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New Materials for Quantum Computing

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This project was a high risk / high reward endeavor directed toward accessing materials that may be used in next generation computing systems. Quantum computing networks require coherent nuclear spin quantum memory, which is challenging to realize. The approaches described herein may enable access to confined and spatially controlled N-V centers in a manner that minimizes detrimental tunneling effects. Ultimately, a new method for using quantum entanglement as a parameter for designing quantum computers of interest to the DoD is targeted. Efforts were primarily directed toward the synthesis and characterization of new materials containing nitrogen atoms as well as sp3-hybridized carbons.

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Summary: This project was a high risk / high reward endeavor directed toward accessing materials that may be used in next generation computing systems. Quantum computing networks require coherent nuclear spin quantum memory, which is challenging to realize. The approaches described herein may enable access to confined and spatially controlled N-V centers in a manner that minimizes detrimental tunneling effects. Ultimately, a new method for using quantum entanglement as a parameter for designing quantum computers of interest to the DoD is targeted. Efforts were primarily directed toward the synthesis and characterization of new materials containing nitrogen atoms as well as sp^3-hybridized carbons.

Introduction: A nitrogen-vacancy (N-V) center is a point defect found in some diamond lattices. It is comprised of a nitrogen atom, which substitutes for a carbon atom, and a lattice vacancy. Materials with N-V centers may potentially form the basis of a new generation of high performance quantum computers due to quantum entanglement of the qubits (N-V centers). To realize materials that contain N-V centers, efforts were directed toward the synthesis of N-containing carbons. These efforts entailed 'top down' approaches where graphene precursors were doped with appropriate heteroatoms as well as 'bottom-up' approaches from appropriately functionalized, diamond-like monomers to grow carbon-rich matrices. The method developed are expected to facilitate access to N-doped, sp^3-hybridized films that can be addressed using contemporary optical methods and thus may find utility in quantum computing systems.

Experiments, Results and Discussion: Chemical doping is an efficient way to tailor the chemical, electronic, and optical properties of various materials[1] and has been successfully employed in a range of electronic and photovoltaic devices.[1,2] Substitutional doping of graphene results in the disruption of the lattice of sp^2-hybridized carbon atoms and thus introduces changes in the material's intrinsic electronic and optical properties as well as chemical reactivity.[1,2] Among the currently known dopants for graphene or graphene oxide (G-O), nitrogen (N) is an archetypal candidate because its incorporation in the graphene lattice requires relatively minor structural perturbations.[1] A series of theoretical studies[3-6] have predicted that N-doped graphene could display a unique set of chemical, electronic, and/or optoelectronic characteristics. Indeed, N-doping is expected to introduce additional electrons in carbon-based networks and offers an effective way to tailor the properties of graphene for use in a variety of applications, including quantum computing.[2]

N-doped graphene has been prepared by several methods including chemical vapor deposition (CVD),[7,8] chemical reduction of an appropriately functionalized G-O precursor,[9,10] Joule heating of G-O in the presence of ammonia,[3,11] as well as from nitrogen-containing precursors like melamine[12] or cyanamide.[13] Plasma and arc-discharge approaches have also been employed for N-doping purposes.[14] While many reductants, such as hydrazine,[15] dimethyl hydrazine,[16] sodium borohydride,[17] sodium hydride,[18] hydrogen sulfide[19] and hydroquinone,[20] have been used to reduce G-O to reduced graphene oxide (rG-O), the introduction of N into carbon lattices generally requires a separate synthetic step. To expedite access to N-doped rG-O (N@rG-O), we developed a one-pot, low temperature synthesis that utilizes a chemical reaction to reduce G-O in liquid ammonia (NH_3) (see Figure 1).

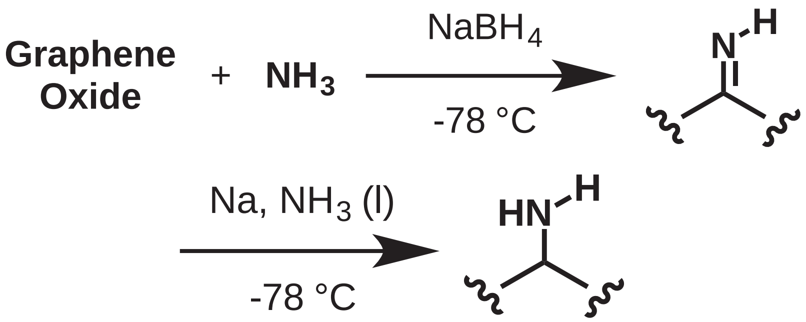

Figure 1. Summary of a synthetic approach that was developed for preparing carbon materials containing nitrogen.

