Soft selective light absorber for efficient photothermal chemical processes in complex reactor geometries

Fuzhen Hu[1, 5], Wei Wang[1, 5], Dachao Yuan[2, 5], Kai Du[1, 5], Jiacong Guo[1], Lin Ma[1], Yuan Tang[1*], Yaguang Li[1*], Jinhua Ye[1, 3.4]

Experimental Section

Chemicals

The industrial CuZnAl was purchased from Sichuan Shutai Chemical Technology Co., Ltd. The PEI/SiO_2 was purchased from Taobao. Ti_3AlC_2 was purchased from Zhongke Leiming Technology Co., Ltd., HCl was purchased from Tianjin Damao Chemical Reagent Factory, LiF was purchased from Aladdin Reagent Co., Ltd., and ethanolamine and anhydrous methanol were purchased from Tianjin Kemio Chemical Reagent Co., Ltd. All commercial chemicals, including ethanol (Beilian Chemical Co., Ltd.), were used without further processing.

The synthesis of MXene ink

The MXene nanosheets with a layered two-dimensional structure were obtained by liquid-phase etching of the titanium aluminium carbide (Ti_3AlC_2) bulk phase. 20 mL of 9 M HCl was added to a 100 mL polytetrafluoroethylene (PTFE) liner, followed by the addition of 1.6 to 2 g of lithium fluoride (LiF). The solution was thoroughly dissolved, turning pale yellow. Ice water was used in the water bath to slow down the intense exothermic reaction at the initial stage. 1.0 g of Ti_3AlC_2 was added in small portions multiple times to the concentrated hydrochloric acid to prevent the solution from boiling excessively due to the exothermic reaction. After Ti_3AlC_2 was fully dissolved, the container was sealed, leaving only a vent hole for the escape of hydrogen gas (H_2). The reaction temperature was maintained at 40 °C for 48 hours. After the reaction was complete, the mixture was centrifuged to separate the precipitate. The precipitate was then washed by centrifugation with 2 M HCl for 4 to 5 cycles, taking advantage of the solubility of lithium fluoride in acid. Centrifugation with deionized water was continued for 3 to 5 cycles. During this process, the colour of the supernatant turned black, and the precipitate exhibited stratification, indicating the formation of a MXene suspension in the upper layer. Due to the low concentration of MXene, multiple centrifugation steps were required, followed by ultrasonic treatment of the precipitate. After ultrasonic treatment, the final centrifugation step was used to separate the precipitate. The resulting black ink contains monolayer or few-layer MXene nanosheets. After concentration calibration, the prepared MXene ink was a nitrogen-saturated deionized water to prevent oxidation. The prepared MXene ink has 1 mg_{MXene}/mL of density.

The synthesis of MXene/Al film

We added 400 mL of ethanol to 100 mL of MXene ink, which needs to be stirred in an ice water bath for 12 hours to form MXene solution. Commercial Al foil was purchased from Taobao, with a thickness of 15 μm. This Al foil is first cleaned by ultrasonic cleaning in ethanol for 30 minutes. After ultrasonic cleaning, the Al foil is spread flat on a heating plate and nitrogen is used to blow and remove ethanol. The MXene solution is placed into a spray gun with a pressure set to 0.3 MPa. The spray gun is fixed 50 cm away from the Al foil, then the MXene solution is sprayed onto the Al foil. The spray gun is moved at a speed of 1m/min to complete the spraying. The time interval between each spraying is 10 seconds. The temperature in the spraying room is maintained at 30 °C, and the humidity is kept below 20% to ensure rapid drying of the spray MXene solution. After the sprayed MXene solution is natural dried, the MXene/Al film is achieved. The MXene/Al film can be coated with adhesive and then directly adhered to the surface of the reactors.

Infrared radiation calculation

According to the Stefan-Boltzmann law, the low-infrared thermal radiation properties of photothermal materials are intrinsically associated with the material's emissivity and temperature (Equation. S1).

$$M_{net} = \varepsilon * \sigma * (T_{sample}^{4} - T_{ambient}^{4})$$

Where ε is the emissivity of the sample (given as 0.95), σ is the Stefan–Boltzmann constant (5.670374419×10^{-8} W m^{-2} K^{-4}), T_{sample} is the thermodynamic temperature of the sample (K), $T_{ambient}$ is the thermodynamic temperature of the surroundings (K).

Photothermal Reverse Water-gas shift reaction (RWGS)

The light intensity ranges from 0 to 6 kW·m^{-2}, with a test point every 1 kW·m^{-2}. The CuZnAl catalyst used in RWGS was firstly reduced in a hydrogen (H_2)

environment at 300 °C for 2 hours. The flow rates of CO_2 and H_2 are 40 mL·min^{-1} and 80 mL·min^{-1}, respectively. The catalyst mass is 20 mg.

Product formation rates (E), CO_2 conversion (X), and CO selectivity (S) were calculated by using the following equations (Equations. S2):

$$E = \frac{V_{CO_2,in} \times R \times 60}{m \times 24.5}$$

$$X_{CO_2} = \frac{E_{CO,out} + E_{CH_4,out}}{M_{CO_2,in}}$$

$$S_{CO} = \frac{E_{CO,out}}{E_{CO,out} + E_{CH_4,out}}$$

where V_{CO_2} is the flow rate of CO_2, R is the CO (or CH_4) volume percentage (%), m is the catalyst quality, and the calculation method for CH_4 is the same as that for CO.

