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Supporting Information

Theoretical Insights into Effective Electron Transfer and Migration Behavior towards CO_2 Reduction on the BiOBr (001) Surfaces

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Surface formation energy

The surface energy is lower meaning that is more stable or more "bulklike". And the molar chemical potential (μ) is known as partial molar free energy. The surface energy can be expressed as [1, 2]:

$$\sigma = \frac{1}{2A}\left(E^{slab} - nE^{bulk}\right) \quad \text{.....(1)}$$

The surface energy of BiOBr{001} can be expressed as:

$$\sigma_{001-O} = \frac{1}{2A}\left(E^{slab}_{001-O} - nE^{bulk}_{BiOBr} - 2\mu^{slab}_{O}\right) \quad \text{.....(2)}$$

$$\sigma_{001-O+H} = \frac{1}{2A}\left(E^{slab}_{001-O+H} - nE^{bulk}_{BiOBr} - 2\mu^{slab}_{O} - 4\mu^{slab}_{H}\right) \quad \text{.....(2)}$$

$$\sigma_{001-Bi} = \frac{1}{2A}\left[E^{slab}_{001-Bi} - nE^{bulk}_{BiOBr} - 2\mu^{slab}_{O} - 2\mu^{slab}_{Bi}\right] \quad \text{.....(3)}$$

$$\sigma_{001-Br} = \frac{1}{2A}\left(E^{slab}_{001-Br} - nE^{bulk}_{BiOBr}\right) \quad \text{.....(4)}$$

The chemical potential of O in the slab (μ^{slab}_{O}) must be less than the chemical potential of O in its bulk phases (μ_O), otherwise, the compound slab will be unstable and more favorable to form bulk phase. Therefore, the thermodynamic range of the O chemical potential is

$$\mu^{slab}_{O} \le \mu_O \le \frac{1}{2}\mu_{O_2} \quad \text{.....(5)}$$

$$\frac{1}{2}\Delta H_f \le \Delta\mu_O \le 0 \quad \text{.....(6)}$$

Where $\Delta\mu_O$ is defined as $\Delta\mu_O = \mu^{slab}_{O} - \mu^{mol}_{O}$.

Internal electric field (IEF) magnitude

The IEF magnitude (E_{IEF}) could be obtained through Eq.(7) [3]

$$E_{IEF} = \left(\frac{-2V_s\rho}{\varepsilon\varepsilon_0}\right)^{1/2} \quad \text{.....(7)}$$

Where, V_s is the surface voltage, ρ is the surface charge density, $\mathcal{E}$ is the low-frequency dielectric constant, and $\mathcal{E}_0$ is the permittivity of free space. These meant that the E_{IEF} is mainly determined by the surface voltage and the charge density because $\mathcal{E}$ and $\mathcal{E}_0$ are two constants.

A surface voltage (V_S) is usually the result of a surface or insulator charge or work function (Φ) difference and it is most commonly detected with a non-contacting probe [4]. Hence, no electric field exists between the sample and the probe making $V_S = \Phi$.

The charge density could be picked up through Eq. (8)

$$\rho = \left(\frac{F}{A}\right)\left[\left(\frac{10^{-2pH} - K_1K_2}{10^{-2pH} + 10^{-2pH}K_1 + K_1K_2}\right)N_T\right] \quad \text{.....(8)}$$

Where F is the Faraday constant, A is the total surface area, N_T is the total number of moles of surface sites, and K_1 and K_2 are the acid equilibrium constants.

From the above, with no external electric field, the E_{IEF} was in direct proportion to work function (Φ) and inversely proportional to the surface area value ($SA=A/N_T$), as Eq. (9) shown:

$$E_{IEF} \propto \frac{\Phi}{A} \quad \text{.....(9)}$$

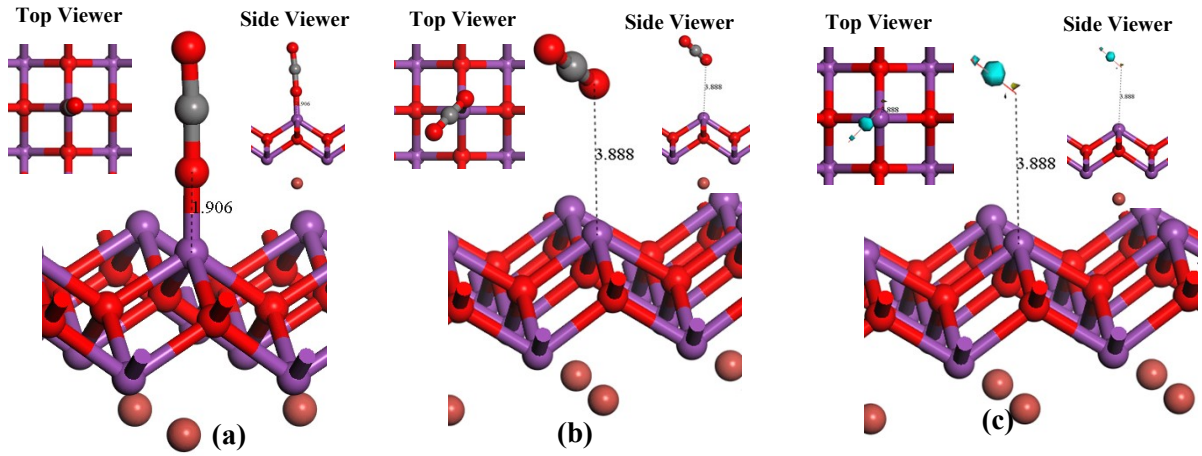

Figure S1 The structure for the O atoms of CO_2 adsorption on BiU adsorption site of BiOBr (001Bi) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

