

Support Information (SI):

Photo-driven selective CO₂ reduction by H₂O into ethanol over Pd/Mn-TiO₂: Suitable synergistic effect between Pd and Mn sites

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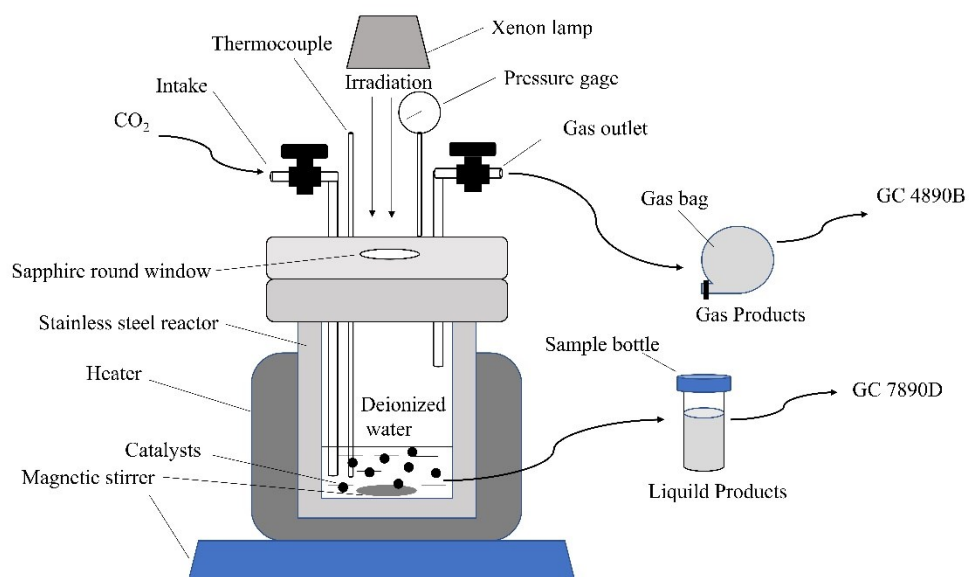


Fig.S1. Diagram of reactor

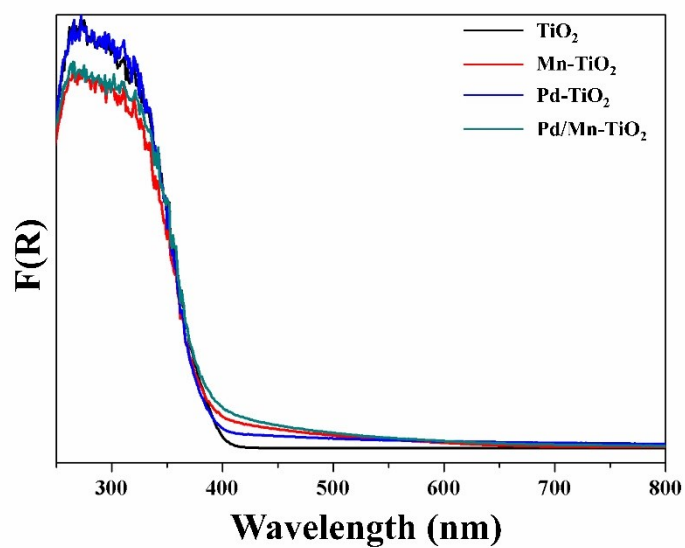


Fig.S2. UV-Vis DRS spectrums of TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂ samples.

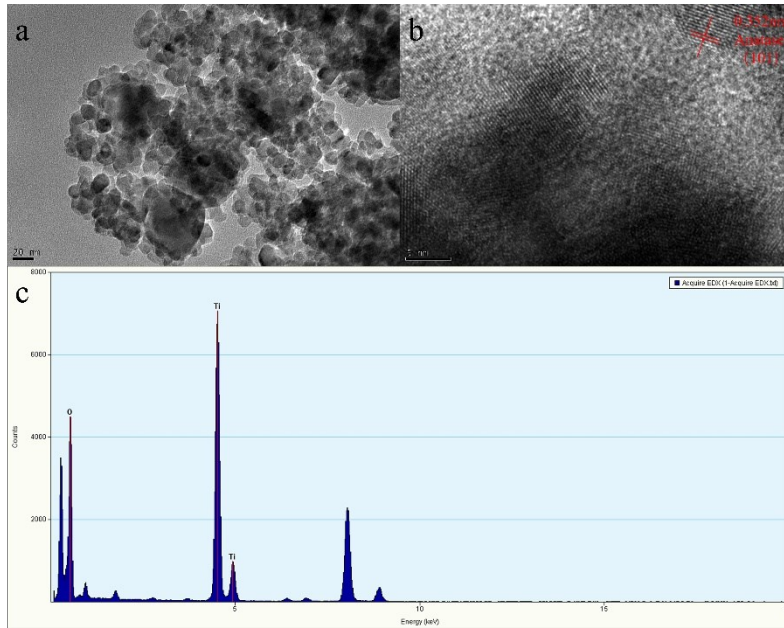


Fig.S3. The images of TEM (a), HRTEM (b) and EDX (c) of TiO₂ sample.