Photothermal CO_2 desorption from PEI/SiO_2

The preparation of saturated PEI/SiO_2 in the CO_2 desorption reaction is carried out through the following steps: First, 20g of PEI/SiO_2 is added to the absorption reactor, and then heated in a water bath at 30°C for 10-15 minutes to reach thermal equilibrium. The mass flow controller is adjusted to ensure that CO_2 flows into the solution at a rate of 120 mL·min^{-1}. Once the outlet CO_2 concentration stabilizes, the solution is considered to have reached absorption saturation. For the photothermal CO_2 desorption from PEI/SiO_2, 3 g of saturated PEI/SiO_2 was loaded into the photothermal reactors and the reactors were irradiated with simulated sunlight.

Photothermal methanol steam reforming

The industrial CuZnAl catalyst used in this reaction undergoes hydrogen reduction treatment under conditions similar to those of the water-gas shift reaction. The catalyst mass is 400 mg. The methanol solution is prepared by mixing anhydrous methanol with deionized water in a 1:13 volume ratio. The solution is injected by an automatic injection system, consisting of an injector and a 50 mL syringe, with an injection rate of 0.25 mL·min^{-1}. The light intensity ranges from 0 to 6 kW·m^{-2}, with a test point every 1 kW·m^{-2}.

Solar to hydrogen efficiency（η）was calculated using the following equation (Equation. S3):

$$\eta = \frac{F_{H_2} \times \triangle H}{C \times S}$$

where F_{H_2} is the H_2 output, $\triangle H$ is the enthalpy change, C is the solar intensity, S is the light-receiving area (6 cm^2).

Characterizations

TEM images are acquired using a JEOL 2100plus transmission electron microscope operating at 200 kV. The samples are prepared by depositing a water/ethanol dispersion onto an ultrathin carbon film, followed by immediate solvent evaporation. Aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM) images and STEM-EDX elemental mappings are obtained using a JEOL JEM-ARM200F transmission electron microscope, also operating at 200 kV, and equipped with a probe spherical aberration corrector. The SEM images are acquired from FEI Nova Nano SEM450 scanning electron microscopes. The AFM images are acquired from MFP-3D Origin Atomic Force Microscope. XRD analysis of the obtained MXene is performed using a Rigaku MiniFlex 600 diffractometer with a Cu-Kα X-ray source (λ = 0.154056 nm). Typically, the sample is placed on an amorphous silica substrate, and the XRD patterns are recorded at a scan rate of 2 min^{-1}. XPS measurements are conducted using a Thermo VG ESCALAB-250 system with Al-Kα and Mg-Kα sources operated at 15 kV. The binding energies are referred to the C 1s peak (284.8 eV) from adventitious carbon. Infrared (IR) photographs are taken with a camera (Fluke Ti300, America). The IR radiation and IR emissivity of the samples are measured using an integrating sphere-equipped FTIR system with a heated substrate (HYPERION 3000, Bruker Optics). The ultraviolet-visible-infrared absorption spectrum (UV-vis-IR) and IR emission were measured by Hitachi Limited U4100

(Japan) and FTIR spectrometer (Bruker, VERTEX 70 FT-IR). The light intensity is measured using a power meter (PM100D + S425C, ThorLabs).

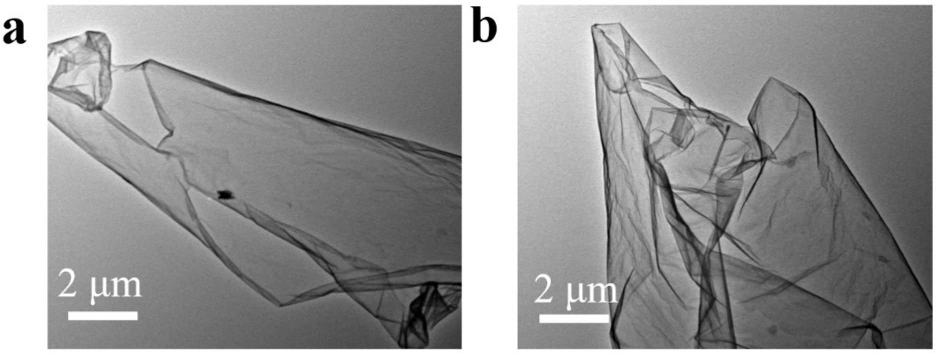

Fig. S1 (a-b) TEM images of MXene.

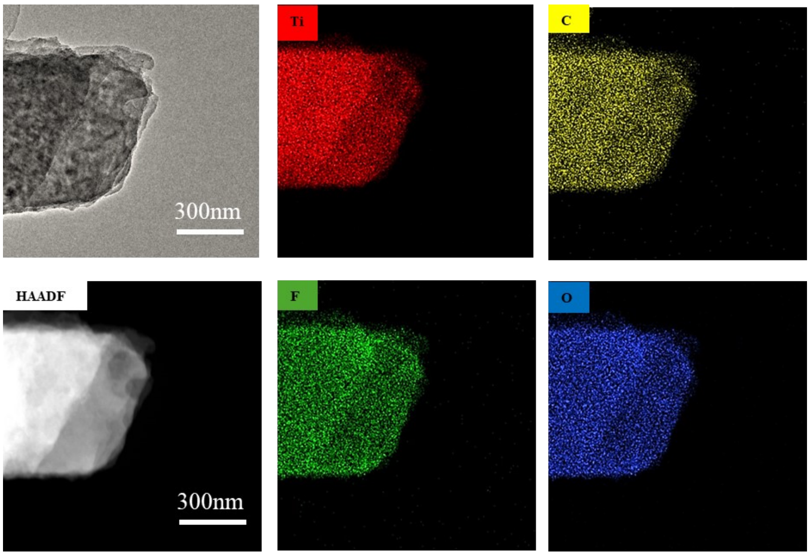

Fig. S2 MXene TEM images of other regions and their corresponding EDS mapping.

