# Cooperative CO<sub>2</sub> capture via oxalate formation on metal-decorated graphene

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 $CO_2$  capture using carbon-based materials, particularly graphene and graphene-like materials, is a promising strategy to deal with  $CO_2$  emissions. However, significant gaps remain in our understanding of the molecularlevel interaction between  $CO_2$  molecules and graphene, particularly in terms of chemical bonding and electron transfer. In this work, we employ random structure search and density functional theory to understand the adsorption of  $CO_2$  molecules on Ca-, Sr-, Na-, K-, and Ti-decorated graphene surfaces. Compared to the pristine material, we observe enhanced  $CO_2$  adsorption on the decorated graphene surfaces. Particularly on group 2 metals and titanium-decorated graphene,  $CO_2$  can be strongly chemisorbed as a bent  $CO_2$  anion or as an oxalate, depending on the number of  $CO_2$  molecules. Electronic structure analysis reveals that the adsorption mechanism involves a charge transfer from the metal adatom to the adsorbed  $CO_2$ . Overall, this study suggests that reducing  $CO_2$  to oxalate on group 2 metals and titanium-decorated graphene surfaces is a potential strategy for  $CO_2$ storage.

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# I. INTRODUCTION

The world faces a severe climate crisis due to the alarming increase of anthropogenic  $CO_2$  emissions. One key strategy to offset  $CO_2$  emissions is to identify new and high-performing materials capable of efficiently trapping  $CO_2$  molecules within an optimal adsorption energy range of -0.4 to -0.8 eV [1–4]. This range is crucial for ensuring moderate binding and subsequent release of  $CO_2$ , facilitating its conversion into valuable chemicals [1–4].

A wide range of porous materials, such as activated carbon, zeolites, graphene, and metal-organic frameworks have been investigated as promising candidates for  $CO_2$  capture because of their high surface areas, stability, and tunable surface chemistries [5–10]. In particular, graphene is a

two-dimensional material with great promise for many applications such as nanoelectronics [11,12], gas storage [13-15], chemical sensors [16,17], and catalytic applications [18,19]. The versatility of graphene can be attributed to its unique electronic structure. Specifically, the semimetallic nature of graphene as a result of its vanishing density of states at the Fermi level enables the electronic properties of this material to be easily tuned [20-22].

As promising as graphene is for gas storage applications,  $CO_2$  has been reported to bind too weakly on pristine graphene below the lower adsorption energy limit for viable  $CO_2$  capture [2–4]. Hence, there is a need to functionalize the surface of graphene. Owing to the reducibility of  $CO_2$  and the tunability of graphene's electronic properties, decoration of graphene with neutral metal adatoms has been found to enhance the interaction between  $CO_2$  and graphene [23,24]. However, this enhanced interaction is typically seen when one  $CO_2$  molecule is adsorbed and little is known about the adsorption of multiple  $CO_2$  molecules on the metal-decorated graphene surface [2,3,24–30]. Investigating the interaction of multiple  $CO_2$  on decorated graphene surfaces could help

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understand the cooperative interaction between  $CO_2$  molecules and provide fundamental insights that aid in the development of next-generation materials for an enhanced  $CO_2$  uptake.

In this work, we investigate the adsorption of multiple  $CO_2$ molecules on metal-decorated graphene (M@Gr) surfaces, identifying high-performing metal decorators and elucidating the underlying mechanism that mediates the interaction between gas molecules and surfaces. To accurately predict the M@Gr properties, we used density functional theory (DFT) and an *ab initio* random structure search (RSS) [31–33] to systematically find stable configurations of 1–5 CO<sub>2</sub> molecules adsorbed on group 1 metals, Na and K, group 2 metals, Ca and Sr, and transition metal, Ti, decorated graphene surfaces.

Our results computed at the PBE-D3 [34,35] level of theory show that decorating graphene with a metal atom can boost the adsorption strength to beyond -1.71 eV—about ten times greater than CO<sub>2</sub> adsorption on the pristine material (-0.17 eV). We find that the enhanced interaction for group 2 and Ti decorators results from the one-electron reduction of CO<sub>2</sub> to a bent CO<sub>2</sub> radical anion and a further reduction to form oxalate when  $\ge 2 \text{ CO}_2$  molecules are adsorbed. The formation of oxalate further enhances the cooperative adsorption of subsequent physisorbed CO<sub>2</sub> molecules due to a strong interaction of CO<sub>2</sub> with the metal cation. This indicates the propensity of group 2 and Ti-decorated graphene for the adsorption of multiple CO<sub>2</sub> molecules.