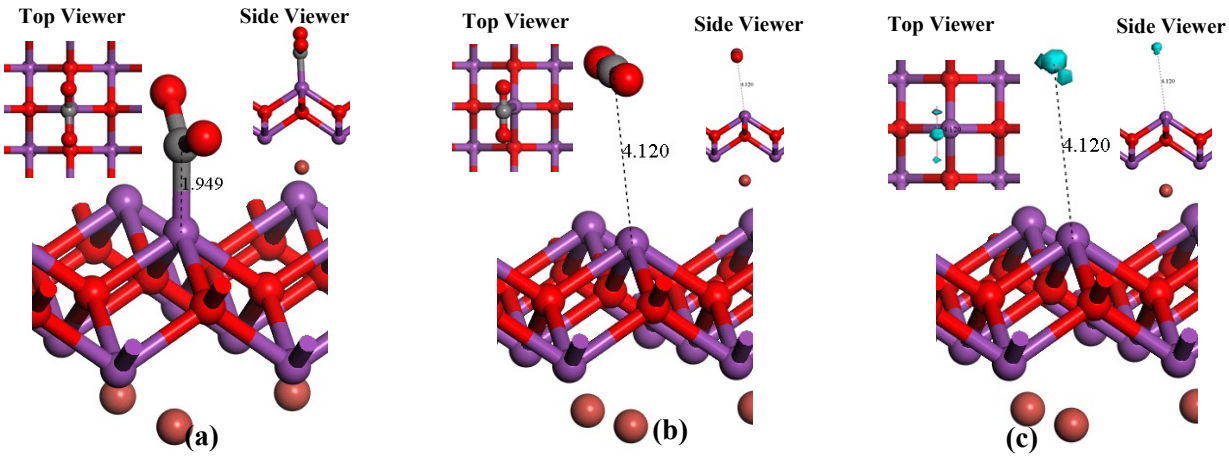

Figure S2 The structure for the C atoms of CO_2 adsorption on BiU adsorption site of BiOBr (001Bi) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

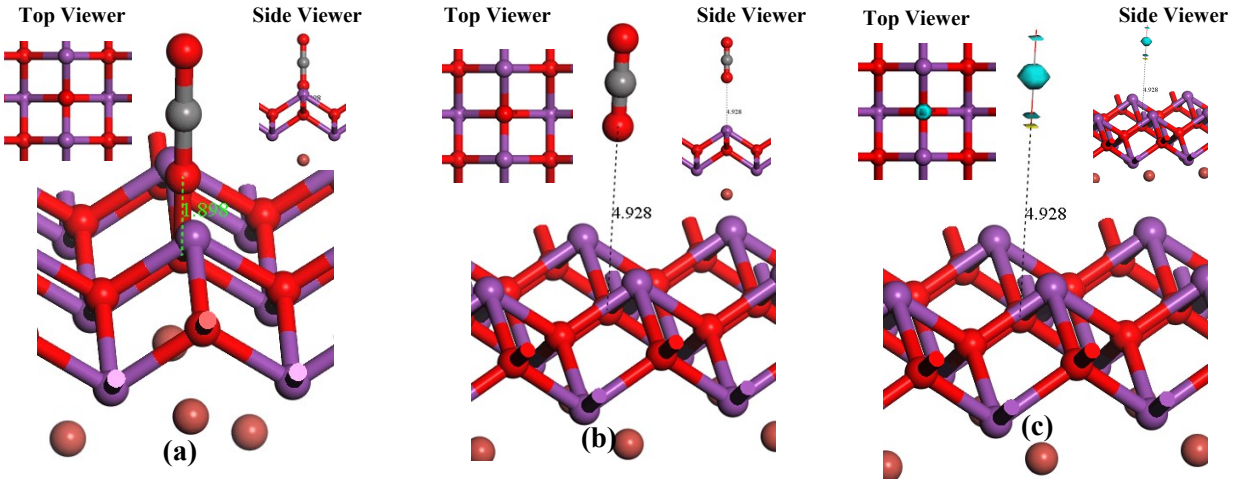

Figure S3 The structure for the O atoms of CO_2 adsorption on O adsorption site of BiOBr (001Bi) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

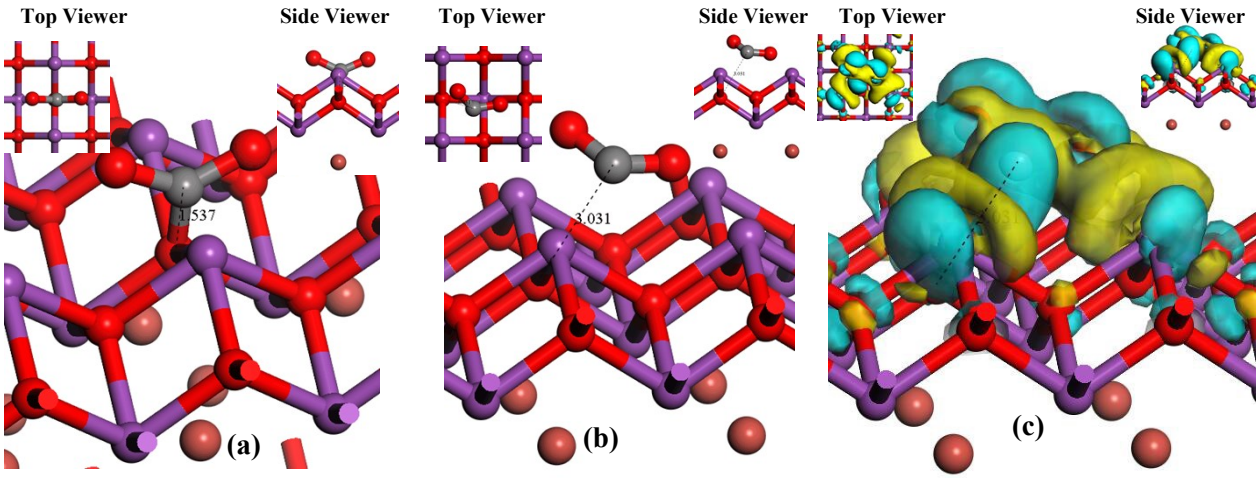

Figure S4 The structure for the C atoms of CO_2 adsorption on O adsorption site of BiOBr (001Bi) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

