Control of CO₂ Capture Process on Transition-Metal-Porphyrin-like Graphene with Mechanical Strain

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ABSTRACT: Nanomaterials, such as zeolites and metal–organic frameworks, have been studied for CO₂ capture and sequestration. However, this application of nanomaterials has been limited largely due to their poor selectivity for flue gases as well as low capture capacity under low pressures. The first-principle density-functional theory calculations for porphyrin-like graphene decorated with a transition metal were performed to investigate the effects of mechanical strain on its CO₂ capture capacity. We found that Sc- and V-decorated porphyrin-like graphenes could capture CO₂ molecules selectively from gaseous mixtures under low CO₂ pressure with compressive strain and release them with tensile strain at room temperatures. The CO₂ binding to these transition metals was understood to be mostly due to the Dewar interaction involving hybridization of the metal d orbitals with π orbitals of CO₂. These results elucidate a novel approach to the CO₂ capture process with the application of the mechanical strain to nanomaterials.

INTRODUCTION

Carbon dioxide has been considered to be the main cause of climate change. Its concentration in the earth’s atmosphere has increased to 391 ppm in 2011, and by 2100 it is expected that the concentration could reach about 600 ppm. Anthropogenic CO₂ emission will give rise to ocean acidification and rising sea levels due to glacial melting. The demands for fossil fuels accelerate these trends, and therefore the identification of new and effective carbon-capturing materials would be an important task to mitigate the climate change.1

Among diverse studies of CO₂ capture,2–16 nanostructured materials, such as zeolites and metal–organic frameworks, have been considered candidates for CO₂-capturing substances. However, applications have been limited, despite fast adsorption kinetics and effective regeneration of CO₂,5,7,9–16 because of their poor selectivity for flue gases and low capacity under near-ambient conditions.5,6,8 For these reasons, traditional adsorbent seems hard to apply for CO₂ capturing from flue gases.17 In response, investigation of novel CO₂ capture materials is emerging.18–21

Recently, transition-metal-porphyrin-like fragments (TM-N₄) on the surface of nanostructures, analogous to the central structure of hemoglobin or myoglobin,22,23 were synthesized by the chemical vapor deposition and pyrolysis methods.24–30 In this structure, a transition metal (TM) atom is surrounded by four nitrogen atoms as in a metal-porphyrin structure.31,32 Considering that the concentration of nitrogen was found to reach ∼8% in carbon nanotubes (CNTs)33 and ∼10% in graphene,34 it is expected that TM-porphyrin-like carbon nanostructures can be synthesized experimentally. Using a combinatorial method of thermodynamics and ab initio density-functional theory (DFT) calculations, some of us investigated the most efficient TM element in graphene-based TM-N₄ structure by high-throughput screening,35 from which it was concluded that TM-decorated porphyrin-like graphene can be a good CO₂-capturing material, and Sc- and V-decorated ones provide high selectivity for CO₂ capture from flue gases.

On the other hand, recent ab initio calculations of Kou et al. revealed substantially enhanced adsorption of several important environmental molecules such as NO and NH₃ on a monolayer MoS₂ in the presence of mechanical strain.36 The variations in the binding energies were understood to result from changes in the charge environment due to distorted atomic structures under mechanical strain. Since a monolayer graphene was reported to endure from −1 to +10% of uniaxial strain37,38 and from −1 to +2% of biaxial strain,39–41 we expect that the CO₂ capacity of TM-decorated porphyrin-like graphene could be tuned by mechanical strain, without any temperature adjustment. Thus, we performed first-principle DFT calculations to investigate the property of CO₂ capture on TM-porphyrin-like graphene under mechanical strain. We here consider biaxial mechanical strain in the range of −3 to +3%, which is theoretically acceptable even though expansion is harder than stretching.
This paper is organized as follows. The section of Flue-Gas Models deals with the chemical potentials of different gas molecules constituting our flue gases. The DFT results along with the related discussions are presented in the section Results and Discussion. We summarize our findings and conclude in the section Conclusions. Finally, computational details, including the description of the TM-porphyrin-like graphene, are presented in the section Computational Methods and Details.

