Carbon Capture Using Amine-modified Carbon Nanotubes

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Abstract
The increasing rise in the rate of both anthropogenic CO₂ emissions and atmospheric CO₂ concentration, combined with an evolving understanding of what this means for global climate change both now, and in the future, has increased the need for novel technologies for CO₂ capture from large point sources. Current industry standards involve the use of amine solvents, which have a large parasitic load, primarily due to the heating and evaporation of water. A robust, inexpensive sorbent material that can operate under flue gas conditions (8 to 12% CO₂ with high humidity) could have a large impact on the economics of CO₂ capture. For this purpose, multi-walled carbon nanotubes (MWNTs) were functionalized with the aminosilane compounds aminopropyltriethoxysilane (APTES) and N-dimethylaminopropyltrimethoxy-silane (DMAPS) and the resulting materials were characterized and tested for CO₂ capture under relevant conditions. Amine loadings were determined to be larger by comparison of silane grafting groups using X-ray Photoelectron Spectroscopy (XPS), when primary amines (APTES) were used. The morphology of the MWNTs with functionalization did not seem to be significantly altered. Porosity measurements indicate insignificant change in both the inner micropore space of the MWNTs and the larger mesopore space due to MWNT bundling. Experiments of CO₂ breakthrough indicated that APTES functionalized MWNTs captured 1.2 mmol CO₂ g⁻¹ sorbent under dry conditions, with an expected decrease in the presence of water. Although the DMAPS functionalized MWNTs were shown to not effectively capture CO₂ under dry or humid conditions, important lessons were learned regarding the need for a novel functionalization procedure, an increase in the loading of the tertiary amine DMAPS and a need for a breakthrough experiment with higher humidity.

Introduction
The purpose of this research project is to develop a robust, inexpensive solid sorbent for CO₂ capture from large point sources. Multi-walled carbon nanotubes (MWNTs) have been chosen for functionalization using both primary and tertiary aminosilane compounds. The use of carbon nanotubes, which are essentially an activated carbon material that can be tuned to achieve desired properties, and aminosilane compounds creates a combination of materials that are well understood, and have been used widely in industry as individual components. Carbon nanotubes offer an advantage over other engineered materials, such as zeolites and metal-organic frameworks, which may preferably adsorb H₂O, making them difficult to work with in humid environments.
The research objectives of this work include the: 1) development of a method for successful functionalization of MWNTs; 2) characterization and testing of sorbents for CO₂ capture and release under relevant conditions; and 3) use of knowledge gained from these experiments to better tune the sorbents for enhanced CO₂ capture.

Background
The increase in atmospheric CO₂ concentrations since the industrial revolution is thought to be the leading contributor to global climate change. Natural sources and sinks for atmospheric CO₂ can be expected to maintain a rough equilibrium according to the carbon cycle, implying the change in atmospheric concentration is the result of anthropogenic emissions. In 2007, global energy-related CO₂ emissions reached 28.8 gigatons (Gts) and are projected to increase to 40.2 Gts by 2030.[1] Carbon-based fossil fuels account for 86% of global energy usage and 75% of anthropogenic CO₂ emissions.[2] Given the world’s current energy portfolio, increasing energy demand due to the rise of large and emerging economies, such as China and India and the global abundance of accessible and relatively cheap carbon-based energy sources, such as coal and natural gas, energy-related CO₂ emissions are expected to continue increasing. Carbon capture at fixed point stations, such as coal-fired power plants (CFPPs) combined with sequestration (CCS) has the potential to mitigate Gts of anthropogenic CO₂ emissions, and is regarded as a key method for global-scale CO₂ emissions reduction.

