# Spacer-Assisted Amine-Coiled Carbon Nanotubes for CO<sub>2</sub> Capture

Mengmeng Deng<sup>†</sup> and Hyung Gyu Park<sup>\*,‡</sup>

<sup>†</sup>Department of Mechanical and Process Engineering, Swiss Federal Institute of Technology (ETH) Zurich, Zurich 8092, Switzerland

<sup>‡</sup>Department of Mechanical Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-ro, Nam-gu, Pohang, Gyeongbuk 37673, Republic of Korea

**Supporting Information** 

**ABSTRACT:** Architecture of a DNA-wrapped carbon nanotube (CNT) inspires rational design of a polymer-wrapped CNT effective for  $CO_2$  capture. Polyethyleneimine (PEI) selected as a spiral wrapper of CNT is modified by insertion of spacer molecules loaded with amino groups such as siloxanes and purine to enhance the  $CO_2$  capture performance. A porous adsorbent made by packing these functional nanowires (e.g., PEI-purine-CNT) reveals  $CO_2$  uptake as large as 3.875 mmol/g. Adsorbent materials from this biomolecule-inspired design drop the adsorption heat to 29.00 kJ/mol if secondary and tertiary amines are adopted, besides the primary one, a value that is one-third of the absorption heat of an industrially deployed, liquid absorbent of  $CO_2$ . The corresponding adsorption and desorption kinetics agree with an Avrami model, indicating that both processes involve multiple sorption pathways. Furthermore, PEI-purine-CNT maintains its adsorption capacity after 50 adsorption-desorption cycles, implying a great potential for carbon capture from smokestacks and air in a stable and cyclic manner.



## ■ INTRODUCTION

Global warming is undoubtedly a major challenge that faces humanity today related closely to anthropogenic greenhouse gas emission. Among the greenhouse gases, CO<sub>2</sub> takes the primary portion which makes up ~68% of the estimated total greenhouse gas emissions.<sup>1</sup> Since the beginning of the industrial revolution in 1850s, the average atmospheric concentration of CO<sub>2</sub> has elevated from 280 to 370 ppm by 2000,<sup>2</sup> reaching around 400 ppm today.<sup>3</sup> According to an estimation, the atmosphere might contain up to 570 ppm CO<sub>2</sub> by the year of 2100, a potential source of raising the average global temperature of ~2 °C.<sup>4</sup>

Aqueous alkylamine has been applied to the CO<sub>2</sub> capture by absorption at an industrial pilot plant scale successfully.<sup>5</sup> This technology, on the other hand, faces issues such as amine degradation and equipment corrosion as well as limited loading of the aqueous adsorbent caused by viscosity increase and energy penalty for regeneration.<sup>6-9</sup> Solid adsorbents functionalized with amines are, therefore, considered in order to resolve the above issues.<sup>10,11</sup> Amines loaded on porous solid matrices pose a number of advantages.<sup>9,12</sup> For example, no need of an aqueous solution could mostly eliminate the equipment corrosion issue. Relatively small energy for the regeneration of the solid adsorbent can be a benefit, too. Additionally, footprint needed for CO<sub>2</sub> capture could be decreased, and the disposal cost of the solid adsorbents would be cheaper than that of liquids. The porous media-embedded amine, nevertheless, shows limited CO<sub>2</sub> capture capacity in general because of a pore blocking issue at very high amine loading.' As a

result, amine-functionalized adsorbents have not been able to catch CO<sub>2</sub> molecules effectively, thus showing low adsorption capacity values relatively. One way to solve the above issue is the adoption of highly porous zeolites with amines as building blocks such as metal-adeninate, which offers promising CO<sub>2</sub> capture capacities.<sup>13,14</sup> Siloxane-modified carbon materials such as carbon nanotubes (CNTs) via covalent bonds showed small sorption heat and good repeatability, but the uptake performance needs to be further improved.<sup>15–17</sup> An artificial pore design with an optimal microstructure has been proposed to address this issue. For instance, an interconnected macropore configuration has enhanced transport of CO<sub>2</sub> molecules within the pores and achieved effective CO<sub>2</sub> capture.' Physical geometry in a porous medium draws numerous interest in improving CO<sub>2</sub> capture significantly. Chemical geometry at the adsorption sites could be referred to as another way of facilitating CO<sub>2</sub> removal. Nevertheless, rare reports on the chemical geometry necessitate an exploration of chemical arrangement at the molecular level.

