Supporting information

Light-driven thermocatalytic CO_2 reduction over surface-passivated β–Mo_2C nanowires: Enhanced catalytic stability by light

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Experimental Section

All chemicals were of reagent grade quality and gained from commercial sources.

1. Synthesis of β–Mo_2C nanowires

2.48g of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and 3.33 ml of aniline were simultaneously added in a 40ml of deionized water under stirring, following by dropwise addition of 1 mol/L hydrochloric acid at room temperature until white precipitate appeared. The slurry was kept at 50 ℃ for 6 hours. After that, it was filtrated, washed with water and ethanol until pH value equals to 7, and dried at 50 ℃ for 6 hours to obtain a white product.

The above-prepared product was heated with a ramping rate of 2 ℃/min and kept at 725 ℃ for 5 hours in a 5%H_2/Ar mixed gas with a flow rate of 50 cm^3/min. After being cooled to room temperature, the resultant was immersed in deionized water without exposure to the air, and then was dried at 50 ℃ for 6 hours under vacuum. The final product was denoted as P-Mo_2C.

2. Characterizations

X-ray powder diffraction (XRD) patterns were taken on a Bruker D8 Advance diffractometer using Cu k α radiation (λ =1.54056 Å) at room temperature. Diffraction intrnsity for 2θ from 20-90°, Scanning speed is 6°/min. SEM and TEM images were obtained on a Hitachi s4800 and FEI Tecnai G2 F20 instrument, respectively. Raman and IR investigation were performed on Horiba LabRAM HR Evolution and Bruker VERTEX 70V, respectively. The surface area and pore size were determined using a Micromeritics ASAP 2460 autosorption analyzer. The pore size distribution curves were derived from the adsorption branch of the isotherms. BET specific surface area was calculated from adsorption data at a relative pressure range from 0.05 to 0.3. UV-Vis-Nir diffuse reflectance spectra (DRS) were measured with a Cary5000. X-ray photoelectron spectroscopy (XPS) were recorded with Thermofisher AXIS SUPRA. Isotherm adsorptions of CO_2 were carried out on a home-made volumetric adsorption system at room temperature. The catalyst was evacuated at 473 K for 2 h before the

measurement. After cooling the catalyst to room temperature, doses of CO_2 were admitted sequentially and the coverages of CO_2 were measured until the equilibrium pressure reached about 20 kPa.

3. Catalytic measurements for CO_2 reduction with H_2O

The catalytic redction of CO_2 with H_2O vapor was carried out in a reaction system equipped with a mechanical vacuum pump and two types of reactors for photocatalysis and thermocatalysis. A 300 W xenon lamp was used as the light source with light intensity of 0.220 W cm^{-2}. 20 mg of tested catalyst powder was evenly deposited on a circular quartz plate with a diameter of 50 mm and placed inside a cylindrical reactor connected to a cooling system. The actual temperatures at the P-Mo_2C surface were immediately measured by using an infrared thermometer once the reaction was over in the work. For thermocatalytic CO_2 conversion, the catalyst was placed into a tubular reactor with a heating furnace. 20 mL of gaseous- and 20 μL of liquid-reactant was injected into the vacuum reactor system, and the catalytic activities were determined for 5 h in each run. The reaction products were monitored by an online gas chromatograph (SP-3420A, BFRL) equipped with a methanation furnace and a flame ionization detector (FID). The isotopic experiment with $^{13}CO_2$ as the reactant over the P-Mo_2C was carried out in a reactor connected to a molecular vacuum pump and a mass spectrometer. 20 mg of the P-Mo_2C was evenly deposited on the reactor and a 300 W xenon lamp was used as the light source.

