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## Pit-embellished low-valent metal active sites customize CO<sub>2</sub> photoreduction to methanol†

Wei Zhao,<sup>a</sup> Miao Ding,<sup>c</sup> Pengxin Yang,<sup>a</sup> Qiang Wang,<sup>a</sup> Kaifu Zhang,<sup>\*a</sup>  
 Xiaowen Zhan,<sup>id e</sup> Yu Yu,<sup>a</sup> Qiquan Luo,<sup>id \*c</sup> Shan Gao,<sup>id \*a</sup> Jinlong Yang<sup>id d</sup> and  
 Yi Xie<sup>id \*b</sup>

Customizing catalytic reaction pathways by precisely designing the metal active sites and electron–hole separated channels of metal oxides to simultaneously achieve a high yield and selectivity of photo-catalytic CO<sub>2</sub> reduction to liquid fuel remains a challenge. Herein, we for the first time propose that low-valent tungsten sites favor the formation of key CHO\* intermediates for highly selective photo-catalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH. *In situ* spectroscopic results and DFT calculations demonstrate that coordinately unsaturated low-valent W sites near the tungsten trioxide (denoted WO<sub>3–x</sub>) pits serve as catalytic sites and electron capture sites enabling the adsorbed CO<sub>2</sub> to selectively form a predominant lower-energy \*CHO intermediate instead of \*CO, thereby triggering a unique reaction pathway for CO<sub>2</sub> reduction to CH<sub>3</sub>OH. Accordingly, the optimal WO<sub>3–x</sub> delivers a notable CH<sub>3</sub>OH selectivity of up to 86% with a high evolution rate of 17 μmol g<sup>–1</sup> h<sup>–1</sup> under sunlight irradiation. This work highlights how low-valent metal active sites in the surface pits can be controlled at the atomic-level to customize the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) pathway to generate valuable liquid fuels.

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### Broader context

Infinite sunlight-driven CO<sub>2</sub> conversion into value-added alternative fuels under mild conditions has emerged as a promising technology to achieve carbon neutrality and ameliorate future energy feedstock supplies. Metal oxides are very promising and efficient catalysts for the photochemical CO<sub>2</sub> reduction to CH<sub>3</sub>OH in practical catalytic systems. However, the rapid electron–hole recombination rate and lack of intrinsic catalytic sites in photocatalysts still limit their photocatalytic performance. Therefore, developing a suitable photocatalyst with selective active sites for both the activation of stable CO<sub>2</sub> molecules and the customization of CO<sub>2</sub> reduction products is urgently needed but it remains a challenge. In this tandem experimental–computational work, we propose that the formation of CHO\* intermediates at low-valent W sites in the surface pits is the key factor determining selectivity. Furthermore, we demonstrate that the unsaturated W atoms on the WO<sub>3–x</sub> surface pits are the actual catalytic sites; meanwhile, exposing the low-valent W active site promotes the formation of the \*CHO intermediates, thereby facilitating CH<sub>3</sub>OH generation. This work highlights product selectivity changes induced by precisely designing the electronic structure of the catalyst surface, while providing deep mechanistic insights into customizing CO<sub>2</sub> reduction to liquid solar fuels.

<sup>a</sup> Anhui Province Key Laboratory of Chemistry for Inorganic/Organic Hybrid Functionalized Materials, Key Laboratory of Structure and Functional Regulation of Hybrid Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Anhui University, Hefei, 230039, China.  
 E-mail: shangao@ahu.edu.cn, kfzhang@ahu.edu.cn

<sup>b</sup> Hefei National Research Center for Physical Sciences at Microscale, University of Science & Technology of China, Hefei, 230026, China. E-mail: yxie@ustc.edu.cn

<sup>c</sup> Institutes of Physical Science and Information Technology, Anhui University, Hefei, 230039, China. E-mail: qluo@ustc.edu.cn

<sup>d</sup> Hefei National Research Center for Physical Sciences at Microscale, Synergetic Innovation Centre of Quantum Information & Quantum Physics, University of Science & Technology of China, Hefei, 230026, China

<sup>e</sup> School of Materials Science and Engineering, Anhui University, Hefei, 230039, China