Inspired by DNA-coiled CNTs in which base pairs contain amino groups within the narrow space in between the sugar phosphate backbone and CNT,<sup>18</sup> we envision that a use of such an architecture could avail  $\text{CO}_2$  molecules effective access to a large number of amine moieties. If a myriad of such aminecoiled CNTs could be entangled into a macroporous medium

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Figure 1. (A) Schematic of amine functionalization of CNT: PEI coiling (top), covalent tethering of the siloxane spacers followed by PEI coiling (middle), and  $\pi - \pi$  attachment of the purine spacers followed by PEI coiling (bottom). (B) As-prepared PEI-purine-CNT powders. (C) Scanning electron microscopy (SEM) of the exposed surface of a PEI-purine-CNT sample, showing the reticular texture of nanotube-based buckypaper.

easily, the medium would potentially act as a cheap and effective adsorbent for CO<sub>2</sub> capture. Here, we report biomolecule-inspired design of amine-coiled CNTs where a polyethyleneimine (PEI) chain spirally wraps each CNT decorated with a bunch of amine-laden spacers that assist the wrapping and create additional adsorption space in between the CNT and PEI chain. Both PEI and the spacers can contribute to CO<sub>2</sub> capture. The spacers with optimal molecular length and amino quantity turn out to improve CO<sub>2</sub> capture capacity up to 3.875 mmol/g. The corresponding heat of adsorption measures 29.00 kJ/mol, a value that is nearly one-third of the absorption heat of the industrialized monoethanolamine (MEA) solution (~88 kJ/mol), attributable to adoption of secondary and tertiary amines as well as the low heat capacity of sorbents. The small adsorption heat of the porous adsorbent based on CNTs coiled with amines leads to a reliable cyclic process of CO<sub>2</sub> capture and release. Potential stability of this adsorbent material is verified with unwithered 50 repetitions of  $CO_2$  uptake and release in a prototype test that illustrates an industrial CO<sub>2</sub> capture process.

#### MATERIALS AND METHODS

**Materials and Equipment.** CNTs were purchased from Shenzhen Nanotech Port Co. Ltd (MWNT-10, MWCNT with diameter of 7–15 nm and purity >97%). Branched PEI (Mw = 1300 g mol<sup>-1</sup>), 3-aminopropyl triethoxysilane (APTS), N-(3trimethoxysilylpropyl)ethylenediamine (2NAPS), N-(3trimethoxysilylpropyl)ethylenediamine (3NAPS), and (6-amino-9H-purin-9-yl)methanol (purine) were purchased from Sigma-Aldrich. Deionized (DI) water (Milli-Q, 18.2 MQ·cm) was used throughout the experiment.

The scanning electron microscopy (SEM) image was collected by FEI Nova NanoSEM 450 field-emission SEM. The sample after vacuum-filtration was dried in the atmosphere first, then transferred to a Si chip, and fixed by a carbon tape.

Composition of the functionalized CNT samples was characterized by Linseis STA PT 1600 TGA (Figure S1A). The sample after preparation was dried in the atmosphere first and transferred to an alumina crucible afterwards. After loading the crucible in the thermogravimetric analyzer (TGA), the maximum temperature was set at 1000  $^{\circ}$ C at a heating rate of 10  $^{\circ}$ C/min. The measurement atmosphere is under the air.

The functional groups were characterized by Thermo Scientific Nicolet iS10 total reflection Fourier transform infrared (FTIR) spectroscopy. The sample after preparation was dried in the atmosphere first. Then, the sample was transferred to a glass substrate followed by fixing the sample on the FTIR test platform via a cantilever. The measurement is operated in the atmosphere.