A major hurdle in the implementation of CCS is that current industrial carbon capture technologies are energy intensive and not cost-effective.[2, 3] To be viable, a capture technology must achieve 90% CO₂ capture with a maximum energy penalty of 10%.[4] The current state-of-the-art capture technology for CFPPs, i.e., aqueous amine solutions, involves countercurrent gas-liquid stripping of CO₂ in a packed column. This method requires the addition of new capital equipment that must be retrofitted to existing CFPPs and may carry a prohibitively high parasitic load due to the energy costs of regeneration.[5] Moreover, the cost of electricity from a CFPP with 90% CO₂ capture using aqueous amine solutions is expected to increase by 81%.[5, 6]

As an alternative to gas-liquid absorption, gas-solid adsorption processes have been proposed as promising technologies for carbon capture.[7-9] Solid sorbents have the potential to reduce the energy demand of capture processes due to potentially higher loading capacities, absence of solvent heating and vaporization during regeneration, lower material heat capacities (i.e., carbon compared to water), and lower heats of sorption.[8, 10-12] Solid sorbents require a large surface area-to-mass ratio and a preferential interaction with CO₂ to be efficient and effective. While a range of solid sorbents have been considered, including activated carbon[13], zeolites[14], and metal-organic frameworks[15], amine-modified carbon nanotubes (amine-CNTs) have recently been identified as promising sorbents for CO₂ capture.[10, 12, 16-21] CNTs are attractive for adsorbing gases because they have high surface areas and relatively controllable porosity. The surfaces of pristine CNTs are relatively inert to covalent modification, but have highly polarizable delocalized π electrons that enable physisorption. CNT growth has been extensively studied[22] and CNT materials can be grown controllably to a range of diameters and number of walls.[23] This control of
porosity and structure allows for a material that can be tuned to specific sorption capacities. CNT interactions with gases may be tuned for chemisorption interactions through functionalization of the nanotube surface with various functional groups. Covalent functionalization of SWNTs has also been well-studied\[24\] and can be performed by facile acid treatment which creates hydroxyl (-OH) and carboxylic acid (-COOH) groups on the ends and walls of the SWNTs.\[25\] These functional groups can be further covalently functionalized by use of commercially available silane grafting agents using condensation chemistry. This results in a material with a large surface area, controllable porosity, and tunable surface chemistry.

Amine moieties tethered to high surface area supports have been shown to adsorb carbon dioxide.\[26\] Depending on the number of moieties, other than hydrogen, attached to the nitrogen atom, an amine is labeled primary (R-NH\(_2\)), secondary (R-NHR\(^1\)) or tertiary (R-NR\(^1\)R\(^2\)). Previous work has shown that the stability of CO\(_2\) reaction products, the reaction rate, and heat of reaction depends not only on the type of amine (primary, secondary, or tertiary) but also on the chemical structure of the sorbent molecule, specifically the steric hindrance of the amine group.\[27-29\] While primary and secondary amines have been applied toward carbon capture more frequently than tertiary amines, the nature of tertiary amine-CO\(_2\) reaction chemistry suggests that tertiary amines might be excellent functional groups for CO\(_2\) sorption. First, tertiary amines physisorb CO\(_2\).\[8\] As mentioned previously, capture by physisorption, rather than chemisorption, may be ideal for minimizing sorbent regeneration costs. Second, unlike primary and secondary amine-CO\(_2\) reactions, where H\(_2\)O competes with CO\(_2\), the tertiary amine-CO\(_2\) reaction requires a 1:1 H\(_2\)O to CO\(_2\) ratio to form bicarbonate. Given the ubiquitous presence of H\(_2\)O in flue gases, the potential for tertiary amines to promote CO\(_2\) sorption in the presence of H\(_2\)O is an important benefit over primary and secondary amines.\[8\]

The proposed reaction for supported primary amines is as follows:

**CO\(_2\) Sorption:**

\[
2 \text{ R-NH}_2 + \text{CO}_2 \rightarrow \text{R-NH}_3^+ + \text{R-NH-COO}^-
\]

**Regeneration:**

\[
\text{R-NH-COO}^- + \text{R-NH}_3^+ + (\text{Heat}) \rightarrow \text{CO}_2 + 2 \text{ R-NH}_2
\]

For the tertiary amines the mechanism is believed to require water:

**CO\(_2\) Sorption:**

\[
\text{R-NR}_1\text{R}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{R-NR}_1\text{R}_2\text{H}^+ + \text{HCO}_3^-
\]

**Regeneration:**

\[
\text{R-NR}_1\text{R}_2\text{H}^+ + \text{HCO}_3^- + (\text{Heat}) \rightarrow \text{R-NR}_1\text{R}_2^2 + \text{CO}_2 + \text{H}_2\text{O}
\]

In the above schemes, the substituent R is an alkyl moiety connecting the amine to the support material and R\(^1\), R\(^2\) are different alkyl moieties.