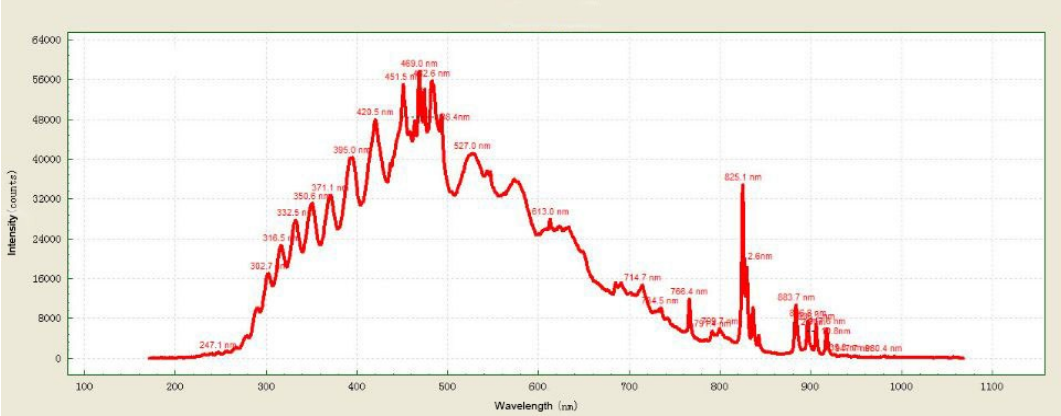

Figure S1. Emission spectrum of the Xenon lamp used in the work

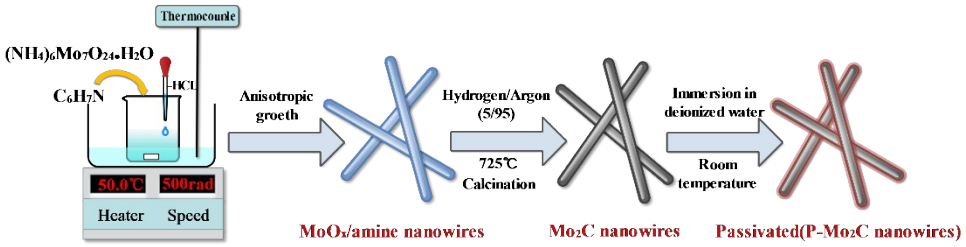

Figure S2. Schematic illustration of the construction of surface-passivated β-Mo_2C nanowires (named P-Mo_2C)

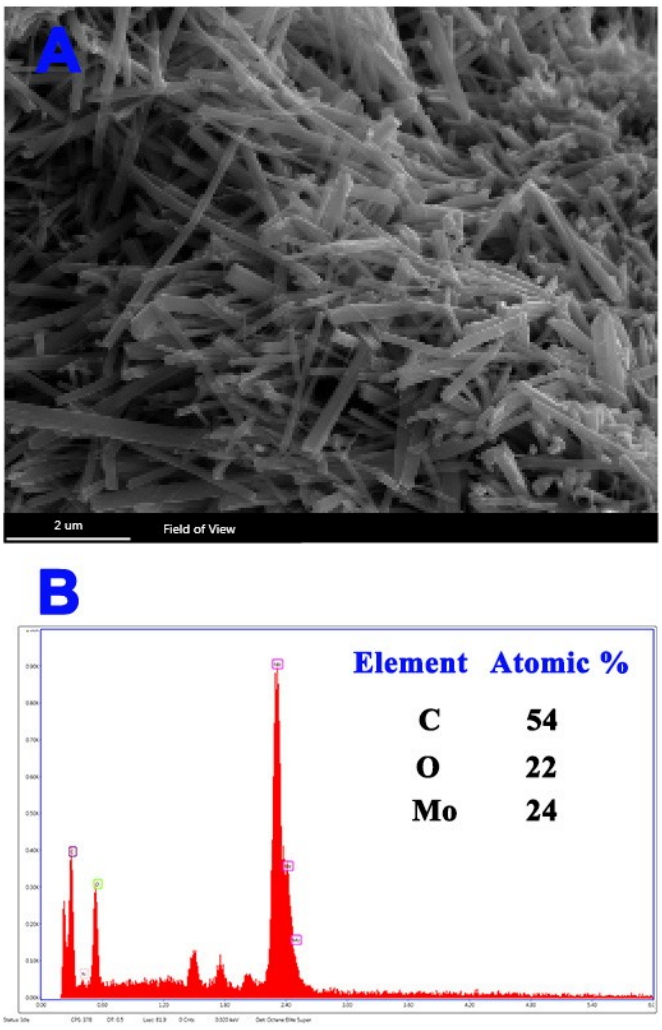

Figure S3. (A) a SEM image with low magnification and (B) EDS elemental analysis for the P-Mo_2C.

