Supporting Information for:

Steam Stable Covalently-Bonded Polyethyleneimine Modified Multiwall Carbon Nanotubes for Carbon Dioxide Capture

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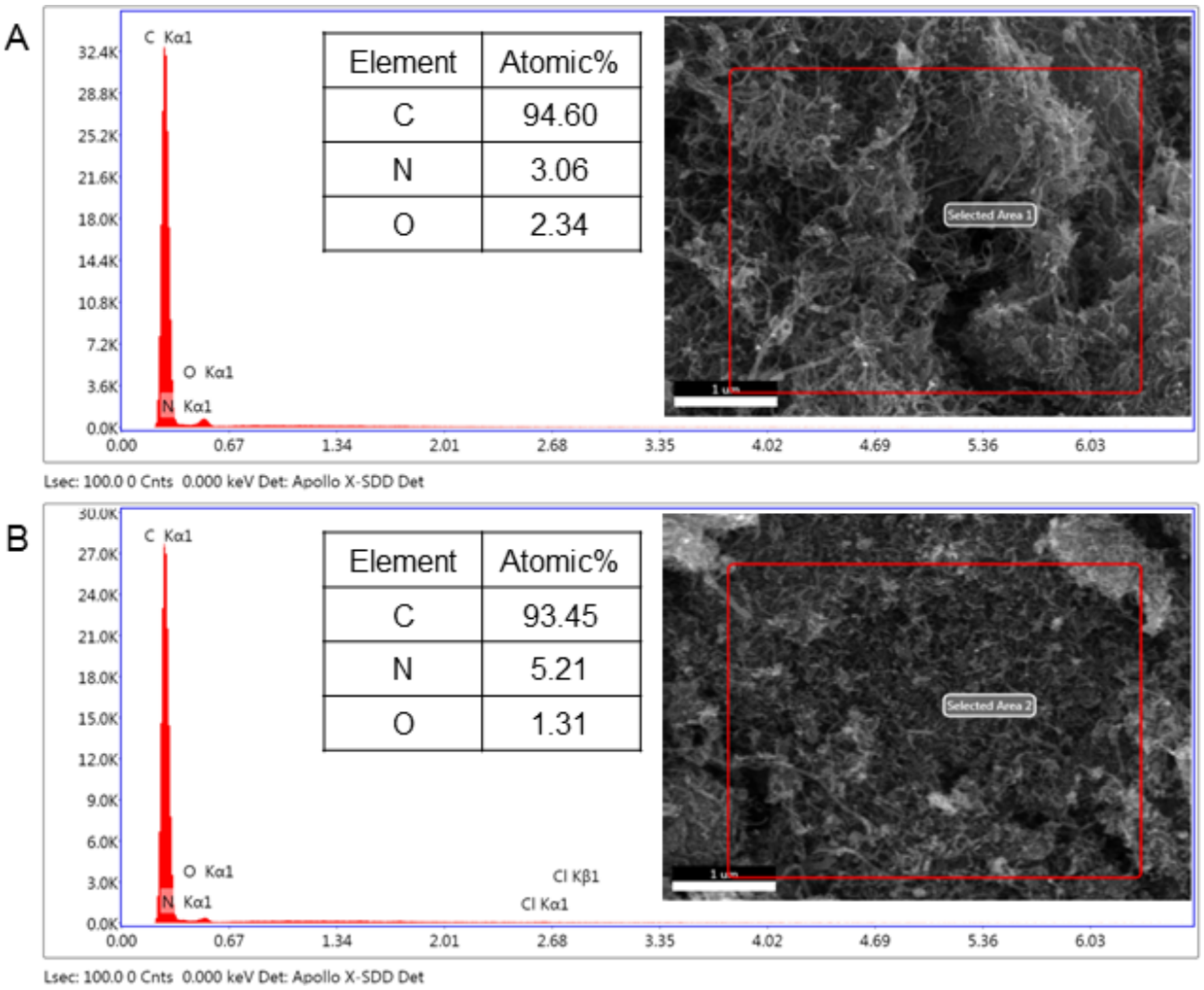


