Supporting Information

Synergetic Promotion by Oxygen Doping and Ca Decoration on Graphene for CO_2 Selective Adsorption

Anqi Liu[†], Jun Long[†], Shandong Yuan[‡], Wanglai Cen[*,‡,§], Jianjun Li[*,†]

†. College of Architecture and Environmental and National Engineering Research Center for Flue Gas Desulfurization, Sichuan University, Chengdu 610065, China

‡. Institute of New Energy and Low Carbon Technology, Sichuan University, Chengdu 610207, China

§. Department of Chemistry and Institute for Computational Engineering and Sciences, University of Texas at Austin, Austin, Texas 78712, USA

*corresponding authors

Dr. Wanglai Cen (cengwanglai@163.com)

Prof. Dr. Jianjun Li (jjli@scu.edu.cn)

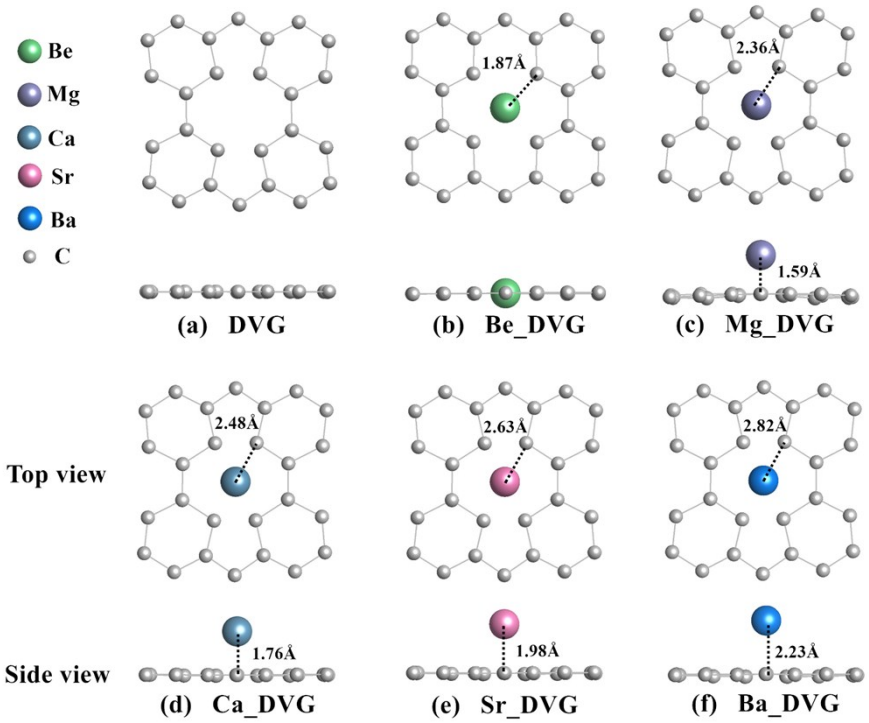

Fig. S1 Relaxed local geometric structures for DVG (a), Be-decorated DVG (b), Mg-decorated DVG (c), Ca-decorated DVG (d), Sr-decorated DVG (e) and Ba-decorated DVG (f), respectively.

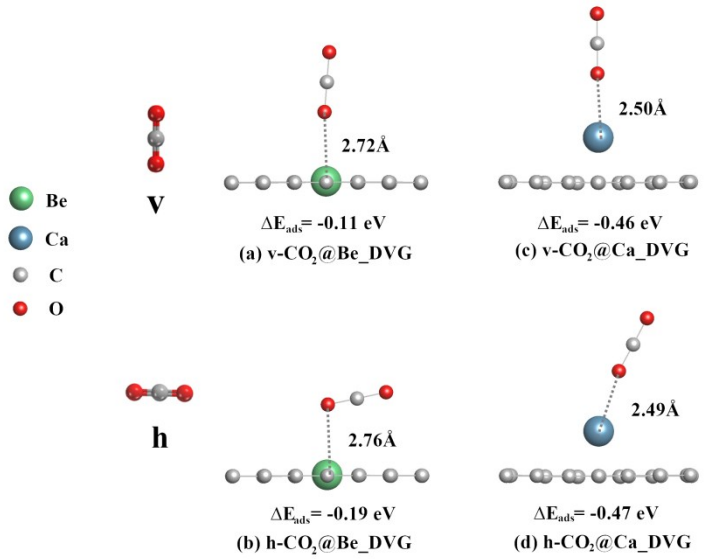

Fig. S2 Relaxed structures for two possible horizontal (h) and vertical (v) configurations of CO_2 molecule adsorbed on Be and Ca decorated DVG.

