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Pretreated Multi-walled Carbon Nanotube adsorbents with Amine-Grafting for CO₂ Removal in confined Space

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Abstract

Three different methods including thermal treatment, HNO₃ acid and O₂ oxidation were employed to pretreat multi-walled carbon nanotubes (MWCNTs) in order for the subsequent grafting with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS). The types and contents of the O-containing groups generated by various pretreatments were investigated and quantified, and the corresponding amine-grafting reactions were also illustrated. The alkoxy groups of AEAPS can react with O-containing groups on the pretreated MWCNTs through silylation reaction in the absence of carboxyl acids induced by O₂ gas oxidation, where primary amino groups can be retained in the compounds which can be accessible to capture more CO₂. A dynamic fixed-bed system was used to characterize the adsorption behavior of low-concentration CO₂. The adsorption/desorption operations of 10 repeated cycles were further conducted for verifying the sustained excellent performance. The highest CO₂ adsorption capacity of 0.64 mmol/g was achieved by the O₂-oxidized MWCNTs with AEAPS-grafting, which is almost 7.1 times of the oxidized-MWCNTs. Therefore, it indicates that O₂ gas oxidation is easy in operation and high in

1 efficiency for the pretreatment of MWCNTs. The obtained adsorbent with high capacity, high
2 thermal stability, high tolerance to moisture and low regeneration cost is promising for direct CO₂
3 capture in confined space.

4 **Keywords:** Oxidative pretreatment; O-containing groups; aminosilane; CO₂ capture;
5 amine-grafting efficiency.

6

1. Introduction

In recent years, CO₂ capture and sequestration technologies (CCS) for reducing the impacts of the increasing atmospheric CO₂ concentration on the global climate changing have been received significant attentions.^{1,2} It is estimated that approximately one-third of global carbon emissions are emitted from the distributed sources such as transportation vehicles, where low-concentration CO₂ shall be directly captured from ambient air (ca.400 ppm CO₂, “air capture”).³ Capture technologies of high concentration CO₂ generated from large point sources, such as coal-fired power plants (ca. 10% CO₂), are relatively mature.^{4,5} In particular, CO₂ capture is also occupied in confined space including submarines, space shuttles, and space stations etc., where CO₂ is emitted from human breathing, emission from mechanical equipment running and oxidation of material.^{6,7} It is because that high CO₂ concentration in enclosed space will threaten human being’s survival.^{8,9}

Approaches utilized to capture CO₂ from a gas mixture including absorption, cryogenic distillation, adsorption and membrane separation have been well-studied.¹⁰⁻¹³ The chemical absorption process frequently using lithium hydroxide or liquid amines with high CO₂ capture capacity is a mature commercial technology. However, it suffers from some drawbacks such as high operational costs, container corrosion, energy intensive, viscosity and foaming issues.¹⁴ The cryogenic distillation and membrane separation processes are expected to be low efficiency and high cost, especially for ambient air capture.¹⁰ Adsorption with porous solid sorbents including carbon materials,^{15, 16} polymers,⁶ silica materials,¹⁷⁻²⁰ and metal-organic frameworks (MOFs)²¹ is more promising, because these materials have the potential to work with low regeneration energy²².

1 Apart from physical adsorbents, amine-functionalized adsorbents are more attractive owing to
2 providing alkaline active sites for CO₂ adsorption.^{15,23} Typically, these chemical adsorbents were
3 prepared by physically immobilizing liquid amines or chemically grafting amino groups onto the
4 surface of porous support.²⁴ Higher loading of amine can be achieved for impregnation method,
5 however they exhibit low thermal stability and poor distribution.²⁵⁻²⁸ The CO₂ adsorption capacity
6 decreases gradually along with the increasing of adsorption/desorption cycles because of the
7 leaching of amines, and meanwhile the amine efficiency is low.²⁹ Herein, intensive research efforts
8 have been devoted to chemically grafting on silica-based solid supports such as SBA-16,¹⁷
9 SBA-15,^{30,31} and MCM-41.^{29,32} Carbon nanotubes (CNTs) are more suitable as the supports
10 because of the tolerance to moisture compared with silica-based adsorbents.^{22,33-35} It has been
11 proved as well that CNTs-based adsorbents are light in weight, high in surface area, thermal and
12 chemical stability and controllable in chemical reactivity.³⁶⁻³⁸ The thermodynamics and
13 regeneration studies demonstrated that amine-grafted CNTs are possibly cost-effective sorbents
14 for CO₂ capture.^{33,34}

15 The introduction of O-containing groups on supports induced by chemical pretreatment is a
16 crucial procedure of chemical grafting for covalently linking with amine functional groups. The
17 commonly used pretreated methods were acid oxidation, UV photo-oxidation, thermal treatment,
18 plasma, and gas phase oxidation.^{37,39,40} Velasco-Santos and coworkers employed the
19 arc-discharge method to oxidize the carbon nanotube surface in order to improve the chemically
20 bonding with different polymer materials. They addressed that the trisilanol groups on
21 organosilanes can react with the hydroxyl groups on the pre-oxidized nanotube surface and

1 therefore organosilanes will be attached on the surface of nanotube.⁴⁰ However, the arc-discharge
2 treatment should be conducted in high-voltage and high cost of power supply hindered it for the
3 industrial application. The acid treatment exhibited the relatively high yields of functional groups
4 including carboxylic acid, phenol, carbonyl, carboxylic anhydride and lactone groups, etc.³⁴
5 However, acid treatment is trouble and time-consuming on the rinsing and drying operation. Gas
6 phase oxidation is more convenient and effective, especially being contaminant-free, where the
7 O-containing groups including phenol, carbonyl/quinone and lactone groups were generated.^{37, 41}
8 Thermal treatment can selectively remove some of functional groups, such as carboxylic acid. An
9 intensive study on the correlation between O-containing groups on the oxidized CNTs and the
10 silylation reaction efficiency was conducted by Gaspar and coworkers.³⁷ It was found that the
11 highest efficiency was achieved by the HNO₃ oxidation with subsequent thermal treatment
12 because it showed a high content of O-containing groups including the phenol groups, but without
13 carboxylic acids. However, they did not concentrate on the study of CO₂ capture.

14 To the best of our knowledge, some pretreatments including thermal, acid and NaOH treatments
15 were employed only to purify CNTs before amine-grafting,^{22, 35, 42} and the tuning of O-containing
16 functional groups induced by the oxidative methods on amine-grafting for CO₂ capture was
17 seldom investigated. Therefore, in the present work multi-walled CNTs (MWCNTs) were first
18 pretreated by acid oxidation, thermal treatment or gas phase oxidation and subsequently
19 N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPS) were selected to tether to the
20 pretreated MWCNTs. We devoted to investigating the effects of types and contents of the
21 O-containing groups on the corresponding amine-grafting reaction as well as the amine-grafting

1 efficiencies for CO₂ capture, and CO₂ adsorption mechanisms were also illustrated. The textural
2 properties, surface chemical composition and morphologies of the resulted modified-MWCNTs
3 were characterized by N₂ adsorption isotherms, thermogravimetry, X-ray photoelectron
4 spectroscopy, Fourier transform infrared spectroscopy, elemental analysis and scanning electron
5 microscopy. Here, the obtained amine-grafted MWCNTs were employed for CO₂ removal in
6 confined space, where the representative CO₂ level is about 2% vol.⁸ The effects of operating
7 temperature and humidity in the gas mixture on CO₂ adsorption behavior were further discussed
8 and the repeated availability was also concerned.

