Supporting Information

Oxygen Vacancy and Nitrogen Doping Collaboratively Boost Performance and Stability of TiO_2-supported Pd Catalysts for CO_2 Photoreduction: A DFT Study

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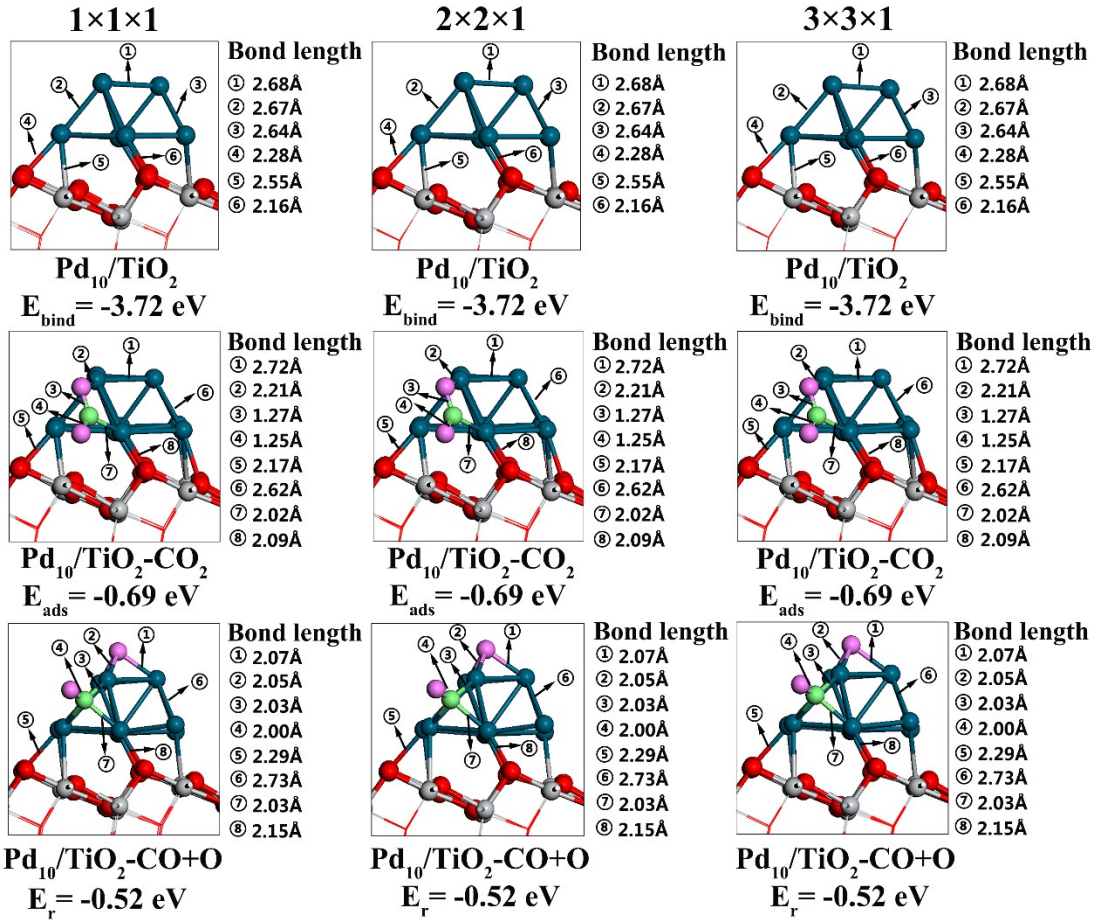

Fig. S1. Optimized structures of Pd_{10}/TiO_2, Pd_{10}/TiO_2-CO_2 and Pd_{10}/TiO_2-CO+O using different κ-point grids (1×1×1, 2×2×1 and 3×3×1). Typical bond lengths are listed beside the corresponding structures (right side). The E_{bind}, $E_{ads\ and}$ E_r are the binding energy of Pd_{10} with TiO_2, the adsorption energy of CO_2 and the reaction energy of CO_2 dissociation to CO and O on Pd_{10}/TiO_2. Color coding: red, O atoms in TiO_2; pink, O atoms in CO_2; green, C atoms; gray, Ti atoms; navy blue, Pd atoms.

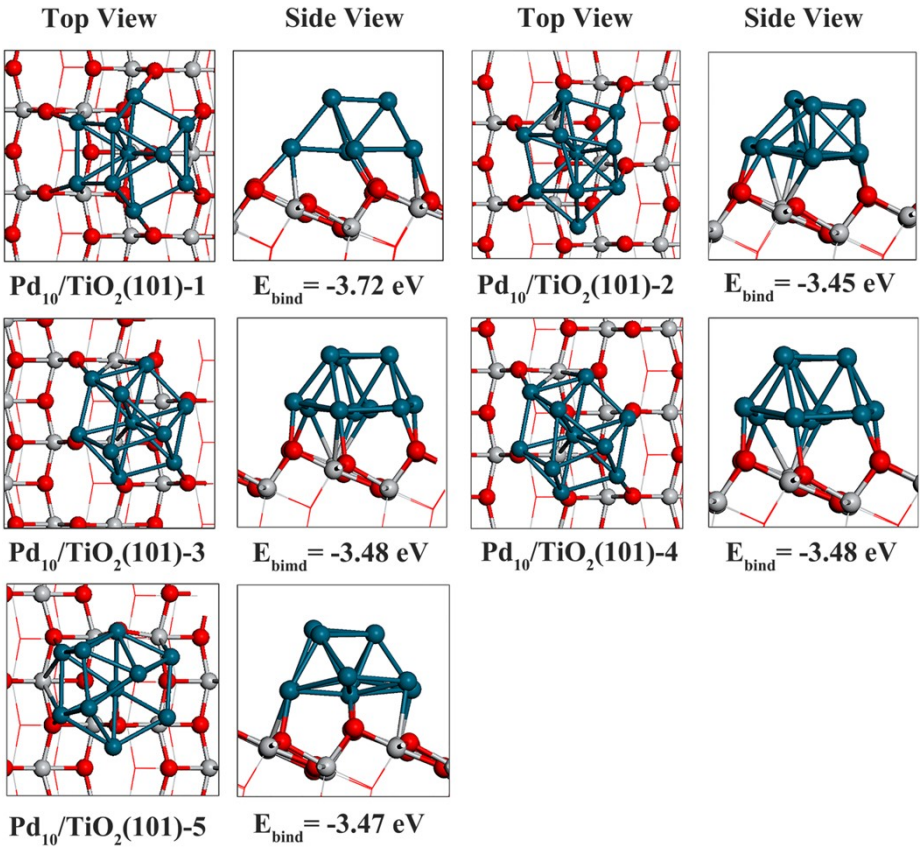

Fig. S2. Optimized configurations and binding energies of Pd_{10} adsorbed at different positions of $TiO_2(101)$ by the bottom atomic plane (denoted as Pd10/TiO_2(101)-b). See Fig. S1 for color coding.