Figure S1. SEM image with EDX of A) o-CNT and B) CNT-PEI

Table S1. Functional group loading of CNT with various oxidative treatments

Entry	Treatment	Time (h)	Functional group (wt%)
1	As received	0	1.27
2a	16 M HNO_3 18 M H_2SO_4 (3:1)	3	2.44
2b	16 M HNO_3 18 M H_2SO_4 (3:1)	16	2.46
3a	16 M HNO_3	3	1.85
3b	16 M HNO_3	16	4.66
3c	16 M HNO_3	24	6.5
3d	16 M HNO_3 (low temperature)	24	5.28
4	3M HNO_3	24	2.29

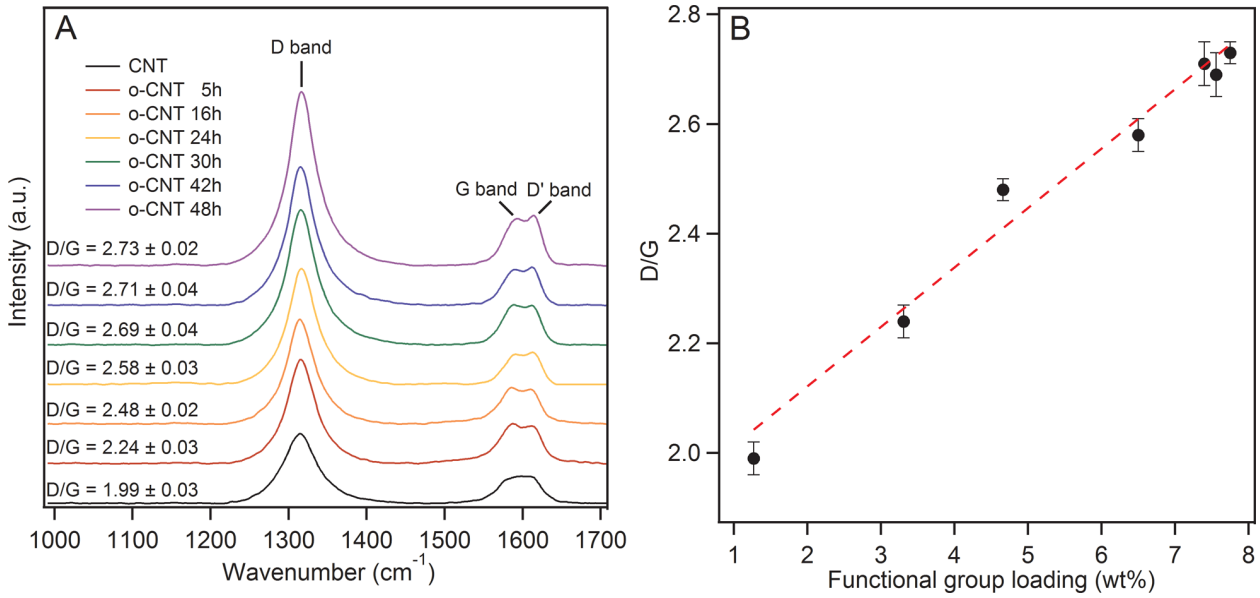


Figure S2. A) Raman spectra and D/G ratios of CNT and o-CNT with various treatment times B) D/G ratios of CNT and o-CNT in relation to functional group loading