To investigate the adsorption behaviors of CO_2 molecules on the alkali earth metal-decorated DVG, it is necessary to determine their optimal adsorption configurations. Considering Be and Ca systems as examples, two possible horizonal and vertical configurations of the CO_2 molecule were considered and are shown in Fig. S2 (v and h). The results indicate that the two horizonal configurations (b and d) are both slightly preferred in the exothermic and thermodynamic aspects. On the other hand, the relaxed CO_2 molecules are inclined to tilt as an oxygen atom approaches the decorated metal, suggesting the major role of the oxygen atom. Hence, the initial configuration of the CO_2 molecule is designed to be tilted. These four structural relaxations are converged to 0.01 eV/Å, ignoring the zero-point energy (ZPE) correction.

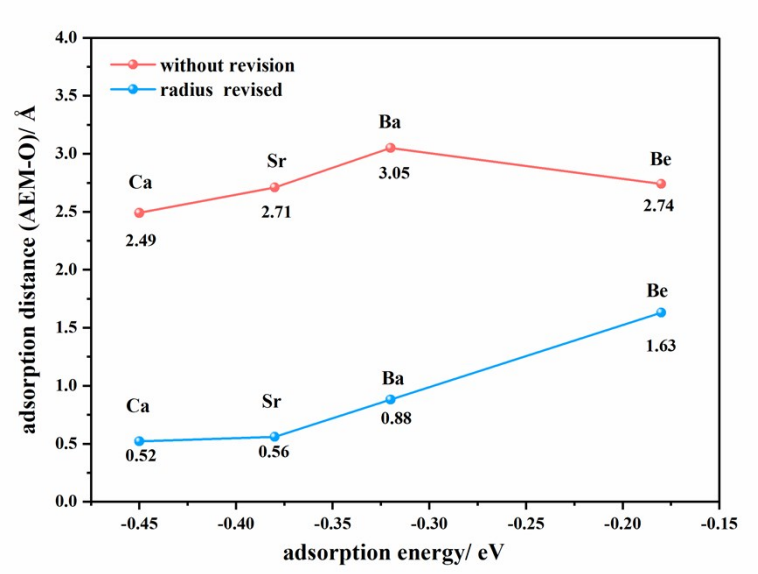

Fig. S3 Relations of CO_2 adsorption energy and AEM-O^1 distance, with the radius of metal atom revised or not.

To further study the relations between CO_2 adsorption energy and the adsorption phenomenon, the radius of metal atom is taken into account to revise the AEM-O^1 distance. As shown in Fig. S3, when the O^1-metal distance is revised by eliminating the radius of metal atom, the adsorption energy monotonically increases (release more energy) as the O^1-metal distance decreases. Without radius correction, the situation for Be_DVG is an exception.