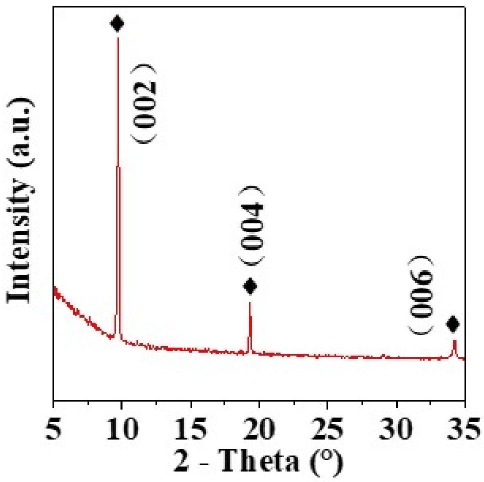

Fig. S3 XRD image of Ti_3AlC_2.

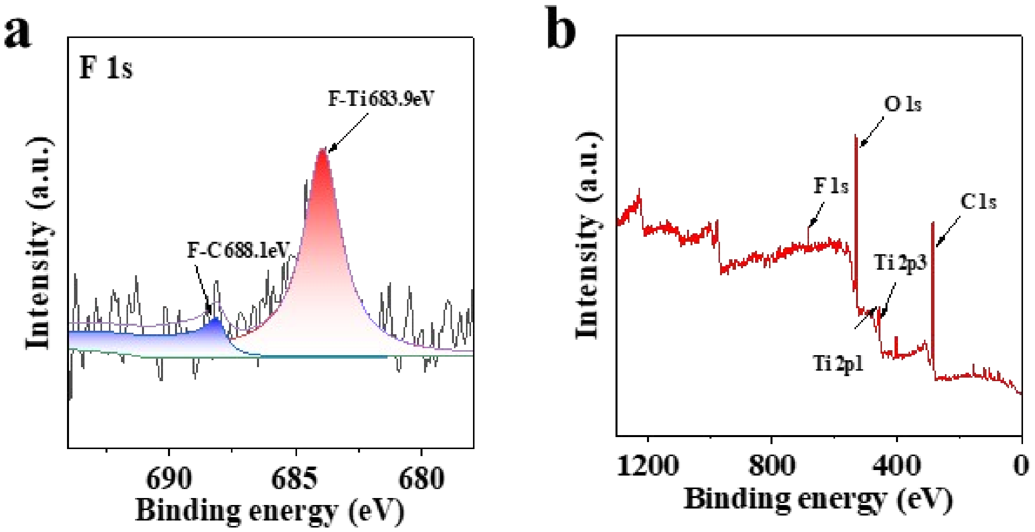

Fig. S4 (a) F 1s spectrum of MXene, (b) The survey of MXene.

Fig. S5 The photograph of MXene ink.