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## Introduction

Converting carbon dioxide (CO<sub>2</sub>) to solar fuels *via* naturally inexhaustible solar energy is a sustainable strategy to simultaneously ameliorate energy feedstock supplies and climate change.<sup>1–4</sup> It is known that the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) process is quite complex and ambiguous, containing the necessary protonation coupled electron transfer to generate various deoxygenated products.<sup>5–7</sup> Among the possible CO<sub>2</sub>RR derivations, the 6H<sup>+</sup>/6e<sup>–</sup> reduction of CO<sub>2</sub> towards CH<sub>3</sub>OH, an appealing platform molecule and liquid commodity chemical that can be easily stored and handled, exhibits great potential and economic feasibility for application in industry and organic synthesis, namely ‘methanol economy’.<sup>8</sup> In terms of the CO<sub>2</sub>RR



process, the metal (M) sites on the photocatalyst surface preferably bond with the C or O atoms in the adsorbed CO<sub>2</sub> through orbital hybridization, resulting in a series of reactive intermediates with the M–C or M–O bond.<sup>9–13</sup> In this regard, the catalyst-reactive intermediate interaction is the key factor determining the performance of photocatalysts in practical catalytic systems. To date, notwithstanding that the most research efforts have shown that semiconductor photocatalysts can generate dominantly CH<sub>4</sub> or CO products with high activity or selectivity during the CO<sub>2</sub>RR, only a few reports were on liquid CH<sub>3</sub>OH production under comparable conditions.<sup>14,15</sup> More unfortunately, both the selectivity and yield of photocatalytic CO<sub>2</sub>-to-CH<sub>3</sub>OH reduction remain extremely unsatisfactory due to the high thermodynamic stability of linear CO<sub>2</sub> molecules, rapid recombination kinetics of photogenerated carriers<sup>4,16,17</sup> and multi-electron side reactions with similar reduction potentials.<sup>18</sup> As a promising approach to addressing these issues, developing a suitable photocatalyst with both high activity and selectivity for CO<sub>2</sub> reduction is urgently desired, while it remains a great challenge.

Given that metal oxides are very promising and efficient catalysts, they have been extensively studied for photocatalytic reduction of CO<sub>2</sub> to CH<sub>3</sub>OH.<sup>19</sup> As a classical metal oxide photocatalyst, tungsten trioxide (WO<sub>3</sub>) seems to be one of the most appropriate candidates to achieve the above goal due to its intriguing advantages such as its beneficial band gap (~2.6 eV), suitable bandgap edge, strong light harvesting ability, high chemical stability, and excellent photoactivity.<sup>13,20,21</sup> Meanwhile, theoretical calculations further indicate that WO<sub>3</sub> has good CO<sub>2</sub> adsorption and activation abilities, which is the premise of the subsequent reduction reaction.<sup>22,23</sup> However, the rapid electron-hole recombination rate and lack of intrinsic catalytic sites in WO<sub>3</sub> still limit the full utilization of photogenerated charge carriers to initiate the highly selective reduction of CO<sub>2</sub> to CH<sub>3</sub>OH. As we all know, constructing surface defects on photocatalysts is an effective strategy to introduce coordinatively unsaturated and catalytically active metal sites and regulate electronic structures.<sup>24,25</sup> This not only promotes local electron delocalization at unsaturated metal sites on the catalyst surface, but also modulates the redox capability of photogenerated charge carriers, activating adsorbed CO<sub>2</sub> molecules and optimizing the reactive intermediates' energy barrier on sites, thereby altering the product selectivity of CO<sub>2</sub> reduction.<sup>26–28</sup> Additionally, to further improve the activity of the catalyst, rational morphology design and precise electron-hole separated channel construction for WO<sub>3</sub> have also offered an opportunity to enable ultra-high specific surface area and expose more accessible active sites, which is beneficial to improving light harvesting while boosting charge carrier separation and migration in the photocatalytic process.<sup>29,30</sup> Nevertheless, as far as we know, the design of highly efficient WO<sub>3</sub> photocatalysts with selective active sites and electron-hole separated channels for customization of the CO<sub>2</sub>RR product is still in its infancy and has not been systematically established yet.

