrogen adsorption/desorption analysis.

2.1 Thermogravimetric analysis (TGA)

We started with thermogravimetric analysis of air-cleaned N-CNOs in air from ambient to 1000 °C in high-resolution dynamic mode. From the TGA under air, it is possible to find out the combustion temperature and inorganic metal content from percent residue.[29, 30]

The TGA of N-CNOs (Figure 2.1) shows that this material is stable up to 550 °C in air and started burning after that. Carbon materials such as graphite powder, carbon nanotubes, nanodiamonds and carbon nano-onions show distinct thermal stabilities with unique combustion temperatures.[31] The single sharp mass loss transition at 600 °C corresponding to the combustion of N-CNOs signifies that the material is a homogeneous single phase with no other carbon materials as impurities. The low thermal stability of N-CNOs compared with that of other carbon materials such as graphite and CNTs (~ 650 °C) may be due to high curvature and presence of structural defects. Structural defects such as edges, dangling bonds, vacancies, dislocations[29] and strain induced through high curvature[32] will lead to the decrease in the combustion temperature. The low residue observed is consistent with the metal catalyst-free preparation of N-CNOs.
Figure 2.1. Thermogravimetric analysis of air-cleaned N-CNOs in air with a combustion temperature of 638 °C and % residue of 3.6.

2.2 Transmission electron microscopy (TEM) analysis

TEM analysis is useful to determine the morphology, diameter and number of graphitic layers of N-CNOs. From a TEM image (Figure 2.2), the diameters of typical N-CNOs range from 6 nm to 8 nm with 8 to 10 concentric graphitic layers. Also, the material consists of mostly N-CNOs with no other carbon materials, which was already evident from TGA.
Figure 2.2. (a) HRTEM image of N-CNOs, (b) N-CNO single particle with a diameter of 7 nm and (c) N-CNO particle with approximate number of carbon atoms of each layer.

Based on TEM analysis, we calculated the approximate number of C atoms in an N-CNO, assuming that all the graphitic layers are perfectly spherical. A $C_{60}$ fullerene with a diameter of 0.66 nm[33, 34] has a surface area of 1.36 nm$^2$ and 60 carbon atoms arrayed in
a spherical arrangement. Knowing the diameter of each spherical layer of N-CNO from TEM image, we calculated the surface area of each layer of N-CNO. From the surface area, we calculated the approximate number of carbon atoms present in each layer with reference to $C_{60}$. The distribution of C atoms in each graphitic layer of N-CNO is given in Figure 2.2(c). The total number of C atoms in one N-CNO with average diameter of 7 nm is 22,600 and corresponding molar mass is 271,200 g/mol.

2.3 Powder X-ray diffraction analysis

For carbon nanomaterials, powder X-ray diffraction is a useful technique to determine interplanar distances and to calculate average crystallite size. The powder XRD pattern of air-cleaned N-CNOs is shown in Figure 2.3. The average interplanar distance of 3.5 Å was calculated from the position of the broad, intense (002) peak at 25.5°. Another broad low intense peak at 43.3° corresponds to (100) crystal planes with inter-planar distance of 2.09 Å and a sharp peak at 44.5° corresponds to (111) planes of traces of nanodiamonds[35] that may be left untransformed during the graphitization.
Figure 2.3. Powder-XRD pattern of N-CNOs (left) showing the peaks corresponding to (002), (100) graphitic planes and (111) diamond planes appearing at 25.5°, 43.3° and 44.5° respectively.

Smaller crystallites give broader powder XRD peaks.[36] The peaks corresponding to both (002) and (100) planes of N-CNOs are broad due to smaller crystallite dimensions along these planes. The crystallite size of carbon materials can be defined by $L_a$ and $L_c$. $L_a$ is longitudinal crystallite size (parallel to graphene sheets along a-direction) that is calculated from the full width at half maximum (FWHM) of a peak appearing at ~43° corresponding to (100) crystal planes. $L_a$ can also be calculated from the ratio of integrated intensities of D and G bands ($I_D/I_G$ ratio) of a Raman spectrum and
energy of incident laser used for the Raman excitation,[37] but this approach is more applicable for materials with larger crystallites. $L_c$ is the thickness of crystallite (perpendicular to graphene sheets and along c-direction) that is calculated from FWHM of peak appearing at $\sim 25^\circ$ corresponding to (002) crystal planes.[38] The crystallite size of N-CNOs can be calculated using Scherrer equation by knowing the FWHM of peaks of (002) and (100) crystal planes. The Scherrer equation is

$$L = \frac{K\lambda}{\beta \cos\theta}$$

Where $L$ is the crystallite size, $K$ is the Scherrer or shape constant ($\sim 0.9$), $\lambda$ is the wavelength of incident radiation (1.542 Å), $\beta$ is the FWHM of peak in radians and $\theta$ is one half of position of peak. The $L_a$ and $L_c$ values calculated by the Scherrer equation for N-CNOs are 1.06 nm and 2.23 nm, respectively.

### 2.4 Raman analysis

Raman analysis with 532 nm excitation wavelength enables investigation of the structure all the way to the core of an N-CNO. The Raman spectrum of air-cleaned N-CNOs is shown in Figure 2.4. The peak at 1584 cm$^{-1}$ corresponds to the G band responsible for $E_{2g}$ vibrational mode of graphitic carbon atoms and the peak at 1340 cm$^{-1}$ corresponds to the D band observed due to translational symmetry breaking at edges or defective sites.[39] The D band is more pronounced for the materials comprised of small crystallites, usually less than 1000 Å.[39] The $I_D/I_G$ ratio in Raman spectrum is the measure of extent of defective sites with respect to the graphitic structure. The $I_D/I_G$ ratio for N-CNOs is 1.57, which significantly higher than other carbon materials such as graphite ($\sim 0.25$),[40] SWCNTs ($\sim 0.12$)[41] and A-CNOs ($\sim 0.45$).
Figure 2.4. Raman spectrum of N-CNOs (right) showing graphitic G band at 1584 cm\(^{-1}\) and disorder induced D band at 1340 cm\(^{-1}\) with \(I_D/I_G = 1.57\).

This high \(I_D/I_G\) ratio indicates a higher density of defects in the structure of N-CNOs, which accounts for higher reactivity of these materials compared with other carbon materials.[42] The smaller crystallite size of N-CNOs observed with powder XRD analysis is also responsible for high \(I_D/I_G\) ratio. Smaller the crystallite, larger will be the number of defects and edges in the structure hence higher will be the \(I_D/I_G\) ratio. These surface defect sites could provide an advantage to functionalize these materials to improve their solubility/dispersion.
From powder XRD data, we found the approximate dimensions of a typical N-CNO crystallite and Raman analysis implies the presence of defects on the surface. A model of defective surface of N-CNOs is proposed based on these results shown in Figure 2.5.

*Figure 2.5.* Model of a part of defective surface (approximately 2 nm along a, b direction) of N-CNOs with hydrogen and oxygen-terminated edges; proposed based on Raman and powder XRD analysis.

### 2.5 BET surface area and pore size distribution

The surface area and porosity distribution of a powder are measured by the physical adsorption of an inert gas onto the surface of the sample at liquid nitrogen.
temperature. The BET (Brunauer, Emmett and Teller) theory is commonly used to evaluate the gas adsorption data and generate a specific surface area (expressed in m²/g) and pore size distribution of a material.[43] The BET equation is

\[
\frac{1}{V[(P/P_0)-1]} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \left( \frac{P}{P_0} \right)
\]

Where \( P/P_0 \) is inert gas relative pressure, \( V \) and \( V_m \) are adsorbed gas quantity and monolayer adsorbed gas quantity, respectively, and \( C \) is the BET constant, related to the strength of interaction between gas and solid material. Specific surface area is the accessible surface area per unit mass of material. It is calculated from monolayer volume \( (V_m) \) of adsorbed gas that can be calculated from the slope \( S \) and intercept \( i \) of the straight line when \( 1/V [(P_0/P)-1] \) is plotted against \( P/P_0 \).

\[
S = \frac{C-1}{V_mC} \quad i = \frac{1}{V_mC}
\]

Solving for \( V_m \) gives

\[
V_m = \frac{1}{S+i}
\]

Porosity is the ratio of the volume of voids plus the volume of open pores to the total volume occupied by the powder.[44] Porous material are classified according to the size of pores: materials with pore diameters less than 2 nm are called microporous, materials with pore diameters between 2 and 50 nm are called mesoporous, and materials with pore diameters greater than 50 nm are macroporous.[45] The total pore volume is often derived from the amount of vapor adsorbed at a relative pressure close to unity.

Nitrogen adsorption/desorption isotherms and DFT pore-size distribution of air-cleaned N-CNOs are displayed in Figure 2.6 and 2.7. The specific surface area calculated
between relative pressures \((P/P_0)\) of 0.01 and 0.2 is 560 m\(^2\)/g. The pore-size distribution curve given in Figure 2.7 indicates that the majority of pore volume lies between 5 nm and 30 nm, showing the material as highly mesoporous (~77%), which is useful for battery applications. This high surface area and mesoporosity of N-CNOs can be attributed to their smaller size and presence of surface defects.

*Figure 2.6.* Nitrogen adsorption/desorption isotherm of air-cleaned N-CNOs.
2.6 Experimental

2.6.1 Preparation of N-CNOs

Ultra-dispersed diamonds (ND-50, 5 – 7 nm) were purchased from Dynalene. ND were graphitized by heating from room temperature to 1650 °C under flowing helium at 20 °C/min and cooling to room temperature at 50 °C/min. The obtained N-CNOs were cleaned by heating at 400 °C under air-flow using a Lindberg/Blue M tube furnace (Model TF55035A) for 4 h to remove amorphous carbon impurities.
2.6.2 Characterization

Thermogravimetric analysis was performed on TA 2950 and TA Q500 in high-resolution dynamic mode (heating rate is controlled with respect to the measured rate of mass loss) from ambient temperature to 1000 °C under air. HRTEM images were taken using a JEOL 2010F field-emission TEM operated at 200 kV. N-CNOs dispersed in ethanol was placed on TEM copper grid with lacey carbon and dried overnight at 60 °C. Powder X-ray diffraction analysis was performed on a Bruker AXS D8 DISCOVER with Cu Kα (1.5418 Å) radiation.

BET (Brunauer, Emmett, and Teller) specific surface area and pore-size distribution of air-cleaned N-CNOs were determined by an automated gas adsorption analyzer, ASAP 2020 (Micromeritics, Instruments Inc.). After degassing of samples at 150 °C, nitrogen adsorption-desorption isotherms were measured by this equipment at -196 °C. The specific surface area was calculated using BET equation and the pore-size distribution was determined using density function theory method. Raman analysis was performed on Thermo Scientific DXR dispersive Raman spectrometer using 532 nm excitation wavelength (diode-pumped, frequency-doubled Nd: YVO₄ laser) focused on sample by 50X objective lens.
Chapter 3 Functionalization of N-CNOs

3.1 Introduction

From the structural analysis, we understood that N-CNOs are small carbon nanoparticles (~ 7 nm) with high surface area (560 m²/g), numerous structural defects (I_D/I_G = 1.5) and smaller crystallite size. These N-CNOs are more reactive than other CNOs (such as arc-discharge and electron-beam CNOs) due to their smaller size, high curvature and surface defects.[42] These carbon materials have potential applications in tribology,[46, 47] optical limiting materials,[48] catalysis,[49] gas storage,[14] electromagnetic shielding[50] and as additives to strengthen carbon nanotube-polymer composites. [51] CNOs are also potentially useful in photovoltaic and fuel cell applications. With much larger surface area than CNTs, CNOs are potential candidates for the development of miniaturized fuel cells.[52] In the field of tribology, they can replace MoS₂ as a solid additive to grease, providing adequate and even superior lubrication compared to the commonly used graphitic particles.[46, 53] In this chapter, we discuss several functionalization methods to improve solubility and dispersion properties of N-CNOs and their characterization using wide range of techniques such as TGA, TG-MS, advanced pH-titrimetry, FT-IR, Raman, MALDI-MS and capillary electrophoresis (CE).

3.1.1 Future applications of functionalized N-CNOs

Solubility is an important criterion to explore the properties and applications of carbon materials. Hence functionalization of N-CNOs for effective solubility and dispersion properties and their characterization are challenging tasks. We would also like to explore the basic and fundamental chemistry of these materials, and we need a reliable, well-functionalized and characterized starting material with versatile functional groups
on the surface having enough solubility properties for biological applications. Polystyrene nanoparticles attached with polyethylene glycols (PEGs) and terminated covalently with derivatized galactose moieties (shown in Figure 3.1) are used to adhesively interact with several *Escherichia coli* in warm-blooded organisms.[54] As the interaction between carbohydrates and bacterial surface is weak, the polymeric nanoparticles carry multiple carbohydrate ligands which can bind to single receptor thereby enhancing the strength of interaction. The idea is to replace the polystyrene nanoparticles with N-CNOs, as the later has relatively small size and due to tremendous electronic properties and microwave absorption, they can bind to bacteria and destroy it.

![Figure 3.1. Polystyrene nanoparticles attached with PEGs and terminated covalently with derivatized galactose moieties](image)

**Figure 3.1.** Polystyrene nanoparticles attached with PEGs and terminated covalently with derivatized galactose moieties

Much research is underway to synthesize and study the properties of CNT-reinforced polymer composites. These composites are more promising and stronger than the polymer composites without CNTs. At a much lower concentrations, due to their high aspect ratios and graphitic structure, the CNTs can establish a highly conductive network inside the polymer matrix and increase its mechanical strength.[55] Although it was reported that the mechanical strength increased up to 50%, still there is a possibility of crack propagation in these CNT-polymer composites due to either inhomogeneous
dispersion[56] or presence of gaps between the CNTs in the polymer matrix. The crack initiation takes place at low-CNT density regions and propagates through weak CNT-polymer interfaces. This drawback can be overcome by the introduction of CNOs into the polymer matrix along with CNTs, thereby reducing the possibility of crack propagation and reducing the crack mouth opening displacement (CMOD) as shown in Figure 3.2.

The long-term goal is to come up with highly pure chemically functionalized CNOs to make CNT/CNO-polymer composites. The chemical nature of the polymer demands compatible functionality on the surface of CNOs.

Figure 3.2. Model of possible crack propagation in CNT-polymer composite (left) and CNT/CNO-polymer composite (right)

3.1.2 Importance of functionalization

To accomplish the goals stated above, the investigation of basic chemistry of N-CNOs is very much needed. N-CNOs should have facile and versatile functional groups on the surface for further derivatization to make individual N-CNO particles suspend or disperse well. For this reason, we are trying various synthetic approaches to functionalize
N-CNO for better solubility and dispersion properties. As N-CNOs are macromolecules without any functional groups on the surface, they have poor solubility in organic and aqueous solvents. This lack of solubility hinders the study of their chemical and physical properties. An illustration of size of N-CNO compared with that of simple molecules such as naphthalene and fullerene is given in Figure 3.3. N-CNO form agglomerates due to van der Waals attractive forces. The main goals of functionalization of N-CNOs can be summarized as:

i. Improve the solubility/displacement properties in aqueous, polar and non-polar organic solvents by introducing functional groups on the surface,

ii. Introduce versatile surface functional groups for further functionalization to use them in biological and CNT-polymer composite applications,

iii. Use N-CNOs in chromatographic techniques (such as size exclusion chromatography) to do size-dependent separations to make homogeneous N-CNO materials.