Graphite oxide was first prepared using a modified Hummers method[21,22] and then subjected to bath sonication in water to induce exfoliation to graphene oxide (G-O). The exfoliation of was confirmed by observation of the Tyndall effect. The dispersion was then centrifuged and the supernatant was separated by vacuum filtration at room temperature to yield a dry 'G-O powder'. The G-O powder was subsequently re-dispersed in water and filtered through a PTFE membrane by vacuum filtration to obtain a 'G-O film'. The G-O powder was dispersed in liquid NH_3 that was condensed at -78 °C in a closed reaction vessel using a dry ice-acetone bath. The mixture was stirred for 1 h until the G-O was dispersed. Sodium borohydride was then added, the cooling bath was removed, and the ammonia underwent evaporation while the mixture warmed to room temperature. The product was isolated by filtration using a PTFE membrane followed by washing to obtain a 'N@rG-O powder'.The N@rG-O powder was subsequently re-dispersed in distilled water and filtered by vacuum filtration to obtain a 'N@rG-O film'.

As summarized in Figure 2, FT-IR analysis of the G-O powder revealed a series of signals characteristic of G-O, including νO–H = 3394 cm^{-1}, νC–OH = 1063 cm^{-1}, νC–C = 1429 cm^{-1}, and νC=C = 1623 cm^{-1}.[26,27] In addition, signals recorded at 1718 cm^{-1} and 1760 cm^{-1} were attributed to the vibrations of the C=O bond[26] and adsorbed water molecules,[28,29] respectively. The N@rG-O powder lacked a signal that may be assigned to the adsorbed water molecules and the intensities associated with C–OH, C=O, and O–H stretches in the product decreased; a signal was also recorded at 1543 cm^{-1} and assigned to the vibration of C–N bonds.[28] A color change of the aqueous suspension from brown, which is typical of G-O, to black was observed upon reduction.

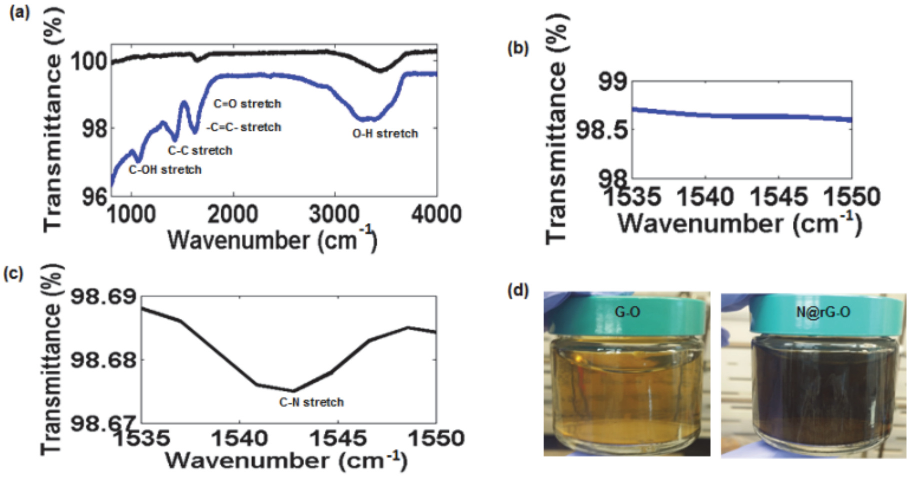

Figure 2. ATR-FTIR spectra recorded for (a) a thin film of stacked and overlapped G-O sheets (blue) and a thin film of stacked and overlapped N@rG-O sheets (black). High-resolution

ATR-FTIR spectra recorded for (b) a thin film of stacked and overlapped G-O sheets and (c) a thin film of stacked and overlapped N@rG-O sheets. (d) A photograph of aqueous suspensions of G-O and N@rG-O.