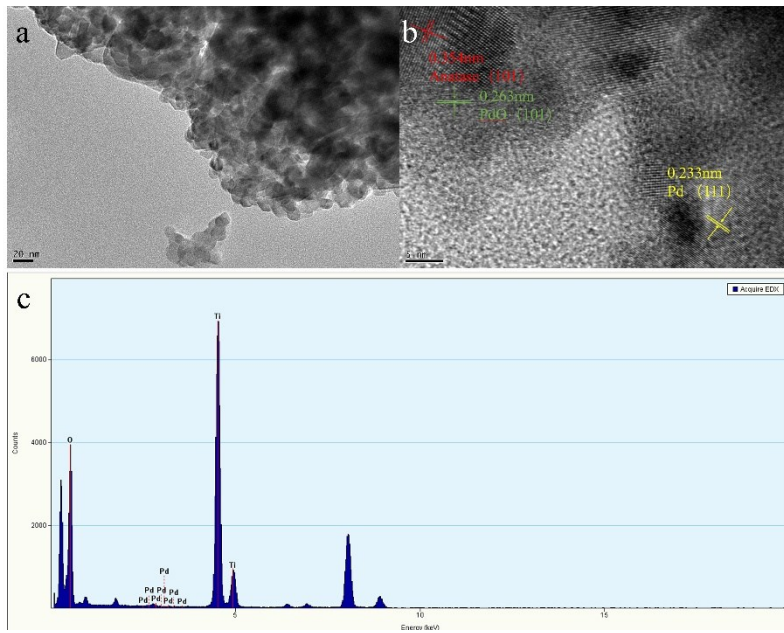


Fig.S4. The images of TEM (a), HRTEM (b) and EDX (c) of Pd-TiO₂ sample.

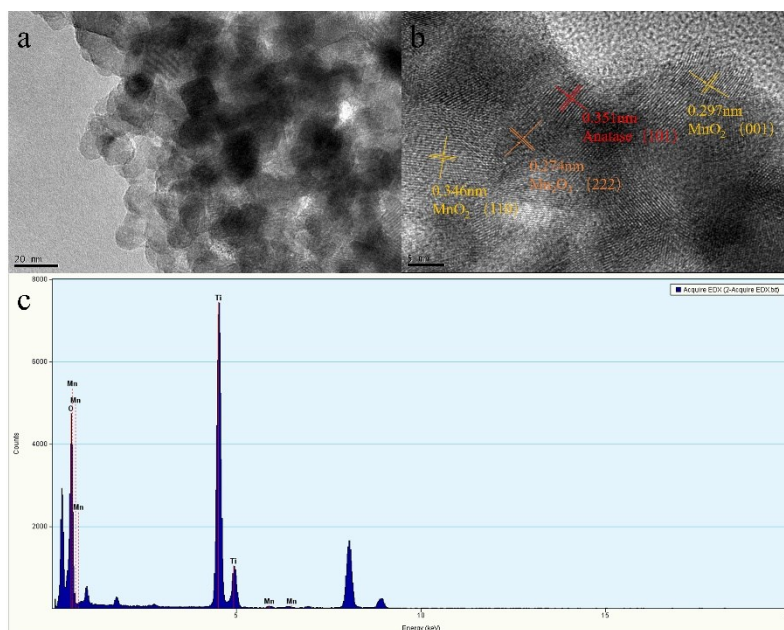


Fig.S5. The images of TEM (a), HRTEM (b) and EDX (c) of Mn-TiO₂ sample.

Table S1 Element contents of TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂.

Sample	Element	Content(mg/kg)
TiO ₂	Ti	607237.7
Pd-TiO ₂		603376.7
Mn-TiO ₂		600777.0
Pd/Mn-TiO ₂		652224.1
TiO ₂	Pd	7.19
Pd-TiO ₂		7762.2
Mn-TiO ₂		7.32
Pd/Mn-TiO ₂		9459.8
TiO ₂	Mn	7.14
Pd-TiO ₂		98.05
Mn-TiO ₂		14894.6
Pd/Mn-TiO ₂		16717.0