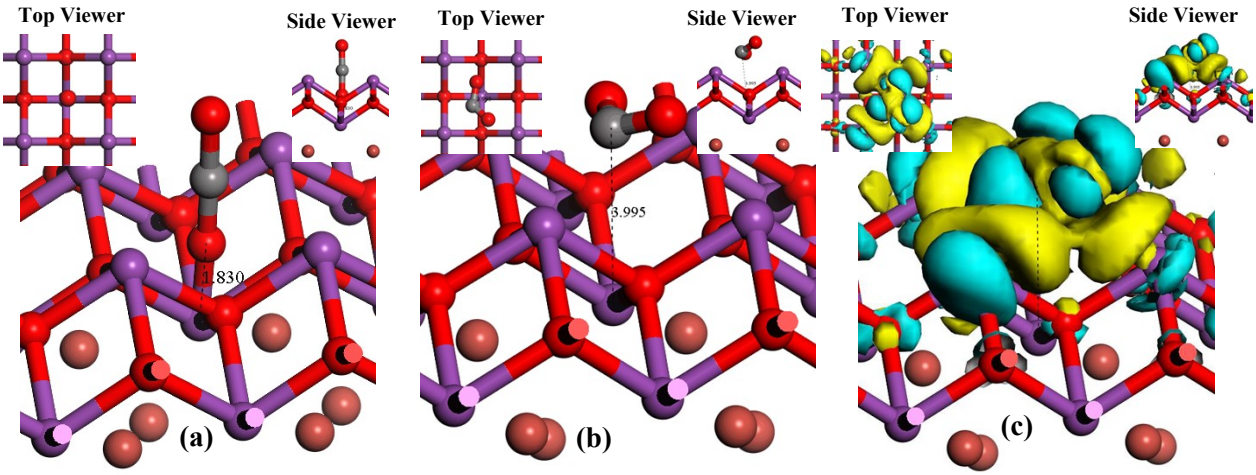

Figure S5 The structure for the O atoms of CO_2 adsorption on BiD adsorption site of BiOBr (001Bi) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

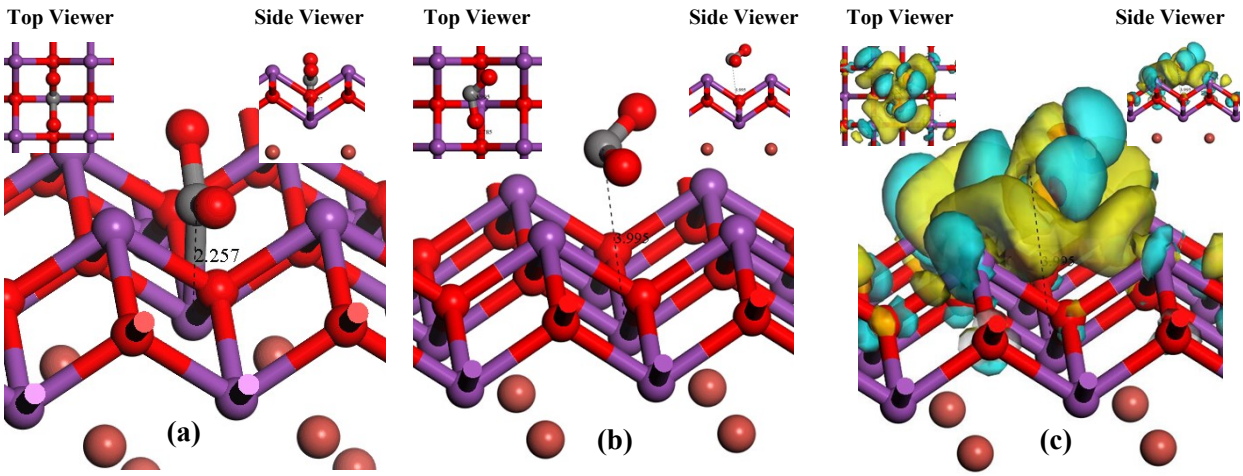

Figure S6 The structure for the C atoms of CO_2 adsorption on BiD adsorption site of BiOBr (001Bi) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

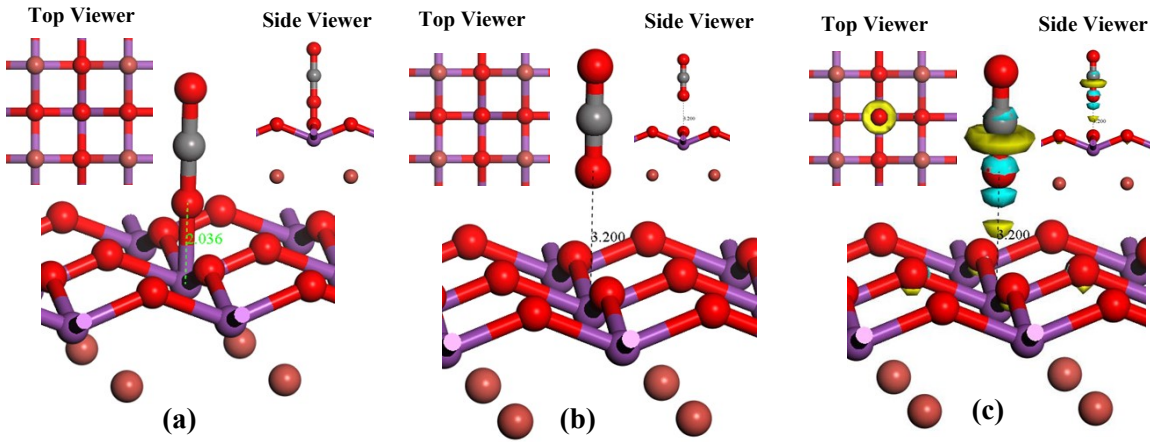

Figure S7 The structure for the O atoms of CO_2 adsorption on Bi adsorption site of BiOBr (001O) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

