

Conversion of CO₂ into Formic Acid on Transition Metal-Porphyrin-like Graphene: First Principles Calculations

Seunghan Lee, Hyeonhu Bae, Amit Singh, Tanveer Hussain, Thanayut Kaewmaraya, and Hoonkyung Lee*



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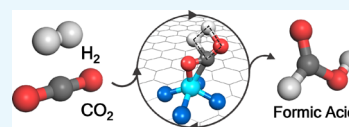


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ABSTRACT: Recently, transition metal (TM)-porphyrin-like graphene has been predicted to be a promising material for CO₂ capturing under favorable conditions. Such materials can capture CO₂ at 300 K and release it at 450 K. However, the captured CO₂ gas is mostly stored in oceans. With the aid of first principles calculations, we herein propose a method in which the captured CO₂ is converted into an environmentally friendly product, formic acid. Addition of H₂ to CO₂ molecules adsorbed on Sc- and Ti-porphyrin-like graphene was found to catalyze this conversion. We also performed nudged elastic band calculations and thermodynamic analysis using the first-order Polanyi–Wigner equation and equilibrium statistical mechanics to investigate the chemical reactions involved in this conversion. In addition, we performed Bader charge analysis to obtain insights into the mechanism of charge transfer and adsorption throughout the conversion. Our study presents a novel method in which the captured CO₂ is treated by converting it into an environmentally friendly product. Since this method does not require CO₂ storage, it is expected to be an effective strategy to manage the rising CO₂ level in the environment.



1. INTRODUCTION

Carbon dioxide (CO₂), a greenhouse gas, is the main cause of global warming.^{1–4} The global surface temperature has increased significantly in recent years because of the drastic increase in CO₂ emissions, and the combustion of fossil fuels contributes significantly to this. As an essential step toward mitigating the climate change, considerable efforts have been made to develop technologies for collecting CO₂ from flue gases.¹ The conventional methods for capturing CO₂ from flue gases rely heavily on the use of aqueous ammonia.^{5–7} However, this approach suffers from poor solvent regeneration and corrosion due to the toxic nature of the amine solution.^{8–10}

Recently, nanostructures or porous materials such as graphene, zeolites, and metal–organic frameworks have gained significant attention as CO₂ capturing materials because of the high regeneration of CO₂ gas through its physisorption on the material surface^{11–21} and the high capacity of the materials due to their large surface area (e.g., ~2600 m²/g for graphene).²² However, their capture capacity significantly reduces under ambient conditions such as room temperature and atmospheric CO₂ pressure because of the low binding energy of CO₂ (approximately few tens of meV per CO₂ molecule) to these materials. Moreover, the selectivity of CO₂ from flue gases toward these materials is poor,^{20–23} and this largely hinders their use in CO₂ capture from flue gases.²³

More recently, through computational high-throughput screening based on first principles thermodynamics,^{24–26} metal-porphyrin-like graphene and Ca-decorated nanoribbons were shown to capture CO₂ from flue gases under ambient

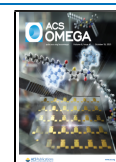
conditions.^{24–26} They could selectively capture CO₂ from other ambient gases such as H₂, N₂, and CH₄, with a CO₂ capture capacity of ~3 mmol/g.^{24–26} The Ca atoms and d orbitals of transition metals (TMs) have a predominant contribution to the binding of CO₂ during its capture.^{27–31} Meanwhile, transition metal-porphyrin-like graphene is synthesized in experiments.³² Therefore, metal-porphyrin-like graphene materials can serve as a promising reversible CO₂ capture material. However, storage of CO₂ in oceans and ground is still a matter of concern because of the high cost of CO₂ storage after its release on Sc- and Ti-porphyrin-like graphene.

Herein, we present a first principles study of a novel method for treating CO₂ following its capture. The proposed method converts CO₂ on metal-porphyrin-like graphene to formic acid (HCOOH) by adding H₂ as shown in Figure 1, which is slightly acidic and harmless; that is, it is environmentally friendly.^{33–37} CO₂ storage in oceans and ground can thus be avoided, resulting in easier management of the captured CO₂. Our results show that the addition of H₂ molecules to the CO₂ molecule adsorbed on the TM atom led to the formation of formic acid. The d orbitals of the TM atoms play a role in catalyzing the reaction between CO₂ and H₂ to form formic

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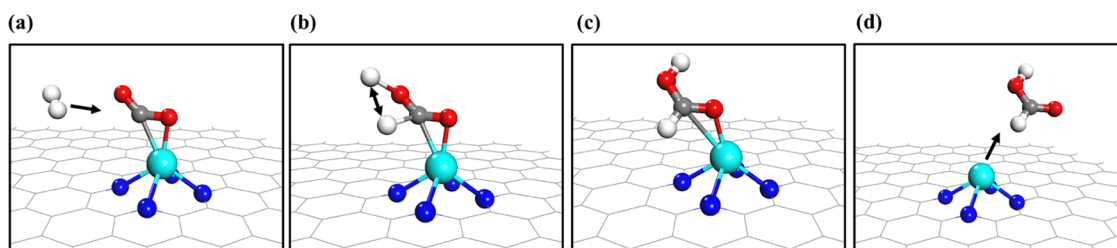