On the basis of the above-mentioned considerations, herein, we developed well-defined low-valent W sites to realize highly efficient electron-hole separation and CO<sub>2</sub> activation at

single-component WO<sub>3–x</sub> nanosheet surface pits, thus customizing the CO<sub>2</sub>RR pathway to generate CH<sub>3</sub>OH. The optimal WO<sub>3–x</sub> exhibits an impressive CH<sub>3</sub>OH evolution rate of 17 μmol g<sup>–1</sup> h<sup>–1</sup> with a high selectivity of up to 86% and appreciable stability for 5 consecutive runs. More importantly, the underlying mechanism is further revealed by experimental and computational results, showing that the unsaturated W atoms on the WO<sub>3–x</sub> surface pits are the actual catalytic sites for CO<sub>2</sub> activation, and the \*CO intermediates adsorbed at the active sites are likely to undergo a more rapid and low-energy-barrier protonation process to generate the key \*CHO intermediates rather than desorption for CO generation, thereby leading to accelerated catalytic kinetics for CH<sub>3</sub>OH production from CO<sub>2</sub> photoreduction.

## Results and discussion

It is widely accepted that the introduction of oxygen vacancies or low-valent metal species could modulate the electronic band structure and create trapping sites to benefit separation of photoinduced charge carriers.<sup>31–33</sup> Furthermore, the existence of defects could broaden the light harvesting range and more importantly regulate the local charge density distribution. Thus, we conducted density functional theory (DFT) to check the influence of low-valent W species on the electronic structure of WO<sub>3</sub> and WO<sub>3–x</sub> (see Calculation details in the ESI†).<sup>34,35</sup> As depicted in Fig. 1a, the Bader charge distribution of the W atom adjacent to the top oxygen vacancy is 2.79 electrons (2.79 e<sup>–</sup>) on an optimized WO<sub>3–x</sub> surface, which is between the charge of W<sup>6+</sup> (2.97 e<sup>–</sup>) in a perfect WO<sub>3</sub> and the charge of W<sup>4+</sup> (2.27 e<sup>–</sup>) in WO<sub>2</sub>. This indicates that the localized electron would transfer to W atoms, resulting in a reduced valence state of around +5.<sup>36,37</sup> Interestingly, the low-valent W species on the WO<sub>3–x</sub> surface exhibits a tremendously enhanced charge density, in which the electron distribution becomes more delocalized, and successively donates its d-orbital electrons to the C=O antibonding orbital (π\*) of adsorbed CO<sub>2</sub> molecules to form highly reactive intermediates. In fact, these intermediates are usually regarded as key factors in redefining the selectivity of the final reduction product.<sup>37</sup> To further unveil the electron-transfer pathway of CO<sub>2</sub> activation on optimized WO<sub>3–x</sub> surfaces, we applied the charge density difference to track their electron behaviours (Fig. 1b). We found that a crucial \*CO intermediate was formed and accumulated on the low-valent WO<sub>3–x</sub> and perfect WO<sub>3</sub> surface.

In fact, the reaction energy change of this \*CO intermediate is a key factor determining the reaction pathway.<sup>37,38</sup> In sharp contrast to the perfect WO<sub>3</sub> surface, there is a strong electron transfer (0.32 e<sup>–</sup> lost) from the low-valent W species on WO<sub>3–x</sub> to the \*CO group, and the C–O bond strength is weakened. The weakened C–O bond in the \*CO intermediate is stretched from 0.114 to 0.117 nm after introduction of the low-valent W species. This phenomenon indicates that low-valent W species can better stabilize the \*CO intermediates and rapidly transfer more electrons to protonate them for production of lower-energy \*CHO intermediates during CO<sub>2</sub> photoreduction, thereby changing the reaction pathway to generate CH<sub>3</sub>OH instead of CO.





**Fig. 1** (a) Distribution of charge density for the original  $\text{WO}_3$  (left) and  $\text{WO}_{3-x}$  (right) plotted from 0 (blue) to  $0.035 \text{ e}^- \text{ bohr}^{-3}$  (red). (b) Charge difference diagrams of  $^*\text{CO}$  adsorption on original  $\text{WO}_3$  (left) and  $\text{WO}_{3-x}$  (right); blue and yellow surfaces represent charge depletion and accumulation, respectively.