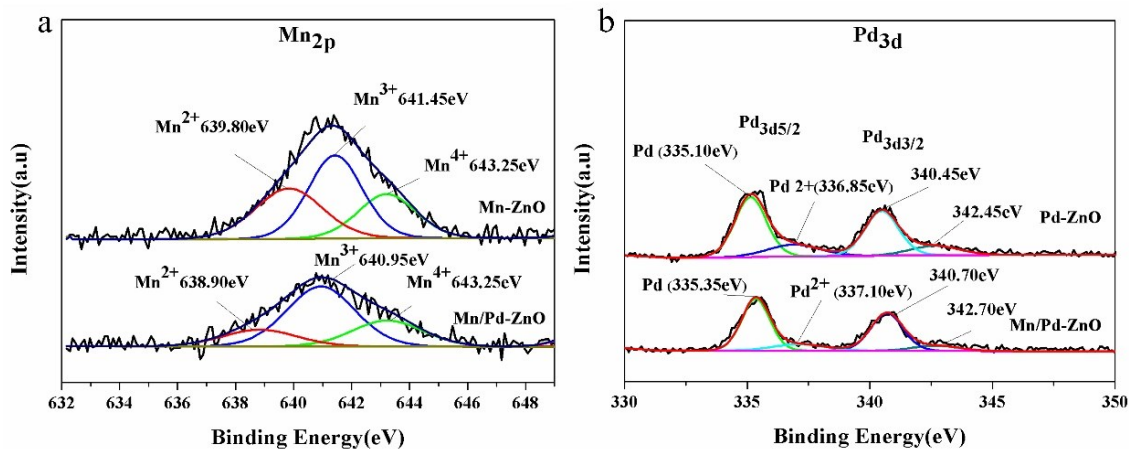


Fig.S6. High-resolution XPS spectra of Mn 2p of Mn-ZnO and Pd/Mn-ZnO samples (a); Pd 3d of Pd-ZnO and Pd/Mn-ZnO samples (b).

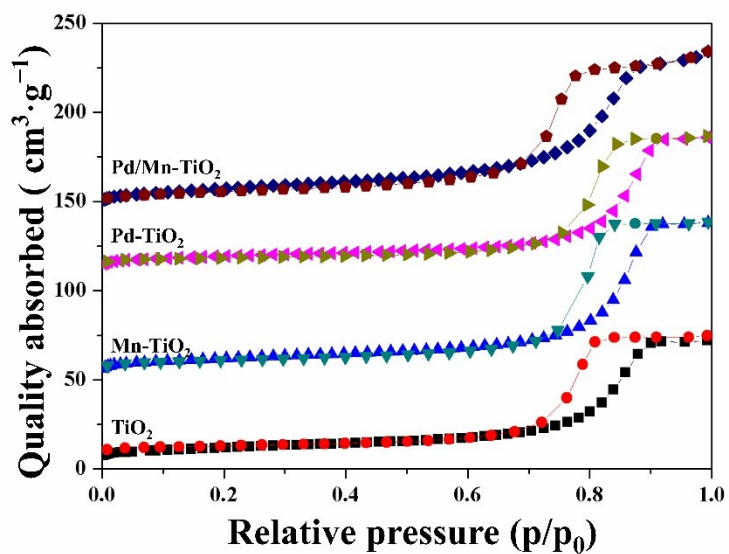


Fig.S7. N₂ adsorption–desorption isotherms of TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂ samples.

Table S2 The textural properties of TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂ samples.

	Specific surface area/(m ² ·g ⁻¹)	Pore volume/(cm ³ ·g ⁻¹)	Pore diameter (nm)
TiO ₂	41.770	0.107	12.149
Mn-TiO ₂	48.812	0.135	13.244
Pd-TiO ₂	40.493	0.117	14.089
Pd/Mn-TiO ₂	58.453	0.140	11.033

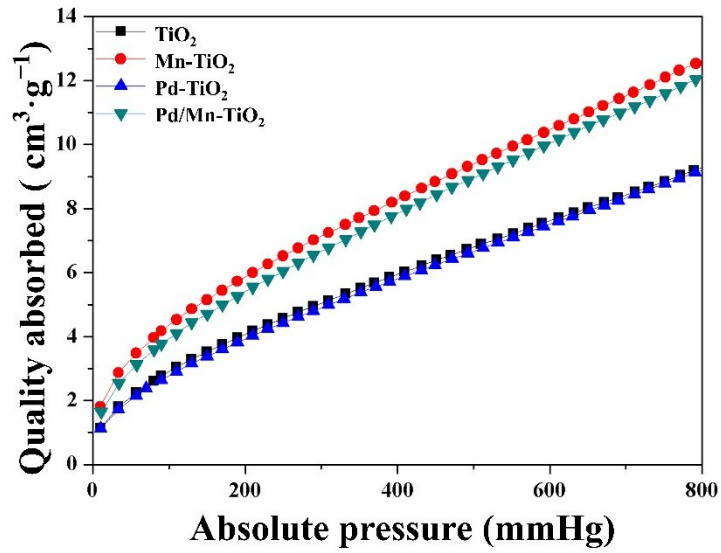


Fig.S8. CO₂ physical adsorption isotherms of TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂ samples.