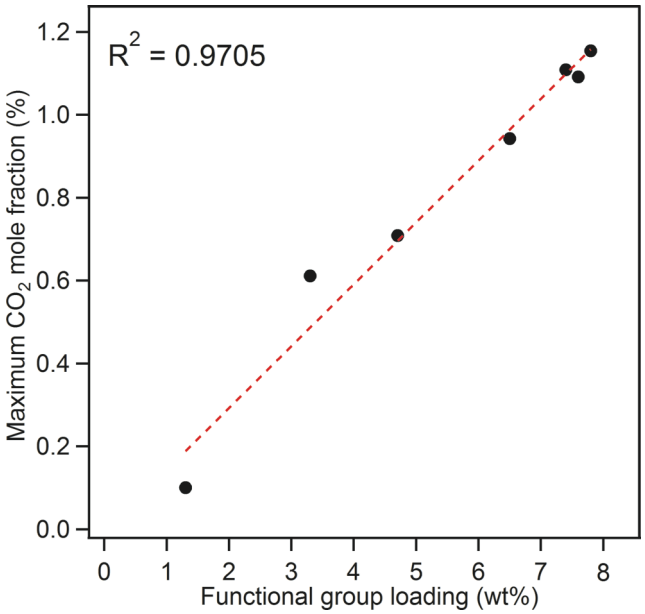


Figure S3. The correlation of carboxylic acid group and functional group loading

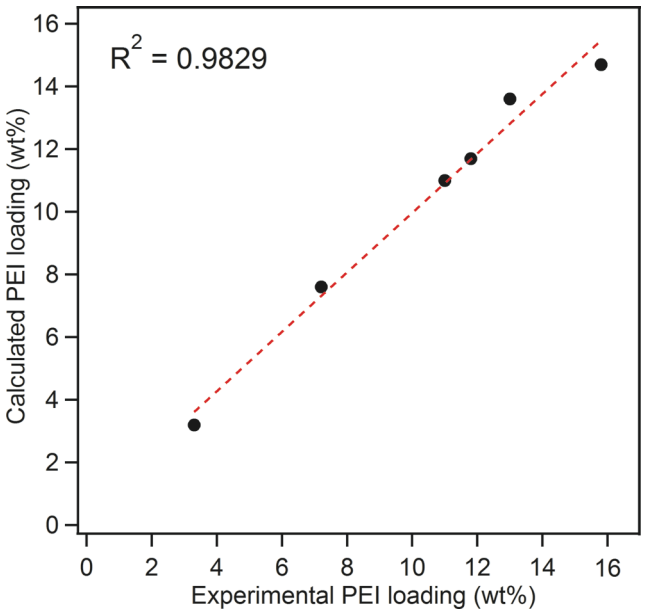


Figure S4. The relationship between calculated and experimental PEI loading

Table S2. Statistical details of modal simulation from Rstudio

Summary (ln(BPEI) = β_0 + β_1*Func + β_2*SA)

Coefficients:	Estimate	Std.Error	t value	Pr(>|t|)
(Intercept, β_0)	-0.073499	0.154134	-0.48	6.66E-01
Func, β_1	0.10292	0.014777	6.97	6.07E-03 **
SA, β_2	0.012208	0.001346	9.07	2.83E-03 **
Signif. codes:	0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1			
Residual standard error:	0.06233 on 3 degrees of freedom			
Multiple R-squared:	0.9928	Adjusted R-squared:	0.988	
F-statistic:	206.6 on 2 and 3 DF	p-value:	6.12E-04	

A multiple linear regression model was built to investigate the significant factors (PEI loading, surface area, pore volume and pore size) on the PEI loading. We built two full models and 20 reduced models to study the relationship between BPEI loading or logarithm of BPEI and all the factors mentioned above. In the model, we use lPEI, FG, SA, PV and PS to describe logPEI, functional group, surface area, pore volume and pore size. The factors are in Table S3 below.

Table S2.A The statistics model of the effect of functional group, surface area, pore volume and pore size on the covalent PEI loading of CNT

Entry	Model	p-value	R^2	FG (p-value)	SA (p-value)	PV (p-value)	PS (p-value)
Full model_1	PEI ~ FG + SA + PV + PS	0.0376	0.999	0.0448*	0.0787	0.0936	0.0713
Red model_10	PEI ~ FG + SA + PV	0.0745	0.950	0.1950	0.8120	0.3840	NA
Red model_11	PEI ~ FG + SA + PS	0.0437	0.971	0.1026	0.0932	NA	0.2009
Red model_12	PEI ~ FG + PV + PS	0.0614	0.959	0.1340	NA	0.1340	0.5450
Red model_13	PEI ~ SA + PV +PS	0.1845	0.873	NA	0.5190	0.6060	0.6670
Red model_14	PEI ~ FG + SA	0.0231	0.919	0.1107	0.0991	NA	NA
Red model_15	PEI ~ FG + PV	0.0119	0.948	0.0060**	NA	0.0501	NA
Red model_16	PEI ~ FG + PS	0.0670	0.835	0.1240	NA	NA	0.3500
Red model_17	PEI ~ SA + PV	0.0541	0.857	NA	0.0277*	0.3012	NA
Red model_18	PEI ~ SA + PS	0.0584	0.849	NA	0.1060	NA	0.3330
Red model_19	PEI ~ PV + PS	0.0674	0.835	NA	NA	0.1242	0.0347*
Full model_2	lPEI ~ FG + SA + PV + PS	0.0206	1.000	0.0522	0.0771	0.1173	0.1062
Red model_20	lPEI ~ FG + SA + PV	0.0102	0.993	0.1240	0.1700	0.7730	NA
Red model_21	lPEI ~ FG + SA + PS	0.0084	0.994	0.0907	0.0142	NA	0.5301
Red model_22	lPEI ~ FG + PV + PS	0.0193	0.987	0.1760	NA	0.0330*	0.3580
Red model_23	lPEI ~ SA + PV +PS	0.0418	0.972	NA	0.4510	0.6340	0.7950
Red model_24	lPEI ~ FG + SA	0.0006	0.993	0.0061**	0.0028**	NA	NA
Red model_25	lPEI ~ FG + PV	0.0033	0.978	0.0016**	NA	0.0154*	NA