9 **2. Experimental Section**

10 **2.1 Preparation of amine-grafted MWCNTs**

11 **2.1.1 Materials**

12 All of the reagents and solvents used in this study were utilized without further purification.
13 Commercial MWCNTs (TNM2, 95 wt% purity, Chengdu Organic Chemicals Co., Ltd.) were
14 prepared through the catalytic decomposition of natural gas over Co-based catalyst. The outer
15 diameter is in the range of 8-15 nm, and the length is around 50 μm. The chemicals used in the
16 oxidation and silylation reactions are listed as below: HNO₃ (65-68 wt%, Gaojing), H₂SO₄ (98
17 wt%, Gaojing), anhydrous toluene (AR, Guoyao), AEAPS (>95 wt%, Aladdin).

18 **2.1.2 Chemical pretreatments**

19 The pristine MWCNTs were pretreated by thermal treatment, acid oxidation, and oxidation in the
20 gas phase, while the obtained samples were denoted as t-MWCNTs, h-MWCNTs, and
21 o-MWCNTs, respectively. The corresponding procedures are described as follows.

1 *Thermal treatment:* The pristine MWCNTs were thermally treated in a fused-silica tube with N₂
2 gas (100 mL/min) at 300 °C for 1 h and then cooled to room temperature.

3 *Acid oxidation:* About 4 g of pristine MWCNTs were refluxed in 300 mL 68 wt% HNO₃ at 80 °C
4 for 8 h and then cooled to room temperature. Subsequently, the samples were filtered and washed
5 with deionized water until the filtrate pH reached neutral. Finally, the obtained samples were dried
6 in vacuum at 60 °C overnight. When the raw MWCNTs were treated by mixture of HNO₃ and
7 H₂SO₄ (1:3, v/v) at 80 °C for 4 h, the obtained samples were denoted as m-MWCNTs.

8 *Gas Oxidation:* The pristine MWCNTs were heated to 500 °C at 4 °C/min by passing 5 vol%
9 O₂/N₂ gas mixtures (100 mL/min), and kept at 500 °C for 3 h. The samples were then cooled to
10 room temperature under N₂ atmosphere.

11 **2.1.3 Amine-grafting of MWCNTs**

12 AEAPS was tethered onto surface of pretreated MWCNTs through silylation reaction.³⁷ Firstly, 5
13 mL AEAPS was dispersed in 95 mL anhydrous toluene and continuously stirred for 5 min. Then
14 about 2 g pretreated MWCNTs were added and refluxed at 110 °C for 24 h under Ar protection.
15 Afterward, the amine-functionalized MWCNTs were filtered and rinsed with toluene. The
16 obtained amine-grafted MWCNTs shall be dried at 80 °C for 8 h. A simple notation was
17 recommended for the obtained sample. For example, o-MWCNTs-AEAPS represents that the
18 sample was pretreated by O₂/N₂ oxidation and subsequently grafted with AEAPS.

19 **2.2 Characterization of adsorbents**

20 The textural characterization of the materials were determined by the N₂ physical

1 adsorption/desorption isotherms (TriStar 3000, Micrometrics) at $-196\text{ }^{\circ}\text{C}$, where the samples were
2 vacuum-dried at $120\text{ }^{\circ}\text{C}$ for 3 h before the determination. The Brunauer-Emmett-Teller (BET) and
3 Barrett-Joyner-Halenda (BJH) methods were used for the calculation of the surface areas and
4 average pore diameter from the isotherm of adsorption branch, respectively. The total pore volume
5 was calculated from the amount of adsorbed N_2 at $P/P_0=0.98$, while the micro surface areas and
6 volume were calculated by t-plot method. The surface morphological features were observed by
7 using a field emission scanning electron microscope (FE-SEM) (SU-70, Hitachi) at 3 kV. Thermal
8 stabilities were performed in a thermogravimetric analyzers (TGA) equipped with differential
9 scanning calorimetry (DSC) (SDT Q600, TA Instrument) in N_2 atmosphere with a flow rate of 120
10 mL/min, and the functional groups under the corresponding decomposition temperature can be
11 quantitatively analyzed. The sample was heated from room temperature to $900\text{ }^{\circ}\text{C}$ at the heating
12 rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in N_2 atmosphere. The X-ray photoelectron spectra (XPS) (Amicus, Shimadzu)
13 equipped with monochromatized Al $K\alpha$ radiation source (1486.7 eV) and Fourier transform
14 infrared spectroscopy (Nicolet 6700) were employed to study and identify the surface chemical
15 properties, especially for the determination of amino groups. The quantitative determination of
16 elemental content in adsorbents was tested with Flash EA 1112 (Thermo Finnigan).

17 **2.3 Adsorption Experiments**

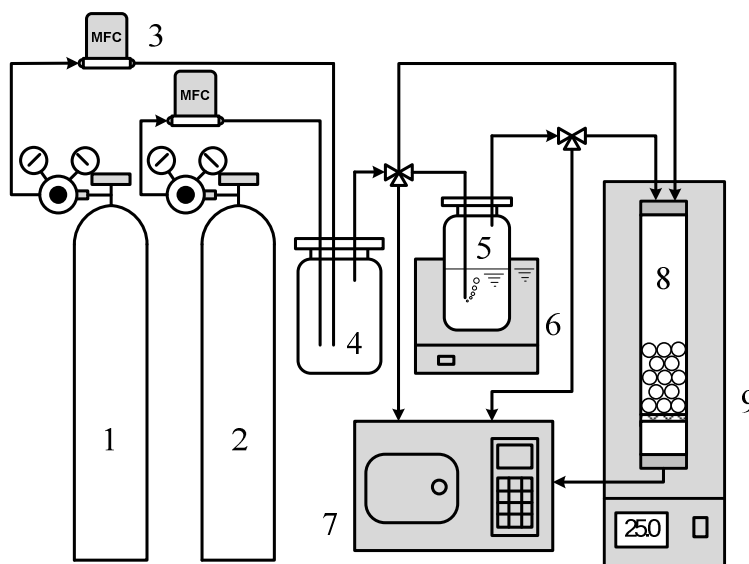
18 The experimental studies on the CO_2 adsorption performances were conducted in a dynamic
19 fixed-bed system, as shown in **Figure 1**. The glass adsorption column packed with 1 g adsorbent
20 was placed in a temperature control box (AT-950, Science Instrument China) in order to maintain
21 a constant temperature. The internal diameter and total length are approximately 1 cm and 20 cm,