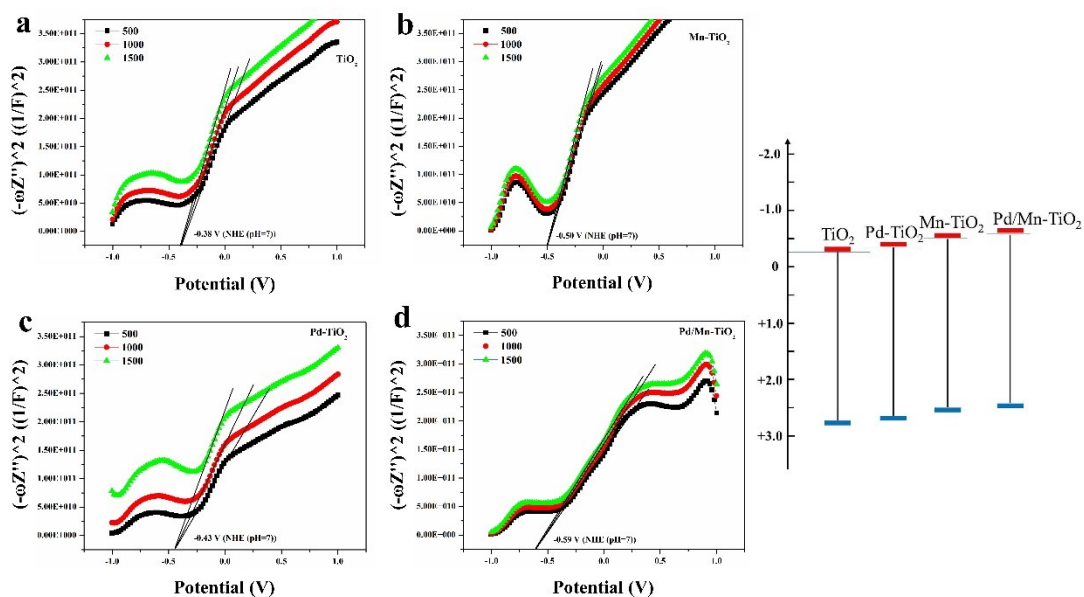


Fig.S9. The Mott-Schottky polt of (a) TiO_2 , (b) Pd-TiO_2 , (c) Mn-TiO_2 and (d) Pd/Mn-TiO_2 samples.

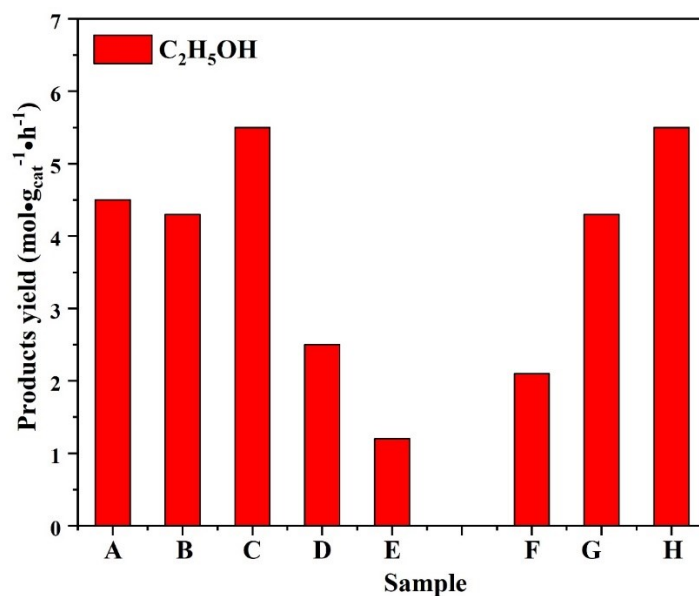


Fig.S10. Product yield of varied ratio of Pd/Mn doped TiO_2 catalysts under UV irradiation, 3.5 MPa and 180 °C (A:0.9%Pd/0.9%Mn- TiO_2 , B:0.7%Pd/0.7%Mn- TiO_2 , C:0.5%Pd/0.5%Mn- TiO_2 , D:0.3%Pd/0.3%Mn- TiO_2 , E:0.1%Pd/0.1%Mn- TiO_2 , F:0.5%Pd/0.1%Mn- TiO_2 , G:0.1%Pd/0.5%Mn- TiO_2 , H:0.5%Pd/0.5%Mn- TiO_2).