Red model_26	lPEI ~ FG + PS	0.0888	0.801	0.2930	NA	NA	0.7860
Red model_27	lPEI ~ SA + PV	0.0050	0.971	NA	0.0025*	0.0529	NA
Red model_28	lPEI ~ SA + PS	0.0058	0.968	NA	0.0151*	NA	0.0622
Red model_29	lPEI ~ PV + PS	0.0081	0.960	NA	NA	0.0210*	0.0040**
Red model_30	lPEI ~ FG	0.0170	0.795	0.0170*	NA	NA	NA
Red model_31	PEI ~ FG	0.0220	0.768	0.022*	NA	NA	NA

*significant, **very significant

Since the mechanism (Scheme 1) showed PEI is covalently bonded to COOH groups on CNT, the functional group loading (FG) has to be included in the model. All models without FG factors are removed from the Table 1 (all red lines). Secondly, the FG factor should have significant effect on the PEI loading, which means the p-value of FG should be less than 0.05; all FG p-value higher than 0.05 are removed (all blue lines). All remaining factors in the model must be significant; therefore any model with an insignificant p-value factor is removed (green line). Finally, the experimental data should be well described by the model. Therefore, any model with relatively low R squared value (R^2) were removed (purple lines). The updated table is as follows:

Table S2.B Final possible regression models from Table S2.A

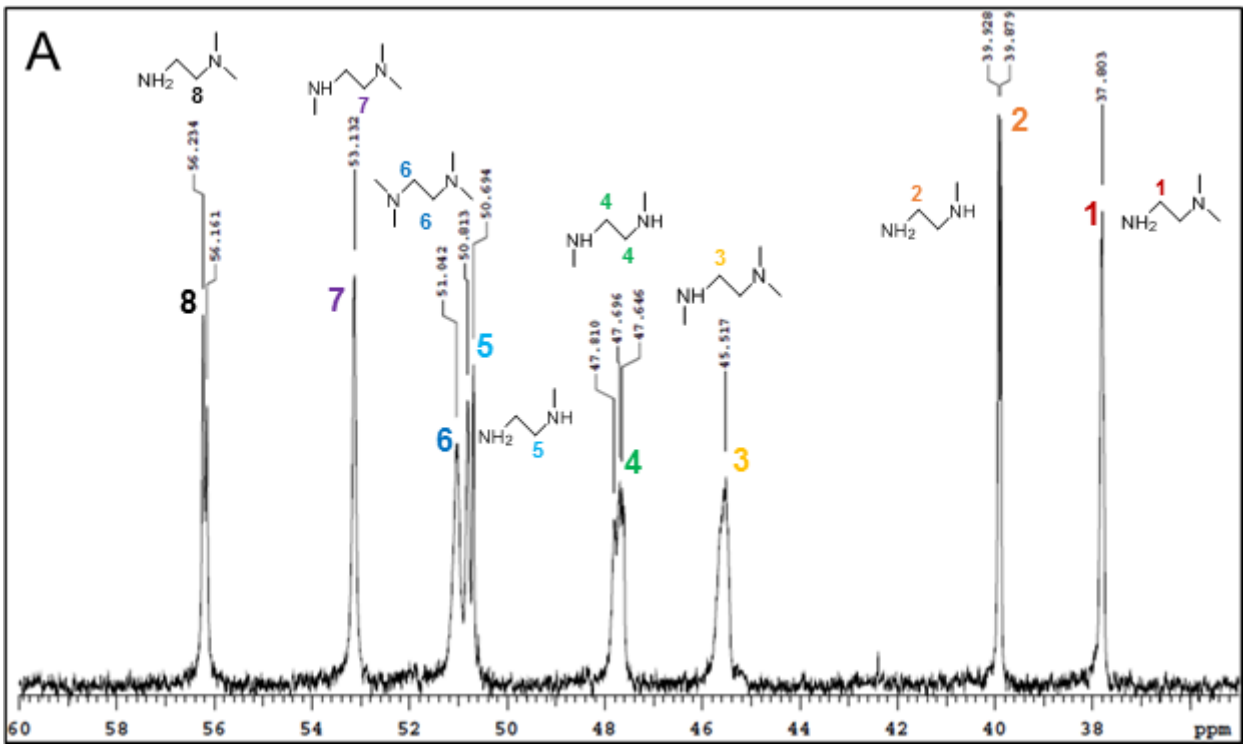
Entry	Model	P-value	R^2	FG	SA	PV	PS
Red model_24	lPEI ~ FG + SA	0.0006	0.993	0.0061**	0.0028**	NA	NA
Red model_25	lPEI ~ FG + PV	0.0033	0.978	0.0016**	NA	0.0154*	NA