The remainder of this paper is organized as follows: We provide the computational details of the DFT and the RSS approach in Sec. II and discuss the adsorption energy trends, formation of oxalate and the underlying adsorption mechanism in Sec. III. In Sec. IV, we briefly discuss our results in context with previous works, and Sec. V ends with conclusions and an outlook on future related research.

#### **II. COMPUTATIONAL DETAILS**

All calculations were performed with the plane-wave DFT code Vienna ab initio simulation package (VASP5, version 5.4) [36–39]. The Perdew, Burke, and Ernzerhof (PBE) exchange-correlation functional [35], and Grimme's D3 dispersion correction with zero damping function [40] were used. This combination was chosen because PBE-D3 can successfully describe interactions between gas molecules and surfaces [41–44]. In addition, the adsorption trends reported in this study are found to be rather insensitive to functional choice—see the Supplemental Material (SM) for details [45] and also Refs. [46-49] therein. Projector augmented wave (PAW) potentials were used to describe the interaction between core states and the semicore and valence states [50,51]. The 2s2p, 2s2p, 3s3p4s (Ca\_sv), 4s4p5s (Sr\_sv), 2s2p3s (Na sv), 3s3p4s (K sv), and 3s3p4s3d (Ti sv) electrons were explicitly included for the C, O, Ca, Sr, Na, K, and Ti atoms, respectively. In this way, semicore states are included for all metal species.

A  $(5 \times 5)$  supercell of graphene containing 50 carbon atoms was used, except where otherwise stated. Periodic boundary conditions were applied, and a vacuum of 20 Å was used in the *z* direction, perpendicular to the graphene sheet. We used a low metal adatom doping concentration of 2%

TABLE I. Stepwise adsorption energies of 1–5 CO<sub>2</sub> molecules adsorbed on Na-, K-, Ca-, Sr-, and Ti-decorated graphene. The adsorption energies ( $E_{M-Gr}^{ads}$ ) and metal-graphene distances ( $d_{M-Gr}$ ) in the absence of CO<sub>2</sub> are also reported. Energies are given in eV and distances in Å.

Adatom	1	2	3	4	5	$E_{M-{ m Gr}}^{ m ads}$	$d_{M-Gr}$
Na K Ca Sr	-0.51 -0.40 -1.16 -0.84	-0.49 -0.41 -1.71 -1.84	-0.45 -0.28 -0.54 -0.47	-0.37 -0.50 -0.50 -0.45	-0.13 -0.17 -0.15 -0.56	-0.77 -1.18 -0.75 -0.75	2.19 2.56 2.30 2.50
Ti	-2.96	-0.86	-0.75	-0.41	-0.22	-1.94	2.35

in this study. This concentration refers to the ratio between the number of metal adatoms and carbon atoms in graphene. Specifically, 2% translates to one metal adatom per  $(5 \times 5)$ graphene supercell. We have selected a low concentration to obtain insights into the individual CO<sub>2</sub> adsorption processes on decorated graphene.

The lowest-energy structures are the most important for predicting the properties of materials because they tend to dominate under equilibrium conditions. To identify the most stable conformers for the adsorption of 1–5 CO<sub>2</sub> molecules on the Ca-, Sr-, K-, Na-, and Ti-decorated graphene (from here on referred to as Ca@Gr, Sr@Gr, K@Gr, Na@Gr, and Ti@Gr, respectively), we screened the adsorption energy of CO<sub>2</sub> on each substrate in a two-stage process. In the initial screening stage, 100 random configurations each for 1-5 CO<sub>2</sub> molecules were generated on Ca@Gr, Sr@Gr, K@Gr, Na@Gr, and Ti@Gr systems. The atoms in the graphene sheets were fixed, and the RSS was done with both linear and bent CO<sub>2</sub> molecules, which were placed at a random distance and angle on the xy plane of the graphene sheet. The distance r between the metal adatom and the carbon atom in  $CO_2$  in the z direction was constrained to be within  $2 \leq r \leq 4$  Å. A spin-polarized  $\Gamma$  point relaxation was performed for all systems using a plane-wave energy cutoff of 300 eV and a Gaussian smearing of 0.05 eV. All geometry and electronic relaxations for 1-5 CO<sub>2</sub> molecules on each substrate were converged to residual forces and energy less than  $0.05 \text{ eV} \text{ Å}^{-1}$ and  $1 \times 10^{-5}$  eV, respectively.