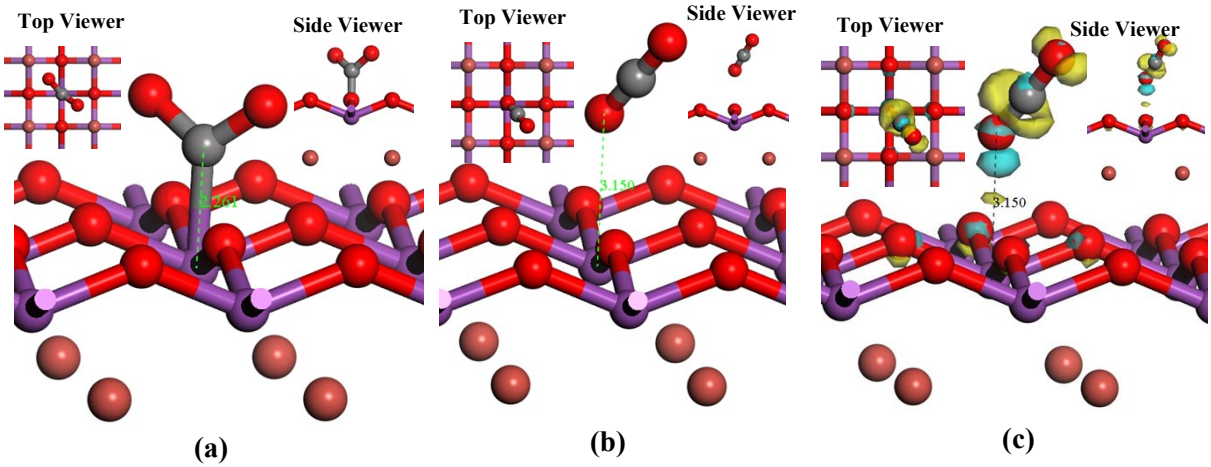

Figure S8 The structure for the C atoms of CO_2 adsorption on Bi adsorption site of BiOBr (001O) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

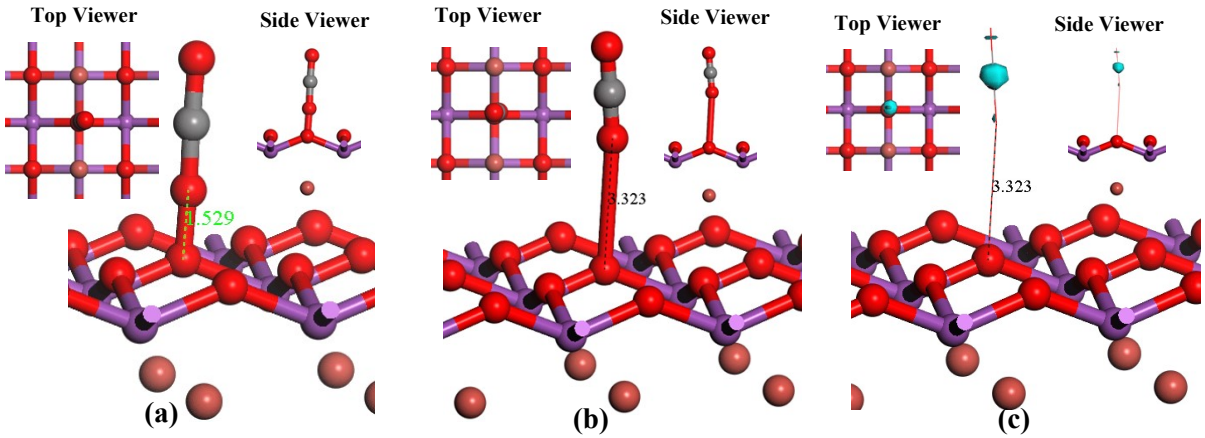

Figure S9 The structure for the O atoms of CO_2 adsorption on O adsorption site of BiOBr (001O) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

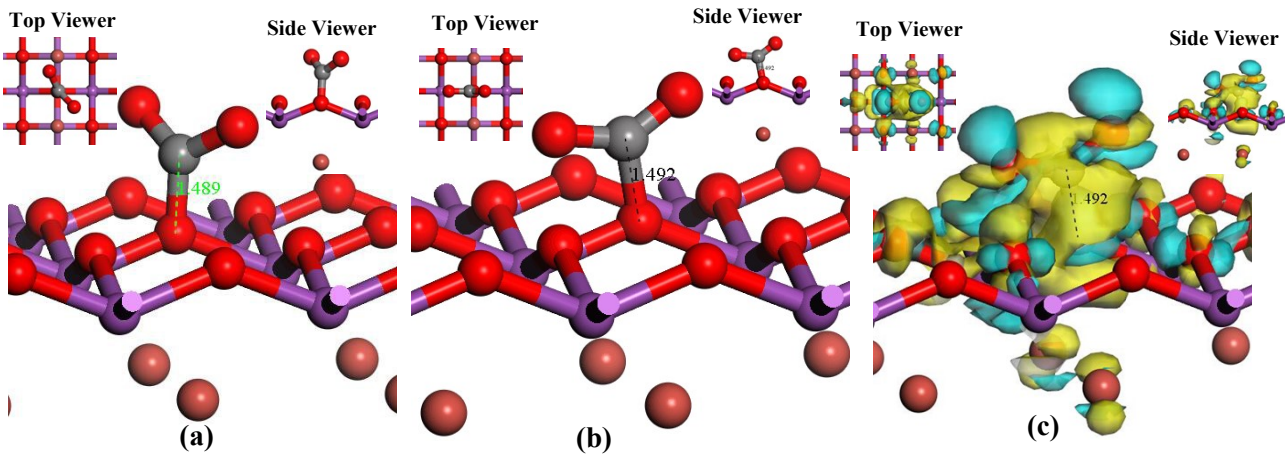

Figure S10 The structure for the C atoms of CO_2 adsorption on O adsorption site of BiOBr (001O) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

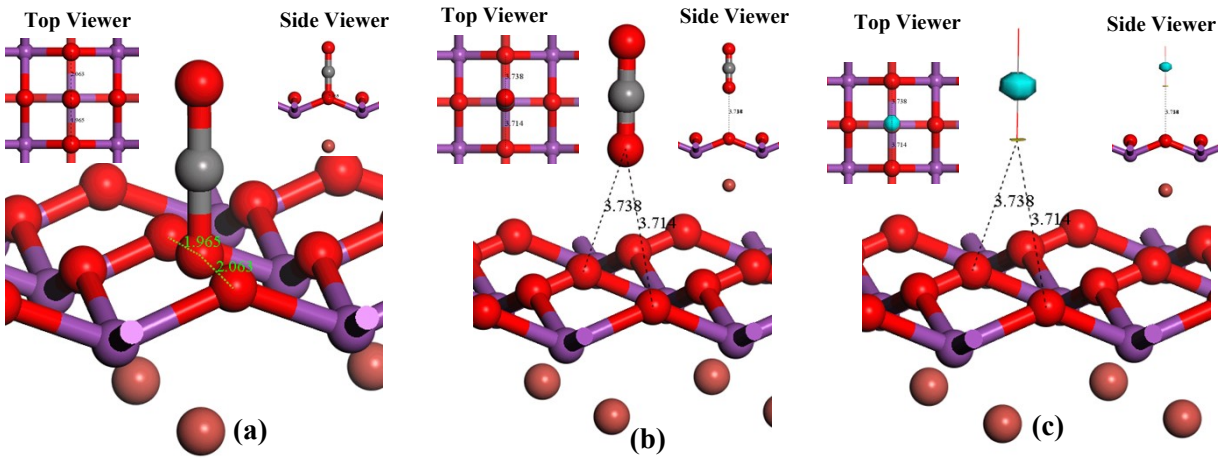

Figure S11 The structure for the O atoms of CO_2 adsorption on Br adsorption site of BiOBr (001O) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