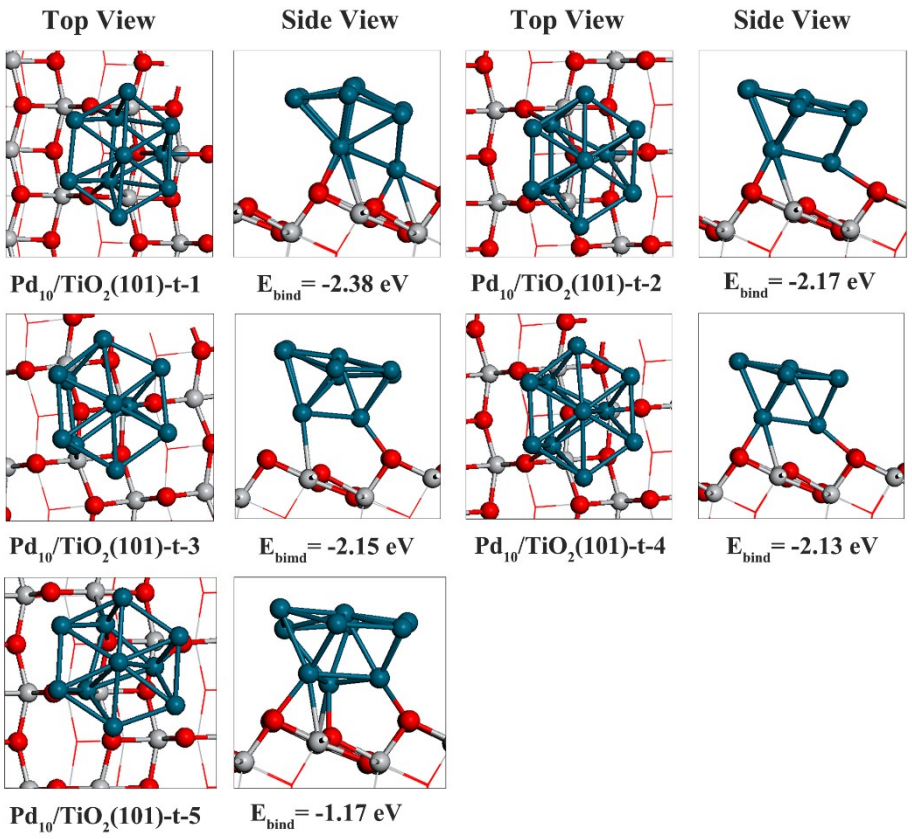

Fig. S3. Optimized configurations and binding energies of Pd_{10} cluster adsorbed at different positions of $TiO_2(101)$ by the top atomic plane (denoted as $Pd_{10}/TiO_2(101)$-t). See Fig. S1 for color coding.

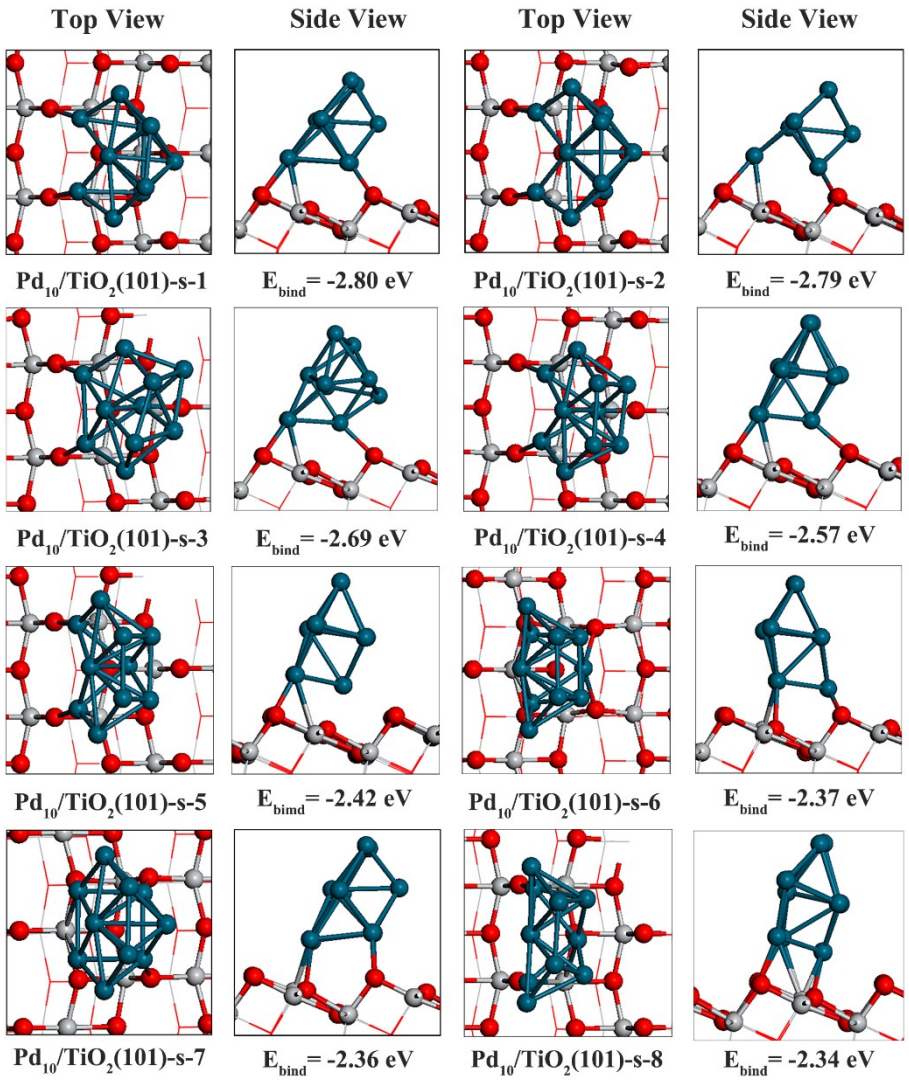

Fig. S4. Optimized configurations and binding energies of Pd_{10} cluster adsorbed at different positions of $TiO_2(101)$ by the side atomic plane (denoted as $Pd_{10}/TiO_2(101)$-s). See Fig. S1 for color coding.