*Figure 3.3.* Size comparison of a N-CNO with naphthalene and C\textsubscript{60} fullerene.
Agglomeration is a common problem during functionalization of N-CNOs, as agglomerated particles have fewer surfaces exposed to reagents during a chemical reaction and therefore are less reactive. The functionalization approach employed should be vigorous enough to disperse the agglomerates into individual primary particles during the reaction. Several surface functionalization methods such as strong oxidation,[57-59] reductive alkylation (Billups reaction),[60] Friedel-Crafts acylation[61] and mechanochemical reactions[62] have been reported to improve the solubility and dispersibility of single-walled carbon nanotubes (SWCNTs) in water, polar and non-polar organic solvents. Oxidation procedures for SWCNTs include reaction with mixture of oleum and concentrated nitric acid[57], treatment with potassium permanganate in presence of an acid[58], reflux with 2.6-M nitric acid[59] and sonication in 8.0-M nitric acid.[59]

Researchers have reported several synthetic approaches that functionalize CNOs to modify their chemical properties and improve their solubility. Specific reactions such as [2+1] cycloaddition of nitrene,[63] oxidation using mixture of mineral acids,[9] 1,3-dipolar cycloaddition,[64] and radical addition of conjugated polymers[65] have been already reported. In this chapter, we discuss our synthetic approaches to functionalize N-CNOs. Mainly we tried acid oxidation, Friedel-Crafts acylation, Billups reductive alkylation and mechanochemical hydroxylation reactions on N-CNOs. In this chapter we will discuss the preparation and characterization of functionalized N-CNOs prepared using these chemical approaches.
3.2 Results and discussion

3.2.1 Acid oxidation

Oleum oxidation is the most successful functionalization method to make ultra-short SWCNTs that are soluble in polar solvents by producing oxygen-containing functional groups on the surface. We optimized Tour’s oxidation reaction conditions for SWCNTs[57] to maximize the yield of ON-CNOs. One h heating with oleum and conc. HNO$_3$ at 75-85 °C gave a 70% yield (by mass) of ON-CNOs that dissolve spontaneously in polar organic solvents such as DMSO (9.8 mg/mL), DMF (6.4 mg/mL) and DI water (1.4 mg/mL) without the aid of sonication. At pH> 7 the solubility in DI water increased to 8.5 mg/mL, giving an indication about the presence of acidic functional groups on the surface. Sequential photographs of spontaneous dissolution of ON-CNOs in water at pH > 7 are shown at 0, 5, 10, 15 and 20 min (Figure 3.4).

Agglomeration is the most common concern for surface functionalization of N-CNOs as they are too small to agglomerate during the reaction, decreasing the extent of functionalization per N-CNO. Here in the first step of oxidation, as explained by Tour and group in case of SWCNTs[57], the oleum (SO$_3$ in H$_2$SO$_4$) is effectively intercalates between individual N-CNOs inside N-CNO agglomerates and makes their surface available for further oxidation. The CNO-oleum intercalation is expected to be due to CNO forming a thermodynamically favorable charge transfer complex with sulfuric acid molecules. In the second step, concentrated HNO$_3$ at 75-85 °C in presence of oleum oxidizes the surface of individual N-CNOs with NO$_2^+$ being the effective oxidant resulting with oxygen-containing functional groups on the surface. So, the solubility of these materials is attributed to these oxygen-containing functional groups such as
hydroxyl, carboxylic, sulfonic and nitro groups, which are evident from TG-MS analysis (Figure 3.5).

**Figure 3.4.** Sequential photographs at 0, 5, 10, 15 and 20 min of the spontaneous dissolution of ON-CNOs in water at pH > 7. After addition of sample to the solvent, the vial was swirled for 5 seconds at 10th minute.
Figure 3.5. TG-MS of ON-CNOs performed by heating the material to 550 °C with a rate of 10 °C/min under argon

TG-MS is the combination of thermogravimetric analysis (TGA) and mass spectrometry (MS), usually used to detect and quantify volatile compounds. By heating the sample in TG apparatus, volatile materials are released through thermal desorption or combustion. These generated gases are transferred to MS where they are identified and quantified. In TG-MS analysis, ON-CNOs were heated to 550 °C at a rate of 10 °C/min under argon flow of 100 mL/min, the evolution of gas species was followed in situ by coupled TG-MS system and mass spectra were acquired. The evolution curves of ion-fragments of various gases released are shown as intensity vs. time curves in Figure 3.5.
Peaks at m/z 17 and 18 corresponding to OH and H₂O respectively evolved early at 6.5 min. A broad peak at m/z 30 corresponding to NO started evolving at 7.0 min. Next significant peak observed at m/z 44 corresponding to CO₂ evolved at 12.0 min. Two significant peaks observed at m/z 48 and 64 corresponding to SO and SO₂ respectively evolved at 12.8 min. These exited gases imply the presence of oxygen-containing functional groups such as hydroxyl, carboxylic acid, nitro and sulfonic acid. The list of exited gases with their corresponding molar mass is given in table 3.1.

**Table 3.1.** List of gases exited from TG furnace with their corresponding molar mass

<table>
<thead>
<tr>
<th>Gases exited</th>
<th>amu</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>17</td>
</tr>
<tr>
<td>H₂O</td>
<td>18</td>
</tr>
<tr>
<td>CO₂, N₂</td>
<td>28</td>
</tr>
<tr>
<td>NO</td>
<td>30</td>
</tr>
<tr>
<td>CO₂, N₂O</td>
<td>44</td>
</tr>
<tr>
<td>NO₂</td>
<td>46</td>
</tr>
<tr>
<td>SO</td>
<td>48</td>
</tr>
<tr>
<td>SO₂</td>
<td>64</td>
</tr>
</tbody>
</table>
We used a two-stage pH-metric titration similar to a Boehm titration[66] of oxidized carbon blacks and Haddon’s acid-base titration of purified SWCNTs[67] to determine the number of strongly and weakly acidic groups on the surface of ON-CNOs. Titration of ON-CNOs dispersed in water against 50-mM NaOH solution resulted in a pH vs. volume of NaOH curve that corresponded to $pK_a$ 4.0, close to that of benzoic acid (Figure 3.6), suggesting the presence of aromatic carboxylic acid groups. The transition is broader than that of benzoic acid, most likely because of a distribution of acidic groups in slightly different environments on the ON-CNO surface, and possibly also because of
slower heterogeneous proton-transfer kinetics. This particular observation encouraged us to find out the type and distribution of acidic functional groups on the surface. To do this we have performed advanced pH-metric titrations.

Figure 3.7. pH-Metric titration curve of ON-CNOs (red) after saturating with base and titrating against HCl along with their corresponding blank titration (blue).

In this experiment, we initially saturated total acidic sites (presumably phenols, carboxylic acids and sulfonic acids) on ON-CNO surface with NaOH for 3 d and titrated excess NaOH after neutralization with HCl to find out total number of acidic sites, which is $2.31 \times 10^{21} \text{ g}^{-1}$. We have saturated strong acidic sites (presumably carboxylic acids and sulfonic acids) exclusively on ON-CNO surface with NaHCO$_3$ and titrated excess NaHCO$_3$ after neutralization with HCl to find out total number of strong acidic sites,
which is $0.88 \times 10^{21} \text{ g}^{-1}$. From this data the percentage of strongly acidic groups (carboxylic acids and sulfonic acid) is around 38% and that of weakly acidic groups (phenols) is 62%.

![TGA graph showing mass losses at ~198 °C and ~430 °C](image)

**Figure 3.8.** TGA of ON-CNOs (blue) under inert atmosphere showing mass losses at ~198 °C and ~430 °C, compared with that of as produced N-CNOs (black).

The TGA under nitrogen of ON-CNOs shows mass loss transitions at ~198 °C and ~430 °C with ~18% and ~20% mass loss, respectively (Figure 3.8). The mass loss at ~198 °C is due to the loss of water and carbon dioxide from oxygen-containing functional groups.[68] The source of the mass loss at ~430 °C is less clear. Salzmann et al. reported that sulfuric/nitric acid-oxidized SWCNTs had polycyclic aromatic hydrocarbon (PAH) adsorbates, which they call as carboxylated carbonaceous fragments (CCFs)[69]. Tour et
al. made a similar observation for oleum/nitric acid-oxidized SWCNTs.[70] Although neither group commented on the source of these CCFs, they stated that these adsorbates are held on the CNT surface with weak van der Waals attractive forces (π-π interactions). Salzmann used base treatment with 8-M NaOH at 100 °C to remove the CCFs from oxidized CNTs by breaking π-π interactions between CCFs and the CNT surface.

Aqueous alkali-metal hydroxide solutions have been reported to have good graphite intercalation properties.[71, 72] Therefore, NaOH is chosen and is able to intercalate between π-stacked structures of the sample to release the CCFs from CNT surface at 100 °C. The efficiency of NaOH in removing CCFs is probably due to the deprotonation of oxygen-containing functional groups on the CCFs, making them more soluble in the basic aqueous solutions. This kind of mechanism was also proposed by Rinzler and group for the purification of nitric acid-treated SWCNTs by washing with alkaline sodium hydroxide solution.[73]

We carried out the same base treatment method on our ON-CNOs to see whether we could isolate any adsorbed carbonaceous material from our material (scheme 3.1). May be due to the complicacy of the procedure, even after making several attempts we ended up with no success to isolate CCFs but a huge mass that may be a mixture of CCFs and insoluble sodium salts. But we could achieve reasonable amount of base treated ON-CNOs (BON-CNOs) with a weight loss of ~15%.
Scheme 3.1. Air-cleaned N-CNOs were oxidized using mixture of oleum and concentrated nitric acid to yield ON-CNOs, which were further heated with 8 M aqueous NaOH to isolate CCFs to yield BON-CNOs.
Figure 3.9. pH-Metric titration curve BON-CNOs after saturating with base and titrating against HCl along with their corresponding blank titration

After the removal of CCFs from surface by base treatment, the BON-CNOs were still soluble in polar organic solvents. If some of the functional groups reside on CCFs, their number should decrease after base treatment. To find that out, we again performed pH-metric titrations with the same method as described earlier on this material and found significant decrease in the total number of acidic functional groups on the surface after removal of CCFs (Figure 3.9). The total number of acidic functional groups decreased by about half, from $2.3 \times 10^{21} \text{ g}^{-1}$ for ON-CNOs to $1.2 \times 10^{21} \text{ g}^{-1}$ for BON-CNOs. This leads to a conclusion that almost half of the total acidic functional groups of ON-CNOs were present on CCFs, which is in a close agreement with Salzmann’s finding that almost 60% of the carboxylic groups are present on CCFs rather than the CNT surface. [69] It is also
possible that 8-M NaOH treatment deoxygenated the ON-CNO surface, similar to the exfoliation of graphene oxide with 8-M NaOH solution at 80 °C reported by Fan et al. [74]

![Figure 3.10. HRTEM images of a) ON-CNOs and b) BON-CNOs showing the preserved concentric graphitic structure after oxidation and base treatment](image)

The TEM images and powder X-ray diffraction patterns show that the structure and interlayer spacing of N-CNOs were not disturbed by oxidation and base treatment. The TEM images of ON-CNOs and BON-CNOs (Figure 3.10) show that they still retain their concentric graphitic structure. From the powder XRD analysis, the interlayer spacing can be calculated from the position of (002) crystal plane of N-CNOs. The position of (002) peak is 25.5° for N-CNOs, ON-CNOs and BON-CNOs, corresponding to an interlayer spacing of 3.5 Å (Figure 3.11), which implies that these materials are structurally intact. Interestingly, the peak at 44.5 corresponding to (111) of ungraphitized nanodiamonds (Section 2.3) is absent for ON-CNOs and BON-CNOs. This may be due to the complete oxidation of residual nanodiamond material under these conditions. Just to
make sure this hypothesis, we did the oxidation of nanodiamonds under the same conditions, and the nanodiamond material got completely oxidized.

**Figure 3.11.** Powder X-ray diffraction pattern of N-CNOs, ON-CNOs and BON-CNOs, showing no change in the position of the (002) peak.

Figure 3.12(a) shows the Raman spectra of N-CNOs, ON-CNOs and BON-CNOs obtained using a 514.5 nm excitation wavelength. As discussed in Chapter 2, all the samples exhibit the graphitic G-band at ~1580 cm\(^{-1}\) and disorder-induced D-band at ~1350 cm\(^{-1}\). The ratio of integrated area under the D-band to the G-band is used to quantify the disorder in carbon nanostructures. Clearly, the average I\(_D\)/I\(_G\) increased for
ON-CNOs and BON-CNOs compared with that of N-CNOs, indicating disorder induced during oxidation and base treatment. Further, FTIR spectra of these samples confirm the presence of functional groups (Scheme 3.1) induced during oxidation and base treatment. The bottom spectrum in Figure 3.12(b) shows the absence of any functional groups in N-CNOs. The ON-CNO samples exhibit strong –COOH and –OH features. These bands are at least ~20 times suppressed for BON-CNOs suggesting lesser extent of functional groups on BON-CNO surface, which is due to removal of CCFs or deoxygenation of functional groups during base treatment at 100 °C.

**Figure 3.12.** (a) Raman spectra of N-CNOs, ON-CNOs and BON-CNOs. The average I_D/I_G ratio increased for ON-CNOs and BON-CNOs compared to that of N-CNOs. (b) FT-IR spectra of N-CNOs, ON-CNOs and BON-CNOs. The absorbance decreased for BON-CNOs compared to that of ON-CNOs as the most of functionalization was removed with base treatment.

So far, we have characterized ON-CNOs and BON-CNOs, finding that they are structurally intact and the number of functional groups decreased significantly for BON-
CNOs compared to that of ON-CNOs after removing CCFs. However, we were not able to isolate enough CCFs from the base extract for characterization. We did not give up the idea of isolating the carbonaceous fragments. To do that we designed a thermal desorption experiment at 200 °C under vacuum. The experimental setup is shown in Figure 3.13. In this experiment, the ON-CNO material was heated at 110 °C for 2 h under vacuum in a tube furnace to dry the material. After drying, ON-CNOs were heated at 200 °C for 10 h under vacuum to desorb CCFs as shown in Figure 3.13. We collected a minute amount of brown to gray condensate at the entrance of U-shaped liquid nitrogen trap. ON-CNOs after thermal desorption were analyzed for TGA and compared with that of ON-CNOs before thermal desorption.

*Figure 3.13.* Thermal desorption setup to isolate CCFs from ON-CNOs at 200 °C under vacuum.

The TGA under nitrogen of ON-CNOs before and after thermal desorption are compared in Figure 3.14. Interestingly, the mass losses at ~198 °C and ~430 °C are significantly reduced for ON-CNOs after thermal desorption. The decrease in the mass loss at ~198 °C is attributed to the loss of oxygen-containing functional groups as
discussed earlier. Heating at 200 °C for 10 h can eliminates most of the oxygen-containing functional groups. The decrease in the mass loss at ~430 °C may be due to the loss of carbonaceous fragments during thermal desorption at 200 °C, because it has been reported that polycyclic aromatic hydrocarbons when analyzed for TGA under nitrogen, usually show mass loss between 400 to 650 °C due to their sublimation.[75] The exact temperature of sublimation depends on the type of structure and molar mass. This experiment suggests that thermal treatment at 200 °C for 10 h under vacuum sublimes the CCFs from the ON-CNO surfaces.

Figure 3.14. TGA under nitrogen of ON-CNOs before (blue) and after (red) thermal desorption compared with that of air-cleaned N-CNOs (black)
Figure 3.15. MALDI-MS spectra of carbonaceous fragments obtained by thermal desorption of ON-CNOs with a possible polycyclic aromatic fragment (inset).
We have analyzed the minute amount of carbonaceous material that was collected at the entrance of U-shaped tube for MALDI-MS analysis. MALDI-MS analysis of the sublimed carbonaceous material using DHB (dihydroxybenzoic acid) as matrix shows peaks corresponding to high molar mass poyaromatic fragments as shown in Figure 3.15. For example, a possible polycyclic aromatic fragment corresponding to the peak at m/z 659 is C$_{53}$H$_{23}$, shown in Figure 3.15 (inset).

