Electronic Supplementary Information

Probing the potential of Al_2CO/SiC heterostructures for visible light driven photocatalytic water splitting using first-principles strategies

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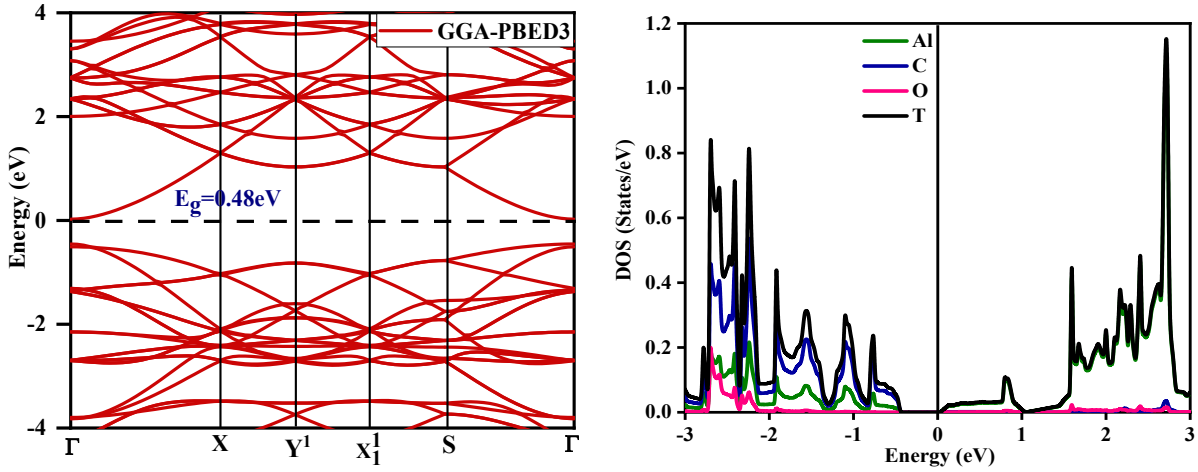
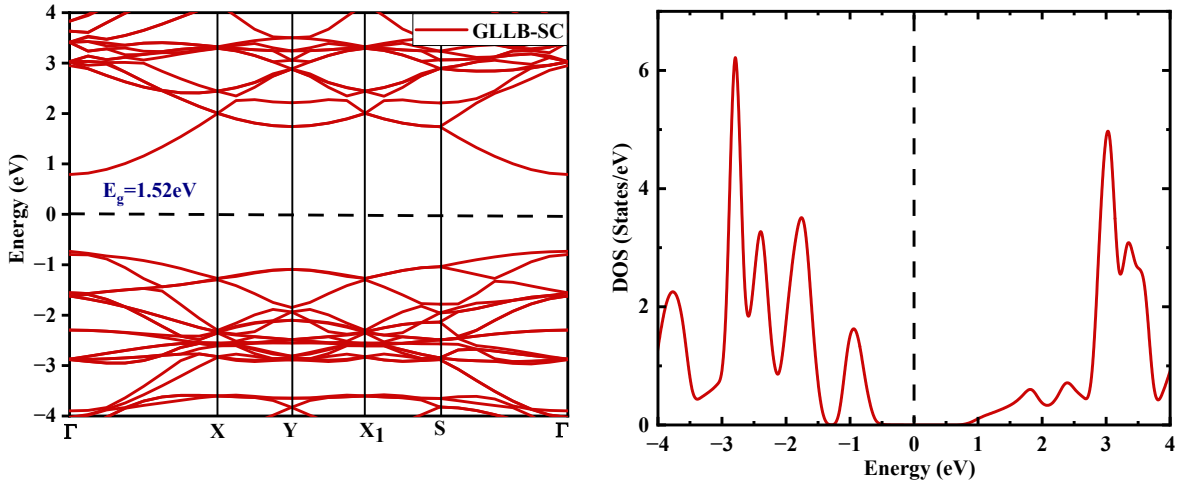
1. Electronic Properties of the Al_2CO, SiC, and Al_2CO/SiC with different functionals.
2. Hirshfeld Charge Analysis of the interface.
3. PEDA Analysis.
4. Calculation method to find Gibbs free energy for HER and OER.

