SUPPLEMENTARY MATERIAL (SM)

Mechanism of formaldehyde and formic acid formation on (101)-TiO_2@Cu_4 system through CO_2 hydrogenation

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Table S1. The variation of bond length between atoms and CO_2 molecule angle in three configurations (1, 2 and 3-configurations) of CO_2 and CO adsorbed on the (101)-TiO_2@Cu_4.

Configuration	R(Cu-O), Å	R(Cu-Ti), Å	R(C-O), Å	R(Cu-Cu), Å	Angle (˚)
1(CO_2)	1.8944-1.8937	2.7108	1.1763-1.1778	2.3537-2.5387	179.29
1(CO)	1.8959-1.8978	2.7738	1.1451	2.3550-2.4605	-
2(CO_2)	1.8665-1.8839	2.7694	1.2345-1.2712	2.3770-2.4583	135.59
2(CO)	1.8708-1.8944	2.9413	1.1618	2.3691-2.4656	-
3(CO_2)	1.8957-1.8972	2.7382	1.1752-1.1768	2.3429-2.5491	178.81
3(CO)	1.9210-1.9254	2.7149	1.1445	2.3580-2.4800	-

Table S2. Calculated absorption energy ($E_{ads.}$), corresponding magnetic moments on 5-fold and 6-fold coordinated Ti atoms (as shown in Figure 1) [$\Delta\mu(\mu_B)$] of the three configurations of CO_2 and CO adsorption on the (101)-TiO_2@Cu_4.

Configuration	Eads. (CO_2/CO), eV		Δμ (μ_B) (CO_2/CO)	
	With vdW (CO_2/CO)	Without vdW (CO_2/CO)	With vdW (CO_2/CO)	Without vdW (CO_2)
1	2.94/0.30	2.65/0.30	0.82/0.84	1.20
2	3.00/0.34	2.56/0.39	1.42/1.41	0.75
3	3.03/0.24	2.66/0.29	0.82/0.83	0.83

Table S3. The variation of total Bader charge and charges of CO_2 and CO molecules adsorbed at different sites on the (101)-TiO_2@Cu_4.

Configuration/ Bader charges	**1**	**2**	**3**
$\Delta q(CO_2)/\lvert e\rvert$	0.30 (loss)	0.17 (gain)	0.34 (loss)
$\Delta q(CO)/\lvert e\rvert$	0.20 (loss)	0.08 (loss)	0.19 (loss)