### 3.2.2 Acid oxidation at varying oxidation time

To learn more about the effect of acid oxidation on the structure of N-CNOs, we gradually increased the time of the second step of the oleum oxidation reaction. We withdrew 15 mL aliquots of reaction mixture at 0, 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 h of oxidation time, isolated and weighed the solid products. As expected the mass of the product significantly decreased as the oxidation time increased; this observation is shown in Table 3.2. These products at various oxidation times were characterized using HRTEM, Raman spectroscopy and capillary electrophoresis.

<table>
<thead>
<tr>
<th>Oxidation Time (h)</th>
<th>Mass of product (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>55.0</td>
</tr>
<tr>
<td>0.5</td>
<td>53.0</td>
</tr>
<tr>
<td>1.0</td>
<td>43.0</td>
</tr>
<tr>
<td>1.5</td>
<td>30.0</td>
</tr>
<tr>
<td>2.0</td>
<td>20.0</td>
</tr>
<tr>
<td>3.0</td>
<td>7.0</td>
</tr>
<tr>
<td>5.0</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Although the HRTEM images shows heavy agglomeration, we observed that as oxidation time increases, the nano-onion size (number of graphitic layers) decreases (Figure 3.16). The initial sample has an average diameter of ~7 to 8 nm. At an oxidation time up to 1 h, N-CNOs retained their original size and structure. At 3 h, the average N-
CNO size decreased to ~5 to 7 nm and other materials resembling pieces of curved graphitic structures appeared in the sample. At 5 h, more tiny N-CNOs with an average diameter of ~4 to 5 nm appeared.

*Figure 3.17.* Raman spectra of ON-CNOs obtained by oxidation of N-CNOs for 1, 3 and 5 h
Raman spectra of ON-CNOs as a function of oxidation time are shown in Figure 3.17; observations are summarized by plotting $I_D/I_G$ ratio and G and D band positions vs. oxidation time (Figure 3.18). Raman analysis shows significant increase in $I_D/I_G$ after 1 h of oxidation. The D and G bands both shifted to higher frequency with increasing in the oxidation time, with most of the change occurring during the first hour. The reason for
the blue shift in G band is due to; (i) overlap of G band with the D’ band that becomes active due to defects; (ii) a reduced number of layers resulting in blue shift as observed for graphite converting to graphene.[76]

Although we wanted to optimize the reaction time for the second step, from this experiment we got valuable information. The reaction time of the second step can be optimized to tune the size of the resulting ON-CNOs, as it is the step where the actual oxidation of outer surface takes place. As the reaction proceeds, the outer layer gets oxidized and inner layers are exposed for further oxidation. This process leads to a decrease in the number of graphitic layers and thereby the size of N-CNOs. This observation also supports the presence of CCFs on the surface of ON-CNOs. The broken outer layer after vigorous oxidation leads to the formation of heavily oxidized polycyclic aromatic fragments with oxygen-containing functional groups.

3.2.3 Friedel-Crafts acylation

Acylation under Friedel-Crafts conditions is a useful synthetic approach to functionalize CNTs with long sidechains to improve their solubility/dispersibility in moderately polar and non-polar solvents.[61] By introducing long side chains, we hoped to improve the dispersibility of N-CNOs in non-polar to moderately polar organic solvents. Friedel-Crafts acylation of N-CNOs is shown in Scheme 3.2.
We used a 1:1 molar ratio of NaCl/AlCl$_3$ as the reaction medium, which is reportedly effective for SWCNTs,[61] to functionalize N-CNOs with lauroyl chloride as electrophile. The lauroylated N-CNOs were continuously washed with boiling toluene in a fritted Soxhlet extraction setup to remove unreacted and adsorbed lauroyl impurities.

Later, we decided to functionalize N-CNOs with two electrophiles, one with chain length less than lauroyl and other with a chain length greater than lauroyl. If these get functionalized, TGA under nitrogen of functionalized N-CNOs should show the mass loss depending on their chain length. We chose 5-carbon pentanoyl chloride and 18-carbon stearoyl chloride as electrophiles to functionalize N-CNOs. The functionalized N-CNOs (pentanoyl N-CNO-C$_5$, lauroyl N-CNO-C$_{12}$ and stearoyl N-CNO-C$_{18}$) were continuously washed with boiling toluene in a fritted Soxhlet extraction setup to remove unreacted and adsorbed materials. We characterized the functionalized N-CNOs using TGA, Raman spectroscopy and checked the dispersibility in chloroform and THF.
The TGA under air of lauroyl functionalized N-CNOs shows two mass loss transitions at ~370 °C and ~480 °C and combustion of N-CNOs at 595 °C (red curve in Figure 3.19), whereas the TGA under nitrogen shows only one mass loss transition at ~380 °C (blue curve in Figure 3.19). The mass loss at ~370 °C under air and ~380 °C under nitrogen is attributed to the loss of functional groups from the N-CNO surface. The mass loss at ~480 °C under air is apparently due to combustion, but not of the N-CNO itself.

Figure 3.19. TGA of lauroylated N-CNOs; TGA of air-cleaned N-CNO under nitrogen (black), TGA of lauroylated N-CNOs under nitrogen (blue) and under air (red)
The TGA under nitrogen of N-CNO-C5, N-CNO-C12 and N-CNO-C18 are shown in Figure 3.20. All three materials show a mass loss transition at ~370 °C. With the increase in the chain length of acyl chloride the % mass loss increased, corresponding to the loss of alkyl chain.

*Figure 3.20.* TGA of acylated N-CNOs under FC conditions, N-CNOs (black), pentanoylated N-CNOs (green), lauroylated N-CNOs (blue) and stearoylated N-CNOs (red)

TGA under inert atmosphere also gave us information about degree of coverage. From the % mass loss we calculated average number of molecules present on the surface of each N-CNO. The degree of coverage (X), is the number carbon atoms for every one functional group, can be calculated by formula,[77]
\[ X = \frac{M_{\text{add}} (1 - W\%) }{M_C W\%} \]

Where \( M_{\text{add}} \) is the molar mass of addend, \( W\% \) is percent mass loss in TGA, \( M_C \) is atomic mass of carbon.

The surface coverage of all three acylated N-CNOs is given in Table 3.3. The \% surface coverage (number of functional groups per 100 surface carbon atoms) decreases with increasing acyl chain length. It is quite reasonable to think that as the chain length or complicacy of the addend increases, surface coverage decreases.

**Table 3.3.** Surface coverage of acylated N-CNOs calculated based on TGA

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>% Mass loss (W %)</th>
<th>Molar mass of addends (M_{\text{add}})</th>
<th>% Surface coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N-CNO-C5</td>
<td>6.8%</td>
<td>85</td>
<td>3.4%</td>
</tr>
<tr>
<td>2 N-CNO-C12</td>
<td>9.7%</td>
<td>163</td>
<td>2.6%</td>
</tr>
<tr>
<td>3 N-CNO-C18</td>
<td>13.1%</td>
<td>267</td>
<td>2.3%</td>
</tr>
</tbody>
</table>
Figure 3.21. Raman spectra of FC acylated N-CNOs, N-CNOs (black), pentanoylated N-CNOs (green), lauroylated N-CNOs (blue) and stearoylated N-CNOs (red)

Table 3.4. $I_D/I_G$ of N-CNOs and their acylated derivatives

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-CNO</td>
<td>1.57</td>
</tr>
<tr>
<td>N-CNO-C5</td>
<td>1.52</td>
</tr>
<tr>
<td>N-CNO-C12</td>
<td>1.51</td>
</tr>
<tr>
<td>N-CNO-C18</td>
<td>1.56</td>
</tr>
</tbody>
</table>
Raman analysis of functionalized N-CNOs (Figure 3.21) shows that the ID/I_G ratio of N-CNO-C5, N-CNO-C12 and N-CNO-C18 are insignificantly less than that of unfunctionalized N-CNOs (Table 3.4). As described in Chapter 2, N-CNOs contain a lot of structural defects according to the proposed model in Figure 2.5, where the defects or edges are terminated with either hydrogen or oxygen atoms. FC acylation apparently takes place at defect sites either by replacing hydrogens or by acylating oxygens or both, leading to no change in ID/I_G ratio. The graphitic network is intact with no contribution to the intensity of D band, hence no change in ID/I_G ratio. A model with proposed sites of FC acylation of N-CNOs is shown in Scheme 3.3.

Scheme 3.3. A model for sites of FC acylation of N-CNO surface defects.

N-CNO-C5, N-CNO-C12 and N-CNO-C18 show improved dispersibility compared to N-CNOs, as shown for chloroform and THF in Table 3.5.

Table 3.5. Solubility (mg/mL) of acylated N-CNOs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chloroform</th>
<th>THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC</td>
<td>&lt; 0.1 *</td>
<td>&lt; 0.1 *</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>--------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>NC-C5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NC-C12</td>
<td>0.27</td>
<td>0.27</td>
</tr>
<tr>
<td>NC-C18</td>
<td>0.40</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Unstable dispersion

### 3.2.4 Billups reductive alkylation of N-CNOs

Birch reduction (often called as Billups reaction[60] for carbon nanomaterials) is a well-known synthetic approach to functionalize CNTs with alkyl and aryl halides[78, 79]. Reductive alkylation allows utilization π-bonds on the surface of CNOs. The typical mechanism involves the addition of organic electrophiles to radical anion intermediates formed by the reduction of double bond with solvated electrons in alkali metal solutions in liquid ammonia.

![Scheme 3.4](image)

**Scheme 3.4.** Air-cleaned N-CNOs reduced with Li in ammonia and further reacted with NH₄Cl, CH₃I, BrCH₂COOCH₂CH₃ and CH₃(CH₂)₁₀COCl

We started with Billups reductive alkylation using the simple electrophiles iodomethane (CH₃I) and ethyl 2-bromoacetate (BrCH₂COOCH₂CH₃) to prepare methyl-
functionalized N-CNOs 1 and ethoxycarbonylmethyl-functionalized N-CNOs 2 (Scheme 3.4). 2 can be hydrolyzed to hydroxycarbonylmethyl (-CH₂COOH) N-CNOs 4 and further functionalized to esters or amides.

**Figure 3.22.** TGA of air-cleaned and methyl- and ethoxycarbonylmethyl-functionalized N-CNOs.

Thermograms under air of air-cleaned, methyl N-CNOs 1 and ethoxycarbonylmethyl N-CNOs 2 are shown in Figure 3.22. TGA clearly shows that the combustion temperature decreases after functionalization. We propose that the surface initiate combustion at lower temperatures than the N-CNOs core, and combustion continues into the core. Both methyl and ethoxycarbonylmethyl N-CNOs started burning at ~220 °C with a higher mass loss for ethoxycarbonylmethyl N-CNOs than for methyl
methyl-CNOs. The surface coverage calculated from this mass loss for 1 and 2 are ~3.3% and ~11%, respectively. Introduction of defects[29] on the surface through functionalization also leads to a decrease in the combustion temperature of functionalized N-CNOs. The mass loss for both of these materials is not pronounced as the molecules attached on the surface of N-CNOs (methyl and ethoxycarbonylmethyl) are significantly small. Keeping this point in view this time we tried some long chain molecules like lauroyl chloride.

**Figure 3.23.** The TGA pattern of lauroyl-functionalized N-CNOs compared with that of air-cleaned and lauroyl adsorbed N-CNOs

TGA in air of lauroyl-functionalized N-CNOs 3 is shown in Figure 3.23. The first mass loss starting at 100 °C is due to the loss of water. The lauroyl chains started burning at ~200 °C with a slow but steady mass loss centered at ~350 °C. A sharp mass loss at
520 °C is due to the combustion of core N-CNOs. The low % mass loss (~10%) is due to a lower degree of functionalization. Similar to 1 and 2, the combustion temperature of 3 was significantly decreased to 520 °C compared to that of air-cleaned N-CNOs (638 °C). The surface coverage of 3 calculated from the mass loss at ~350 °C is ~2.7%.

A control reaction was performed to determine whether the mass loss at ~350 °C is due to the loss of covalently attached groups rather than adsorbed molecules. For this, N-CNOs were stirred for 5 h and bath-sonicated for 24 h with lauric acid in ethanol. The filtered and dried product was analyzed by TGA (red curve in Figure 3.23). This lauric acid-treated material showed no mass loss transition, but did show a decrease in the combustion temperature to 580 °C. It appears that the Billups reaction of N-CNOs with lauroyl chloride gives covalently attached laroyl groups.

Ethoxycarbonylmethyl N-CNOs 2 were hydrolyzed to hydroxycarbonylmethyl N-CNOs 4. Conversion to chlorocarbonylmethyl N-CNOs 5 followed by reaction with ferrocenyl methanol through an ester linkage gave ferrocenylmethoxycarbonylmethyl N-CNOs 6 (scheme 3.5). This material was characterized by using cyclic voltammetry (CV). CV is a versatile electroanalytical technique[80] to identify and quantify electroactive species in an analyte. In this technique, the working electrode potential is ramped linearly versus time, and when an end potential is reached the potential ramp of working electrode is reversed. During this process the current is between the working electrode and counter electrode is measured. The magnitude of the current is directly proportional to the concentration of electroactive species. From this technique, one can find out the redox activity of electroactive material within a potential window.
Scheme 3.5. Ethoxycarbonylmethyl N-CNOs 2 hydrolyzed to hydroxycarbonylmethyl N-CNOs 4, which further converted to chlorocarbonylmethyl N-CNOs 5. 5 reacted with ferrocenyl methanol to give ferrocenylmethoxycarbonylmethyl N-CNOs 6.

Cyclic voltammetry of compound 6 showed a reversible redox process (Figure 3.24) compared with air-cleaned, unfunctionalized N-CNOs. 6 showed an anode potential ($E_{pa}$) at 0.26 V due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$. The cathode potential ($E_{pc}$) for the reduction of Fe$^{3+}$ to Fe$^{2+}$ is at 0.32 V.
Mechanochemistry is a process where covalent chemical bonds are activated by an external mechanical force.\cite{81} In this solid-phase reaction, mechanical energy or motion is imparted to reaction system to generate highly reactive centers for further chemical reaction.\cite{62} It is a successful method for chemical modification of carbon materials such as fullerenes and carbon nanotubes.\cite{62, 82} Mechanochemistry has been used to covalently attach hydroxyl and cyano to the surface of carbon nanomaterials. We carried out mechanochemical reaction N-CNOs with solid potassium hydroxide (KOH) and analyzed the product using TGA.