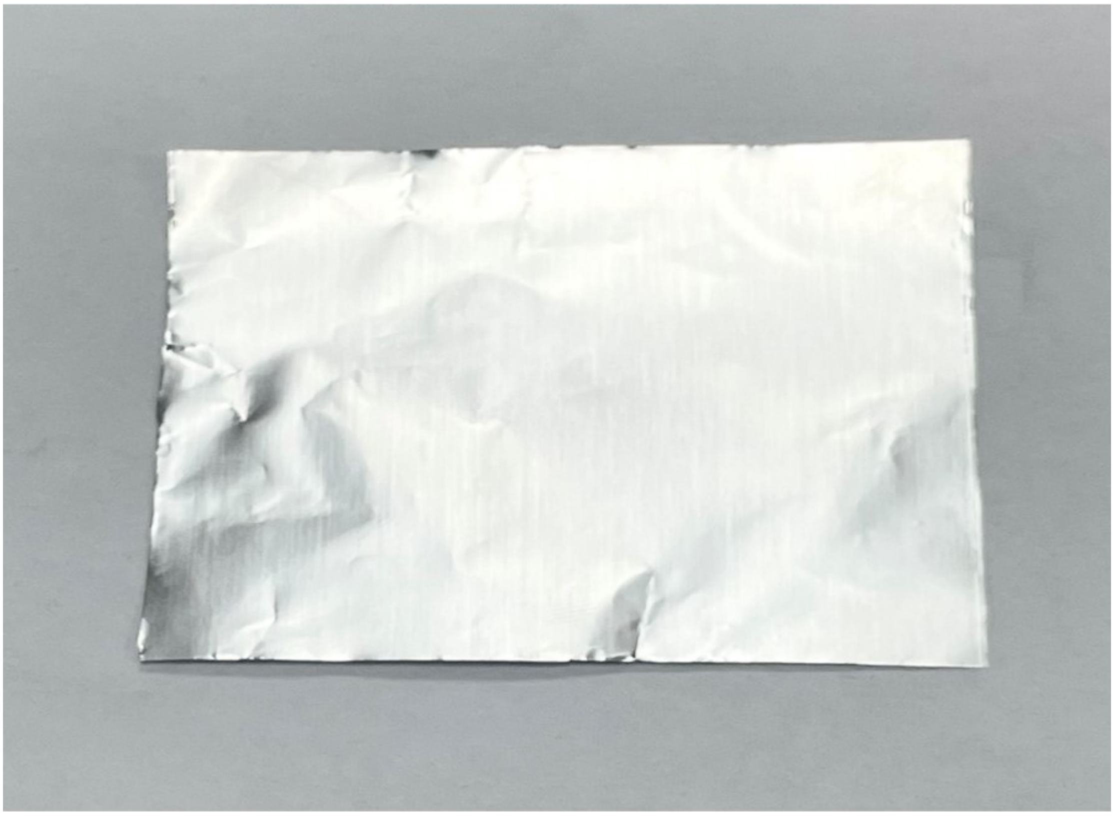

Fig. S6 The photograph of commercial Al foil.

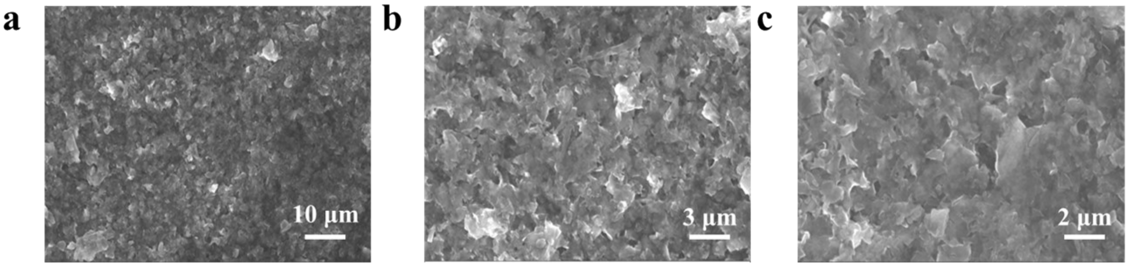

Fig. S7 SEM of 150nm MXene/Al photothermal film. (a) 10 μm, (b) 3 μm, (c) 2 μm.

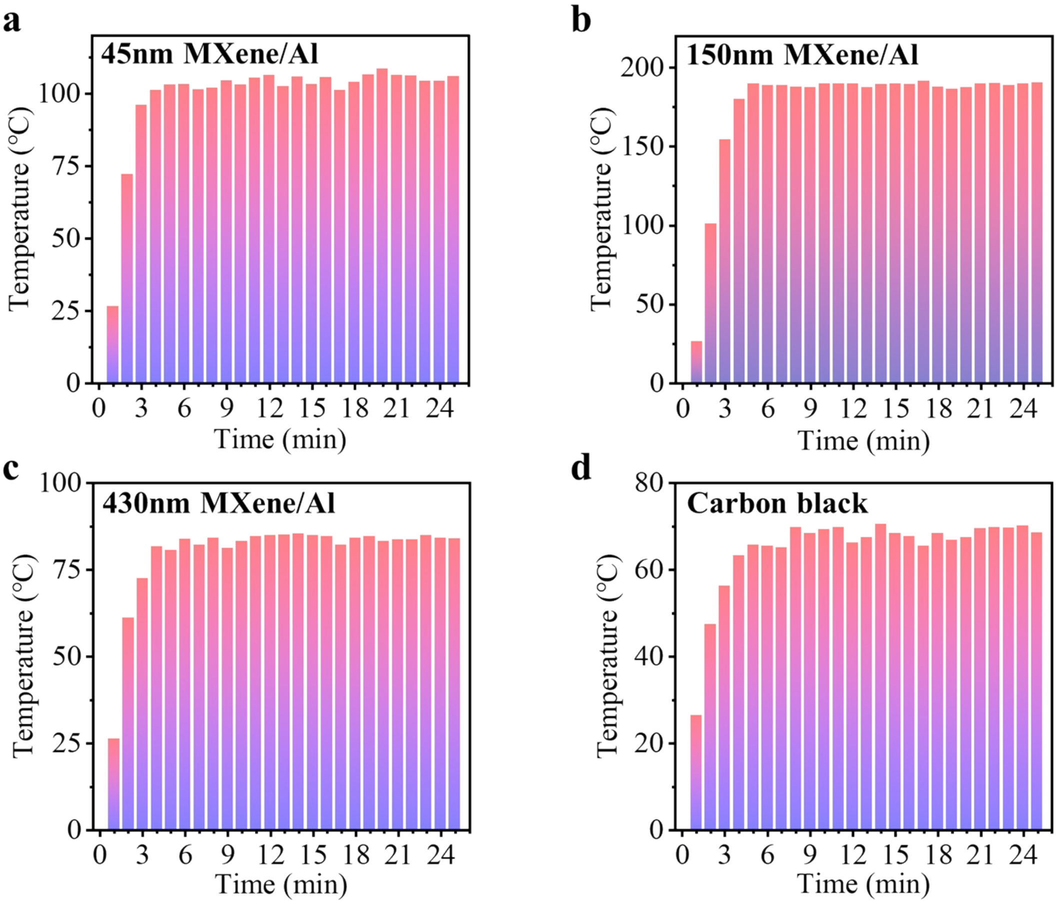

Fig. S8 Temperature rises under 1 kW m^{-2} solar radiation. (a) 45 nm MXene/Al, (b) 150 nm MXene/Al, (c) 430 nm MXene/Al, (d) Carbon black.