**Polyethyleneimine-Carbon Nanotube.** Briefly, 80 mg of the aspurchased CNTs was soaked in 10 mL acid  $(HNO_3/H_2SO_4 (v/v) = 1:3)$  and stirred at 70 °C for 1 h.<sup>19</sup> The acid-treated CNTs were washed with DI water and sieved several times to remove the excess acid. Obtained CNTs were dispersed in 30 mL of a PEI aqueous solution at a given concentration and stirred at room temperature for 12 h. Then, the mixed solution was vacuum-filtrated and washed by DI water.

**PEI–Siloxane–CNT.** The acid-treated CNTs were dispersed first in 20 mL ethanol with 6 mL siloxane. Then, the mixture was refluxed at 70  $^{\circ}$ C for 4 h. After cooling down to room temperature, the mixture was filtrated and washed with DI water to remove the access siloxane. Finally, the siloxane–CNTs were further wrapped with PEI using the same method above.

**PEI–Purine–CNT.** The as-purchased CNTs (80 mg) were dispersed in 20 mL DI water by tip sonication for 2 h. Then, 80 mg of purine was added into the CNT solution at room temperature with stirring for another 4 h. The mixture was filtrated and washed with DI water to remove the excess purine. The purine–CNTs were further wrapped with PEI as shown above.

CO<sub>2</sub> Adsorption and Desorption Measurement. CO<sub>2</sub> sorption was measured by Linseis STA PT 1600 TGA. Briefly, ~20 mg CNTs were loaded into an alumina crucible and pretreated at vacuum and 50 °C for 12 h to clean the sample. Then, the adsorption measurement started at 50 °C by exposing the sample to a pure CO<sub>2</sub> atmosphere at 1 bar. Desorption measurement was performed right after the completion of adsorption. The temperature was increased to 100 °C at 10 °C/min, and the gas atmosphere was changed to N2. The adsorption and desorption heats were measured at the same condition with differential scanning calorimetry (DSC). Sorption heat was calculated from measured values of CO<sub>2</sub> uptake in  $mmol/g\mbox{-}adsorbent$  and heat in J/g-adsorbent. Sorption heat was calculated from measured values of CO2 uptake (TG) in mmol/gadsorbent and heat (DSC) in J/g-adsorbent (Table S3), as reported in literature.  $^{17}$  The heat in J/g-adsorbent was obtained based on the integrated area below the heat flow curve presented in Figure 3.

Sorption heat = heat  $(DSC)/CO_2$  uptake (TG)



Figure 2. (A) Time evolution of  $CO_2$  uptake of various amine-coiled CNT adsorbents at 50 °C and 1 bar. (B) Time evolution of  $CO_2$  desorption at 100 °C and 1 bar. (Dotted line: Avrami model fitting).

The cyclic sorption test was conducted by repeating the above adsorption and desorption steps, while the adsorption takes 1 h and the desorption takes another 1 h. After one adsorption–desorption cycle, it takes  $\sim 1$  h to cool down for another cyclic measurement.

Construction and Characterization of a Prototype CO<sub>2</sub> Capture Column. PEI-purine-CNT powders were packed into a column for adsorption and desorption processes. The column has a diameter of ~0.4 cm and a length of 15 cm. The temperature of the column was controlled by a heating tape (BriskHeat, HSTAT052002-C). A mass spectroscope (MKS, Cirrus 2) was connected at the end of the column to analyze postcolumn contents of gas species. The schematic of the prototype is shown in Figure 4B and the photograph of the setup is shown in Figure S3. A CO<sub>2</sub>/N<sub>2</sub> mixture (15% CO<sub>2</sub>) was blown to the column line at 50 °C for an adsorption process. The adsorption operation took around 3 h. After the adsorption, Ar was blown to purge the entire line. Then, the temperature of the column was increased to 100 °C for the desorption process while blowing the carrier gas of Ar. The desorption operation took around 3 h. After desorption, the entire system was cooled down below 50 °C for a new cycle. The cyclic CO<sub>2</sub> capture-release performance was characterized by repeating the above operations.