*significant, **very significant

The resulting table showed only two models (Red model_24 and Red model_25) left. Besides FG, both SA and PV have a significant effect on the optimal covalent PEI loading. However, the effect of SA (**) was more significant compared to PV (*). Moreover, model_24 could better describe the experimental data compared to model_25 according to their R^2 values. In other research by Barron et. al, (ref.33) it was established that a large surface area is good for covalent attachment of organic molecules. Considering these three reasons, we proposed that SA and FG are the two major factors affecting the optimal covalent PEI loading on acid-treated CNT.

Table S3. The effect of PEI concentration on PEI loading of o-CNT

	PEI : o-CNT	0.25	1	2	3
PEI loading	No $SOCl_2$	3.1	3.29	2.81	2.51
	$SOCl_2$	13.95	15.81	15.90	13.04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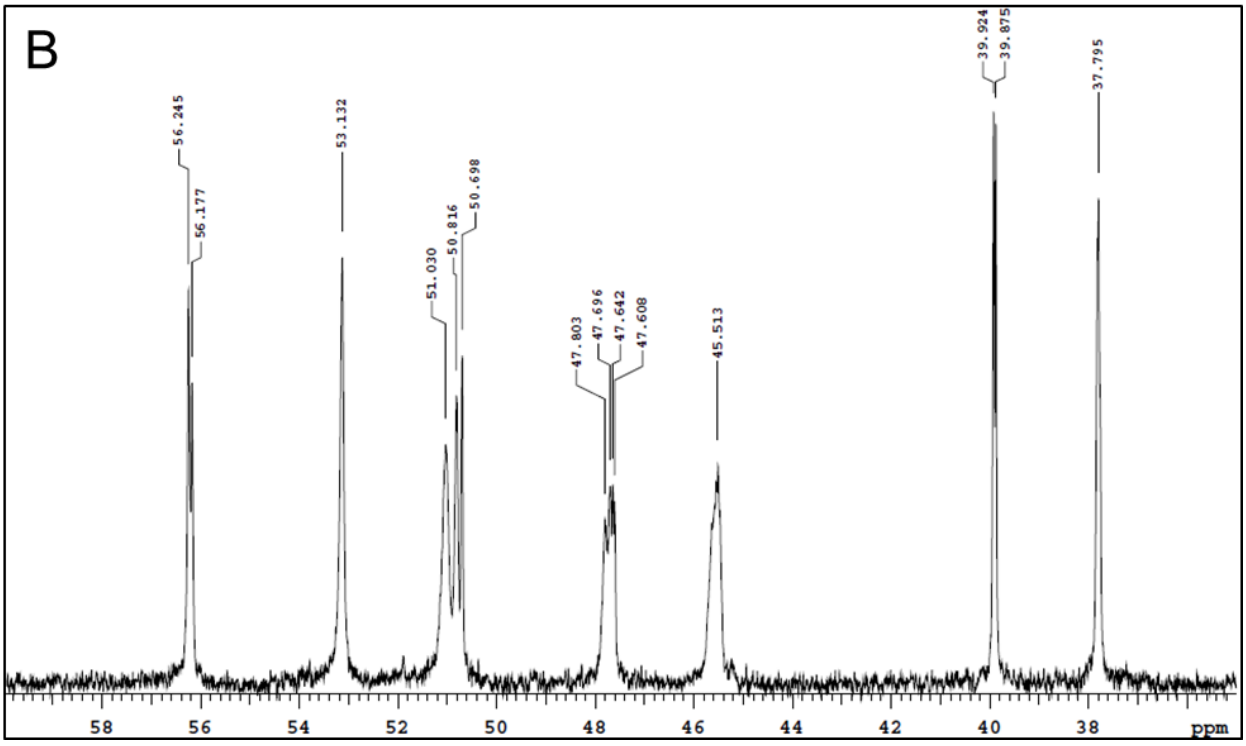
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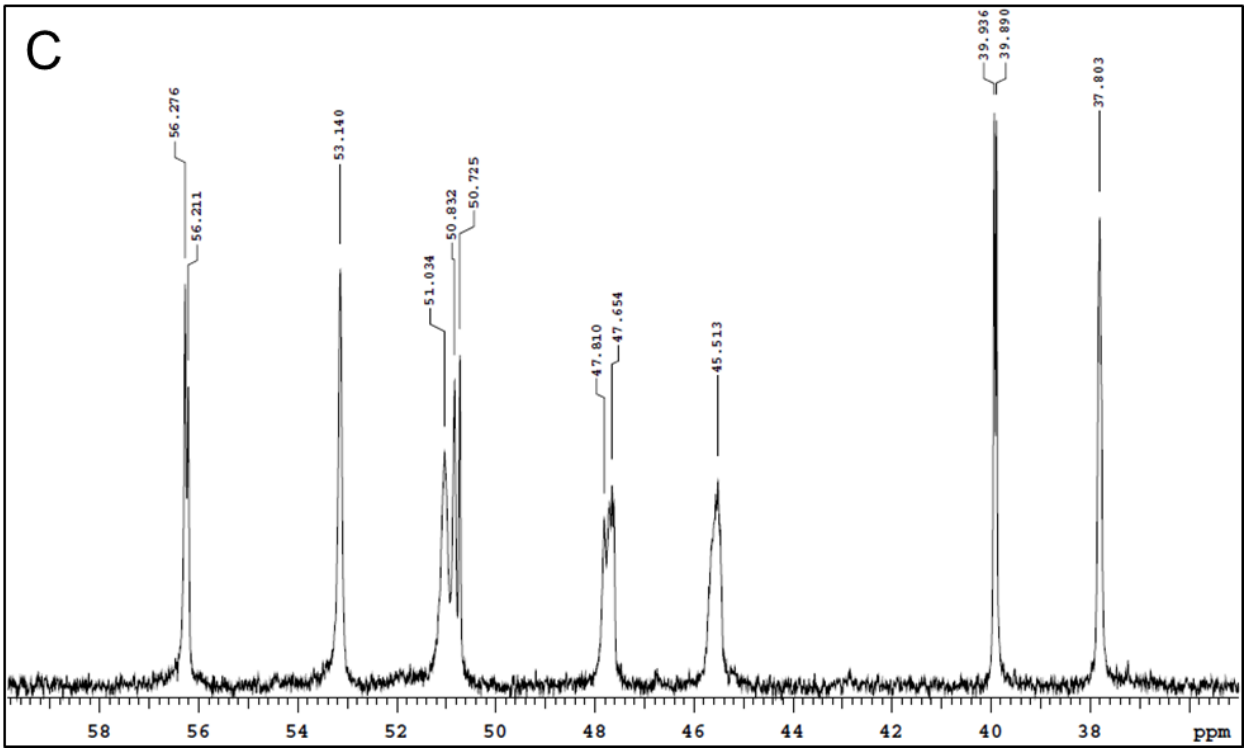

Figure S5. ^{13}C-NMR of PEI A) standard, B) treated with N_2 and C) treated with steam and N_2 at 120 °C for 24 h

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Table S4. Surface area and pore volume of CNT-PEI and CNT/PEI before and after (in parenthesis) steam treatment of the sorbents