The current industrially scalable post-combustion CO\(_2\) capture process involves aqueous absorption with alkanolamines. Although adsorption (the focus of the current work) is
different from absorption separation processes, a great deal can be learned through the vast number of studies associated with amine-based solvent approaches to CO\textsubscript{2} capture based upon absorption. In other words, the mechanism and chemical pathway of CO\textsubscript{2} binding in a solvent is similar to that of a porous solid sorbent. Most commonly used are monoethanolamine (MEA) and diethanolamine (DEA).[30] Recently, Chowdhury et al. investigated the CO\textsubscript{2} sorption rate, loading capacity, and heat of reaction measurements of twenty-five amine-based absorbents. They were able to correlate their findings to the differences in chemical structure of the amines.[31] The results suggest that the specific amine moieties and structures used may be selected or modified to tune the CO\textsubscript{2} capture process.

Tertiary amine-CO\textsubscript{2} reaction chemistry suggests that the tertiary amine-CNTs may have high CO\textsubscript{2} capacity with a relatively low heat of sorption, which makes tertiary amine-CNTs promising sorbents for CO\textsubscript{2} capture. The primary goal of the proposed work is to synthesize and investigate tertiary amine modified CNTs as CO\textsubscript{2} capture sorbents. Initial investigations have been designed to compare the material and CO\textsubscript{2} capture properties of tertiary amine-modified CNTs with primary amine modified CNTs.

Results

Materials and Methods
OH-functionalized MWNTs (OH-MWNTs) with outer diameters of 10-20 nm were purchased from Sun Innovations (Item #SN32547). Aminosilanes: 3-aminopropyltriethoxysilane (APTES) (99%) and N-dimethylaminopropyltrimethoxy-silane (DMAPS) were purchased from Gelest, Inc. Anhydrous toluene was purchased from Arcos Organics.

Method 1: Functionalization procedures were based on the methods reported earlier by Su et al.[19] Prior to silane functionalization, the MWNTs were heated in a quartz tube under a nitrogen flow at 300°C for one hour to remove water, amorphous carbon material and other volatile impurities. The silane functionalization was carried out in an inert argon atmosphere to increase batch-to-batch reproducibility by limiting exposure to ambient water. Two grams of heat-treated MWNTs were dispersed in 100 mL of toluene and 10 mL of silane. The reaction was conducted under reflux with continuous stirring for 18 hours in a Schlenk flask in a silicon oil bath at 125°C. The solution was allowed to cool and the dispersion was vacuum filtered through 0.45-µm PTFE filter (Millipore FH) with excess toluene. The product was then dried in a quartz tube under a nitrogen flow at 125 °C for 1.5 hours to remove any residual silane and toluene. The synthesis of primary and tertiary amine functionalized CNTs was repeated into two batches. For the second batch of tertiary amine CNT functionalization, the reaction was reduced from 96 hours to 24 hours. No observable difference in material properties was found between the two batches.

Method 2: Functionalization procedures were based on the methods reported by Su et al.[32] The CNT support used in this method, C\textsubscript{Tube} 100 MWNT from CNT Co. Ltd., is the same support as that used by Su et al.[32] The silane functionalization was carried out in an ambient atmosphere to facilitate water-induced silane polymerzation. Two
grams of as-produced MWNTs were dispersed in 70 mL of toluene and 30 mL of silane. The reaction was conducted under reflux with continuous stirring for 2 hours in a Schlenk flask in a silicon oil bath at 125 °C. The solution was allowed to cool and the dispersion was vacuum filtered through 0.45-μm PTFE filter (Millipore FH). The product was then dried in a vacuum oven at 80°C for 1.5 hours to remove any residual silane and toluene.