Figure 1. Schematic for the consecutive reaction of CO₂ adsorbed on TM-porphyrin-like graphene to produce HCOOH upon addition of H₂. (a) The H₂ molecule approaches the CO₂ molecule adsorbed on the TM-porphyrin-like graphene. (b) H₂ is dissociatively adsorbed on the TM atom. (c) The product of the reaction between H₂ with CO₂ on the TM atom is HCOOH. (d) Release of the HCOOH molecule adsorbed on TM-porphyrin-like graphene.

acid. This provides a novel framework for converting CO₂ into environmentally friendly products, without the need for a CO₂ storage process. Furthermore, formic acid has different uses in the form of food preservation additives, preservatives, and antibacterial agents and in dyeing and processing of leather and rubber. The conversion of CO₂ into formic acid and its derivatives³³ or CO₂ conversion for fuel cells and hydrogen storage has already been studied.^{34–37}

2. RESULTS AND DISCUSSION

To investigate the possibility of conversion of CO₂ into formic acid on TM-porphyrin-like graphene, we performed the first principles calculations of CO₂ adsorption on Sc- and Ti-porphyrin-like graphene. CO₂ adsorption on TM results in the formation of the η^2 – CO₂ structure through Dewar interaction.²⁷ The TM-promoted reaction pathway of CO₂ and H₂ to form formic acid was obtained using the NEB method.^{38–42} The process by which the Sc and Ti atoms participate in this reaction can be divided into four stages involving four intermediate states. Each step was investigated with various trial coordinates. Here, we assume that the real process occurs in an energy surface, which corresponds to the minimum energy path for reaction. Thus, the minimum energy path of CO₂ conversion that we presented in our paper is the most probable process in experiments.

When CO₂ is adsorbed on the TM atom, it may adopt three configurations depending on the number of bonds. Based on hapticity, these three configurations can be classified as η^1 , η^2 , and η^3 as shown in Figure 2a–c. In the case of the Sc atom, CO₂ has the strongest binding in the η^2 mode formed using two bonds, with a binding energy of 0.75 eV. Meanwhile, in the case of the Ti atom, the largest binding energy of 1.09 eV was observed in the η^2 mode. This suggests that CO₂ binds to Sc- and Ti-porphyrin-like graphene by adopting the η^1 configuration.

We added H₂ molecules to the CO₂-adsorbed Sc-porphyrin-like graphene to obtain the optimized geometry upon adsorption. The distance between the Sc atom and H₂ molecule was 3.41 Å, and the bond length was 0.75 Å. Moreover, formic acid could be generated from this configuration (Figure 1a). We performed the NEB calculations to investigate the energy barrier for the conversion of CO₂ and H₂ to formic acid on the Sc atom. Four transition states (TS1, TS2, TS3, and TS4) and five metastable states were found for this conversion (Figure 2d). The energy barriers corresponding to TS1, TS2, TS3, and TS4 were 13.5, 1.1, 10.5, and 9.0 kcal/mol, respectively. There were four intermediates (IM1, IM2, IM3, and IM4) corresponding to these transition states. For TS1, the H₂ molecule is dissociated to HCOOH@Sc, in which

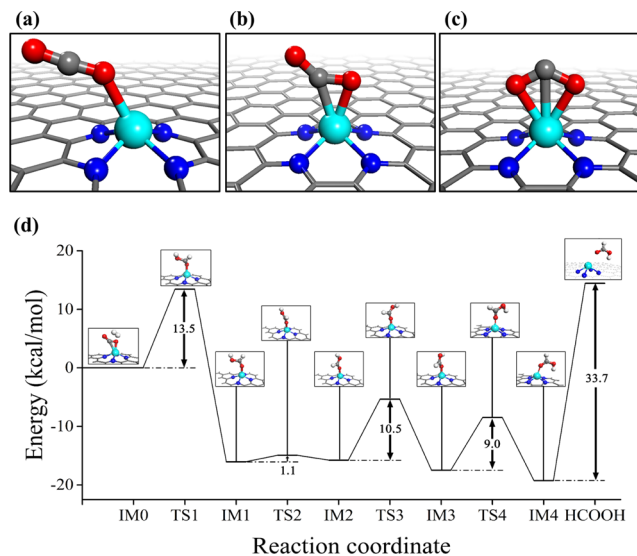


Figure 2. (a–c) Optimized atomic structures of CO₂ binding to TM-porphyrin-like graphene with η^1 , η^2 , and η^3 configurations, respectively. (d) Calculated reaction energy of H₂ dissociation on CO₂ on Sc-porphyrin-like graphene to afford HCOOH obtained using the NEB method. Four transition states and five metastable states exist in the reaction pathway for the conversion of H₂ and CO₂ to HCOOH on Sc-porphyrin-like graphene.

the distance between the H atoms is 2.12 Å. Formic acid was generated with a net energy barrier of 33.7 kcal/mol, via the formation of four transition states and five intermediates (Figure 2d).

In Sc-porphyrin-like graphene, first, the H₂ molecule dissociates into two hydrogen atoms that bind to a carbon atom and an extra oxygen atom that is not involved in TM binding. The bound CO₂ combines with a H₂ molecule to adopt the η^1 – CO₂ configuration, eventually driving the binding reaction to generate formic acid via several stages. The NEB calculations confirmed that there were five steps in this reaction (Figure 2d). The H₂ molecule adjacent to CO₂ binds to the C and O atoms that do not participate in the η^2 bond formation. The energy barrier of this reaction is ~13.5 kcal/mol according to the NEB calculations. The step with the highest activation energy barrier according to the Arrhenius equation is the rate-determining step of the overall reaction; the other steps do not contribute to the overall rate of the reaction.