1. **Electronic Properties of the Al_2CO, SiC, and Al_2CO/SiC with different functionals.**

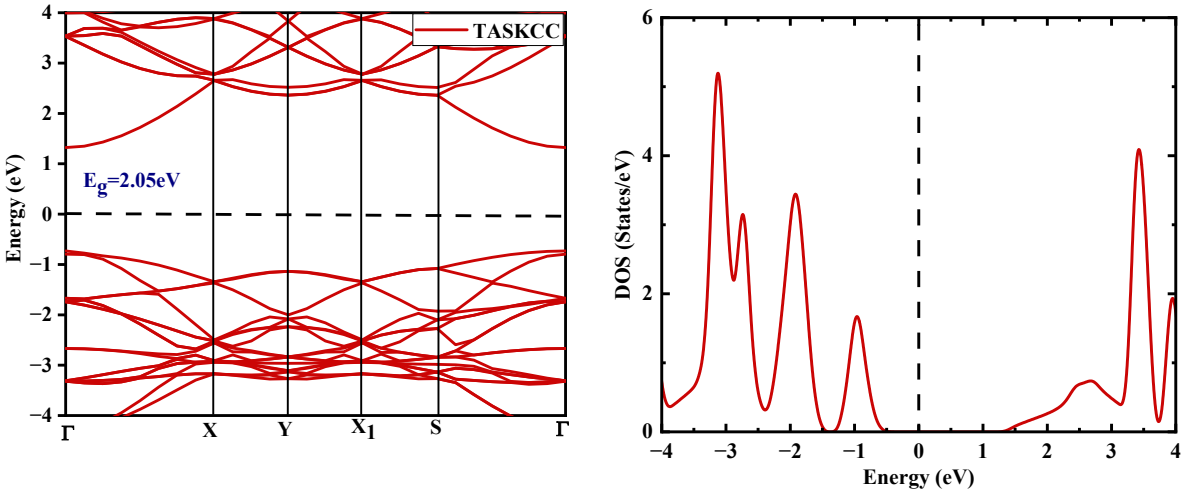
(a)



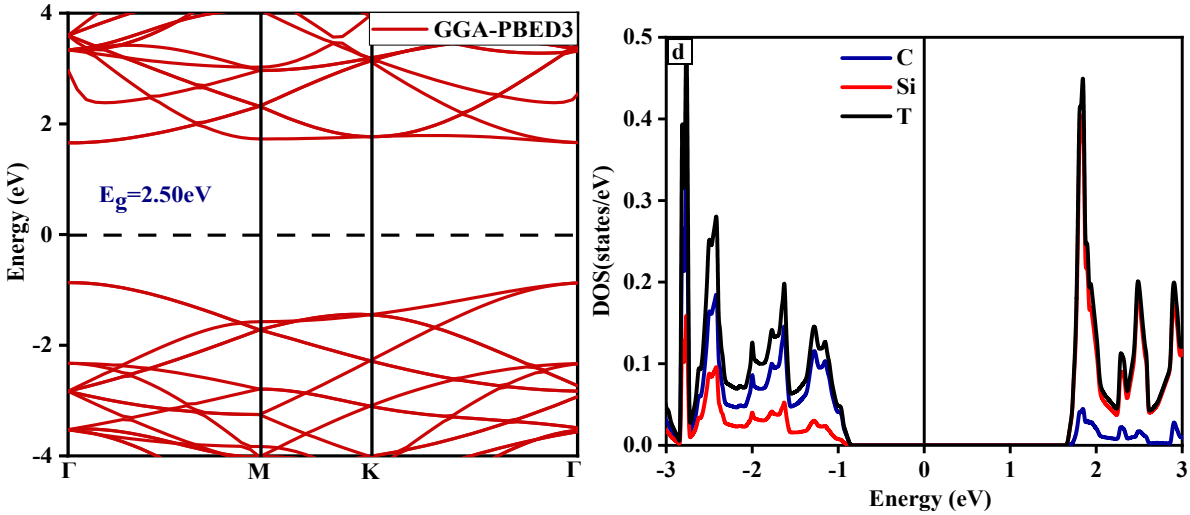
(b)