**Figure 3.24.** Cyclic voltammograms of 6 (red) and air-cleaned N-CNOs (black).
Scheme 3.6. Mechanochemical hydroxylation of N-CNOs using KOH

TGA of mechanochemically hydroxylated N-CNOs shows a high residue of 17% with decreased combustion temperature of 355 °C (red curve in Figure 3.25) compared with that of air-cleaned N-CNOs (black curve in Figure 3.25). The high residue is due to the iron oxide contaminants from the steel reaction containers. Two modifications were done to the procedure to overcome this problem of high residue. The reaction time was reduced to 2 h instead of 4 h and the produced material was sonicated for 1 h with 5% HNO₃ to remove the iron oxide impurities. After HNO₃ treatment, there is a significant decrease in the residue (5% w/w) and combustion temperature increased to 480 °C as shown in Figure 3.25 (blue curve). In the previous case the iron oxide impurities may be catalyzing the combustion reaction resulting in lower combustion temperature, which is also observed in the case of SWCNTs purification.[83]
**Figure 3.25.** TGA of hydroxylated N-CNOs compared with that of air-cleaned N-CNOs (black). As obtained product (red) and 5% HNO$_3$ treated product (blue)

With this approach significant surface derivatization of N-CNOs was achieved, which is evident from huge decrease in the combustion temperature.
3.3 Experimental

3.3.1 Billups reductive alkylation

3.3.1.1 General procedure

*Table 3.6.* Electrophiles used in Billups reactions

<table>
<thead>
<tr>
<th>Electrophile</th>
<th>Amount</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$I (iodomethane)</td>
<td>0.28 mL/0.64 g</td>
<td>N-CNO- CH$_3$ 1</td>
<td>96 mg</td>
</tr>
<tr>
<td>BrCH$_2$COOEt (ethyl 2-bromoacetate)</td>
<td>0.5 mL/0.75 g</td>
<td>N-CNO- CH$_2$COOEt 2</td>
<td>98 mg</td>
</tr>
<tr>
<td>CH$_3$(CH$<em>2$)$</em>{10}$COCl (lauroyl chloride)</td>
<td>1.04 mL/0.988 g</td>
<td>N-CNO-CO(CH$<em>2$)$</em>{10}$CH$_3$ 3</td>
<td>99 mg</td>
</tr>
</tbody>
</table>

A 100 mL three-necked round-bottom flask with a Dewar condenser was cooled to a -78 °C using dry ice–acetone bath. Approximately 50 mL of anhydrous ammonia was condensed into the flask under nitrogen. Li metal (24.3 mg) was added and the resulting blue solution was stirred for 5 min. Air-cleaned N-CNOs (100 mg) were charged to the flask and allowed to stir for 30 min. The electrophile (Table 3.6) was added dropwise slowly with a syringe and the reaction mixture was stirred, slowly brought to room temperature and kept overnight for complete evaporation of ammonia. Milli-Q water was added and the mixture was stirred for 15 min. The resulting dispersion was filtered through a 0.2-µm nylon membrane filter and the resulting retentate was washed with water until the filtrate was neutral, rinsed with ethanol and finally rinsed with dichloromethane and dried under vacuum. The yields were listed in table 3.6.
3.3.1.2 Hydrolysis of ethoxycarbonylmethyl N-CNOs [2]

Material 2 (100 mg) and methanol (10 mL) were charged to a 25-mL round-bottom flask. Potassium hydroxide (0.56 g, 10 mmol) was added with stirring. After stirring for 8 h at room temperature under N₂, 6-N HCl was added dropwise until the reaction mixture was acidic while checking with a pH paper. Reaction mixture was filtered through a 0.2-µm nylon membrane filter and the resulting retentate was washed with water (20 mL) and dried overnight under vacuum to get 98 mg of material 4.

3.3.1.3 Reaction of N-CNO-CH₂COOH with ferrocenyl methanol

Oxalyl chloride (7.0 mL, 82 mmol) was charged to a 50-mL round-bottom flask under nitrogen. Material 4 (50 mg) was added and the dispersion was stirred for 15 min. N,N-Dimethylformamide (1 drop) was added and the mixture was stirred for 1 h at room temperature under N₂. The remaining oxalyl chloride was removed in vacuo to get a black solid of 5, which was stored under N₂ for further reaction.

Ferrocenyl methanol (100 mg, 0.46 mmol) was dissolved in THF (10 mL), and triethylamine (1 mL, 7.2 mmol) was added. This solution was transferred into the round-bottom flask containing material 5 under nitrogen at 0 °C. The reaction mixture was stirred for 15 min at 0 °C and slowly brought to room temperature and refluxed for 8 h. This reaction mixture was filtered through a 0.2-µm nylon membrane washed with THF (5 mL) followed by methanol (10 mL) and diethyl ether (5 mL) and dried under vacuum to get 48 mg of material 6.
3.3.2 Friedel-Crafts acylation

3.3.2.1 General procedure

Table 3.7. Acyl chloride used in FC acylation of N-CNOs

<table>
<thead>
<tr>
<th>Acyl chloride</th>
<th>Amount</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentanoyl chloride (CH₃(CH₂)₃COCl)</td>
<td>2.5 mL</td>
<td>N-CNO-(CO)C₄H₉</td>
<td>55 mg</td>
</tr>
<tr>
<td>Lauroyl chloride (CH₃(CH₂)₁₀COCl)</td>
<td>4.8 mL</td>
<td>N-CNO-(CO)C₁₁H₂₃</td>
<td>58 mg</td>
</tr>
<tr>
<td>Stearoyl chloride (CH₃(CH₂)₁₆COCl)</td>
<td>7.1 mL</td>
<td>N-CNO-(CO)C₁₇H₃₅</td>
<td>58 mg</td>
</tr>
</tbody>
</table>

NaCl (1.4 g, 24 mmol) and AlCl₃ (3.2 g, 24 mmol) were charged to a 50-mL three-necked round-bottom flask and mixed well under N₂. The mixture was heated to melting at 160 °C. To the melt, acyl chloride (Table 3.7) was added, followed by 50 mg of N-CNOs. A reflux condenser was attached, the temperature was raised to 180 °C and the reaction mixture stirred for 3 to 4 h. After cooling the reaction mixture to 50 °C, 5% v/v HCl solution (15 mL) was added and the mixture was stirred for 6 h. The reaction mixture was filtered through 0.2-μm nylon membrane, washed with water (15 mL), acetone (10 mL) and ethanol (5 mL) and vacuum dried overnight at 80 °C. Obtained product was charged to the fritted Soxhlet extractor and continuously extracted with toluene (40 mL) for 24 h under N₂. The apparatus was cooled to room temperature and
the product was washed with acetone (5 mL), ethanol (5 mL) and vacuum dried overnight at 80 °C. The yields were listed in table 3.7.

3.3.2.2 Blank reaction1: FC reaction without acyl chloride

Exactly as described in 3.3.2.1, N-CNOs (50 mg) heated in NaCl/AlCl3 but without addition of an acyl halide. An identical workup gave 48 mg of black solid.

3.3.2.3 Blank reaction2: Stirring N-CNOs in refluxing acyl chloride

A sample of N-CNOs (50 mg) was charged to a 25-mL round-bottom flask containing 5 mL of lauroyl chloride. A reflux condenser was attached and the mixture was refluxed for 3 to 4 h with stirring. The was mixture cooled to room temperature; filtered through 0.2-µm nylon membrane, washed with water (15 mL), acetone (10 mL) and ethanol (5 mL) and vacuum dried overnight at 80 °C to get 48 mg of black solid.

3.3.3 Oxidation of N-CNOs

3.3.3.1 Oxidation of N-CNOs to ON-CNOs

Using a modification of Tour’s carbon nanotube oxidation,[57] air-cleaned N-CNOs (100 mg) were charged to a 100 mL Schlenk flask. Oleum (20% SO3, 20 mL) was added and the mixture was stirred for 24 h under nitrogen atmosphere at room temperature. After cooling to 0 °C, a 2:3 mixture of oleum and conc. HNO3 (25 mL) was added slowly and stirred for 15 min at 0 °C. The suspension was warmed to room temperature, stirred for 15 min and heated to 75–85 °C for 1 h. After cooling to room temperature, the reaction mixture was poured into 100 mL of ice-cold water. The suspension was transferred into polycarbonate centrifuge tubes and centrifuged for 2 h at 3000 RPM to precipitate the oxidized CNOs. The black precipitate from all the tubes was combined, diluted with 40 mL
of water and vacuum filtered through a 0.2-µm nylon membrane filter. The solid was washed with 15 mL of methanol followed by 10 mL of ethyl ether and dried under vacuum at 60 °C to give 70 mg of ON-CNOs.

### 3.3.3.2 Base treatment of ON-CNOs

A sample of ON-CNOs (50 mg) was charged to a Schlenk flask with 40 mL of 8-M NaOH solution and stirred for 48 h at 100 °C under nitrogen. The cooled reaction mixture was vacuum filtered through a 0.2-µm nylon membrane filter to give a red-brown filtrate and black solid. The red-brown filtrate was neutralized with 12-M HCl to give a pale brown solid, which was collected by filtering through a 0.2-µm nylon membrane filter to give 500 mg of a mixture of CCFs and insoluble sodium salts. The black solid on the membrane filter was rinsed with the DI water (25 mL) to give a black filtrate, which was neutralized with 1-M HCl and filtered through 0.2-µm nylon membrane filter to give a black solid, which was washed with methanol (5 mL) and ethyl ether (5 mL) and dried in vacuum at 60 °C to give 44 mg of base treated ON-CNOs (BON-CNOs).

### 3.3.3.3 Thermal desorption of ON-CNOs

As shown in Figure 3.14, a 9-mm Pyrex tube charged with a sample of ON-CNOs (120 mg) was placed horizontally in a tube furnace and a U-tube was attached to it with a 15-mm Teflon Lab-Crest Fisher-Porter joint. The other end of the U-tube was connected to a Schlenk vacuum line with rubber vacuum hose. The furnace was closed and heated initially to 110 °C under vacuum for 3 h to dry the sample. After 3 h, the U-tube was immersed in liquid nitrogen and the furnace temperature increased to 200 °C. After 6–7 h, the furnace was cooled to room temperature, the liquid nitrogen bath was removed and the
The apparatus was vented. The U-tube was disconnected and the brown solid (~5 mg) that deposited near the tube entrance was scraped off and analyzed by MALDI-MS.

### 3.3.3.4 pH-Metric titrations

NaOH, NaHCO₃ and HCl solutions (50 mM) were freshly prepared with water boiled under nitrogen to remove CO₂. NaOH and HCl solutions were standardized using potassium hydrogen phthalate and sodium carbonate as primary standards. The exact concentration of NaHCO₃ was found by titrating a known amount of 50 mM NaHCO₃ against previously standardized HCl. ON-CNOs (20 mg) were transferred into a 20-mL glass vial with 6 mL of water and the contents were bath-sonicated for 15 min. The vial was sealed with a rubber septum through which a pH electrode and a nitrogen purge line were inserted (Figure 3.26).
Figure 3.26. pH-metric titration setup

While stirring the contents, titrant (50 mM NaOH) was added from a 1-mL gas-tight syringe in 0.05 mL increments with pH recorded after each addition. After adding ~4 mL of titrant, the pH was plotted against volume of titrant and pKₐ was found from the curve. Advanced pH-metric titrations were carried out to find out the distribution of strong and weak acidic functional groups of ON-CNOs. In a typical procedure, 20 mg of ON-CNOs were transferred into a 25-mL round-bottom flask with 8 mL of freshly prepared 50 mM NaOH solution and a magnetic stir bar under nitrogen. A tube containing Ascarite® (NaOH-coated silica) was fitted to the flask to exclude CO₂. The suspension was stirred for 3 d under nitrogen to ensure complete equilibrium between the base and the CNO’s acidic
functional groups. The suspension of base-neutralized ON-CNO was transferred to a 20-mL glass vial sealed with a rubber septum through which pH electrode and nitrogen purge line were inserted (Figure 3.26). Titrant (50 mM HCl) was added from a 1-mL gas-tight syringe in 0.05-mL increments with pH recorded after each addition. After adding 10 mL of titrant, pH was plotted against the volume of titrant to find out the endpoint. To perform a blank titration, 8 mL of the same 50 mM NaOH solution was titrated under the same conditions without CNO present. The volume of HCl consumed by base-neutralized ON-CNOs was found by subtracting the endpoint of 50 mM NaOH with CNOs from that of without CNOs. A similar procedure was followed for titration with sodium bicarbonate (NaHCO₃) to determine the number of strong acid groups (carboxylic acids and sulfonic acids) per gram of ON-CNOs.

3.3.4 Oxidation of N-CNOs with varying the reaction times

Air-cleaned N-CNOs (500 mg) were stirred with oleum (20% SO₃, 100 mL) at room temperature as described above. A 2:3 mixture of oleum and conc. HNO₃ (125 mL) was added slowly at 0 °C, stirred for 15 min and warmed to room temperature. A 15-mL aliquot of the reaction mixture was collected in a 50-mL polycarbonate tube. After heating the remaining reaction mixture to 75-85 °C, 15-mL aliquots were collected in 50-mL polycarbonate tubes at 0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 h. Each fraction was diluted with 40 mL of ice-cold water and centrifuged for 2 h at 3000 RPM. The black centrifugate was diluted again to 40 mL with water, vacuum filtered through a 0.2-µm nylon membrane filter, washed with 15 mL of methanol followed by 10 mL of ethyl ether and dried under vacuum at 60 °C. The mass of products obtained at various oxidation times is shown in table 3.2.
3.3.5 Mechanochemical hydroxylation of N-CNOs

Air-cleaned N-CNOs (70 mg) and KOH (1.2 g) were added to a stainless steel capsule equipped with a stainless steel ball. After placing a stainless steel cap, the loaded capsule was locked into place on the ball mill and shaken for 2 h at 80% of maximum amplitude. After completion of the reaction, the reaction mixture was sonicated in 5% nitric acid for 1 h. The resulting mixture was filtered through a 0.2-µm Nylon filter, washed with methanol (5 mL), diethyl ether (5 mL) and dried overnight at 80 °C under vacuum to get 45 mg of product.

3.4 Conclusion

Among the discussed functionalization approaches, oleum-assisted oxidation is effective in improving the dispersion properties of N-CNOs in polar organic and aqueous solvents. We found that ON-CNOs contain several acidic, oxygen-containing functional groups and it is interesting to know that almost 50% of the functionality is carried by the adsorbates (CCFs) that are attached to ON-CNO surface with weak van der Waals attractive forces. We also isolated and characterized these high molar mass adsorbates using MALDI-MS. We investigated the structure of ON-CNOs of increased oxidation times using HRTEM and Raman, and found a decrease in number of layers with an increase in the oxidation time.

We functionalized N-CNOs with long-chain molecules under Friedel-Crafts conditions and observed an improvement in dispersion properties in moderately polar solvents. We observed a trend in TGA under N₂ of N-CNOs functionalized with molecules of different chainlengths; the mass loss in TGA under N₂ increased with an increase in the chainlength of electrophile. We also proposed a model that illustrates
possible sites of FC acylation. We also observed significant surface derivatization of N-CNOs through Billups reductive alkylation and mechanochemical hydroxylation.
Chapter 4 Graphene from A-CNOs

4.1 Introduction

Graphene and graphene-based materials have attracted intensive research interest due to their fascinating properties.[84, 85] Although several starting materials such as graphite and CNTs were used to synthesize graphene, here we introduce the preparation of curved graphene structures from arc-produced carbon nano-onions (A-CNOs). After a brief review of preparative methods for graphene, this chapter focuses on synthesis and characterization of graphene structures prepared by unzipping A-CNOs.

4.1.1 A-CNOs

Several methods of CNO synthesis were discussed in Chapter 1. Underwater arc-discharge between carbon electrodes is useful to produce larger quantities of A-CNOs. This economical and environmentally benign method consists of two submerged graphite rods one as anode and other as cathode, and arc plasma was produced by the contact between anode and cathode at a discharge voltage and current of 16-17 V and 30 A respectively.[86] The arc-plasma produced under such conditions has an average temperature of 4000–6500 K. An experimental setup showing anode-cathode assembly of graphite rods is shown in Figure 4.13.

This method yields CNOs of 20–40 nm diameter with 25–35 graphitic layers with an interlayer spacing of ~3.4 Å, along with other carbon materials such as CNTs and graphitic particles as side-products.[42] Arc powers from 825 W to 1325 W have been used to synthesize A-CNOs, with 825 W being most efficient to produce A-CNOs in high yield with less graphitic impurities. The HRTEM image of purified A-CNOs prepared under these experimental conditions is shown in Figure 4.1. These A-CNOs have both
spherical and polygonal shapes with hollow cores of diameter between 10–12 nm. A-CNOs have larger crystallites compared to that of N-CNOs and the $L_a$ and $L_c$ of A-CNOs calculated from powder XRD analysis are ~62 Å and ~46 Å respectively.

