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### Photoelectrocatalysis

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# Efficient Photoelectrochemical Conversion of Methane into Ethylene Glycol by WO<sub>3</sub> Nanobar Arrays

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Abstract: Photoelectrochemical (PEC) conversion of methane (CH<sub>4</sub>) has been extensively explored for the production of value-added chemicals, yet remains a great challenge in high selectivity toward  $C_{2+}$  products. Herein, we report the optimization of the reactivity of hydroxyl radicals ('OH) on WO<sub>3</sub> via facet tuning to achieve efficient ethylene glycol production from PEC CH<sub>4</sub> conversion. A combination of materials simulation and radicals trapping test provides insight into the reactivity of 'OH on different facets of WO<sub>3</sub>, showing the highest reactivity of surface-bound 'OH on {010} facets. As such, the WO<sub>3</sub> with the highest {010} facet ratio exhibits a superior PEC  $CH_4$  conversion efficiency, reaching an ethylene glycol production rate of 0.47  $\mu$ mol cm<sup>-2</sup> h<sup>-1</sup>. Based on in situ characterization, the methanol, which could be attacked by reactive 'OH to form hydroxymethyl radicals, is confirmed to be the main intermediate for the production of ethylene glycol. Our finding is expected to provide new insight for the design of active and selective catalysts toward PEC CH<sub>4</sub> conversion.

Methane conversion is a highly important process to the energy system optimization, as well as promotes the understanding of C–H bonds activation. The utilization of the  $CH_4$ as a building block for the production of high-value chemicals such as ethane ( $C_2H_6$ ), methanol ( $CH_3OH$ ) and formic acid (HCOOH) is gaining traction from the scientific commuity.<sup>[1–3]</sup> Currently, the industrial  $CH_4$  conversion mainly focuses on  $H_2$  or syngas production through  $CH_4$  reforming, which is accomplished relying on harsh operating conditions such as high temperature and pressure due to the symmetrical tetrahedral structure and extremely stable C–H bonds.<sup>[2,4]</sup> Therefore, the search for the CH<sub>4</sub> conversion technique that could be performed under ambient condition is of scientific and technological significance.<sup>[4,5]</sup>

It is known that hydrogen peroxide  $(H_2O_2)$  or molecular  $O_2$  has been widely used as oxidant in CH<sub>4</sub> conversion.<sup>[6,7]</sup> For example, AuPd colloids have been demonstrated to activate  $CH_4$  with  $H_2O_2$ .<sup>[6]</sup> However, the relatively high cost of  $H_2O_2$ and molecular O<sub>2</sub> for CH<sub>4</sub> conversion hindered the development of economically chemical system. Here we report the photoelectrochemical (PEC) catalyzed CH<sub>4</sub> conversion under mild conditions, without additional oxidant. PEC catalysis, combining the advantages of photocatalysis and electrocatalysis, has recently been arisen as an extraordinary candidate for various chemical reactions. For CH<sub>4</sub> oxidation, PEC can produce reactive oxygen species, especially 'OH, through water oxidation by photoexcited holes for attacking and activating the stubborn C-H bonds, as well as reduce the oxidation barrier of the CH4 molecules by providing external potential for producing various value-added compounds.[8-10] We show that by the optimization of photo-generated radicals, a substantial improvement is achieved without any additional oxidant.

Over the past several decades, various semiconductors have been employed for constituting such a PEC system.<sup>[11,12]</sup> Among them, tungsten oxide  $(WO_3)$  has been known as one of the most promising candidates because of its non-toxicity, high oxidation ability and suitable band gap.<sup>[8,13]</sup> However, the present PEC methane conversion rates are still unsatisfactory with a high selectivity toward low-value  $CO^{[11]}$  and  $C_2H_6^{[12]}$ mainly due to the inappropriate active sites on the surface of catalyst. Herein, we take insight into the facet-dependent performance of WO<sub>3</sub> in CH<sub>4</sub> conversion with the goal of boosting the production of oxygenated derivatives, especially alcohol derivatives. The WO<sub>3</sub> photoanode with the highest {010} facet ratio among all the prepared samples achieves the greatest PEC CH<sub>4</sub> conversion performance, reaching an ethylene glycol (EG) generation rate of 0.47  $\mu$ mol cm<sup>-2</sup> h<sup>-1</sup> and 66% selectivity under a moderately positive applied potential (1.3 V vs. reversible hydrogen electrode (RHE)). More importantly, the optimized WO<sub>3</sub> photoanode shows high stability during PEC CH<sub>4</sub> oxidation for 12 h.

Based on the previous research, 'OH plays a key role in photocatalytic  $CH_4$  activation.<sup>[9,10]</sup> For this reason, density functional theory (DFT) is first employed to investigate 'OH adsorption behaviors on {010}, {100} and {001} facets of monoclinic WO<sub>3</sub> (Figure S1–S4). The lowest-energy adsorp-

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**Figure 1.** The atomic structures of 'OH adsorption on twinning W atoms of a) {010} facet, b) {100} facet and c) {001} facet. The values at the bottom are their corresponding adsorption energy. The white and red spheres represent the hydrogen and oxygen atoms, respectively.

tion structures of 'OH on {010}, {100} and {001} facets are presented in Figure 1. The adsorption energy of two 'OH on  $\{010\}$ ,  $\{100\}$  and  $\{001\}$  facets are -1.742, -1.826 and -1.935 eV, respectively, indicating that  $\cdot$ OH could be strongly adsorbed on twinning W atoms of all the three facets of WO<sub>3</sub>. Notably, the adsorption behaviors of the 'OH bound on different facets are distinct. For {100} facet, two adsorbed 'OH are spatially close (1.872 Å) forming hydrogen bond on {100} facet, and spontaneously form H<sub>2</sub>O and surface-bound O that are connected with hydrogen bond on {001} facet, both of which reduce their further reactivity. In contrast, hydrogen bond could hardly be formed between the surface-bound 'OH on  $\{010\}$  facet because of the vast distance (3.342 Å) between two neighboring 'OH. Consequently, the strong reactivity of the surface-bound OH could be preserved on the {010} facets, allowing it to be more favorable for CH<sub>4</sub> oxidation.