We next investigated the conversion of CO₂ into formic acid on Ti-porphyrin-like graphene. CO₂ was adsorbed on the Ti atom with a binding energy of 1.09 eV, and the distance

between CO₂ and the Ti atom was 2.06 Å. We performed NEB calculations to identify the TS and IM states between CO₂@Ti (initial state) and HCOOH + Ti (final state). Four TS and five IM states were also found between the initial and final states (Figure 3). The dissociation of CO₂ is similar to that on Sc-porphyrin-like graphene.

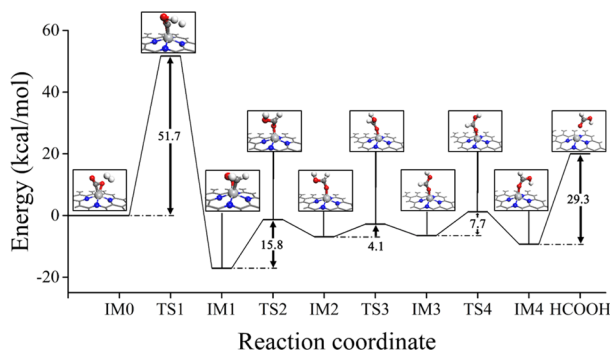


Figure 3. Calculated reaction energy of H₂ dissociation on CO₂ on Ti-porphyrin-like graphene to afford HCOOH obtained using the NEB method. Four transition states and five metastable states exist in the reaction pathway for the conversion of H₂ and CO₂ to HCOOH on Ti-porphyrin-like graphene.

Now, we calculated the escape time from the initial state (IM0) to the first intermediate state (IM1) to investigate the practical conditions of the conversion because the step with the highest activation energy barrier is the rate-determining step of the overall reaction (Figure 4a), while the other steps do not contribute to the overall rate of the reaction. Using the first-order Polanyi–Wigner equation,⁴³ adsorption coverages (θ) between the two states in time t are expressed as

$$\frac{d\theta_1}{dt} = -k\theta_1 \quad (1)$$

$$\frac{d\theta_2}{dt} = k\theta_1 \quad (2)$$

where i and k indicate the index for representing the states ($i = 1$ for the initial state and $i = 2$ for the first intermediate state) and reaction rate constant, i.e., the frequency of collisions resulting in a reaction, respectively. The rate is expressed as follows by the Arrhenius equation

$$k = \nu e^{-E_a/k_B T} \quad (3)$$

where ν , k_B , and T denote the trial frequency, Boltzmann constant, and temperature, respectively.

$$\theta_1(t) = \theta_0 e^{-kt} \quad (4)$$

$$\theta_2(t) = \theta_0(1 - e^{-kt}) \quad (5)$$

where θ_0 indicates the initial value of the coverage at the initial state.

The calculated coverage for given temperatures is shown in Figure 4b, where the trial frequency is chosen to be 0.5 THz. The characteristic time for escape is from a few seconds to a few microseconds. From this result, we suggest that a suitable experiment condition for the conversion is ~ 300 to 500 K.

To achieve the conversion of CO₂ to HCOOH, HCOOH attached to Sc or Ti should be released. Here, we carried out the evaluation of the desorption of HCOOH in equilibrium between the HCOOH molecule attached to Sc or Ti and HCOOH gas using the grand partition function. The fractional occupancy for the adsorption site, $f(P, T)$, is expressed by the formula²⁴

$$f(P, T) = \frac{e^{(\mu(P, T) - E_{\text{ads}})/k_B T}}{1 + e^{(\mu(P, T) - E_{\text{ads}})/k_B T}} \quad (6)$$

where P , $\mu(P, T)$, and E_{ads} indicate the pressure of a gas, chemical potential of a gas at a given P and T , and adsorption energy, respectively. The chemical potential of HCOOH gas was parameterized by the following formula

$$\mu_{\text{real}}(P, T) = \mu_{\text{ideal}}(P, T) + (A + B \times T) \quad (7)$$

where $\mu_{\text{ideal}}(P, T)$ denotes the chemical potential of the ideal gas model and constants A and B in a linearized excess part are 0.09350 eV and -1.09233 meV/K for HCOOH with $R^2 = 0.999$ in the range from 1 atm to 1 natm and 200 to 700 K, respectively. A pressure-dependent term in an excess part is negligible in this range. HCOOH molecules are released on Sc- and Ti-porphyrin-like graphene at ~ 500 K and $\sim 10^{-6}$ bar as shown in Figure 5. In addition, we have already shown that the reaction for the conversion of CO₂ to HCOOH gas occurs at easily achievable conditions (Figure 4). Therefore, the activity for the conversion of CO₂ on Sc- and Ti-porphyrin-like graphene can be controlled by varying the temperature.