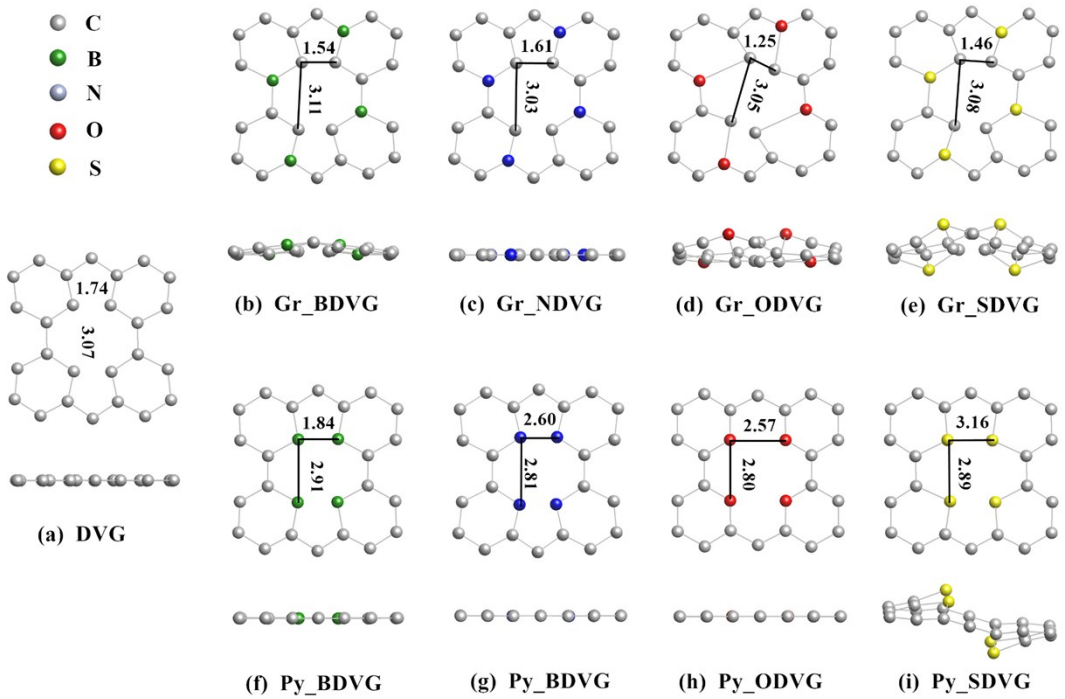

Fig. S4 Optimized structures of B-doped DVG (b, f), N-doped DVG (c, g), O-doped DVG (d, h) and S-doped DVG (e, i) in Py-type and Gr-type, respectively. All lengths are given in Å.

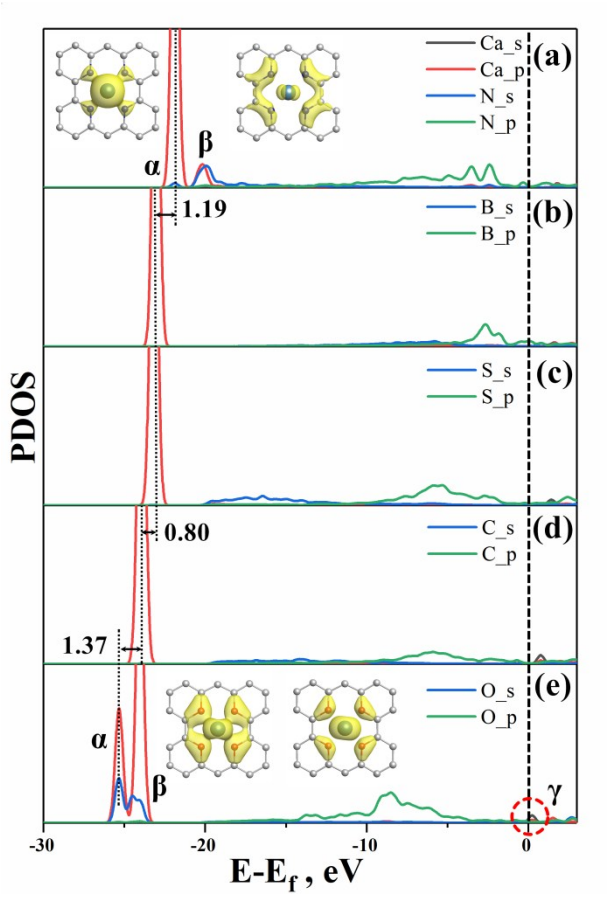

Fig. S5 PDOS of the Ca adatom and heteroatoms doped in Ca_PyNDVG (a), Ca_PyBDVG (b), Ca_PySDVG (c), Ca_DVG (d), and Ca_PyODVG (e) before CO_2 adsorption. The insets are the decomposed charge density corresponding to the labeled two peaks in sequence.