Inspired by the above analysis, we present that creating favourable atomic-level low-valent W species around the pits on the surfaces of  $\text{WO}_{3-x}$  nanosheets can remarkably improve the performance of photocatalytic  $\text{CO}_2$  reduction. The preparation of  $\text{WO}_{3-x}$  nanosheet catalysts *via* a two-step method is illustrated in Fig. 2a (see the Experimental section in the ESI† for more details). Initially, the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  precursor was produced using a wet-chemistry approach by adding sodium tungstate dihydrate into nitric acid solution at a certain concentration. The multilayer  $\text{WO}_3 \cdot \text{H}_2\text{O}$  precursor shows a sheet-like morphology and a relatively smooth and flat surface confirmed by the powder X-ray diffraction (XRD) pattern and transmission electron microscopy (TEM) results in Fig. S1 (ESI†). The  $\text{WO}_{3-x}$  nanosheets with surface pit-decoration and suitable low-valent W sites were subsequently synthesized by an atomic clipping engineering method (Fig. S2, ESI†). The density of low-valent W sites of the  $\text{WO}_{3-x}$  nanosheets can be adjusted by changing the atmosphere (air or hydrogen) and annealing time. The model catalysts were obtained by calcining the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  precursor at  $450^\circ\text{C}$  for 40 and 60 min in hydrogen or calcined at  $700^\circ\text{C}$  for 5 s in air (denoted H-40, H-60, and A-5), respectively. The XRD pattern shown in Fig. S3 (ESI†) for the obtained products could be indexed to the monoclinic tungsten oxide with a distorted  $\text{ReO}_3^-$  type unit (JCPDS No. 83-0950). As presented in the Fourier-transform infrared spectroscopy (FT-IR) spectra, the main peaks located at around  $743$ ,  $811$ , and  $966 \text{ cm}^{-1}$  belong to the O–W–O and O–W stretching modes. This result is in good agreement with the XRD results that all as-prepared samples are the pure monoclinic phase of  $\text{WO}_3$  (Fig. S4, ESI†). The representative morphology

of H-40 is presented in Fig. 2b–d, characterized by TEM and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). H-40 inherits the two-dimensional sheet-like morphology from the  $\text{WO}_3 \cdot \text{H}_2\text{O}$  precursor and contains numerous highly monodisperse pits. We speculate that the formation of surface pits may be due to the loss of crystal water during pyrolysis. The HAADF-STEM and fast Fourier transform (FFT) images in Fig. 2d and e, respectively, confirm the single crystalline structure and the  $[001]$  orientation of H-40. The interplanar spacings of  $0.376$  and  $0.365 \text{ nm}$  for H-40 can be assigned to  $(020)$  and  $(200)$  planes, respectively. In addition, the local  $(020)$  interplanar spacing ( $0.357 \text{ nm}$ ) in the pits is also smaller than its standard value of monoclinic  $\text{WO}_3$  ( $0.376 \text{ nm}$ ), further demonstrating the existence of defects in H-40 (Fig. 2f and g). Elemental mappings (Fig. 2c) further confirm a uniform distribution of W and O elements across H-40, which also agrees well with the XRD results. To further confirm the existence of defective structures, a series of spectroelectrochemistry characterization studies were performed. As shown in Fig. 2h, an obvious electron paramagnetic resonance (EPR) signal at  $g = 2.003$  is observed for A-5, H-40, and H-60, which indicates electrons trapped on metal W species. Furthermore, the stronger EPR signal of H-60 confirms the richer low-valent W species formed during material preparation. This result can be further verified by X-ray photoelectron spectroscopy (XPS). Apparently, the deconvolution of the characteristic W 4f band yields two pairs of peaks, corresponding to the  $\text{W}^{6+}$  (located at  $37.6$  and  $35.5 \text{ eV}$ ) and  $\text{W}^{5+}$  (located at  $36.5$  and  $34.3 \text{ eV}$ ) oxidation states, respectively. Notably, a slightly negative shift of W 4f binding energy and the higher proportion of the peaks at  $36.5$  and  $34.3 \text{ eV}$  in H-60, corroborating the existence of more low-valent  $\text{W}^{5+}$  (Fig. 2i and Fig. S5, Table S1, ESI†).<sup>39–41</sup> This change also affects the electronic structure of oxygen atoms: the H-60 shows the strongest O 1s peak possibly adjacent to the  $\text{W}^{5+}$  at  $531.4 \text{ eV}$  (Fig. 2j).<sup>42–44</sup> Furthermore, the Raman bands of H-60 with numerous defective low-valent  $\text{W}^{5+}$  sites show peak broadening and a redshift compared to the other counterparts, which may be attributed to phonon softening or enhanced electron–phonon coupling at low-valent W sites. All the above mentioned experimental results support the enrichment of low-valent W sites in H-60 (Fig. 2k).