Material	Surface area (m^2/g)	Pore volume (cm^3/g)
CNT/PEI	26.28 (28.73)	0.20 (0.36)
CNT-PEI	54.10 (56.94)	0.21 (0.21)

Discussion of Raman spectroscopy of CNT in relation to functional group loading

Raman spectroscopy was used to investigate the degree of degradation of CNT in relation to the functional group loading measured by TGA. The intensity of the D band (~ 1320 cm^{-1}) and the G band (~ 1585 cm^{-1}) in Raman spectroscopy are related to the defects or disorder of graphitic structure and the sp^2 carbon graphitization of HNO_3 treated CNT (o-CNT) respectively (**Figure S2A**).[1,2] D/G ratio was used to evaluate the degree of degradation where a higher value indicates a higher degree of functionalization on CNT while the D' band is a resonance feature.[3,4] The results showed that the D/G ratio increased as treatment time increased, which indicates that in the range of 0 to 48 hours, extension of treatment times favors CNT structure degradation and functional group generation.[5,6] The degradation of CNT decreased upon longer treatment times and did not show a significant change after 30 h. The total functional group loading measured by

TGA was linearly related to D/G ratio (R^2 = 98%), indicating the functional group generation is accompanied with CNT structure degradation (**Fig. S2B**).[7]

Discussion of CO_2 capture under dry and steam conditions.

One CO_2 molecule is captured by two amine groups and form carbamates in dry conditions (1-2).[8] In steam conditions, one CO_2 molecule is captured by only one amine group and form bicarbonate (3-5).[9,10] Besides primary and secondary amines, tertiary amine can also capture CO_2 in steam conditions (5). Therefore, compared to dry conditions, CO_2 capture should be enhanced with steam.

CO_2 capture in dry conditions

(1) Primary amine:

$$2\ R_1NH_2 + CO_2 \longleftrightarrow R_1NH_3^+R_1NHCOO^-$$

(2) Secondary amine:

$$2\ R_1R_2NH + CO_2 \longleftrightarrow R_1R_2NH_2^+R_1R_2NCOO^-$$

CO_2 capture in steam conditions

(3) Primary amine:

$$R_1NH_2 + CO_2 + H_2O \longleftrightarrow R_1NH_3^+HCO_3^-$$

(4) Secondary amine:

$$R_1R_2NH + CO_2 + H_2O \longleftrightarrow R_1R_2NH_2^+HCO_3^-$$

(5) Tertiary amine:

$$R_1R_2R_3N + CO_2 + H_2O \longleftrightarrow R_1R_2R_3NH^+HCO_3^-$$

Table S5. The effect of treatment time on the functional group loading on CNT (Data for Fig. 1)

Treatment time (h)	0*	5	16	24	30	42	48
Functional groups (wt%)	1.3	3.3	4.7	6.5	7.6	7.4	7.8

*CNT received as is

Table S6. The effect of functional group on PEI loading (Data for Fig. 3B)

Functional group (wt%)	1.3	2.3	3.3	4.7	5.3	6.5	7.7	7.8
PEI loading (wt%)	3.3	5.0	7.2	11.0	14.0	15.8	13.0	11.8
PEI loading standard deviation (wt%)	0.1	0.2	0.2	0.2	0.4	0.1	0.4	0.4

Table S7. CO_2 capture of CNT, CNT-PEI and CNT/PEI without steam

PEI loading (wt%)	CO_2 capture (mmol/g)	Adsorbent
0	0.284 ± 0.011	NA
7	0.505 ± 0.007	CNT-PEI
11	0.697 ± 0.015	CNT-PEI
16	0.981 ± 0.010	CNT-PEI
17	1.328 ± 0.023	CNT/PEI