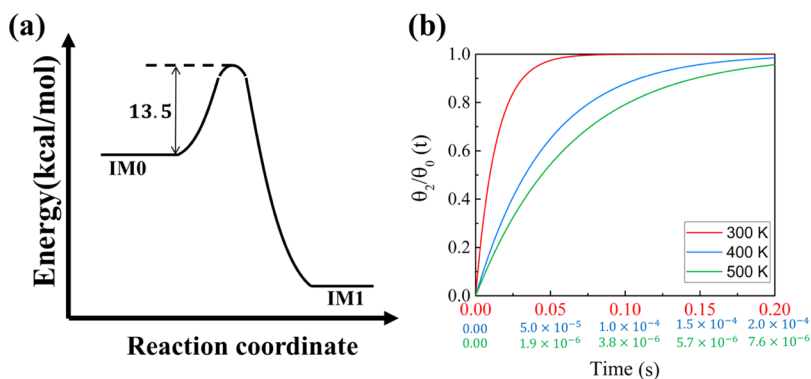


Figure 4. (a) Schematic of the reaction energy of conversion of CO₂ on Sc-porphyrin-like graphene with H₂ to HCOOH, where the value of the activation barrier corresponds to 13.5 kcal/mol (TS1) between the initial state (IM0) and the first intermediate state (IM1) from the NEB calculations (Figure 3). (b) Calculated adsorption coverages as a function of time at 300, 400, and 500 K using eq 5.

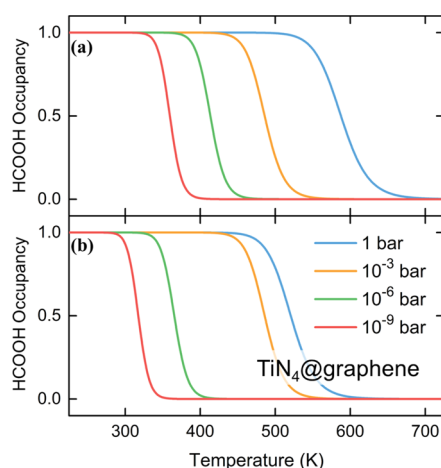


Figure 5. Calculated fractional occupancy of HCOOH on (a) Sc- and (b) Ti-porphyrin-like graphene as a function of temperature at the isobaric process.

We also studied the binding mechanism of formic acid on a TM-porphyrin-like graphene. It was found that the π states of CO_2 and formic acid were significantly involved in hybridization with the d states of Sc and Ti (Figure 6a–d). The charge density in the occupied states and charge density difference are shown in Figure 6e–h. This indicates that the presence of chemical bonding between the CO_2 molecule and Sc and Ti atoms can be explained using the Dewar–Chatt–Duncanson model, which describes TM–organic complexes in terms of electron donation (hybridization of empty TM d states with filled π states) and back donation (hybridization of filled TM d states with empty π states).^{27,28}

We also performed the Bader charge analysis^{44–47} to better understand the charge transfer mechanism throughout the conversion. The positive value indicates that the charge is transferred from the surroundings to the atoms, while a negative value indicates the opposite phenomenon. In the case of Sc-porphyrin-like graphene, CO_2 adsorption results in a charge transfer of -2.33 , -3.44 , 1.97 , and 2.25 electrons for the Sc, C, O^1 , and O^2 atoms, respectively (Figure 7a), while the adsorption of HCOOH results in the charge transfer of -2.34 , -2.58 , 1.93 , 1.99 , -0.13 , and -1.00 electrons for the Sc, C, O^1 , O^2 , H^1 , and H^2 atoms, respectively (Figure 7b). In the case of Ti-porphyrin-like graphene, adsorption of CO_2 results in charge transfer of -2.35 , -2.32 , 1.53 , and 1.87 electrons for the Ti, C, O^1 , and O^2 atoms, respectively (Figure 7c), while the adsorption of HCOOH results in charge transfer of -2.27 , -2.45 , 1.93 , 1.95 , -0.14 , and -1.00 electrons for the Ti, C, O^1 , O^2 , H^1 , and H^2 atoms, respectively (Figure 7d). For both Sc- and Ti-porphyrin-like graphene, the Bader charge transfer analysis suggested that CO_2 was strongly chemisorbed. Further addition of H_2 resulted in the formation of formic acid, which was weakly adsorbed relative to CO_2 , and therefore, the release of formic acid was practically feasible.

3. CONCLUSIONS

We investigated the feasibility of the TM-porphyrin-like graphene-mediated conversion of CO_2 to formic acid using first principles calculations. There were three significant findings in this study: (1) TM atoms aid the conversion of CO_2 into formic acid, (2) the d orbitals play an important role in this conversion, and (3) there are three TS and four IM