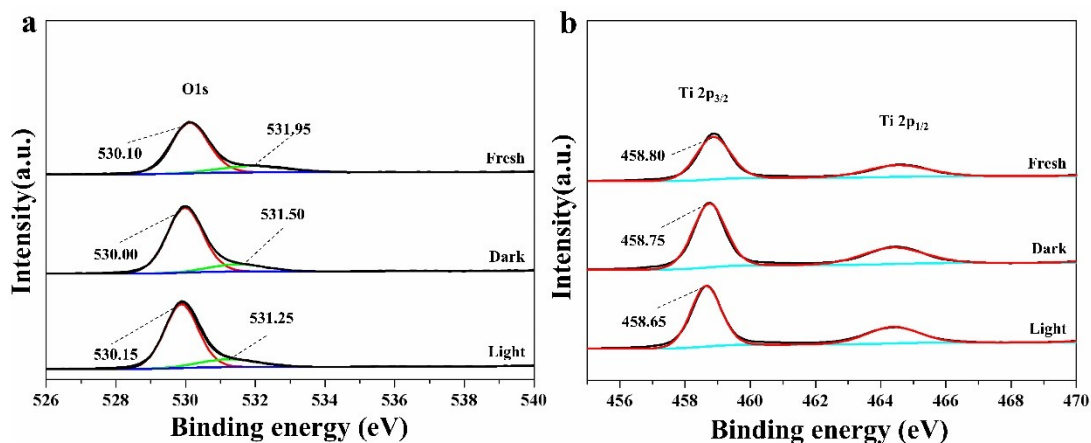


Fig.S11. High-resolution XPS spectra of O 1s (a) and Ti 2p (b) of TiO_2 after various treatments: fresh, reaction in dark, reaction under irradiation.

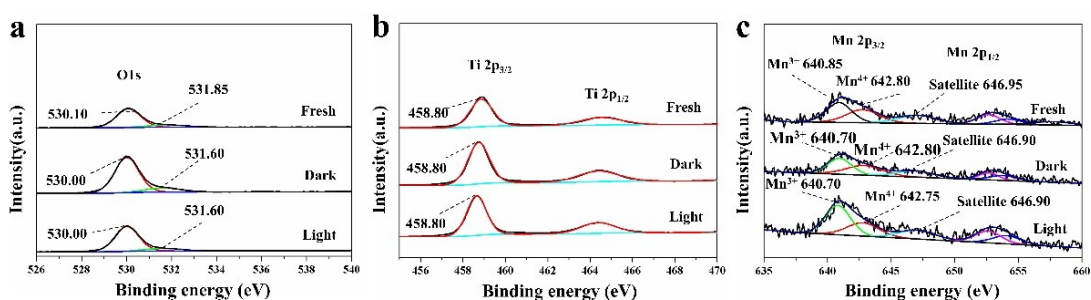


Fig.S12. High-resolution XPS spectra of O 1s (a), Ti 2p (b), and Mn 2p(c) of Mn-TiO_2 after various treatments: fresh, reaction in dark, reaction under irradiation.

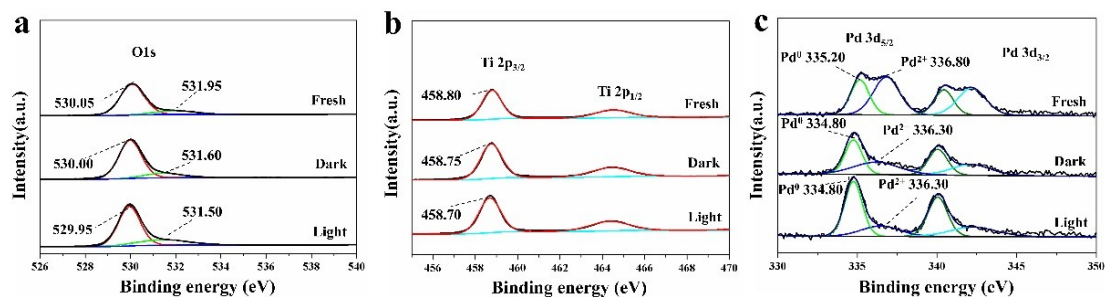


Fig.S13. High-resolution XPS spectra of O 1s (a), Ti 2p (b), and Pd 3d(c) of Pd-TiO_2 after various treatments: fresh, reaction in dark, reaction under irradiation.