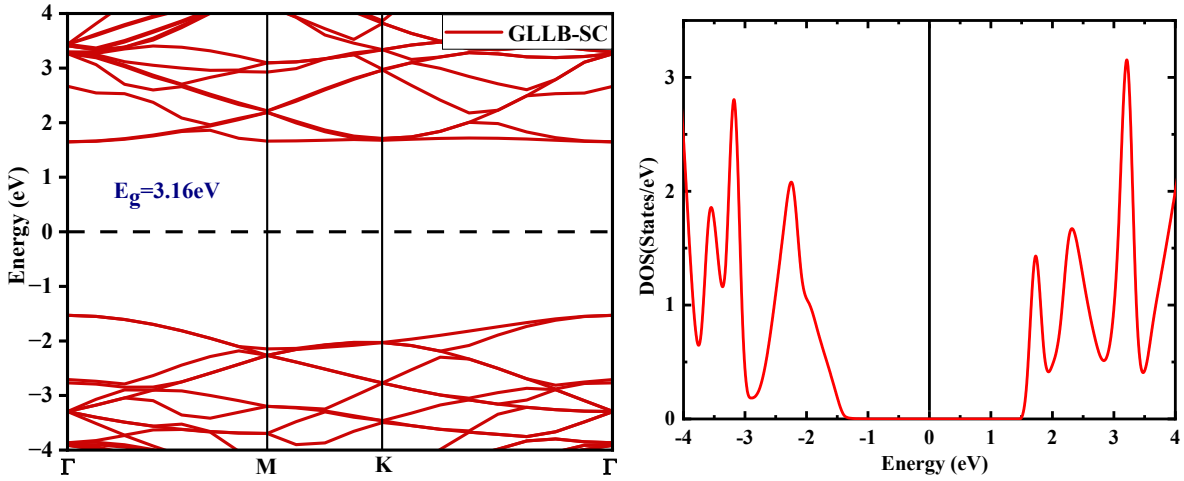
(c)


TASKCC
E_g=2.05eV
Energy (eV)
Γ
X
Y
X_1
S
Γ
DOS (States/eV)
Energy (eV)

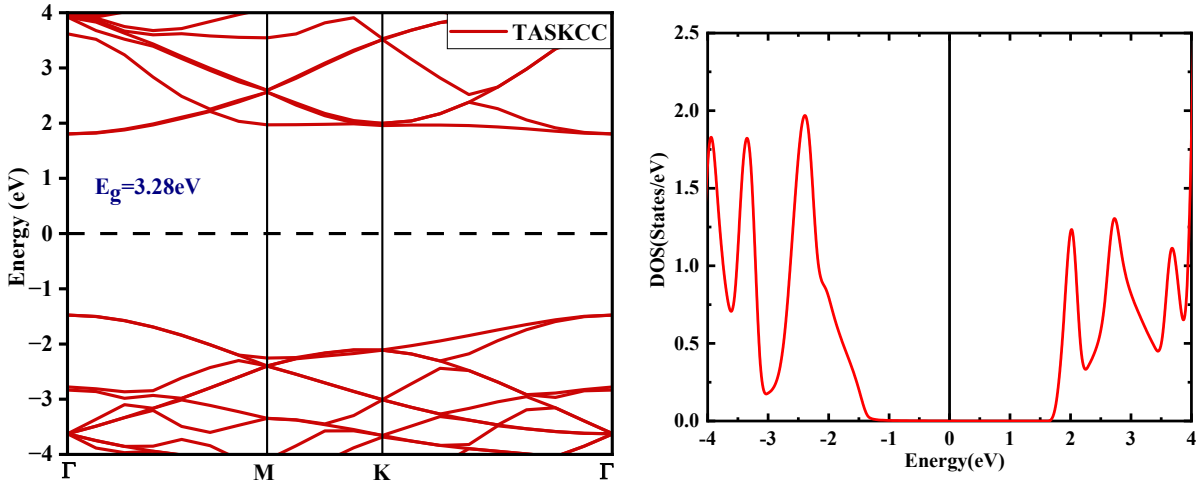
(d)


GGA-PBED3
E_g=2.50eV
Energy (eV)
Γ
M
K
Γ
d
C
Si
T
DOS(states/eV)
Energy (eV)