To unravel the influence of unsaturated low-valent W sites on the photocatalytic performance, we probe into the  $\text{CO}_2\text{RR}$  properties of the obtained catalysts. The gaseous and liquid products were quantitatively evaluated by gas chromatography and H nuclear magnetic resonance spectroscopy (Fig. S6–S8, ESI†), respectively. As shown in Fig. 3a, the reduction products on the different obtained catalysts upon illumination are  $\text{CO}$ ,  $\text{CH}_4$ , and  $\text{CH}_3\text{OH}$ , which gradually accumulated with increasing reaction time. Meanwhile, the  $^{13}\text{CO}_2$  isotope labelling experiment and a series of control experiments were operated in Ar or without the sample or in the dark to provide direct proof for the origin of the products (Fig. S9, ESI†), and the molecular ion peaks at  $m/z$  17 and 33 were assigned, respectively, to  $^{13}\text{CH}_4$  and  $^{13}\text{CH}_3\text{OH}$  when  $^{13}\text{CO}_2$  was used as the reactant, demonstrating that the carbon atoms of the obtained products stemmed from







Fig. 2 (a) Schematic illustration of the synthetic process of 2D  $\text{WO}_{3-x}$  nanosheets. Characterization of the pit-rich  $\text{WO}_{3-x}$  nanosheets. (b) TEM image, (c) HAADF-STEM EDX elemental mappings, (d) atomic-resolution HAADF-STEM image of H-40, and (e) the corresponding fast Fourier transform (FFT) electron diffraction pattern along the [001] zone axis. (f and g) Intensity distribution measured from the HAADF-STEM image in the perfect crystal face (orange) and pits (green). (h) EPR spectra, (i) W 4f XPS spectra, (j) O 1s XPS spectra and (k) Raman spectra of A-5, H-40, and H-60.

$\text{CO}_2$  feedstock instead of any other impurities.<sup>45,46</sup> Besides, the production of  $\text{O}_2$  in the control experiment verified that  $\text{O}_2$  stemmed from  $\text{H}_2\text{O}$  (Fig. S10, ESI†). Notably, H-40 manifests the highest  $\text{CH}_3\text{OH}$  production rate of up to  $17 \mu\text{mol g}^{-1} \text{h}^{-1}$ , which is about 4.6 times higher than that of the A-5 material. Furthermore, the quantum efficiency (QE) of the H-40 photocatalyst was measured to be as high as  $\sim 0.2\%$  under monochromatic visible light (675 nm) irradiation.<sup>47</sup> The trend of the  $\text{CH}_3\text{OH}$  yield agrees well with the photoabsorption of the obtained photocatalysts, demonstrating a high utilization of photogenerated charge carriers (Fig. 3b, 4a and Fig. S11, ESI†). More intriguingly, H-40 achieves the highest  $\text{CH}_3\text{OH}$  selectivity of  $\sim 86\%$  among all materials (Fig. 3c). Surprisingly, both the

$\text{CH}_3\text{OH}$  yield and selectivity of the achieved cheap H-40 surpass those of most previously reported state-of-the-art photocatalysts (Fig. 3e).<sup>38,48–60</sup> To further evaluate its stability, H-40 was repeatedly used in the  $\text{CO}_2\text{RR}$  for five cycles and the product yield was tested every 5 h. No obvious variations are observed during measurements, reflecting the high stability of H-40 (Fig. 3d and Fig. S12, ESI†). Besides, XRD, EPR, XPS and TEM measurements of the used H-40 after photocatalysis also support its high structural stability (Fig. S13, S14 and Table S2, ESI†). Clearly, the above results demonstrate that H-40 has high efficiency and selectivity for  $\text{CO}_2$  photoreduction, which raises the question: how the density of low-valent W sites in  $\text{WO}_{3-x}$  thermodynamically and kinetically influences the photocatalytic activity of the  $\text{CO}_2\text{RR}$ ?