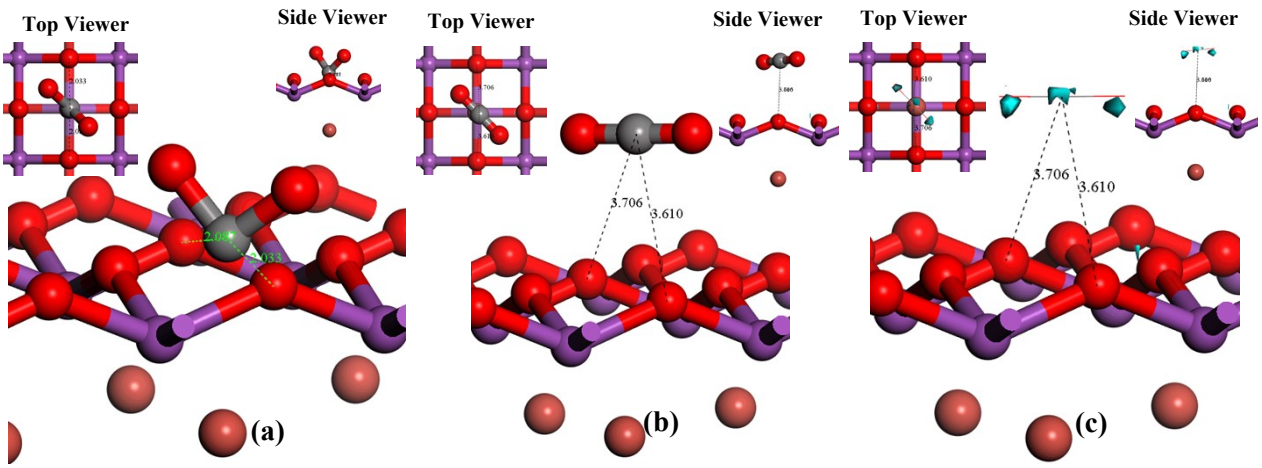

Figure S12 The structure for the C atoms of CO_2 adsorption on Br adsorption site of BiOBr (001O) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

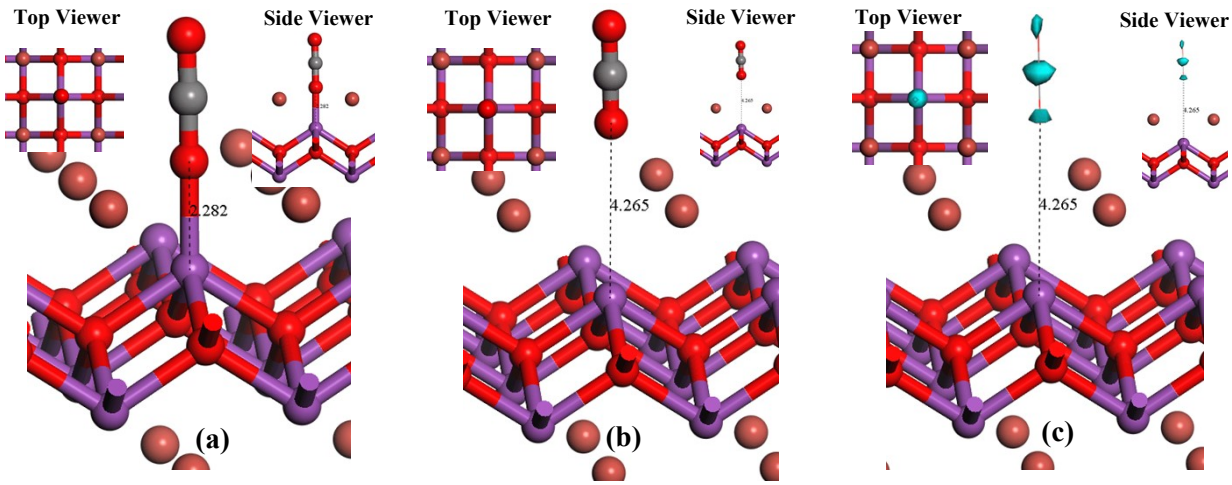

Figure S13 The structure for the O atoms of CO_2 adsorption on Bi adsorption site of BiOBr (001Br) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

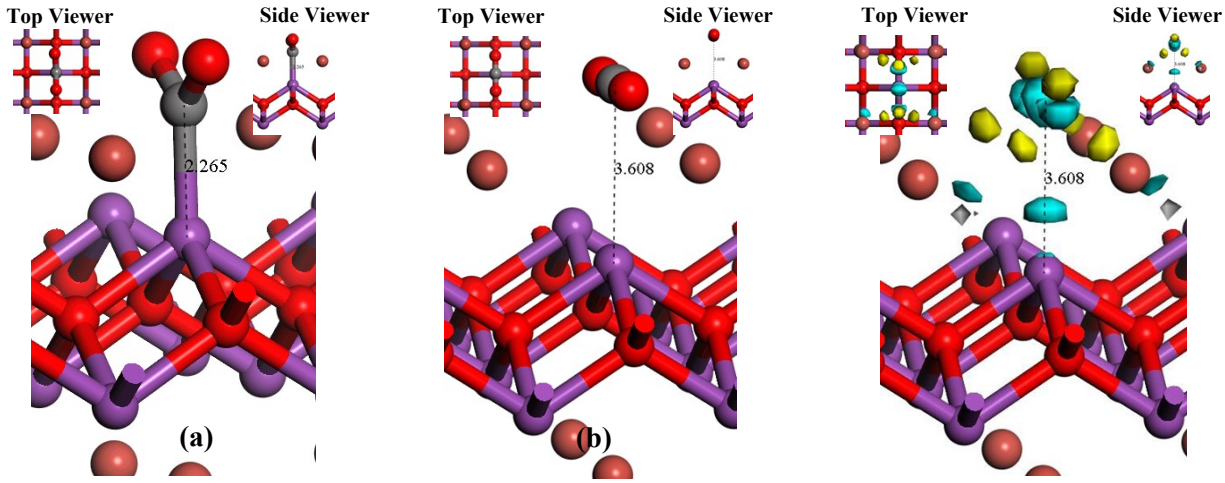

Figure S14 The structure for the C atoms of CO_2 adsorption on Bi adsorption site of BiOBr (001Br) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