# RESULTS AND DISCUSSION

**Characterization of PEI-Spacer-CNT Adsorbents.** An architecture of the amine-coiled CNT (Figure 1A) comprises CNT spirally wrapped with a PEI chain in between which multiple amine spacers are inserted. Spiral wrapping of branched PEI around CNT is well known.<sup>20</sup> The spacer material we conceive is either purine ((6-amino-9*H*-purin-9-yl) methanol) or siloxanes of various chain lengths and amine moieties. The role of the spacer is to create free volume for easy access of CO<sub>2</sub> molecules in between PEI and CNT,<sup>10</sup> a nanostructure that poses great specific area, as well as to capture them therein. In addition, use of secondary and tertiary amines at the spacers would help decrease the regeneration energy.<sup>21,22</sup>

Interactions at the interface between PEI and CNT are characterized by a van der Waals interaction and dipolar zwitterions.<sup>20,23</sup> For difference in surface tension (~136 kJ/mol·nm for CNT and ~17 kJ/mol·nm PEI),<sup>24</sup> PEI-coiled CNTs can be dispersed stably in an aqueous solution. Siloxane is covalently grafted to CNT (siloxane–CNT), while purine is noncovalently attached onto the CNT exterior surface (purine–CNT) through a  $\pi-\pi$  interaction.<sup>17,25</sup> Infrared spectroscopy manifests the successful engagement of siloxane, purine, and PEI onto CNT (Figure S2). A subsequent vacuum filtration process (PTFE filter, Whatman, 0.2  $\mu$ m in pore diameter) produces powders of PEI–spacer–CNT (e.g., PEI–purine–CNT, Figure 1B) that have the texture of buckypaper or porous morphology of entangled nanowires (Figure 1C).

Thermogravimetric characterization reveals a maximum PEI loading of  $\sim 18$  wt % on CNTs (Figure S1).

CO<sub>2</sub> Uptake of PEI–Spacer–CNT Adsorbents. Characterization of  $CO_2$  uptake onto various amine-coiled CNT adsorbents at 50 °C and 1 bar shows that a  $CO_2$  capture capacity can vary widely depending on the spacer design (Figure 2A and Table 1). Among functionalized samples, PEI–

Table 1. CO<sub>2</sub> Uptake Capacity and Sorption Heats

sample	CO <sub>2</sub> uptake (mmol/g)	adsorption heat (kJ/mol)	desorption heat (kJ/mol)
PEI-CNT	0.6520		
PEI-APTS-CNT	1.504	61.35	65.65
PEI-2N(APS)-CNT	2.900	54.15	65.50
PEI-3N(APS)-CNT	0.7930	35.45	12.55
PEI-purine-CNT	3.875	29.00	29.10

CNT with no spacer gives the smallest CO<sub>2</sub> uptake of 0.6520 mmol/g. Use of a siloxane spacer (PEI-siloxane-CNT) enhances the CO<sub>2</sub> uptake because it introduces extra amine moieties in a brushy configuration in between the CNT exterior and PEI. Among siloxane spacers herein tested, a 2N(APS) spacer shows the highest uptake value of 2.900 mmol/g, perhaps attributable to an optimal amine content and free volume for CO<sub>2</sub> access. Use of a longer 3N(APS) spacer, nevertheless, less enhances CO<sub>2</sub> uptake to a value just slightly above that of PEI-CNT. Speculatively, it might be because too long a molecular chain could undermine the morphology of PEI attached on the CNT surface as well as the effective attachment, suggesting that the use of spacers having an optimal or moderate chain length would be crucial. It needs further elucidation to unveil the mechanism of the steric hindrance and to answer what determines the optimal chain length. Inspired by DNA-wrapped CNTs in which nucleobases containing amino groups interact with CNTs through the  $\pi$ - $\pi$ interaction, we made an attempt to attach purine as a spacer onto the CNT exterior surface. Interestingly, this biomoleculeinspired PEI-purine-CNT sample exhibits quite a high CO<sub>2</sub> adsorption capacity (3.875 mmol/g), a value that exceeds those of the siloxane-grafted samples. The nucleobase-like purine spacer on the CNT surface does not only offer free space for the gas access but also provides more number of amine moieties than siloxanes do. Desorption characterization at 100 °C and 1 bar (Figure 2B) claims a fast and complete  $CO_2$  disengagement process, implying a potential reusability of the adsorbents to be demonstrated later.