Fig. 3 (a) Product yields of the CO<sub>2</sub>RR using the different photocatalysts. (b) QE and (c) CH<sub>3</sub>OH selectivity values of different samples. (d) Photocatalytic stability of H-40 for five consecutive runs. (e) Comparison of CO<sub>2</sub>RR performance of WO<sub>3-x</sub> and other reported photocatalysts.

To answer this question, a series of photoelectrochemical characterization studies were conducted to elucidate the excellent CO<sub>2</sub>RR activity of the obtained photocatalysts. As shown in Fig. 4a, the existence of low-valent W<sup>5+</sup> sites results in the formation of abundant internal transition energy levels, which could efficiently narrow the band gap to enhance the visible-light harvesting ability for photocatalytic reactions and tune the sample color range from yellow to dark blue (inset: sample color). The band gaps of A-5, H-40, and H-60 were detected to be 3.18, 2.42, and 2.15 eV, corresponding to their valence band (VB) potentials of 2.61, 1.91, and 1.65 eV (*versus* normal hydrogen electrode, *vs.* NHE) (Fig. 4a and b). Compared with the thermodynamic potential (CO<sub>2</sub>/CH<sub>3</sub>OH = −0.38 V), the calculated conduction band potential of H-40 is more negative, which is essential to facilitate electron transfer for CO<sub>2</sub> conversion into CH<sub>3</sub>OH (Fig. 4c). Furthermore, the formation of pits on the surface significantly enlarged the surface area, which could provide more accessible catalytic sites to improve the catalytic activity. Notably, the numerous low-valent W sites in H-60 significantly improve the light absorption, while the excessive defect sites on the metal oxide surfaces simultaneously generate more photogenerated charge carrier recombination sites for various chemical reactions, resulting in a decrease in catalytic activity.<sup>61,62</sup> Therefore, accurately achieving a suitable density of low-valent W active sites is vital to maximize the photocatalytic activity. This is further verified by the result of the transient photocurrent measurement shown in Fig. 4d, where the enhanced photocurrent of H-40 relative to the other counterparts reveals the

promoted generation and separation of photogenerated charge carriers in H-40. The carrier density can be calculated according to the following formula:

$$N_d = (2/e_0\epsilon_r\epsilon_0)[d(1/C^2)/dE]^{-1} \quad (1)$$

where  $e_0$  ( $1.602 \times 10^{-19}$  C) is the electron charge,  $C$  is the capacitance of the space charge layer,  $N_d$  is the carrier density,  $\epsilon_r$  (20 for WO<sub>3</sub>) is the dielectric constant, and  $\epsilon_0$  ( $8.85 \times 10^{-14}$  F cm<sup>−1</sup>) is the vacuum permittivity.<sup>63</sup> The  $N_d$  value was calculated to be  $3.32 \times 10^{19}$  cm<sup>−3</sup>, approximately 7.8 times higher than the  $0.4 \times 10^{19}$  cm<sup>−3</sup> for A-5 (Fig. 4e and Table S5, ESI†). In addition, the scanning Kelvin probe (SKP) technique was used to probe the work function to determine the electron separation efficiency of the as-prepared photocatalysts. Fig. 4f shows that H-40 achieves the lowest work function value, causing a higher Fermi level of H-40 in comparison with the other counterparts. This means that the built-in electric field and surface energy band bending are enhanced, indicating that a suitable density of low-valent W<sup>5+</sup> sites is beneficial to improve the efficiency of charge separation. The electrochemical impedance spectroscopy (EIS) further supports the SKP results that H-40 has a lower interfacial charge-transfer resistance resulting from its superior electrical conductivity (Fig. 4g). Meanwhile, the charge separation efficiencies of A-5, H-40, and H-60 nanosheets were characterized by steady-state photoluminescence (PL) emission spectroscopy; the weaker PL intensity of H-40 reveals efficient inhibition of charge recombination (Fig. 4h). Furthermore, transient PL emission spectroscopy was employed to determine the specific charge carrier dynamics of the catalysts. The much slower electron decay kinetics of H-40 reveals a distinctly prolonged lifetime of the photogenerated charge carriers by introducing suitably reduced W<sup>5+</sup> sites on H-40 (Fig. 4i and Table S4, ESI†).<sup>64–66</sup> All these results provide solid evidence for the proposition that low-valent W<sup>5+</sup> sites on H-40 can efficiently promote the generation and separation of photoinduced charge carriers.

