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# Regulating protonation paths for enhanced photocatalytic CO<sub>2</sub> methanation by coupling Pt sites on WO<sub>2.9</sub>/TiO<sub>2</sub>†

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CO<sub>2</sub> methanation *via* photocatalysis with water vapor is a sustainable technique for reducing CO<sub>2</sub> emission but is challenged by the high energy barrier associated with the initial adsorption, activation and protonation of CO<sub>2</sub> molecules. In this work, a substoichiometric WO<sub>2.9</sub> thin film with strong Lewis acidity was coated on TiO<sub>2</sub> microspheres, followed by the deposition of Pt cocatalysts on WO<sub>2.9</sub> with controlled Pt single atoms and clusters (Pt-WO<sub>2.9</sub>/TiO<sub>2</sub>). The methane production rate reached 10.74 μmol h<sup>-1</sup> g<sup>-1</sup> with a selectivity of 99.8%, which was ~40 times higher than that of bare TiO<sub>2</sub> (0.27 μmol h<sup>-1</sup> g<sup>-1</sup>). The high methane production rate was attributed to the synergy of Pt sites on the WO<sub>2.9</sub>/TiO<sub>2</sub> heterojunction, where the Pt clusters facilitated water dissociation, thereby providing H\* through hydrogen spillover on the surface, and the presence of a substoichiometric WO<sub>2.9</sub> surface further enhanced the spillover process. The high density of active H\* promoted the protonation pathway for CO<sub>2</sub> activation (CO<sub>2</sub> → COOH\* → \*COOH), which improved the adsorption of the essential intermediate \*CO on Pt single atoms and displayed a significantly reduced energy barrier for the protonation reaction of C1 intermediates, resulting in a mixed reaction pathway. This work provides new insights into a mechanism to regulate the reaction path to facilitate efficient photocatalytic CO<sub>2</sub> methanation.

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## 1. Introduction

Methane is the main component of natural gas and is widely used as a clean energy source or raw material for bulk production of chemicals.<sup>1</sup> In industry, CH<sub>4</sub> is synthesized using CO<sub>2</sub> and H<sub>2</sub> as raw materials *via* the Sabatier reaction,<sup>2</sup> but the carbon emission and energy consumption of the process need to be improved. With the increasing demand for natural gas in the coming decades,<sup>3</sup> CH<sub>4</sub> synthesis *via* a green and sustainable approach is highly promising, with photocatalysis emerging as a method to achieve CO<sub>2</sub> methanation from solar energy. However, owing to the high thermodynamical stability of CO<sub>2</sub>, it is challenging to achieve high methane yield *via* photocatalysis.<sup>4</sup> Moreover, the conversion from CO<sub>2</sub> to CH<sub>4</sub> is an eight-electron reduction

reaction that requires a high density of protons and electrons, resulting in relatively slow reaction kinetics.<sup>5</sup> In addition, the competing reaction for CO<sub>2</sub> reduction is the recombination of protons to form hydrogen. Therefore, photocatalysts that can accumulate photogenerated electrons and promote the migration of protons to carbon intermediates may enhance methane production.<sup>6</sup>

The substoichiometric tungsten oxides, such as WO<sub>2.72</sub>, W<sub>24</sub>O<sub>68</sub> and WO<sub>2.9</sub>, are stable in air,<sup>7</sup> and the light absorption of WO<sub>3-x</sub> can be extended to the near-infrared region owing to the defect states below the conduction band minimum (CBM).<sup>8,9</sup> The V<sub>O</sub> (oxygen vacancy) and unsaturated metal coordination sites pair can be used as Lewis acid sites to adsorb and activate CO<sub>2</sub> molecules by reducing the activation energy barrier of CO<sub>2</sub> molecules.<sup>10</sup> In addition, W(vi) sites in WO<sub>3-x</sub> can be used as electron reservoirs by reducing them to W(v).<sup>11</sup> The tungsten oxide with oxygen deficiency (V<sub>O</sub>) as substoichiometric tungsten oxides (WO<sub>3-x</sub>) are introduced to construct a heterojunction with TiO<sub>2</sub> to improve the charge transfer kinetics of titania and increase the electron density on the surface. Titania is the most investigated semiconductor in photocatalysis due to its high abundance, high chemical stability and resistivity, but it is limited by its overall low reaction rate. In this work, mesoporous TiO<sub>2</sub> microspheres were used as a support for substoichiometric

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tungsten oxide loading. The mesoporous structure and high surface area can provide abundant exposed active sites for surface reduction reactions and facilitate the construction of heterojunctions with intimate interfacial contact. The closely contacted anatase/rutile phase junctions, combined with highly crystalline anatase and rutile nanoparticles, may synergistically promote charge separation and transport.<sup>12,13</sup>

For methane production, noble metal cocatalysts can effectively enhance photocatalytic activity because of their electron transfer ability.<sup>14–16</sup> However, hydrogen evolution reaction, which is a competing reaction in CO<sub>2</sub> reduction, can also be accelerated by noble metals as well.<sup>17</sup> Previous studies have shown that the coordination environment,<sup>16,18</sup> size and distribution<sup>19</sup> of Pt can effectively inhibit hydrogen evolution. It was reported in the 1960s that hydrogen spillover from noble metals to the oxide support occurred at the interface between the metal and the support.<sup>20</sup> For example, it has recently been demonstrated that Pt nanoparticles (Pt NPs) dissociate H<sub>2</sub>O into adsorbed H atoms (\*H) and spillover from Pt NPs to the CO<sub>2</sub> adsorption sites on the support to produce methane.<sup>16</sup>

Moreover, the activation of CO<sub>2</sub> during photoreduction involves two different pathways: activation by electrons (CO<sub>2</sub> → ·CO<sub>2</sub><sup>-</sup>) and protonation (CO<sub>2</sub> → COOH<sup>+</sup>). Recently, experiments have demonstrated that CO<sub>2</sub> activation *via* protonation on semiconductor photocatalysts, forming an O=C=O-H<sup>+</sup> intermediate,<sup>21</sup> can significantly decrease the reaction energy barrier when such an intermediate undergoes further multiple proton-electron coupling reactions. Therefore, it is essential to design photocatalysts that favor the protonation of CO<sub>2</sub>. In this work, substoichiometric WO<sub>2.9</sub> was fabricated on TiO<sub>2</sub> microspheres for photocatalytic CO<sub>2</sub> methanation, where the deposition of Pt cocatalysts and substoichiometric WO<sub>2.9</sub> with good distribution can be expected to control the hydrogen spillover and improve the methane production rate (Scheme 1).

## 2. Experimental

### 2.1 Chemicals and materials

Pluronic F127 ((H(OC<sub>2</sub>H<sub>4</sub>)<sub>x</sub>(OC<sub>3</sub>H<sub>7</sub>)<sub>y</sub>(O<sub>2</sub>H<sub>4</sub>)<sub>z</sub>OH), M<sub>w</sub> = 15 000 g mol<sup>-1</sup>), H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, WCl<sub>6</sub> (99.9%), tetrahydrofuran (THF,

99.9%), sodium bicarbonate (99%) and tetrabutyltitanate (TBOT, 99%) were purchased from Adamas. Acetic acid (AcOH, 99%), absolute ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH, 99.8%), and hydrochloric acid (HCl, 37 wt%) were purchased from Chron in Chengdu. Ultrapure water (resistivity: 17.38 MΩ cm) was used in the synthetic process. All reagents were used as received without further purification.

### 2.2 Synthesis of the catalysts

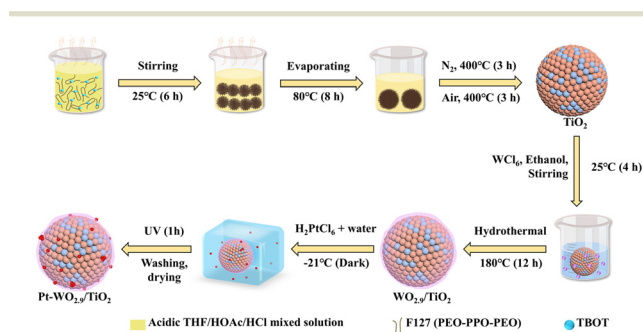
**Synthesis of TiO<sub>2</sub> microspheres.** In a typical procedure, 1 mL of HOAc and HCl (37 wt%) was dropped in 15 mL of THF. 0.75 g F127 yellow powder was slowly introduced into the above solution. The mixture was vigorously stirred to form a clear and transparent solution. Subsequently, 1.7 mL of TBOT was dropped under vigorous stirring to form a clear yellow solution. The yellow solution was then left in a drying oven to evaporate the THF solvents at 40 °C for 20 h and at 80 °C for another 10 h. The obtained precipitate was calcined in a tubular furnace under N<sub>2</sub> flow at 400 °C for 3 h. Finally, the white powder was obtained by calcination in a muffle furnace at 400 °C for 3 h.