### FLUE-GAS MODELS

The chemical potential of gases, \( \mu = (H - TS)/N \), where \( H \) is the enthalpy, \( S \) is the entropy, and \( N \) is the number of gas molecules, respectively, was calculated from the enthalpy and entropy data in NIST Standard Reference Data. Also, we considered three different compositions of flue gas based on previous literature: \(^{10,43}\) (1) \( \text{CO}_2/N_2 = 89:11 \) (oxy-fuel), (2) \( \text{CO}_2/H_2/\text{CH}_4 = 20:75:5 \) (precombustion), and (3) \( \text{CO}_2/N_2 = 17:83 \) (postcombustion). Table 1 presents chemical potentials of different gas molecules in our flue-gas models at a temperature of 298 K and at a pressure of 1 bar.

**Table 1. Chemical Potentials of Gases with Partial Pressures in Our Three Compositions of Flue Gas**

| gas compositions | \( \mu_{\text{CO}_2} \) | \( \mu_{\text{H}_2} \) | \( \mu_{\text{CH}_4} \) |
|------------------|-----------------|-----------------|-----------------|
| oxy-fuel         | −0.57           | −0.56           |                 |
| precombustion    | −0.61           | −0.33           | −0.55           |
| postcombustion   | −0.61           | −0.51           |                 |

The chemical potentials are in units of electronvolt (eV).

### RESULTS AND DISCUSSION

#### Geometric Configurations and Distance Change.

Figure 1 presents optimized geometric configurations of four different gas molecules adsorbed on TM-porphyrin-like graphene. For this, we considered various hapticities (e.g., \( \eta_1-\text{CO}_2, \eta_2-\text{CO}_2 \)) of the adsorbed gas molecules. Among them, \( \eta_2-\text{CO}_2, \eta_1-\text{N}_2, \eta_1-\text{CH}_4 \), and \( \eta_2-\text{H}_2 \) shown in Figure 1 were selected because they resulted in the lowest adsorption energies for the corresponding gas molecules. These optimized geometric structures were observed to change very little even with the change in the distance between a TM atom and a porphyrin-like plane under mechanical strain.

Structural effects of the gas adsorptions are further investigated by analyzing the gas–TM and TM–substrate distance changes while adjusting the mechanical strain to the substrate. As seen in Figure 2, the distance between a TM atom and the substrate increases, regardless of the type of gas molecules, when altering from a tensional strain to a compressive strain. However, no significant change in the gas–TM distance is observed, except for the case of \( \text{CH}_4 \) on the V-decorated substrate where the \( \text{CH}_4 \) molecule is much further away from a V atom (3.6–5.0 Å) than the other gas molecules (1.8–2.0 Å). This indicates that under compressive mechanical strain, a TM atom is bound less to the surrounding nitrogen atoms in porphyrin-like graphene, and its orbitals could be more involved in the adsorption process of a gas molecule.