Substantially, the reactant (H<sub>2</sub>O and CO<sub>2</sub>) adsorption and product desorption on the H-40 surface are crucial during the CO<sub>2</sub>RR because the activation and protonation of CO<sub>2</sub> molecules are involved. As revealed by the N<sub>2</sub> adsorption and desorption curves shown in Fig. S15 and S16a (ESI†), moderate pits decorated on H-40 enable a higher surface area, more low-valent W<sup>5+</sup> sites, and more electron–hole separation channels, which can promote the adsorbate on its surface for subsequent surface redox reactions. As expected, H-40 with larger surface area exhibits higher CH<sub>3</sub>OH activity and selectivity. CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) shows a similar adsorption ability to the obtained samples (Fig. S16b, ESI†). The enhanced peaks of H-40 at higher temperatures indicate that the existence of suitable low-valent W<sup>5+</sup> sites can dramatically promote the chemisorption ability of CO<sub>2</sub>. Moreover, this result is further reinforced by the contact angle measurements (Fig. S17, ESI†). Hence, all these results demonstrate that the introduced coordination unsaturated low-valent W<sup>5+</sup> sites endow it with higher surface hydrophilicity and enhanced CO<sub>2</sub> adsorption capacity.





Fig. 4 (a) UV-vis absorption spectra (inset: Tauc plots), (b) VB XPS spectra, (c) energy band structure alignments, (d) transient photocurrent responses (0.5 V vs. Ag/AgCl, pH 7), (e) Mott-Schottky plots, (f) SKP maps, (g) EIS spectra, (h) steady-state PL spectra, and (i) time-resolved transient PL decay of A-5, H-40, and H-60, respectively.

Achieving excellent activity and controllable product selectivity for  $\text{CO}_2$  photoreduction is generally considered as the bottleneck because of the complicated and sluggish multielectron transfer processes. To probe the evolution of the adsorbed active intermediates on the obtained catalyst surface, *in situ* FT-IR characterization was performed to track the dynamics process of the  $\text{CO}_2\text{RR}$ . As for H-40 (Fig. 5a), the emergence of infrared peaks at 1051, 1430, 1623, and 2065  $\text{cm}^{-1}$  can be assigned to  $\text{*CHO}$ ,  $\text{HCO}_3^*$ ,  $\text{*COOH}$ , and  $\text{*CO}$  species, as well as two peaks at 2962 and 1197  $\text{cm}^{-1}$  corresponding to  $\text{*OCH}_3$  species; in the meantime, the  $\text{CH}_3\text{OH}$  peak of the target product at 2850  $\text{cm}^{-1}$  was also observed, consistent with previously reported studies,<sup>67–69</sup> and these peak intensities gradually strengthened as a function of irradiation time from 0 to 25 min. Among them, the major preponderant  $\text{*CHO}$  species is generally regarded as the most significant intermediate during the photocatalytic  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  reduction process. It is worth noting that the energy levels of key reactive intermediate species on the catalyst surface can determine whether an easy or complex reaction pathway is present.

As expected, the surface coverage of  $\text{*CHO}$  species on H-40 is much larger relative to other samples, leading to high  $\text{CH}_3\text{OH}$  selectivity and a superior yield (Fig. S18, ESI†). Therefore, we deduce that the most likely reaction path for the  $\text{CO}_2$ -to- $\text{CH}_3\text{OH}$  reduction process is outlined below:



where \* denotes the active sites of the catalysts.





Fig. 5 (a) *In situ* FT-IR spectra of H-40. Free energy diagrams for reduction of CO<sub>2</sub> to CH<sub>3</sub>OH over (b) WO<sub>3</sub> and (c) WO<sub>3-x</sub> based on DFT calculation as well as the corresponding structure models for every reaction step. Key steps of CO<sub>2</sub> photoreduction of (d) WO<sub>3</sub> and (e) WO<sub>3-x</sub>. White, dark brown, light yellow, red and pink balls indicate H, C, O (in WO<sub>3</sub>), O (in CO<sub>2</sub>) and W atoms, respectively.