XPS was used to characterize the elemental compositions of the G-O and N@rG-O powders (see Figure 3). The C1s data recorded for the G-O powder revealed signals at 284.3 eV, 286.3 eV, and 288.4 eV, and were assigned to C–C, C–O, and C=O moieties, respectively.[27-29] In comparison, the C1s spectrum recorded for N@rG-O featured signals with relatively low intensities at 286.9 eV and 288.7 eV, and were attributed to C–O and C=O binding energies, respectively.[27-29] The C/O ratio measured for the N@rG-O powder (3.7) was greater than that of the G-O powder (0.9), as calculated by integrating the corresponding signals in the XPS survey spectra and were consistent with the elemental analyses. The relatively high C/O ratio measured for the N@rG-O powder was consistent with the removal of oxygen-containing functional groups from the starting material upon reduction. A series of elemental analyses (by combustion) indicated that the abundance of oxygen decreased from 51 wt.% in the G-O starting material to 19 wt.% in N@rG-O. In contrast, the nitrogen content of the N@rG-O powder was measured to be approximately 4%. The N1s XPS spectrum recorded for the N@rG-O powder revealed two signals at 399.2 eV and 401.7 eV, and were assigned to nitrogen atoms in "pyridine-like" and "graphitic-like" configurations,[30-33] respectively. The ratio of signal intensity (based on the peak areas) for pyridine-like N atoms to that of graphitic-like N atoms was found to be 3:2. Signals consistent with the formation of nitrogen in a pyrollic-like configuration were not observed.

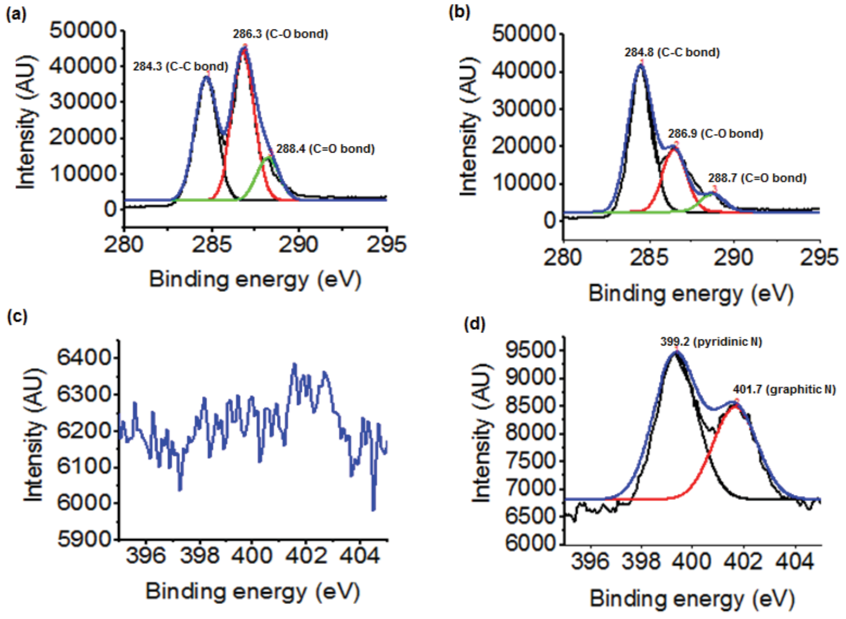

Figure 3. C1s XPS data recorded for (a) G-O and (b) N@rG-O. N1s XPS data recorded for (c) G-O and (d) N@rG-O.

A series of XRD analyses facilitated a comparison of the structures of the G-O and N@rG-O films (Figure 4). The G-O film exhibited an intense and sharp (002) reflection at 2θ = 11.1° (corresponding to an interlayer spacing of 0.83 nm) with a full width at half-maximum (FWHM) of 0.6°. The intensity of the (002) reflection shown by the N@rG-O film was significantly lower, and the peak position had shifted to a higher angle: 2θ = 12.6o (which corresponded to an interlayer spacing of 0.79 nm; the FWHM of the signal was measured to be 1.1°). In addition, two broad halos appeared with center positions at about 2θ = 17.7o and 2θ = 24.1o, respectively. These were attributed to the significant decrease in the interlayer spacing due to the elimination of oxygen-containing functional groups and the removal of intercalated water molecules.[39] The cross sections of the G-O and N@rG-O films were imaged using SEM. A 10 μm thick G-O film consisted of stacked G-O sheets was observed whereas a N@rG-O film consisting of stacked N@rG-O sheets was measured to 14 μm thick.