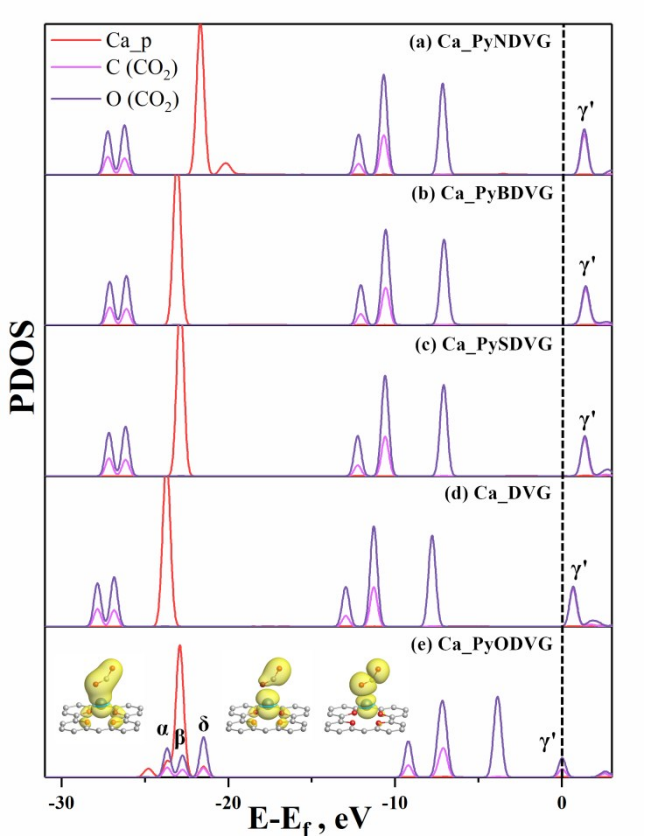

Fig. S6 PDOS of a CO_2 molecule interacting with Ca adatom anchored on Ca_PyNDVG (a), Ca_PyBDVG (b), Ca_PySDVG (c), Ca_DVG (d) and Ca_PyODVG (e) after CO_2 adsorption. The insets are the decomposed charge density corresponding to the labeled three peaks (α，β and γ) in sequence.

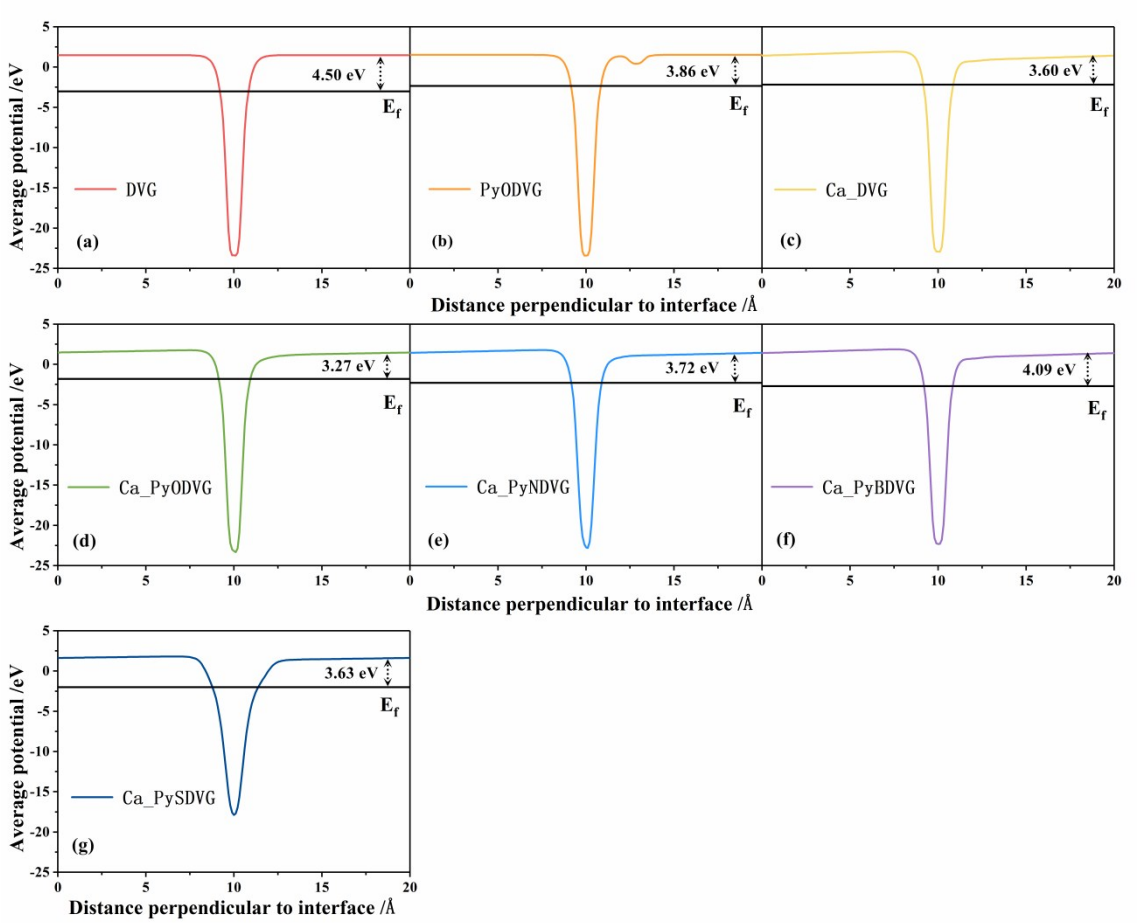

Fig. S7 Average potentials of seven kinds of graphene substrates. Fermi level and the values of work functions are marked, respectively.

Table S1 Formation energies **(E_f)** required for AEMs to form a dimer and trimer on DVG or O-doped DVG.