#### Charge Density Differences and Density of States.

We now analyze the changes in charge density distributions in the process of capturing gas molecules on TM-porphyrin-like graphene. The charge density difference is defined by \( \Delta \rho = \rho_{\text{gas–substrate}} - \rho_{\text{substrate}} - \rho_{\text{gas}} \), where \( \rho_{\text{gas–substrate}}, \rho_{\text{substrate}}, \) and \( \rho_{\text{gas}} \) denote the charge densities of gas-adsorbed TM-porphyrin-like graphene complex, TM-porphyrin-like graphene alone, and an isolated gas molecule, respectively. The results for Sc-porphyrin-like graphene under the mechanical strain of −2% are illustrated in Figure 3. One can see in Figure 3a that the domain of the largest charge depletion observed near a TM atom accompanies the largest charge accumulation region near the bottom side of \( \text{CO}_2 \), indicating some hybridization of TM orbitals with \( \text{CO}_2 \) orbitals. The charge density difference in the case of \( \text{N}_2 \) adsorption shows that the charge accumulation below \( \text{N}_2 \) is correlated with the charge depletion proximal to a TM atom, yet the depletion is smaller in magnitude when compared to the \( \text{CO}_2 \) case (see Figure 3b). Figure 3c shows the charge density difference for \( \text{CH}_4 \) adsorption on TM-
decorated porphyrin-like graphene, displaying charge accumulation under a methane molecule and a much smaller depletion near the TM atom than CO₂ and N₂ adsorption. In Figure 3d, an adsorbed hydrogen molecule is observed to cause charge accumulation to the direction of the TM atom and a nearly invisible charge shortage near the TM atom, which is understood to be due to the well-known Kubas interaction.⁴⁴ Considering that the d orbitals near the TM atom are the most active for CO₂ capture when compared to the adsorption of the other gases, we understand that the Dewar interaction is a dominant mechanism for CO₂ capture on TM-decorated porphyrin-like graphene even under mechanical strain.

For further analysis of the orbital properties near a TM atom and CO₂, we present in Figure 4 the density of states for a Sc
atom and a CO₂ molecule in the CO₂–Sc-porphyrin-like graphene complex, where one can identify an overlap between d orbitals of Sc and π-orbitals of CO₂ near -1.6 and +1.6 eV. This means that there exists an evident hybridization between d orbitals of a Sc atom and π-orbitals of CO₂, which accounts for the charge density difference shown in Figure 3a. The analysis of the charge density distributions and the density of states confirms that CO₂ capture on TM-porphyrin-like graphene takes place due to the Dewar interaction, which was first reported in our previous study for CO₂ capture on strainless TM-porphyrin-like graphene.

**CO₂ Capture Capacity and Selectivity.** To examine the feasibility of controlling the CO₂ capture process with mechanical strain, we estimated the thermodynamic CO₂ capture capacity. To define the capture capacity at a certain mechanical strain of X%, we start from the grand-canonical partition function

\[
Z(X) = \left[ 1 + \sum_{i} \sum_{n_i=1} g_n \exp \{n_i (\mu'_i - \epsilon'_{\text{di}}(X)/k_B T) \} \right]^{N_i} \tag{1}
\]

where \(g_n\) denotes the degeneracy of the configurations with \(n_i\) adsorbed gas molecules of type i.\(^{34,45}\) While \(N_i\) is the number of distinguishable adsorption sites on the system, \(\mu'_i\) and \(\epsilon'_{\text{di}}(X)\) represent the chemical potential (<0) of the i-type gas and its average adsorption energy (<0) under the mechanical strain of X%, respectively. Because we assume that only one molecule can be adsorbed per adsorption site, neither mixed adsorptions of different molecules nor multiple adsorptions of the same molecule are considered, that is, \(g_n = 1 = n_i = 1\), which is a reasonable assumption because we deal with gas molecules, including CO₂, at low pressures less than 1 bar. Then, the thermally averaged number of adsorbed i-type gas molecules at the mechanical strain of X% can be derived from

\[
\langle N_i \rangle = k_B T \frac{\partial \ln Z(X)}{\partial \mu'_i} \tag{2}
\]

Therefore, the mean CO₂ occupancy per adsorption site can be written as

\[
f_{\text{CO}_2}(X, T) = \frac{N_{\text{CO}_2}}{N_i} = \frac{\exp[(\mu'_{\text{CO}_2} - \epsilon'_{\text{di}}(X))/k_B T]}{1 + \sum \exp[(\mu'_i - \epsilon'_{\text{di}}(X))/k_B T]} \tag{3}
\]

From this, the thermodynamic CO₂ capture capacity of the TM-porphyrin-like graphene at a certain mechanical strain of X% for a mixed gas can be set up as

\[
C(X, T) = \frac{N_f f_{\text{CO}_2}(X, T)}{\sum M_i m_i} \tag{4}
\]

where \(M_i\) and \(m_i\) are an atomic mass and the number of each element in the substrate, respectively.