**Synthesis of WO<sub>2.9</sub>/TiO<sub>2</sub> microspheres.** In the N<sub>2</sub> atmosphere, 17.1 mg WCl<sub>6</sub> and 100 mg TiO<sub>2</sub> microspheres were dispersed and dissolved in 40 mL of anhydrous ethanol, and the mixture was continuously stirred for 3 hours in an ice-water bath. After that, it was poured into a 50 mL hydrothermal kettle and kept in an oven at 180 °C for 12 hours. After natural cooling to room temperature, the samples were washed three times with deionized water, dried in a vacuum oven at 60 °C, and calcined at 400 °C in a 5% Ar/H<sub>2</sub> atmosphere for 2 hours.

**Synthesis of Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> microspheres.** 100 mg WO<sub>2.9</sub>/TiO<sub>2</sub> microspheres were dispersed in 20 mL DI water, 1 mg chloroplatinic acid was added and sonicated in N<sub>2</sub> atmosphere and ice water bath for 40 minutes. After freezing in the refrigerator (-20 °C) for 16 hours, keep it frozen and irradiate it with 275 nm ultraviolet light for 1 h in an ice/water bath. After the natural melting of the ice and the temperature reaching room temperature, the powders were centrifuged, washed three times with DI water and dried overnight at 80 °C in a vacuum oven.

### 2.3 Material characterization

The morphology of all samples was observed on a field emission scanning electron microscope (FESEM) (JEOL, JSM-7500, Japan). Transmission electron microscope (TEM) images were acquired with a Japan JEOL-F200 at an acceleration voltage of 200 kV. Samples were dispersed in ethanol, and 10 μL suspension was dropped on an ultra-thin carbon film supported by a 300-mesh copper TEM grid and dried for 1 h under an IR light. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku MiniFlex600 instrument equipped with a Cu Kα radiation (λ = 0.154178 nm) in the 2θ range of 10–80° with a step size of 0.01°. The lattice spacing d was calculated using Bragg's law: 2d sin θ =



**Scheme 1** Schematic of the synthesis of TiO<sub>2</sub> microspheres, WO<sub>2.9</sub>/TiO<sub>2</sub>, and Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> photocatalyst.

$n\lambda$ . The Rietveld refinement line of TiO<sub>2</sub> was obtained using Maud software, in which the crystal structure models of anatase (9008213.cif) and rutile (9004141.cif) were introduced, respectively, and background and scale parameters, basic phase parameters, microstructure parameters, crystal structure parameters and all parameters for texture were adjusted in turn to calculate the ratio of rutile and anatase in TiO<sub>2</sub> microspheres. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha instrument with a monochromatic Al K $\alpha$  X-ray source (12 kV, 6 mA). The vacuum in the analysis room is  $5.0 \times 10^{-7}$  mbar. The binding energies of all the spectra were calibrated to the binding energy of C 1s at 284.6 eV.

## 2.4 Photocatalytic reduction of CO<sub>2</sub>

The photocatalytic CO<sub>2</sub> reduction experiments were performed using a solid-vapor reaction in a Pyrex glass batch reactor with a window on top for light illumination (Labsolar 6A, Beijing Perfect light, China). The reaction temperature was controlled at approx. 10 °C by circulating cooling reagents at 5 °C. A 300 W Xe-lamp equipped with an AM 1.5 filter was placed on top and the optical power density was 100 mW cm<sup>-2</sup>. 20 mg sample was dispersed in 1 mL of DI water and dipped on a porous ceramic substrate (Beijing Perfect Light Technology Co., Ltd) with a 30 mm diameter, then dried at 80 °C for 30 minutes. After drying, the substrate loaded with the catalyst was placed on the quartz support in the center of the reactor, 10 cm above the bottom of the reactor. The reactor was filled with 50 mL DI water at the bottom. After the reactor was sealed, it was continuously vacuum-treated for 10 minutes and purged three times with high-purity CO<sub>2</sub> (99.999%) gas, where CO<sub>2</sub> gas was bubbled through the water at the bottom of the reactor and continuously flowed until the pressure inside the reactor reached ~50 KPa. During irradiation, the products in the gas phase at different reaction times were analyzed by an online gas chromatograph (GC2030, SHIMADZU, Japan) with a barrier discharge ionization detector (BID) using high-purity helium (99.999%) as the carrier gas and Carboxen@1010 PLOT (30 m  $\times$  0.53 mm) as a chromatographic column. In blank experiments, in which there was no light source or photocatalyst, high-purity N<sub>2</sub> was used instead of CO<sub>2</sub>.

The selectivity of CO<sub>2</sub> reduction ( $S_{\text{CO}_2}$ ) and CH<sub>4</sub> ( $S_{\text{CH}_4}$ ) are calculated using the following equations:

$$S_{\text{CO}_2} = \frac{8 \times \text{Yield}(\text{CH}_4) + 2 \times \text{Yield}(\text{CO})}{8 \times \text{Yield}(\text{CH}_4) + 2 \times \text{Yield}(\text{CO}) + 2 \times \text{Yield}(\text{H}_2)}$$

$$S_{\text{CH}_4} = \frac{8 \times \text{Yield}(\text{CH}_4)}{8 \times \text{Yield}(\text{CH}_4) + 2 \times \text{Yield}(\text{CO})}$$

## 2.5 Photoelectrochemical measurements

The photoelectrochemical measurements of TiO<sub>2</sub>, Pt-TiO<sub>2</sub>, WO<sub>2.9</sub>/TiO<sub>2</sub>, and Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> were performed in a three-electrode quartz electrolytic cell using an electrochemical

workstation (Autolab PGSTAT 204A Instruments by Metrohm, Utrecht, Netherlands). The counter electrode was Ag/AgCl and the reference electrode was a platinum sheet (1  $\times$  1 cm). The working electrode was prepared by the spin-coating method. 5 mg of the samples and 20  $\mu$ L Nafion solution were placed into 0.5 mL of ethanol and sonicated for 1 h to obtain a uniform suspension, which was then uniformly coated on the glassy carbon electrode and dried in a vacuum oven at 80 °C. 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution was used as the electrolyte.

The transient photocurrent spectra were tested at a bias of 0.5 V with an on/off period of 40 s for each transient. The EIS measurements were carried out in the frequency range of 0.01–10<sup>5</sup> Hz at a bias of 0.5 V<sub>OCP</sub>. Mott-Schottky (M-S) curves were obtained at frequencies of 600 Hz, 800 Hz, 1000 Hz and 1200 Hz in the potential range of -1.5–1.2 V.

## 2.6 DRIFTS measurements

DRIFTS measurements were conducted using a Thermo Scientific Nicolet FTIR spectrometer equipped with a liquid nitrogen-cooled HgCdTe (MCT) detector. The spectra were obtained by applying an average of 128 scans with a spectral resolution of 2 cm<sup>-1</sup>. The final spectra were obtained after removing the background spectra.

**DRIFTS for CO Adsorption.** The chamber was purged with Ar (99.999%) at room temperature (RT) for 30 min to eliminate air after loading the samples and then the background spectrum was recorded. Subsequently, 8% CO in Ar was purged until the adsorption equilibrium was reached. The CO was then stopped by purging Ar into the chamber to remove the CO in the gas phase.

**DRIFTS for *in situ* CO<sub>2</sub> reaction.** The reaction chamber was purged with N<sub>2</sub> (99.999%) at 100 °C for 30 min to remove moisture and air from the sample and then cooled to RT. After recording the background spectrum in N<sub>2</sub>, CO<sub>2</sub> (99.999%) and H<sub>2</sub>O vapor *via* bubbling of CO<sub>2</sub> gas through water were introduced into the reaction chamber until adsorption equilibrium was reached. The chamber was then sealed and the spectra were recorded at certain time intervals under the illumination of a 300 W Xe lamp with an AM 1.5 filter.

## 2.7 DFT calculations

All the DFT calculations were performed using the Vienna *ab initio* simulation package (VASP)<sup>22</sup> with the projector augmented wave (PAW) method.<sup>23</sup> The exchange-functional is treated using the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE)<sup>24</sup> functional. The energy cutoff for the plane-wave basis expansion was set to 450 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method with a width of 0.2 eV. The WO<sub>2.9</sub> (010) and anatase TiO<sub>2</sub> (101) surfaces were constructed, where the Pt cluster with 10 Pt atoms was established loading on the surface. In addition, single atom Pt was constructed by replacing the W and Ti atoms on WO<sub>2.9</sub> (010) and anatase TiO<sub>2</sub> (101) surfaces, respectively. The

$k$ -point of  $2 \times 1 \times 1$  and  $1 \times 1 \times 1$  was used for the calculations on  $\text{WO}_{2.9}$  (010) and anatase  $\text{TiO}_2$  (101) surfaces, respectively. The self-consistent calculations applied a convergence energy threshold of  $10^{-5}$  eV, and the force convergence was set to  $0.05 \text{ eV } \text{\AA}^{-1}$ .