AEMs	Slab	$E_{f\text{-}21}$ (eV)	$E_{f\text{-}31}$ (eV)	$E_{f\text{-}32}$ (eV)
Be	DVG	5.98	3.94	-2.04
Ca	DVG	1.30	2.70	1.40
Ca	PyODVG	0.40	1.65	1.25
Sr	DVG	1.29	2.74	1.45
Ba	DVG	1.54	2.35	0.81

The formation energies (Ef) form single metal atom to dimer and trimer are defined as:

$$E_{f-21} = E_{dimer\_slab} - (2 \times E_{single_{slab}} - E_{slab})$$

$$E_{f-31} = E_{trimer\_slab} - (3 \times E_{single_{slab}} - 2 \times E_{slab})$$

Then, the formation energy from dimer or trimer can be calculated by:

$$E_{f-32} = E_{f-31} - E_{f-21}$$

Where E_{slab}, E_{single_slab}, E_{dimer_slab} and E_{trimer_slab} refer to the energy of graphene slab, a single metal atom, metal dimer and trimer decorated slab, respectively.

As listed in Table S1, all the positive values indicate the corresponding formation processes are thermodynamically unfavorable. For Be bound DVG, although the formation energy from dimer to timer is negative, the formation referring to single atom dispersion is positive. Consequently, all the four alkali earth metals prefer to form single metal atom dispersion.

Table S2 Selection of doping-types for heteroatoms, and their stability testing.

Doing-types		E_d (eV)	Substrates	E_b (eV)	E_{co} (eV)	Stability
BDVG	PyBDVG	1.02	Ca_PyBDVG	-4.05	-1.89	acceptable
	GrBDVG	4.49	-	-		-
NDVG	PyNDVG	-3.36	Ca_PyNDVG	-6.37		acceptable
	GrNDVG	2.84	-	-		-
ODVG	PyODVG	-9.20	Ca_PyODVG	-2.01		acceptable
	GrODVG	1.50	-	-		-
SDVG	PySDVG	-0.92	Ca_PySDVG	-2.79		acceptable
	GrSDVG	10.31	-	-		-

Table S3 Bader charge of the selected atoms in different substrates.

Substrates	Adsorption state	Δq (4*Pya)	Δq (Ca)	Δq (CO_2)
Ca_DVG	before adsorption	-0.89	1.45	-
	after adsorption	-0.89	1.46	0.04
Ca_PyNDVG	before adsorption	-4.94	1.50	-
	after adsorption	-4.90	1.50	0.04
Ca_PyBDVG	before adsorption	4.36	1.41	-
	after adsorption	4.37	1.43	0.03
Ca_PySDVG	before adsorption	0.06	1.42	-
	after adsorption	-0.01	1.43	0.01
Ca_PyODVG	before adsorption	-4.35	1.47	-
	after adsorption	-4.35	1.57	-0.70

Here, Δq stands for the total charge of the selected atoms and is given in e. A negative value means the electron acquirement.

4*Pya represents the four atoms in the pyridine position. The atoms are C, N, B, S and O atoms in Ca_DVG, Ca_PyNDVG, Ca_PyBDVG, Ca_PySDVG and Ca_PyODVG, respectively.

The Bader charge listed in Table S2 shows that the Δq values of all selected atoms has no evident change before and after CO_2 adsorption, except for those of Ca and CO_2 in Ca_PyODVG. By comparison, it is found that CO_2 obtains 0.70e, while the Ca atom loses 0.10e. Given that the oxygen atoms in the pyridine position have no electron gain or loss, the CO_2 molecule still needs to accept a large number of electrons from the carbon atoms on graphene.

Table S4 Adsorption energies (E_{ads}) of CO_2 on GP, DVG and heteroatom-doped DVG.

Configurations	GP	DVG	PyBDVG	PyNDVG	PyODVG	PySDVG
E_{ads}(eV)	-0.14	-0.12	-0.15	-0.28	-0.16	-0.08

As listed in Table S4, all the adsorption energies of CO_2 on pristine graphene, DVG and heteroatom-doped DVG are rather limited. Therefore, our work aims to enhance the adsorption by introducing AEM atoms.

Table S5 Adsorption energies of four different gases on Ca-decorated graphene and the selectivity factors of CO_2 to competitive gases.

Configurations	Gas adsorption energies (eV)			
	CO_2	N_2	CH_4	H_2
Ca_DVG	-0.45	-0.28	-0.28	-0.11
Ca_PyODVG	-0.74	-0.58	-0.44	-0.21