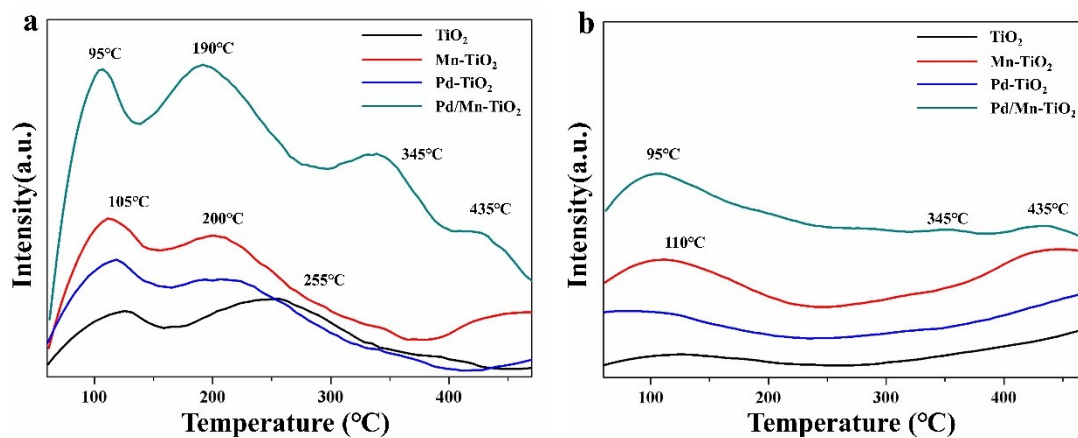


Fig.S14. TPD-MS spectra of CH₄ desorption (a), and CO desorption (b) on TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂ samples.

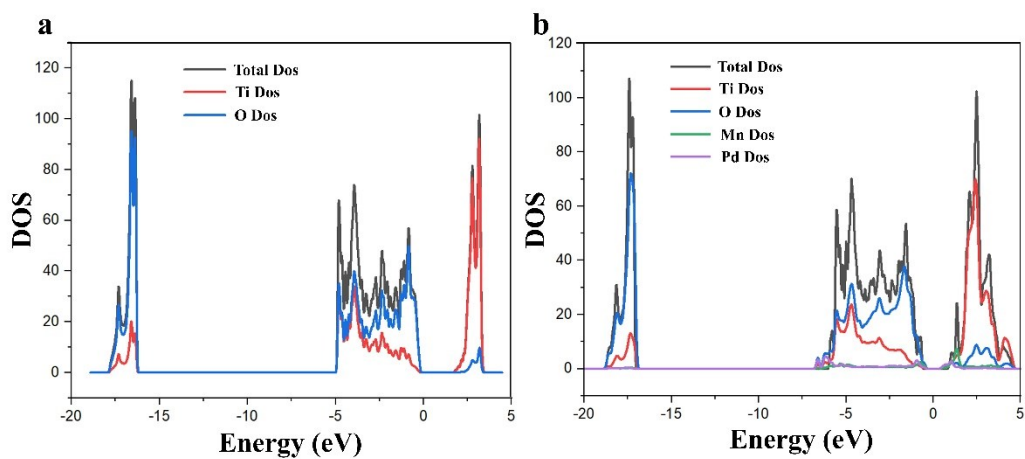


Fig.S15. Calculated density of states of TiO₂ and Mn/Pd-TiO₂.

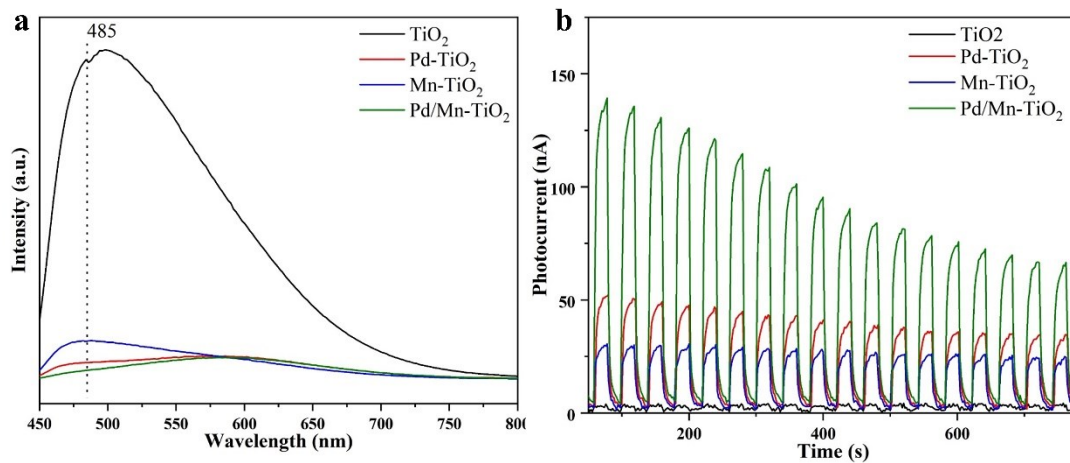


Fig.S16. PL spectra (a) and photocurrent experiments (b) results of TiO₂, Mn-TiO₂, Pd-TiO₂ and Pd/Mn-TiO₂ samples.