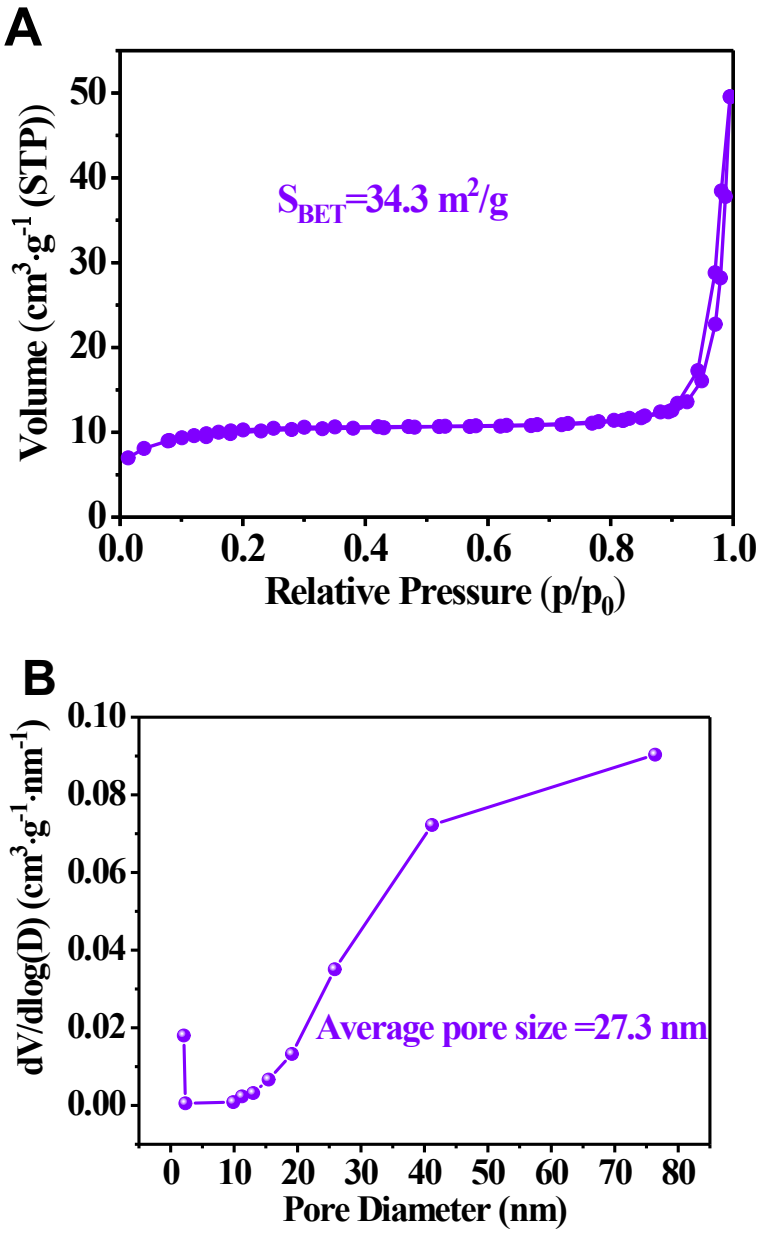

Figure S4. (A) N_2 adsorption–desorption isotherms and (B) pore size distribution curve of the P-Mo_2C