*Figure 4.1.* HRTEM image of arc-produced CNOs (A-CNOs) produced with a power of 850 W showing both spherical and faceted shapes with hollow cores

4.1.2 Graphene

Graphene is an allotrope of carbon that is a one-atom-thick planar sheet of sp$^2$ carbon atoms, densely packed in a honeycomb lattice.[87] It is a two-dimensional
building material for other carbon materials, it can be wrapped up into zero-dimensional fullerene, rolled into one-dimensional nanotubes and stacked into three-dimensional graphite as shown in Figure 4.2.[88]

**Figure 4.2.** Model showing graphene as the building block of fullerenes, CNTs and graphite (Ref [88])

Graphene is the thinnest but strongest, dense and transparent material that conducts electricity as efficiently as copper. In recent years, graphene grabbed considerable attention as a next-generation electronic material due to its exceptional properties such as high current density, high electron mobility,[84] chemical stability,
These characteristic properties make graphene a unique material:

i. Purest form of carbon
ii. High theoretical specific surface area (2360 m²⋅g⁻¹)
iii. High intrinsic mobility (200,000 cm²⋅V⁻¹⋅s⁻¹)
iv. High tensile modulus (~ 1 TPa)
v. Good thermal conductivity (~ 5000 W⋅m⁻¹⋅K⁻¹)
vi. Optical transmittance (~ 97.7%)

Graphene was first prepared by mechanical exfoliation of highly ordered pyrolytic graphite (HOPG) and its electrical conductivity was measured in 2004 by scientists at University of Manchester in 2004.[91] Later researchers synthesized graphene by several physical and chemical methods starting with graphite and CNTs. The mechanical exfoliation or micromechanical cleavage involves peeling of HOPG several times using Scotch tape to give thin flakes and finally few-or single-layer graphene. This material was then transferred onto a silicon wafer for characterization (Figure 4.3).[91, 92] Arcing of graphite electrodes under high pressure of hydrogen[93] is another physical method to yield few-layer graphene, generally containing 2–4 layers. With this method, it is possible to dope graphene with boron and nitrogen by carrying out the electric discharge in the presence of B₂H₆ or pyridine. Single-layer and few-layer graphene has been also synthesized by thermal chemical vapor deposition (CVD) of camphor on a nickel substrate.[94]
Alkali metal intercalation of graphite is another efficient method to make scrolled graphene sheets.\cite{95} A highly exothermic reaction between alkali metal intercalated graphite and polar aprotic solvents leads to the exfoliation of graphite and formation of scrolled graphene structures as shown in the Figure 4.4.

![Figure 4.4. The intercalation/exfoliation process of graphite to scrolled graphene structures (adapted from Ref [95])](image)

Figure 4.3. Scotch-tape method: mounting of peeled graphite onto a silica wafer (Ref [91])
4.1.3 Graphite oxide

Graphite oxide (GO) is another widely used precursor for large-scale production of graphene. Graphite oxide, also known as graphitic oxide or graphitic acid, is a hydrophilic derivative of graphite obtained by treating graphite with strong oxidizing agents such as fuming nitric acid/potassium chlorate or sulfuric acid/potassium permanganate.[96] GO consists of graphene sheets decorated on both sides with epoxide (C—O—C), hydroxyl (—OH), carbonyl (C=O) groups and terminated with —OH and —COOH groups.[97, 98] In 1859, British chemist B. C. Brodie prepared GO for the first time by reacting potassium chlorate (KClO₃) with a slurry of graphite in fuming nitric acid (HNO₃).[99] In 1957, Hummer and Offeman developed an alternate oxidation method by reacting graphite with mixture of concentrated sulfuric acid (H₂SO₄) and potassium permanganate (KMnO₄).[100] This method is widely used, as it is safer, more economical and more efficient, although scientists have modified this procedure to suit their materials.

Due to the presence of various oxygen-containing functional groups, the inter-layer distance of GO is double that of parent graphite. GO is an electrical insulator, as its sp² network is disrupted due to the introduction of oxygen-containing functional groups along the basal plane and peripheries. GO is hydrophilic when dispersed in water and certain other solvents, it is partially or fully exfoliated by solvent molecules, and thus can be referred as graphene oxide. Similar to graphite oxide, graphene oxide is also an electrical insulator due to the disruption of sp² carbon network during oxidation. In order to restore the electrical conductivity, simultaneous removal of oxygen-containing functional groups (reduction) and restoration of the sp² carbon network is needed.
Scheme 4.1. Graphite oxidized to graphite oxide, which is further reduced to graphene or reduced graphene oxide to restore conductivity properties

Reduction of graphene oxide is an established procedure to make graphene in large quantities. Several thermal, electrochemical and solution-based chemical methods are reported to reduce graphene oxide back to graphene.[68, 76, 98, 101-105] Among solution-based chemical methods, the most widely used reducing reagent is hydrazine hydrate, which efficiently restores the conductivity by reducing the oxygen-containing functional groups.[98] A series of sulfur-containing compounds such as NaHSO₃, Na₂SO₃, Na₂S₂O₃, Na₂S•9H₂O, SOCl₂ and SO₂ were also used as reducing reagents to reduce graphene oxide.[103] Other chemical methods involve heating at 150 °C in propylene carbonate[101] and reacting with sodium borohydride (NaBH₄) at room temperature.[102] Thermal reduction at 1000 °C under argon[68] and flash reduction using a pulsed xenon flash[105] are two other successful physical methods to reduce graphene oxide to graphene. Recently, electrochemical reduction methods also have been introduced.[76, 104] As the structure of graphene oxide is still not clear, all the above mentioned reduction methods can’t achieve 100% restoration of sp² carbon network or conductivity. Therefore, graphene obtained by reduction of graphene oxide is usually called reduced graphene oxide (RGO), functionalized graphene, chemically converted
graphene, chemically modified graphene or reduced graphene.[106] Scheme 4.1 depicts the type of structural changes that take place during the oxidation of graphite to graphene oxide followed by reduction of graphene oxide to graphene.

4.1.4 Graphene from CNTs

After graphite and graphite oxide, another significantly used precursor of graphene is carbon nanotubes (CNTs). Graphene nanoribbons (GNRs), thin elongated strips of graphene with straight edges were synthesized by longitudinal unzipping of CNTs.[58, 107-110] Some of the successful unzipping procedures include oxidation of CNTs using a mixture of potassium permanganate (KMnO₄) and concentrated sulfuric acid (H₂SO₄),[58] intercalation-exfoliation of CNTs by treatment with lithium and ammonia followed by acid treatment,[107] cutting of CNTs using transition metal nanoparticle catalysts,[108] inducing resistive heating into CNT structure by electrical current in vacuum[109] and argon plasma etching of CNTs partially embedded in polymer film.[110, 111] Among these methods, unzipping of CNTs using a mixture of KMnO₄ and H₂SO₄ is most promising, simple and economical as it involves a sequential longitudinal cutting. Some CNT unzipping methods are shown in Figure 4.5.
Figure 4.5. Unzipping CNTs into GNRs. (a) Intercalation-exfoliation using NH₃ and Li, (b) using mixture of H₂SO₄ and KMnO₄ as oxidizing agents, (c) catalytic approach, using transition metal nanoparticles as cutting agents, (d) an electrical method, by passing an electric current and (e) a physicochemical method, by Ar plasma etching of polymer embedded CNTs (adapted from Ref [111])

4.1.5 Graphene from CNOs

Graphene isolated from graphite is two-dimensional (2D, both length and breadth > 100 nm) and the graphene nanoribbons synthesized from unzipping of CNTs is one-dimensional (1D, either breadth < 100 nm). The most effective problem of bulk production of graphene is restacking back to the original graphitic structures. Several better methods were devised to synthesize novel graphene structures while avoiding the
restacking problem. Carbon nano-onions, specifically A-CNOs upon oxidation with KMnO₄/H₂SO₄, can lead to the formation of curved graphene structures with dimensions under 100 nm. These curved graphene structures are expected to have a low tendency to restack and high surface area, which are desired for battery and supercapacitor applications. Curved graphene structures tend to restack less than traditional graphene structures, and their curved morphology enables the formation of mesopores, which is desirable for energy storage applications.[112] Also, with the dimensions less than 100 nm, these structures should possess high specific surface area.

![Scheme 4.2](image)

**Scheme 4.2.** Schematic of unzipping/oxidation of A-CNOs to A-CNO-GO which is further reduced to curved graphene structures

Scheme 4.2 gives an outline of how A-CNOs are unzipped to form curved graphene structures. First, they are oxidized using a mixture of conc. H₂SO₄ and KMnO₄ similar to that of CNTs.[58] During oxidation, A-CNOs are unzipped to curved graphene
oxide (GO) structures with simultaneous introduction of several oxygen-containing functional groups like hydroxyl, epoxide, carbonyl and carboxylic acid on the surface as shown in Scheme 2. Tour’s proposed mechanism of nanocarbon unzipping[58] involves formation of a manganate ester in the first step and further oxidation to dione in second step (Figure 4.6). The orientation of ketones distorts β, γ- alkenes (shown in red) making them more strained and prone to further oxidation. This process of unzipping continues until there is no more strain on β, γ- alkenes. The preference for sequential bond cleavage over random attack on non-neighboring carbon atoms is due to the concerted attachment to the neighboring carbon atoms by permanganate.

![Diagram of chemical mechanism](image)

**Figure 4.6.** Proposed chemical mechanism of CNT/CNO unzipping during KMnO₄ oxidation (adapted from ref [25])

4.2 Results and discussion

Scheme 4.3 is a summary of reactions that we carried out to make graphene from A-CNOs. A-CNOs are unzipped using a mixture of KMnO₄ and H₂SO₄ to make oxidized
A-CNOs (A-CNO-GO). To restore A-CNO-GO’s sp² carbon network and thereby its electrical conductivity, we used several reducing methods. Some of the solution-based chemical reduction methods include reacting with hydrazine hydrate at 100 °C[98] and heating in propylene carbonate at 150 °C[101] to get A-CNO-HZ-RGO and A-CNO-PC-RGO respectively. As 100% reduction of GO to graphene is impossible, we prefer to call the reduced product reduced graphene oxide (RGO) instead of graphene. To determine the extent to which the chemical reduction of A-CNO-GO restores the electrical conductivity of the graphitic network, we measured the room-temperature electrical conductivities of compressed A-CNO, A-CNO-GO and A-CNO-HZ-RGO powders.[113] Since both A-CNO-HZ-RGO and A-CNO-PC-RGO show very low conductivity, we used thermal reduction method to reduce A-CNO-GO to A-CNO-TH-RGO, which showed significantly higher conductivity than chemically reduced GO.
Scheme 4.3. A-CNOs oxidized to A-CNO-GO which is further reduced to regain the conductivity by chemical and thermal methods

4.2.1 Powder conductivity measurements

We carried out extensive studies of compressed carbonaceous powders and the measurement of their electrical conductivity.\cite{113-117} Performing these experiments is very simple, rapid and cheap. Measuring the conductivity of powder requires pressing on a bed of grains in order to ensure electrical contact between particles. The pressure-induced rearrangement of particles increases their mean coordination number, further increasing electrical conductivity.\cite{113} The electrical conductivity of a compressed carbonaceous powder depends upon the applied pressure and is a combination of electrical conductivity of individual particles, the degree of contact between them and their packing.\cite{116} More interparticle contacts establish more channels for electrical
current transport. The typical experimental setup for the measurement of electrical conductivity in compressed state is shown in Figure 4.14. In a compressed powder conductivity measurement, ca. 20 mg of powder was pressed between two steel electrodes by applying pressures of 101, 236 and 784 kPa. Current was measured by applying voltage across the steel pistons. To see the ohmic behavior of the material, the applied voltage is plotted against corresponding current. From the slope of the I-V curve, electrical resistance can be found and electrical conductivity at that particular pressure is measured by

$$\sigma = \frac{l}{RA}$$

Where \(\sigma\) is electrical conductivity of the material at that particular pressure, \(l\) is the length of compressed material in cm, \(R\) is the electrical resistance found from the slope of the current-voltage (I-V) curve in ohms (\(\Omega\)) and \(A\) is the cross-sectional area of compressed material in cm\(^2\) (Figure 4.7).

**Figure 4.7.** A description of length and cross-sectional area of compressed material
Table 4.1. Conductivities (S•m⁻¹) of A-CNO materials at three pressures

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>A-CNOs</th>
<th>A-CNO-HZ-RGO (hydrazine)</th>
<th>A-CNO-TH-RGO (Δ, 1050 °C, Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>227.3</td>
<td>5.2</td>
<td>47.4</td>
</tr>
<tr>
<td>236</td>
<td>357.1</td>
<td>13.3</td>
<td>135.2</td>
</tr>
<tr>
<td>785</td>
<td>909.1</td>
<td>34.5</td>
<td>344.8</td>
</tr>
</tbody>
</table>

The electrical conductivities of A-CNOs and A-CNO-RGOs at various applied pressures are listed in Table 4.1. The data shown are average of two measurements. The effect of increase in pressure on electrical conductivity of A-CNO-RGOs and A-CNOs is shown by the conductivity vs. pressure curve in Figure 4.8b. A-CNOs showed an electrical conductivity of ~900 S/m at a pressure of 785 kPa. A-CNO-GO showed zero conductivity at all pressures as it is an electrical insulator. The chemically reduced GO (A-CNO-HZ-RGO) showed very low conductivity compared to that of A-CNOs, which is not desirable. This low restoration after reduction could be either due to residual oxygen-containing functional groups due to incomplete reduction or high contact resistance. It is clear that hydrazine reduction was not efficient enough to restore sp² carbon network by removing most of oxygen-containing functional groups. It is reported that hydrazine is efficient enough in reducing epoxides, and researchers came up with mechanism associated with this de-epoxidation. However, hydrazine’s ability to reduce other oxygen-containing functional groups such as hydroxyl is still unclear.[118] It is also reported that hydrazine reduction leaves high sheet resistance due to the formation of C—N bonds.[119] To improve the conductivity of RGO, we used a thermal reduction method...
where A-CNO-GO was heated at 1050 °C under argon for one minute. This material (A-CNO-TH-RGO) shows considerably higher conductivity than A-CNO-HZ-RGO. At a pressure of 785 kPa, A-CNO-TH-RGO shows an electrical conductivity of 345 S/m, which is ~ 40% to that of precursor A-CNOs. Thermal reduction is more efficient than chemical reduction in restoring electrical conductivity of graphene sheets by removing most of the oxygen-containing functional groups.

**Figure 4.8.** Plots of a) density vs. pressure, b) conductivity vs. pressure and c) density normalized conductivity (DNC) vs. pressure for A-CNO-RGOs and A-CNOs.
From the mass and volume of compressed powder at various pressures, bulk density at that particular pressure is calculated by

$$\rho = \frac{4m}{\pi d^2 l}$$

Where $\rho$ is bulk density of the material at that particular pressure, $m$ is the mass of the material in grams, $d$ is the width and $l$ is the length of compressed material in cm.