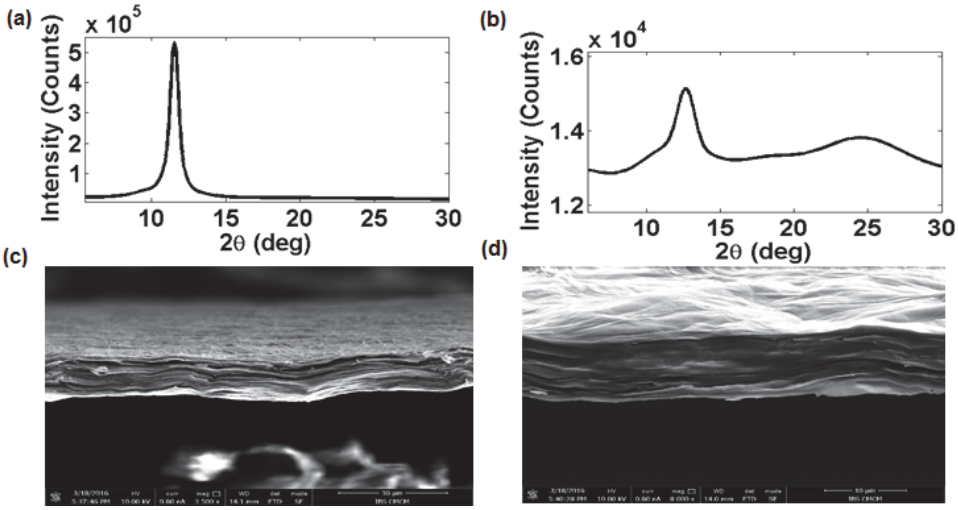

Figure 4. XRD data collected for a (a) graphene oxide film and (b) N@rG-O film; SEM images of the fracture cross-sections of a (c) graphene oxide film and (d) N@rG-O film.

In parallel with the efforts described above, a new method directed toward the synthesis of polymers enriched with sp^3-hybridized carbons and nitrogen atoms based on Wurtz-type coupling and sonochemically-driven chemistry was also explored. As summarized in Figure 5, tetrabromoadamantane was treated to reductive conditions in the presence of hexamethylene tetraamine. We hypothesized that the adamantane-based monomers would undergo coupling and effectively trap the N-containing analogues in carbon matrices that were rich in sp^3-hybridized carbons.

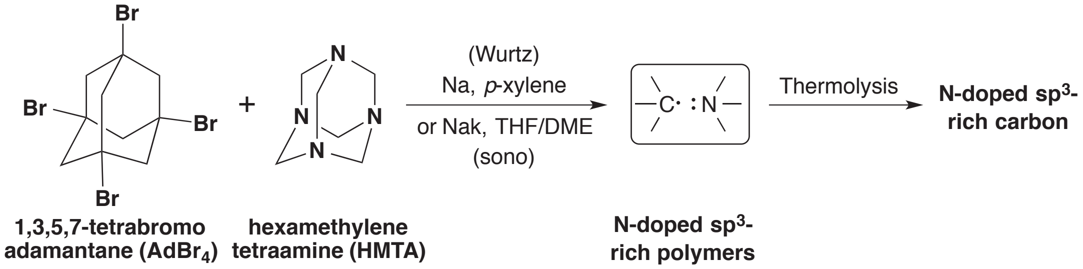

Figure 5. Summary of a synthetic approach used to access N-doped carbons.

As summarized in Figure 6, X-ray photoelectron spectroscopy revealed that sp^3-hybridized carbons as well as nitrogen atoms were present in the products, conclusions that were subsequently confirmed by elemental analysis. Due to strong fluorescence, the Raman signals for the synthesized polymers were difficult to distinguish. Regardless, signals corresponding to D and G bands were recorded which suggested to us that amorphous carbon may form by subjecting the polymers to elevated temperatures.