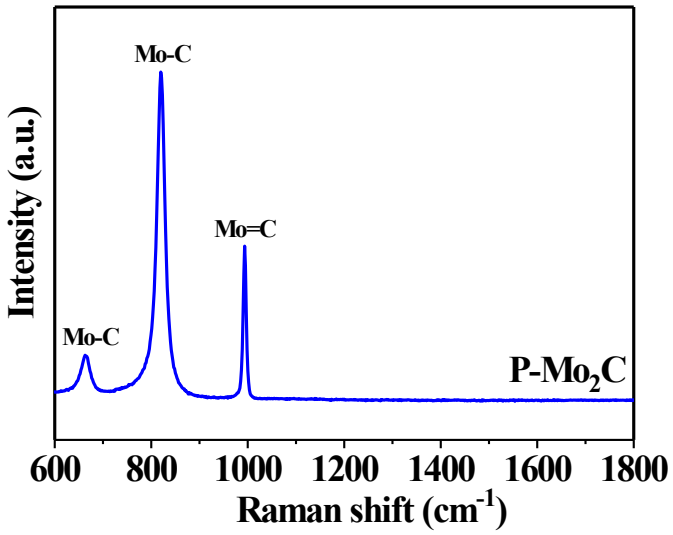

Figure S5. Raman spectrum of the P-Mo_2C

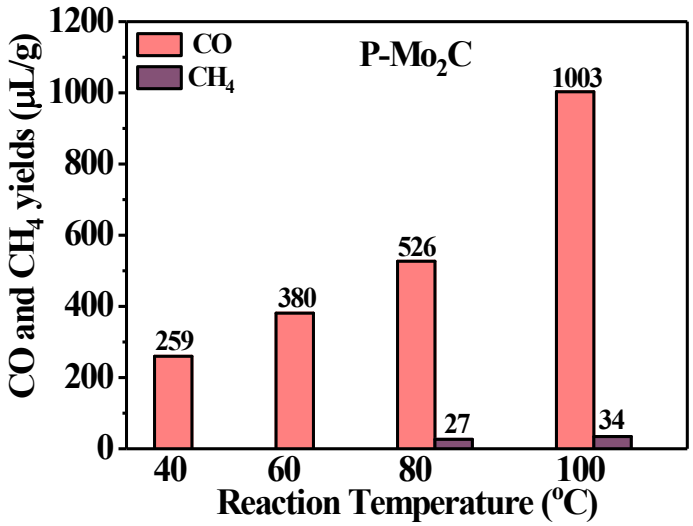

Figure S6. CO and CH_4 yields for the CO_2 reduction with H_2O at different reaction temperatures

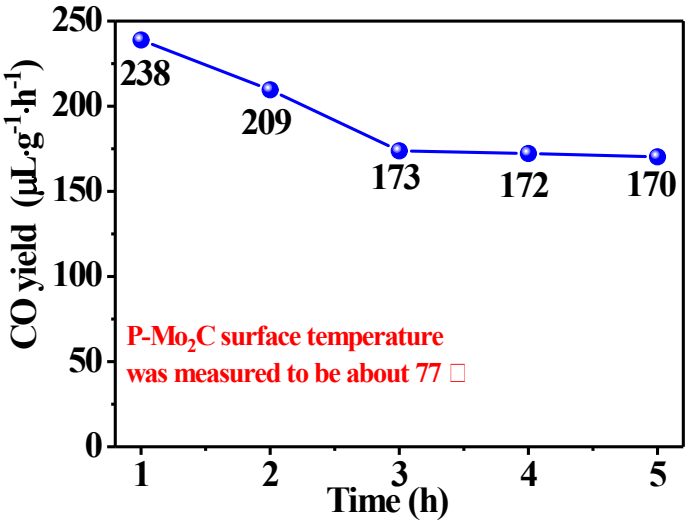

Figure S7. CO yield over the P-Mo_2C under light irradiation in a flow system under normal pressure with a CO_2/H_2O (vapor) flow rate of 6 mL/min.

