High-throughput screening of metal-porphyrin-like graphenes for selective capture of carbon dioxide

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Nanostructured materials, such as zeolites and metal-organic frameworks, have been considered to capture CO2. However, their application has been limited largely because they exhibit poor selectivity for flue gases and low capture capacity under low pressures. We perform a high-throughput screening for selective CO2 capture from flue gases by using first principles thermodynamics. We find that elements with empty d orbitals selectively attract CO2 from gaseous mixtures under low CO2 pressures (~10−3 bar) at 300 K and release it at ~450 K. CO2 binding to elements involves hybridization of the metal d orbitals with the CO2 π orbitals and CO2−transition metal complexes were observed in experiments. This result allows us to perform high-throughput screening to discover novel promising CO2 capture materials with empty d orbitals (e.g., Sc− or V−porphyrin-like graphene) and predict their capture performance under various conditions. Moreover, these findings provide physical insights into selective CO2 capture and open a new path to explore CO2 capture materials.

Carbon dioxide gas is a greenhouse gas that is a primary cause of global warming, which is known to cause severe climate change1. In recent years, the temperature of the earth has increased because of significant increase in CO2 emission. The emission of this gas is expected to continuously increase as the demand for fossil fuels increases, and thus the development of technologies for CO2 capture is essential for addressing climate change1. The technology involving the capture of CO2 gas from the flue gas is currently not sufficiently developed, particularly in the backdrop of the urgent need to reduce CO2 emission.

Nanostructured materials, such as graphene, zeolites, and metal-organic frameworks, have been considered to capture CO2. These materials are potentially useful because of their high capacity, fast CO2 adsorption kinetics, and effective regeneration2–11. However, their application has been limited largely because they exhibit poor selectivity for flue gases and low capture capacity under low pressures (~10−3 bar)11–14, thereby limiting CO2 capture from flue gases in power plants14. Thus, there is an increasing demand to search for novel CO2 capture materials15–17.

Recently, Fe−porphyrin-like fragments (FeN4) to carbon nanotubes18 and Co−porphyrin-like fragments (CoN4) to nanostructures19 were synthesized using the chemical vapour deposition and the pyrolysis methods, respectively, where Fe or Co is located at the center of four nitrogen atoms similar to metal-porphyrin structure20,21. We herein refer to this MN4 structure as an M−porphyrin-like structure. Fused transition metal (TM)−porphyrin-like nanoclusters have been synthesized experimentally22–28. Furthermore, the porphyrin-like structure is analogous to the local structure of Fe in hemoglobin27 or myoglobin28, which deliver O2 to the organs in the body. The concentration of nitrogen in carbon nanotubes and graphene has been found to reach ~8%29 and ~10%30, respectively. Thus, we expect that TM−porphyrin-like nanostructures can be synthesized experimentally. In this article, we perform first-principles thermodynamics based high-throughput screening for suitable M elements as selective CO2 attractors using M−porphyrin-like graphene.

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Results

To measure the CO2 capture capabilities of nanomaterials from a mixed gas, we constructed a thermodynamic model of CO2 adsorption on an adsorbent using the grand-canonical partition function. We assumed a surface containing the number of identical, independent, and distinguishable adsorption sites \( N_i \) with no mixed adsorption of different molecules per adsorption site, wherein the number of adsorbed \( i \)-type gas molecules on the surface is \( N_i \). If the adsorbed molecules and gases are in equilibrium, the grand partition function of the system can be written as

\[
Z = \left( 1 + \sum_i \sum_{n_i} \exp \left( \frac{\mu_i - \mu^\otimes}{k_B T} \right) / k_B T \right)^{N_i},
\]

where superscript \( i \) indicates the type of gas, \( \mu^\otimes \) denotes the chemical potential of the \( i \)-type gas, and \( \exp \left( \frac{\mu_i - \mu^\otimes}{k_B T} \right) / k_B T \) denotes the average adsorption energy and degeneracy of configuration (for a given adsorption number \( n_i \)) of the \( i \)-type gas molecules, respectively. When the thermally average number of \( i \)-type CO2 is calculated from \( \langle N_i \rangle = k_B T \ln Z / \partial \mu_i \), the occupation function (i.e., coverage) of CO2 for an adsorption site can be written as

\[
f_{\text{CO}_2}(P, T) \equiv \left( \frac{\langle N_{\text{CO}_2} \rangle}{N_i} \right) = \frac{1}{1 + \sum_i \sum_{n_i} \exp \left( \frac{\mu_i - \mu^\otimes}{k_B T} \right) / k_B T},
\]

Therefore, the thermodynamic CO2 capture capacity of nanomaterials from a mixed gas can be computed as

\[
C(P, T) = N_i f_{\text{CO}_2}(P, T) / \sum_j M_j m_j,
\]

where \( M_i \) and \( m_i \) denote the atomic mass and number of elements comprising the adsorbent, respectively.