 $CO_2$  capture could be also affected by moisture content and oxidation.<sup>26,27</sup> For example, the little amount of moisture could

enhance the uptake capacity due to the formation of bicarbonates, and the oxidation of amines known as degradation would undermine the capture performance.<sup>17,28</sup> Besides, dependence of  $CO_2$  capture performance on temperature and pressure can be a generally interesting question. Therefore, systematic investigations on the effects of moisture and oxidation as well as the effects of temperature and pressure on the  $CO_2$  capture capacity deserves further exploration with these spacer-assisted adsorbents in the future.

 $CO_2$  uptake capacities among various adsorbents are summarized in Table 2.<sup>29</sup> The inorganic matrix such as

Table 2.	Comparison	of (	$O_2 U$	ptake	Capacit	y
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adsorbent	adsorption temperature (°C)	CO <sub>2</sub> partial pressure (bar)	CO <sub>2</sub> uptake (mmol/g)
PEI-mesoporous silica <sup>35</sup>	50	0.1	1.000
1,2-epoxybutane-PEI-silica <sup>28</sup>	60	0.15	1.620
PEI-SBA-15 <sup>36</sup>	45	1	1.818
tetraethylenepentamine—silica <sup>37</sup>	30	0.15	2.000
PEI—hierarchical silica <sup>38</sup>	75	1	2.432
APTS–silsesquioxane aerogel <sup>39</sup>	50	0.01	3.045
PEI-MCM-41 <sup>40</sup>	25	1	3.523
tetraethylenepentamine-KCC-1 <sup>41</sup>	50	0.15	3.864
PEI-purine-CNT	50	1	3.875
polyethylene polyamine–nanoporous silica <sup>42</sup>	50	1	3.909

silica-based adsorbents has been intensively studied due to the effective working capability and low cost. Among various adsorbents, the spacer-assisted sorption media such as PEI–purine–CNT show promising capture performance. Because the adsorbent support and amines come from various sources, it is still ambiguous to have a direct comparison of the adsorbent price, although it is significant for industrial applications.

Adsorption and desorption curves reveal a three-stage process. For the adsorption process, the early stage shows a lower adsorption rate due to phase transformation and overcoming of energy barrier for adsorption. The middle stage exhibits a higher adsorption rate. Finally, the uptake is saturated because of the limitation of free adsorption sites in the end. For the desorption process, the early stage has a lower desorption rate due to the overcoming of the interaction energy between  $CO_2$  and amine. The middle stage resumes a finite desorption rate as a balance between desorption energy and thermal energy. At the final stage, depletion of the gasoccupied sites brings an end to desorption.

CO<sub>2</sub> Capture Kinetics. Functionalized CNTs can follow multiple pathways for adsorption and desorption of CO<sub>2</sub>.<sup>30,31</sup> CO<sub>2</sub> could be physisorbed directly onto pristine graphitic surfaces of CNTs, as shown in formula 1. CO<sub>2</sub> molecules would also interact with primary or secondary amines to form carbamates (formulas 2 and 3); it is possible that one  $CO_2$ molecule interacts with two types of amine moieties to form a carbamate (formula 4). Considering that multiple complex sorption mechanisms are involved, the Avrami model is known to be instrumental to describe the sorption kinetics.<sup>32,33</sup> Indeed, the Avrami model agrees with our sorption kinetic data greatly (dotted lines in Figure 2, Tables S1 and S2). According to the sorption kinetics parameters (Tables S1 and S2), the adsorption rate (proportional to  $n \cdot k_A^n$ ) tends to increase with an engineered molecular structure compared with PEI-CNT, implying an effective sorption process based on the steric design. An exceptionally large rate constant of 3N(APS) for both adsorption and desorption cases might be related to its rather trivial CO<sub>2</sub> uptake capacity. Neglecting this sample, the adsorption and desorption rates descend in the following order: 2N(APS) > purine > APTS > no spacer for adsorption and purine > 2N(APS) > APTS for desorption. PEI-purine-CNT presenting a moderate adsorption rate may attribute to its largest uptake capacity. It is assumed that the largest desorption rate of PEI-purine-CNT could result from the smallest heat of desorption (Table 1). For both adsorption and desorption processes, the exponent, n, is larger than 1 among all samples, suggesting a nonhomogeneous sorption mechanism with the existence of both chemi- and physisorption that follow multiple pathways.<sup>32</sup>