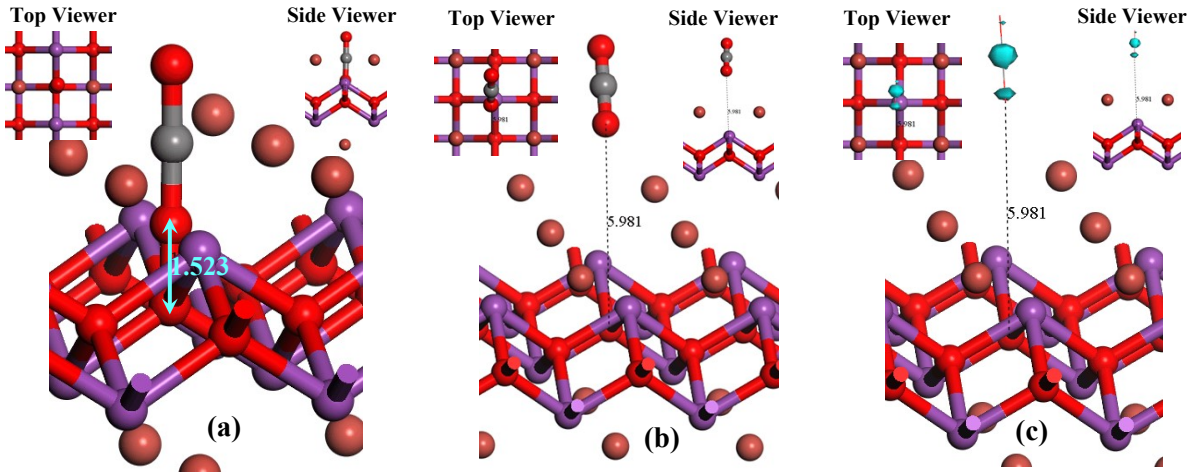

Figure S15 The structure for the O atoms of CO_2 adsorption on O adsorption site of BiOBr (001Br) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

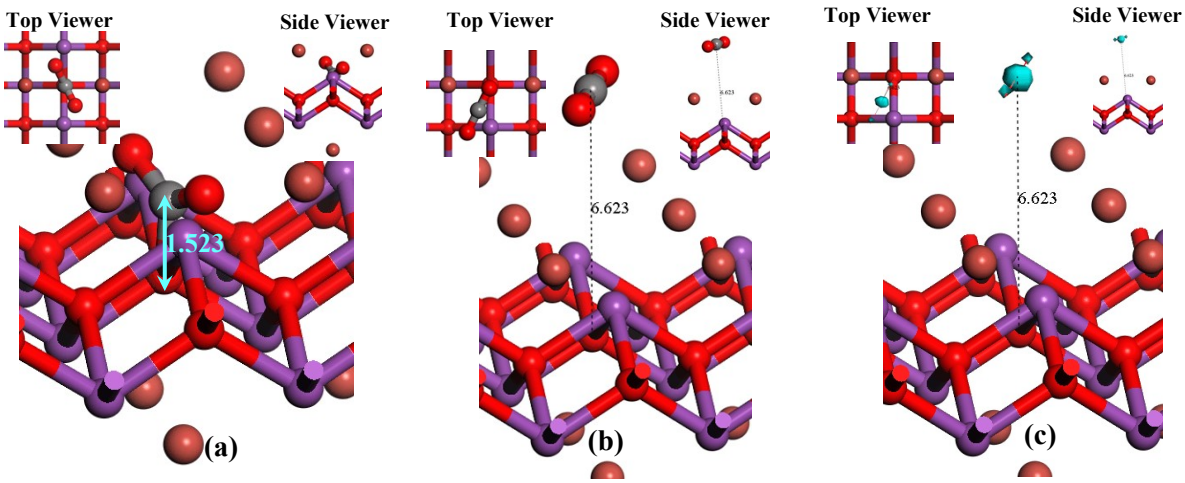

Figure S16 The structure for the C atoms of CO_2 adsorption on O adsorption site of BiOBr (001Br) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

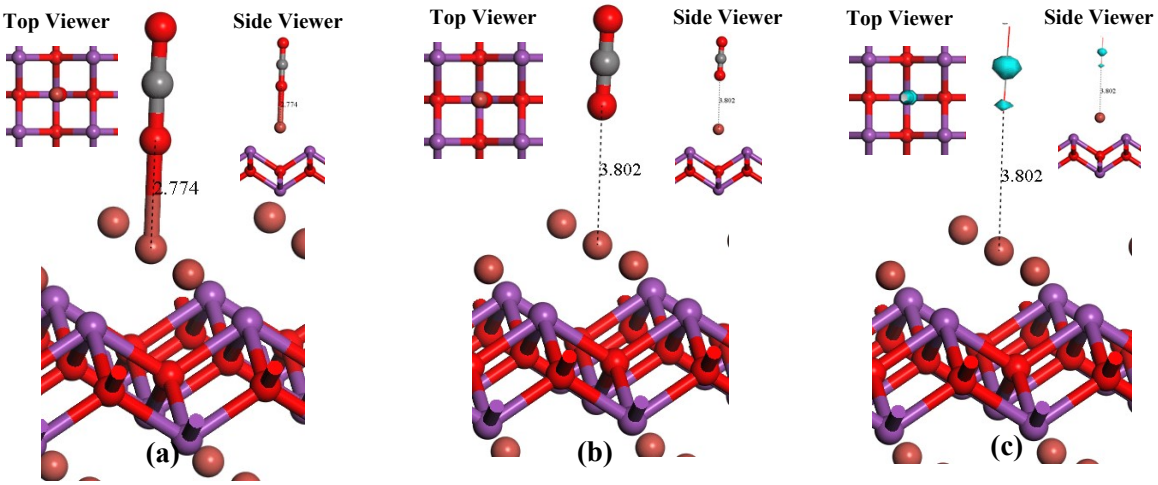

Figure S17 The structure for the O atoms of CO_2 adsorption on Br adsorption site of BiOBr (001Br) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