1 respectively. A mixture of pure N₂ and CO₂ was blended in glass bottle, and the influent CO₂
2 concentration was commonly kept at 2 vol%. Mass flow controllers (D07-19C, Sevenstar
3 Electronics China) were used to control the influent mixture gas flow rate at 50 mL/min. The
4 influent gas then passed through the adsorption column and CO₂ would be adsorbed and removed.
5 Once the CO₂ adsorption process reached the equilibrium, the saturated adsorbents would be
6 undergone in desorption where the temperature of adsorption column raised to 75 °C and its
7 vacuum was kept at 5 kPa. After 5min operation, the desorbed CO₂ concentration of effluent gas
8 decreased to zero, indicating that the adsorption ability of adsorbents was recovered and they
9 would be available for next round adsorption study. Gas chromatography (GC) equipped with a
10 chromatographic column (3.0 mm × 4.0 mm, Proapak QS) and a thermal conductivity detector
11 (TCD) (GC9790, Fuli, China) was utilized to automatically detect the CO₂ concentration of the
12 influent and effluent gas streams. The operating temperatures of injection, column and detector
13 were set at 100 °C, 140 °C, and 150 °C, respectively. Moisture of the influent gas mixture was
14 generated from the water bubbler, where N₂ stream was bubbling in the deionized water and
15 carrying a certain amount of water by adjusting temperature of the water bath. Higher temperature
16 could obtain higher water vapor content. The water content was calculated by the following
17 equation.

$$18 \quad \text{Water content}(\%) = \frac{Q_1 \times p^* / p}{Q_2} \times 100\% \quad (1)$$

19 where Q₁ and Q₂ are the flow rates of N₂ and influent gas mixture, respectively. p* represents the
20 saturated vapor pressure of water in the certain temperature and p is the atmospheric pressure.
21 Similar installation was used by Ye and coworker and the maximum 7% in water content can be

1 obtained²⁸. Actually, the calculated water content represents the inputted percentage in the influent
 2 gas mixture rather than the real equilibrium content. The water fog will be formed when it reached
 3 above 3%. Since the length of the transport pipe between water bubbler and adsorption column is
 4 short, water fog can be quickly transferred into the adsorption column and adsorbed by adsorbents.



5
 6 1. Nitrogen, 2. Carbon dioxide, 3. Mass flow controller, 4. Gas blending bottle, 5. Water bubbler,
 7 6. Water bath, 7. Gas chromatograph, 8. Adsorption column, 9. Temperature control box

8 **Figure 1.** Diagram of the adsorption experimental setup

9 The CO₂ adsorption capacity (q , mmol/g) at a certain time (t , min) was calculated as follows:

$$10 \quad q = \frac{1}{m} \left(\int_0^t Q \frac{C_{in} - C_{out}}{1 - C_{out}} dt \right) \frac{1}{T} \frac{T_0}{V_m} \quad (2)$$

11 where m is the weight of the virgin adsorbents (g) and Q is the flow rate of influent gas (mL/min).

12 C_{in} and C_{out} represent the influent and effluent CO₂ concentration (% vol/vol), respectively. T

13 represents the operating temperature, K. The molar volume of gas, V_m , is 22.4 L/mol at the

14 standard temperature of T_0 at 273 K.

1 The calculation of amine-grafting efficiencies for CO₂ capture (η , CO₂/N molar ratio)
2 recommended by Sculley and Zhou,⁴³ indicating that how many effective amino groups per total
3 weight of adsorbent are accessible to capture CO₂, was further evaluated.

$$4 \quad \eta = \frac{q_e}{C_N} \quad (3)$$

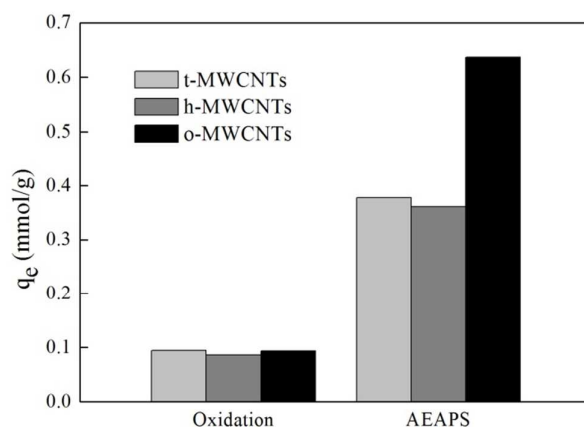
5 where q_e is the CO₂ equilibrium adsorption capacity (mmol/g). C_N is the N content in the
6 modified-MWCNTs (mmol/g) detected by elemental analysis.

7 **3. Results and discussion**

8 **3.1 CO₂ adsorption performance on modified-MWCNTs**

9 **Figure 2** shows the CO₂ equilibrium adsorption capacity of the modified-MWCNTs. It is observed
10 that pre-oxidative MWCNTs exhibited dramatic enhancements after AEAPS-grafting for each
11 pretreatment. It may be attributed to the sufficient effective amino groups on AEAPS-grafted
12 MWCNTs surface, which can capture more CO₂. The CO₂ adsorption capacity of
13 o-MWCNTs-AEAPS is 0.64 mmol/g, which is almost 7.1 times of that of o-MWCNTs, being 0.09
14 mmol/g. Besides, the capacities of t-MWCNTs-AEAPS and h-MWCNTs-AEAPS are 0.38 mmol/g
15 and 0.36 mmol/g, respectively, which are both significantly improved in comparison to those
16 without being AEAPS-grafted. However, it shows that O₂ oxidation exhibited beneficial to
17 AEAPS-grafting in comparison to thermal and HNO₃ pretreatment on the basis of the CO₂
18 adsorption capacities. Some literatures as well addressed the purification of MWCNTs by various
19 pretreatments for amine-grafting in order to improve the CO₂ adsorption. For example, Su *et al.*
20 reported an amine-modified MWCNTs pretreated by NaOH with the CO₂ adsorption capacity of

1 0.984 mmol/g at 20 °C for 15 vol% CO₂.⁴² Gui *et al.* employed H₂SO₄/HNO₃ (3:1 vol/vol) as the
2 pretreatment for amine-grafting of MWCNTs and the CO₂ uptake at 60 °C for 5 % CO₂ was 1.71
3 mg/g.³⁵ The relatively higher adsorption capacity was mainly attributed to the high level of treated
4 CO₂. However, few comparative studies of different pretreatments on AEAPS-grafting for
5 low-concentration CO₂ capture were investigated, especially of the advantage of O₂ oxidation.



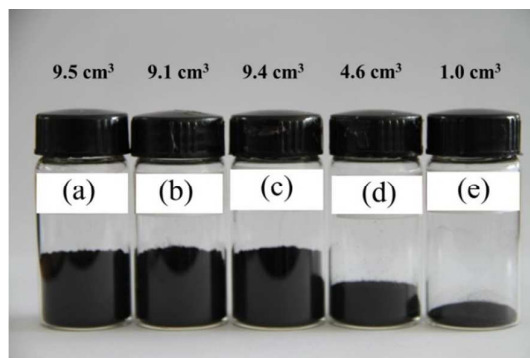
6
7 **Figure 2.** CO₂ adsorption capacity of the modified-MWCNTs at 25 °C with a C_{in} of 2 vol%

8 **3.2 Characterization of modified-MWCNTs**

9 **3.2.1 Direct observation of pretreated MWCNTs**

10 **Figure 3** shows the photo of the pretreated MWCNTs by different pretreatments at the weight of
11 0.5 g, where the variations of bulk volume are also presented. It is observed that the bulk volumes
12 of MWCNTs by thermal and O₂ treatments remained unchangeable in comparison with the
13 pristine MWCNTs. However, MWCNTs significantly shrank owing to acid treatment, especially
14 to mixed H₂SO₄/HNO₃ treatment. The severe agglomeration may be attributed to the enhanced
15 interaction with hydrogen bonds of carboxylic acids generated by acid treatment,⁴⁴ and it was
16 adverse to CO₂ diffusion and its corresponding adsorption capacity was low. Therefore, it is

1 obvious that the conventional acid pretreatment was not suitable for the amine-grafting for CO₂
2 adsorption.