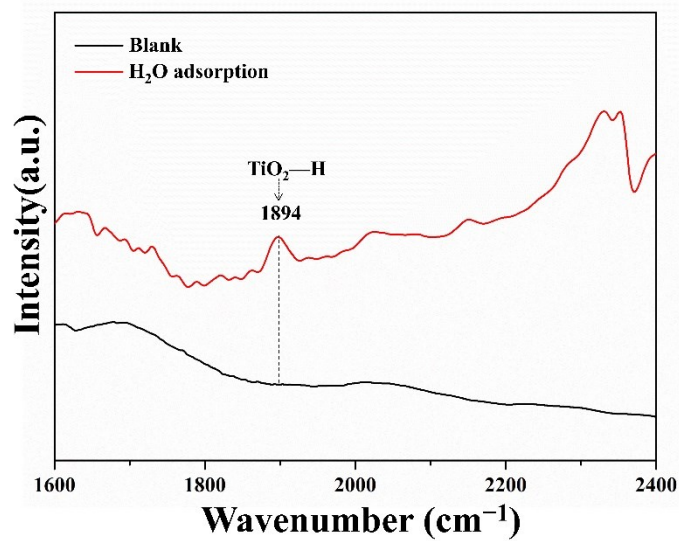


Fig.S17. In situ DRIFTS spectra of H₂O adsorption on Pd/Mn-TiO₂ sample.

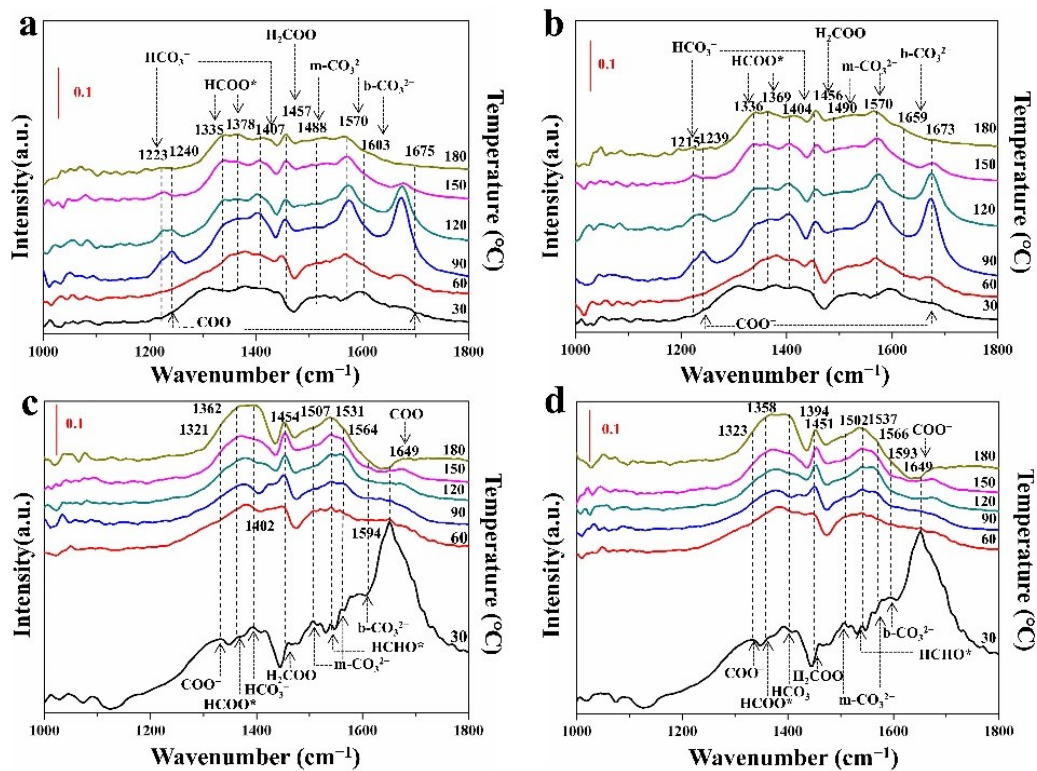


Fig.S18. In situ DRIFTS spectra of CO₂ adsorption at various condition: in dark (a) and under irradiation (b); CO₂+H₂O adsorption in dark (c) and under irradiation (d) on TiO₂ sample.