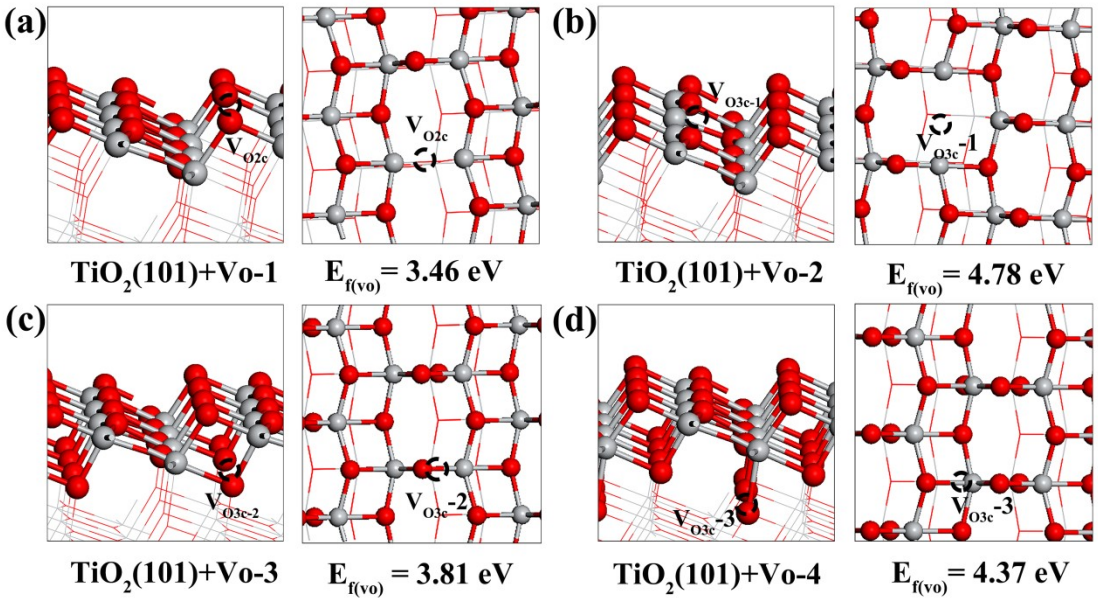

Fig. S5. Optimized structures and formation energies of different types of oxygen vacancy. (a) V_{O2c} on surface layer; (b) V_{O3c} on surface layer; (c-d) V_{O3c} on the sublayer. See Figure S1 for color coding. The dotted circle represents the oxygen vacancy.

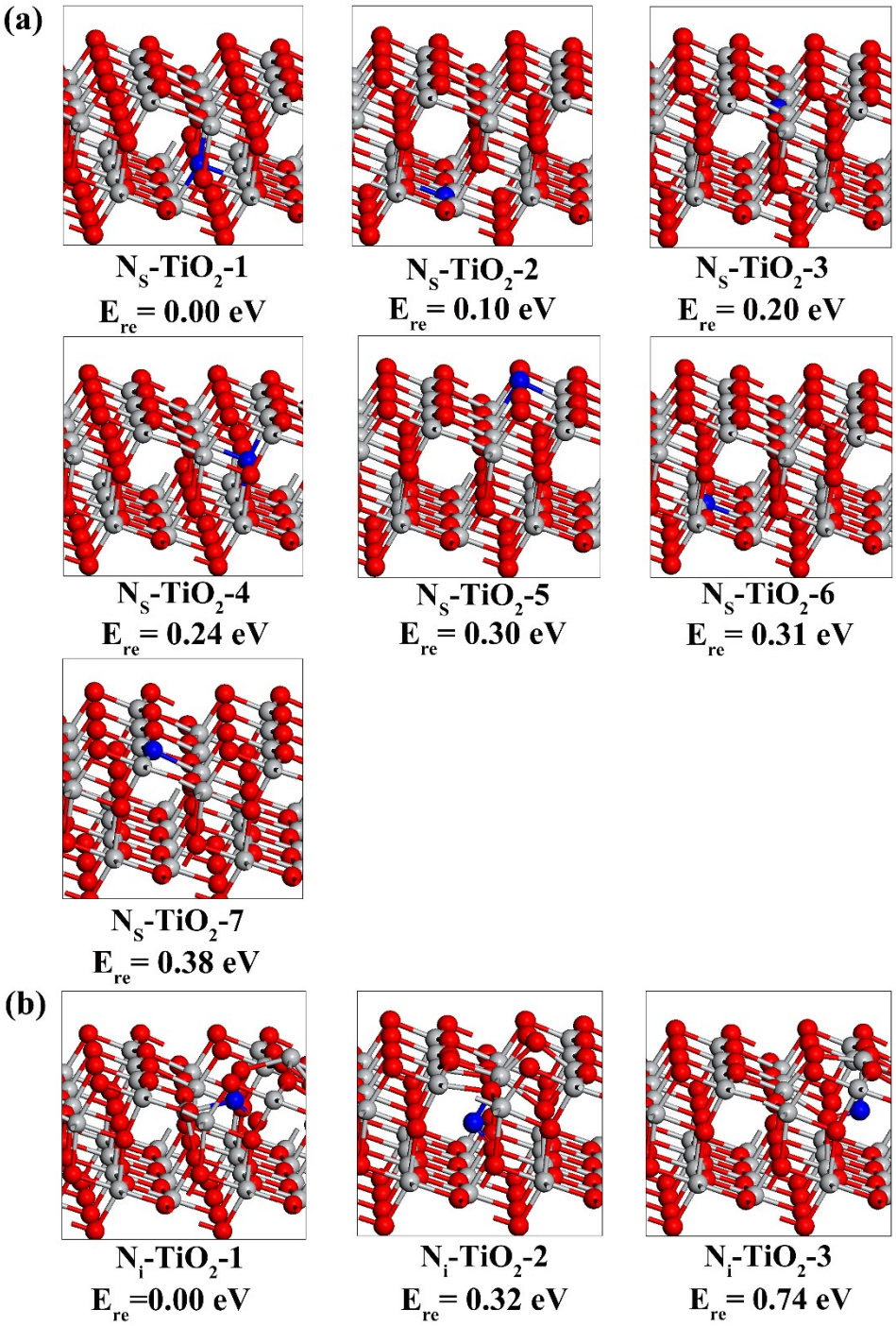

Fig. S6. Possible nitrogen doping sites for (a) substitutional N doping (N_S-TiO_2) and (b) interstitial N doping (N_i-TiO_2). The value under each configuration indicates its relative energy (E_{re}) with respect to the most stable N_S-TiO_2 and N_i-TiO_2, respectively. See Fig. S1 for color coding.