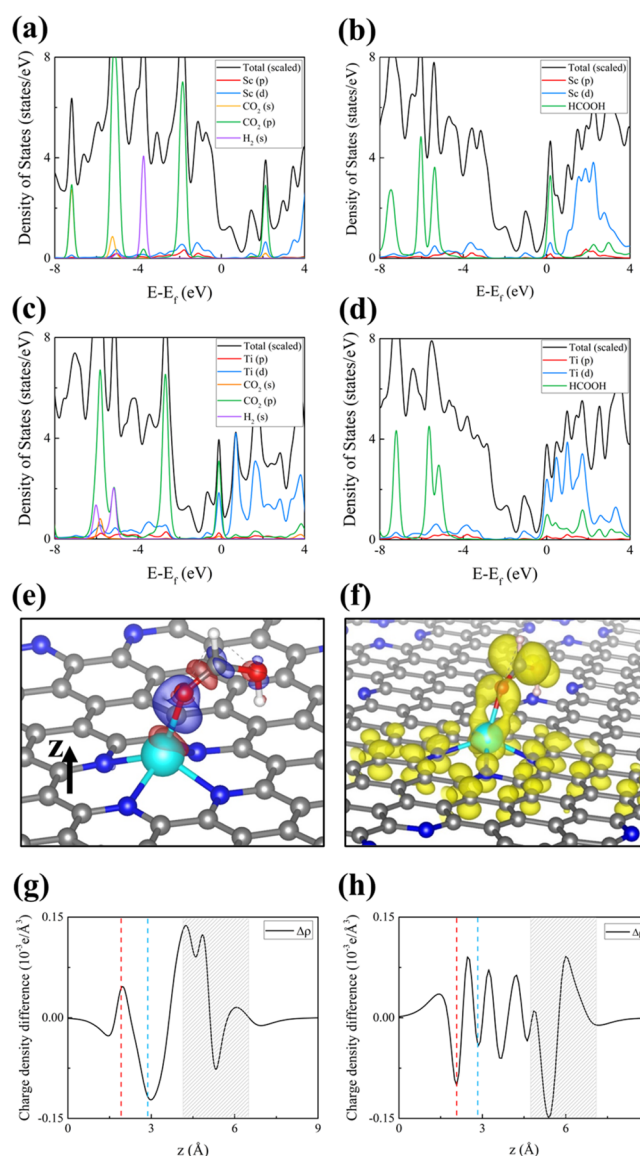


Figure 6. Density of states of Sc- and Ti-porphyrin-like graphene, charge density difference, and charge density at the Fermi level. (a) Projected density of states (PDOS) of CO_2 , H_2 , and Sc of Sc-porphyrin-like graphene. (b) PDOS of HCOOH and Sc of Sc-porphyrin-like graphene. (c) PDOS of CO_2 , H_2 , and Ti of Ti-porphyrin-like graphene. (d) PDOS of HCOOH and Ti of Ti-porphyrin-like graphene. (e) Charge density difference between Sc-porphyrin-like graphene and HCOOH; red and blue colors indicate depletion and accumulation of electrons, respectively. (f) Charge density at the Fermi level of Sc-porphyrin-like graphene with HCOOH; the value of the isosurface is $0.002764 \text{ e}/\text{\AA}^3$. (g) Planar averaged charge density difference along the z direction of Sc-porphyrin-like graphene with HCOOH. (h) Planar averaged charge density at the Fermi level along the z direction of Ti-porphyrin-like graphene with HCOOH. The red and blue dashed lines indicate the position of the graphene and TM atom, respectively. The gray zone indicates the position of HCOOH.

states in this reaction pathway. Our results show that TM-porphyrin-like graphene can be used for the conversion of CO_2 into formic acid upon addition of H_2 . When exposed to H_2 gas, TM-porphyrin-like graphene can capture CO_2 and convert and release it in the form of formic acid. The Bader analysis reveals that CO_2 was strongly chemisorbed, and the addition of H_2

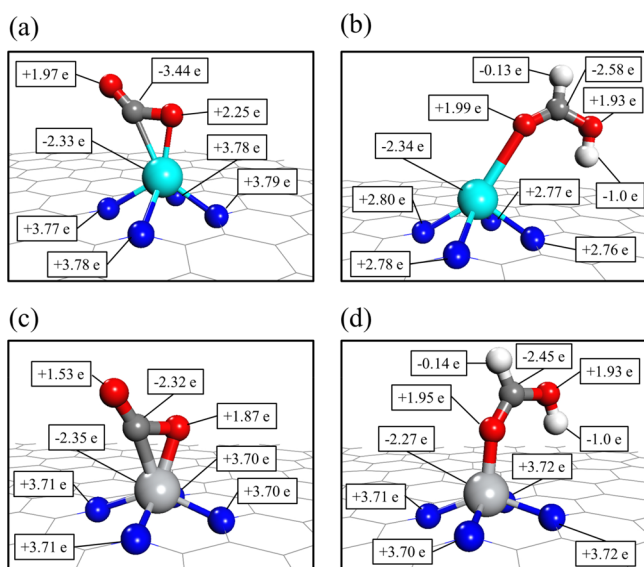


Figure 7. Bader charge analysis for (a) Sc-porphyrin-like graphene with adsorbed CO_2 , (b) Sc-porphyrin-like graphene with adsorbed HCOOH , (c) Ti-porphyrin-like graphene with adsorbed CO_2 , and (d) Ti-porphyrin-like graphene with adsorbed HCOOH . The values mentioned near the atoms indicate transferred charges, e indicates the elementary charge (1.602×10^{-19} C), and + and - signs indicate accumulation and depletion of the electrons, respectively.

resulted in the formation of formic acid, which was relatively weakly adsorbed, thereby assisting the release of formic acid at a feasible temperature. Thus, we conclude that TM-porphyrin-like graphene can selectively capture CO_2 and transform it into formic acid, which is an environmentally friendly compound.