XPS analyses were performed using a Physical Electronics (PHI) 5000Versa Probe Scanning XPS system at the Stanford Nanocharacterization Laboratory at Stanford University. Spectra were collected under high vacuum (10^-11 Torr) at ambient temperature using monochromatic Al Kα radiation at 1486 eV. All spectra were calibrated to the C1s peak located at 284.6 eV. Samples were prepared by dispersing the functionalized MWNT using bath sonication in deionized water and then filtering the dispersion through 0.4-mm polycarbonate filters. Scanning Electron Microscopy (SEM) was conducted using a FEI XL30 Sirion SEM at 5 KV and using a FEI Magellan 400 XHR at 5 KV. The SEM samples were prepared by dispersing the functionalized MWNT using bath sonication in deionized water. A drop of this dispersion was placed on a heated (120 °C) bare silicon wafer plate. Micro-Raman spectroscopy was performed in a LabRamAramis confocal Raman spectrophotometer (Horiba). Measurements were carried out at 633 nm (1.96 eV) excitation at 100x magnification and 1-mm spot size, and 1800 grating. Samples for Raman spectroscopy were made in a similar manner as the SEM samples. Data was normalized to the G’-band. FTIR was performed in a Thermo Nicolet Nexus 470 ESP FTIR spectrophotometer. FTIR pellet samples were made by grinding CNT samples with KBr and then pressing in a pelletizer.

The porosity and surface area analysis was performed using a Quantachrome Autosorb iQ gas sorption analyzer. Each sample was outgassed at 0.03 torr with a 2 °C/min ramp to 110 °C, followed by a 5 °C/min ramp to 140 °C, where the sample was held for 3 hours and tested for continuing outgassing. If the sample was still outgassing, it was further held at 140 °C for up to 3 additional hours, with a test performed every 15 minutes. The sample was then held at vacuum (0.03 torr) until the analysis was run. Pore analysis was performed using N₂ at 77 K (P/P₀ range of 1×10⁻⁵ to 0.995) and Ar at 87 K (P/P₀ range of 1×10⁻⁵ to 0.995). Mesopore distributions were estimated using N₂ and Ar desorption isotherms in combination with the Barrett-Joyner-Halenda (BJH) method, while micropore distributions were estimated using N₂ and Ar adsorption isotherms in combination with the Dubinin-Astakhov (DA) method.

Breakthrough experiments were performed in a quartz reactor with packed beds ranging from 100 mg to 200 mg of CNT. The experimental schematic can be seen in Figure 1. Nitrogen is passed through a bubbler containing H₂O (the bubbler is bypassed in dry experiments) at 20 mL/min and passed through the packed bed. At a designated time, 2 mL/min of CO₂ is passed into the flow stream. Breakthrough is measured downstream of the packed bed using an Extrel 300Max-LG quadrupole MS. Both CO₂ and H₂O concentrations are monitored, and CO₂ is not sent to the bed until the H₂O concentration has stabilized. Typical experimental parameters are 9.09% CO₂ and 2.1% H₂O, with a balance of N₂. Residence times across the bed are on the order of several seconds. The bed is held at a constant temperature of 40 °C for adsorption experiments. The reactor
may be rapidly heated to 120 °C for desorption measurements. The capacity of the sorbent is determined by measuring the difference between CO$_2$ breakthrough curves through an empty reactor and through the packed bed. Experiments were performed to determine the effect of pressure drop across the bed using a 500 mg bed of Sigma Aldrich 50-70 mesh quartz sand. Changes due to pressure drop were determined to be minimal, and within the experimental error.

![Schematic for CO$_2$ breakthrough experiments.](image)

**Figure 1**: Schematic for CO$_2$ breakthrough experiments.

MWNTs were functionalized with primary (APTES) and tertiary (DMAPS) aminosilanes and the material properties of the functionalized MWNTs were investigated. The results of this characterization analysis are described in the following sections.