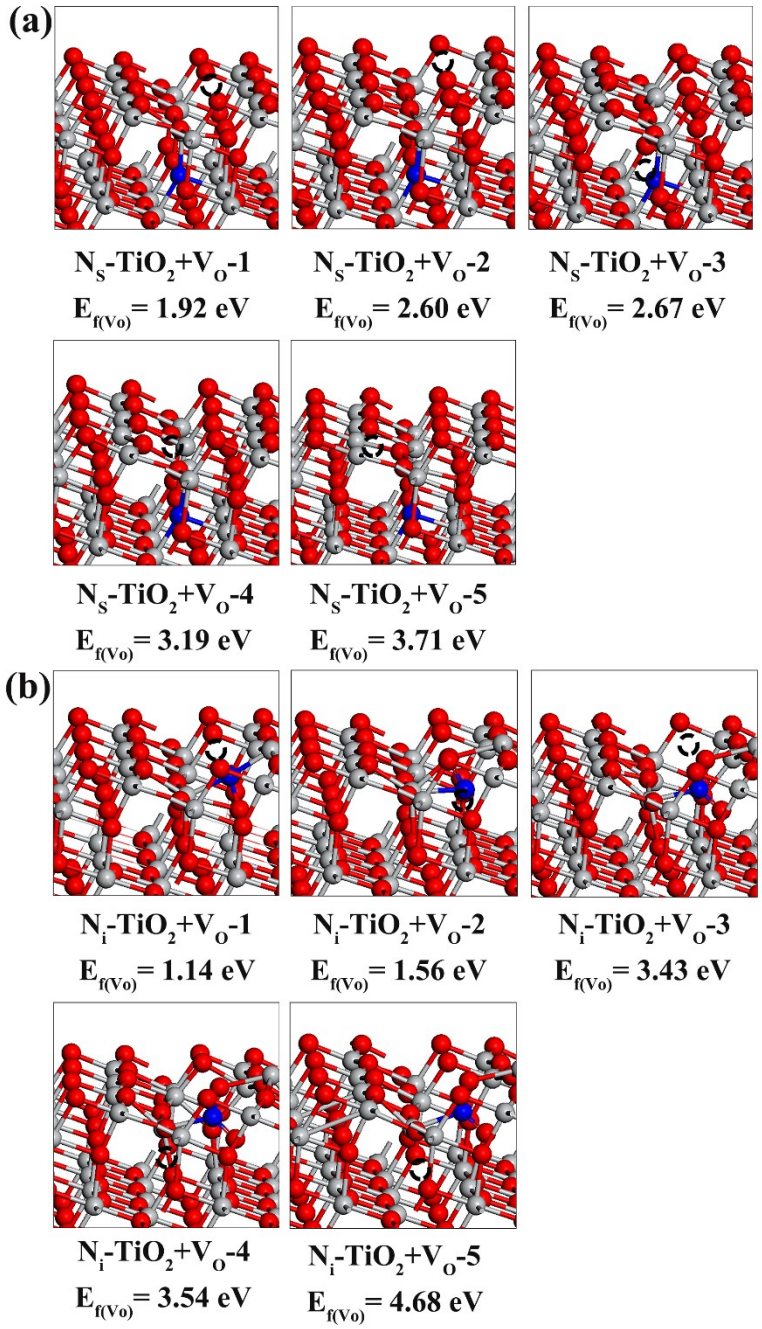

Fig. S7. The optimized structure and the forming energy of different V_Os in (a) N_S-TiO_2+V_O and (b) N_S-TiO_2+V_O. See Fig. S1 for color coding. The dotted circle represents the oxygen vacancy.

Table S1. The coordinate numbers of each Pd atoms on various catalysts. The value in red is the coordinate number of the Pd atom serves as the active site.

	Pd_{10}/TiO_2	Pd_{10}/TiO_2+Vo	Pd_{10}/N_S-TiO_2+Vo	Pd_{10}/N_i-TiO_2+Vo
Pd-1	**5**	**5**	**5**	**5**
Pd-2	**5**	**5**	**5**	**5**
Pd-3	**5**	**5**	**5**	**5**
Pd-4	**4**	**5**	**4**	**6**
Pd-5	**5**	**6**	**5**	**6**
Pd-6	**5**	**6**	**6**	**6**
Pd-7	**4**	**5**	**5**	**5**
Pd-8	**5**	**4**	**5**	**3**
Pd-9	**5**	**4**	**5**	**3**
Pd-10	**8**	**8**	**9**	**8**

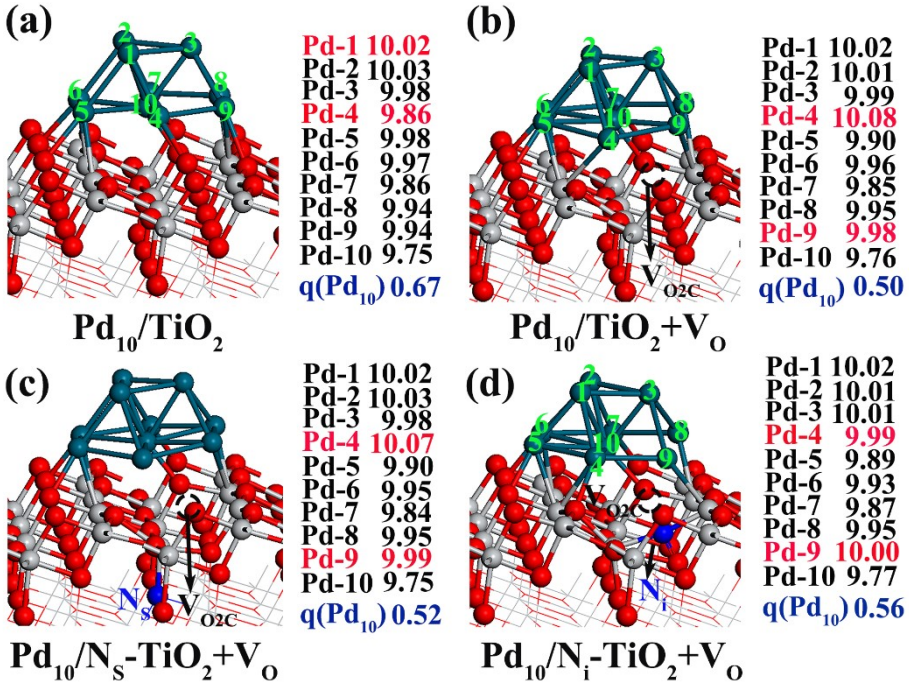

Fig. S8. The Bader charge analysis of (a) $Pd_{10}/TiO_2(101)$, (b) $Pd_{10}/TiO_2(101)+V_O$, (c) $Pd_{10}/N_s\text{-}TiO_2(101)+V_O$, and (d) $Pd_{10}/N_i\text{-}TiO_2(101)+V_O$. The unit of the Bader charge is e.