The free energy corrections were calculated at 298 K using the following equation:

$$\Delta G = \Delta E + \Delta G_{\text{ZPE}} + \Delta G_{\text{U}} - T\Delta S$$

where  $\Delta E$ ,  $\Delta G_{\text{ZPE}}$ ,  $\Delta G_{\text{U}}$ , and  $\Delta S$  refer to the DFT-calculated energy change, the correction from zero-point energy, the correction from inner energy and the correction from entropy.<sup>25</sup>

### 3. Results and discussion

#### 3.1 Morphology and structure analysis

In brief,  $\text{TiO}_2$  microspheres were synthesized *via* solvent evaporation-driven oriented assembly using tetrabutyltitanate precursors.<sup>12</sup> A typical scanning electron microscopy (SEM) image of  $\text{TiO}_2$  (Fig. 1a) exhibits a regular spheric shape with a diameter of  $1.57 \pm 0.10 \mu\text{m}$ , consisting of anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276), with an  $R$  ( $R = I_{\text{A}}/I_{\text{R}}$ ) of 23.6%, as determined by Rietveld refinement ((Fig. 1b, Table S1 and Fig. S1†). The homojunction between anatase and rutile in the microspheres allows for improved charge-carrier separation efficiency, higher reduction potential of electrons ( $E_{\text{CB}}$  of rutile  $\leq 0.6$  eV) and light absorption ability ( $E_{\text{g}}$  of rutile:  $\sim 3.0$  eV).<sup>26</sup>

A substoichiometric tungsten oxide film was loaded onto  $\text{TiO}_2$  microspheres *via* a hydrothermal method using tungsten hexachloride ( $\text{WCl}_6$ ) as a metal precursor in deoxygenated anhydrous ethanol. The morphology of

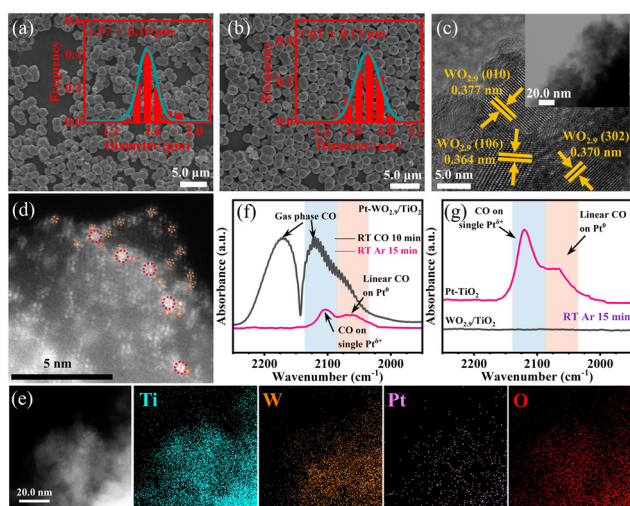
tungsten oxide depends on the concentration of  $\text{WCl}_6$  in solution, but with  $\text{TiO}_2$  microspheres as support, the morphology of tungsten oxide is directed by the support, where  $\text{W}^{6+}$  ions adsorb on the oxide sites, form nuclei and grow as a film (Fig. S2†).

The XRD spectrum (Fig. S1b†) for  $\text{WO}_{2.9}/\text{TiO}_2$  shows no corresponding diffraction peaks for  $\text{WO}_{2.9}$ , which may be attributed to the high dispersion of  $\text{WO}_{2.9}$  on the surface of  $\text{TiO}_2$  microspheres. For reference, pure tungsten oxide in a dark blue color was synthesized using the same hydrothermal method. The XRD spectrum of the tungsten oxide (Fig. S3†) shows obvious diffraction peaks at  $23.6^\circ$  and  $48.3^\circ$ , which can be ascribed to the (010) and (020) facets in the  $\text{WO}_{2.9}$  phase (JCPDS 05-0386). The Raman spectroscopy (Fig. S4†) revealed characteristic Raman active modes with symmetries  $E_{\text{g}}$  at  $443 \text{ cm}^{-1}$  and  $A_{1\text{g}}$  at  $609 \text{ cm}^{-1}$  for rutile  $\text{TiO}_2$ , and  $E_{\text{g}}$  at  $144 \text{ cm}^{-1}$  for anatase. The broad peak at about  $230 \text{ cm}^{-1}$  is aroused from the multiple phonons scattering. The attenuation of the peak at  $144 \text{ cm}^{-1}$  may be due to the change in the anatase phase in the  $\text{TiO}_2$  microspheres. The coating amount of  $\text{WO}_{2.9}$  was optimized based on the catalytic performance to be 10 wt% (Fig. S5a†).

The deposition of Pt was performed using photochemistry under restricted conditions.<sup>27</sup> The ice lattice naturally confines the dispersion of precursors, nucleus formation and crystal size. The density, size, dispersion and allocation of Pt atoms can be fine-regulated by the density of photoelectrons,<sup>28</sup> and the Pt precursor concentration. In this work, Pt cocatalysts were deposited as single atoms and nanoclusters on  $\text{WO}_{2.9}$  film, reduced by photogenerated electrons under irradiation of ultraviolet light at  $\lambda = 275 \text{ nm}$ . For reference, Pt cocatalysts were deposited on  $\text{TiO}_2$  microspheres *via* the same photochemistry method and annotated as Pt- $\text{TiO}_2$ . The amount of the Pt precursor was optimized based on the catalytic performance to be 1 wt% (Fig. S5b†).

The diameter of  $\text{TiO}_2$  microspheres in Pt- $\text{WO}_{2.9}/\text{TiO}_2$  is  $1.61 \pm 0.11 \mu\text{m}$ , where the increase of 40 nm was attributed to the coating of  $\text{WO}_{2.9}$  film (Fig. 1b). The lattice fringes at the edge of the microsphere were analyzed to be 0.377 nm, 0.370 nm and 0.364 nm from the HRTEM image (Fig. 1c and S6a†), corresponding to the (010), (302) and (106) crystal planes of  $\text{WO}_{2.9}$ , respectively.

The atomic dispersion of Pt was analyzed using aberration-corrected high-angle annular dark-field scanning TEM (AC HAADF-STEM) imaging (Fig. 1d and S6b†), which clearly resolves isolated Pt single atoms (marked by orange circles) and uniformly dispersed Pt clusters (marked by red circles) composed of several Pt atoms on  $\text{WO}_{2.9}$ , with no evidence of Pt nanoparticles exceeding 1 nm in size. The compositions of the elements were analyzed with a uniform distribution of Pt and W ((Fig. 1e). To further clarify the distribution of Pt, CO-adsorption diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) measurements for Pt- $\text{WO}_{2.9}/\text{TiO}_2$  are performed (Fig. 1f). First CO coverage saturation is reached with two strong IR peaks for gas phase



**Fig. 1** SEM image and statistical analysis on particle size of (a)  $\text{TiO}_2$  microspheres and (b) Pt- $\text{WO}_{2.9}/\text{TiO}_2$ ; (c) HRTEM image (inset: TEM image); (d) AC-HAADF-STEM image and (e) EDS elemental mapping of Pt- $\text{WO}_{2.9}/\text{TiO}_2$ ; CO-DRIFTS for (f) Pt- $\text{WO}_{2.9}/\text{TiO}_2$  and (g) Pt- $\text{TiO}_2$ ,  $\text{WO}_{2.9}/\text{TiO}_2$ .

CO. Then, gas phase CO and physically adsorbed CO were removed, which leaves chemical adsorption of CO with two sets of absorption bands centered at  $2103\text{ cm}^{-1}$  and a broad peak at  $2070\text{ cm}^{-1}$ . The former is ascribed to linearly adsorbed CO on single-atom  $\text{Pt}^{\delta+}$ ,<sup>29</sup> and the latter is assigned to linearly adsorbed CO on  $\text{Pt}^0$  in Pt particles.<sup>30</sup>

The CO-DRIFTS spectrum of  $\text{WO}_{2.9}/\text{TiO}_2$  exhibits no clear bands for adsorbed CO (Fig. 1g), indicating that the CO adsorption bands observed for Pt- $\text{WO}_{2.9}/\text{TiO}_2$  originate from the CO adsorbed on the Pt species. For Pt- $\text{TiO}_2$ , two sets of CO absorption bands are observed, with one centered at  $2119\text{ cm}^{-1}$  and another broad band centered at  $2070\text{ cm}^{-1}$ , where the former peak at  $2119\text{ cm}^{-1}$  is attributed to CO adsorption on single  $\text{Pt}^{\delta+}$  atoms. Compared with CO on Pt- $\text{WO}_{2.9}/\text{TiO}_2$  ( $2103\text{ cm}^{-1}$ ), there is a blue shift in the CO adsorption peak on single  $\text{Pt}^{\delta+}$  sites, indicating that the back donation from  $\text{WO}_{2.9}$  to  $\text{Pt}^{\delta+}$  is stronger than that from  $\text{TiO}_2$ . To evaluate the stability of Pt on  $\text{TiO}_2$  and  $\text{WO}_{2.9}/\text{TiO}_2$ , the photocatalysts were pretreated in  $\text{Ar}/\text{H}_2$  at  $100\text{ }^\circ\text{C}$  and CO-DRIFTS spectra were collected after the treatment (Fig. S7†).