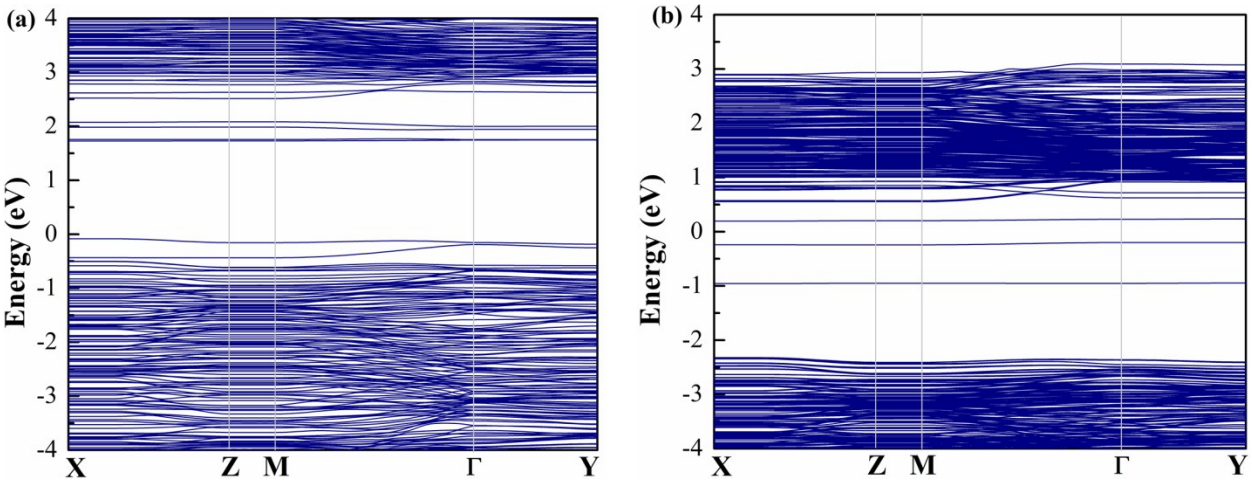

Figure S1: The electronic band structures of (a) (101)-TiO_2 and (b) (101)-TiO_2@Cu_4. The Fermi-level is set at zero.