The occupation function of CO2 would have a positive value, i.e., \( f_{\text{CO}_2} > 0 \), if \( \mu^\otimes (300 \text{K}) > \mu_{\text{CO}_2} \) and \( \Delta_{\text{CO}_2} > \Delta_{\text{other}} \) at the adsorption (capture) conditions as shown in Fig. 1a, wherein \( \Delta^\prime \equiv \mu^\otimes - \mu \) is set and the superscript 'other' denotes molecules other than CO2. In this case, selective CO2 adsorption occurs through competitive adsorption between CO2 and other molecules; this is attributed to the fact that the Gibbs factor for CO2 adsorption is much greater than unity and the Gibbs factors of other molecules, i.e., \( \exp \left( \frac{\mu_i - \mu^\otimes}{k_B T} \right) / k_B T \gg 1 \). However, the occupation function would be zero, i.e., \( f_{\text{CO}_2} = 0 \), if \( \mu^\otimes (450 \text{K}) < \mu_{\text{CO}_2} \), at the desorption (release) conditions \( \exp \left( \frac{\mu_i - \mu^\otimes}{k_B T} \right) / k_B T \ll 1 \) as shown in Fig. 1b, indicating that CO2 adsorbed on the metal sites is released. Under a CO2 pressure of \( \sim 1 \text{ bar} \), the ideal conditions for adsorption and desorption are assumed to be 300 and 450 K, respectively, where \( \mu_{\text{CO}_2} \) is approximately \( -0.75 \) and \( -1.20 \) eV, respectively, at ambient conditions. Thus, the key thermodynamic conditions for reversible and selective CO2 capture from a mixed gas are as follows: (i) \( -1.20 \text{ eV} < \epsilon_{\text{CO}_2} < -0.75 \text{ eV} \) and (ii) \( \Delta_{\text{CO}_2} > \Delta_{\text{other}} \).

From this we construct a computational approach to efficiently predict selective CO2 capture materials based on first principles thermodynamics shown in Fig. 1c. The thermodynamic conditions and capacity requirements11 for screening are as follows: \( -1.20 \text{ eV} < \epsilon_{\text{CO}_2} < 0.75 \text{ eV} \) and \( \Delta C(P, T) > 3 \text{ mmol g}^{-1} \) for CO2 gas, and \( \Delta_{\text{CO}_2} > \Delta_{\text{other}} \) and \( \Delta C(P, T) > 3 \text{ mmol g}^{-1} \) for a mixed gas. \( \Delta C(P, T) \) denotes the difference between \( C(P, T) \) at 300 K and \( C(P, T) \) at 450 K under a pressure of \( \sim 1 \) bar, which indicates the CO2 working capacity. These requirements may need to be revised depending on the operational environments.

We performed calculations on the adsorption energy of CO2 molecules on the M sites of M–porphyrin-like graphene (Fig. 2a). Elements of atomic numbers up to 92 for the M site were considered, and the others were ruled out because of their heavy weight. Sc-, V-, Tc-, Os-, and Th–porphyrin-like graphenes out of many candidates met the reversibility requirements, viz. \( -1.2 \) to \( 0.8 \text{ eV} \) (Fig. 2a), where a CO2 molecule adsorbs on a TM atom with the distance of \( \sim 2.5 \text{ Å} \) between the TM atom and the CO2 molecule. Therefore they were considered for the next step. We also performed CO2 adsorption calculations on carbon allotropes such as carbon nanotubes, graphene, and C60. The adsorption energy of the CO2 molecule is ca. \(-0.05 \text{ eV} \), and the distance between their surface and the molecules is \( \sim 3.5 \text{ Å} \). In this case, since the adsorption energy of CO2 molecules is much smaller than the required adsorption energy, pristine carbon nanostructures may not be suitable for use as CO2 capture media under low pressure at room temperature. Notably, our approach significantly reduces the computational load because it is not necessary to calculate \( \Delta C(P, T) \) for all the candidates in CO2 gas or a mixed gas.

To predict the capture capabilities of the candidates, the CO2 working capacities, \( \Delta C(P, T) \), of the structures were computed using Eq. (3) (Fig. 2b). The experimental values of the chemical potentials of CO2 gas and calculated adsorption energies \( \epsilon_{\text{CO}_2} \) were used in these calculations. Since the working capacities of Sc–, V–, and Tc–porphyrin-like graphenes satisfied the capacity requirement \( (> 3 \text{ mmol g}^{-1}) \), they were considered for the next selectivity screening step.