**Table 4.2.** Bulk densities (g•cm$^{-3}$) of A-CNO materials at three pressures

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>A-CNOs</th>
<th>A-CNO-HZ-RGO (hydrazine)</th>
<th>A-CNO-TH-RGO (Δ, 1050 °C, Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>0.748</td>
<td>0.459</td>
<td>0.229</td>
</tr>
<tr>
<td>236</td>
<td>0.808</td>
<td>0.546</td>
<td>0.288</td>
</tr>
<tr>
<td>785</td>
<td>0.962</td>
<td>0.722</td>
<td>0.386</td>
</tr>
</tbody>
</table>

The bulk densities of A-CNOs and A-CNO-RGOs at various applied pressures are listed in Table 4.2. The data shown are average of two measurements. The effect of increase in pressure on bulk densities of A-CNO-RGOs and A-CNOs is shown by the density vs. pressure curve (Figure 4.8a). For all the materials, a similar trend in increase in the bulk density with applied pressure was observed. The morphology of carbon powders consists of agglomerates, built up of many primary particles. At lower pressure, due to the presence of large voids between agglomerates and loose packing, low bulk density values were observed. At this low pressure, the observed density is mainly due to rearrangement and fragmentation of relatively weak agglomerates controlled by particle-particle friction. At higher pressures, with high compression of agglomerates, the rearrangement and reduction of intra-agglomerate primary particle distances takes place.
and bulk density increases.[120] As both A-CNO-RGO materials are more expanded and highly dispersed, they show low bulk density values compared to starting material (A-CNOs). During thermal reduction of graphene oxide, when material is heated under inert atmosphere at 1050 °C, the gases released from oxygen-containing functional groups will significantly kick the graphene sheets away from each other. Because of this, thermally reduced GO (A-CNO-TH-RGO) is more expanded than A-CNO-HZ-RGO, hence showing very low bulk density.

The materials for electrical conductivity comparison exhibit different densities at a particular pressure. For example, at a pressure of 785 kPa, A-CNOs, A-CNO-HZ-RGOs and A-CNO-TH-RGOs have bulk densities of 0.962, 0.722 and 0.386 g·cm⁻³ respectively. So the packing and extent of contact between the particles is not similar at that particular pressure. Hence we came up with a parameter called ‘density normalized conductivity (DNC)’, which is electrical conductivity over bulk density at a particular pressure,

\[
\text{DNC} = \frac{\sigma}{\rho}
\]

Where \(\sigma\) is electrical conductivity in S/m and \(\rho\) is bulk density in g·cm⁻³.

**Table 4.3.** Density normalized conductivity (DNC, S·m⁻¹·g⁻¹·cm³) of A-CNO materials at three pressures

<table>
<thead>
<tr>
<th>Pressure (kPa)</th>
<th>A-CNOs</th>
<th>A-CNO-HZ-RGO (hydrazine)</th>
<th>A-CNO-TH-RGO (Δ, 1050 °C, Ar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>303.88</td>
<td>11.2</td>
<td>206.9</td>
</tr>
<tr>
<td>236</td>
<td>441.96</td>
<td>24.4</td>
<td>469.4</td>
</tr>
<tr>
<td>785</td>
<td>945.01</td>
<td>47.7</td>
<td>893.2</td>
</tr>
</tbody>
</table>
Our intention was to consider the effect of bulk density while comparing the electrical conductivity of materials. The DNC values of A-CNO, A-CNO-HZ-RGO and A-CNO-TH-RGO are listed in table 4.3. The effect of increase in the pressure on DNC of A-CNO and A-CNO-RGO samples is shown by the DNC versus pressure curve in Figure 4.8c. The DNC of A-CNO-RGO is almost equal to that of A-CNOs, implying that thermal reduction is effective enough to restore almost 100% of conductivity, unlike hydrazine reduction. Under similar pressure, A-CNO-TH-RGO shows electrical conductivity almost equal to that of A-CNOs.

4.2.2 Powder XRD analysis

The interlayer distance of the CNO materials after oxidation and reduction processes was monitored using powder X-ray diffraction. As mentioned in chapter 2, the interlayer spacing can be calculated from the position of peak corresponds to (002) crystal planes. The powder XRD pattern of A-CNOs, A-CNO-GOs, A-CNO-HX-RGOs and A-CNO-TH-RGOs is shown in Figure 4.9.
For A-CNOs, the (002) peak was observed at $2\theta = 26^\circ$, corresponding to an interlayer distance of 3.4 Å. In the XRD pattern of A-CNO-GO, the strong peak at $2\theta = 11.6^\circ$ corresponds to an interlayer distance of 7.6 Å is due to (002) crystal planes. This increase in interlayer distance is due to the introduction of several oxygen-containing functional groups on the basal planes of unzipped structures of A-CNOs. There is one very low intense peak at $2\theta = 26^\circ$ corresponding to (002) of A-CNOs that may be left unoxidized. For chemically reduced graphene oxide (A-CNO-HZ-RGO), the peak at $2\theta = 11.6^\circ$ is almost absent as most of oxygen-containing functional groups are removed.
during oxidation. Also a broad peak was observed that can be fitted by using Lorentzian function into at least three peaks centered at $2\theta = 19^\circ$, $23^\circ$ and $26^\circ$, corresponding to an interlayer distances of 4.7 Å, 3.9 Å and 3.4 Å respectively. These XRD results clearly support the reduction processes of intervening oxygen-containing functional groups of A-CNO-GO and exfoliation of graphene structures. This kind of observation is also related to an irregular orientation of reduced graphene structures without a significant re-stacking. The XRD pattern of thermally reduced graphene oxide (A-CNO-TH-RGO), shown in Figure 4.9, indicates an amorphous structure with no significant peaks except one very low intense peak at $2\theta = 26^\circ$. We assign this peak to (002) of A-CNOs that is left unoxidized is carried over.

### 4.2.3 Thermogravimetric analysis

Thermograms of A-CNOs, A-CNO-GO, A-CNO-HZ-RGOs and A-CNO-TH-RGOs are shown in Figure 4.10. All the samples were heated from ambient temperature to 750 °C under argon with high resolution dynamic mode. A-CNOs showed no mass loss in this temperature range, as there are no functional groups on the surface and no possibility of oxidation under inert atmosphere. For A-CNO-GOs, the mass loss (~ 7%) before 100 °C is due to the absorbed water as the material is highly hydrophilic. A dramatic mass loss (~ 25%) at 200 °C is due to the loss of oxygen-containing functional groups. This loss can be in the form of liberated gases such as CO$_2$ and H$_2$O. [68]
Figure 4.10. Thermograms of A-CNOs, A-CNO-GOs and A-CNO-RGOs under nitrogen

4.2.4 BET surface area

The specific surface area of A-CNO materials was calculated from BET nitrogen adsorption/desorption studies. Both chemically and thermally reduced GOs showed at least 3-fold increase in the surface area compared to A-CNOs. The surface area of A-CNOs, A-CNO-GOs, A-CNO-HZ-RGOs and A-CNO-TH-RGOs is shown in Table 4.4.
Table 4.4. BET surface area (m$^2$/g) of A-CNOs, GOs and RGOs

<table>
<thead>
<tr>
<th>Material</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-CNO</td>
<td>30</td>
</tr>
<tr>
<td>A-CNO-GO</td>
<td>240</td>
</tr>
<tr>
<td>A-CNO-HZ-RGO</td>
<td>120</td>
</tr>
<tr>
<td>A-CNO-TH-RGO</td>
<td>95</td>
</tr>
</tbody>
</table>

4.2.5 Atomic force microscopy (AFM) analysis

The number of layers in RGO material was studied from the height profile of atomic force microscopy (AFM) analysis. Several attempts were made to get suitable dispersion of GO to deposit on the silica wafer. Lack of proper dispersion of GO on silica wafer resulted in undesired height profiles that are not informative in understanding the morphology and actual size of graphene fragments. In order to get the GO dispersed evenly, in situ reduction of GO to RGO on silica wafer was carried out under argon at 1050 °C (Figure 4.11).
Figure 4.11. In-situ thermal reduction of A-CNO-GOs to A-CNO-TH-RGOs on silica wafer for AFM analysis.

The phase and topography images of A-CNO-TH-RGOs that were acquired through tapping mode AFM are shown in Figure 4.12. Phase image usually reveals the homogeneity of the material. The surfaces with different chemical nature will show different color contrast in a phase image. The similar contrast shown in phase image of Figure 4.12 implies homogeneity of A-CNO-TH-RGO. In the topography image, the intensity of the color refers to the height of the material from the substrate. The topography image and corresponding height profiles are given in Figure 4.13. The height profiles show that in situ reduction is successful enough to get as low as bilayer graphene, evident from the height of 0.8 nm. Most of the AFM images corresponding to graphene fragments show the dimensions less than 100 nm (~60 nm), which is expected from unzipping of A-CNOs with diameters between 25–40 nm.
Figure 4.12. AFM analysis of A-CNO-TH-RGOs: topography image and height profiles of three different spots and phase image.

From the AFM analysis, it is evident that graphene fragments with dimensions less than 100 nm (nanographene structures) were synthesized. The powder conductivity measurements show that the graphene material synthesized through thermal reduction was equally conductive as A-CNOs and has surface area three times to that of A-CNOs. But, from the characterization data that we have, it is still not clear whether these graphene structures are curved. Our next aim would be to analyze for HRTEM to see actual morphology of these structures.
4.3 Experimental

4.3.1 Preparation of A-CNOs

An automated arc-discharge setup was built in the laboratory and its anode-cathode contact assembly is shown in Figure 4.13. 3 L of DI water was charged into a 4 L Pyrex beaker surrounded by a circulating ice-water bath. High-purity graphite rods (McMaster) were used as anode (6”× 1/4”) and cathode (3”× 1/2”). The arc assembly shown was lowered into the bottom of the beaker and N\textsubscript{2} was passed through the nozzle. The N\textsubscript{2} pressure was maintained such that water did not rise up to the terminal connections inside the hollow tube. Power of 825 W is supplied from a modified Chicago Electric Dual MIG 151T/2 welder to produce arc-plasma in water. The controller maintains a 30% duty cycle to control the arc and prevent overheating.

After the experiment, the floating material on the water was collected on 0.2-\textmu m Nylon membrane filter, washed with ethanol (10 mL) and dried overnight in vacuum at 80 °C. The obtained material sieved through 250 \textmu m mesh to remove bulky graphitic particles and remaining material was ball-milled for 30 min using Teflon balls. The ball-milled material was air-cleaned at 450 °C to remove any amorphous carbon impurities.
Figure 4.13. Experimental setup of arc-discharge of graphite rods in water with anode-cathode contact assembly.

4.3.2 Unzipping of A-CNOs to A-CNO-GOs

A sample of CNOs (100 mg) was charged to a Schlenk flask with 50 mL of conc. H$_2$SO$_4$ and stirred for 24 h at room temperature. KMnO$_4$ (500 mg) was added to the reaction mixture and stirred for 1 h at room temperature. The reaction mixture was heated in an oil bath and stirred for 30 min at 55 °C and 1 h at 75–85 °C. The reaction mixture was cooled to room temperature and poured into 200 mL of ice-cold water with 3 mL of 30% H$_2$O$_2$ (to prevent precipitation of insoluble MnO$_2$). This dispersion was transferred into 50-mL polycarbonate tubes, centrifuged for 30 min at 3000 RPM and the supernatant was removed from the dark brown precipitate. The dark brown solid was dispersed in 50 mL of DI water by bath-sonicating for 30 min. The material from this dispersion was...
flocculated by adding 20% v/v HCl (10 mL) and the contents were filtered and the solid collected on a 0.2-µm nylon membrane filter, washed with water (10 mL), acetone (5 mL) and ether (5 mL) and dried under vacuum at 60 °C to give 125 mg of graphene oxide.

4.3.3 Hydrazine reduction of A-CNO-GO

A sample of graphene oxide (100 mg) was dispersed in 100 mL of DI water by bath-sonicating for 15 min and horn-sonicating for 20 min (with 25% duty cycle). This dispersion was transferred into a Schlenk flask and hydrazine hydrate (1.5 mL) was added slowly, followed by stirring at 95 °C for 24 h. The reaction mixture cooled to room temperature, filtered and the solid was collected on a 0.2-µm nylon membrane, washed with water (20 mL), acetone (10 mL) and ethanol (5 mL) and dried under vacuum at 80 °C to give 80 mg of hydrazine-reduced graphene oxide of A-CNOs (A-CNO-HZ-RGOs).

4.3.4 Propylene carbonate reduction of A-CNO-GO

A graphene oxide suspension (1 mg/mL) was obtained by dispersing a sample of A-CNO-GO (100 mg) in anhydrous propylene carbonate (PC, 100 mL) with the aid of bath sonication for 1 h and horn sonication for 20 min at 25% duty cycle. This suspension was transferred to a Schlenk flask and heated with stirring in an oil bath for 12 h at 180 °C. After cooling to room temperature, this suspension was filtered and solid was collected on a 0.2-µm nylon membrane filter. After draining PC completely, the black RGO solid was washed with acetone (5 mL) and ethanol (5 mL) and dried overnight under vacuum at 80 °C to give 85 mg of propylene carbonate-reduced graphene oxide of A-CNOs (A-CNO-PC-RGOs).
4.3.5 Thermal reduction of A-CNO-GO

A sample of graphene oxide (100 mg) was charged to a 25 cm long quartz tube (id = 1.2 cm). Argon inlet and outlet were inserted through rubber stoppers and the sample was purged with argon for 20 min. While the sample was under argon, the quartz tube was kept in a preheated tube furnace and heated for 1 min at 1050 °C. The quartz tube was removed from furnace, allowed to cool to room temperature and the reduced graphene oxide sample (50 mg) was collected.

4.3.6 Electrical conductivity measurement

The device used to measure the conductivity of powders is schematically shown in Figure 4.14. It consists of a thick-walled glass tube (inner diameter = 1.3 mm) with its bottom closed by a stationary steel piston. Around 20 mg of sample (A-CNOs, A-CNO-HZ-RGO and A-CNO-TH-RGO) was accurately weighed and poured into the tube from the top using a tiny glass funnel. A close-fitting steel plunger/piston, which is allowed to move down in the glass cylinder, closes the compression chamber. Loads equivalent to pressures 101, 236 and 784 kPa were applied to the movable upper steel piston to compress the powder. The distance between two pistons was measured before and after compression using a Vernier caliper; the difference between these two values is the length of the compressed sample. The DC electrical resistance of the pressed powder was determined by two-probe method by connecting both the steel pistons to an external power circuit as shown in Figure 4.14. Known voltages were applied via two plugs fitted to two steel pistons, and corresponding currents flowing through compressed powder were measured. The currents were plotted against voltages to check the ohmic behavior of the sample. The DC electrical resistance was determined from the slope of the current.
vs. voltage (I-V) curve. Thus, both apparent density $\rho$ and electrical conductivity $\sigma$ were determined for the sample at each applied pressure.

![Diagram showing a two-probe experimental setup for the measurement of electrical conductivity of compressed powders.](image)

**Figure 4.14.** Two-probe experimental setup for the measurement of electrical conductivity of compressed powders

### 4.3.7 In-situ thermal reduction of A-CNO-GO

A sample of A-CNO-GO (5 mg) was transferred into a 50-mL polycarbonate tube with 25 mL of N-methylpyrrolidone (NMP), horn-sonicated for 10 min with 25% duty cycle and bath-sonicated for 24 h. After sonication, this dispersion was centrifuged at 3000 rpm for 2 h to settle remove undispersed material. Two drops of supernatant dispersion were placed onto a 1 cm $\times$ 1 cm silica wafer and dried overnight under vacuum at 110 °C. The dried silica wafer was placed in a 25 cm long quartz tube (id = 1.2
Argon inlet and outlet were inserted through rubber stoppers and the sample was purged with argon for 20 min. This tube with a slight argon flow was placed into a tube furnace preheated to 100 °C and the furnace temperature was gradually raised 1050 °C with a ramp rate of 25 °C/min. After that, the furnace was cooled to room temperature, the quartz tube was taken out and the silica wafer with reduced A-CNO-GO was analyzed by AFM.

