Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Achieving a direct band gap in oxygen functionalized-monolayer scandium carbide by applying an electric field

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Geometric properties of each model of monolayer Sc_2CO_2

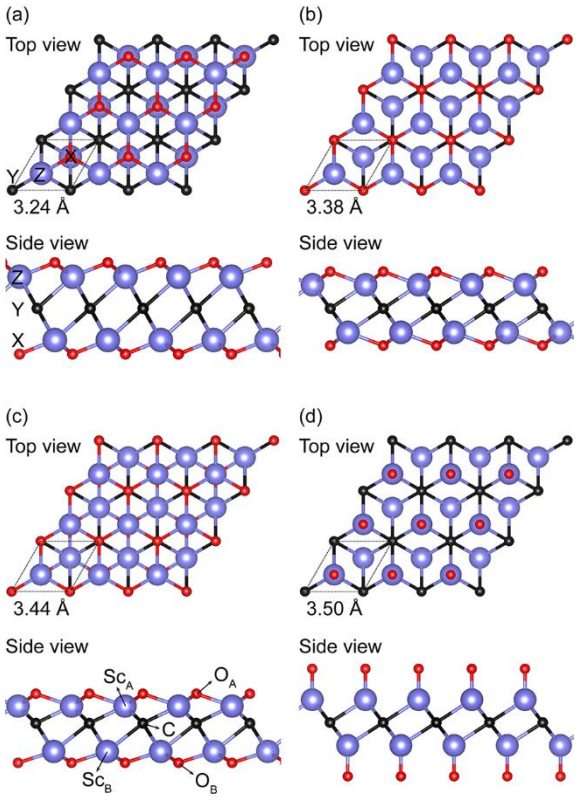

Fig. S1. Geometry of the four models of monolayer Sc_2CO_2: (a) Model 1, (b) Model 2, (c) Model 3, and (d) Model 4, respectively.

The configurations of each model of monolayer Sc_2CO_2 are shown in Fig. S1. From previous studies, it is known that two terminated O layers can be positioned with four types on both sides of this single-layer Sc_2C: Model 1 has each terminated O layer stacked on the X and Z sites, which are the hollow sites of the Sc layer on the same side; Model 2 has both terminated O layers stacked on top of the C layer (Y site); Model 3 is the mixing structure of Model 1 and 2; Model 4 has two terminated O layers stacked on the X and Z sites, which are the top sites of the Sc layer on the same side.[1] The geometric properties of each model of

monolayer Sc_2CO_2 are listed in Table S1.

Table S1. Geometric properties of each model of monolayer Sc_2CO_2. The properties listed are the lattice parameter of the unit cell (a), Sc-C bond length (d_{Sc-C}), Sc-O bond length (d_{Sc-O}), C-O bond length (d_{C-O}), and thickness (t). Model 3 has two bond lengths due to its asymmetric structure. The first one is related to the Sc_A (O_A) atom and the other one is related to the Sc_B (O_B) atom. The thickness is defined as the distance along the z-axis between the O_A and O_B atoms.

	a (Å)	d_{Sc-C} (Å)	d_{Sc-O} (Å)	d_{C-O} (Å)	t (Å)
Model 1	3.24	2.52	2.02	3.07	4.86
Model 2	3.38	2.35	2.08	2.05	4.09
Model 3	3.44	2.21, 2.53	2.10, 2.09	1.65, 2.97	3.86
Model 4	3.50	2.41	1.77	3.86	6.15

References

[1] Naguib, M., Mochalin, V. N., Barsoum, M. W. & Gogotsi, Y., *Adv. Mater.* 2014, **26**, 992-1005.

Most stable model of monolayer Sc_2CO_2 under an external E-field

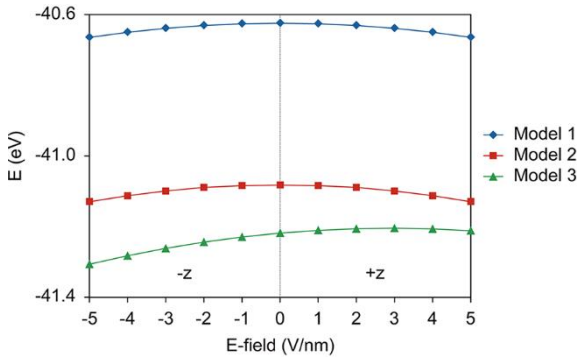

Fig. S2. Total energy of each model of monolayer Sc_2CO_2 as a function of the external E-field. The blue, red, and green lines represent Model 1, 2, and 3, respectively. The case of Model 4 is not shown here because its total energy is too high compared to the other cases.