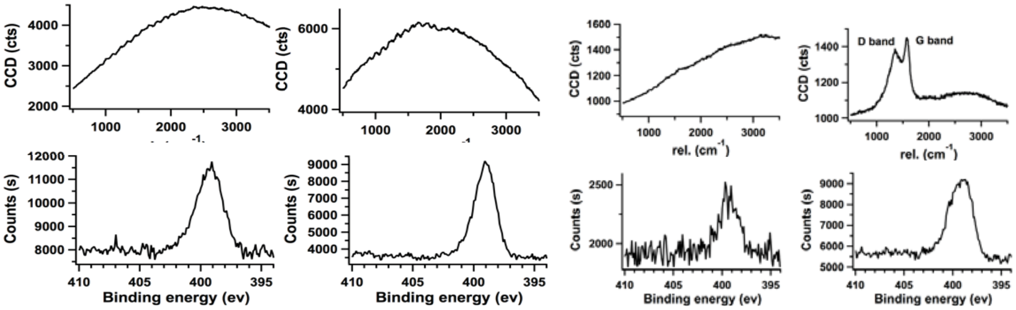

Figure 6. Summary of Raman and XPS data collected for various materials before (left) and after (right) thermal analysis.

The aforementioned structural assignments were support by FT-IR spectroscopy (Figure 7, left). Likewise, thermogravimetric data recorded for the materials indicated that the monomers employed (i.e., 1,3,5,7-tetrabromoadamantane, hexamethylene tetraamine and 3,5,7-tribromo-1-azaadamantane) completely decomposed at temperatures below 400 ºC; however, their respective products were relatively stable (Figure 7, right). At elevated temperatures (up to 1000 ºC), large residues were obtained from the product prepared under sonochemical conditions which may reflect a crosslinked structure and/or a high intrinsic stability.

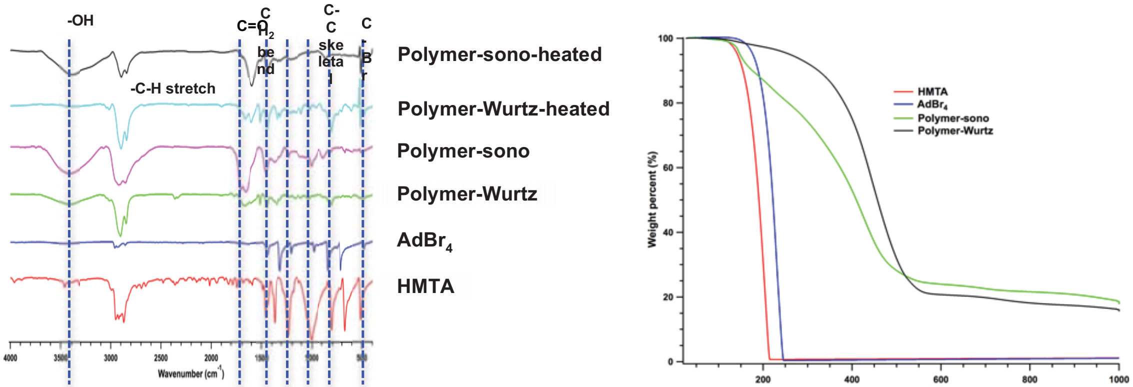

Figure 7. Summary of Raman and XPS data collected for various materials before (left) and after (right) thermal analysis.

Collectively, these results suggested to us that a synthesis of N@rG-O using a one-pot, low temperature chemical reduction of G-O in liquid NH_3 and in the presence of $NaBH_4$ was successfully developed. The method facilitates the insertion of pyridinic as well as graphitic nitrogen atoms in the rG-O during the reduction process. The removal of oxygen-containing groups in the G-O starting material and the formation of a network of sp^2-hybridized carbon atoms were confirmed using XPS and other techniques. Likewise, a new method that enables the synthesis of materials that contain nitrogen and are rich in sp^3-hybridized carbons was also explored. These methods are envisioned to enable access to films rich in sp^3-hybridized carbon atoms that are doped with nitrogen. Large area films comprised of such materials should be readily addressable using optical methods and may hold potential for use in information storage and processing applications.

List of Publications and Significant Collaborations That Resulted from Your AOARD Supported Project: Although a paper was previously submitted for publication, more data are needed before it can be published. Manuscripts summarizing other aspects of the work performed through support of this grant are under development.

DD882: See attachment.

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