Fig. S9 The photographs of 150 nm MXene/Al film with various nest fold shapes.

Fig. S10 The photograph of 150 nm MXene/Al film with large scale.

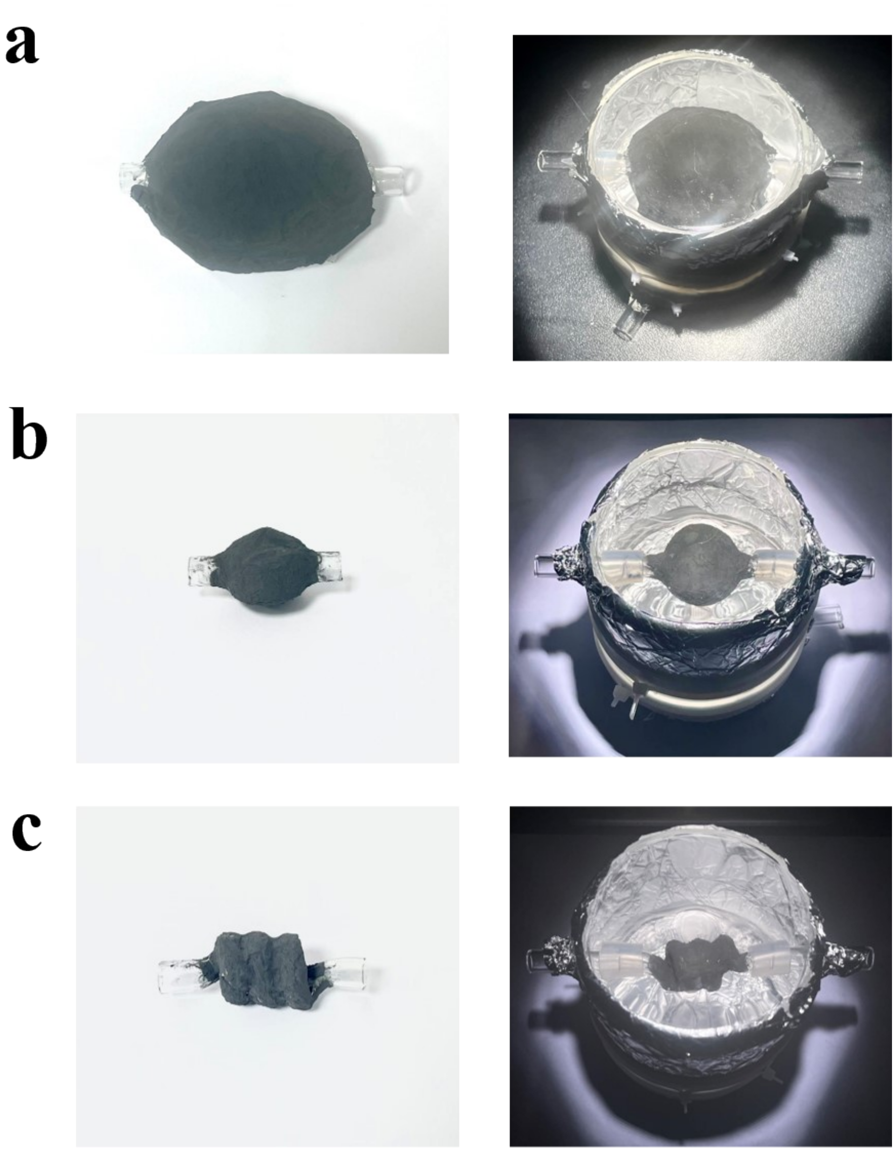

Fig. S11 (a) Carbon black powder coating disc device, (b) Carbon black powder coated conical component device, (c) Carbon black powder coated spiral component device.

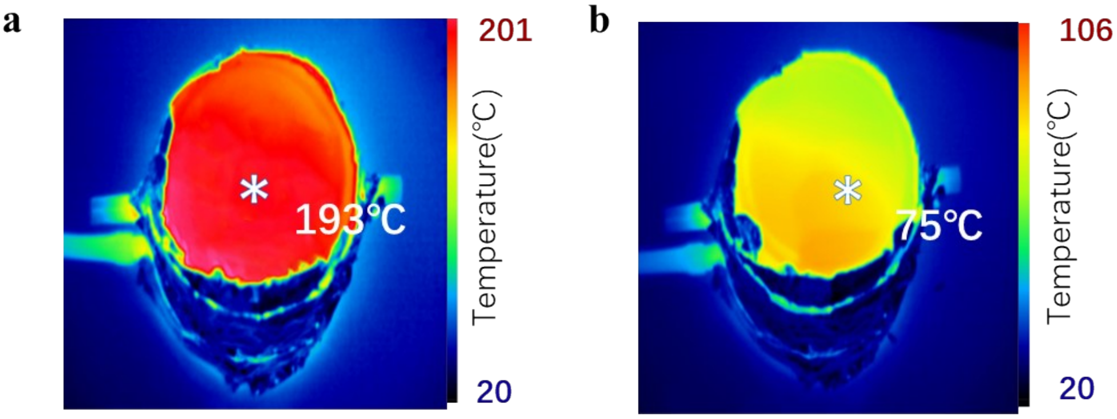

Fig. S12 Infrared thermal imaging of reactor under light irradiation. (a) 150nm MXene/Al, (b) Carbon black.