X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical species of the photocatalysts. The XPS survey spectra of  $\text{TiO}_2$ , Pt- $\text{TiO}_2$ ,  $\text{WO}_{2.9}/\text{TiO}_2$  and Pt- $\text{WO}_{2.9}/\text{TiO}_2$  demonstrate that no impurity elements were present in the as-synthesized samples, except for Pt, W, O, Ti and C (Fig. S8†). The XPS Ti 2p spectrum of  $\text{TiO}_2$  shows four symmetric peaks after deconvolution of the spectrum, with a pair of binding energy at  $458.4\text{ eV}$  and  $464.1\text{ eV}$  for Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  of  $\text{Ti}^{4+}$ , and another pair at  $456.9\text{ eV}$  and  $462.6\text{ eV}$  representing Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$  for  $\text{Ti}^{3+}$ , with an area ratio of 36.5% for  $\text{Ti}^{3+}$  (Fig. 2a).

With the coating of  $\text{WO}_{2.9}$ , for the Ti 2p spectra of  $\text{WO}_{2.9}/\text{TiO}_2$  and Pt- $\text{WO}_{2.9}/\text{TiO}_2$ , a doublet peak at  $458.4\text{ eV}$  for Ti  $2p_{3/2}$  and  $464.1\text{ eV}$  for Ti  $2p_{1/2}$  of  $\text{Ti}^{4+}$  can be detected, where the shoulder peak of  $\text{Ti}^{3+}$  vanishes, which may be attributed

to the oxidation during hydrothermal reaction in solution. During the formation of  $\text{WO}_{2.9}$ , electrons are preferentially extracted from  $\text{Ti}^{3+}$ -associated oxygen vacancies in  $\text{TiO}_2$ , thereby oxidizing  $\text{Ti}^{3+}$  to  $\text{Ti}^{4+}$ .

For Pt- $\text{TiO}_2$ , the shoulder peak for  $\text{Ti}^{3+}$  vanished, possibly because of Pt deposition on the vacancy sites. However, the binding energy of  $\text{Ti}^{4+}$  shifts to lower energy ( $\sim 0.30\text{ eV}$ ), suggesting either the defects partially exist, or the electrons transfer from Pt to  $\text{TiO}_2$  at the interface, which may induce upward surface band bending of  $\text{TiO}_2$ .

In the W 4f XPS spectrum of  $\text{WO}_{2.9}/\text{TiO}_2$ , two doublets can be deconvoluted-peaks with a binding energy of  $35.2\text{ eV}$  and  $37.3\text{ eV}$  attributed to  $\text{W}^{6+}$ , and another doublet at  $33.9\text{ eV}$  and  $36.0\text{ eV}$  attributed to  $\text{W}^{5+}$  (Fig. 2b). With Pt deposition, the peak of  $\text{W}^{6+}$  for Pt- $\text{WO}_{2.9}/\text{TiO}_2$  shifts to higher binding energy ( $\sim 0.13\text{ eV}$ ), indicating a decrease in the electron density of the W species, probably due to the transfer to the Pt sites. The shoulder peak for  $\text{W}^{5+}$  exists after the photodeposition of Pt, with an area ratio of 13.7%, which is close to the ratio for  $\text{W}^{5+}$  in  $\text{WO}_{2.9}/\text{TiO}_2$  (13.0%) (Table S2†). Compared with the change in Ti 2p for Pt- $\text{TiO}_2$  after deposition of Pt, the defect sites in  $\text{WO}_{2.9}$  remain for Pt- $\text{WO}_{2.9}/\text{TiO}_2$ , suggesting a stable structure of substoichiometric  $\text{WO}_{2.9}$ .

The Pt 4d<sub>5/2</sub> spectrum of Pt- $\text{WO}_{2.9}/\text{TiO}_2$  was resolved into three components,  $\text{Pt}^{4+}$  at  $316.8\text{ eV}$ ,  $\text{Pt}^{2+}$  at  $314.4\text{ eV}$ , and  $\text{Pt}^0$  at  $311.6\text{ eV}$  (Fig. 2c). Compared with the Pt 4d<sub>5/2</sub> spectrum for Pt- $\text{TiO}_2$ , the binding energies of  $\text{Pt}^{2+}$  show a shift to lower binding energy ( $\sim 0.20\text{ eV}$ ,  $314.6\text{ eV}$ ), indicating an overall increase in the electron density of Pt on Pt- $\text{WO}_{2.9}/\text{TiO}_2$ . For both samples, the  $\text{Pt}^{2+}$  species is dominant ( $\sim 55\%$ ), but the concentration of  $\text{Pt}^0$  species in Pt- $\text{TiO}_2$  (22.6%) is higher than that in Pt- $\text{WO}_{2.9}/\text{TiO}_2$  (15.7%) (Table S2†).

The O 1s XPS spectrum (Fig. 2d) of  $\text{TiO}_2$  shows three components at  $527.8\text{ eV}$ ,  $529.6\text{ eV}$ , and  $531.7\text{ eV}$ , possibly corresponding to electron-rich oxygen ( $\text{O}_R < 529.0\text{ eV}$ ), lattice O ( $\text{O}_L$ , Ti-O), and hydroxyl O ( $\text{O}_C$ , -OH), respectively.<sup>31</sup> With the coating of  $\text{WO}_{2.9}$ , for the O 1s spectra of  $\text{WO}_{2.9}/\text{TiO}_2$  and Pt- $\text{WO}_{2.9}/\text{TiO}_2$ , the peak related to electron-rich oxygen disappeared, which may be attributed to the oxidation during the hydrothermal reaction in solution. An additional peak at  $\sim 531.2\text{ eV}$  appears, which is characteristic of the oxygen-deficient tungsten oxide ( $\text{O}_V$ ). Compared with the O 1s spectra for  $\text{TiO}_2$  and  $\text{WO}_{2.9}/\text{TiO}_2$ , the O 1s spectra for Pt- $\text{TiO}_2$  and Pt- $\text{WO}_{2.9}/\text{TiO}_2$  show a shift to lower binding energy, which may be due to photoreduction and the interaction between the surface and deposited Pt.

The Mott-Schottky spectra show that the flat band ( $E_{fb}$ ) potential of  $\text{TiO}_2$  and  $\text{WO}_{2.9}$  is  $-0.85$  and  $0.10\text{ V}$  vs.  $\text{Ag}/\text{AgCl}$  (about  $-0.65$  and  $0.30\text{ V}$  vs. NHE,  $E_{\text{NHE}}(\text{V}) = E_{\text{Ag}/\text{AgCl}} + 0.197$ ), respectively. (Fig. 3a) Furthermore, for n-type semiconductors, the conduction band minimum (CBM) is typically  $\sim 0.2\text{ V}$  more negative than the flat-band potential. Consequently, the CBM positions of  $\text{TiO}_2$  and  $\text{WO}_{2.9}$  were measured to be  $-0.85\text{ V}$  and  $0.10\text{ V}$  (vs. NHE), respectively. The optical band gap was obtained from Tauc plots according to the following equation:

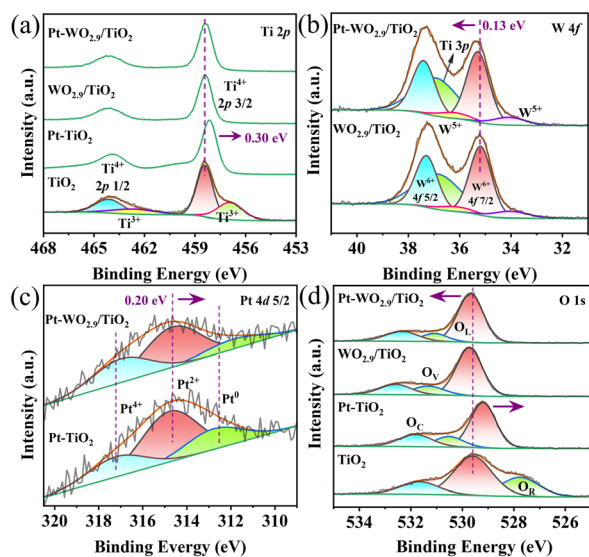


Fig. 2 High-resolution XPS spectra of (a) Ti 2p; (b) W 4f; (c) Pt 4d<sub>5/2</sub>; and (d) O 1s.

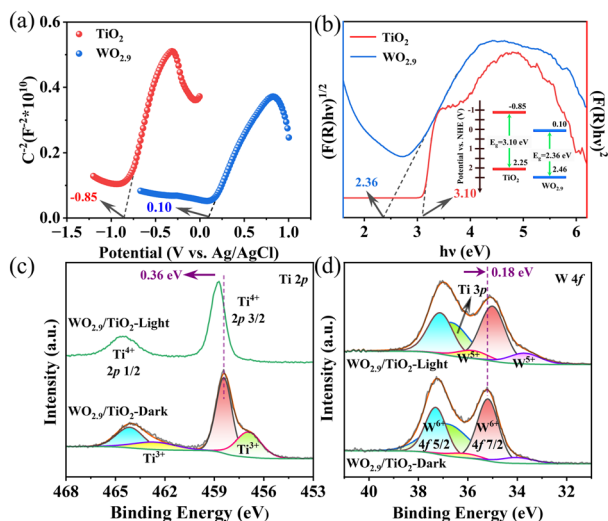


Fig. 3 (a) Mott-Schottky spectra and (b) Tauc plots of  $\text{TiO}_2$  and  $\text{WO}_{2.9}$ . inset: proposed band structures of  $\text{TiO}_2$  and  $\text{WO}_{2.9}$ . High-resolution XPS spectra of (c) Ti 2p, and (d) W 4f of  $\text{WO}_{2.9}/\text{TiO}_2$  before and after light irradiation.