 $CO_2 + CNT \rightarrow CO_2 - CNT$  (1)

$$CO_2 + 2RNH_2 = RNHCO_2^{-} + RNH_2^{+}$$
(2)

$$CO_2 + 2R_2NH = R_2NCO_2^- + R_2NH_2^+$$
 (3)

$$CO_{2} + RNH_{2} + R_{2}NH/R_{3}NH$$
  
= RNHCO\_{2}^{-} + R\_{2}NH\_{2}^{+}/R\_{3}NH^{+} (4)

The Avrami kinetics follows  $q_t = q_e \{1 - \exp[-(k_A t)^n\}$ , where  $q_e$  is the CO<sub>2</sub> uptake at an equilibrium state,  $q_t$  represents the CO<sub>2</sub> uptake at time t,  $k_A$  is an Avrami rate constant, and n is the Avrami exponent related to the occurrence of multiple sorption pathways.

**Sorption Heat Analysis.** Energetics of  $CO_2$  sorption can provide another guideline for a suitable adsorbent for energyefficient  $CO_2$  capture and release. By characterizing heat addition and discharge kinetics over the sorption events



Figure 3. DSC profiles of various amine-functionalized CNT samples for (A) CO<sub>2</sub> adsorption at 50 °C and (B) desorption at 100 °C, respectively.



Figure 4. (A)  $CO_2$  adsorption by PEI-purine-CNT with 50 cycles. (B) Schematic of the laboratory-scale prototype setup and (C,D) 1st cycle of adsorption and desorption measurements. (E,F) Adsorption and desorption repeatability by using the prototype.

through DSC profiling (Figure 3), we obtained the sorption enthalpies of our amine-coiled CNT samples (Table 1). For the grafted amine spacer, both adsorption and desorption heats decrease as the spacer length or the number of the secondary and tertiary amine moieties increases (Table 1). PEI-purine-CNT shows the sorption heats similar to those of PEI-3N(APS)-CNT presumably because of the secondary and tertiary amine moieties in the purine molecules. The corresponding value of the adsorption heat (29.00 kJ/mol) is on par with the best performed solid adsorbents (i.e., the lowest adsorption heat) hitherto reported<sup>7,17</sup> and one-third of the adsorption heat of the MEA liquid absorbent. The low adsorption energy is not only caused by the diverse types of amine moieties employed in our adsorbent architecture but also by the heat capacity of the CNT matrix ( $\sim 2 \text{ kJ/kg} \cdot \text{K}$ )<sup>34</sup> smaller than that of water (4.2 kJ/kg·K). PEI-coiled CNTs with the 3N(APS) spacers [PEI-3N(APS)-CNT] give the smallest desorption heat, which is likely the result of the insignificant CO<sub>2</sub> capture capacity of this adsorbent. Remarkably, the desorption heat of PEI-purine-CNT is quite similar to its adsorption heat, implying a reversible sorption process desirable for the energy-efficient CO<sub>2</sub> capture and release.

Stability Test of the PEI–Purine–CNT Adsorbent. Stability of the CNT-supported amines is crucial for the regeneration of adsorbents. We characterized the cyclic performance of PEI–purine–CNT in order to demonstrate the sorption stability of this adsorbent as well as to obtain the  $CO_2$  capture lifetime. Within 50 cycles of adsorption and desorption in a TGA chamber (Figure 4A), there is no significant loss observed about the  $CO_2$  uptake, which maintained the uptake capacity of ~3.900 mmol/g, except for minor fluctuations, potentially suggesting the adsorbent reusability. The PEI–purine–CNT adsorbent turns out to be better in stability than previously reported PEI-laden porous adsorbents, attributable to the large molecular weight of PEI, a mild desorption temperature (100 °C), and the specific interactions among PEI, purine, and CNT rather than a physical attachment alone.<sup>43,44</sup>