Using the first-principle DFT calculations, we computed the adsorption energy of each gas molecule captured on the substrate, which is defined by

\[
\epsilon'(X) = E_i - \epsilon_{\text{substrate}}(X) - E_{\text{substrate}}(X) - E_i \tag{5}
\]

here, \(E_{\text{substrate}}(X)\) and \(E_{\text{substrate}}(X)\) correspond to the total energies of a gas–substrate complex and a TM-porphyrin-like graphene at the mechanical strain of X%, while \(E_i\) is the energy of an i-type gas molecule. Figure 5 shows our DFT results of the adsorption energy for each gas molecule captured on the substrate. For all TM atoms considered in this study, the CO₂ adsorption energy is observed to decrease steadily as the mechanical strain to the substrate changes from a tension to a compression. This indicates that as the distance between a decorated TM atom and the four nitrogen atoms in the graphene sheet increases with compressive strain, its d orbitals are more activated for hybridization with CO₂ π-orbitals to result in stronger Dewar interaction.
Figure 5a shows the adsorption energies of different flue-gas molecules captured on Sc-porphyrin-like graphene under mechanical strain. Like CO$_2$, H$_2$, CH$_4$, and N$_2$ molecules are seen to have lower adsorption energies with stronger compressional mechanical strain. We note that the adsorption energy curves of CO$_2$ (red) and N$_2$ (blue) have an intersection point at the mechanical strain of +1.5%, below which the CO$_2$ adsorption energy is lower than the adsorption energy of N$_2$.

Figure 5b exhibits the adsorption energies of the flue gases as a function of the mechanical strain to the Ti-decorated substrate. This figure shows that CO$_2$ has the lowest adsorption energy among the flue-gas molecules over the whole range of the mechanical strain considered here. In addition, the CO$_2$ adsorption energy is found to vary depending on the strength of applied mechanical strain, while those of the other molecules do not. The adsorption energies of gases captured on V-porphyrin-like graphene are displayed in Figure 5c, where the adsorption energy of CH$_4$ hardly changes but the ones of the other gas molecules decrease monotonically with the CO$_2$ adsorption energy showing the largest decrease, as the mechanical strain changes from +3 to −3%. Interestingly, CO$_2$ is observed to have higher adsorption energies than N$_2$ in the whole range of the mechanical strain considered here for V-porphyrin-like graphene. This suggests that regardless of the magnitude of the applied mechanical strain, N$_2$ adsorption would be favored over CO$_2$ adsorption on the V-porphyrin-like graphene under our flue-gas models where the chemical potential of CO$_2$ is lower than that of N$_2$ (see Table 1).

Figure 6 exhibits our results for the CO$_2$ capture capacity C(X, T) of TM-porphyrin-like graphenes, which were estimated using eq 4, for the three flue-gas models as functions of the mechanical strain to the substrate. In Figure 6a, one can...
see the dependence of the CO$_2$ capture capacity of Sc-decorated porphyrin-like graphene on the applied mechanical strain. In the oxy-fuel and precombustion compositions, the CO$_2$ capture capacity shows similar values of $\sim 2.33$ and $\sim 2.40$ mmol/g for $-3$ to $0$% strain with very little strain dependence, whereas they drastically fall to $\sim 0.11$ and $\sim 0.18$ mmol/g within the range of $0$ to $+3$% strain. In the postcombustion composition, the CO$_2$ capture capacity follows a similar trend, with near complete depletion at $+2$% strain from the value of $\sim 2.15$ mmol/g at $-2$% strain. One can see in Figure 6b that Ti-decorated porphyrin-like graphene has the CO$_2$ capture capacity of $\sim 2.42$ mmol/g, regardless of our flue-gas composition, for the entire range of the mechanical strain considered here. However, the CO$_2$ capture capacity on V-decorated porphyrin-like graphene is seen in Figure 6c to be definitely impacted by the flue-gas composition. The oxy-fuel composition shows the maximum CO$_2$ capture capacity of $\sim 0.61$ mmol/g at $-3$% strain, and it gradually decreases for $-3$ to $-0.5$% strain until it reaches $0$ mmol/g for $-0.5$ to $+3$% strain. On the other hand, the precombustion model has a CO$_2$ capture capacity of $\sim 2.42$ mmol/g below the $+0.5$% strain, beyond which it decreases abruptly and falls to $\sim 0$ mmol/g at $+2$% strain. Lastly, the postcombustion flue gas shows a fixed CO$_2$ capture capacity of $\sim 0$ mmol/g for the entire range of mechanical strain. Thus, among the three different substrates, Sc- and V-decorated porphyrin-like graphene have controllability of CO$_2$ capture with the mechanical strain, whereas the CO$_2$ capture capacity of Ti-porphyrin-like graphene shows no dependence on the mechanical strain.