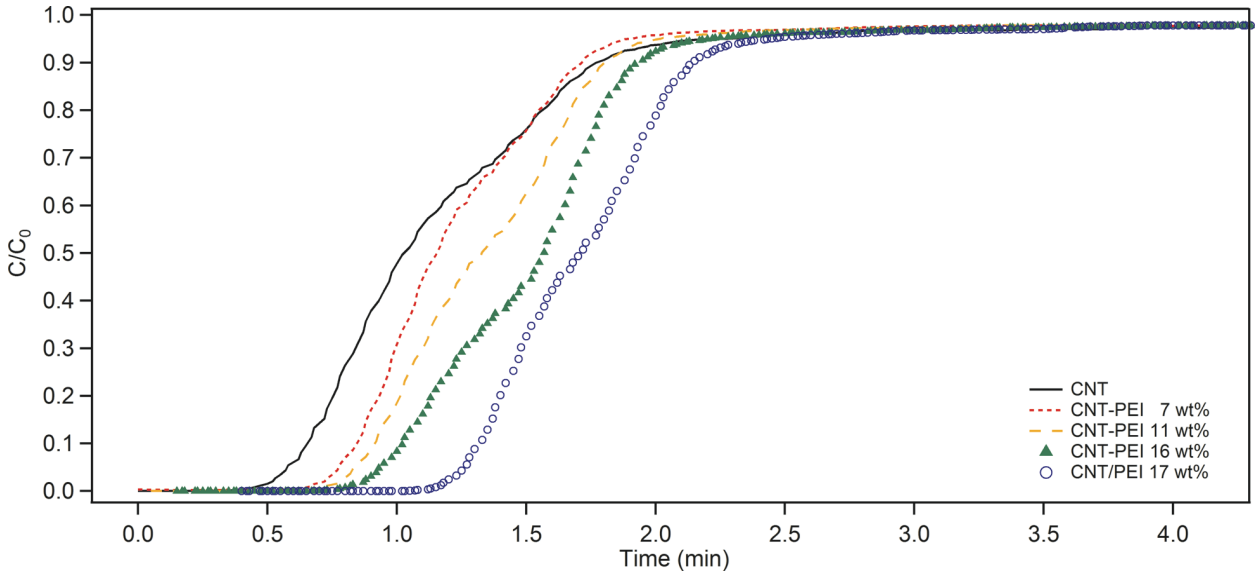

Figure S6. CO_2 capture breakthrough curve of CNT, covalently and physically PEI modified CNT

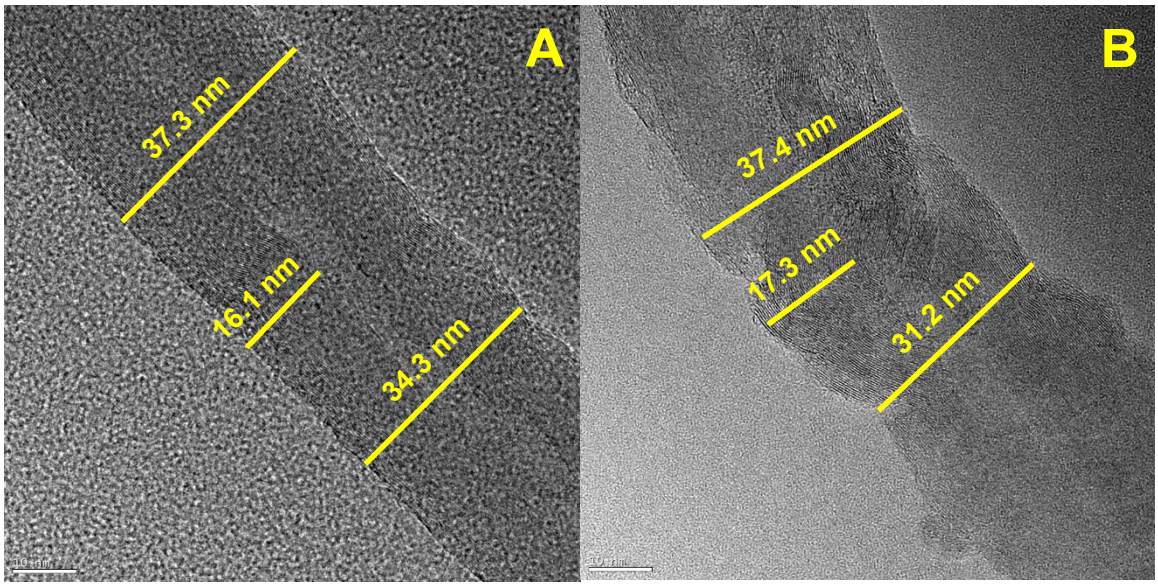

Figure S7. The TEM image and diameter of A) as is CNT and B) CNT-16wt%PEI

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