In the refined screening, an energy cutoff of 400 eV and a  $3 \times 3 \times 1$   $\Gamma$ -centered **k**-point mesh were used to obtain more accurate adsorption energies for the lowest energy structures from the initial screening stage. At this setting, the adsorption energy is converged within 10 and 1 meV for the **k**-point and the energy cutoff, respectively (see Fig. S5 in SM for **k**-point and energy cutoff convergence [45]). All geometry and self-consistent field electronic relaxations were converged to residual forces and energy less than 0.01 eV Å<sup>-1</sup> and 1 × 10<sup>-6</sup> eV, respectively.

The stepwise adsorption energies were computed using Eq. (1) and reported in Table I:

$$E_{\text{ads}}^n = E_{M@\text{Gr}+n\text{CO}_2}^{\text{tot}} - E_{M@\text{Gr}+(n-1)\text{CO}_2}^{\text{tot}} - E_{\text{CO}_2}^{\text{tot}}.$$
 (1)

In Eq. (1),  $E_{ads}$  is the stepwise adsorption energy of the *n*th CO<sub>2</sub> molecule,  $E_{M@Gr+nCO_2}^{tot}$  and  $E_{M@Gr+(n-1)CO_2}^{tot}$  are the total energies for CO<sub>2</sub> molecules adsorbed on M@Gr where *n* is



FIG. 1. Optimized geometries of 1–5 CO<sub>2</sub> on (a) Ca-, (b) Sr-, (c) K-, (d) Na-, and (e) Ti-decorated graphene systems. The first adsorbed CO<sub>2</sub> is seen to bend on Ca@Gr and Sr@Gr. From the adsorption of 2–5 CO<sub>2</sub> molecules, an oxalate is formed alongside with other physisorbed CO<sub>2</sub> molecules on Ca@Gr and Sr@Gr. The first adsorbed CO<sub>2</sub> on Ti partially dissociate to CO and O, the O passivate Ti to form TiO. The adsorption of second CO<sub>2</sub> molecules on Ti@Gr forms a bent CO<sub>2</sub>, and oxalate is formed when three CO<sub>2</sub> molecules are adsorbed on TiO@Gr. For 4–5 CO<sub>2</sub> molecules on Ti@Gr, oxalate is formed alongside physisorbed CO<sub>2</sub> molecules on TiO@Gr. For all number of CO<sub>2</sub> molecules are radially coordinated to the metal adatoms and no bent CO<sub>2</sub> or oxalate is formed at higher loading of CO<sub>2</sub> molecules on these systems.

the number of  $CO_2$  molecules adsorbed, and  $E_{CO_2}^{tot}$  is the total energy of the gas-phase relaxed  $CO_2$  molecule.

To understand the charge transfer processes for  $CO_2$  adsorption on different metal atoms, a charge density distribution analysis was done on the lowest energy structures using the Bader charge approach [52]. Density of states (DOS) and projected density of states (PDOS) were also examined and these were obtained using a  $\Gamma$ -centered 15 × 15 × 1 **k**-point mesh and the SUMO code for post-processing the data [53].