**Prototype Measurement of the PEI–Purine–CNT Adsorbent.** To illustrate a simple CO<sub>2</sub> capture process feasible for an industrial application, we designed and built a laboratory-scale prototype (Figures 4B and S3). The PEI– purine–CNT adsorbent was packed into a single column (length: ~15 cm and diameter: ~0.4 cm) for both adsorption and desorption. Briefly, the adsorption takes place at 50 °C in the atmosphere of a CO<sub>2</sub>/N<sub>2</sub> gas mixture (15% CO<sub>2</sub>) and desorption at 100 °C with Ar as a sweeping and carrier gas. For adsorption, the postcolumn CO<sub>2</sub> content is undetectable at the beginning because of nearly complete adsorption (Figure 4C). The CO<sub>2</sub> content, then, increased with time, implying that more CO<sub>2</sub> molecules escaped from the column (Figure 4C).

#### Langmuir

Finally, the curve almost reached a plateau, hinting at that the adsorbent was saturated (Figure 4C). During the desorption process, the postcolumn  $CO_2$  content increased with time using Ar as the carrier gas, showing that  $CO_2$  molecules had been detached from the adsorbent increasingly (Figure 4D). After reaching a maximum  $CO_2$  content value, it decreased until no  $CO_2$  partial pressure was detected (Figure 4D), indicating complete desorption of the adsorbed  $CO_2$  molecules. For both adsorption and desorption processes, curves of the similar trend are repeatedly obtainable for 50 cycles (Figure 4E,F), supporting a cyclic operation capability by use of the PEI–purine–CNT adsorbent.

# CONCLUSIONS

From the facts that PEI chains have tendency to wrap around CNT spirally and that large specific area of CNT can be integrated to a buckypaper format easily, one can conceive of a buckypaper-type CO<sub>2</sub> adsorbent that would benefit from both the large specific area of CNTs and the renowned affinity of CO<sub>2</sub> to PEI. On top of this architecture, a biomoleculeinspired incorporation of amine-laden spacers in between the PEI coil and the CNT exterior can drastically improve the sorption performance by providing PEI with legs that would open up the amine-rich space for CO<sub>2</sub> gas access. Various amine-laden spacers are engaged onto the CNT exterior surface either by  $\pi - \pi$  interactions of amino-aromatic rings (e.g., purine) to the graphitic surface or by covalent functionalization of the oxidized CNT surface with aminoaliphatic chains of various lengths and amino content (e.g., APTS, 2NAPS, and 3NAPS) via silane chemistry. At an optimal chain length, the amino-aliphatic chains can endow the corresponding modified adsorbent as large a CO2 uptake capacity as 2.900 mmol/g, although enthalpies of sorption for the adsorbent regeneration are not very small. On the other hand, the DNA-mimic PEI-purine-CNT adsorbent exhibits as high CO<sub>2</sub> uptake capacity as 3.875 mmol/g and as small sorption heats as 29.00 kJ/mol, that is, only one-third of that of the MEA liquid absorbent. This biomolecule-inspired adsorbent architecture also poses additional advantages including fast sorption kinetics, equivalently low ad- and desorption heats, and outstanding stability of well-maintained CO<sub>2</sub> capture performance after 50 adsorption-desorption measurements, an attribute that a prototype porous-plug adsorbent reproduces for practical adaptation. Our investigation offers an insight that the biomolecule-inspired rational nanoarchitecture can play a powerful role in bringing effective improvement to such a sustainability solution as CO<sub>2</sub> capture from smokestacks and air.

## ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.lang-muir.8b03980.

Description of the PEI loading characterization, FTIR characterization of functional groups on CNTs, kinetic model fitting parameters, DSC measurement data, and lab-scale prototype (PDF)

# AUTHOR INFORMATION

Corresponding Author

\*E-mail: parkhg@postech.ac.kr.

#### ORCID 0

Mengmeng Deng: 0000-0002-4042-8402 Hyung Gyu Park: 0000-0001-8121-2344

# Notes

The authors declare no competing financial interest.

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