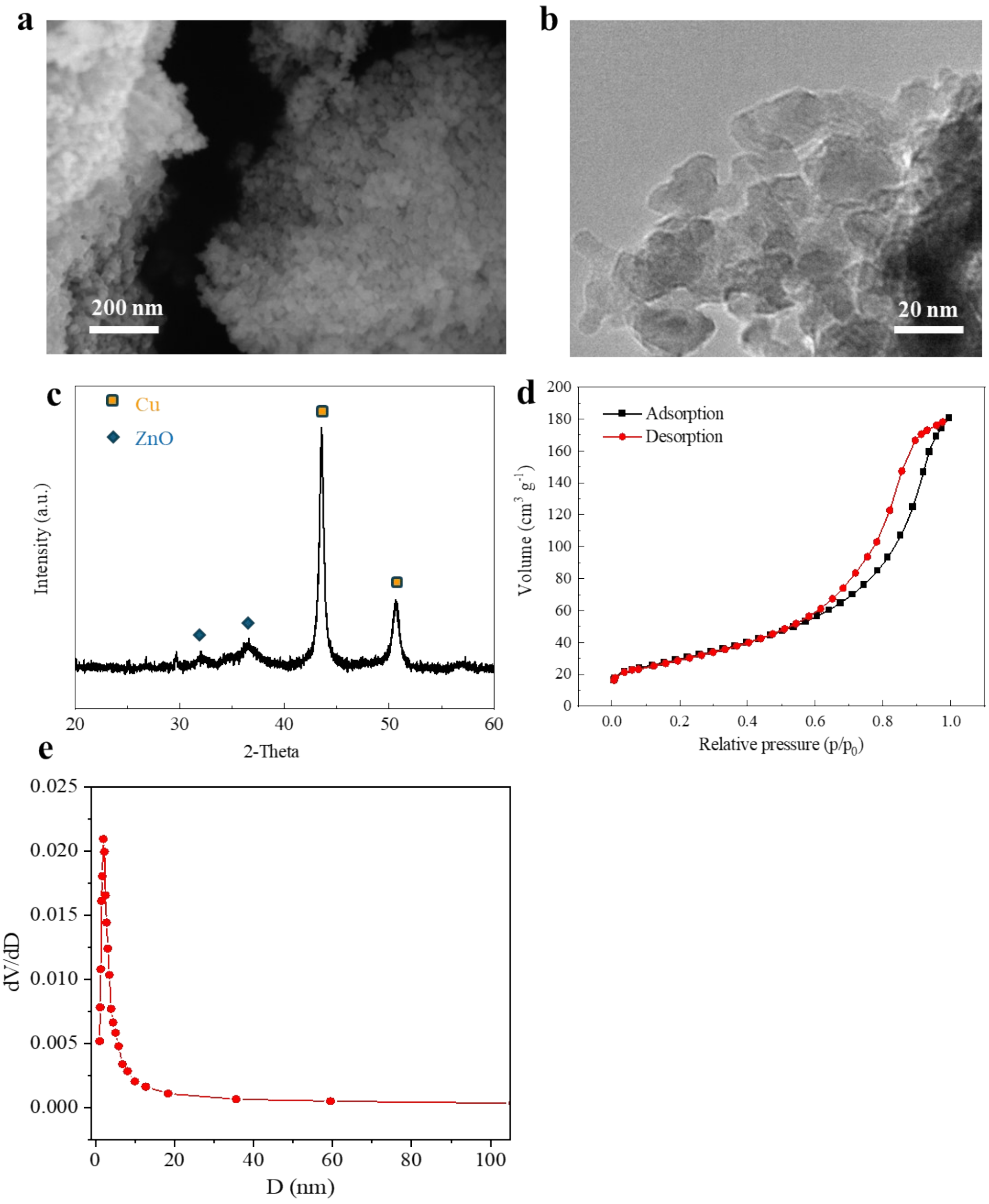

Fig. S13 Characterization of Industrial CuZnAl Catalyst. (a) SEM image, (b) TEM image, (c) XRD pattern, (d) nitrogen adsorption and desorption isotherm, (e), pore size distribution.

The N_2 adsorption–desorption isotherms of the CuZnAl catalyst exhibit a typical Type IV profile, indicating the presence of a mesoporous structure. The pore size distribution curve shows that the pore sizes are predominantly concentrated in the mesoporous range of 2-10 nm, providing active sites and mass transfer pathways for catalytic reactions.