3
4 **Figure 3.** Photo of the pretreated MWCNTs by different pretreatments: (a) pristine MWCNTs, (b)
5 t-MWCNTs, (c) o-MWCNTs, (d) h-MWCNTs, (e) m-MWCNTs

6 3.2.2 Textural properties and morphologies

7 **Textural properties:** The N₂ adsorption/desorption isotherms of the pretreated and
8 AEAPS-modified MWCNTs are shown in **Figure 4**. The described IV shape and H1 type of
9 hysteresis loop according to IUPAC classification indicate that all samples exhibit mesoporous
10 with cylindrical pores in spite of being pretreated and amine-grafted.³¹ The sharp increment of
11 adsorption isotherms at high P/P_0 and adsorption hysteresis loop may be caused by the capillary
12 condensation with mesoporous pores. In particular, o-MWCNTs has the highest N₂ adsorption
13 capacity among the pretreated MWCNTs, as shown in **Figure 4 (a)**, indicating that the highest
14 amounts of porosities appear after O₂ oxidation treatment. However, there are no significant
15 changes in the N₂ adsorption isotherms induced by thermal and HNO₃ pretreatments. The obtained
16 physical properties shown in **Table 1** can provide the detailed information of the variations.
17 Accordingly, the specific surface areas (S_{BET}) and pore volume (V_p) of o-MWCNTs are 151.8 m²/g
18 and 0.394 cm³/g, respectively, which are increased by almost 18.8% and 15.9% in comparison to

1 pristine MWCNTs. The S_{BET} and V_p of t-MWCNTs and h-MWCNTs show slight changes as
2 expected. High specific surface areas and pore volume would be beneficial to amine-grafting and
3 CO_2 transport for MWCNTs. It is observed in **Table 1** as well that amine-grafting leads to a drastic
4 decrease in the surface area in comparison to the pretreated precursor because of the introduction
5 of organic amines. The S_{BET} of t-MWCNTs-AEAPS, h-MWCNTs-AEAPS and
6 o-MWCNTs-AEAPS are $102.74 \text{ m}^2/\text{g}$, $66.22 \text{ m}^2/\text{g}$, and $67.05 \text{ m}^2/\text{g}$, respectively, which is almost
7 reduced by 19.1%, 47.6 %, and 55.8 %. The grafted amines are the main contributors to the partial
8 or complete blockage of the pores and result in the decrease of S_{BET} and V_p .³⁷ However, the S_{BET} of
9 the modified-MWCNTs was not in accordance with the obtained CO_2 adsorption capacity. The
10 S_{BET} of t-MWCNTs-AEAPS is relatively higher, indicating that the AEAPS loading may be lower.
11 The average pore diameters (APDs) all increased after amine-grafting due to the coverage of the
12 well-distributed and uniform AEAPS. The APDs of the t-MWCNTs-AEAPS, h-MWCNTs-AEAPS
13 and o-MWCNTs-AEAPS are 13.3 nm, 11.8 nm, and 11.1 nm, respectively, almost increased by
14 11.3 %, 5.9 %, and 6.63 %. Thermal treatment resulted in higher APD, because it only removed
15 some oxygen groups originally from pristine MWCNTs and subsequently AEAPS were mainly
16 grafted onto the dominated sidewalls of nanotubes. HNO_3 or O_2 oxidation can react on the end
17 caps as well as the sidewalls of nanotubes and more O-containing groups were generated.

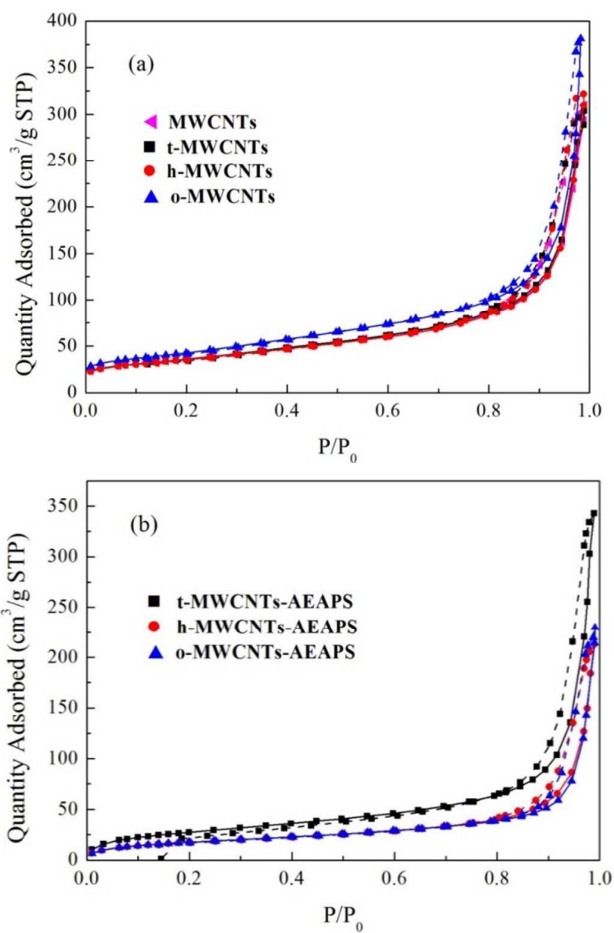
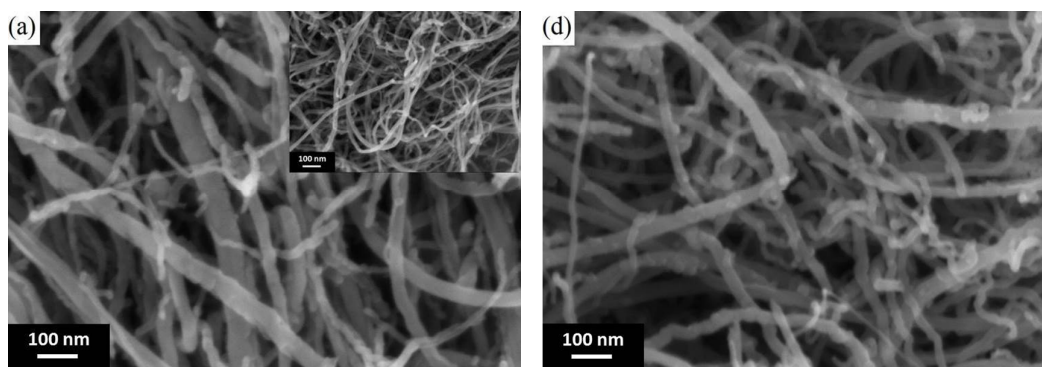