The total energies of each model of monolayer Sc_2CO_2 under the perpendicular external electric field (E-field) from -5 to 5 V/nm are plotted in Fig. S2. Here, all the total energies represent the values that were calculated using the PBE functional. Under all the intensities of the E-field, Model 3 has the lowest total energies. Thus, although the external E-field is applied to monolayer Sc_2CO_2, the most stable structure is maintained as Model 3.

Existence of an internal E-field in monolayer Sc_2CO_2

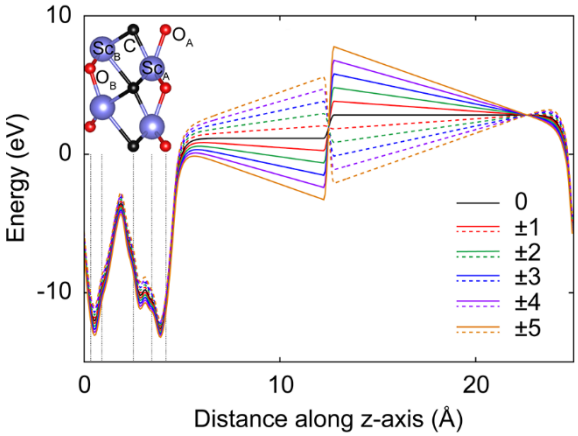

Fig. S3. Electrostatic potential along the normal direction to the monolayer Sc_2CO_2 sheet. The different colored lines represent the electrostatic potential under each intensity of the external E-field. The solid and dotted lines indicate the positive and negative E-field, respectively. The sharp slope at a near vacuum level of 12.5 Å represents an artificial dipole for the calculation of the external E-field.

The electrostatic potential along the normal direction to the monolayer Sc_2CO_2 sheet under each external E-field is shown in Fig. S3. The calculations of the external E-field were implemented by adding an artificial dipole to the vacuum level. At the E-field-free condition, however, there is also an artificial dipole. For this reason, it can be supposed that the artificial dipole is introduced by an internal E-field in monolayer Sc_2CO_2. In addition, by comparing the artificial dipole at the no E-field state with one under an external E-field, it is also confirmed that the direction of the internal E-field is the same as that of a positive external E-field.

Major factors of the band gap properties in monolayer Sc_2CO_2

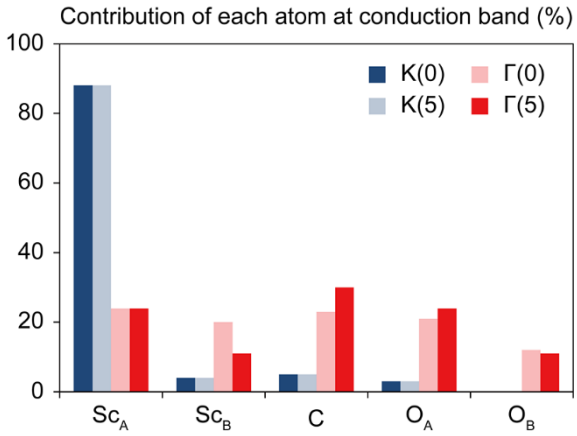

Fig. S4. Bar graph of the contribution of each atom in monolayer Sc_2CO_2 to the *K* and Γ points in the lowest conduction band under 0 and 5 V/nm. The blue and red bar represent the K and Γ points, respectively. Also, the vivid one indicates the conduction band minimum under each external E-field.

The contribution of each atom in monolayer Sc_2CO_2 to the *K* and Γ points in the lowest conduction band under 0 and 5 V/nm is presented in Fig. S4. The contribution of each atom at the *K* point is maintained despite applying an external E-field to monolayer Sc_2CO_2. On the other hand, the contribution of each atom at the Γ point is slightly varied as the E-field is applied. However, in spite of the change of the contribution of each atom, the composition of the in-plane (p_x, p_y, d_{xy}, d_{x2-y2}) and out-of-plane orbitals (p_z, d_{xz}, d_{yz}, d_{z2}) of all atoms at each point in the lowest conduction band is preserved under the external E-field as 92 % in-plane orbitals at the K point and 100 % out-of-plane orbitals at the Γ point. Thus, this fact supports the assumption that the major factor in the variation of the band gap characteristics is the difference in the composition of the orbital at each point in the lowest conduction band.