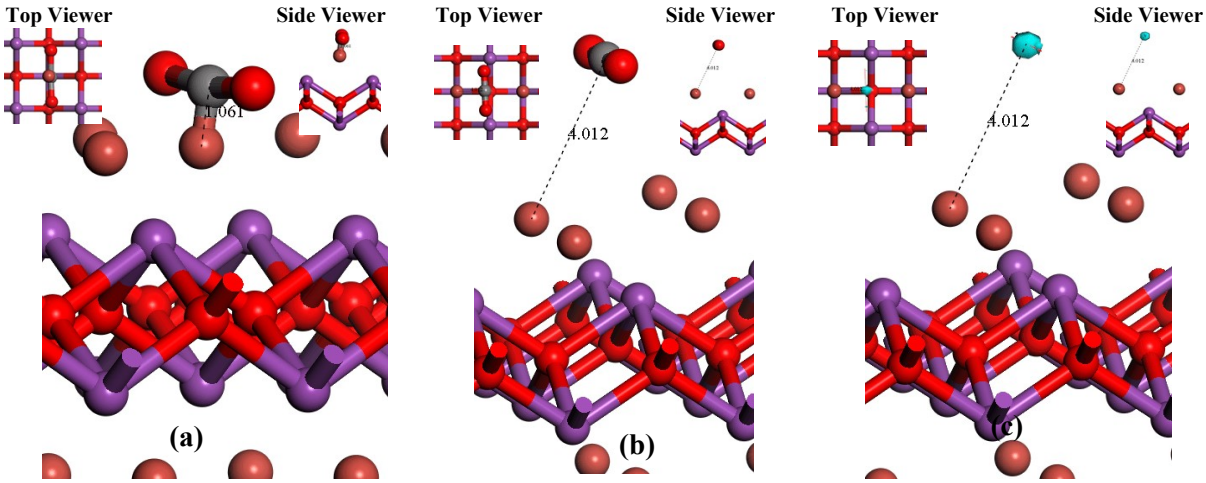

Figure S18 The structure for the C atoms of CO_2 adsorption on Br adsorption site of BiOBr (001Br) surface: (a) before optimization, (b) after optimization and (c) electron difference density.

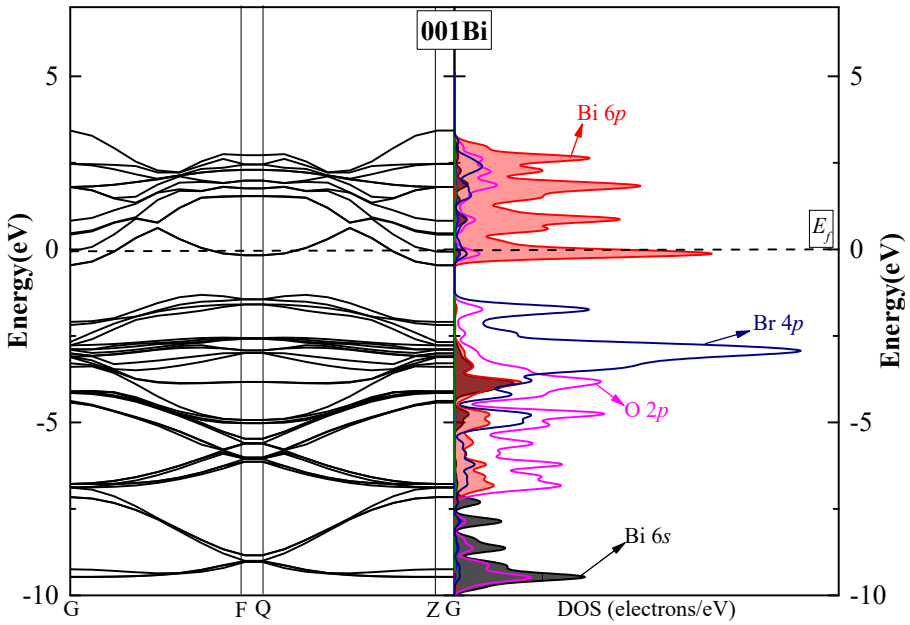

Figure S19 Band structures and density of states for BiOBr (001Bi) surface.

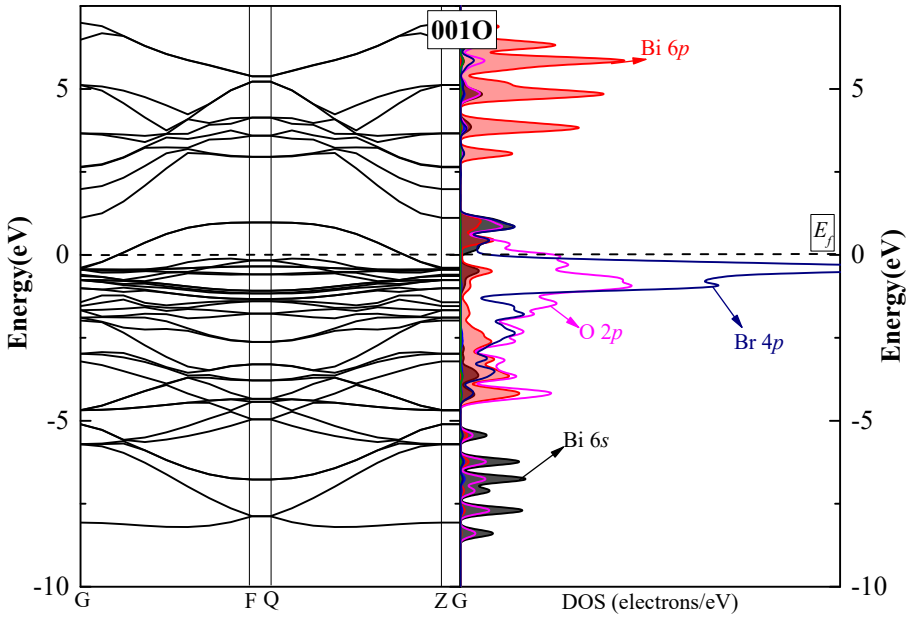

Figure S20 Band structures and density of states for BiOBr (001O) surface.