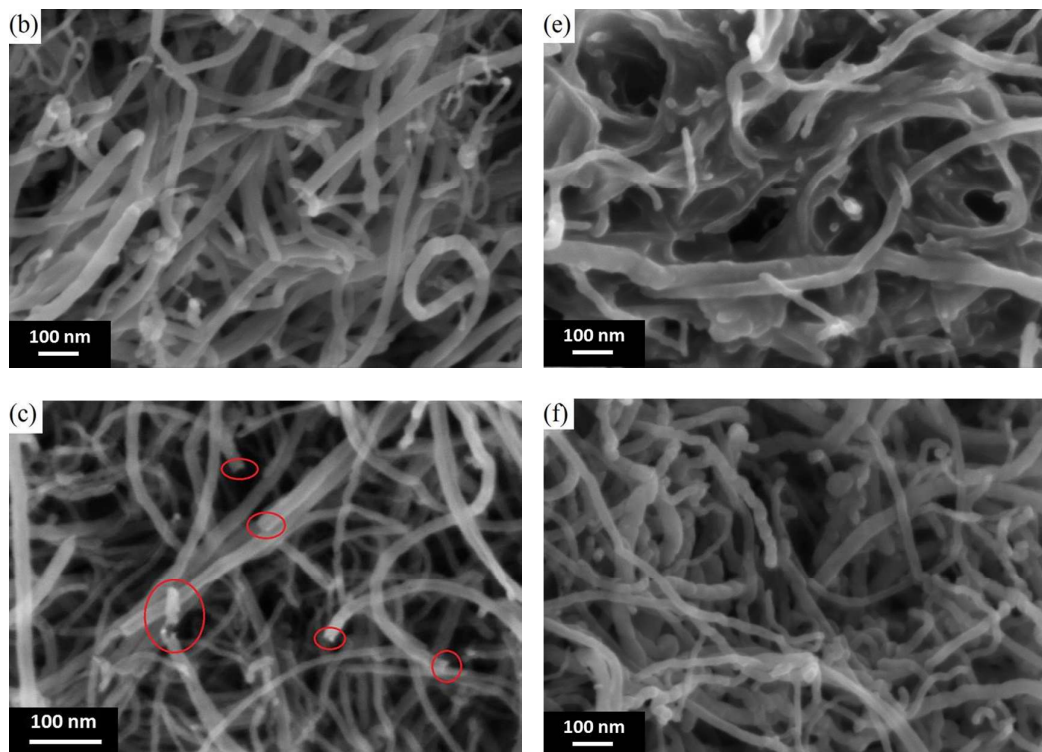
Figure 4. N₂ adsorption (solid line)/desorption (dash line) isotherms of the pretreated (a) and AEAPS-grafted MWCNTs (b)

Table 1. Textural and structural properties of the modified MWCNTs

Samples	S_{BET} (m ² /g)	V_{p} (cm ³ /g)	APD (nm)
MWCNTs	127.8	0.340	10.6
t-MWCNTs	126.9	0.379	11.9
h-MWCNTs	126.3	0.353	11.2
o-MWCNTs	151.8	0.394	10.4
t-MWCNTs-AEAPS	102.7	0.341	13.3
h-MWCNTs-AEAPS	66.2	0.196	11.8
o-MWCNTs-AEAPS	67.1	0.186	11.1

1 **Morphologies:** The morphologies of pretreated MWCNTs and corresponding AEAPS-grafted
2 MWCNTs are shown in **Figure 5**. There are no obvious changes between t-MWCNTs and pristine
3 MWCNTs, shown in **Figure 5 (a)** and its inset, respectively. The surfaces of h-MWCNTs and
4 o-MWCNTs appear clear, since most of the impurities were removed by HNO₃ or O₂ treatment.
5 Owing to the aggressive treatment of O₂ oxidation, the open and cut-off structures of MWCNTs
6 can be found more readily, which is highlighted by circles in **Figure 5 (c)**. With respect to the
7 corresponding AEAPS-grafted samples, it is observed that AEAPS was tethered onto the nanotube
8 surfaces successfully. The AEAPS loading on t-MWCNTs was relatively scattered and low, as
9 shown in **Figure 5 (d)**. The h-MWCNTs-AEAPS shown in **Figure 5 (e)** tends to serious
10 cross-linking. This fact may be related to the limitation of CO₂ diffusion to reach deep amino
11 groups inside the pores and possibly to a certain blocking of pore entrances. Herein, their obtained
12 CO₂ adsorption capacities were low. The nanotube density of o-MWCNTs-AEAPS showed large
13 due to the coverage of the well-distributed and uniform AEAPS, as shown in **Figure 5 (f)**. It
14 demonstrated that O₂ oxidation was suitable for the AEAPS grafting, and the obtained uniform
15 distribution of amine groups would be beneficial to capture more CO₂.



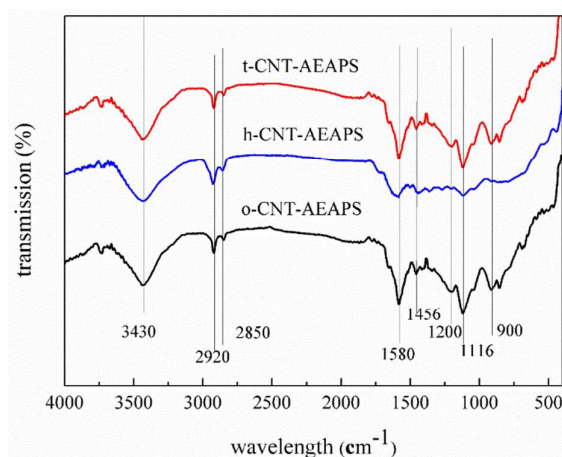


1 **Figure 5.** Morphologies of the modified MWCNTs: (a) t-MWCNTs, pristine MWCNT shown in
2 the inset of (a); (b) h-MWCNTs; (c) o-MWCNTs; (d) t-MWCNTs-AEAPS; (e)
3 h-MWCNTs-AEAPS; (f) o-MWCNTs-AEAPS.

4 3.2.3 Composition analysis

5 The functional groups on the AEAPS-grafted MWCNTs were characterized by FT-IR analysis,
6 and the spectra is shown in **Figure 6**. It is observed that the characteristic bands for the
7 AEAPS-grafted MWCNTs show no significant differences. The band at 1580 cm^{-1} assigns to the
8 typical stretching vibration of C=C bonds in MWCNTs, and the band at 1200 cm^{-1} is associated
9 with the scissoring vibration of C-C bond and stretching vibration of C-O bond.⁴⁵ The broad band
10 of 3440 cm^{-1} results from the presence of free and associated hydroxyl groups due to intercalated
11 water and structural hydroxyl groups (-COOH and -COH). The occurrence of 2920 cm^{-1} and 2850
12 cm^{-1} bands is verified the presence of C-H bond from alkyl and alkoxy groups in aminosilane. In

1 particular, the band of 1116 cm^{-1} assigns to the asymmetric stretching vibration of Si-O-R bond,
2 accompanying with the bending vibration of Si-C and Si-OH bonds. The weak band at 1456 cm^{-1}
3 is contributed to the bending vibration of N-H bond in aminosilane.⁴⁶ Herein, it demonstrates that
4 aminosilane has been successfully grafted onto the pretreated MWCNTs induced by the silylation
5 reactions.