To examine the selectivity of CO$_2$ capture from flue gases with our model compositions, we now consider the differences between chemical potentials of flue gases and their adsorption energies on a TM-porphyrin-like graphene

$$\Delta(X) = \mu - \epsilon(X)$$

Figure 6. CO$_2$ capture capacities of TM-porphyrin-like graphenes decorated with three different TM atoms of (a) Sc, (b) Ti, and (c) V as functions of the mechanical strain, which were estimated under our three flue-gas models of oxy-fuel (black), precombustion (red), and postcombustion (blue).
Thermodynamically, CO$_2$ capture is more dominant than adsorption of other gas molecules on a certain substrate when $\Delta$CO$_2$($X$) is larger than $\Delta$other($X$). In this regard, we set region (i) for $\Delta$CO$_2$ > $\Delta$other and region (ii) for $\Delta$CO$_2$ < $\Delta$other. Figure 7 presents our results for $\Delta$CO$_2$($X$) on Sc- and V-decorated porphyrin-like graphenes under the mechanical strain of |$X$%|. We here omit the discussion of $\Delta$CO$_2$($X$) for the Ti-decorated substrate because the substrate does not show controllable capability of CO$_2$ capture with the applied mechanical strain as seen in Figure 6. For the Sc-decorated substrate, the precombustion system shows a region (i) of $\Delta$CO$_2$ > $\Delta$other for the full range of mechanical strain, while region (i) appears at mechanical strain below +1% for the oxy-fuel and below −1% for the postcombustion model (see Figure 7a). For the V-decorated substrate, the precombustion model shows region (i) below +2.5% of the mechanical strain, whereas the oxy-fuel and the postcombustion models manifest no region (i) for the entire range of the mechanical strain considered here.

Our results for $\Delta$(X, T) presented in Figure 6 show that the CO$_2$ capture capacity on Sc- and V-decorated porphyrin-like graphenes could be controlled with the application of mechanical strain, while the CO$_2$ capture on the Ti-decorated substrate could not. Because selective CO$_2$ capture from flue gases could be realized in region (i) defined above, the controllable CO$_2$ capture capacity with mechanical strain is defined by the difference between the maximum CO$_2$ capture capacity and the minimum capacity in region (i). According to Figure 7, the Sc-decorated substrate shows the controllable CO$_2$ capture capacity of ~1.43 mmol/g for the oxy-fuel, ~2.22 mmol/g for the precombustion, and ~1.25 mmol/g for the postcombustion gas model, whereas the respective values for the V-decorated substrate are ~0, ~2.42, and ~0 mmol/g. As summarized in Table 2, the precombustion gas system shows the maximum selective controllable CO$_2$ capture capacity on Sc- and V-decorated porphyrin-like graphenes. On the other hand, the oxy-fuel and the postcombustion flue-gas models exhibit controllability of selective CO$_2$ capture with mechanical strain only on the Sc-decorated substrate.