We observed three different geometries for the adsorbed CO2 molecules on the TM atoms, which were designated as \( \eta^1\text{-CO}_2 \), \( \eta^2\text{-CO}_2 \), and \( \eta^\otimes\text{-CO}_2 \), corresponding to the coordination numbers of the TM atom, i.e., 1, 2, and 3, respectively (Fig. 3a). The adsorption energies of the CO2 molecules were calculated to be \(-0.54 \) to \(-0.79 \), and \(-0.78 \text{ eV} \) per CO2 for the Sc–\( \eta^1\text{-CO}_2 \), Sc–\( \eta^2\text{-CO}_2 \), and Sc–\( \eta^\otimes\text{-CO}_2 \) geometries, respectively. The preferred CO2 geometry depends on the metal type. The distance between the CO2 molecule and TM atoms is 2.2–2.5 Å, which
is much smaller than the equilibrium van der Waals distance (~3.4 Å), and the bond lengths of CO₂ are elongated by ~5%. Thus, the bonding between the TM atoms and CO₂ molecules must be chemical in nature.

To understand the enhanced interaction between early d orbital–containing elements and CO₂ molecules, we focused on a binding mechanism that appears between TM atoms and olefin molecules and is well known in organometallic chemistry. The Dewar–Chatt–Duncanson model explains the type of chemical bonding between a π-orbital acid alkene and d-orbital metal atom by electron donation (i.e., hybridization of the empty d states with filled π states) and back-donation (i.e., hybridization of the filled d states with empty π states). The interaction...
between the TM d orbitals and the olefin π orbitals is called the “Dewar interaction”. Therefore, empty d-orbital metals are expected to attract CO₂ molecules. The Dewar interaction is based on chemical bonding between the TM and CO₂ and can enhance the strength of the M–CO₂ bond beyond that of the van der Waals interaction. It is noteworthy that Ca²⁺ also has empty 3d orbitals near the Fermi level that could participate in the Dewar interaction.

Next, we investigated whether the enhanced adsorption observed with early TM atoms is caused by the Dewar interaction. We observed the hybridization of the Sc 3d states with the CO₂ states at around −2.5, −2.0, and −2.0 eV for the η¹-CO₂, η²-CO₂, and η³-CO₂ geometries, respectively (Fig. 3b). The difference in charge density between the Sc atom and CO₂ molecule (Fig. 3c) indicates chemical bonding between CO₂ and the metal atoms. From this, we concluded that the enhanced binding of CO₂ to the metal atom originates from the Dewar interaction. The distinct adsorption geometries of CO₂ can be explained by the different hybridization states of the TM d orbitals with the CO₂ π orbitals (Fig. 3d).

To examine the selectivity of CO₂ adsorption on Sc, V, and Tc sites in the presence of a mixed gas, we also carried out calculations on the adsorption of multiple CO₂ molecules or ambient gas molecules such as N₂, CH₄, and H₂ onto the metal atoms. Several CO₂, H₂, N₂, and CH₄ molecules bound to Sc, V, and Tc atoms (Figs 4a,b and 5). The difference between the chemical potential at 300 K and 10⁻³ bar and the adsorption energy of CO₂ (or other gas molecules) was calculated (Fig. 4c) using experimental values of the chemical potentials of CO₂, H₂, N₂, and CH₄ gases. The chemical potentials of gases were obtained by fitting the experimental values to the following expression \( \mu^i(P,T) = \mu^i_{\text{ideal}}(P,T) + A_i + B_i \times T \) where upper subscript \( i \) indicates the type of gases, \( \mu^i_{\text{ideal}}(P,T) \) denotes the chemical potential of an ideal monatomic i-type gas for a given the pressure \( P \) and the temperature \( T \), and \( A_i \) and \( B_i \) are fitted coefficients of i-type gas. The fitted coefficients are presented in Table 1. Since Sc and V, but not Tc, were found to satisfy the conditions for selective CO₂ adsorption (\( \Delta \text{CO}_2 > \Delta \text{other} \)), they were considered for the next screening step.

We also considered the zero-point vibrational energy of the gas molecules adsorbed onto the TM atoms. This energy was calculated to be in the order of a few meV regardless of the metal. Since the zero-point vibrational energy is negligible compared to the (static) adsorption energy (Fig. 4a), we ignored the influence of the
zero-point vibrational energy on adsorption in all cases except for H₂. Since the zero-point energy of the H₂ molecules adsorbed on TM atoms was not negligible (25% of the calculated values), we corrected the H₂ adsorption energies to determine the true adsorption energy.