**Scanning Electron Microscopy**

Morphology was investigated by scanning electron microscopy (SEM) by drop casting dispersions of MWNTs in deionized water onto clean and heated silicon/silicon oxide wafers. There was no significant difference in appearance of the OH-MWNTs before or after heat treatments prior to functionalization (not shown). Figure 2 shows high-resolution images of large aggregates of MWNTs with and without functionalization. The SEM images show MWNTs with a large available surface area and little order in aggregation. In addition to the large surface area outside the SWNTs, this loose architecture should allow some access to the interior pore space inside the MWNT. However, some of the higher contrast particles observed in the micrographs could be metal catalyst, which could block this inner pore space. It should be noted that the silane molecules are not expected to be observable by SEM unless there is extensive polymerization of the silane resulting in large aggregates. Toluene was also used as a dispersion media and no significant differences in MWNT morphology were observed. However, the “coffee ring effect” due to material deposited during solvent evaporation was observed in the low-resolution images on the SiO$_2$ surface of the APTES-MWNT samples (not shown). It is likely that these are due to residual APTES dissolved in
X-ray Photoelectron Spectroscopy
For elemental analysis of the functionalized materials, X-ray photoelectron spectroscopy was performed. In Figure 3, the spectra of two batches of OH-MWNT are shown. As expected, the OH-MWNTs do not contain N or Si, but have a small oxygen peak associated with the hydroxyl groups bound to the CNT. Calculating from the XPS cross sections of N and Si, the atomic percentages of N and Si correspond to the 1:1 atomic ratio of N to Si in both APTES-MWNT and DMAPS-MWNT samples. The corresponding change in the oxygen signal from the OH-MWNTs to the APTES-MWNT and DMAPS-MWNT samples is also consistent with the attachment of APTES and DMAPS to the MWNTs. The ratio of O to Si throughout the silanization process should range between 1:1 to 2:1, depending on whether the silane binds to one or two hydroxyl groups on the CNT surface.
**Figure 3:** XPS spectra for A. Carbon (C1s), B. Nitrogen (N1s), C. Oxygen (O1s) and D. Silicon (Si2p) regions from both batches of the the OH-MWNT, APTES-MWNT and DMAPS MWNTs. The spectra are shifted and normalized according to the C1s spectra.

The C1s spectra of all samples are primarily due to the C-C bonds of the CNTs; however, a shoulder of the APTES-MWNTs C1s spectra is evident at 286.5 eV, and may be due to carbon in an oxidized state present on the APTES-MWNTs. DMAPS-MWNT shows a similar shoulder, but at a smaller intensity. Due to the low signal-to-noise ratio for the N1s spectra, it is difficult to determine how N is configured. The O1s spectra of OH-MWNTs appear broadened, likely due to the presence of O-Si, O-C and O-H bonds. The Si2p spectrum present in APTES and DMAPS samples was due to silicon, as it is not present in the non-functionalized OH-MWNT samples. While it is difficult to determine the exact coordination of APTES and DMAPS on the CNT surface, the APTES-CNTs XPS spectra do support the covalent attachment of APTES to the OH-CNTs.

Both batches of functionalization result in the same spectral shapes. For the OH-MWNTs, these were from the same material, but scanned at different times. The APTES-MWNTs were produced using the same functionalization method, indicating this procedure is reproducible. The DMAPS-MWNTs were fabricated with 96-h and 24-h reactions, yet the XPS analysis indicates a similar amount of functionalization. This difference in reaction time with DMAPS does not appear to significantly affect the coverage of DMAPS on the MWNTs.
Resonant Raman Spectroscopy

**Figure 4**: Resonant Raman spectra of the D-band and G-band of OH-MWNT and APTES-MWNT. The spectra were normalized and shifted to the G-band. There is no significant difference in the spectra indicating functionalization process did not increase or decrease the defects on the MWNTs.

Resonant Raman spectroscopy was performed on the OH-MWNTs and APTES-MWNTs. The OH-MWNTs display a very large D-band/G-band ratio indicating a large amount of defect sites from the –OH functionalization by the manufacturer. The D/G band ratio did not change with functionalization. Also, the 300 °C annealing step performed before functionalization was not at a temperature high enough to heal defect sites.