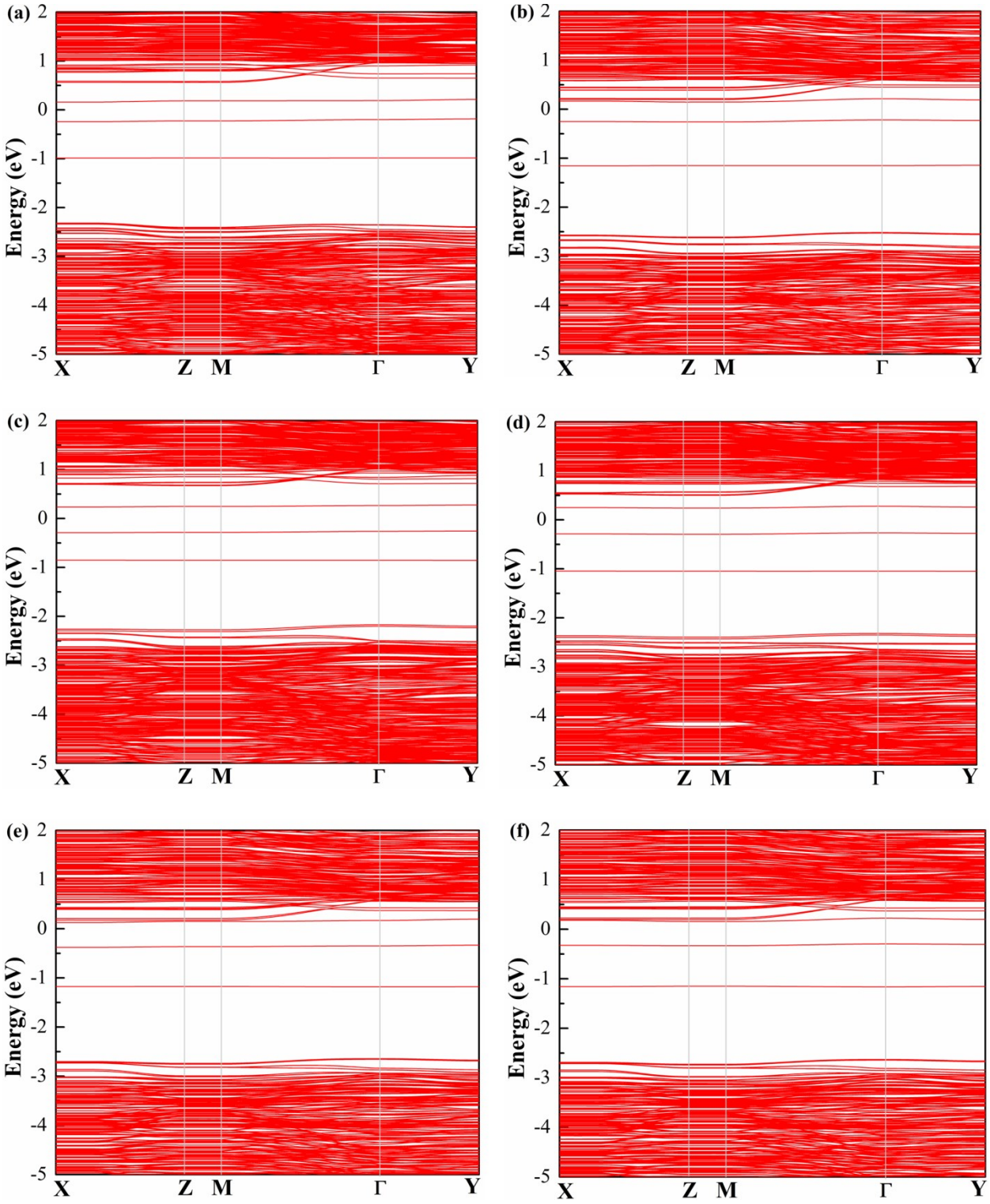

Figure S2: The electronic band structures of (101)-TiO_2@Cu_4 (a, b) CO2 and CO with conf-1, (c, d) CO2 and CO with conf-2 and (e, f) CO2 and CO with conf-3. The Fermi-level is set at zero.

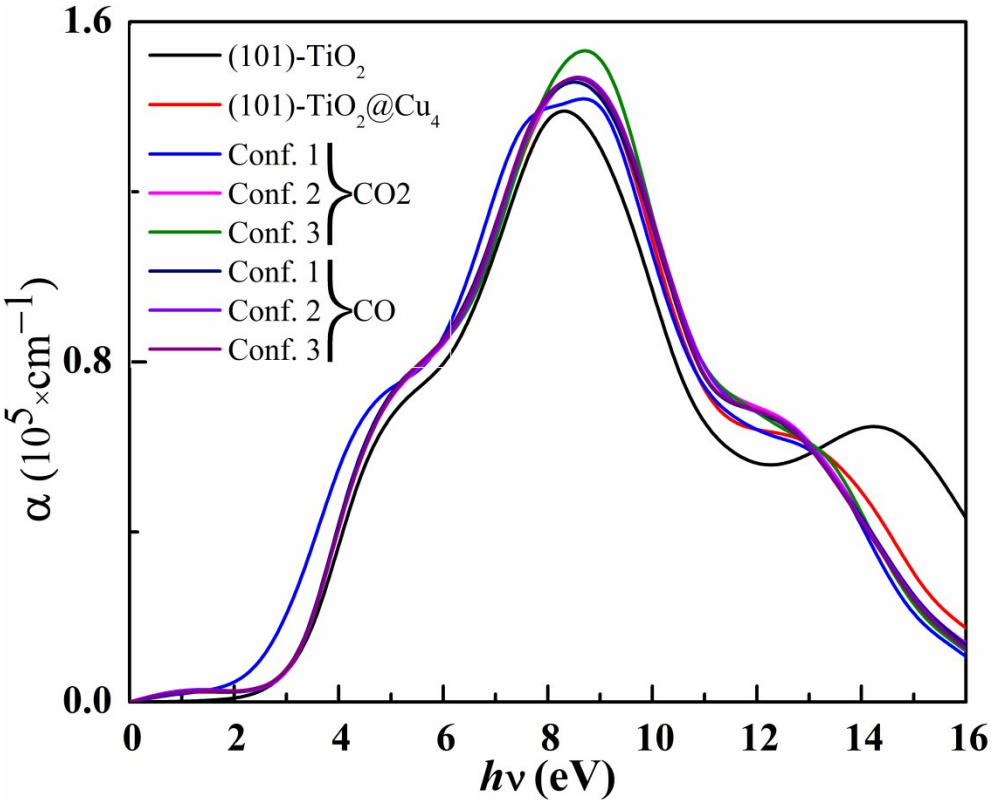

Figure S3: The optical absorption of (a) (101)-TiO_2 and (b) (101)-TiO_2@Cu_4. The optical absorption spectra with gas molecules on the surface of (101)-TiO_2@Cu_4 (a, b) CO2 and CO with conf-1, (c, d) CO2 and CO with conf-2 and (e, f) CO2 and CO with conf-3.