6

7

Figure 6. FT-IR spectra of the AEAPS-grafted MWCNTs

8 The quantitative results of the obtained samples by XPS analysis are presented in **Table 2**. The
9 highest O content of 7.8 % was achieved by HNO_3 pretreatment. The elements of Si and N
10 appeared on all samples, indicating that AEAPS was successfully grafted onto the pretreated
11 MWCNTs. The N contents of t-MWCNTs-AEAPS, h-MWCNTs-AEAPS, and
12 o-MWCNTs-AEAPS are 6.15 %, 8.33 % and 7.28 %, respectively. However, high N content is not
13 as a linear function with high CO_2 adsorption capacity. It is because that CO_2 adsorption capacity
14 is dependent on the effective amine groups, especially on the primary amine groups.³⁰ The
15 amine-grafting for o-MWCNTs-AEAPS is more effective on the basis of the obtained
16 performance of CO_2 adsorption is higher than the others.

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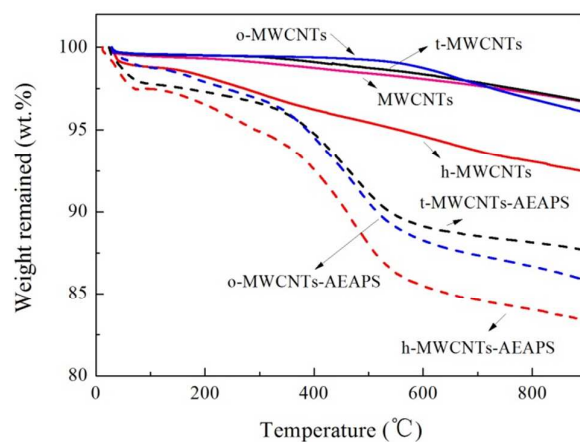
Table 2. The surface atomic percentages of pretreated and amine-modified MWCNTs

Samples	C 1s	O 1s	N 1s	Si
MWCNTs	95.13	4.23	0.64	/
t-MWCNTs	97.26	2.74	/	/
h-MWCNTs	91.74	7.8	0.46	/
o-MWCNTs	97.26	2.74	/	/
t-MWCNTs-AEAPS	80.59	9.43	6.15	3.84
h-MWCNTs-AEAPS	72.09	14.42	8.33	5.16
o-MWCNTs-AEAPS	76.63	11.42	7.28	4.67

7

8 The TG curves of the pretreated and AEAPS-grafted MWCNTs are shown in **Figure 7**. It is
9 observed that the weight loss from room temperature to ~ 110 °C for all samples, which is mainly
10 contributed to the evaporation of adsorbed water, is less than 2 %. The h-MWCNTs shows the
11 highest percentage of the total weight loss among three pretreated samples, indicating that the
12 amount of O-containing groups introduced by HNO₃ treatment is the highest. The weight of
13 pristine MWCNTs gradually lost during the whole heating process, verifying that some of
14 O-containing groups existed on the surface.^{36, 37} The differences between thermal stability on the

1 decomposition temperature can provide some qualitative information about O-containing
2 functional groups.^{37,47} For example, carboxylic acids groups can be selectively removed through
3 thermal treatment at 300 °C. The weight loss of o-MWCNTs at high temperature is mainly
4 attributed to the decomposition of phenols and carbonyl/quinone groups as well as lactones. With
5 respect to AEAPS-grafted samples, the highest weight loss was obtained by h-MWCNTs-AEAPS,
6 corroborating the result that its AEAPS loading was high. High silylation reaction yield may be
7 attributed to high amount of O-containing groups in the pretreated MWCNTs.



8
9 **Figure 7.** Thermogravimetric curves of the pretreated and AEAPS-grafted MWCNTs

10 The types and contents of the O-containing functional groups on the pretreated MWCNTs can be
11 quantified on the basis of the decomposition temperature and the corresponding differential weight
12 loss in a simplified manner recommended by some scientific researchers.^{37, 41} The typical
13 functional groups including carboxylic acids, phenols and carbonyls/quinones are in accordance
14 with the decomposition temperature of 200~450 °C, 600~750 °C, and 700~950 °C, respectively.³⁷
15 The contributions of other groups such as carboxylic anhydrides and lactones were relatively low
16 and can be omitted. Here we assumed that the weight loss between 700 °C and 750 °C for phenols

1 and carbonyls/quinones was equal. The types and contents of O-containing groups in the pretreated
 2 MWCNTs are summarized in **Table 3**. The total contents of O-containing groups in t-MWCNTs,
 3 h-MWCNTs, and o-MWCNTs are 2.6 %, 5.0 % and 3.3 %, respectively. As for HNO₃
 4 pretreatment, the content of carboxylic acids is 2.4 %, which possesses the percentage of 48 %
 5 among the O-containing groups. However, no carboxylic acids existed in o-MWCNTs because O₂
 6 pretreatment was conducted at 500 °C, and the phenols and carbonyls/quinones groups were
 7 dominated. Herein, it demonstrates that the high obtained N loading was attributed to the high
 8 content of carboxylic acids, and the absence of carboxylic acids in o-MWCNTs was the root of the
 9 effective AEAPS-grafting which would obtain high CO₂ adsorption capacity for
 10 o-MWCNTs-AEAPS. The possible reasons would be clarified in the following section.

11 **Table 3.** The types and contents of O-containing groups in the pretreated MWCNTs

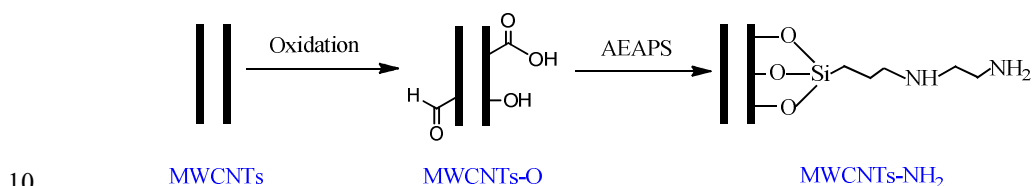
Samples	Functional groups	Decomposition temperature	Δ%
t-MWCNTs	carboxylic acids	200 °C ~450 °C	0.6
	phenols	600 °C ~750 °C	0.8
	carbonyls/quinones	700 °C ~950 °C	1.2
	total		2.6
h-MWCNTs	carboxylic acids	200 °C ~450 °C	2.4
	phenols	600 °C ~750 °C	1.3
	carbonyls/quinones	700 °C ~950 °C	1.3
	total		5.0
o-MWCNTs	phenols	600 °C ~750 °C	1.5
	carbonyls/quinones	700 °C ~950 °C	1.8
	total		3.3

12

1 3.3 Understanding the amine-grafting reaction on MWCNTs for CO₂ capture

2 3.3.1 Amine-grafting reaction

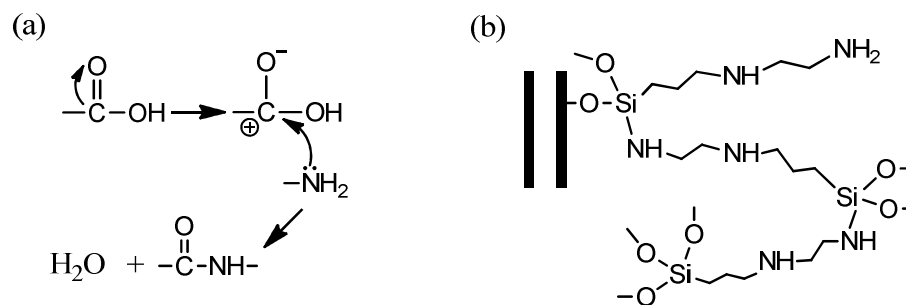
3 The AEAPS-grafting reaction with pretreated MWCNTs is illustrated in **Figure 8**. Priority is given
 4 to retain primary amine groups for CO₂ capture rather than be consumed during the amine grafting.
 5 Herein, the alkoxy groups in the AEAPS can react with O-containing groups on the pretreated
 6 MWCNTs by the silylation reaction, where there are no influences on the amine groups in the
 7 compounds. Therefore, aminosilane is the proper amino compound of the amine grafting for CO₂
 8 adsorption other than an aliphatic amine. The grafted primary amino groups can be accessible to
 9 capture the maximum amount of CO₂.