*Fourier Transform Infrared Spectroscopy*

Fourier Transform Infrared Spectroscopy (FTIR) analysis of the samples was performed in transmission mode by KBr pellets with the MWNTs. Observed in the spectra was a clear reduction in the broad –OH peak, which appears at approximately 3400 cm\(^{-1}\). This indicates effective consumption of the –OH group during silanization. The weak band at 1130 cm\(^{-1}\) in the DMAPS-MWNT spectrum can be assigned to the C-N stretching. Weak bands at 1040 cm\(^{-1}\) in both APTES-MWNT and DMAPS-MWNT spectra are due to Si-O stretching. It should be noted that the characteristic bands are weak and not evident. The FTIR tests will be repeated in future work with better control of the amount of samples in the KBr pellets. Furthermore, strong bands appear at 2320 cm\(^{-1}\), 2430 cm\(^{-1}\) and 2430 cm\(^{-1}\) for OH-MWNT, APTES-MWNT and DMAPS-MWNT, respectively. These bands are probably due to C=O stretching induced by oxidation of the carbon nanotubes in air.
CO₂ Breakthrough Analysis
Breakthrough experiments were performed on MWNTs functionalized by aminosilanes using both methods described in the Materials and Methods section. The samples were initially tested in dry conditions at 40 °C in 9.1% CO₂. This ideal state approximates the CO₂ concentration in flue gases, but eliminates the effects of other flue gas constituents, especially H₂O. As a proof of concept, several known materials (soda lime, the commercial metal-organic framework ZIF-18 and the commercial zeolite 13X) were tested in the system before analysis of the functionalized MWNTs was commenced. One of these materials can be seen in Figure 7, which can also serve as a discussion of the breakthrough calculations in general.

Figure 5: FTIR Spectra of the OH-MWNTs and the silane-functionalized MWNTs
The black line in Figure 6 is the empty bed breakthrough curve for CO$_2$, which is averaged over 4 experimental runs, with the error bars indicating the standard deviation of 0.12%. This corresponds to an error of 0.1 mmol CO$_2$ g$^{-1}$ sorbent in the final calculation. The red line is the CO$_2$ breakthrough curve for a 197.3-mg bed of powdered 13X zeolite (obtained from Sigma Aldrich in pellet form). The difference between the two curves is equivalent to a CO$_2$ capacity of 0.97 mmol g$^{-1}$ of 13X sorbent. A recent paper by Mulgundmath et al. reported a capacity for 13X from a different supplier at 0.8 mmol g$^{-1}$ sorbent in N$_2$/CO$_2$ binary systems at a CO$_2$ partial pressure of 0.1 and 40 °C.[33] When factoring in the unknown impact of the pellet binding material and system error, this is a strong indication that the system is performing as expected.

Testing of both the APTES and DMAPS functionalized OH-MWNT (functionalization method 1) indicates that the materials did not adsorb CO$_2$ as expected under the experimental conditions. For this reason, the 2$^{nd}$ functionalization method was performed, with a different source of MWNTs. The source MWNTs were tested for CO$_2$ capture in a 73.0 mg bed under standard test conditions and showed a CO$_2$ capacity of 0.48 mmol g$^{-1}$ sorbent. This was higher than expected and could potentially be related to the depth of the bed (the non-functionalized material has a very low bulk density, resulting in a bed depth 4 to 5 times larger than the functionalized material) and the size of the bed (smaller bed weights will increase the experimental error due to the calculation method).
Figure 7: CO₂ breakthrough experiment for 208.8 mg of CNT Co. LTD. Cₜₐₜ₈ 100 modified with APTES. This material was created using the 2nd functionalization method. The red, blue and green lines indicate cycles 1, 2 and 3, respectively.