### 4.4 Conclusion

A-CNOs were unzipped to make graphene structure with dimensions within 100 nm and improved specific surface area. Electrical conductivity and bulk density were measured in compressed state for A-CNOs and A-CNO-derived graphene materials during oxidation and subsequent reduction. The compressed state conductivity measurements suggests that thermal reduction of A-CNO-GO is more effective in restoring conductive network compared to hydrazine-assisted reduction. A-CNO-TH-RGO showing density normalized conductivity almost equal to that of A-CNOs. We also devised *in-situ* thermal reduction method for AFM analysis to find out the width and dimensions of thermally reduced graphene oxide.
Chapter 5 Negative Electrode Materials for Lithium Ion Batteries

5.1 Introduction

An electrochemical cell is a chemical device for generating electricity. It contains positive and negative electrodes separated by an electrolyte, which conducts ions but not electrons. The chemical reactions at two electrodes, called half-cell reactions, generate electricity. An electrode contains an active material, which is a chemical that undergoes chemical reaction, and a metal component attached to it called a current collector. The driving force for the external current is the difference between the electrode potentials of the two half-cell reactions. During the discharge of a cell, the current collector of the negative electrode gathers the electrons liberated by a half-cell reaction. These electrons pass through the external load, do useful work, and are accepted by the current collector of the positive electrode with its complementary half-cell reaction. When two or more cells are joined together electrically, either in series (positive electrode of one cell to negative electrode of other) or in parallel, the resulting assembly is called a battery.[121]
Figure 5.1. Classification of batteries; Lithium ion batteries are primary rechargeable batteries.

Batteries are mainly classified into chemical batteries and physical batteries. Chemical batteries that produce electric energy by chemical reaction are further classified into primary non-rechargeable (disposable) batteries and secondary rechargeable batteries (Figure 5.1). Lithium-ion batteries (LIBs) are secondary chargeable batteries that are widely used in modern society since their commercialization in the early 1990s by Sony. Due to their high energy and power densities and stable cycling performances, LIBs are used as portable electrical energy storage systems.[122, 123]
Figure 5.2. Comparison of various electrochemical energy storage systems in terms of gravimetric and volumetric energy densities (Ref [122]).

Usually batteries are compared in terms of their volumetric and gravimetric energy densities to use them for a commercial purpose. Stored energy per unit mass is gravimetric energy density or specific energy (expressed in W h kg\(^{-1}\)) and stored energy per unit volume is volumetric energy density or energy density (expressed in W h dm\(^{-3}\)).[121] A comparison of various batteries in terms of gravimetric and volumetric energy densities is shown in Figure 5.2. LIBs outperform other batteries with high volumetric and gravimetric densities, as they are smaller and lighter than other batteries such as lead-acid, nickel-cadmium and nickel-metal hydride.
5.1.1 Lithium ion battery

The enormous interest for LIBs is due to the following characteristics.

1. High gravimetric (~125 W h kg\(^{-1}\)) and volumetric (~ 300 W h dm\(^{-3}\)) energy density;
2. High average operating voltage (3.6 V);
3. Excellent charge-discharge properties, with more than 500 cycles;
4. Low self-discharge on standing (< 10% per month);
5. No memory effect as observed in case of Ni-Cd batteries;
6. Rapid recharging is possible, i.e. within 2 to 3 h;
7. Safer than equivalent cells that use lithium metal, with no special transportation regulations.[121]

A typical LIB consists of a positive electrode (cathode), a negative electrode (anode) separated by an ionically conducting and electronically insulating liquid electrolyte. Layered lithium-transition metal oxides such as LiCoO\(_2\) and LiNiO\(_2\) and spinel-structured LiMn\(_2\)O\(_4\) are used commercially as cathode materials in LIBs, among which LiCoO\(_2\) is the most popular.[124, 125] The structure of layered oxides is favorable to rapid Li insertion and extraction. Aluminum metal is used as the current collector on the positive electrode side. Since the launch of Sony’s first commercial LIB, graphite has been used predominantly as anode material. Silicon, tin, graphene and other carbon nanomaterials such as CNTs and CNOs were also tested as anode materials for LIBs.[126-131] Copper metal is used as the current collector at negative electrode side. Liquid electrolytes in LIBs consist of an organic solvent, typically a combination of ethylene carbonate, dimethyl carbonate, and diethyl carbonate, with a dissolved lithium salt such as LiPF\(_6\), LiBF\(_4\), LiBOB (lithium bis(oxalato)borate), or LiClO\(_4\). The primary
function of the electrolyte is shuttling Li ions between two electrodes. Before discussing
the mechanism of LIB, it is worth getting familiar with the following terms.

**Cell potential:** The difference between anode oxidation potential and cathode reduction
potential is the standard cell potential.

**Capacity/storage capacity:** Capacity of a battery is the amount of charge, usually
expressed in ampere-hours that can be withdrawn from a fully charged battery under
specified conditions. Also, the capacity/storage capacity is the product of current and the
number of hours for which the cell/battery can be discharged to a defined cut-off voltage
when a battery is discharged at constant current. The value of capacity depends greatly
upon the rate of discharge; the higher the rate of discharge, the lower will be the available
capacity

**C-rate:** The discharge rate or charge rate, in amperes, is expressed relative to the rated
capacity. For example, for LIBs, C/10 (37.2 mA, where C is theoretical capacity of
graphite, i.e. 372 mA·h/g) draws a current of 37.2 mA for 1 h.

**Columbic efficiency:** The ratio, usually expressed as a percentage of the ampere-hours
removed from a battery during a discharge, to the ampere-hours required to restore the
initial capacity. For a material such as graphite, the columbic efficiency is the ratio of
amount of lithium extracted to the amount of lithium inserted.
Figure 5.3. Schematic of charge/discharge mechanism in a conventional LIB with metal oxide cathode vs. graphite anode. Charge is indicated by blue arrows and discharge is indicated by red arrows. (Ref [133])

LIBs shuttle Li ions from positive to negative electrode on charging and from negative to positive electrode on discharging, while the electrons travel through external circuit giving out electrical energy. The electrodes, being intercalation materials, will accommodate Li ion between their layers and spaces during charge/discharge processes.
The charge/discharge mechanism, usually called as “rocking chair mechanism” of a conventional LIB, is illustrated in Figure 5.3.

In a fully charged state, lithium is stored in a negative electrode material (e.g., graphite) by intercalating between the graphene layers, forming LiC₆. During the discharge, lithium ions deintercalate from the negative electrode material and migrate toward the positive electrode (e.g., LiCoO₂ or LiNiO₂) and insert into the electrode material. Simultaneously, the electrons removed from the negative electrode (oxidation); are transferred through external circuit, which creates current to do a useful work; and enter the cathode (reduction). This process is reversed during charging.[132] The electrochemistry at positive and negative electrodes during charging and discharging of LIB is shown as follows.

At the positive electrode,

\[ \text{LiCoO}_2 \xrightarrow{\text{Charging}} \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^- \xrightarrow{\text{Discharging}} \]

At the negative electrode,

\[ x\text{Li}^+ + xe^- + 6\text{C} \xrightarrow{\text{Charging}} \text{Li}_x\text{C}_6 \xrightarrow{\text{Discharging}} \]

5.1.2 Negative electrode materials

In 1972, Exxon introduced lithium as a negative electrode with TiS₂ as a positive electrode.[122, 133] The motivation for using lithium as negative electrode is that lithium is the most electropositive (-3.04 V vs. standard hydrogen electrode) and lightest (specific gravity = 0.53 g cm⁻³) metal, which is a suitable parameter to construct a battery with high energy density. But very soon, it was realized that lithium is not a safe negative
electrode because it forms dendrites (uneven growths of lithium)[134] at electrolyte-electrode interfaces, which could lead to a short circuit in the battery. In 1991, Sony commercialized carbonaceous material (graphite) as a negative electrode material; since then, graphite is the most widely used commercial material for negative electrodes in LIBs, offering a theoretical capacity of 372 mA•h•g⁻¹.[135] There are different kinds of graphitic negative electrode materials, such as natural graphite, mesocarbon microbeads (MCMB) and highly disordered or amorphous carbon.[136-138] The theoretical specific capacity (stored charge per unit mass) and theoretical capacity density (stored charge per unit volume) calculated from final lithiated product of graphite (LiC₆) is 372 mA•h•g⁻¹ and 840 mA•h•mL⁻¹ respectively. The reaction of graphite and lithium during lithiation and delithiation is,

\[
\text{Li} + 6\text{C} \quad \xrightarrow{\text{Lithiation}} \quad \text{LiC}_6
\]

\[
\text{De-lithiation}
\]

With its crystalline and layered structure consisting of individual graphene sheets separated with 3.35 Å, graphite has good cycling stability and safety features.[137, 139] With sufficient interlayer spacing, the volume change upon lithium intercalation/deintercalation during charge/discharge is very small (less than 10%).[137] Because of this, the commercial electrochemical-grade graphite delivers stable capacity over several hundred cycles.

Research has been done to develop alternative negative electrode materials with higher stability and capacity than that of graphite. There are many elements that perform better than graphite in terms of specific capacity. For example, silicon shows a theoretical capacity of ~4200 mA•h•g⁻¹,[140] which is the highest among all the elements for
negative electrodes except for pure lithium metal itself. Although silicon attracted significant attention of researchers because of its highest theoretical capacity, it can’t withstand the large volume change (~310%)[141] during cycling, which is not desired as it leads to the pulverization of electrode material that in turn deteriorates the cycling stability. Similar to silicon, tin shows a significant theoretical capacity of ~990 mA•h•g$^{-1}$,[142] but can’t withstand the volume change (~260%) during cycling.[141]

Besides graphite, several other carbon nanomaterials such as carbon nanotubes[127, 129] and graphene[128] have been studied for higher capacity and energy density. So there is a huge scope for the development of new anode materials that can deliver better capacities and stable enough for higher number of cycles.

As discussed in Chapters 1 and 2, N-CNOs are largely unexplored carbon nanomaterials with unique structural properties. In this chapter, we discuss the performance of air-cleaned N-CNOs as negative electrode materials for LIBs for both slow (C/10) and fast (C) charge/discharge rates and examine the ex-situ Raman analysis of N-CNOs before and after cycling. In Chapter 4, we discussed the preparation of graphene materials from the unzipping of arc-discharge CNOs (A-CNOs). We have also performed some preliminary experiments to study A-CNOs, A-CNO-GOs and A-CNO-TH-RGOs as negative electrode materials for LIBs.

5.2 Results and Discussion

5.2.1 N-CNOs

N-CNOs were structurally analyzed using TGA, TEM, powder-XRD, Raman spectroscopy and BET nitrogen adsorption/desorption before testing for electrochemical performances and the results were discussed in Chapter 2. To summarize the results
discussed in chapter 2, N-CNOs are multi-layered fullerenes with diameters ranging from 6–8 nm with 8–10 graphitic layers separated with an interlayer distance of 3.5 Å. N-CNOs contain many structural defects with smaller crystallite size evident from Raman and powder XRD analysis. BET nitrogen adsorption/desorption studies show that N-CNOs has huge surface area (560 m²/g) with about 77% mesoporosity.

Figure 5.4. Galvanostatic charge/discharge of N-CNOs at a rate of C/10 (potential vs. capacity). The first cycle (blue), second cycle (red), fifth cycle (green), tenth cycle (black) and fifteenth cycle (yellow); solid lines corresponding to discharge and dashed line corresponding to charge.
In order to study the capacity performance, the galvanostatic discharge/charge method was used to cycle the coin cells. Figure 5.4 shows the first 15 cycles of potential vs. capacity curves, at a charge/discharge rate of C/10 (37.2 mA\textsuperscript{•}g\textsuperscript{−1}). Here discharging corresponds to delithiation of lithium metal (which is a counter electrode) and lithiation of electrode containing N-CNOs as active material. Charging corresponds to delithiation of electrode containing N-CNOs as active material. A very large capacity of 1944 mA\textsuperscript{•}h\textsuperscript{•}g\textsuperscript{−1} was observed during the first discharging cycle (lithiation), and a reversible capacity of 530 mA\textsuperscript{•}h\textsuperscript{•}g\textsuperscript{−1} was observed during the first charging cycle (delithiation). As mentioned in Chapter 2, the surface area of N-CNO is 560 m\textsuperscript{2}/g. When large surface area electrode material is in contact with electrolyte, a large irreversible capacity (1344 mA\textsuperscript{•}h\textsuperscript{•}g\textsuperscript{−1}) is observed due to the formation of solid electrolyte interface (SEI).[139] A long plateau observed between 0.6 – 0.9 V in Figure 5.5 (blue solid line) corresponds to SEI formation.
Figure 5.5. Cycling performance of N-CNO under charge/discharge rate of C/10; showing a reversible capacity of ~530 mA•h•g⁻¹

For the second cycle, there is no similar plateau observed as there is no formation of SEI phase. For the second to the fifteenth cycles, the reversible capacity is stabilized around 530 – 550 mA•h•g⁻¹ with a coulombic efficiency of 99.5% (Figure 5.5). This capacity is approximately 1.5 times that of graphite theoretical capacity (372 mA•h•g⁻¹, forming LiC₆),[139] corresponding to stoichiometres from Li₁.₄₂C₆ to Li₁.₄₈C₆. Unlike graphite and other carbon nanomaterials, where several phases (i.e. LiC₁₈, LiC₁₂, LiC₆ compounds) were formed during charging,[139, 143] there is no specific phase formed for N-CNOs. Figure 5.6 shows the cyclic voltammetry (CV) curves for the 1ˢᵗ, 2ⁿᵈ and 5ᵗʰ cycle at a scan rate of 0.05 mV/s between 0 and 3.0 V. During the first cycle, there is a strong peak around 0.6 V, which indicates the SEI formation, corresponding well with the
large plateau on 1st discharge curve of Figure 5.5. After the first cycle, no strong peak exists, indicating that there is no identical phase formed thereafter.

Figure 5.6. Cyclic voltammetry (CV) plots of N-CNOs for the first (black line), second (red line) and fifth (blue line) cycles under scan rate of 0.05 mV/s.
Figure 5.7. Cycling performance of N-CNOs under high charge/discharge rate of C for first 150 cycles. Performance of commercial graphite MCMB) under the same testing conditions (inset).

Figure 5.7 shows the cycling performance of N-CNO under higher charge and discharge rate of C (C corresponding to 372 mA•g⁻¹) for 150 cycles. Under the rate of C, the initial capacity is around 540 mA•h•g⁻¹, and then the capacity stabilized around 420 mA•h•g⁻¹ after 20 cycles. Up to 150 cycles, the N-CNOs maintains a stable capacity of ~410 mA•h•g⁻¹ with a coulombic efficiency approaching 99.9%. As stated earlier, the available capacity greatly depends upon the charge/discharge rate, i.e. with an increase in the charge/discharge rate, available capacity decreases. The capacity of N-CNO electrode with a charge/discharge rate of C is 410 mA•h•g⁻¹, which is less than its capacity with a charge/discharge rate of C/10, which is ~530 mA•h•g⁻¹.
The cycling performance of commercial graphite (mesocarbon microbeads, MCMB) electrode is shown in Figure 5.7 (inset). This material shows poor capacity and cycling stability under high charge/discharge rates. For the first 10 cycles MCMB showed contrasting performance as that of N-CNOs. The capacity increased from ~60 mA\(\cdot\)h\(\cdot\)g\(^{-1}\) (1\(^{\text{st}}\) cycle) to ~200 mA\(\cdot\)h\(\cdot\)g\(^{-1}\) (10\(^{\text{th}}\) cycle). Due to the faster charge/discharge rate, the initial lower capacity is due to the formation of only SEI, but not due to lithium intercalation. After 10 cycles, the capacity achieved was 200 mA\(\cdot\)h\(\cdot\)g\(^{-1}\), and then kept decreasing for the following cycles. After 150 cycles, the capacity remains only ~120 mA\(\cdot\)h\(\cdot\)g\(^{-1}\), which is around 30% of the theoretical capacity.