The statistical model obtained here can correctly describe the adsorption of CO₂ onto TM–porphyrin-like graphene in the presence of a mixed gas because the mixed adsorption of different molecules onto a TM atom is not energetically favorable. For instance, the adsorption energy at which both a CO₂ and N₂ molecule adsorb onto a Sc atom was calculated to be −0.9 eV, which is much higher than that (−1.3 eV) at which single CO₂ or N₂ molecules adsorb on different sites.

The CO₂ capture capacities, \( C(P, T) \), from mixed gases with different compositions were calculated for Sc– and V–porphyrin-like graphenes (Fig. 6a,b). The ratios of the mixed gases were based on experimental measurements \(^{33,35} \) from pre-combustion, post-combustion, and oxyfuel-combustion CO₂ capture. These results show high CO₂ selectivity of Sc– and V–porphyrin-like graphene in mixed gases, which is consistent with the prediction of the selectivity requirement of \( \Delta \) (CO₂) > \( \Delta \) (other). The CO₂ working capacities, \( \Delta C(P, T) \), of Sc– and V–porphyrin-like graphenes can reach ~4 mmol g\(^{-1}\) (Fig. 6c,d), which meets the capacity requirement of 3 mmol g\(^{-1}\) in a mixed gas. Therefore, Sc– and V–porphyrin-like graphene were found to be suitable for highly selective CO₂ capture from

Figure 3. Origin of distinct geometries of CO₂ adsorption: (a) Atomic structures showing CO₂ molecule adsorbed onto Sc–4N graphene for the various CO₂ adsorption geometries designated as \( \eta^1 \)-CO₂, \( \eta^2 \)-CO₂, and \( \eta^3 \)-CO₂, respectively. (b) The density of states for \( \eta^1 \), \( \eta^2 \), and \( \eta^3 \) geometries, respectively. (c) The difference in the total charge density \( \Delta \rho = \rho(GP + 4N + Sc + CO₂) - \rho(GP + 4N + Sc) - \rho(CO₂) \) for \( \eta^1 \), \( \eta^2 \), and \( \eta^3 \) geometries, respectively. Yellow and green indicates the charge accumulation and depletion. (d) The schematic of the hybridization of the Sc 3d orbitals with the CO₂ p\(_z\) orbitals for \( \eta^1 \), \( \eta^2 \), and \( \eta^3 \) geometries, respectively. Red and blue colors of the orbitals indicate the different phases, respectively.
flue gases at ambient conditions. Furthermore, the CO$_2$ pressure range covers the pressure (~0.4 × 10$^{-3}$ bar) of CO$_2$ in the atmosphere because the concentration of CO$_2$ in the atmosphere is ~400 ppm.

**Discussion**

We performed first-principles total energy calculations regarding CO$_2$ adsorption onto metal–porphyrin-like structures to explore the feasibility of achieving room-temperature CO$_2$ capture under low pressures. We found that transition metal–porphyrin-like structures adsorb CO$_2$ molecules with the desirable binding energy range.
and the practical (usable) capacity under ambient conditions can reach ~3 mmol/g. Equilibrium thermodynamics studies showed that Sc– or V–porphyrin-like graphene structures were found to be suitable for use as room-temperature CO2 capture media. These results indicate that nanostructures containing empty d orbitals may be applied for selective adsorption of CO2 from flue gases. We believe our results provide a new approach to achieving CO2 capture at room temperature.

**Methods**

We performed first-principles calculations based on the density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave (PAW) method. The
generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof scheme was used for the exchange correlation energy functional, and the kinetic energy cutoff was taken to be 800 eV. For calculations of gas molecule adsorption, our model for the graphene-based system comprised a 3 × 3 hexagonal supercell, and the composition of the supercell was C2H2N4M5. Geometrical optimization of the grapheme-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. 4 × 4 k-point sampling was used for the 3 × 3 graphene supercells. The chemical potential of gases, , where H, S, and N denote the enthalpy, the entropy, and the number of particles was calculated from the data of the enthalpy (H) and entropy (S) in the reference: http://webbook.nist.gov/chemistry/fluid/.

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Author Contributions
H.B. and M.P. contributed equally to this work. H.L.+ conceived and designed the study. H.B., M.P., B.J. and J.P. performed the calculations. Y.K.+, H.L.+, H.C., C.C., S.H., Y.K.+, B.I.Y., and H.L.+ interpreted the data. C.C. and H.L.+ wrote the manuscript. All authors revised the manuscript and approved the final version of the manuscript.

Additional Information
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Corrigendum: High-throughput screening of metal-porphyrin-like graphenes for selective capture of carbon dioxide

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This Article contains an error in Table 1, where ‘Bi (eV/K)’ should read ‘Bi (meV/K)’.

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