11 **Figure 8.** Schematic diagrams of the AEAPS-grafting reaction with pretreated MWCNTs

12 The primary amino groups can react with CO₂ at a 1:1 mole ratio and exhibit a higher capacity.⁴⁸
 13 Herein, the low CO₂ adsorption capacities for t-MWCNTs-AEAPS and h-MWCNTs-AEAPS are
 14 mainly attributed to the consumption of primary amino groups by possible side reactions including
 15 the NH₂-silicon polymerization and amide reaction of amines, as illustrated in **Figure 9**. AEAPS is
 16 a kind of bifunctional organosilane and the N of -NH₂ group is a nucleophilic atom. The oxygen of
 17 carboxylic acids generated by acid oxidation shows strong electron withdrawing properties, and it
 18 would make the carbon connect to the oxygen display δ⁺ and promote the nucleophilic attack of
 19 NH₂ groups, as shown in **Figure 9 (a)**. Besides, the solvent of toluene is a good water-carry agent,

1 which as well may promote the amide reaction. **Figure 9 (b)** shows the direct attack of
 2 nucleophilic amino groups on the silicon center in the presence of acidic carboxylic acids, where
 3 the methoxyl group acted as a leaving group under acid-catalyzed condition. The polymerization
 4 caused by the excessive AEAPS-grafting on the MWCNTs surface would block the pore and limit
 5 the CO₂ diffusion into the internal pores.³⁴ Although the highest loading of amino groups was
 6 anchored to the pretreated MWCNTs by HNO₃ pretreatment, some NH₂ groups were hindered and
 7 not be free to act as adsorption active sites for CO₂. Herein, the obtained adsorption capacity was
 8 low.



9
 10 **Figure 9.** Possible side reactions of AEAPS-grafting in the presence of carboxylic acids: (a) amide
 11 reaction and (b) NH₂-silicon polymerization

12 3.3.2 Amine-grafting efficiency for CO₂ capture

13 **Table 4** provides the amine efficiencies of CO₂ capture (η , CO₂/N, mol/mol) for AEAPS-grafted
 14 MWCNTs, where some reported results of other amine-modified adsorbents are listed for
 15 comparison. It is observed that the amine efficiency (CO₂/N) of h-MWCNTs-AEAPS is 0.13
 16 mol/mol, being only 54.2% of o-MWCNTs-AEAPS although the N content is high. The low
 17 amine efficiency is contributed to the reduction of primary amino groups by the side reactions.
 18 The N contents of the AEAPS-grafted adsorbents detected by elemental analysis range from 1.81

1 to 2.77 mmol/g, which are much lower than those of other adsorbents by PEI-impregnation and
2 tri-grafting samples. However, the amine efficiencies for low-concentration CO₂ capture are close.
3 The adsorption capacity for high-concentration CO₂ at 15 vol% is 1.31 mmol/g and the
4 corresponding η is 0.49, which is close to the theoretical maximum value of 0.5. It is observed that
5 the obtained amine efficiency is much higher than those of other adsorbents listed here. The
6 well-distributed amino groups on the support surface by chemically grafting methods are
7 beneficial to promote the amine efficiency of CO₂ adsorption in comparison to impregnation.

Table 4. Summary of amine-grafted MWCNTs adsorbents on the CO₂ adsorption performance

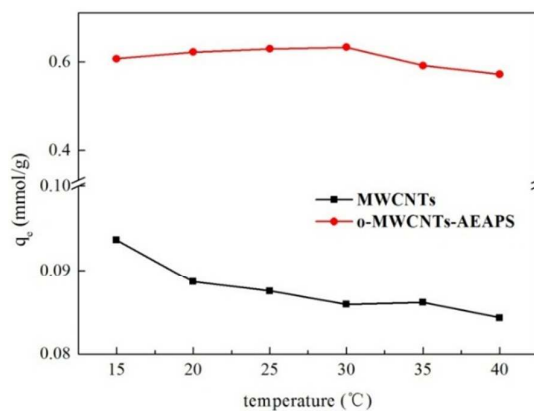
Support materials	Amine type	Methods	C_N (mmol/g)	Adsorption capacity		Operating conditions		CO ₂ / N mol/mol	References
				mg/g	mmol/g	C_{in}	T		
t-MWCNTs			1.81	0.38		2 %			
h-MWCNTs	AEAPS	Grafting	2.77	0.36	2 %	25 °C	0.13	This work	
o-MWCNTs			2.66	0.64	2 %		0.24		
o-MWCNTs			2.67	1.31	15 %		0.49		
MCM-41			Anhydrous-grafting	5.75*	1.04				0.181
PE-MCM-41	tri	Anhydrous-grafting	6.10*	1.55	5 %	25 °C	0.254	Harlick et al. ³	
PE-MCM-41		Water-aided-grafting	7.98*	2.65			0.332		
HMS-C	45% PEI	Impregnation	10.19*	94	2.14*	100 %	75 °C	0.21	Chen et al. ⁴⁹
	70% PEI		16.33*	108	2.45*			0.15	
HMS-T90	60% PEI		13.93*	184	4.18*			0.3	
	70% PEI		16.30*	165	3.75*			0.23	
SBA-15	30% TEPA+20%DEA	Impregnation			100%	75 °C	0.4	Yue et al. ⁵⁰	

C_{in} , the influent concentration of CO₂; tri: aminoethylaminoethylaminopropyltrimethoxysilane; PEI: polyethyleneimine; *, calculated values

1 3.4 Optimization of CO₂ capture on AEAPS-grafted MWCNTs

2 3.4.1 Effects of operating temperature

3 The effect of operating temperature on CO₂ adsorption is shown in **Figure 10**. It is observed that
4 the CO₂ adsorption capacities of o-MWCNTs-AEAPS maintained the high level in spite of the
5 increasing of operating temperature. The adsorption capacity showed a modest increase from 0.61
6 to mmol/g 0.64 mmol/g from 15 °C to 30 °C. It is because that the elevated temperature promoted
7 the reaction between CO₂ and amino groups and improved the CO₂ diffusion into the internal pore
8 of adsorbent. The slight decrease occurred when the temperature increased to 40 °C, implying the
9 exothermic nature of the chemisorption adsorption process. The adsorption capacities of pristine
10 MWCNTs with the increasing of operating temperature were also presented for comparison. The
11 gradually decreasing capacities reveals that the physisorption may be dominant.²⁸ Therefore, the
12 comfortable temperature of 17-25 °C in confined space is suitable for the applications. Since the
13 room temperature in confined space was usually set at 25 °C, it was chose for the following
14 adsorption experiment.