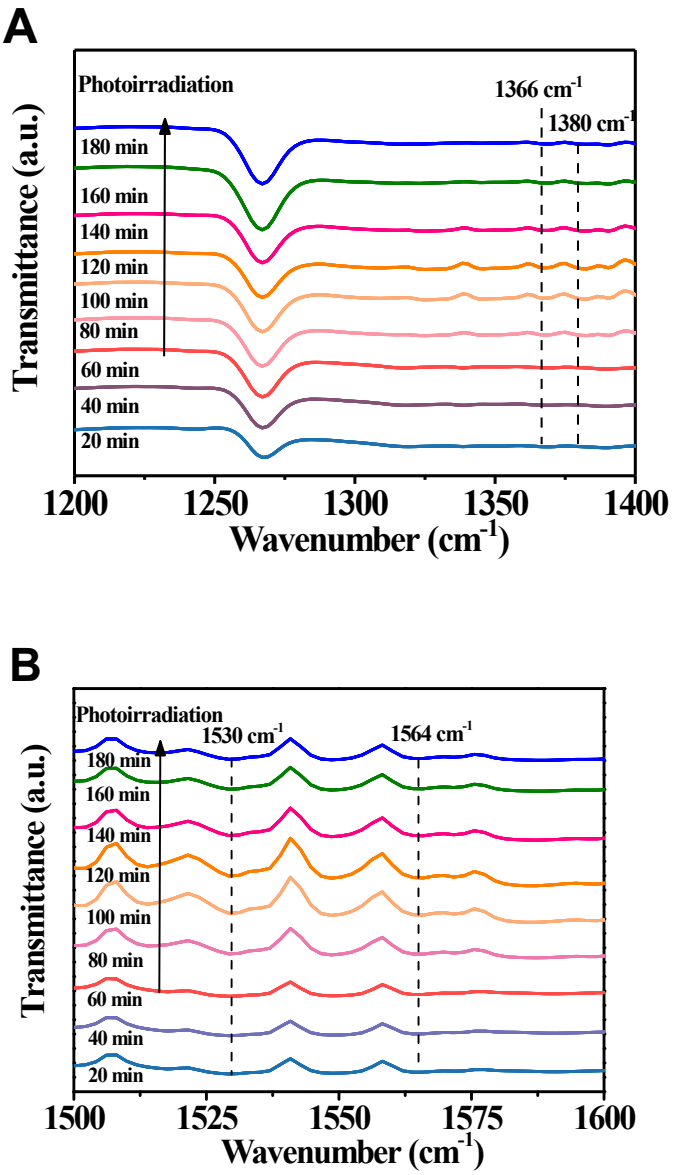

Figure S8. In situ FTIR spectra for coadsorption of a 1:1 mole ratio mixture of CO_2 and H_2O vapor on the P-Mo_2C. The spectra were recorded with light-irradiation time.

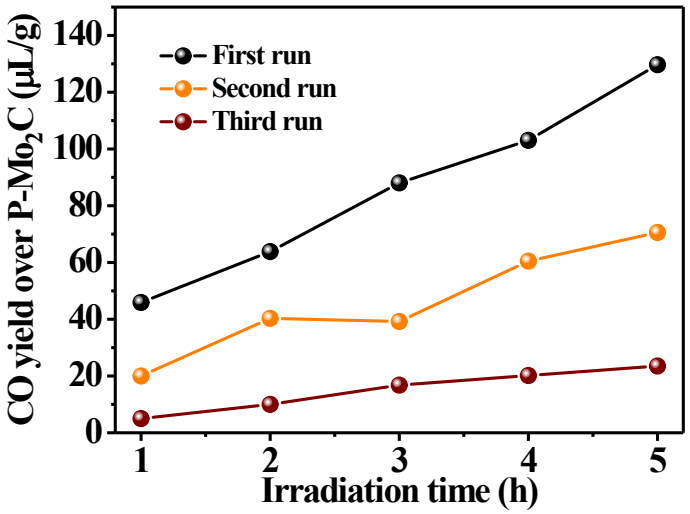

Figure S9. CO production in a blank experiment by using 15 ℃ of cooling water, where the P-Mo_2C was illuminated in the absence of CO_2 and H_2O for three successive cycles.