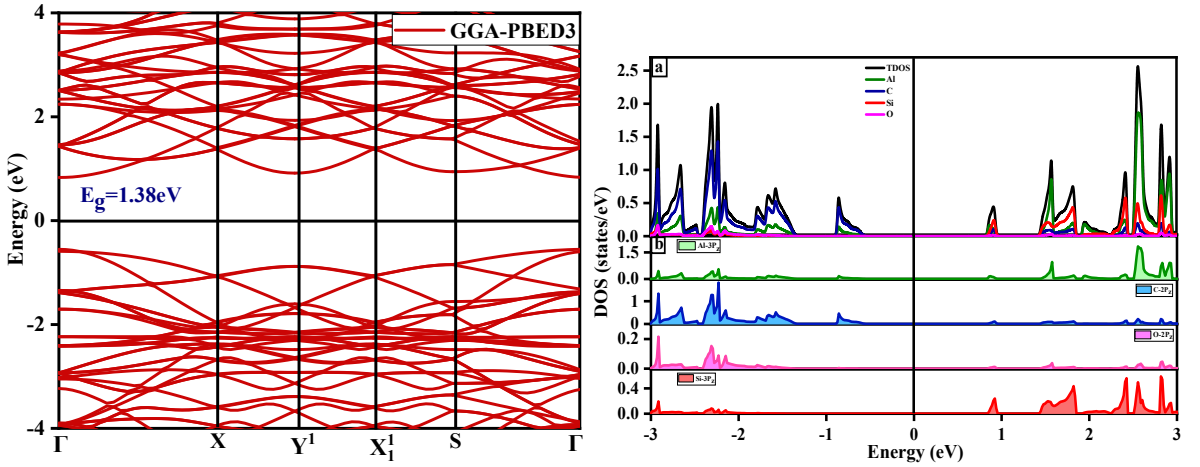
(e)


GLLB-SC
E_g=3.16eV
Energy (eV)
Γ
M
K
Γ
DOS(States/eV)
Energy (eV)

(f)


TASKCC
Eg=3.28eV
Energy (eV)
Γ
M
K
Γ
DOS(States/eV)
Energy(eV)

(g)


GGA-PBED3
Eg=1.38eV
Energy (eV)
Γ
X
Y1
X11
S
Γ
a
TDOS
Al
C
Si
O
b
Al-3Pz
C-2Pz
O-2Pz
Si-3Pz
DOS (states/eV)
Energy (eV)

(h)