# **III. RESULTS**

Our RSS procedure was used to obtain the most stable configuration of 1-5 CO<sub>2</sub> molecules adsorbed on Ca@Gr,

Sr@Gr, Na@Gr, K@Gr, and Ti@Gr, and the stepwise adsorption energies computed for the most stable configurations of adsorbed CO<sub>2</sub> on each substrate (as shown in Fig. 1) are reported in Table I and Fig. 2. The metal atoms are adsorbed at 2.19–2.56 Å on the hollow site above the graphene sheet with adsorption energies reported in Table I. In contrast with the weak interaction of CO<sub>2</sub> with pristine graphene (-0.17 eV), the interaction of CO<sub>2</sub> with *M*@Gr systems is generally much stronger for all metal decorators. The maximum adsorption strength of the metal decorators follows the order of Ti > Sr > Ca > Na > K, with Ti exhibiting the strongest adsorption and K the weakest. Overall, the adsorption energy of group 2 decorated graphene and the Ti@Gr for the first few CO<sub>2</sub> molecules is outside the ideal adsorption energy window



FIG. 2. Stepwise adsorption energy plot of 1-5 CO<sub>2</sub> molecules adsorbed on metal-decorated graphene. The stepwise adsorption energies (in eV) for the lowest-energy structures found with the RSS are shown. The symbols indicate the adsorption motif of CO2 molecules around the metal atoms. The filled triangles indicate the formation of a bent CO<sub>2</sub> anion; empty triangle indicates dissociated CO<sub>2</sub>; and the circles indicate the radial orientation of the physisorbed CO<sub>2</sub> molecules to the metal atom. The filled squares indicate the exclusive formation of oxalate, and the empty squares represent the system with oxalate and physisorbed CO2 molecules. The single black circle represents the adsorption energy of CO2 on pristine graphene. Examples of optimized orientations of CO2 on K-decorated (purple) and Ca-decorated (green) graphene are shown above. Group 1 metals are indicated by dotted lines, group 2 metals by dashed lines, and transition metal Ti by the solid line. The shaded gray region shows the ideal adsorption and desorption energy window (-0.4 to -0.8 eV) for carbon capture [54].

(-0.4 to -0.8 eV) for adsorption and desorption of CO<sub>2</sub> (see the shaded gray region in Fig. 2), while the adsorption on group 1 decorated graphene falls within the range.

## A. Enhanced CO<sub>2</sub> adsorption via metal decoration of graphene

CO<sub>2</sub> has been previously reported to be weakly physisorbed on pristine graphene, exhibiting an adsorption energy of about -0.2 eV, which is below the adsorption limit for viable CO<sub>2</sub> capture [2–4]. The most stable configuration of CO<sub>2</sub> on pristine graphene from our RSS is a linear CO<sub>2</sub> molecule, flatly adsorbed on a C–C bond of pristine graphene with a weak adsorption energy of -0.17 eV, in agreement with previous works [2–4], and at a distance of 3.4 Å to the graphene sheet (see the inset in Fig. S1 of the SM [45]). The equilibrium C–O bond length of 1.18 Å remains unchanged upon adsorption, indicating a weak interaction of CO<sub>2</sub> with the graphene sheet.

For the first adsorbed CO<sub>2</sub> molecule on Ca@Gr and Sr@Gr, the CO<sub>2</sub> molecule undergoes a significant bending and symmetrical C–O bond elongation to  $125^{\circ}$  and 1.28 Å for Ca. Similar bending of CO<sub>2</sub> with an angle of  $134^{\circ}$  and bond elongation to 1.30 Å is seen for Sr. This change in structure

is a result of charge transfer of  $\approx 1e^{-1}$  from the metal adatom to the  $\pi^*$  orbital of the adsorbed CO<sub>2</sub> with no hybridization of the *p* state and the *s*, *d* metallic states of the Ca adatom as reported in Ref. [24] [see Fig. S4(b) in SM [45]]. The rearrangement of the linear CO<sub>2</sub> to the bent CO<sub>2</sub> anion on group 2 decorated graphene and the observed structural changes in this study agree well with previous studies that investigated the adsorption of CO<sub>2</sub> on Ca@Gr [24,30].

The bent  $CO_2$  anion formation on the group 2 decorated graphene results in the chemisorption energies -1.16 and -0.84 eV for 1 CO<sub>2</sub> on Ca@Gr and Sr@Gr, respectively, reported in Table I. The weakening and elongation seen for the intramolecular C–O bond on Ca@Gr and Sr@Gr is described by Hoffmann [55] as the chemisorption compromise, explaining the strengthening of the interaction between the adsorbate and the surface occurs at the expense of the bonding within the *M*@Gr and the adsorbed molecules (CO<sub>2</sub>) [55]. This increases the intramolecular bond length within the adsorbates and surfaces involved, as seen for the bent CO<sub>2</sub> in this work.