The above CO$_2$ capture capacities of the TM-porphyrin-like graphenes were obtained for flue gases under the pressure of 1 bar at a temperature of 298 K. For all our flue-gas models, the CO$_2$ capture capacities are found to significantly decrease when the temperature increases to 473 K, but they show small increases with the pressure increasing to 2 bar. The controllable CO$_2$ capture capacities predicted for the TM-porphyrin-like graphenes with the application of mechanical strain are only about a half of the capture capacity of ~4.3 mmol/g reported for N-doped porous carbon via the chemical activation of polypyrrole/graphene composites using potassium hydroxide solution. Practical significance of our DFT results lies in the fact that they could be achieved through the selective capture process of CO$_2$ from mixed flue gases without any thermodynamic combustion. First-principle DFT calculations are known to have some limitation in estimating the CO$_2$ adsorption energy accurately. Especially, the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) scheme we used for the exchange correlation functional tends to underestimate the adsorption energy of a molecule on a substrate because of its inability of describing weak van der Waals interaction. This suggests that the

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Difference between the gas chemical potential of i-type molecule and its adsorption energy, $\Delta_i(X) = \mu_i - \epsilon_i(X)$, on (a) Sc- and (b) V-porphyrin-like graphenes for each flue-gas model as a function of the mechanical strain $X$%. Red, yellow, olive, and blue symbols represent $\Delta_i(X)$ of CO$_2$, H$_2$, CH$_4$, and N$_2$ for each model composition, respectively.

| Model                | oxy-fuel | precombustion | postcombustion |
|----------------------|----------|---------------|----------------|
| Sc                   | 1.43     | 2.22          | 1.25           |
| V                    | 0        | 2.42          | 0              |

*The capture capacities are in units of mmol/g.

| Model                | oxy-fuel | precombustion | postcombustion |
|----------------------|----------|---------------|----------------|
| Sc                   | 1.43     | 2.22          | 1.25           |
| V                    | 0        | 2.42          | 0              |

Table 2. Controllable CO$_2$ Capture Capacities of Sc- and V-Decorated Porphyrin-like Graphenes for Our Flue-Gas Models
actual CO₂ capture capacities of TM-porphyrin-like graphenes could be higher than the values reported in this paper.

**Substrate Bending Effects.** As discussed above, the distance between a decorated TM atom and the graphene sheet increases when a compressive mechanical strain is applied to a TM-porphyrin-like graphene. This allows d orbitals of a TM atom to be more activated for hybridization with CO₂ π-orbitals, resulting in the lowering of the CO₂ adsorption energy due to stronger Dewar interaction. In addition to the increase of the TM—substrate distance, actual application of compressive strain could cause some bending of the graphene surface. To investigate the effects of substrate bending on the CO₂ capture process, we performed additional first-principle DFT calculations for the adsorption of flue gases on Sc-porphyrin-like carbon nanotubes (CNTs) with various curvatures.

Figure 8 presents the adsorption energy of each flue gas depending on the curvature of the CNT substrate. As can be seen, the adsorption energies of CH₄ and H₂ change very little with the increase in substrate bending from graphene to (8,0) CNT, where they show similar values around ~0.3 and ~0.2 eV, respectively. On the other hand, one can observe a clear trend that both CO₂ and N₂ adsorption energies get lower as the substrate bends from graphene to (8,0) CNT. But they have significantly higher values on smaller (6,0) and (4,0) CNTs than on (8,0) CNT. It is found that the CO₂ adsorption energy has the highest value of ~0.53 eV on (4,0) CNT and the lowest value of ~0.94 eV on (8,0) CNT.