As can be seen in Figure 7, the APTES functionalized MWNT captured CO₂ under dry conditions. The sorbent was exposed to CO₂ under standard operating conditions. The bed was then raised to 120 °C in pure N₂ to drive the CO₂ off the sorbent, then allowing the sorbent to return to 40 °C. This occurred for 3 adsorption-desorption cycles on the same 208.8 mg bed. The average CO₂ capacity of the sorbent was 1.21 mmol g⁻¹ sorbent over the 3 experiment sample, showing a high degree of repeatability. Su et al., who performed a similar functionalization of the same MWNTs, observed a CO₂ capacity of 3.58 mmol g⁻¹ at 50 °C in 15% CO₂ and longer residence times.[18] Carbon dioxide was observed on the MS system being desorbed from the APTES MWNTs, but due to potential changes in MS inlet conditions from the heating of the packed bed, the exact amount is unknown at this time. The DMAPS functionalized MWNT was tested under the same dry conditions and as expected due to the absence of H₂O, no CO₂ capture was detected.
Figure 8: CO$_2$ breakthrough experiment for 197.3 mg of CNT Co. LTD. C$_{\text{Tube}}$ 100 modified with DMAPS under wet conditions. This material was created using the 2$^{\text{nd}}$ functionalization method. The red, blue and green lines indicate cycles 1, 2 and 3, respectively.

The APTES and DMAPS functionalized MWNTs were also tested under humid conditions, where N$_2$ was humidified by passing the gas stream through a bubbler. The water concentration in the gas was expected to be 2.1%, and this was further confirmed by observation on the MS. The APTES functionalized MWNTs continued to capture CO$_2$, although the capacity was decreased from an average of 1.2 mmol g$^{-1}$ sorbent to 0.6 mmol g$^{-1}$ sorbent. Since the H$_2$O concentration was allowed to equilibrate before the bed was exposed to CO$_2$, the H$_2$O and CO$_2$ concentration were not competitively adsorbing, and this may account for some of the decrease in CO$_2$ capacity. The decrease may also be attributed to a change in the CO$_2$ concentration (down to 6.9% from 9.1% due to a mass flow controller issue not noted until experiment completion). Unfortunately, as seen in Figure 8, the DMAPS functionalized MWNTs did not capture CO$_2$ under humid conditions. While the reasons for this are still being explored, it may be due to the CO$_2$ to H$_2$O ratio being closer to 3 than the desired 1 or the experimental procedure of allowing H$_2$O to equilibrate with the sorbent before CO$_2$ exposure.

Porosity Analysis
The pore size distribution was measured by performing isothermal sorption and desorption measurements using N$_2$ at 77 K. Nitrogen chemisorbs onto amine groups, thus measurements of the functionalized MWNT pores sized on the order of nanometers are not possible with this procedure. The pore distribution estimates presented in Figure 9 are for the non-functionalized MWNTs used in methods 1 and 2. The Sun Innovations OH-MWNT is presented in red, while the CNT Co. Ltd. MWNT used in method 2 is
presented in black. First, the micropore data obtained using the DA method and the adsorption isotherm indicates that the inner pore of the MWNTs is approximately 1.5 to 2 nm for both sources. However, the mesopore data obtained from the BJH method and the desorption isotherms indicate there is a substantial difference in the pore size distribution of the MWNT bundles. The pore size distribution for the OH-MWNTs and APTES-MWNTs is very similar indicating that further functionalization did not change the aggregate packing and effective pore size. The increased pore size in the bundles is perhaps one reason why the second functionalization method performed substantially better than the initial attempt. Although not presented here due to the ineffectiveness of the sorbent, a N$_2$ analysis of the APTES and DMAPS functionalized OH-MWNTS (the first method) indicates that there is not a substantial change in pore distribution or volume upon functionalization.

![Figure 9](image)

**Figure 9**: Pore distribution measured by nitrogen sorption at 77 K. The pore distribution is estimated using the Dubinin-Astakhov method for micropores (solid lines) and the Barrett-Joyner-Halenda method for mesopores (dotted lines). The red lines are the OH-MWNT used in method one and the black lines are the MWNT used in method 2.