For the adsorption of one CO2 molecule on Na@Gr (-0.51 eV) and K@Gr (-0.40 eV), there is no reduction of the linear  $CO_2$  molecule to a bent  $CO_2$  anion, despite these adatoms having the required one valence electron to reduce  $CO_2$  to a bent  $CO_2$  anion. Instead, graphene is reduced by the valence electrons of these metal atoms and the negatively charged graphene layer does not possess a sufficiently strong reduction potential to reduce CO<sub>2</sub>. The most stable configuration of  $CO_2$  on group 1 decorated graphene is found to be radially coordinated to the adatom (see inset for physisorbed  $CO_2$  in Fig. 2) with the nearest oxygen atom at a distance of 2.34 Å, with an unchanged C-O bond length of 1.18 Å. This structural reorientation of CO<sub>2</sub> on group 1 decorated graphene suggests an electrostatic interaction of the adsorbed  $CO_2$  with the oxidized group 1 cations in the system. The lack of bent CO<sub>2</sub> anion formation on group 1 decorators explains the weaker interaction seen for these systems compared with other metal decorators [29].

For the adsorption of one  $CO_2$  on Ti@Gr, the lowestenergy structure is a partially dissociated  $CO_2$  molecule, forming CO and O [as can be seen in Fig. 1(e)] with a strong adsorption energy of -2.96 eV. This is well known both experimentally and theoretically with Ti decorators [56–59]. The strong dissociative adsorption of a single  $CO_2$  on Ti@Gr is well beyond the energy window for reversible  $CO_2$  capture. However, given the formation of stable TiO on graphene, subsequent RSS was performed at TiO@Gr and Ti@Gr for 2-5  $CO_2$  molecules. We found that the TiO@Gr system supports more stable adsorption structures than Ti@Gr and, as such, the adsorption energies reported in Fig. 2 and Table I for 1–5  $CO_2$  molecules for the Ti decorator correspond to TiO@Gr, as can be seen from Fig. 1(e).

#### B. Enhanced interaction of CO<sub>2</sub> via oxalate formation

For the adsorption of a second  $CO_2$  molecule on group 2 metal-decorated graphene, the RSS approach finds an oxalate molecule forms with a stepwise adsorption energy of -1.71 and -1.84 eV for  $CO_2$  on Ca@Gr and Sr@Gr, respectively. In the oxalate, two  $CO_2$  molecules form a carbon-carbon covalent bond of 1.6 Å length. The oxalate coordinates with

the metal ion and carries a charge of about -2|e|. The metaloxalate complex on graphene can be seen in Fig. 1. As shown in Fig. 2, the strongest adsorption energy is observed for two CO<sub>2</sub> molecules on Ca@Gr and Sr@Gr due to the oxalate formation in these systems. In the case of TiO@Gr, the addition of a second  $CO_2$  molecule leads to the stepwise adsorption energy of  $-0.86 \,\text{eV}$  and the formation of the bent  $CO_2$  anion—as seen when one  $CO_2$  molecule is adsorbed on group 2 metal-decorated graphene. TiO is indeed analogous to group 2 metals, having two valence electrons to reduce CO<sub>2</sub> and therefore interacting in the same manner as a Ca or Sr decorator. In the same vein, when a third CO<sub>2</sub> molecule is adsorbed on TiO@Gr, a TiO-oxalate complex is found to be the most stable structure through RSS, with a stepwise adsorption energy of -0.75 eV. Oxalates do not form in group 1 decorated graphene systems (see Fig. 1) because group 1 metals can only donate one electron, whereas the formation of oxalate requires two electrons. As a result, the stepwise adsorption energy of 1-4 CO2 molecules remains relatively flat for Na@Gr and K@Gr.