Our DFT results for the flue-gas adsorptions on Sc-porphyrin-like CNTs have shown that the bending of carbon substrates tends to lower the adsorption energies of CO₂ and N₂ between a flat graphene surface and (8,0) CNT. Since TM-porphyrin-like graphene substrate could bend under compressive strain as noted above, these results indicate that as a result of substrate bending, the CO₂ adsorption energies under compressive strain could be lower than the values presented in Figure 5. This would result in higher CO₂ capture capacities than the ones predicted in Table 2. Sudden decrease in the magnitudes of CO₂ and N₂ adsorption energies on (6,0) and (4,0) CNT substrates is understood to be due to the fact that carbon atoms other than those adjacent to nitrogen atoms forming a porphyrin-like structure, even those located on the opposite side of the TM atom on the CNT surface, could affect the adsorption on the CNT substrates with small radii. This suggests that the adsorption processes of flue gases on TM-porphyrin-like CNT substrates smaller than the (8,0) CNT cannot be understood purely by the substrate bending effects.

**CONCLUSIONS**

We performed first-principle DFT calculations for CO₂ capture on Sc-, Ti-, and V-decorated porphyrin-like graphenes under mechanical strain to explore the feasibility of controlling the capture process at room temperature under low pressures. Application of compressive strain to a TM-porphyrin-like graphene was found to increase the distance between the decorated TM atom and the graphene sheet, which allowed d orbitals of the TM atom to be more activated for hybridization with CO₂ π-orbitals and resulted in the lowering of the CO₂ adsorption energy due to stronger Dewar interaction. From this, we discovered that TM-porphyrin-like nanostructures could selectively capture CO₂ molecules with compressive strain and release them under tensional strain. While the Ti-decorated porphyrin-like graphene did not show controllability of CO₂ capture with mechanical strain, the Sc- and V-decorated substrate exhibited significant CO₂ capture controllability. These results lead us to conclude that nanostructures containing TM elements with empty d orbitals can be applied to control selective CO₂ capture from flue gases with mechanical strain.

Bending effects of the graphene substrate under compressive strain were investigated through DFT calculations of the adsorption energies of flue gases on TM-porphyrin-like CNTs with various curvatures. Both CO₂ and N₂ adsorption energies were found to lower significantly with the increase in the substrate curvature from graphene to (8,0) CNT, while the adsorption energies of other flue gases such as CH₄ and H₂ showed little dependence on CNT curvature. From this, we expect that a possible bending of the substrate under compressive strain would make the control of selective CO₂ capture process from flue gas with mechanical strain more feasible. The first-principle results discussed in this study have the potential for use in the development of a new approach to engineer controlling media for CO₂ capture at room temperature by applying mechanical strain without the thermodynamic process of combustion. Experimental realization of this new approach for CO₂ capture could be expedited by recent development in strain engineering as demonstrated for graphenes and nanowires suspended over a trench.

**COMPUTATIONAL METHODS AND DETAILS**

Our first-principle DFT calculations were performed as implemented in the Vienna ab initio simulation package with the projector augmented wave method. The GGA-PBE exchange correlation functional was used, and the kinetic energy cutoff was taken to be 900 eV. For calculations of gas molecule adsorption on a substrate, the model substrate of the graphene-based system comprised a 4 × 4 hexagonal supercell,
whose composition was TM-N\textsubscript{4}C\textsubscript{26}. Geometrical optimization of the graphene-based system was carried out until the Hellmann–Feynman force acting on each atom was less than 0.01 eV/Å. The first Brillouin zone integration was performed using the Monkhorst–Pack scheme. A 2 × 2 k-point sampling was used for the 4 × 4 graphene supercells.

Biaxial mechanical strain was uniformly applied to the TM-decorated porphyrin-like graphene. The range of strain we considered was +3% (extension) to −3% (compression) with 0.5% regular intervals in all directions. It was assumed that only one molecule could be captured on the central metal in a unit cell.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This paper was supported by the Basic Science Research Program (2015R1D1A1A09056745) through the National Research Foundation of Korea funded by the Ministry of Education and was written as part of Konkuk University’s research support program for its faculty on sabbatical leave in 2018. We also acknowledge the support from the Supercomputing Center/Korea Institute of Science and Technology Information with supercomputing resources including technical support (KSC-2016-C-3-001).

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