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where  $\alpha$  is the absorption coefficient,  $h$  is Planck's constant and  $n$  is the vibration frequency ( $n = 2$  for  $\text{TiO}_2$ ,  $n = 1/2$  for  $\text{WO}_{2.9}$ ). The band gap ( $E_g$ ) of  $\text{TiO}_2$  and  $\text{WO}_{2.9}$  was thus calculated to be 3.10 and 2.36 eV (ref. 32 and 33) (Fig. 3b), respectively. The band structures of  $\text{TiO}_2$  and  $\text{WO}_{2.9}$  are thus proposed to be a type II heterojunction.

*In situ* XPS Ti 2p and W 4f spectra under illumination (Fig. 3c and d) demonstrate that the Ti 2p peaks shifted +0.36 eV to higher binding energy, and the W 4f peaks shifted -0.18 eV, accompanied by an increase in  $\text{W}^{5+}$  content (13.7 → 24.0%). These observations confirm the directional electron transfer from  $\text{TiO}_2$  to  $\text{WO}_{2.9}$ , consistent with a type II heterojunction mechanism.

### 3.2 Photocatalytic $\text{CO}_2$ reduction and photoelectrochemical performance

The above XPS analysis demonstrates the electronic interactions between  $\text{WO}_{2.9}$  and Pt, and between  $\text{WO}_{2.9}$  and  $\text{TiO}_2$ , which may contribute to the photocatalytic methane production. The photocatalytic  $\text{CO}_2$  reduction performance of the Pt- $\text{WO}_{2.9}/\text{TiO}_2$  composites was evaluated and measured, leading to the production of  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{H}_2$  in the gas phase. Each experiment was repeated three times for the reference samples as  $\text{TiO}_2$ , Pt- $\text{TiO}_2$ , and  $\text{WO}_{2.9}/\text{TiO}_2$ , to ensure reproducibility. The comparison of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  yield over reaction time under illumination is shown in Fig. S10†

For  $\text{TiO}_2$ , the yield of  $\text{CH}_4$  after 6 hours is  $1.61 \mu\text{mol g}^{-1}$  (Fig. 4a), which increased to  $3.68 \mu\text{mol g}^{-1}$  after coating with  $\text{WO}_{2.9}$  for  $\text{WO}_{2.9}/\text{TiO}_2$ . For Pt- $\text{WO}_{2.9}/\text{TiO}_2$ , the yield of  $\text{CH}_4$  reaches  $64.41 \mu\text{mol g}^{-1}$ , which is 17.5 times higher than that

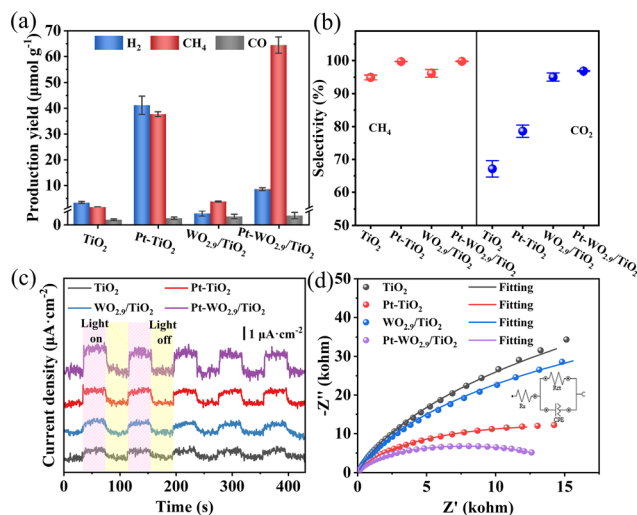


Fig. 4 Photocatalytic production yield (a) and selectivity (b) of  $\text{TiO}_2$ ,  $\text{WO}_{2.9}/\text{TiO}_2$ , Pt- $\text{WO}_{2.9}/\text{TiO}_2$  and Pt- $\text{TiO}_2$  in a 6 h reaction time. (c) Photocurrent transient spectra and (d) electrochemical impedance spectra (EIS) of  $\text{TiO}_2$ , Pt- $\text{TiO}_2$ ,  $\text{WO}_{2.9}/\text{TiO}_2$ , and Pt- $\text{WO}_{2.9}/\text{TiO}_2$ .

of  $\text{WO}_{2.9}/\text{TiO}_2$ . However, for Pt- $\text{TiO}_2$ , the  $\text{CH}_4$  yield is  $37.63 \mu\text{mol g}^{-1}$ , which is about half of that for Pt- $\text{WO}_{2.9}/\text{TiO}_2$ .

Compared with the methane production rate reported in the literature, the value reported in this work is among the top values (Table S4†). In the reference experiments, there was no detection of the gas product, e.g.  $\text{CH}_4$  or  $\text{CO}$ , in the experiments without  $\text{CO}_2$  (using substituted  $\text{N}_2$ ), without light irradiation, or as a photocatalyst (Fig. S11†).

In addition, the  $\text{H}_2$  yield is  $3.34 \mu\text{mol g}^{-1}$  for  $\text{TiO}_2$  and  $0.80 \mu\text{mol g}^{-1}$  for  $\text{WO}_{2.9}/\text{TiO}_2$ , suggesting that the  $\text{WO}_{2.9}/\text{TiO}_2$  heterojunction significantly improved the overall  $\text{CO}_2$  conversion rate and suppressed the competing reaction for hydrogen evolution. Moreover, the hydrogen yield is  $41.12 \mu\text{mol g}^{-1}$  for Pt- $\text{TiO}_2$ , which is 4.8 times higher than that for Pt- $\text{WO}_{2.9}/\text{TiO}_2$  ( $8.47 \mu\text{mol g}^{-1}$ ), indicating that the deposition of Pt promotes the hydrogen evolution reaction, but with  $\text{WO}_{2.9}$ , hydrogen evolution can be effectively inhibited.

The selectivity of  $\text{CO}_2$  reduction ( $S_{\text{CO}_2}$ ) and  $\text{CH}_4$  ( $S_{\text{CH}_4}$ ) are calculated based on the yield, where  $S_{\text{CO}_2}$  refers to the selectivity for electron consumption  $\text{CO}_2$  reduction (see Fig. S12†) in competition with hydrogen evolution, and  $S_{\text{CH}_4}$  refers to the methane selectivity among  $\text{CH}_4$  and  $\text{CO}$  (Fig. 4b). The  $S_{\text{CO}_2}$  is 67.1% for  $\text{TiO}_2$  microspheres, which increases significantly to 95.0% with the loading of  $\text{WO}_{2.9}$  and reaches a remarkably high value of 96.8% for Pt- $\text{WO}_{2.9}/\text{TiO}_2$ . However,  $S_{\text{CO}_2}$  for Pt- $\text{TiO}_2$  decreases to 78.6%, which suggests that the presence of  $\text{WO}_{2.9}$  facilitates the electron transfer to  $\text{CO}_2$  reduction reaction.

The stability of Pt- $\text{WO}_{2.9}/\text{TiO}_2$  was evaluated by performing six consecutive reaction cycles (6 hours for each). The average methane production rate in the fifth cycle was 73.3% of the first cycle (Fig. S13†), showing a slight decrease in the activity, which may stem from partial deactivation of the Pt active sites or surface contamination by intermediates.

To understand the impact of Pt sites on the CO<sub>2</sub> reduction reaction, Pt NP-WO<sub>2.9</sub>/TiO<sub>2</sub> was prepared by annealing Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> in N<sub>2</sub> to convert Pt to nanoparticles. The methane production rate of Pt NP-WO<sub>2.9</sub>/TiO<sub>2</sub> significantly decreased to 5.25 μmol g<sup>-1</sup> h<sup>-1</sup>, and the hydrogen production rate increased to 19.19 μmol g<sup>-1</sup> h<sup>-1</sup> (Fig. S14†), that gives a S<sub>CO<sub>2</sub></sub> of 52.4%. These results indicate that the competitive reaction of hydrogen evolution is favoured on Pt nanoparticles.

The S<sub>CH<sub>4</sub></sub> among CH<sub>4</sub> and CO for TiO<sub>2</sub> was 94.9%, that is like S<sub>CH<sub>4</sub></sub> for WO<sub>2.9</sub>/TiO<sub>2</sub> (96.2%). In the presence of Pt, the S<sub>CH<sub>4</sub></sub> is 99.8% for Pt-WO<sub>2.9</sub>/TiO<sub>2</sub>, 99.7% for Pt-TiO<sub>2</sub>, and 99.9% for Pt NP-WO<sub>2.9</sub>/TiO<sub>2</sub>, which suggests that Pt can significantly improve the methane selectivity, possibly contributing to the proton production and spillover during the reaction.