When 3–5 CO<sub>2</sub> molecules are adsorbed on the group 2 and Ti substrates, along with the oxalate formed, there are physisorbed CO<sub>2</sub> molecules in the system, as can be seen in Fig. 1. The stepwise adsorption energy seen in Fig. 2 for physisorbed  $CO_2$  molecules is weaker than for chemisorbed CO<sub>2</sub>, given the absence of strong charge transfer interactions but stronger than for pristine graphene. Physisorption energies range from -0.13 to -0.56 eV across all substrates, as can be seen in Table I. The difference in physisorption energies (<0.43 eV) is relatively small with respect to the strong chemisorption energies found in these systems (-0.84 to) $-1.84 \,\mathrm{eV}$ ) and can be attributed to the complex potential energy surface (PES) for physisorption, whereby there are many rotational and translational degrees of freedom. While an RSS can be effective for exploring the PES, it is still considerably challenging to find the global minimum for physisorption due to the many available degrees of freedom. However, even without finding the global minima for physisorbed CO<sub>2</sub> molecules it can still be seen that the physisorption of  $CO_2$ is generally stronger on these decorated substrates than on pristine graphene, where it is  $-0.17 \,\text{eV}$ .

### C. Sticky oxalate

In systems with more than two  $CO_2$  molecules, we find that when oxalate is present, other  $CO_2$  molecules bind more strongly. The role of oxalate in the physisorbed  $CO_2$ molecules is shown in Fig. 3. On the left-hand side [Fig. 3(a)], we show that bringing a physisorbed  $CO_2$  towards a Ca adatom results in a +0.03 eV change in energy. Note that physisorbed  $CO_2$  on Ca@Gr is a single-point evaluation to avoid the formation of bent  $CO_2$ . However, the interaction of a physisorbed  $CO_2$  molecule with Ca-oxalate on graphene leads to an energy gain of about -0.38 eV, as shown in Fig. 3(b). This shows that the physisorbed  $CO_2$  interacts more strongly with the calcium-oxalate complex in the system than with pristine graphene.

For the stepwise addition of a third and fourth  $CO_2$  molecule to oxalate on Ca@Gr,  $CO_2$  is stabilized by an energy of -0.37 and -0.33 eV, respectively, relative to



FIG. 3. Schematic representation of enhanced CO<sub>2</sub> adsorption in the presence of oxalate. Panel (a) shows the energy difference from adsorbing a CO<sub>2</sub> on the pristine graphene to adsorbing it on a Ca-decorated graphene system, where the Ca and graphene have  $a + 1e^-$  and  $-1e^-$  charge, respectively. Panel (b) shows the energy change from adsorbing CO<sub>2</sub> on pristine graphene to adsorbing it on Ca@Gr in the presence of calcium-oxalate. It is worth noting that in systems where calcium oxalate forms it contributes -2.87 eV to the total adsorption energy of the system.

physisorbing on pristine graphene. This further confirms that oxalate enhances the adsorption of CO<sub>2</sub>. Upon adding the fifth CO<sub>2</sub> molecule, there is a +0.02 eV increase in energy, indicating that the adsorption of the fifth CO<sub>2</sub> molecule is slightly destabilized relative to pristine graphene because it is located further away (about 8.95 Å) from the Ca-oxalate moiety in the system. Overall, these results reveal that for the third and fourth CO<sub>2</sub> molecules, the Ca-oxalate complex formed in this system is sticky, yielding a stronger interaction with physisorbed CO<sub>2</sub> than pristine graphene.

Our results show that group 2 decorated graphene and Ti-decorated graphene demonstrate stronger adsorption than group 1 metal decorators. This strength is due to the ability of metal atoms to reduce a linear  $CO_2$  molecule to a bent  $CO_2$  anion and form an oxalate upon the adsorption of more  $CO_2$  molecules. The formation of the fully oxidized cation (+2) by oxalate enhances the adsorption of multiple  $CO_2$  molecules up to four  $CO_2$  molecules for the group 2 decorated graphene system.

With our results, being aware of the limitation of the PBE-D3 functional used, we have performed additional calculations with other types of functionals: optB86b-vdW [46], optB88-vdW [47], SCAN + rVV10 [48], and r2SCAN + rVV10 [49], as can be found in the SM [45]. We find that the adsorption energies are shifted on the order of 0.25 eV, but the overall trends remain the same.

## D. Chemisorption of CO<sub>2</sub> as oxalate on decorated graphene

To gain insight into the redistribution of electrons and the nature of the bond formed between  $CO_2$  and the decorated graphene surfaces, a Bader charge analysis was performed on the Ca@Gr and TiO@Gr systems as representative systems where an oxalate forms and on K@Gr where no oxalate forms.