To further verify our hypothesis, the remarkable selectivity of the low-valent W<sup>5+</sup> mediated WO<sub>3</sub> (WO<sub>3-x</sub>) catalyst was examined by DFT simulation, in which the structural model based on the (001) facet of WO<sub>3</sub> was employed. The Gibbs free energy profiles and their optimized reactive intermediate adsorption configurations of each possible step for CO<sub>2</sub> reduction to CH<sub>3</sub>OH on the surface of the perfect WO<sub>3</sub> and WO<sub>3-x</sub> are displayed in Fig. 5b–d. Take the perfect WO<sub>3</sub> as an example; the potential-determining step (PDS) is CO<sub>2</sub> protonation to generate \*COOH with a reaction free-energy-barrier of 1.76 eV. After the introduction of the low-valent W species, this PDS has a lower \*COOH formation energy of 0.67 eV, which facilitates the whole reaction. This result indicates that the different adsorption sites likely have a decisive influence on the formation energies of crucial intermediates.<sup>33</sup>

To clarify this, we performed a precise analysis of the above two models and found a very clear difference in the step of protonation of the \*CO intermediate to generate \*CHO. Most interestingly, we also find that the \*CHO formation energy is higher than the desorption energy of the CO molecules on the perfect WO<sub>3</sub>, while the CO desorption energy and \*CHO

formation energy on WO<sub>3-x</sub> are diametrically opposite. This change might indicate that the low-valent W species induced the redistribution of the photogenerated electrons on the WO<sub>3-x</sub> surface, thereby efficiently stabilizing and promoting the protonation of \*CO to generate \*CHO instead of desorbing CO molecules from its surface, which is also supported by the *in situ* FT-IR results.<sup>30,70</sup> Furthermore, the CO-TPD isotherm (Fig. S19, ESI†) confirms the fact that the introduction of suitable low-valent W sites can regulate the CO adsorption and desorption capacity to a certain extent, thereby favouring the subsequent CO protonation and relieving the CO poisoning. This result further suggests that appropriate defect density is critical for customizing liquid products. More importantly, the desorption energy of the CH<sub>3</sub>OH molecules on the WO<sub>3-x</sub> surface is much lower than that on the perfect WO<sub>3</sub> surface, indicating that suitable low-valent W species are more beneficial for the CH<sub>3</sub>OH desorption process and efficiently boost its activity and selectivity. The above results demonstrate that the suitable surface pit-embellished low-valent W sites in the WO<sub>3-x</sub> system could modulate the reaction intermediate's formation energy to change the reaction pathway, which accounts for highly selective photocatalytic CO<sub>2</sub> reduction to CH<sub>3</sub>OH.

## Conclusions

In summary, we proposed a general strategy to prepare an extremely efficient WO<sub>3-x</sub> catalyst and elucidated the origin of its superior CO<sub>2</sub>RR activity. More specifically, the unique WO<sub>3-x</sub> nanosheets with abundant surface pits promoted the creation of low-valent W sites to interact with the adsorbed reactant. *In situ* FT-IR spectra and computational results demonstrate that the delocalized charge near the low-valent W sites not only reduces the reaction energy for CO<sub>2</sub> transformation into the key \*CHO intermediate, but also regulates the energy level of reaction intermediates to prevent the production of other multi-electron carbon-based products, which is a key characteristic for achieving high CH<sub>3</sub>OH selectivity. Consequently, a suitable low-valent W concentration enables the H-40 catalyst to show a drastically enhanced yield of CH<sub>3</sub>OH as well as appreciable stability, which outperformed most previously reported state-of-the-art photocatalysts operated under similar conditions. This work puts forward some inspirations for the rational design of surface electronic structures of photocatalysts and the precise control of the reaction pathways, while providing deep mechanistic insights into customizing the conversion of CO<sub>2</sub> into valuable solar fuels.

## Author contributions

Y. X. and S. G. conceived and designed the research. W. Z., P. X. Y. and Q. W. carried out the experiments. J. L. Y., Q. Q. L. and M. D. conducted the DFT calculations. K. F. Z., X. W. Z. and Y. Y. participated in the experimental data analyses and scientific discussions. S. G. and K. F. Z. wrote the manuscript. W. Z., M. D., and P. X. Y. contributed equally to this work.



## Conflicts of interest

There are no conflicts to declare.

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