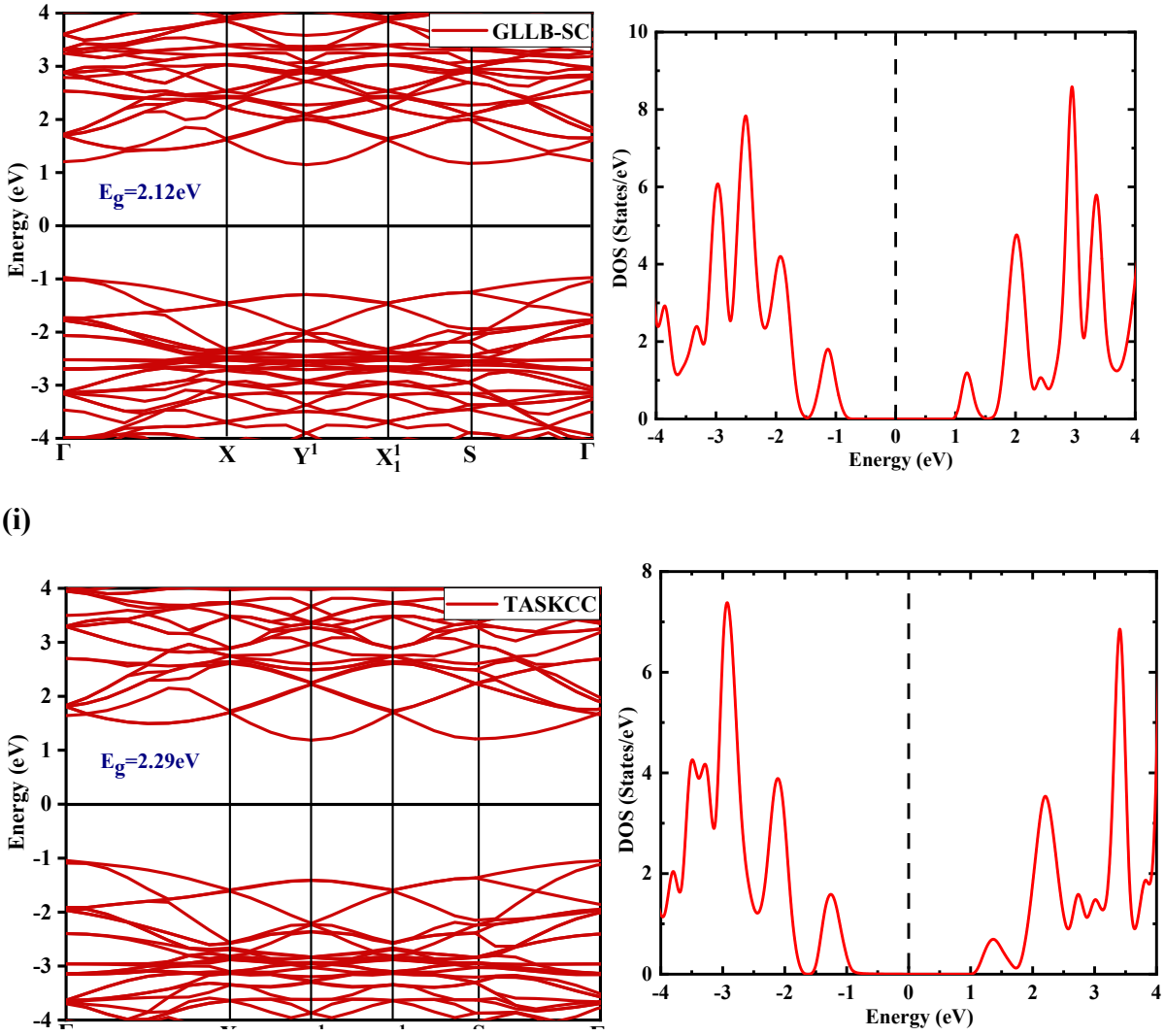


Fig. S1. The calculated band structure and DOS of Al_2CO (a, b, c) SiC (d, e, f), and Al_2CO/SiC (g, h, i) with different functionals such as GGA-PBED3, GLLB-SC, and TASKCC.

2. Hirshfeld Charge Analysis of interface

The value of Hirshfeld charges on the Al_2CO/SiC interface as indicated in Fig. 6(c) are O(1) = O(2) = O(3) = O(4), O(32) = O(33) = O(34) = O(35) = O(36) = -0.231 e, Al(5) = Al(6) = Al(7) = Al(8), Al(10) = Al(11) = Al(13) = 0.390 e, Al(9) = Al(12) = 0.391 e, Al(14) = Al(15) = Al(17) = Al(19) = Al(20) = Al(21) = 0.324 e, Al(16) = Al(22) = 0.323 e, Al(18) = 0.325, C(23) = C(24) = C(26) = C(27) = C(29) = C(30) = -0.470 e, C(25) = C(28) = C(31) = -0.471 e, C(37) = C(52) = -0.339 e, C(38) = -0.340 e, Si(39) = Si(40) = Si(41) = Si(42) = Si(43) = Si(44) = Si(45) = Si(46) = Si(47) = 0.327 e, C(48) = C(49) = C(50) = C(51) = -0.340 e, C(53) = C(54) = -0.340 e. This indicates that Al and Si atoms have more positive charge behaves as a donor

while O and C atoms have more negative charge behaves as an acceptor so, the overall values of Hirshfeld charge are Al (0.391 e), Si (0.327 e), O (-0.231 e) and C (-0.471 e).

3. PEDA Analysis

The value of ionization energies (IE) was calculated using PEDA analysis to investigate the type of interaction between interface and water molecule. Lower total energy values or more favourable energy components (e.g., larger negative $E_{electrostatic}$, $E_{orbital}$, and smaller positive E_{steric} values) indicate greater stability in PEDA analysis. From Table S1 it can be seen that AD site forms the most stable structure and this illustrates that magnitude of IE in interface is higher than all other sites. These results are consistent with previous results such as adsorption energies and Hirshfeld charge analysis.