FIG. 4. Bader charge analysis and schematic representation of charge transfer from metal adatoms. (a) Bader charges on K (purple circle), linear CO<sub>2</sub> molecules (blue circle), and the graphene sheet (gray circle). (a)(i)–(iv) Schematics of charge transfer for K@Gr and 1–3 CO<sub>2</sub> molecules on K@Gr, respectively. (b) Bader charges in the Ca@Gr systems for Ca (green circle), bent CO<sub>2</sub> (brown filled triangle), and oxalate molecules (red squares). Filled squares represent the exclusive formation of oxalate and the empty red squares show the charge on the oxalate molecule where oxalate and physisorbed CO<sub>2</sub> are present. (b)(i)–(iv) Schematics of charge transfer for Ca@Gr, bent CO<sub>2</sub> on Ca@Gr, oxalate on Ca@Gr, and oxalate and physisorbed CO<sub>2</sub> on Ca@Gr, respectively. (c) Bader charges in the Ti-decorated systems, showing Ti (magenta circle) and TiO (inverted magenta triangle). The empty triangle represents the charge on the CO molecule. (c)(i)–(iv) show the schematics of charge transfers for Ti@Gr, dissociated CO<sub>2</sub> on Ti@Gr, CO<sub>2</sub> and CO on TiO@Gr, and oxalate and CO on TiO@Gr, respectively.

Figure 4 shows the net charge on graphene, K, Ca, Ti, TiO, and  $CO_2$  molecules as the number of  $CO_2$  increases from zero to five.

When K, Ca, and Ti are adsorbed on the substrate, they reduce the graphene sheet by donating about one electron [see Figs. 4(a)(i), 4(b)(i), and 4(c)(i)]. For 1–5 CO<sub>2</sub> on K@Gr in Fig. 4(a), the  $0.9e^-$  charge on the K adatom is donated to the graphene sheet. As such, the fully oxidized K adatom and the reduced graphene sheet are unable to reduce CO<sub>2</sub> to a bent anion. This explains the relatively weak adsorption energy of CO<sub>2</sub> on group 1 decorated graphene compared to group 2 and Ti-decorated graphene.

Contrary to what is seen for K@Gr, when a  $CO_2$  molecule is adsorbed on Ca@Gr,  $CO_2$  is reduced to a bent  $CO_2$  anion by transfer of about one  $e^-$  from Ca, while the graphene sheet remains reduced by the other electron donated from Ca [see Fig. 4(b)(ii)]. For the adsorption of two  $CO_2$  molecules where oxalate is formed, the  $+1.5e^-$  on Ca is donated solely to the oxalate, showing an ionic bonding between the oxalate and the metal adatom. Note that Bader charges are not equivalent to formal charges and we interpret a  $+1.5e^-$ Bader charge as Ca being in the +2 oxidation state. At 2–5 CO<sub>2</sub>, where one oxalate is consistently formed, the  $+1.5e^-$  on Ca is donated to oxalate entirely to form the Ca-oxalate complex and the graphene sheet becomes neutral [see Fig. 4(b)(iii)].

With the first CO<sub>2</sub> molecule dissociatively adsorbing on Ti@Gr, the Ti atom donates  $0.7e^-$  to oxygen, forming TiO,  $0.3e^-$  to CO, and  $0.4e^-$  to graphene, according to Bader charges. With the adsorption of a bent CO<sub>2</sub> anion on TiO@Gr, the CO molecule and graphene sheet become neutral [as shown in Fig. 4(c)(iii)]. The charge transfer from TiO to oxalate on graphene exhibits a similar trend to Ca@Gr, with TiO donating  $0.8e^-$  to the oxalate molecule.

Graphene also makes a small contribution of around 0.3e<sup>-</sup> to reducing the oxalate, according to the Bader charge analysis.

In general, the charge and type of formed species determines the adsorption strength of  $CO_2$  on the substrate. When the valence electrons from the metal adatom are donated to graphene, physisorption of  $CO_2$  is seen. On the other hand, the transfer of the valence electrons from the metal adatom to the adsorbed  $CO_2$  molecule (as in the case of oxalate formation), results in a strong ionic chemisorption of  $CO_2$  molecules on the substrate. These conclusions are consistent with a partial density of state analysis reported in the SM [45]; see also Refs. [9,10] therein.