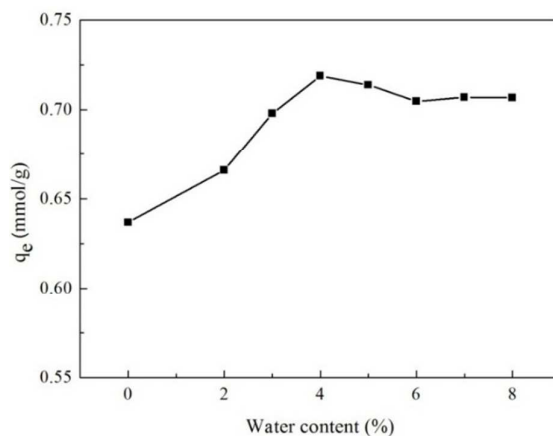


15

16 **Figure 10.** Effect of operating temperature on CO₂ adsorption17 (C₀=2 vol%, Q=50mL/min, dry gas mixture)

1 3.4.2 Effects of moisture in influent gas stream

2 The humidity in confined space is high, since several persons live or stay in the very limited space
3 for long time. Not only water vapor but also water fog existed in atmosphere. Therefore, the
4 effects of high water content on CO₂ adsorption process shall be investigated in confined space.
5 The study on the competitive adsorption of H₂O and CO₂ can be investigated. Moisture in gas
6 mixture plays an important role in CO₂ adsorption. The adsorption was hindered in humid
7 conditions for many hydrophilic adsorbents. **Figure 11** depicts the CO₂ adsorption capacities for
8 o-MWCNTs-AEAPS under different water content in gas streams at 25 °C. The capacity
9 remarkably improved to 0.72 mmol/g with the increase at the water content to 4 vol %, which is
10 almost 13 % higher than that in dry gas. However the capacity slightly decreased to 0.71 mmol/g
11 at 7 vol % water content, which may be caused by the competitive adsorption of H₂O and CO₂
12 with the adsorption sites. With the further increase in water content, the capacity remained stable.
13 It demonstrates that MWCNTs exhibited the high tolerance to moisture compared with
14 silica-based adsorbents.^{22, 33-35} Since the dissolved CO₂ in the surface adsorbed water is
15 inconspicuous, the promoting effects were attributed to the formation of bicarbonate ions (HCO₃⁻)
16 in a direct or indirect way where amino groups reacted with CO₂ at the mole ratio of 1:1 with the
17 assistance of H₂O.³² On the contrary, two molecular amino groups were required for bonding a
18 molecular CO₂ in anhydrous conditions. Therefore, the promoted amine efficiency of CO₂
19 adsorption resulted in high capacity.



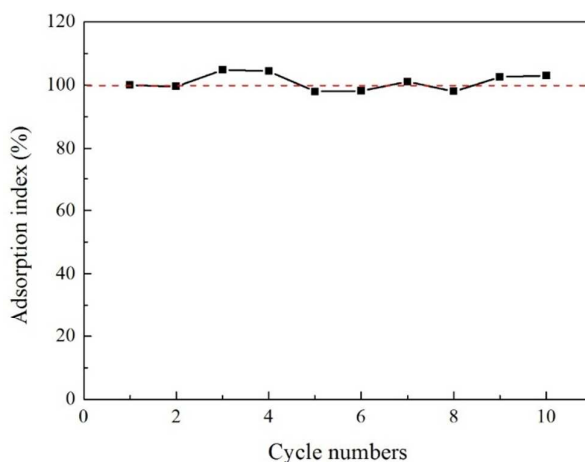
1
2 **Figure 11.** Effect of water content on CO₂ adsorption for o-MWCNTs-AEAPS

3 (C₀=2 vol%, T=25 °C, Q=50mL/min)

4 **3.4.3 Adsorption performance of repeated availability**

5 The sustained excellent adsorption performance of adsorbents on multi-run adsorption/desorption
6 operations was valuable for practical applications. The adsorption index was calculated on the
7 ratio of the obtained adsorption capacity to the first-run one. **Figure 12** shows the variation of
8 adsorption performance on the basis of the adsorption index for 10 repeated cycles. It is observed
9 that the adsorption performance showed a little fluctuation with the original capacity and no
10 significant reduction was obtained. It indicates that the adsorption capacity of the adsorbent can be
11 readily recovered. The desorption process is high in efficiency where the operation was conducted
12 at 75 °C with the vacuum of 5 kPa for 5min. It was addressed that the regeneration temperature of
13 the common solid amine sorbents was typically from 50 to 100 °C.⁴⁸ The relatively low
14 temperature in the present work indicates the low required energy cost. Similarly, Su and
15 coworker conducted the desorption process on the APTS-grafted CNTs adsorbent at 120 °C with
16 the vacuum of 0.145 atm (14.7 kPa) and the regeneration time of 5 min was consumed.⁴² Although

1 similar time was spent, the lower temperature was applied and one third of vacuum value were
2 required. It is estimated that half of the total energy cost can be saved. The adsorbent exhibited
3 high thermal stability and low regeneration cost, and it is promising for direct CO₂ capture
4 especially on low concentration.



5

6 **Figure 12.** Adsorption performance for 10 repeated cycles

7

(C₀=2 vol%, T=25 °C, Q=50mL/min)

8 **4. Conclusion**

9 The effects of types and contents of O-containing groups on MWCNTs induced by different
10 pretreatments were investigated. The alkoxy groups of AEAPS can react with O-containing
11 groups on the pretreated MWCNTs through the silylation reaction, and the obtained adsorbents
12 were employed for CO₂ removal in confined space at ambient temperature. High silylation
13 efficiency can obtain high amine loading due to the high contents of O-containing groups on the
14 pretreated MWCNTs, and however it was not in proportion to high CO₂ adsorption capacity. The
15 presence of carboxylic acids generated by HNO₃ treatment resulted in the occurrence of side
16 reactions including the amide reaction and NH₂-silicon polymerization, which consumed the

1 primary amine groups and resulted in low capacity. The O₂ pretreated MWCNTs adsorbents with
2 the AEAPS-grafting showed high CO₂ adsorption capacity of 0.64 mmol/g, which is almost 7.1
3 times of that of o-MWCNTs. The amine-grafting efficiencies at 2 vol% and 15 vol % are 0.24 mol
4 CO₂/ mol N and 0.49 mol CO₂/ mol N, respectively, of which the latter one is close to the
5 theoretical maximum value of 0.5. The capacity maintained the high level in spite of the operating
6 temperature up to 40 °C. The adsorbent of adsorption capacity can be readily recovered and no
7 significant reduction was observed after 10 repeated adsorption/desorption operations. The lower
8 desorption temperature was applied and one third of vacuum value were required, which would
9 significantly reduce the energy cost. Therefore, it indicates that O₂ gas oxidation is easy in
10 operation and high in efficiency for the pretreatment of MWCNTs and the subsequent grafting
11 with aminosilane was employed. The obtained adsorbent with high capacity, high thermal stability,
12 high tolerance to moisture and low regeneration cost is promising for direct CO₂ capture in
13 confined space.

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