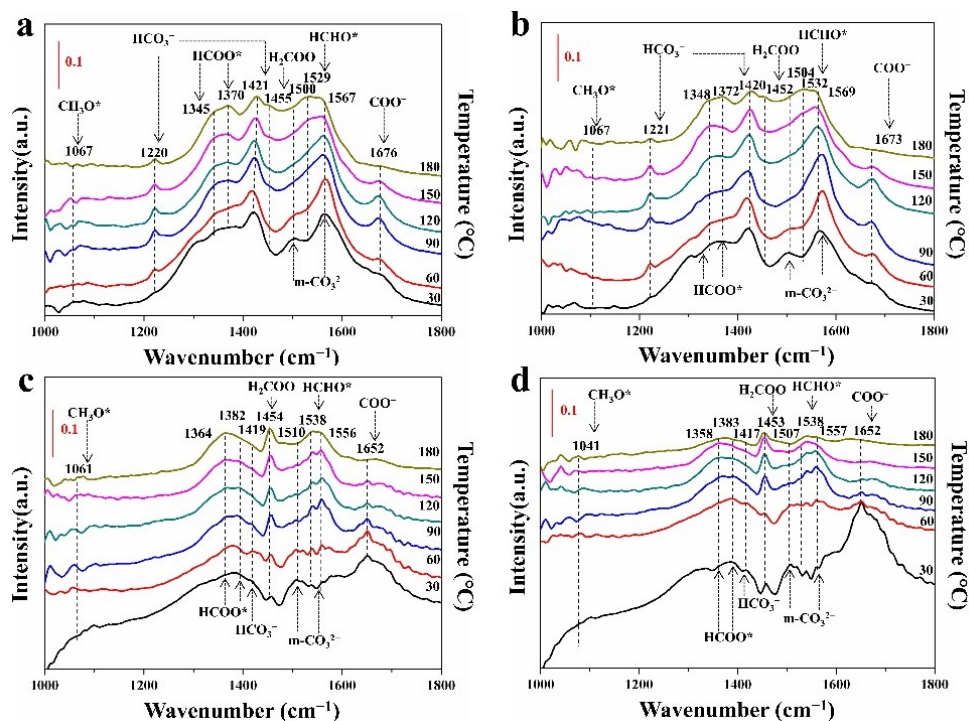


Fig.S19. In situ DRIFTS spectra of CO₂ adsorption at various condition: in dark (a) and under irradiation (b); CO₂+H₂O adsorption in dark (c) and under irradiation (d) on Mn-TiO₂ sample.

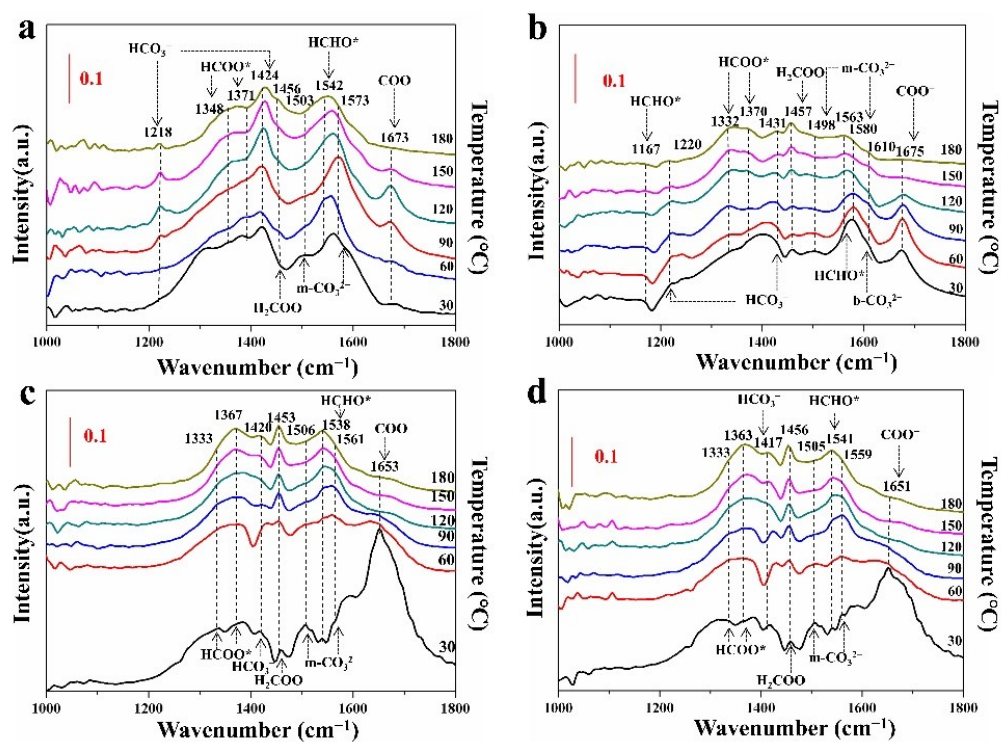


Fig.S20. In situ DRIFTS spectra of CO₂ adsorption at various condition: in dark (a) and under irradiation (b); CO₂+H₂O adsorption in dark (c) and under irradiation (d) on Pd-TiO₂ sample.