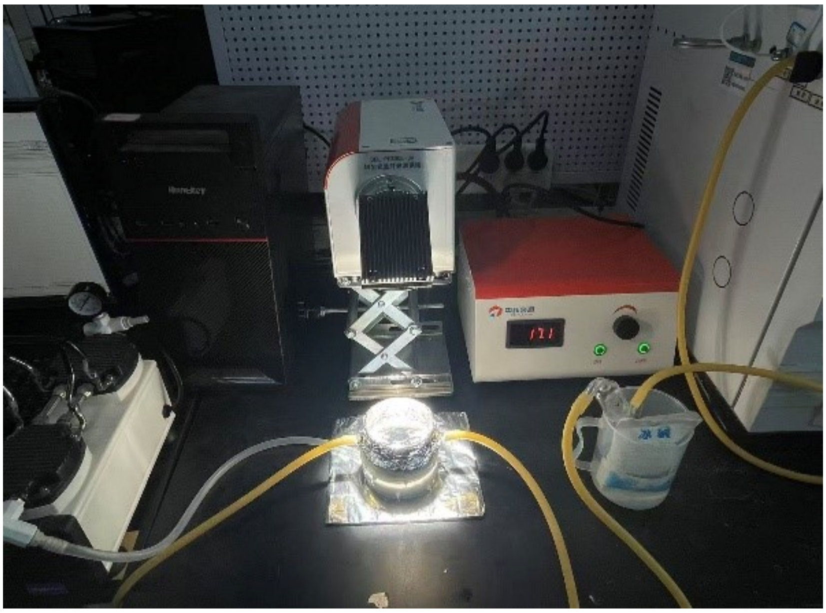

Fig. S14. Physical connection diagram of the disc device for photothermal RWGS.

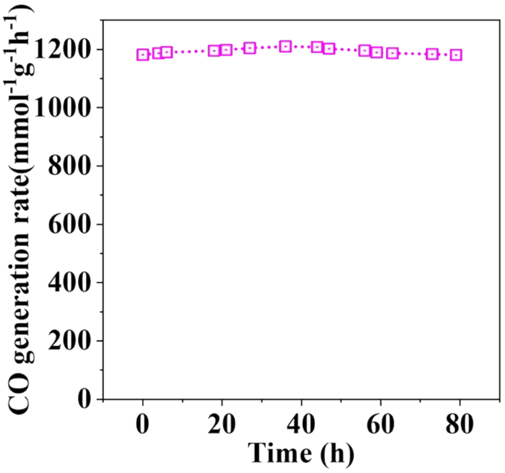

Fig. S15 Stability testing of photothermal RWGS over MXene/Al coated disc device under 6 suns irradiation.

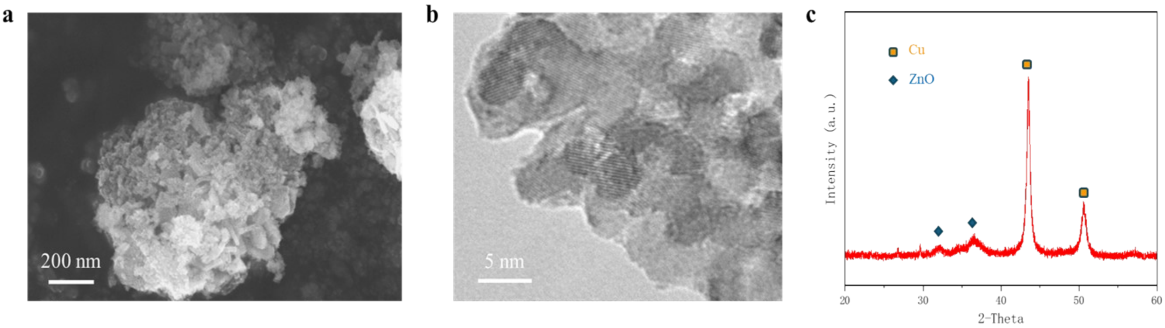

Fig. S16 Characterization of industrial CuZnAl after 80 hours of reaction. (a) SEM image, (b) TEM image, (c) XRD pattern.

