Supplementary Information

First-Principles Study of CO$_2$ and H$_2$O Adsorption on the Anatase TiO$_2$(101) Surface: The Effect of Au Doping

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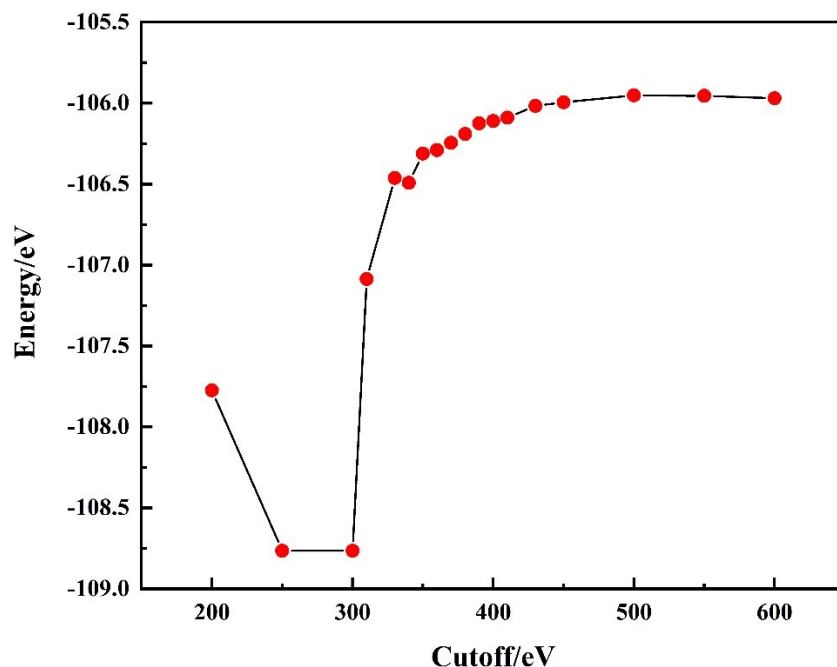** Corresponding author，email：dushuangli@tyut.edu.cn*

Fig. S1 Truncation energy convergence test results

Table S1

Surface energy of $TiO_2(101)$ surface system.

Surface	Esur/(J/m^2)
TiO_2	0.56
[45]	0.61

The surface energy of $TiO_2(101)$ surface system was calculated according to the formula S1:

$$E_{surf} = \frac{1}{2A}\left(E_{total}^{unrelax} - N*E_{bulk}\right) + \frac{1}{A}\left(E_{total}^{relax} - E_{total}^{unrelax}\right)$$

(S1)

Here, E_{surf} represents the surface energy of the system, $E_{total}^{unrelax}$ and E_{total}^{relax} represent the energy of the system before and after relaxation, N represents the number of single cells in the system, and E_{bulk} represents the energy of single cells. The calculated surface energy of the $TiO_2(101)$ surface system is 0.56 J/m^2, as shown in Table S5. Due to the different calculation details, the final calculation results are slightly different from the previous research results[45], but the overall results are similar, indicating that the selected $TiO_2(101)$ surface is the most stable surface.

Table S2

Adsorption energy (E_{ads}, kcal/mol), C-O bond length(Å), average bond length(Å), bond angle(°) and adsorption distance (d, Å) of CO_2 on $TiO_2(101)$ surface.

adsorption site	E_{ads}	chemical bond length		average bond length	bond angle	d
I	-11.1	C-O1	1.170	1.176	177.3	2.625
		C-O2	1.181			
II	-9.7	C-O1	1.171	1.176	179.1	2.629
		C-O2	1.181			
III	-7.8	C-O1	1.170	1.177	178.5	2.614
		C-O2	1.183			

Data from Ref.[49].

Table S3

Adsorption energy (E_{ads}, kcal/mol), H-O bond length (Å), average bond length (Å), distance between O and surface Ti atom in H_2O ($d1$, Å) and distance between H and surface O atom ($d2$, Å) of H_2O on $TiO_2(101)$ surface.

adsorption site	E_{ads}	chemical bond length		average bond length	$d1$	$d2$
1	-19.7	H1-O	0.988	0.988	-	2.201
		H2-O	0.988			
2	-19.1	H1-O	0.982	0.982	-	-
		H2-O	0.982			

Data from Ref.[50].

Table S4

Charge transfer of CO_2 adsorption on $TiO_2(101)$ surface at physical adsorption sites.

Atom		Before	After			
			Short-bridge	$\Delta q/e$	Long-bridge	$\Delta q/e$
C		2.042	1.979	-0.063	2.093	0.051
O	O1	-1.022	-0.989	0.033	-1.078	-0.056
	O2	-1.02	-1	0.02	-1.002	0.018
CO_2		0		-0.01		0.013

When adsorbed at the short-bridge site, the C atom gains electrons, the O atom loses electrons, resulting in a net electron gain. Charge moves from catalyst surface to CO_2 molecule. The charge at the long-bridge site is transferred from the CO_2 molecule to catalyst surface.

Table S5

Charge transfer of CO_2 adsorption on Au-$TiO_2(101)$ surface at physical adsorption sites.

Atom		Before	After					
			Short-bridge	$\Delta q/e$	Long-bridge	$\Delta q/e$	Au-site	$\Delta q/e$
C		2.042	2.092	0.05	2.11	0.068	2.101	0.059
O	O1	-1.022	-1.088	-0.066	-1.085	-0.063	-1.047	-0.025
	O2	-1.02	-0.986	0.034	-1.045	-0.025	-1.063	-0.043
CO_2		0		0.018		-0.02		-0.009

It can be found that the direction of electron movement at the short-bridge site and the long-

bridge site is reversed after the doping of Au, and the amount of charge transfer increased. For the newly added sites, at the Au site, the C atom gains electrons, the O atom loses electrons, resulting in an overall increase in charge, with charge transferring from catalyst surface to the CO_2 molecule. The doping of Au atoms increases the amount of charge transfer at the physical adsorption sites and promotes the adsorption of CO_2 molecules on catalyst surface.