The photocurrent density of Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> (1.77 μA cm<sup>-2</sup>) is nearly 3 times as compared to TiO<sub>2</sub> (0.56 μA cm<sup>-2</sup>), demonstrating a significant improvement in the separation and transfer of photogenerated charge carriers (Fig. 4c). The electrochemical impedance spectroscopy (EIS) spectra show that the charge transfer resistance of Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> is 15.31 kΩ, which is lower than the R<sub>ct</sub> of Pt-TiO<sub>2</sub> (27.92 kΩ, Table S5†). The lower charge transfer resistance favoured the transport and separation of photogenerated electron-hole pairs (Fig. 4d). The coating of WO<sub>2.9</sub> on TiO<sub>2</sub> not only extends the absorption edge but improves the separation efficiency of photogenerated carriers.

After five cycles of experiments, the post-reaction photocatalyst was analysed. A slight decrease in photocurrent density (Fig. S15a†) and an increase in charge transfer resistance (Fig. S15b†) are in line with a decrease in photocatalytic activity, possibly due to partial deactivation of the Pt active sites.

### 3.3 CO<sub>2</sub> photoreduction mechanism

Except for the charge transfer kinetics, the surface reaction rate also determines the overall reaction rate. The reaction intermediates during the photocatalytic methane production were thus detected by *in situ* DRIFTS measurements (Fig. 5 and S16†). After the adsorption equilibrium of CO<sub>2</sub> and water vapor, the DRIFTS for Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> (Fig. 5a, bottom spectrum) show the peaks at 1273 cm<sup>-1</sup>, 1372 cm<sup>-1</sup>, 1424 cm<sup>-1</sup>, 1700 cm<sup>-1</sup>, that could be attributed to the features of the \*COOH intermediates, that is, OH deformation, C-O stretch, symmetric stretch and C=O stretch, respectively. The signals appeared at 1067 cm<sup>-1</sup>, 1464 cm<sup>-1</sup>, 1150 cm<sup>-1</sup> can be assigned to \*CHO, \*CH<sub>2</sub>O and \*OCH<sub>3</sub>, respectively. Furthermore, the \*CO absorption band at ~2077 cm<sup>-1</sup> can be detected, indicating abundant CO intermediates were generated on the surfaces after the adsorption of CO<sub>2</sub> and the \*CHO intermediate originated from \*CO. The bands at 2987 cm<sup>-1</sup> to 2898 cm<sup>-1</sup> can be attributed to the -CH<sub>3</sub>/-CH<sub>2</sub> stretch and the wide band at 1637 cm<sup>-1</sup> can also be observed, which is attributed to physically adsorbed H<sub>2</sub>O. The results suggest that the dissociation of CO<sub>2</sub>, H<sub>2</sub>O and proton reactions occur

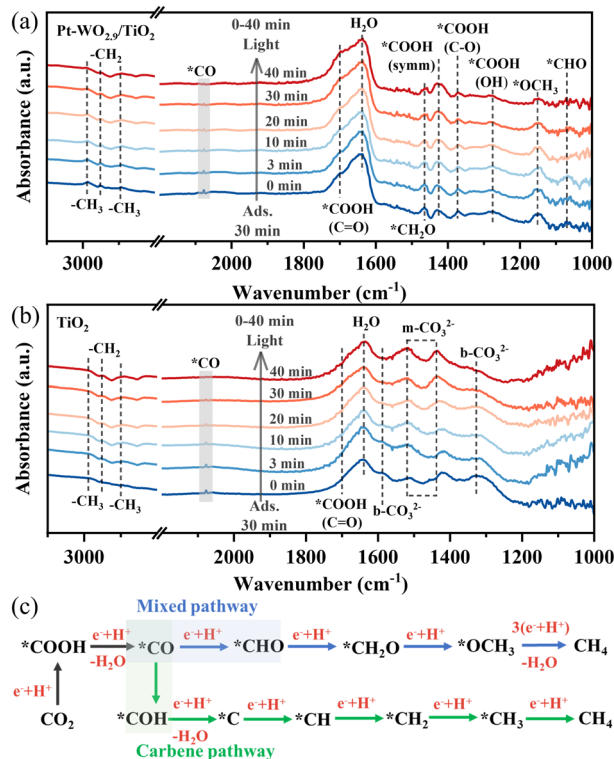


Fig. 5 *In situ* DRIFTS spectra recorded during the photocatalytic CO<sub>2</sub> reduction of (a) Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> and (b) TiO<sub>2</sub>. (c) Proposed pathways for CO<sub>2</sub> methanation.

on the surface after the adsorption of CO<sub>2</sub> and H<sub>2</sub>O in the dark.

After illumination of the Xe lamp with AM 1.5 filter, the DRIFTS feature for \*CO at ~2077 cm<sup>-1</sup> and the bands at 2987 to 2898 cm<sup>-1</sup> for -CH<sub>3</sub>/-CH<sub>2</sub> stretching almost vanishes, suggesting that the intermediates were consumed during the reaction. The intensity for the \*CHO at 1067 cm<sup>-1</sup>, \*OCH<sub>3</sub> at 1150 cm<sup>-1</sup> and \*CH<sub>2</sub>O at 1464 cm<sup>-1</sup> decrease during the 40 min illumination duration. However, the intensity of the signals for the \*COOH intermediate features increased over the illumination time, that is OH deformation at 1273 cm<sup>-1</sup>, symmetric stretch at 1424 cm<sup>-1</sup>, and C=O stretch at 1700 cm<sup>-1</sup>. Based on the above analysis, the pathway of CO<sub>2</sub> methanation on Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> photocatalyst is a mixed pathway (Fig. 5c).

For the DRIFTS of TiO<sub>2</sub> (Fig. 5b), after the adsorption of CO<sub>2</sub>, the peaks of monodentate carbonates at 1518 cm<sup>-1</sup> and 1437 cm<sup>-1</sup> (m-CO<sub>3</sub><sup>2-</sup>), bidentate carbonates at 1587 cm<sup>-1</sup>, and 1327 cm<sup>-1</sup> (b-CO<sub>3</sub><sup>2-</sup>) can be detected, as well as \*CO at 2077 cm<sup>-1</sup>, physically adsorbed H<sub>2</sub>O at 1638 cm<sup>-1</sup> and -CH<sub>3</sub>/-CH<sub>2</sub> at 2987 to 2898 cm<sup>-1</sup>. After illumination of AM1.5 for 40 min, the signal of the IR peaks related to b-CO<sub>3</sub><sup>2-</sup> and \*CO intermediates completely vanishes, but the intensity for the bands at 1518 and 1437 cm<sup>-1</sup> for m-CO<sub>3</sub><sup>2-</sup> increases over illumination time. Moreover, the intensity of the characteristic peak at 1700 cm<sup>-1</sup> of \*COOH (C=O) hardly changes with illumination. The above phenomena indicate

that light excitation enhances the adsorption and activation ability of  $\text{TiO}_2$  for  $\text{CO}_2$  gas ( $\text{CO}_2$  to adsorbed carbonate species), but the protonation process of the intermediates is limited, resulting in low catalytic efficiency. In addition,  $\text{CO}_2$  methanation on  $\text{TiO}_2$  occurs *via* the carbene pathway. The formation of the  $^*\text{CO}$  intermediate needs to overcome a high energy barrier to form the  $^*\text{C}$  intermediate, so  $\text{CH}_4$  production through the mixed pathway is favoured instead of the carbene pathway.<sup>34</sup> Hence, the  $\text{CH}_4$  yield and selectivity of  $\text{Pt-WO}_{2.9}/\text{TiO}_2$  are higher than those of  $\text{TiO}_2$ , consistent with the yield and reaction rate detected in the  $\text{CO}_2$  photoreduction experiments.

The DRIFTS spectra of  $\text{Pt-TiO}_2$  and  $\text{WO}_{2.9}/\text{TiO}_2$  were acquired as a reference (Fig. S16†). Compared to  $\text{TiO}_2$ , the peaks of  $\text{b-CO}_3^{2-}$  disappear and the intensity of peaks related to  $\text{m-CO}_3^{2-}$  significantly decreased in the DRIFTS spectra of  $\text{WO}_{2.9}/\text{TiO}_2$  acquired after adsorption and under illumination, and the intensity of the peak related to  $^*\text{COOH}$  (C=O) significantly increased with the extension of illumination time (Fig. S16a†). The  $^*\text{COOH}$  species is a key intermediate in the photoreduction of  $\text{CO}_2$  to  $\text{CO}$  or  $\text{CH}_4$ , and its formation and adsorption behavior significantly affect the yield and selectivity of the  $\text{CO}_2$  reduction reaction relative to the hydrogen evolution reaction.

For the DRIFTS of  $\text{Pt-TiO}_2$  in the dark and under illumination (Fig. S16b†), the intensity of the peaks related to  $^*\text{COOH}$  (C=O) also increased. The peak corresponding to  $^*\text{CH}_3\text{O}$  at  $1150\text{ cm}^{-1}$  appears after adsorption of  $\text{CO}_2$  and the intensity decreased over time under illumination, demonstrating that the Pt sites regulate the  $\text{CO}_2$  methanation pathway from carbene to mixed pathway.

Based on the above discussion and analysis, it is clear that the most significant adsorption peak of the  $^*\text{COOH}$  species appears for  $\text{Pt-WO}_{2.9}/\text{TiO}_2$ , but no observation of the adsorption peak corresponding to the carbonate species before and after illumination suggests that the synergy between  $\text{WO}_{2.9}$  and Pt sites can promote the conversion of  $\text{CO}_2$  into the  $^*\text{COOH}$  intermediate. The absence of carbonate intermediates indicates that the reaction followed a proton-induced pathway for  $\text{CO}_2$  reduction ( $\text{CO}_2 \rightarrow \text{COOH}^+ \rightarrow ^*\text{COOH}$ ).