## **IV. DISCUSSION**

Through comprehensive exploration of the potential energy surface with RSS, we found group 2 metal (Ca and Sr) oxalates form on graphene upon the adsorption of  $CO_2$ . Ti similarly forms a TiO-oxalate complex after dissociatively adsorbing one  $CO_2$  molecule.

Previous theoretical studies have reported enhanced adsorption due to the reduction of one CO<sub>2</sub> molecule to a bent CO<sub>2</sub> anion on Ca-decorated surfaces. For instance, Tawfik et al. [30] found only the first adsorbed  $CO_2$  to bend on single and double vacancy Ca@Gr with strong adsorption energies of -1.10 eV and -1.30 eV, respectively. Upon the subsequent addition of CO<sub>2</sub>, there was no further reduction of the  $CO_2$  molecules [30]. However, in our work, two  $CO_2$ molecules are reduced to oxalate on group 2 decorated and Ti-decorated graphene systems. To examine the stability of the oxalate molecule with respect to a  $CO_2$  anion and a physisorbed CO<sub>2</sub> molecule on metal-decorated graphene, we performed nudged elastic band calculations for the Ca@Gr substrate. We find that the formation of oxalate is almost barrierless, with a small energy barrier of 2 meV, and it is  $\approx 1.3 \text{ eV}$  more stable than a CO<sub>2</sub> anion and a physisorbed CO<sub>2</sub> molecule. The details are reported in the SM [45]; see also Refs. [60–62] therein.

There are many possible reasons why an oxalate was not formed in Ref. [30]. First, differences in the system, such as unit cell size and defects on the graphene [30]. More importantly, previous work might have missed the oxalate formation because wider configuration spaces of  $CO_2$  on metal-doped graphene were not sampled with sampling techniques such as RSS. The latter is supported by the observation that the CaO clusters reported in Ref. [30] were seen in some of the highenergy structures discovered by the RSS technique performed in our work.

Experimental works [63–65] have reported the electrocatalytic conversion of  $CO_2$  to oxalate by transition metals. The reduction of  $CO_2$  to bent  $CO_2$  anion is the first step to the conversion of  $CO_2$  to higher  $C_2$  compounds such as oxalate; however, the large energy needed for the reduction of  $CO_2$  to bent  $CO_2$  anion makes it challenging for experiments. In this work, our results demonstrate that the RSS technique could be a suitable modeling tool to screen for bent  $CO_2$  molecules and other higher  $C_2$  compounds such as oxalate when investigating  $CO_2$  reduction on low-dimensional materials. Furthermore, the binding energies found vary

from physisorption to chemisorption strengths and, therefore, we might expect well-defined peaks if investigated with temperature programmed desorption (TPD) experiments. We include an estimation of TPD peaks (invoking the Redhead approximation) in the SM [45], see also Ref. [66] therein.

### V. CONCLUSION AND OUTLOOK

By systematically exploring a relatively wide configuration space of  $CO_2$  molecules on a decorated graphene system with random structure search, we have gained the following insights: (i) There is enhanced adsorption of  $CO_2$  molecules on M@Gr compared with pristine graphene. (ii) Oxalates form on group 2 metal-decorated and Ti-decorated graphene and give the strongest adsorption energy of  $CO_2$  in Ca@Gr and Sr@Gr systems. (iii) The adsorption mechanism observed for the enhanced  $CO_2$  adsorption is facilitated by charge transfer. (iv) Oxalate formation enhances the adsorption of additional  $CO_2$  molecules on the metal-decorated graphene surface because a fully oxidized metal cation is formed which strongly interacts with the  $CO_2$  molecules.

This study is primarily aimed at understanding how  $CO_2$ interacts with decorated graphene surfaces, and many factors that might affect the practical use of these materials for  $CO_2$ capture have not been considered because they are beyond the scope of this work. However, the fundamental insights about the formation of oxalate and its cooperative effect in enhancing the adsorption of other  $CO_2$  molecules suggest a potential strategy for higher  $CO_2$  uptake on decorated graphene systems. It would be extremely valuable to confirm the formation of oxalates experimentally while considering other important factors such as defects, water, and temperature on these types of materials.

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