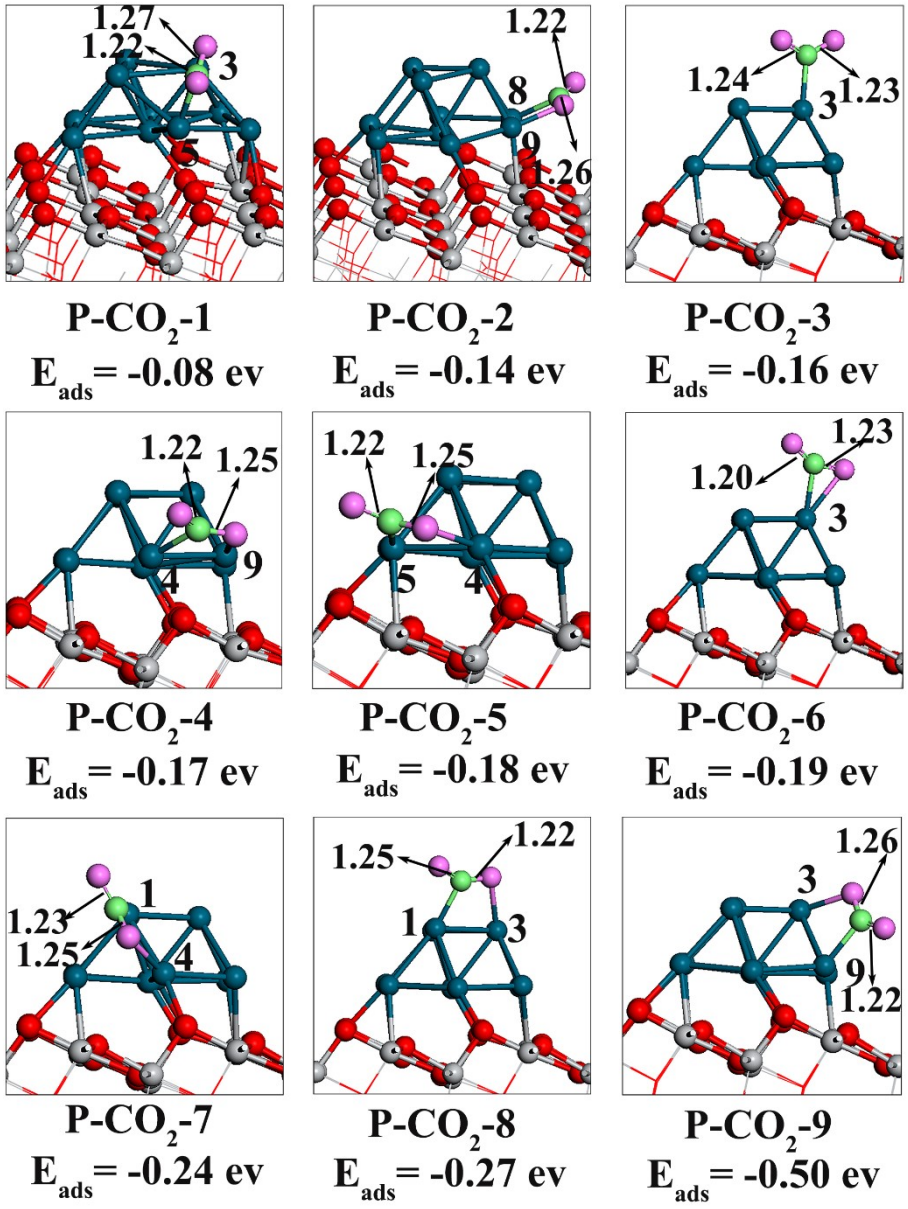

Fig. S9. Various adsorption configurations of CO_2 on $Pd_{10}/TiO_2(101)$. Color coding is the same as in Fig. S1. The adsorption energy (E_{ads}) have been marked in the figure. The bond length is quoted in Å.

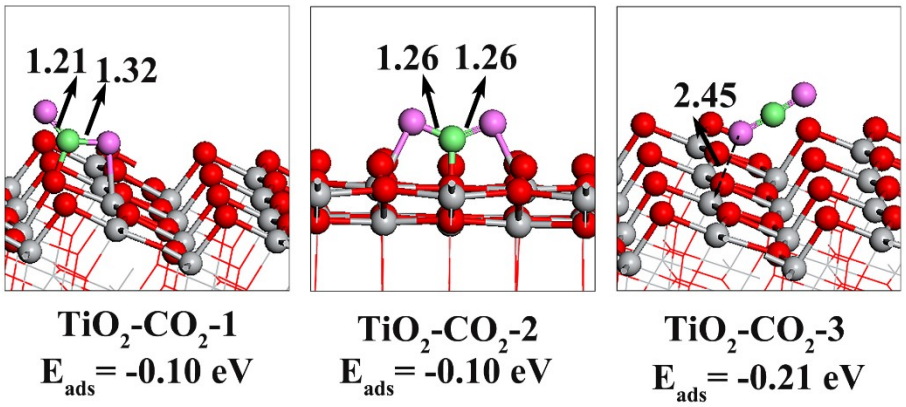

Fig. S10. Adsorption configurations of CO_2 on TiO_2(101). Color coding is the same as in Fig. S1. The adsorption energy (E_{ads}) have been marked in the figure. The bond length is quoted in Å.