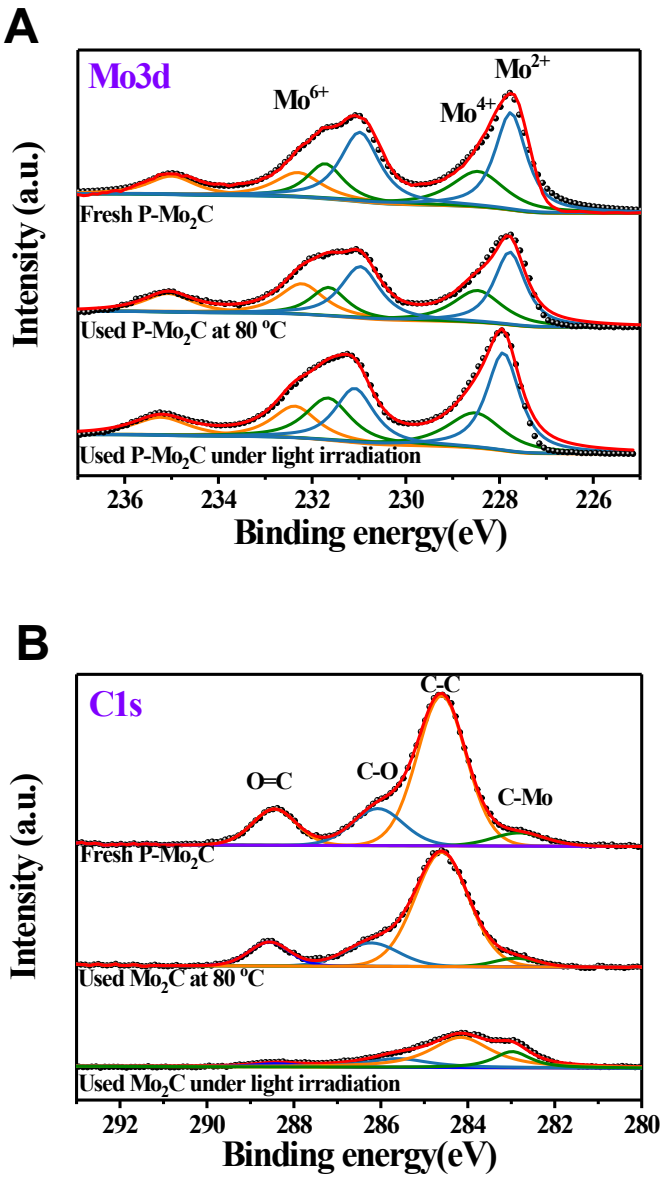

Figure S10. Mo 3d and C 1s core level XPS spectra of the fresh P-Mo_2C, used P-Mo_2C at 80 ℃ and used P-Mo_2C under light irradiation.