Table. S1. The calculated values of E_{Pauli}, $E_{electrostatic}$, E_{steric}, $E_{orbital}$, and IE per PEDA energy terms (in eV)

Site	E_{Pauli}	$E_{electrostatic}$	E_{steric}	$E_{orbital}$	IE
AA	2.80	-2.24	0.56	-1.14	-0.58
AB	3.22	-2.49	0.73	-1.38	-0.65
AC	3.09	-2.39	0.69	-1.29	-0.61
AD	9.96	-6.16	3.81	-11.22	-7.42

4. Calculation method to find Gibbs free energy for HER and OER

The value of ΔG can be calculated by using equation (1):

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE(H)} - T\Delta S_H \quad (1)$$

Where ΔE_H represents the E_{ad} of H atom and can be calculated using equation (2),

$$\Delta E_H = E_{H^*} - E_* - \frac{1}{2} E_{H_2} \quad (2)$$

E_{H^*} and E_* represent E_{ad} of the interface with and without the adsorbed hydrogen atom. The difference in zero-point energies and entropies of adsorbed H atom and ½(H_2) in the gas phase

is represented by $\Delta E_{ZPE(H)}$ and ΔS_H at temperature 298.15 K. The $\Delta E_{ZPE(H)}$ can be calculated using equation (3).

$$\Delta E_{ZPE(H)} = E_{ZPE(H^*)} - E_{ZPE(*)} - \frac{1}{2} E_{ZPE(H_2)} \quad (3)$$

Where $E_{ZPE(H^*)}$, $E_{ZPE(*)}$, and $\frac{1}{2} E_{ZPE(H_2)}$ are zero-point energy of the adsorbed H atom on the catalyst, zero-point energy of the catalyst, and gas phase H_2.

To identify the potential determining steps (PDS) of the OER Gibbs free energy differences (ΔG) for every elementary reaction step were determined by using the formulas (4) to (8) [1, 2]:

$$\Delta G_1 = G(HO*) \quad (4)$$

$$\Delta G_2 = G(O^*) - G(HO^*) \quad (5)$$

$$\Delta G_3 = G(HOO^*) - G(O^*) \quad (6)$$

$$\Delta G_4 = 4.92 - G(HOO^*) \quad (7)$$

$$G(H^+ + e^-) = G(\frac{1}{2} H_2) \quad (8)$$

The E_{ad} of the intermediates such as HO^*, O^*, and HOO^* can be calculated using equations (9) to (11) [3]:

$$\Delta E_{HO^*} = E(HO^*) - E(*) - (E_{H_2O} - 1/2\, E_{H_2}) \quad (9)$$

$$\Delta E_{O^*} = E(O^*) - E(*) - (E_{H_2O} - E_{H_2}) \quad (10)$$

$$\Delta E_{HOO^*} = E(HOO^*) - E(*) - \left(2E_{H_2O} - \frac{3}{2} E_{H_2}\right) \quad (11)$$

Table. S2. The calculated adsorption energy (E_{ads}), zero-point energy (ZPE), entropic corrections (TS), Gibbs free energy change

of different intermediate adsorbed on Al_2CO/SiC surface such as HO^*, O^*, HOO^*.

Al_2CO/SiC	E_{ads} (eV)	ZPE (eV)	TS (eV)	ΔG (eV)
HO^*	-1.27	2.53	-0.38	1.64
O^*	-0.43	2.49	-0.18	2.24
HOO^*	-0.26	2.49	-0.52	2.75

References:

[1] S. Lu, H. L. Huynh, F. Lou, K. Guo, and Z. Yu, Nanoscale., 2021, **13**, 12885-12895.

[2] X. Xu, H. Xu, and D. Cheng, Nanoscale., 2019, **11**, 20228-20237.

[3] P. Zhai, M. Xia, Y. Wu, G. Zhang, J. Gao, B. Zhang, S. Cao, Y. Zhang, Z. Li, Z. Fan, C. Wang, X. Zhang, J. T. Miller, L. Sun and J. Hou, Natur. Commu., 2021, **12**, 4587.