4. COMPUTATIONAL METHODS

We performed first principles density functional theory⁴⁸ calculations using the Vienna Ab Initio Simulation Package (VASP) with the projector augmented wave (PAW)

method^{49,50} for conversion of CO_2 on TM-porphyrin-like graphene adsorption, our model for the TM-porphyrin-like graphene comprised a 4×4 hexagonal supercell (Figure 8), and the composition of the supercell was $\text{C}_{26}\text{N}_4\text{TM}_1$, where C, N, and TM denote carbon, nitrogen, and transition metal atoms, respectively. The kinetic energy cutoff was set at 600 eV to ensure accurate calculations. The structure was geometrically optimized till the Hellmann–Feynman force acting on each atom was less than 0.01 eV/Å. We used $4 \times 4 \times 1$ k-point sampling for each case, and the Brillouin zone integration was performed using the Monkhorst–Pack scheme.⁵¹ There is no dependence of the lattice constant as to the type of TM. Since the strength of the interaction between CO_2 and TM is ~ 1 eV, which is much greater than that of a few meV, we did not consider the van der Waals interaction for the conversion process of CO_2 . The nudged elastic band (NEB) calculations^{52,53} were performed to obtain the transient states between a particular configuration of $\text{CO}_2 + \text{H}_2$ and formic acid.

AUTHOR INFORMATION

Corresponding Author

Hoonkyung Lee – Department of Physics, Konkuk University, Seoul 05029, Korea; orcid.org/0000-0002-6417-1648; Email: hkiee3@konkuk.ac.kr

Authors

Seunghan Lee – Department of Physics, Konkuk University, Seoul 05029, Korea; orcid.org/0000-0002-6932-6362

Hyeonhu Bae – Department of Physics, Konkuk University, Seoul 05029, Korea; orcid.org/0000-0001-7276-6636

Amit Singh – Department of Mechanical Engineering, National Yang Ming Chiao Tung University, Hsinchu 30010, Taiwan; Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan; orcid.org/0000-0003-1005-1779

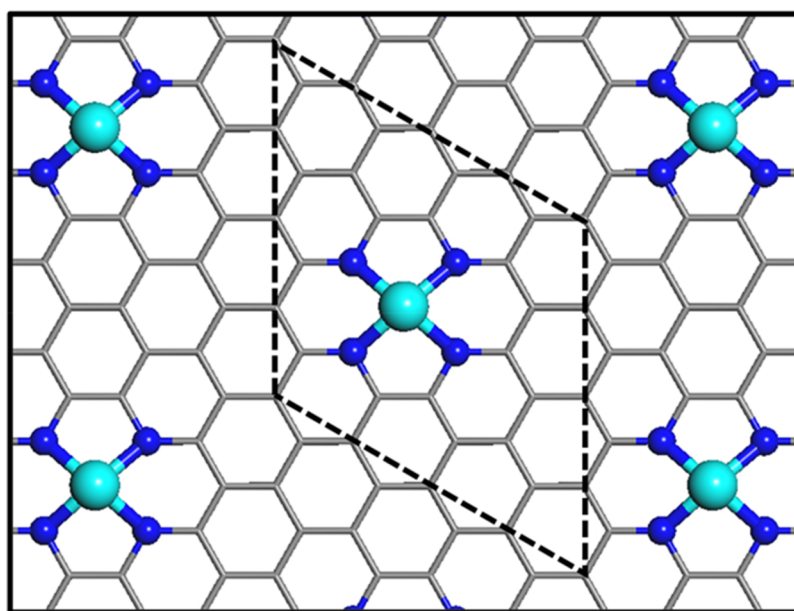


Figure 8. Periodic calculation model for the 4×4 TM-porphyrin-like-graphene. The dotted line indicates the supercell for our calculations with a lattice constant of 9.88 Å.

Tanveer Hussain – School of Chemical Engineering, The University of Queensland, St Lucia 4072, Australia; orcid.org/0000-0002-0300-0503

Thanayut Kaewmaraya – Department of Physics and Institute of Nanomaterials Research and Innovation for Energy (INRIE), NANOTEC -KKU RNN on Nanomaterials Research and Innovation for Energy, Khon Kaen University, Khon Kaen 40002, Thailand; orcid.org/0000-0002-0139-1571

Complete contact information is available at:

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Intergovernmental Panel on the Climate Change (IPCC) *Climate Change 2013 - The Physical Science Basis*. Cambridge Univ. Press 2014, DOI: [DOI: 10.1017/CBO9781107415324](https://doi.org/10.1017/CBO9781107415324)
- (2) Davis, L. W.; Gertler, P. J. Contribution of air conditioning adoption to future energy use under global warming. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, 5962–5967.
- (3) Masson-Delmotte, V.; Zhai, P.; Portner, H.-O.; Roberts, D.; Skea, J.; Shukla, P. R.; Pirani, A.; Moufouma-Okia, W.; Pean, C.; Pidcock, R.; Connors, S.; Matthews, J. B. R.; Chen, Y.; Zhou, X.; Gomis, M. I.; Lonnoy, E.; Maycock, T.; Tignor, M.; Waterfield, T. *Global warming of 1.5°C* 2018.
- (4) Peters, G. P.; Andrew, R. M.; Canadell, J. G.; Friedlingstein, P.; Jackson, R. B.; Korsbakken, J. I.; Le Quéré, C.; Peregon, A. Carbon dioxide emissions continue to grow amidst slowly emerging climate policies. *Nat. Clim. Change* **2020**, 10, 3–6.
- (5) Samanta, A.; Zhao, A.; Shimizu, G. K. H.; Sarkar, P.; Gupta, R. Post-Combustion CO₂ Capture Using Solid Sorbents: A Review. *Ind. Eng. Chem. Res.* **2012**, 51, 1438.
- (6) Han, K.; Ahn, C. K.; Lee, M. S.; Rhee, C. H.; Kim, J. Y.; Chun, H. D. Current status and challenges of the ammonia-based CO₂ capture technologies toward commercialization. *Int. J. Greenhouse Gas Control* **2013**, 14, 270–281.
- (7) Wang, F.; Zhao, J.; Miao, H.; Zhao, J.; Zhang, H.; Yuan, J.; Yan, J. Current status and challenges of the ammonia escape inhibition technologies in ammonia-based CO₂ capture process. *Appl. Energy* **2018**, 230, 734–749.
- (8) Wang, H.; Lustig, W. P.; Li, J. Sensing and capture of toxic and hazardous gases and vapors by metal–organic frameworks. *Chem. Soc. Rev.* **2018**, 47, 4729.
- (9) Cuccia, L.; Dugay, J.; Bontemps, D.; Louis-Louis, M.; Vial, J. Analytical methods for the monitoring of post-combustion CO₂ capture process using amine solvents: A review. *Int. J. Greenhouse Gas Control* **2018**, 72, 138–151.
- (10) Mazari, S. A.; Ghalib, L.; Sattar, A.; Bozdar, M. M.; Qayoom, A.; Ahmed, I.; Muhammad, A.; Abro, R.; Abdulkareem, A.; Nizamuddin, S.; Baloch, H.; Mubarak, N. M. Review of modelling and simulation strategies for evaluating corrosive behavior of aqueous amine systems for CO₂ capture. *Int. J. Greenhouse Gas Control* **2020**, 96, 103010.
- (11) Liu, Y.; Wang, Z. U.; Zhou, H.-C. Recent advances in carbon dioxide capture with metal-organic frameworks. *Greenhouse Gases: Sci. Technol.* **2012**, 2, 239.
- (12) Cinke, M.; Li, J.; Bauschlicher, C. W., Jr.; Ricca, A.; Meyyappan, M. CO₂ adsorption in single-walled carbon nanotubes. *Chem. Phys. Lett.* **2003**, 376, 761.
- (13) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. Carbon Dioxide Capture in Metal–Organic Frameworks. *Chem. Rev.* **2012**, 112, 724.
- (14) Wang, B.; Côté, A. P.; Furukawa, H.; O’Keeffe, M.; Yaghi, O. M. Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs. *Nature* **2008**, 453, 207–211.
- (15) Bezerra, D. P.; Oliveira, R. S.; Vieira, R. S.; Cavalcante, C. L., Jr.; Azevedo, D. C. S. Adsorption of CO₂ on nitrogen-enriched activated carbon and zeolite 13X. *Adsorption* **2011**, 17, 235.
- (16) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O’Keeffe, M.; Kim, J.; Yaghi, O. M. Ultrahigh Porosity in Metal-Organic Frameworks. *Science* **2010**, 329, 424–428.
- (17) Sun, W.; Yeung, M. T.; Lech, A. T.; Lin, C.-W.; Lee, C.; Li, T.; Duan, X.; Zhou, J.; Kaner, R. B. High Surface Area Tunnels in Hexagonal WO₃. *Nano Lett.* **2015**, 15, 4834.
- (18) Kondo, A.; Noguchi, H.; Ohnishi, S.; Kajiro, H.; Tohdoh, A.; Hattori, Y.; Xu, W.-C.; Tanaka, H.; Kanoh, H.; Kaneko, K. Novel Expansion/Shrinkage Modulation of 2D Layered MOF Triggered by Clathrate Formation with CO₂ Molecules. *Nano Lett.* **2006**, 6, 2581–2584.
- (19) Kim, S.; Jinschek, J. R.; Chen, H.; Sholl, D. S.; Marand, E. Scalable Fabrication of Carbon Nanotube/Polymer Nanocomposite Membranes for High Flux Gas Transport. *Nano Lett.* **2007**, 7, 2806–2811.
- (20) Lin, L. C.; Berger, A. H.; Martin, R. L.; Kim, J.; Swisher, J. A.; Jariwala, K.; Rycroft, C. H.; Bhowan, A. S.; Deem, M. W.; Haranczyk, M.; Smit, B. In silico screening of carbon-capture materials. *Nat. Mater.* **2012**, 11, 633–641.
- (21) Liu, H.; Liu, B.; Lin, L.-C.; Chen, G.; Wu, Y.; Wang, J.; Gao, X.; Lv, Y.; Pan, Y.; Zhang, X.; Zhang, X.; Yang, L.; Sun, C.; Smit, B.; Wang, W. A hybrid absorption–adsorption method to efficiently capture carbon. *Nat. Commun.* **2014**, 5, 5147.
- (22) Sorokin, P. B.; Lee, H.; Antipina, L. Y.; Singh, A. K.; Yakobson, B. I. Calcium-Decorated Carbyne Networks as Hydrogen Storage Media. *Nano Lett.* **2011**, 11, 2660–2665.
- (23) Xiang, S.; He, Y.; Zhang, Z.; Wu, H.; Zhou, W.; Krishna, R.; Chen, B. Microporous metal-organic framework with potential for carbon dioxide capture at ambient conditions. *Nat. Commun.* **2012**, 3, 954.
- (24) Bae, H.; Park, M.; Jang, B.; Kang, Y.; Park, J.; Lee, H.; Chung, H.; Chung, C.; Hong, S.; Kwon, Y.; Yakobson, B. I.; Lee, H. High-throughput screening of metal-porphyrin-like graphenes for selective capture of carbon dioxide. *Sci. Rep.* **2016**, 6, 21788.
- (25) Bae, H.; Huang, B.; Lee, H. Steric effects of CO₂ binding to transition metal-benzene complexes: A first-principles study. *Curr. Appl. Phys.* **2016**, 16, 1124–1129.
- (26) Koo, J.; Bae, H.; Kang, L.; Huang, B.; Lee, H. Calcium-decorated carbon nanostructures for the selective capture of carbon dioxide. *Phys. Chem. Chem. Phys.* **2016**, 18, 29086–29091.
- (27) Kubas, G. J. Metal–dihydrogen and σ -bond coordination: the consummate extension of the Dewar–Chatt–Duncanson model for metal–olefin π bonding. *J. Organomet. Chem.* **2001**, 635, 37.
- (28) Mingos, D. M. P. A historical perspective on Dewar’s landmark contribution to organometallic chemistry. *J. Organomet. Chem.* **2001**, 635, 1–8.
- (29) Kim, G.; Jhi, S.-H.; Lim, S.; Park, N. Crossover between multipole Coulomb and Kubas interactions in hydrogen adsorption on metal-graphene complexes. *Phys. Rev. B* **2009**, 79, 155437.
- (30) Hoang, T. K. A.; Antonelli, D. M. Exploiting the Kubas Interaction in the Design of Hydrogen Storage Materials. *Adv. Mater.* **2009**, 21, 1787–1800.