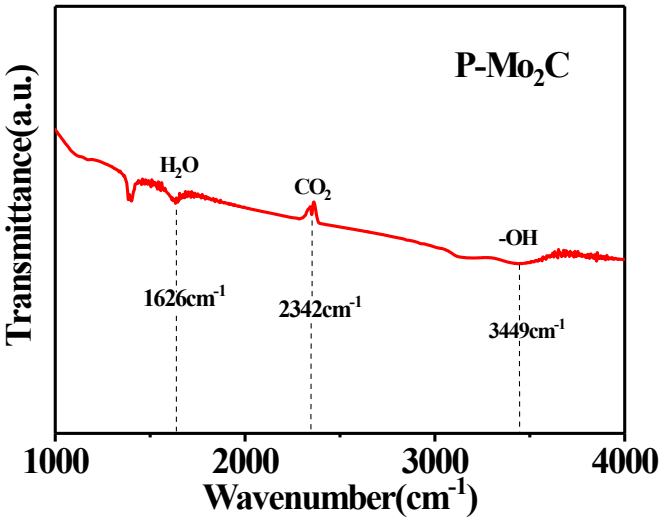

Figure S11. FTIR spectrum of the P-Mo_2C

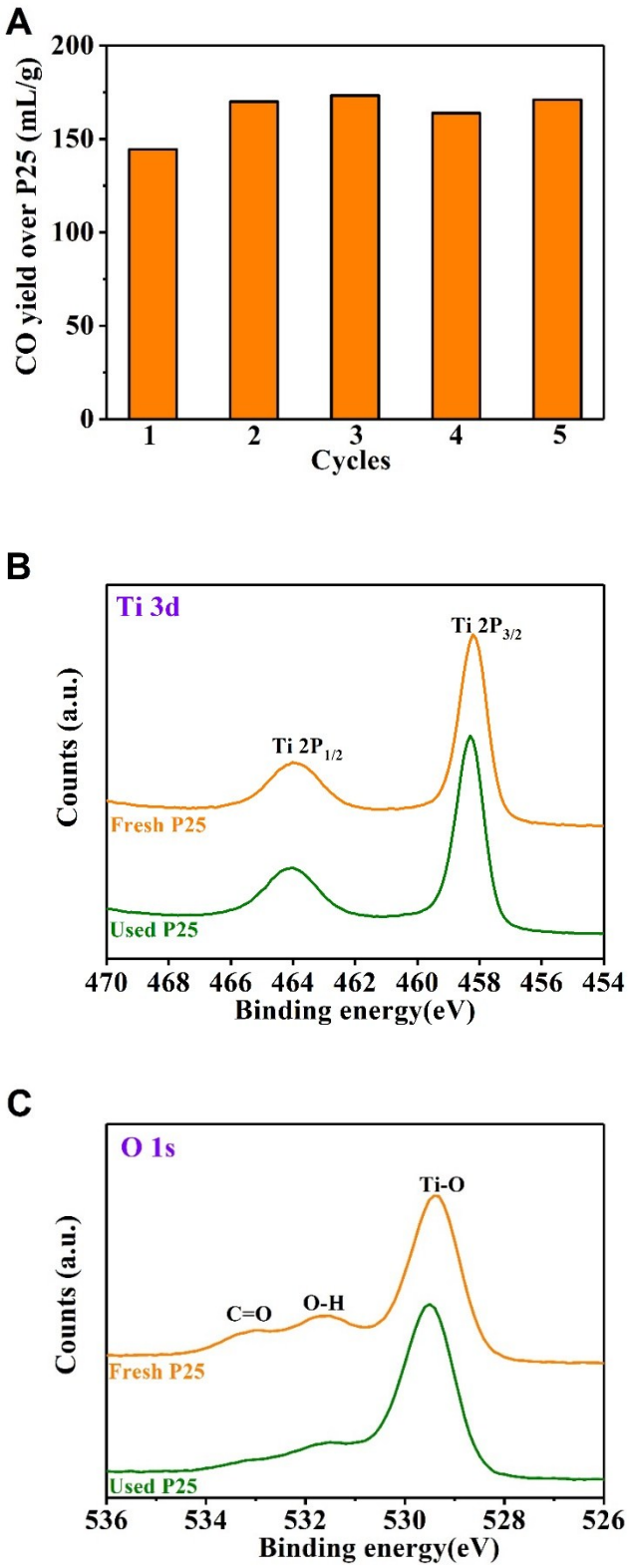

Figure S12. (A) Catalytic stability text of P25 for CO_2 reduction with H_2O under light irradiation. (B, C) Ti 3d and O 1s core level XPS of the P25 before and after use.

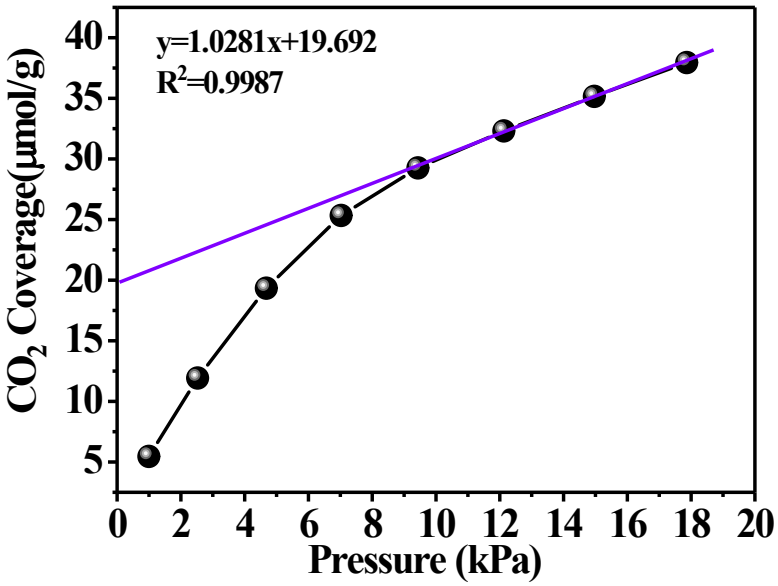

Figure S13. Coverage vs. pressure of CO_2 on the P-Mo_2C at room temperature.

Table 1 CO yields over the P-Mo_2C and P25 under light irradiation at different cooling water temperatures

Parallel group	15 ℃ (P25)	5 ℃ (P-Mo_2C)	15 ℃ (P-Mo_2C)	R.T. (P-Mo_2C)
1	145.2	89.6	648.7	924.9
2	125.5	47.0	638.0	736.0
3	138.3	73.2	560.4	1049.0

Table 2 CO yields over the P-Mo_2C under light irradiation for five successive cycles

Parallel group	1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}
1	637.1	581.3	483.4	471.5	528.2
2	648.7	572.9	491.5	485.2	452.6
3	560.4	498.2	466.2	452.3	442.6

Table 3 CO yields over the P-Mo_2C at 80 ℃ for five successive cycles

Parallel group	1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}
1	526.8	471.5	414.2	331.5	214.1
2	507.2	392.0	332.0	257.2	192.9
3	539.3	442.9	392.5	303.6	198.2