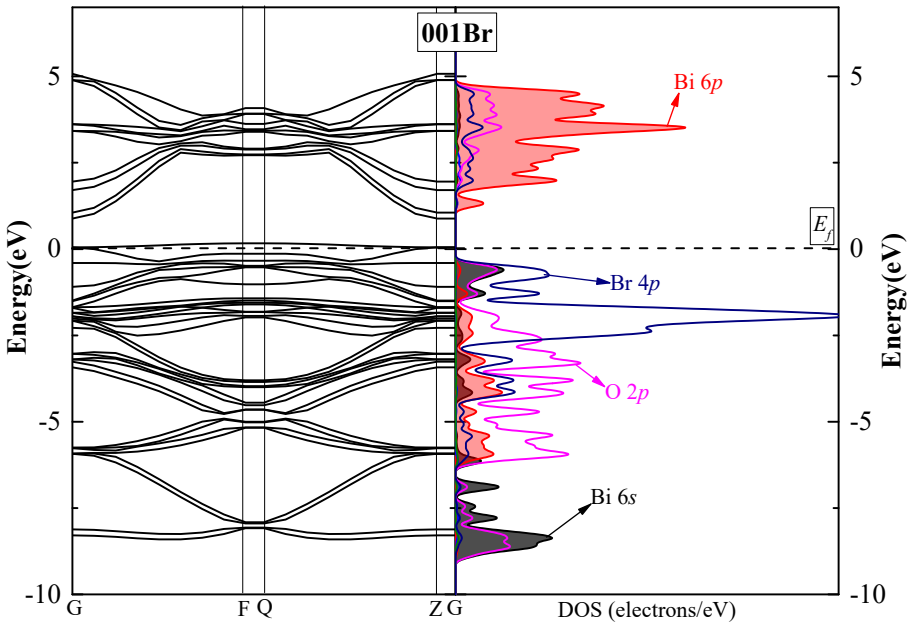

Figure S21 Band structures and density of states for BiOBr (001Br) surface.

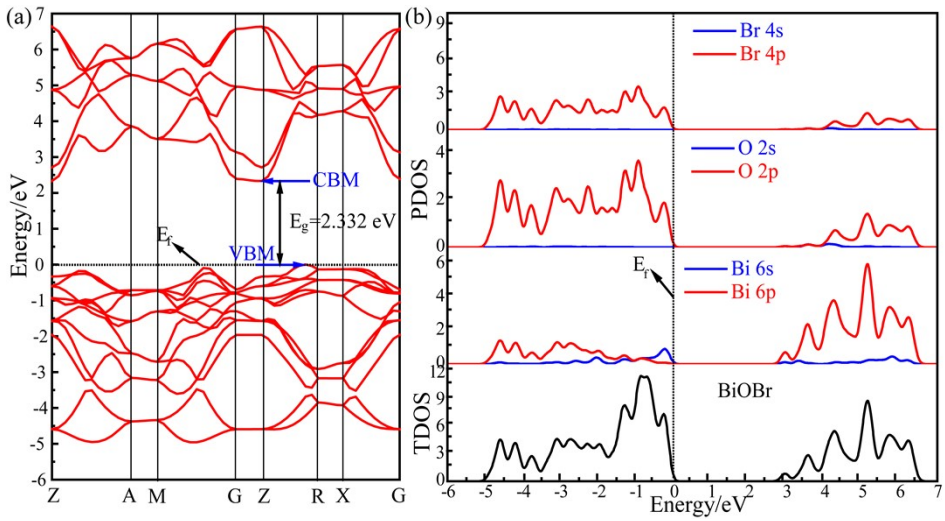

Figure S22 Band structure and density of states for bulk BiOBr.

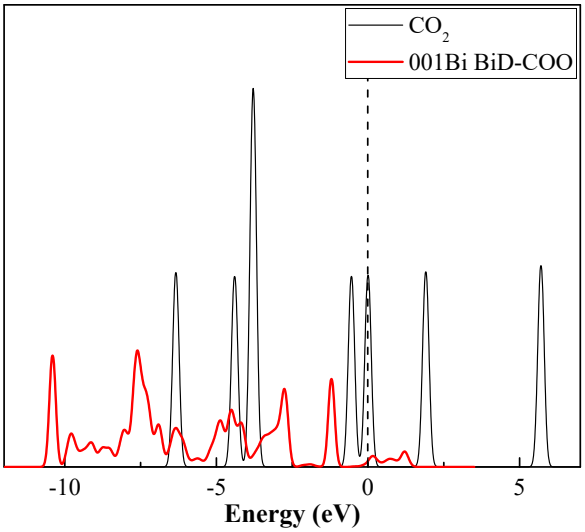

Figure S23 The LDOS of CO_2 before and after chemisorption on BiD site of BiOBr (001) surface with Bi-termination.

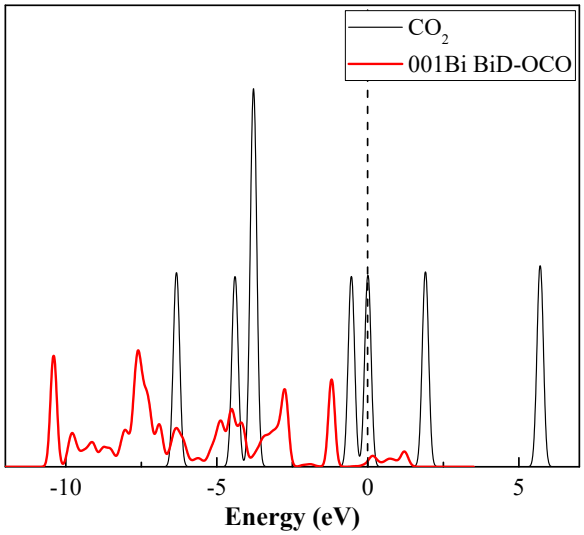

Figure S24 The LDOS of CO_2 before and after chemisorption on BiD site of BiOBr (001) surface with Bi-termination.

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