- (31) Anikina, E. V.; Banerjee, A.; Beskachko, V. P.; Ahuja, R. Influence of Kubas-type interaction of B–Ni codoped graphdiyne with hydrogen molecules on desorption temperature and storage efficiency. *Mater. Today Energy* **2020**, *16*, 100421.
- (32) Krishna, M. B. M.; Venkatramiah, N.; Venkatesan, R.; Rao, D. N. Synthesis and structural, spectroscopic and nonlinear optical measurements of graphene oxide and its composites with metal and metal free porphyrins. *J. Mater. Chem.* **2012**, *22*, 3059–3068.
- (33) Leitner, W. Carbon Dioxide as a Raw Material: The Synthesis of Formic Acid and Its Derivatives from CO₂. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2207–2221.
- (34) Rees, N. V.; Compton, R. G. Sustainable energy: a review of formic acid electrochemical fuel cells. *J. Solid State Electrochem.* **2011**, *15*, 2095–2100.
- (35) Luo, Q.; Beller, M.; Jiao, H. Formic acid dehydrogenation on surfaces – A review of computational aspect. *J. Theor. Comput. Chem.* **2013**, *12*, 1330001.
- (36) Yu, X.; Pickup, P. G. Recent advances in direct formic acid fuel cells (DFAFC). *J. Power Sources* **2008**, *182*, 124–132.
- (37) Proietto, F.; Patel, U.; Galia, A.; Scialdone, O. Electrochemical conversion of CO₂ to formic acid using a Sn based electrode: a critical review on the state-of-the-art technologies and their potential. *Electrochim. Acta* **2021**, *389*, 138753.
- (38) Taqui, M. M. T.; Halligudi, S. B.; Shukla, S. Reduction of CO₂ by molecular hydrogen to formic acid and formaldehyde and their decomposition to CO and H₂O. *J. Mol. Catal.* **1989**, *57*, 47–60.
- (39) Choi, H.; Park, Y. C.; Kim, Y.-H.; Lee, Y. S. Ambient Carbon Dioxide Capture by Boron-Rich Boron Nitride Nanotube. *J. Am. Chem. Soc.* **2011**, *133*, 2084–2087.
- (40) Yoo, J. S.; Abild-Pedersen, F.; Nørskov, J. K.; Studt, F. Theoretical Analysis of Transition-Metal Catalysts for Formic Acid Decomposition. *ACS Catal.* **2014**, *4*, 1226–1233.
- (41) Moret, S.; Dyson, P. J.; Laurenczy, G. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. *Nat. Commun.* **2014**, *5*, 4017.
- (42) Kortlever, R.; Peters, I.; Koper, S.; Koper, M. T. M. Electrochemical CO₂ Reduction to Formic Acid at Low Overpotential and with High Faradaic Efficiency on Carbon-Supported Bimetallic Pd–Pt Nanoparticles. *ACS Catal.* **2015**, *5*, 3916–3923.
- (43) Lee, H.; Li, J.; Zhou, G.; Duan, W.; Kim, G.; Ihm, J. Room-Temperature Dissociative Hydrogen Chemisorption on Boron-Doped Fullerenes. *Phys. Rev. B* **2008**, *77*, 235101.
- (44) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A fast and robust algorithm for Bader decomposition of charge density. *Comput. Mater. Sci.* **2006**, *36*, 354–360.
- (45) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. Improved Grid-Based Algorithm for Bader Charge Allocation. *J. Comput. Chem.* **2007**, *28*, 899–908.
- (46) Tang, W.; Sanville, E.; Henkelman, G. A grid-based Bader analysis algorithm without lattice bias. *J. Phys. Condens. Matter* **2009**, *21*, No. 084204.
- (47) Yu, M.; Trinkle, D. R. Accurate and efficient algorithm for Bader charge integration. *J. Chem. Phys.* **2011**, *134*, No. 064111.
- (48) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140*, A1133.
- (49) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758.
- (50) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (51) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188.
- (52) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- (53) Henkelman, G.; Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **2000**, *113*, 9978–9985.