In addition to the photoelectric performance and spectroscopic analysis, it can be determined that the formation of  $\text{WO}_{2.9}/\text{TiO}_2$  heterojunction and the loading of Pt sites on the  $\text{WO}_{2.9}$  film significantly improve the light absorption and achieve a higher separation efficiency of photogenerated carriers. Furthermore, the strong Lewis acidity of the  $\text{WO}_{2.9}$  film, the electron-rich nature of the Pt sites and the hydrogen spillover channel from Pt clusters (Pt NPs) to Pt single atoms ( $\text{Pt}_1$ ) optimize the adsorption and activation processes of  $\text{CO}_2$ , significantly promoting the generation of key intermediates for  $\text{CO}_2$  methanation, such as  $^*\text{COOH}$  and  $^*\text{OCH}_3$ . Consequently, the highest  $\text{CH}_4$  production and selectivity in  $\text{Pt-WO}_{2.9}/\text{TiO}_2$  are simultaneously achieved.

Hydrogen spillover occurs between noble metal particles and oxide supports (particularly reducible support), which

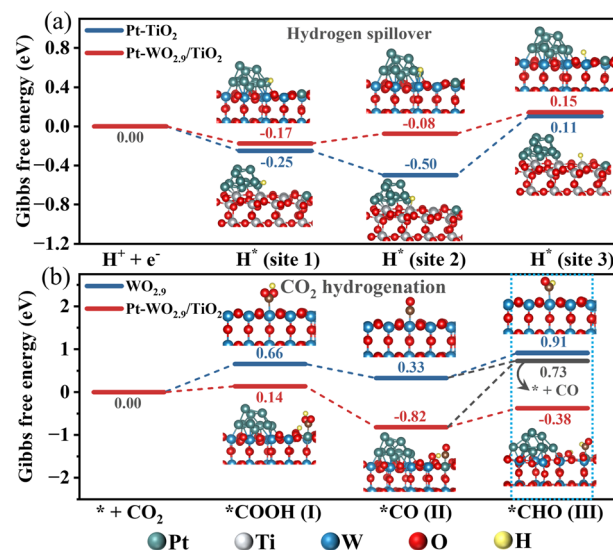


Fig. 6 Calculated free energy diagram for (a) hydrogen spillover on  $\text{Pt}/\text{WO}_{2.9}$  in comparison to  $\text{Pt}/\text{TiO}_2$  and (b)  $\text{CO}_2$  to  $^*\text{CHO}$  or  $\text{CO}$  on  $\text{Pt}_1/\text{WO}_{2.9}/\text{TiO}_2$  and on  $\text{WO}_{2.9}$ . The insets are stick-ball models, showing the stable adsorption configuration of intermediates on the active sites.

allows the migration of active hydrogen atoms from metal particles (where a hydrogen atom is generated) to the support.<sup>35,36</sup> In the hydrogen evolution reaction, the hydrogen spillover effect can significantly enhance reaction rates.<sup>37–39</sup> Therefore, the rational design of spillover pathways on the catalyst can effectively improve  $\text{CO}_2$  hydrogenation rates by suppressing competitive HER.<sup>16,40</sup>

To further evaluate the hydrogen spillover assisted by  $\text{WO}_{2.9}$ , density functional theory (DFT) calculations were performed using  $\text{Pt}/\text{TiO}_2$  and  $\text{Pt-WO}_{2.9}/\text{TiO}_2$ . Fig. 6a shows that on the  $\text{Pt-WO}_{2.9}$  surface,  $\text{H}^*$  preferentially adsorbs at the  $\text{Pt}/\text{WO}_{2.9}$  interface with  $\Delta G_{\text{H}}$  values of  $-0.17\text{ eV}$  (site 1) and  $-0.08\text{ eV}$  (site 2), where the negative values indicate spontaneous hydrogen adsorption. The  $\Delta G_{\text{H}}$  at the W top site (site 3, between Pt NPs and  $\text{Pt}_1$ ) was  $0.15\text{ eV}$ , resulting in a thermodynamic energy barrier from site 2 to site 3 of  $0.23\text{ eV}$ . On the surface of  $\text{Pt-TiO}_2$ , the values of  $\Delta G_{\text{H}}$  on site 1 and site 2 were  $-0.25\text{ eV}$  and  $-0.50\text{ eV}$ , respectively, indicating spontaneous hydrogen bonding at the interface between the Pt cluster and  $\text{TiO}_2$ . The  $\Delta G_{\text{H}}$  for  $\text{H}^*$  adsorption on the Ti top (site 3) was  $0.11\text{ eV}$ , leading to a considerably higher thermodynamic energy barrier ( $0.61\text{ eV}$ ) from site 2 to site 3, compared to the  $\text{Pt-WO}_{2.9}/\text{TiO}_2$ , which may hinder hydrogen spillover from site 2 to site 3 on the surface of  $\text{TiO}_2$ .

Based on the results of  $\text{CO}_2$  photoreduction experiments, the highest  $\text{H}_2$  production rate ( $19.19\text{ }\mu\text{mol g}^{-1}\text{ h}^{-1}$ ) is observed for Pt NPs on  $\text{WO}_{2.9}/\text{TiO}_2$  without  $\text{Pt}_1$ , suggesting that protons may accumulate on Pt NPs and recombine to form hydrogen gas, which is a competitive reaction process for methane production. With  $\text{Pt}_1$  and Pt clusters ( $\text{Pt-WO}_{2.9}/\text{TiO}_2$ ),  $\text{H}_2$  production rate decreased significantly ( $1.42\text{ }\mu\text{mol g}^{-1}\text{ h}^{-1}$ ), and the methane production rate greatly increased ( $10.74\text{ }\mu\text{mol g}^{-1}\text{ h}^{-1}$ ). In addition, for  $2\text{Pt-WO}_{2.9}/\text{TiO}_2$  (with nominal  $2.0\text{ wt}\%$  Pt precursor), the hydrogen evolution rate

was nearly two times higher than that of Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> (Fig. S5b†). Therefore, Pt SAs optimize CO<sub>2</sub> adsorption/activation, and Pt clusters enhance H<sub>2</sub>O dissociation, which synergistically determines the overall activity and selectivity for CO<sub>2</sub> methanation.

For the sample without WO<sub>2.9</sub> (Pt-TiO<sub>2</sub>), the methane production rate is 6.27 μmol g<sup>-1</sup> h<sup>-1</sup> and the H<sub>2</sub> production rate is 6.85 μmol g<sup>-1</sup> h<sup>-1</sup>, which may be due to the limited spillover of hydrogen. The experimental results and DFT calculations demonstrate that during the photocatalytic reduction reaction, protons at the Pt clusters transfer from the interface between the Pt clusters and the oxide support to the surface of the oxide, then desorb and participate in the reaction with CO<sub>2</sub> molecules on adjacent Pt<sub>1</sub>, where the spillover is favoured on the WO<sub>2.9</sub>, in comparison to TiO<sub>2</sub>. The synergistic effect of Pt clusters and Pt<sub>1</sub> and the promotion of WO<sub>2.9</sub> on hydrogen spillover led to high efficiency for CO<sub>2</sub> methanation and inhibited HER activity.

To further demonstrate the role of the synergistic Pt sites, calculations on the Gibbs free energy pathways of CO<sub>2</sub> reduction from adsorbed CO<sub>2</sub> to \*CHO or CO were performed using Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> and bare WO<sub>2.9</sub> (Fig. 6b). On the surface of bare WO<sub>2.9</sub>, ΔG<sub>H</sub> value of CO<sub>2</sub> to \*COOH was 0.66 eV, which decreased to 0.14 eV for Pt-WO<sub>2.9</sub>/TiO<sub>2</sub>. The lower energy barrier on the surface of Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> can be ascribed to the electronic structure of Pt<sub>1</sub> favouring the adsorption compared to that of W. Moreover, due to the hydrogen spillover to the O atom adjacent to Pt<sub>1</sub>, an OH bond forms near Pt<sub>1</sub>, which can significantly weaken the original Pt-O bond (Fig. S17†). Consequently, when a C<sub>1</sub> intermediate adsorbs and forms a chemical bond with Pt<sub>1</sub>, the Pt-O bond strengths further decrease and may break, leading to stable adsorption of the C<sub>1</sub> intermediate on the Pt<sub>1</sub> site (inset in Fig. 6b).

In addition, on Pt-WO<sub>2.9</sub>/TiO<sub>2</sub>, the energy barrier from \*CO to \*CHO was 0.44 eV, which was significantly lower than the energy barrier for \*CO desorption (1.55 eV). Therefore, \*CO tends to further protonation reaction rather than desorption of CO on Pt-WO<sub>2.9</sub>/TiO<sub>2</sub>. However, in WO<sub>2.9</sub>, the energy barrier from \*CO to desorbed CO molecules was 0.40 eV, which was lower than the energy barrier from \*CO to \*CHO (0.58 eV). Therefore, \*CO intermediates tend to desorb from the WO<sub>2.9</sub> surface to free CO molecules, which is in line with the experimental results, in which the CO production rate is higher for WO<sub>2.9</sub>/TiO<sub>2</sub> without Pt presence on the surface.