Due to the issues with N$_2$ interaction with amines, a surface and pore analysis of the MWNTs using Ar adsorption and desorption at 87 K are underway. Initial results can be seen in Figure 10. The non-functionalized MWNT is in black, the APTES functionalized MWNT in red and the DMAPS functionalized MWNT analysis is in the process of being completed, thus it is not included. The Ar adsorption analysis combined with the DA method indicates (as N$_2$ did) that the inner pore space of the MWNT is located at about 1.5 to 2 nm. The presence of APTES does not impact this pore space distribution significantly, although there may be some loss at the larger end of the micropore volume. The mesopore distribution, as determined through the BJH method, shows a similar
distribution to that obtained by N\textsubscript{2} on the non-functionalized MWNT. However, APTES functionalization decreases the pore volume available at the larger end of the mesopore region and results in the creation of pore space between 2 and 10 nm that is not present in the non-functionalized MWNT. A similar analysis for the DMAPS functionalized MWNT is currently underway.

![Figure 10](image.png)

**Figure 10**: Pore distribution measured by argon sorption at 87 K. The pore distribution is estimated using the Dubinin-Astakhov method for micropores (solid lines) and the Barrett-Joyner-Halenda method for mesopores (dotted lines). The red lines are the non-functionalized MWNTs (method 2) and the black lines are the APTES functionalized MWNT (method 2).

**Discussion**
Materials characterization of MWNTs functionalized by aminosilanes was performed in order to highlight characteristics that may be useful for CO\textsubscript{2} capture. Loadings of APTES, a primary amine, on MWNTs were much higher than the tertiary DMAPS as shown by the XPS elemental analysis. This could be due to the large molecular size of DMAPS and steric considerations with the bulky methyl groups on the DMAPS, which prevent higher loadings. Also, it is well known that APTES can be grafted onto surfaces with the siloxane moiety as well as with interactions with the lone pair and hydrogen groups on the nitrogen moiety[34]. The smaller molecular size and head and tail functional groups on APTES allow the molecule to polymerize and it is possible that higher loading is also due to polymerization of APTES. The functionalization reaction was performed under dry conditions to increase the reproducibility of the results by reducing polymerization; however, the vacuum filtration was performed under ambient conditions. Humidity from the air could have introduced water and resulted in polymerization. Polymerization of the silane group might not result in adverse
performance as these increases the amine loading of the MWNTs. Future work will explore the reaction conditions in ambient conditions as well as the controlled introduction of water during reaction.

Pore size analysis indicates that functionalization does not significantly affect the pore size distribution. However, it may affect total pore volume at specific pore diameters, but increased control over analysis sample weight is needed, as well as an increased number of runs to determine error, in order to confidently conclude that this is the case. Breakthrough results indicated that only the APTES functionalized MWNTs created through method 2 captured a measurable amount of CO$_2$. The DMAPS functionalized MWNTs did not capture CO$_2$, potentially due to low loading, poor functionalization or a poor CO$_2$ to H$_2$O ratio in the breakthrough experiments.

**Conclusions**

MWNTs were functionalized with aminosilane compounds and the resulting materials were characterized. Comparing the amine loading by using silane-grafting groups, primary amines had higher loadings as determined by XPS. The morphology of the MWNTs with functionalization did not seem to be significantly altered. The porosity measurements indicate insignificant change in both the inner micropore space of the MWNT and the larger, mesopore space due to MWNT bundling. The FTIR measurements need to be repeated with lower loadings of MWNT into the KBr pellet to clarify the lack of expected nitrogen containing peaks in the spectra. Additionally, methods to explore higher amounts of amine loading need to be explored. There have been studies with APTES-SWNTs with high loading and this procedure, which the procedures used here are derived from, needs to be explored for higher loadings of tertiary amines[18]. The addition of water during silane functionalization may help in creating polymerization of aminosilane and result in higher amine loadings in the final sorbent material.

**Progress**

The current path of the research is revealing important lessons in both the functionalization of MWNTs for carbon capture and the general difficulties with dealing with solid sorbents.

**Future Plans**

The remainder of the research project will focus on developing a procedure to successfully functionalize MWNTs with the tertiary amine DMAPS. Since this is the potential advancement desired by the project, an iterative process involving functionalization and CO$_2$ capacity analysis will be performed. This plan will highlight both the best method for functionalization and the best conditions under which to perform CO$_2$ capture.

**Publication and Patents**

None to report at this stage.

**References**


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