Under high charge and discharge rate, the N-CNOs outperform MCMB as negative electrode material for LIB. There are several reasons for the stable and enhanced capacity N-CNOs. (1) The unique structure of N-CNOs, containing lots of defects and more edges, provide more possible active sites for lithium ion storage; (2) The smaller size (diameter ~6 nm) and large surface area (560 m\(^2\)/g) offer short pathways for lithium ion and electron transport.[143] The disadvantage of this large surface area is to form large SEI, which is evident from the large irreversible capacity during the first cycle. But for the following cycles, when SEI is stabilized, the large surface area is beneficial for the high performance of N-CNO as negative electrode material for LIB under high charge/discharge rate.

To investigate the stability of cycled N-CNO material, we performed \textit{ex-situ} Raman studies. Cycled cells were disassembled in a glove box and the active material (N-CNO electrode) was sealed between thin glass slides and analyzed by Raman spectroscopy. For comparison, the active N-CNO material from a non-cycled cell was
also tested by Raman analysis; both spectra are shown in Figure 5.8. Figure 5.8 shows the Raman spectra of N-CNO electrode before and after cycling for 200 cycles with a charge/discharge rate of C. The $I_D/I_G$ ratio of N-CNOs was $\sim 2.41$ before cycling $\sim 2.44$ after cycling. The high $I_D/I_G$ ratio ($\sim 2.4$) of the electrodes compared with that of as produced N-CNOs ($\sim 1.5$) is due to the presence of conductive activated carbon present along with N-CNOs in electrodes contributing to the intensity of D band. The lack of change in $I_D/I_G$ ratio implies that N-CNO electrodes retain their structural stability during electrochemical cycling.

![Figure 5.8. Raman spectra of N-CNO electrode before and after 200 cycles with a charge/discharge rate of C](image-url)
5.2.2 A-CNOs

The cycling performance of arc-prepared CNOs (A-CNOs) is shown in Figure 5.9 with a charge/discharge rate of C/10. Unlike N-CNOs, A-CNOs show poor performance with a reversible capacity of ~200 mA•h•g⁻¹.

Figure 5.9. Cycling performance of A-CNOs under charge/discharge rate of C/10

The capacity vs. potential curve of A-CNOs for the 1st cycle (Figure 5.10) shows a plateau between 0.9 V to 0.6 V due to the formation of SEI, similar to N-CNOs, but the irreversible capacity shown by A-CNOs (~150 mA•h•g⁻¹) due to the formation of SEI is very small compared to that of N-CNOs (~1344 mA•h•g⁻¹). If surface area is the contributing factor for the capacity (amount of lithium stored) of CNOs, surface area should lead to higher capacity and larger SEI contributing to large irreversible capacity. As the surface area of A-CNOs (30 m²/g) is very less than that of N-CNOs (560 m²/g), A-
CNOs show very less capacity than that of N-CNOs and show low irreversible capacity due to SEI formation.

**Figure 5.10.** Capacity vs. potential curve of A-CNOs for 1st cycle (C/10 charge/discharge rate) showing SEI between 0.6 – 0.9 V and 2nd to 10th cycles (inset)

### 5.2.3 A-CNO-GOs

A-CNO-GOs are obtained by oxidative unzipping of A-CNOs and contain several oxygen-containing functional groups such as hydroxyl, epoxide and carboxylic acid on the surface and along the edges (Chapter 4). The surface area of A-CNOs is 30 m²/g and there is eight-fold increase in the surface area after unzipping of A-CNOs to A-CNO-GOs (240 m²/g). The cycling performance of A-CNO-GOs is shown in Figure 5.11 for the charge/discharge rate of C/10. The huge irreversible (~650 mA•h•g⁻¹) capacity during the first charge/discharge cycle is due to the formation of SEI. From second to tenth cycle, the capacity stabilized at ~600 mA•h•g⁻¹, which is ~1.6 times that of graphite.
Huge surface area is definitely a significant contributing factor for the high initial capacity. We still didn’t have any experimental evidence about other significant contributing factors for the high capacity. But, it is reported for oxidized graphene nanoribbons (ox-GNRs) that presence of oxygen in GNRs induces the formation of a more stable and chemically bonded SEI, and this lithium-rich SEI likely prevents electrode degradation and enhances the lithium exchange and storage capacity of the electrode.[144, 145] With these preliminary experimental results, we can say that A-CNO-GO is definitely an interesting material for negative electrode material in LIBs.
5.2.4 A-CNO-TH-RGOs

A-CNO-TH-RGO is the graphene material obtained by thermal reduction of A-CNO-GO at 1050 °C under argon. The cycling performance of A-CNO-TH-RGO is shown in Figure 5.12 for the first 10 cycles at a charge/discharge rate of C/10. An irreversible capacity of ~440 mA•h•g⁻¹ observed during the first charge/discharge cycle is due to the formation of SEI. From 2nd cycle the capacity kept falling gradually and stabilized at 6th cycle with a capacity of ~380 mA•h•g⁻¹.

Figure 5.12 Cycling performance of A-CNO-TH-RGO at a charge/discharge rate of C/10
5.3 Experimental

5.3.1 Preparation of active materials

Please refer Chapter 2 for the preparation of air-cleaned N-CNOs and refer Chapter 4 for the preparation of A-CNOs, A-CNO-GOs and A-CNO-TH-RGOs.

5.3.2 Electrochemical testing

A sample of active material (such as N-CNO, A-CNO, A-CNO-GO, A-CNO-TH-RGO and MCMB) was mixed with polyvinylidene difluoride (PVdF) (Alfa Aesar) binder and active carbon (Alfa Aesar) as conducting material in 8:1:1 weight ratio. Then N-methylpyrrolidinone (NMP) (Alfa Aesar) was added to the mixture to make slurry with suitable viscosity for slurry-coating. The slurry was spread onto a copper foil evenly while controlling the thickness of 5 mils (0.005", 0.127 mm) and this electrode was heated to 80 °C in the oven overnight until all the solvent was evaporated. The working electrodes were punched with a diameter of 1 cm, and then precisely weighed on a microbalance (XS 205, Mettler Toledo).
Figure 5.13. Schematic of the parts used to construct 2025 coin-type half-cell.

Samples were assembled into CR 2025 coin-type cells (Figure 5.13) in an argon-filled glovebox with the moisture and oxygen levels controlled under 0.1 ppm. Lithium metal (Sigma-Aldrich) was used as counter electrode, and 1.0 M LiPF$_6$ dissolved in ethyl carbonate and dimethyl carbonate (EC/DMC in 1:1 volume ratio) was used as electrolyte. For each cell, a piece of Celgard 3501 separator was used between the working electrode and lithium metal. The electrochemical tests were conducted with a Bio-Logic potentiostat (VMP3) at room temperature. The cells were galvanostatically cycled from 0.02 V to 3 V at rates of C and C/10. Cyclic voltammetry (CV) was conducted at scan rates from 0.05 mV/s to 2.0 mV/s. All cells rested for 3 h before conducting electrochemical tests and some cells were pre-cycled for 2 – 5 cycles to stabilize the cell.
5.3.3 Characterization

Please refer Chapter 2 for the characterization of air-cleaned N-CNOs and Chapter 4 for the characterization of A-CNOs, A-CNO-GOs and A-CNO-TH-RGOs.

5.3.3.1 Ex-situ Raman analysis

Ex-situ Raman tests were conducted before and after cycling. For this, the cycled cells were disassembled and electrode material was sealed between two glass slides (2.5 cm × 2.5 cm, 0.2 mm thickness) in the glove box and taken out and analyzed for Raman. Raman analysis was performed on a Thermo Scientific DXR dispersive Raman spectrometer using 532 nm excitation wavelength (diode-pumped, frequency-doubled Nd: YVO₄ laser) focused on the sample by a 50× objective lens.

5.4 Conclusion

In conclusion, among all the materials tested, N-CNOs performed best in terms of capacity (1.5 times that of graphite) and columbic efficiency at a charge/discharge rate of C/10. At faster charge/discharge rate of C, N-CNOs outperform MCMB with a capacity of 410 mA•h•g⁻¹ (over twice that of MCMB) and columbic efficiency of 99.5% after 150 cycles. Ex-situ Raman analysis shows that the structure of N-CNOs is intact even after 200 faster charge/discharge cycles, which is a unique property for carbon materials. The unique structure of N-CNOs with many surface defects and high surface area are beneficial for stable cycling performance and high capacity. A-CNOs with less surface area than N-CNOs and fewer structural defects than N-CNOs show poor performance as negative electrode materials. This is another proof of the fact that the surface defects and edges on N-CNOs are active sites for lithium storage during the cycling. N-CNOs are promising materials as negative electrode material for lithium-ion batteries.
On the other hand, A-CNO-GO with huge surface area and several oxygen-containing functional groups on the surface also performs better in terms of capacity (600 mA•h•g⁻¹, 1.6 times that of graphite) and cumbic efficiency, whereas A-CNO-TH-RGO, a thermally reduced A-CNO-GO, shows moderate performance with a capacity of ~400 mA•h•g⁻¹ for first 10 cycles. To see whether A-CNO-GOs and A-CNO-TH-RGOS are promising materials, their cycling performance needs to be tested for more number of cycles at different charge/discharge rates. More ex-situ experiments need to be performed to comment on the contributing factors for the available capacity of these materials.
Chapter 6 Future Directions

Nanocrystalline diamond particles (ND) are members of a diverse structural family of carbon nanomaterials with excellent mechanical and optical properties, high surface areas and tunable surface structures. A brief outline of their properties and applications was given in Chapter 1. Other than using them as precursors for N-CNOs, we didn’t get a chance to throw much light on their chemistry. After doing thorough literature research on these materials, we found that there are still few unanswered issues related to their purification and chemical modification.

6.1 Objectives

The presence of large amounts of non-diamond carbon and metal impurities in detonation synthesis of ND confines their applications. In addition to diamond carbon, the ND soot obtained through detonation synthesis also contains of amorphous and graphitic carbon impurities and incombustible metal and metal oxides impurities.\[25, 146\] On an industrial scale, ND is purified by liquid oxidants \[25, 147\] to remove non-diamond carbon particles. This wet purification is considered to be not environmentally benign and requires expensive corrosion-resistant equipment and costly waste disposal processes. Alternatively, the non-diamond carbon impurities of ND can be oxidized in an environmentally friendly manner using air and ozone-enriched air oxidation.\[146, 148\] The air-oxidation method proposed by Osswald and group involves oxidation of ND soot in a narrow temperature range of 400–430 °C, is effective enough in removing non-diamond carbon impurities.

The purity of ND can be improved to large extent by introducing methods to remove impurities that are confined within ND aggregates. Although few attempts were
made in this direction, our primary objective would be to come up with simple and economical purification procedure to remove the aggregate-trapped impurities. Mild ball milling in a chemically inert PTFE or ZrO$_2$ capsule container with ZrO$_2$ ball could break the ND aggregates releasing the impurities, which further can be removed by air-oxidation.

Several oxygen-containing functional groups were introduced on the surface of ND (Figure 1.3) during purification. To get precise control over surface chemistry, a pure sample of ND with only one kind of functional groups on the surface is required. So far, ozone oxidation is the method that could produce purified ND with exclusively acid anhydride groups on the surface.[148] Our second objective is to develop environmentally friendly chemical methods to produce purified ND with single-functional group surfaces.

6.2 Methodology to be adopted

6.2.1 Purification

Ball-milling followed by air-oxidation could improve the purity to large extent. We will optimize:

- A chemically inert experimental setup using PTFE or ZrO$_2$ milling jar and ball
- The frequency and time of milling that minimally changes the size distribution of primary ND particles. Particle size can be determined either by electron microscopy or laser diffraction.
- The sharp purification temperature range will be measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).
• Maximum sp³ carbon content and minimum metal oxide impurities comparison will be monitored using Raman spectroscopy and TGA.

6.2.2 Functionalization

We mainly propose three different chemical approaches to introduce one kind of functional group on the surface and intend to use environmentally benign, solvent-free mechanochemical methods to introduce versatile functional groups such as hydroxyl, ester, carboxylic acid and cyanide on ND surface. Mechanochemistry is a very successful method for chemical modification of carbon materials such as fullerenes and carbon nanotubes (CNT).[62, 82]

**Approach 1:** In this approach, the air-cleaned ND with several types of O-containing functional groups were defunctionalized by heating under inert atmosphere to give defunctionalized ND (DND). These DND needs to be analyzed for electron resonance spectroscopy (ESR) to see the presence of free radicals. DND can be further mechanochemically reacted with compounds such as KOH, KCN and CH₃COONa under optimized experimental conditions to give hydroxyl, cyanide and acetate functionalized ND respectively (Scheme 6.1).
Scheme 6.1. Preparation of hydroxyl, cyano, ester and carboxylic acid functionalized ND

**Approach 2:** DND can be chlorinated similar to fluorination[149] by heating under Cl₂ (Scheme 6.2). The C—Cl bonds on the surface can further be converted using strong nucleophilic reagents to new ND derivatives. Cyanide- and hydroxyl- functionalized ND can be prepared by treating chlorinated ND with KOH and KCN under mechanochemical conditions.
**Scheme 6.2.** Preparation of hydroxyl and cyano functionalized ND from chlorinated ND

**Approach 3:** During the graphitization of ND, the transformation proceeds from the surface to the core. Hence partial graphitization of ND will create ND with fullerene-like graphitic surface (PND) that can be further functionalized using olefinic chemistry. Certain approaches such as acid oxidation, Friedel-Crafts acylation and reductive alkylation on N-CNOs were successful enough to introduce various functional groups to improve CNO dispersion properties. These approaches can be manipulated on PND (Scheme 6.3) to get chemically modified ND with their inner diamond core intact.
Scheme 6.3. Partial graphitization of ND and further functionalization

6.3 Significance of the work

ND are highly desirable materials for biological applications as they are chemically inert and biocompatible with negligible cytotoxicity. To use ND as drug delivery platforms, they need to be pure, biocompatible, dispersible in water and able to carry a wide range of therapeutics. For this purpose, the following issues need to be addressed.

- Development of purification methods.
- Improve the solubility of ND in water.
- Dense polar functional group atmosphere on the surface with diamond core intact.
- Versatile functional groups on the surface to carry wide range of drug molecules.
- The functional groups on the surface of ND will control the chemical properties.

Presence of different kinds of functional groups on ND surface will lead to an ambiguity while studying their chemical properties and exploring applications. So, there is a need to develop chemical approaches to create homogeneous functional group atmosphere on the ND surface.
The modified purification methods of this proposal should produce ND with sp³ carbon content close to 100%. The three synthetic approaches of this proposal should produce functionalized ND with improved solubility properties. A homogenous functional group atmosphere introduced on the ND surface will give a chance to control the surface chemistry. Also the functional groups introduced through these methods - hydroxyl, carboxylic acid, cyanide and chloride can be further derivatized to tune the solubility and chemical properties.

6.4 Long-term project

After achieving pure and well functionalized ND, stable dispersions/solutions can be made in various organic and aqueous solvents. For any application, it is always desirable to have homogeneous size distribution of ND material. The next goal would be to develop chromatographic methods for size dependent separation of ND particles using size-exclusion chromatography. More research can be done focusing on biological properties such as their pH-dependent affinity for various therapeutics, binding capability to targeted cells (such as tumor cells) and cytotoxic behavior towards various body tissues.
References


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EDUCATION

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