For Pt-WO<sub>2.9</sub>/TiO<sub>2</sub>, CH<sub>4</sub> selectivity reaches almost 100% with highest production rate under simulated solar light. Hydrogen spillover from Pt clusters to the vicinity of Pt<sub>1</sub> sites not only regulates the coordination environment of Pt<sub>1</sub> sites for CO<sub>2</sub> adsorption and activation but also provides protons for CO<sub>2</sub> methanation.

## 4. Conclusion

In this work, CO<sub>2</sub> molecules were converted to methane using a Pt-WO<sub>2.9</sub>/TiO<sub>2</sub> photocatalyst, achieving a high CH<sub>4</sub>

selectivity of 99.8% and an average CH<sub>4</sub> production rate of 10.74 μmol g<sup>-1</sup> h<sup>-1</sup> under simulated solar light. Dissociated water on the Pt clusters provides active H\* for CO<sub>2</sub> methanation through the hydrogen spillover channel, while the Pt single atoms act as the adsorption and activation sites for CO<sub>2</sub>. The strong Lewis acidity of WO<sub>2.9</sub> enhances hydrogen spillover, effectively inhibiting the competitive hydrogen evolution activity. Moreover, the hydrogen spillover influences the coordination of Pt<sub>1</sub> for the adsorption of C<sub>1</sub> intermediates and reduces the energy barrier for further protonation. The yield of CH<sub>4</sub> is thus enhanced by promoting the activation of CO<sub>2</sub> molecules and the CH<sub>4</sub> production pathways. Therefore, this work provides insights into the atomic design of cost-effective photocatalysts for CO<sub>2</sub> methanation.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 X. Meng, X. Cui, N. P. Rajan, L. Yu, D. Deng and X. Bao, *Chem*, 2019, **5**, 2296–2325.
- 2 M. Tommasi, S. N. Degerli, G. Ramis and I. Rossetti, *Chem. Eng. Res. Des.*, 2024, **201**, 457–482.
- 3 U. Ulmer, T. Dingle, P. N. Duchesne, R. H. Morris, A. Tavasoli, T. Wood and G. A. Ozin, *Nat. Commun.*, 2019, **10**, 3169.
- 4 T. Zhang, X. Han, N. T. Nguyen, L. Yang and X. Zhou, *Chin. J. Catal.*, 2022, **43**, 2500–2529.
- 5 X. Li, J. Yu, M. Jaroniec and X. Chen, *Chem. Rev.*, 2019, **119**, 3962–4179.
- 6 J. Fu, K. Jiang, X. Qiu, J. Yu and M. Liu, *Mater. Today*, 2020, **32**, 222–243.
- 7 T. Paik, M. Cargnello, T. R. Gordon, S. Zhang, H. Yun, J. D. Lee, H. Y. Woo, S. J. Oh, C. R. Kagan, P. Fornasiero and C. B. Murray, *ACS Energy Lett.*, 2018, **3**, 1904–1910.
- 8 K. Manthiram and A. P. Alivisatos, *J. Am. Chem. Soc.*, 2012, **134**, 3995–3998.

- 9 H. Khan, M. G. Rigamonti and D. C. Boffito, *Appl. Catal., B*, 2019, **252**, 77–85.
- 10 C. Lu, J. Li, J. Yan, B. Li, B. Huang and Z. Lou, *Appl. Mater. Today.*, 2020, **20**, 100744.
- 11 F. Riboni, L. G. Bettini, D. W. Bahnemann and E. Selli, *Catal. Today*, 2013, **209**, 28–34.
- 12 Y. Liu, R. Che, G. Chen, J. Fan, Z. Sun, Z. Wu, M. Wang, B. Li, J. Wei, Y. Wei, G. Wang, G. Guan, A. A. Elzatahry, A. A. Bagabas, A. M. Al-Enizi, Y. Deng, H. Peng and D. Zhao, *Sci. Adv.*, 2015, **1**, e1500166.
- 13 L. Yang, J. Du, J. Deng, N. H. M. Sulaiman, X. Feng, C. Liu and X. Zhou, *Small*, 2024, **20**, 2307007.
- 14 J. Ran, M. Jaroniec and S.-Z. Qiao, *Adv. Mater.*, 2018, **30**, 1704649.
- 15 C. Dong, C. Lian, S. Hu, Z. Deng, J. Gong, M. Li, H. Liu, M. Xing and J. Zhang, *Nat. Commun.*, 2018, **9**, 1252.
- 16 Y. Wang, J. Zhao, Y. Li and C. Wang, *Appl. Catal., B*, 2018, **226**, 544–553.
- 17 S. Xie, Y. Wang, Q. Zhang, W. Deng and Y. Wang, *ACS Catal.*, 2014, **4**, 3644–3653.
- 18 H. Wang, L. Zhang, Y. Zhou, S. Qiao, X. Liu and W. Wang, *Appl. Catal., B*, 2020, **263**, 118331.
- 19 X. Shi, Y. Huang, Y. Bo, D. Duan, Z. Wang, J. Cao, G. Zhu, W. Ho, L. Wang, T. Huang and Y. Xiong, *Angew. Chem., Int. Ed.*, 2022, **61**, e202203063.
- 20 L. Kuai, Z. Chen, S. Liu, E. Kan, N. Yu, Y. Ren, C. Fang, X. Li, Y. Li and B. Geng, *Nat. Commun.*, 2020, **11**, 48.
- 21 S. Yin, Y. Zhou, Z. Liu, H. Wang, X. Zhao, Z. Zhu, Y. Yan and P. Huo, *Nat. Commun.*, 2024, **15**, 437.
- 22 G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 23 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 24 J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671–6687.
- 25 C. Guo, X. Tian, X. Fu, G. Qin, J. Long, H. Li, H. Jing, Y. Zhou and J. Xiao, *ACS Catal.*, 2022, **12**, 6781–6793.
- 26 C. Gao, T. Wei, Y. Zhang, X. Song, Y. Huan, H. Liu, M. Zhao, J. Yu and X. Chen, *Adv. Mater.*, 2019, **31**, 1806596.
- 27 H. Wei, K. Huang, D. Wang, R. Zhang, B. Ge, J. Ma, B. Wen, S. Zhang, Q. Li, M. Lei, C. Zhang, J. Irawan, L.-M. Liu and H. Wu, *Nat. Commun.*, 2017, **8**, 1490.
- 28 A. Kubiak, *Sci. Rep.*, 2024, **14**, 13827.
- 29 W. Zhang, H. Wang, J. Jiang, Z. Sui, Y. Zhu, D. Chen and X. Zhou, *ACS Catal.*, 2020, **10**, 12932–12942.
- 30 K. Ding, A. Gulec, A. M. Johnson, N. M. Schweitzer, G. D. Stucky, L. D. Marks and P. C. Stair, *Science*, 2015, **350**, 189–192.
- 31 M. Kan, C. Yang, Q. Wang, Q. Zhang, Y. Yan, K. Liu, A. Guan and G. Zheng, *Adv. Energy Mater.*, 2022, **12**, 2201134.
- 32 L. Li, X. Dai, C. Cheng, F. Chen, S. M. Wabaidur, W. Wang and Y. Hu, *Chem. Eng. J.*, 2025, **507**, 160101.
- 33 L. Li, H. Liu, C. Cheng, X. Dai, F. Chen, J. Ning, W. Wang and Y. Hu, *ACS Catal.*, 2024, **14**, 10204–10213.
- 34 Ş. Neaţu, J. A. Maciá-Agulló, P. Concepción and H. Garcia, *J. Am. Chem. Soc.*, 2014, **136**, 15969–15976.
- 35 W. C. Conner, Jr. and J. L. Falconer, *Chem. Rev.*, 1995, **95**, 759–788.
- 36 M. D. Marcinkowski, A. D. Jewell, M. Stamatakis, M. B. Boucher, E. A. Lewis, C. J. Murphy, G. Kyriakou and E. C. H. Sykes, *Nat. Mater.*, 2013, **12**, 523–528.
- 37 Z. Gu, M. Li, C. Chen, X. Zhang, C. Luo, Y. Yin, R. Su, S. Zhang, Y. Shen, Y. Fu, W. Zhang and F. Huo, *Nat. Commun.*, 2023, **14**, 5836.
- 38 J. Li, J. Hu, M. Zhang, W. Gou, S. Zhang, Z. Chen, Y. Qu and Y. Ma, *Nat. Commun.*, 2021, **12**, 3502.
- 39 J. Li, H.-X. Liu, W. Gou, M. Zhang, Z. Xia, S. Zhang, C.-R. Chang, Y. Ma and Y. Qu, *Energy Environ. Sci.*, 2019, **12**, 2298–2304.
- 40 P. Liu, Z. Huang, X. Gao, X. Hong, J. Zhu, G. Wang, Y. Wu, J. Zeng and X. Zheng, *Adv. Mater.*, 2022, **34**, 2200057.