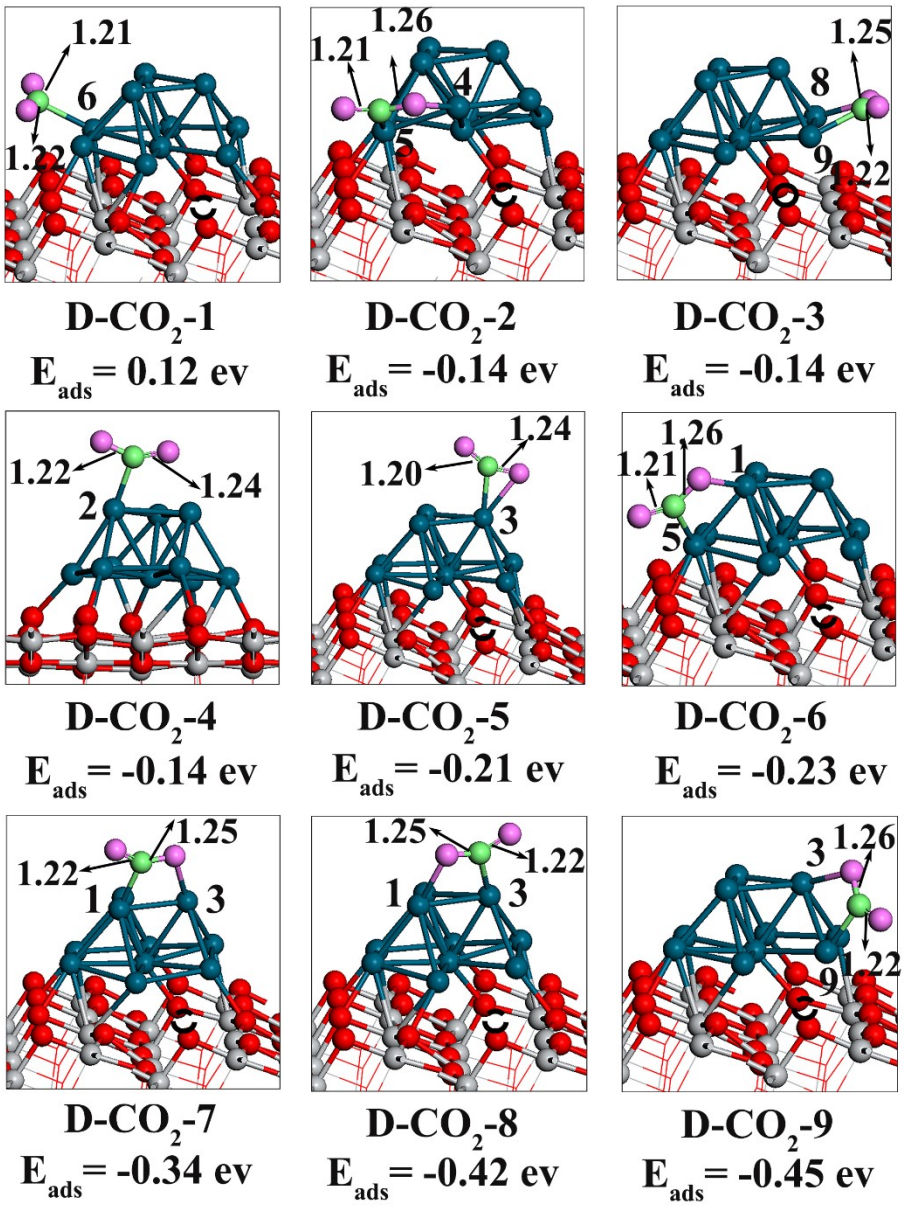

Fig. S11. Various adsorption configurations of CO_2 on $Pd_{10}/TiO_2(101)+V_O$ (denoted as D). The dotted circle represents the V_O. Color coding is the same as in Fig. S1. The adsorption energy (E_{ads}) have been marked in the figure. The bond length is quoted in Å.

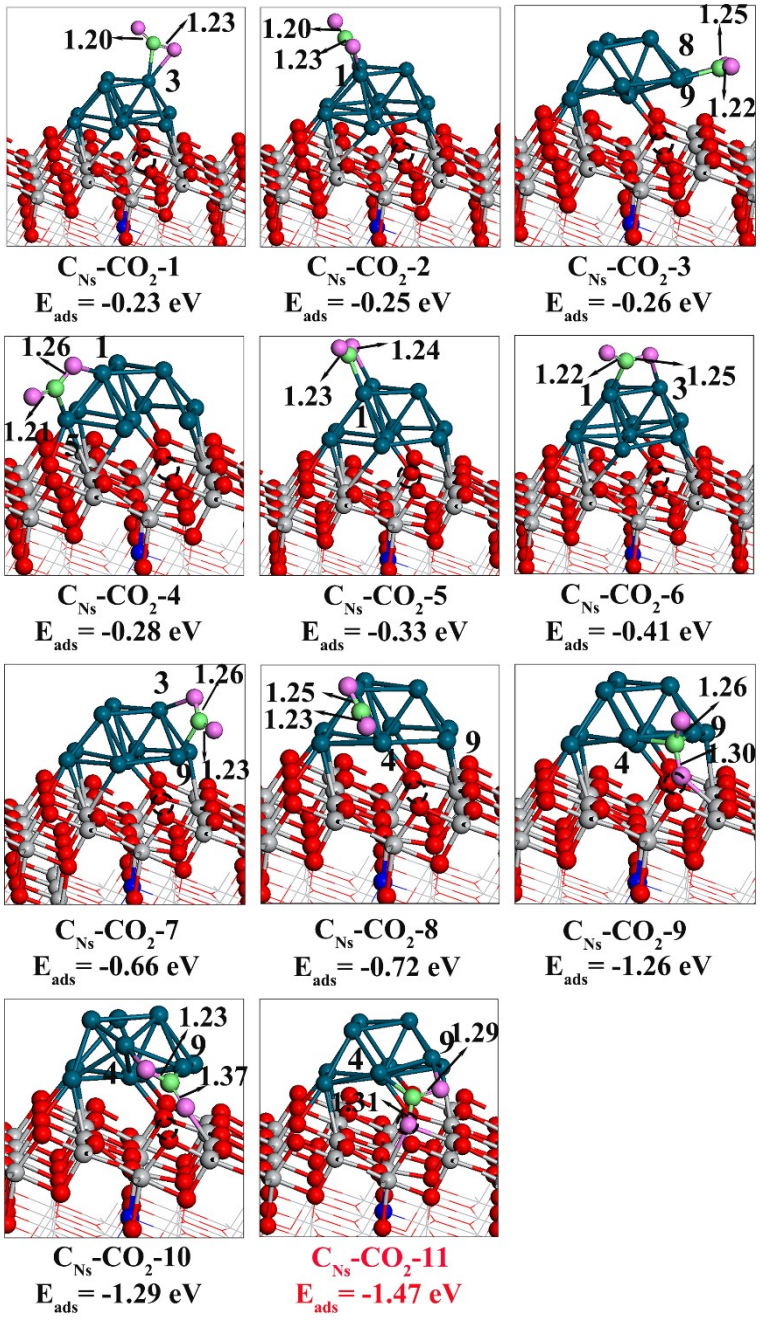

Fig. S12. Adsorption configurations of CO_2 on Pd_{10}/N_S-$TiO_2(101)$+V_O (denoted as Cs). Color coding: blue, N atom; other atoms are the same as Fig. S1. The dotted circle represents the oxygen vacancy.