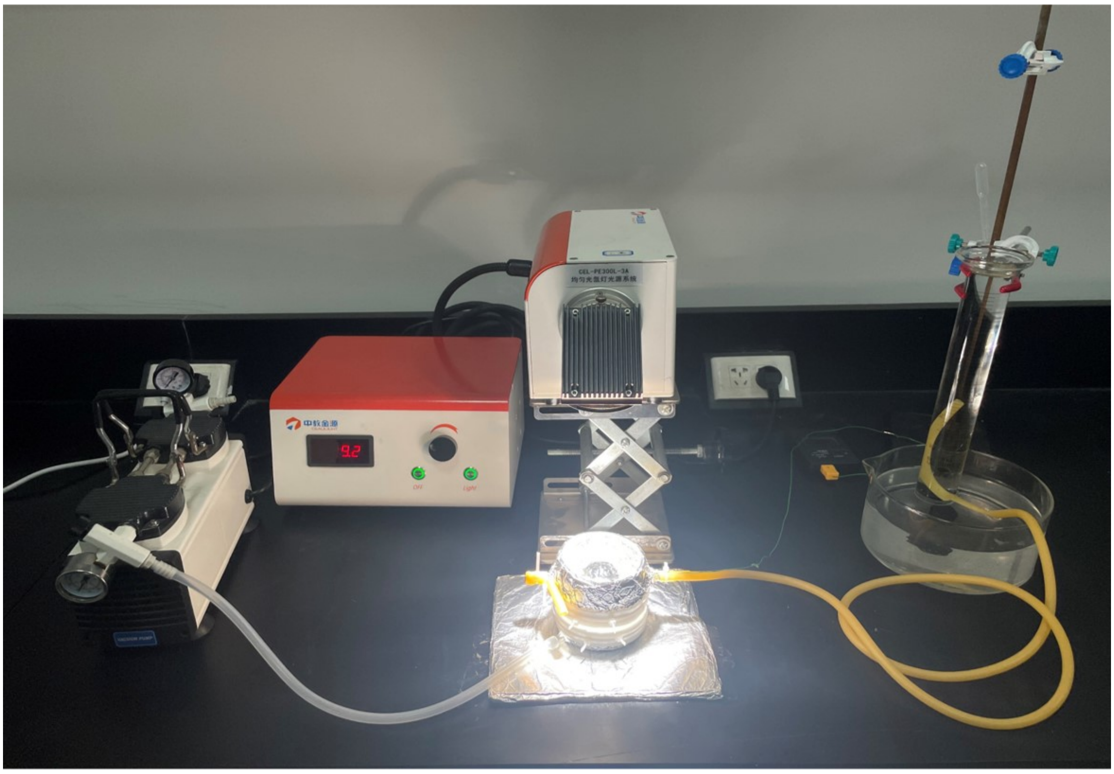

Fig. S17 Supplement on the PEI/SiO_2 derived CO_2 desorption in MXene/Al coated conical device.

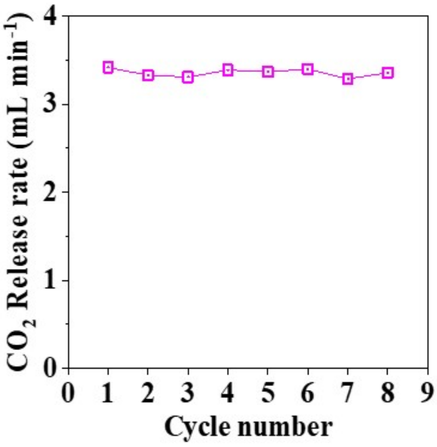

Fig. S18 Stability test of CO$_2$ desorption reaction system under 1.5 suns irradiation (8 cycles).

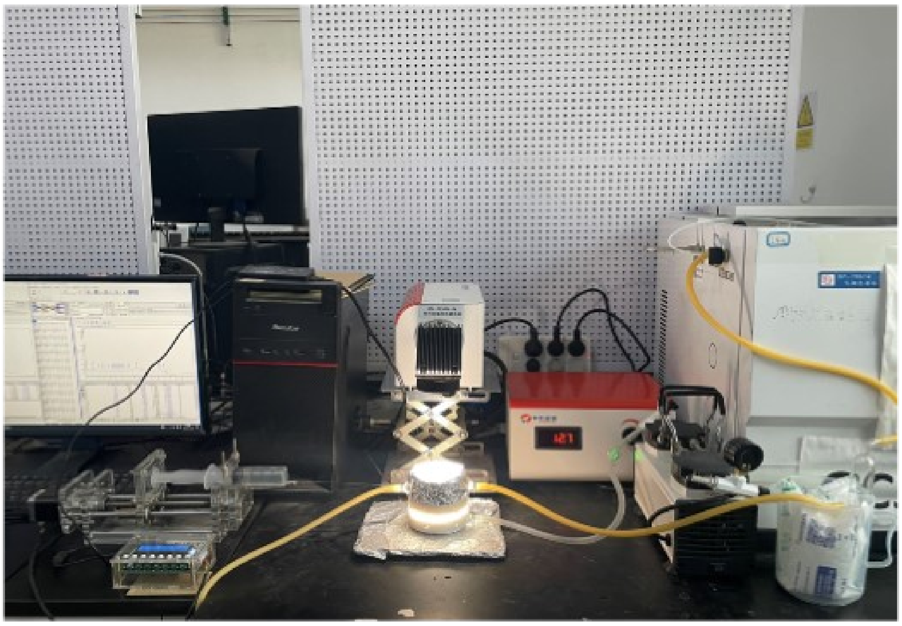

Fig. S19 Physical connection diagram of the MXene/Al coated spiral device for photothermal methanol-to-hydrogen reaction.

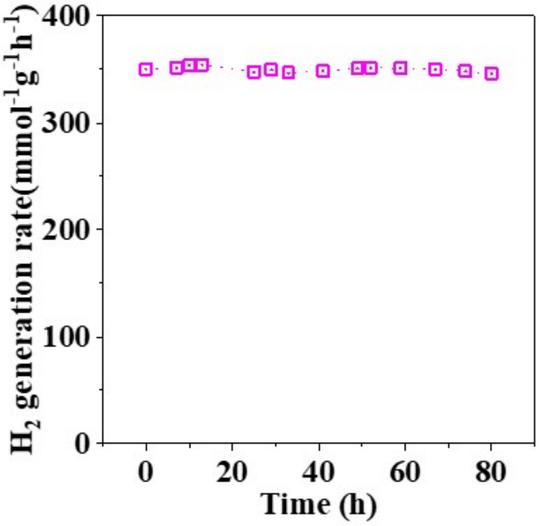

Fig. S20 Stability testing of methanol hydrogen production reaction system under 6 suns irradiation.