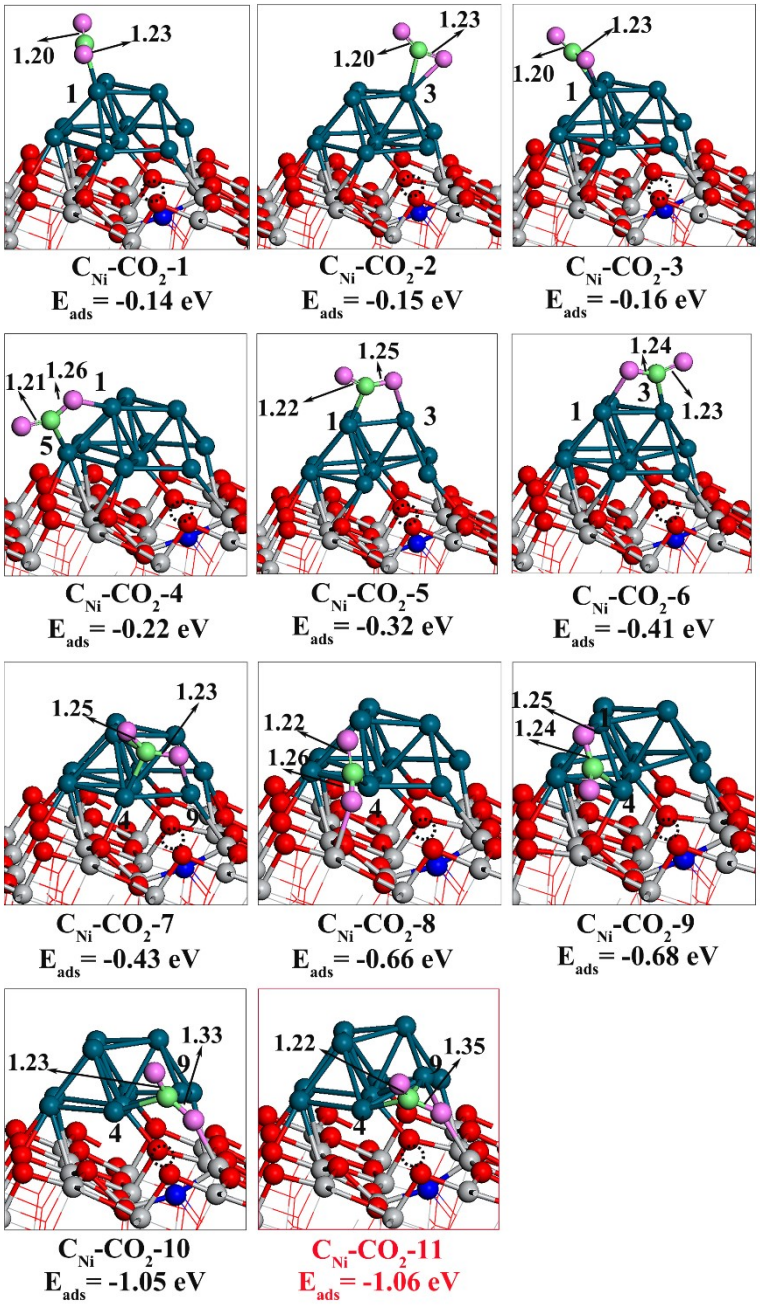

Fig. S13. Adsorption configurations of CO_2 on Pd_{10}/N_i-$TiO_2(101)$+V_O (denoted as C_{Ni}). See Fig. S1 for color coding. The dotted circle represents the oxygen vacancy.

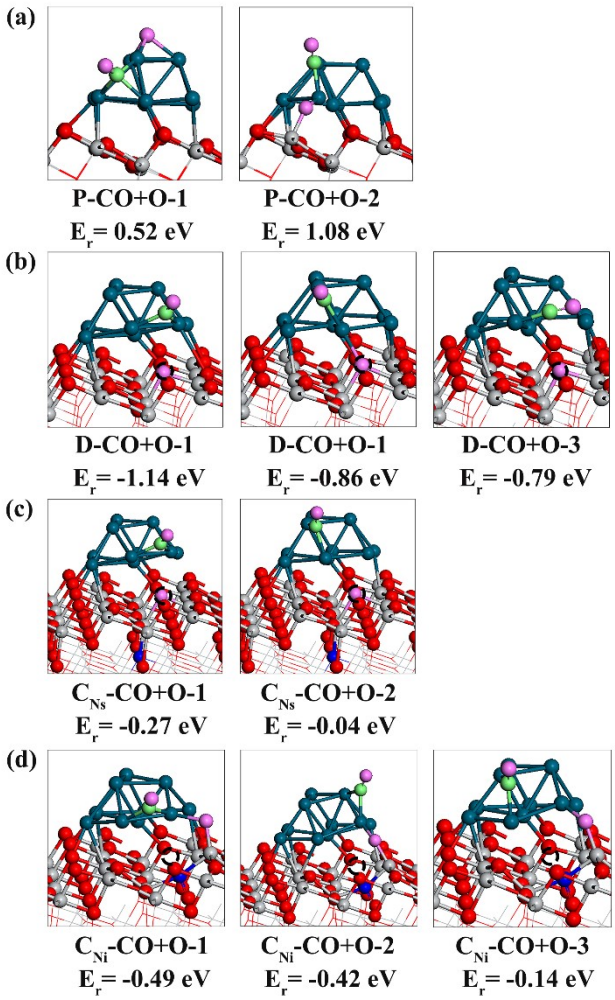

Fig. S14. CO_2 dissociation configurations on (a) Pd_{10}/TiO_2, (b) Pd_{10}/TiO_2+V_O, (c) $Pd_{10}/N_s\text{-}TiO_2+V_O$, and (d) $Pd_{10}/N_i\text{-}TiO_2+V_O$. The reaction energy ($E_r$) have been marked in the figure. See Fig. S1 for color coding. The dotted circle represents the oxygen vacancy.

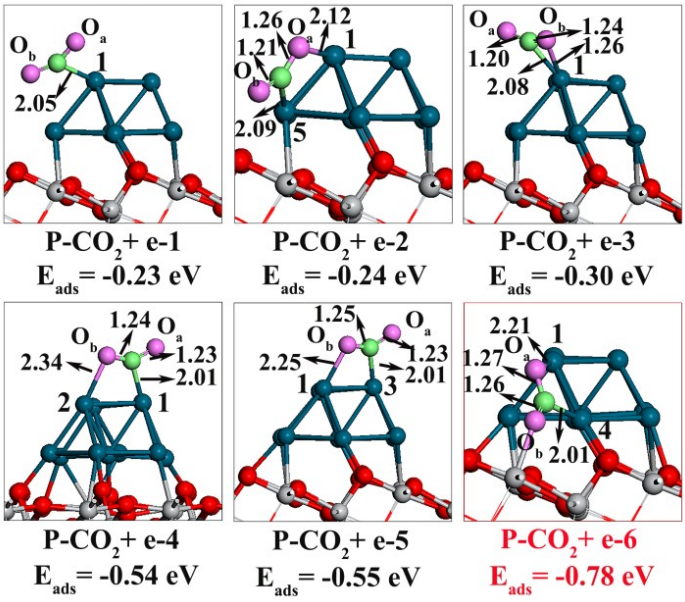

Fig. S15. Adsorption configurations of CO_2 on $Pd_{10}/TiO_2(101)$ (denoted as P) in the presence of photoexcited electron. See Figure S7 for color coding.

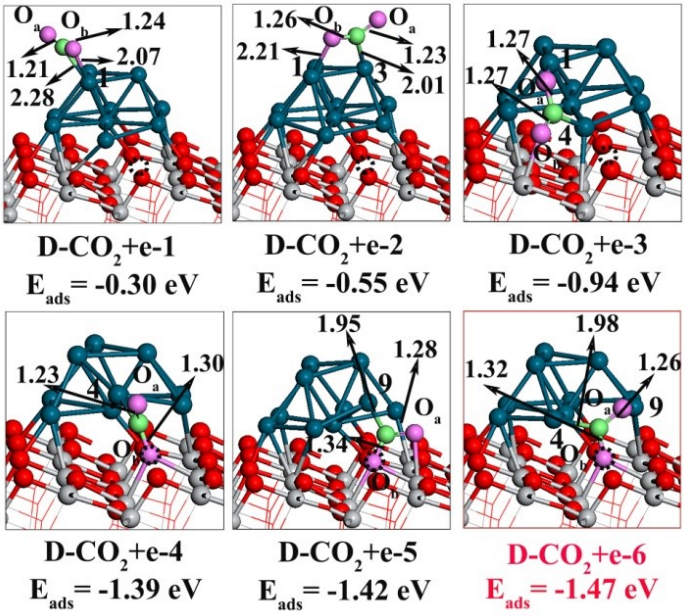

Fig. S16. Adsorption configurations of CO_2 on $Pd_{10}/TiO_2(101)+V_O$ (denoted as D) in the presence of photoexcited electron. See Figure S7 for color coding. The dotted circle represents the oxygen vacancy.

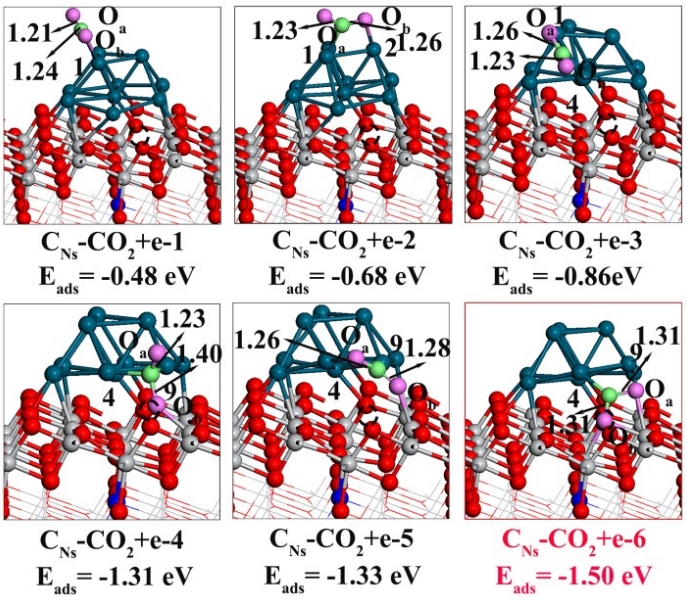

Fig. S17. Adsorption configurations of CO_2 on Pd_{10}/N_s-$TiO_2(101)$+V_O (denoted as C_{Ns}) in the presence of photoexcited electron. See Figure S7 for color coding. The dotted circle represents the oxygen vacancy.

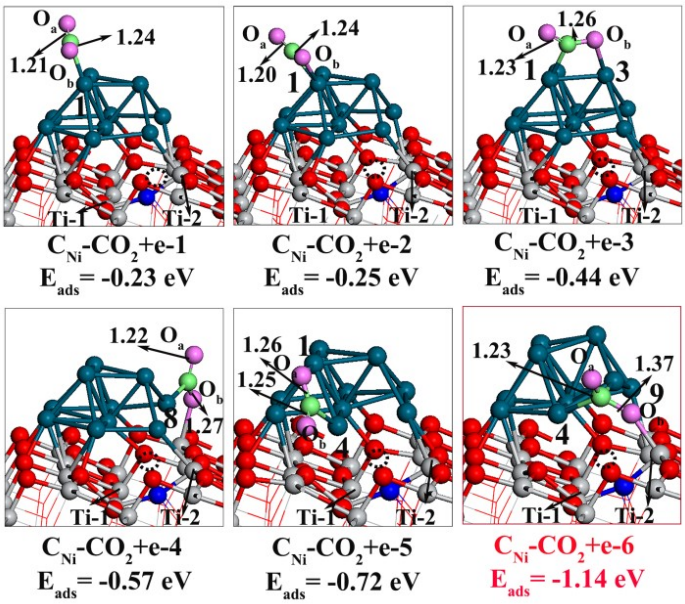

Fig. S18. Adsorption configurations of CO_2 on Pd_{10}/N_i-$TiO_2(101)+V_O$ (denoted as C_{Ni}) in the presence of photoexcited electron. See Figure S7 for color coding. The dotted circle represents the oxygen vacancy.

Table S2. Bader charge on CO_2 and Pd_{10} cluster before and after the addition of photoexcited electron.

	Without photoelectron			With photoelectron		
	E_{ads}(eV)	$q_{(CO2)}$ (|e|)	$q_{(Pd)}$ (|e|)	E_{ads}(eV)	$q_{(CO2)}$ (|e|)	$q_{(Pd)}$ (|e|)
$Pd_{10}/TiO_2(101)$	**-0.69**	**-0.55**	**0.67**	**-0.78**	**-0.64**	**0.34**
$Pd_{10}/TiO_2(101)$+Vo	**-1.58**	**-0.96**	**0.50**	**-1.47**	**-0.99**	**0.28**
$Pd_{10}/N_sTiO_2(101)$+Vo	**-1.47**	**-0.95**	**0.52**	**-1.50**	**-1.05**	**0.30**
$Pd_{10}/N_iTiO_2(101)$+Vo	**-1.06**	**-0.73**	**0.56**	**-1.14**	**-0.87**	**0.31**