To complement the above theoretical study, we seek to design WO<sub>3</sub> photoanode with different {010} facet ratios for PEC CH<sub>4</sub> oxidation. To this end, WO<sub>3</sub> nanobar arrays (WO<sub>3</sub>NB), WO<sub>3</sub> nanoplate arrays (WO<sub>3</sub>NP) and WO<sub>3</sub> nanoflake arrays (WO<sub>3</sub>NF), which all have {010} facets on their side faces, are grown on fluorine-doped tin oxide (FTO) glass substrates by hydrothermal methods. The crystal phase on WO<sub>3</sub> photoanodes is attested by X-ray diffraction characterization (Figure S5), in which the diffraction patterns of all the prepared samples are well indexed to monoclinic WO<sub>3</sub> (PDF#43-1035), with three characteristic peaks of {002}, {020} and {200} facets at 23.1°, 23.6° and 24.4°, respectively. As revealed by scanning electron microscopy (SEM) images (Figure 2a-c and S6), all the nanostructures are uniformly distributed on FTO substrates. The thicknesses of WO<sub>3</sub>NB, NP and NF are 250-400 nm, 80 nm and 25 nm, respectively. The nanostructures are further determined by high-resolution transmission electron microscopy (HRTEM, Figure S7), which turn out to have the orientations as shown in Figure 2d.<sup>[14]</sup> Combined with the orientations, SEM images reveal that the  $\{010\}$  facet ratios on the prepared WO<sub>3</sub> photoanodes change in the following sequence: WO<sub>3</sub>NB >  $WO_3NP > WO_3NF$ . To further examine the band structures of WO<sub>3</sub> photoanodes, UV-vis diffuse reflectance spectroscopy



**Figure 2.** SEM images of a)  $WO_3NB$ , b)  $WO_3NP$  and c)  $WO_3NF$ . d) Schematic illustration for monoclinic  $WO_3$  nanostructures with different {010} facet ratios on substrates.

and ultraviolet photoelectron spectroscopy are also collected (Figure S8–S11). It is apparent that valance band maximums for all these  $WO_3$  are sufficiently high for water oxidation to produce 'OH.<sup>[15,16]</sup>

To elucidate the facet effect on 'OH reactivity of WO<sub>3</sub>, electron paramagnetic resonance (EPR) spectroscopy is carried out to detect 'OH produced on these prepared WO<sub>3</sub> photoanodes using 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin-trapping agent. Figure 3 a shows the EPR spectra of DMPO-'OH adduct for WO<sub>3</sub> samples, which contain typical quartet signals with an intensity ratio of 1:2:2:1.<sup>[17]</sup> Obviously, the signal for DMPO-'OH produced on WO<sub>3</sub>NB is stronger than that for WO<sub>3</sub>NP and WO<sub>3</sub>NF. It is straightforward to understand this feature because the highest ratio of {010} facets on WO<sub>3</sub>NB has ensured the highest



**Figure 3.** a) EPR detection of 'OH using DMPO as a spin-trapping agent under 30 s illumination in the presence of WO<sub>3</sub>NB, WO<sub>3</sub>NP and WO<sub>3</sub>NF. b) Current density-potential profiles of WO<sub>3</sub> photoanodes measured at a range of potentials under 100 mWcm<sup>-2</sup> illumination. c) Production rate and d) carbon selectivity of EG produced in PEC CH<sub>4</sub> conversion on WO<sub>3</sub> photoanodes with different {010} facet ratios at a range of potentials under 100 mWcm<sup>-2</sup> illumination.

reactivity of the surface-bound 'OH so that the produced 'OH can easily react with DMPO to form DMPO-'OH adduct. Note that superoxide radical cannot be produced given the conduction band minimum of  $WO_3$ .<sup>[18]</sup> Moreover, no  $H_2O_2$  formation is observed in our experiments.

Upon recognizing the capability of tuning 'OH reactivity, we next appraise the performance of the WO<sub>3</sub> photoanodes for PEC CH<sub>4</sub> conversion. To suppress competing oxygen production reaction, PEC CH<sub>4</sub> conversion is performed in acidic medium of 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with pH adjusted to 2 using sulfuric acid.<sup>[19]</sup> In the absence of CH<sub>4</sub>, the photocurrent density is mostly resulted from water oxidation (Figure 3b). After flowing CH<sub>4</sub> gas into the reaction system for 30 min, the photocurrent density significantly increases, accompanied with obvious onset shift toward lower potentials for all the prepared samples (Figure S12), indicating that the CH<sub>4</sub> oxidation is more preferable than oxygen production on the WO<sub>3</sub>. Furthermore, WO<sub>3</sub>NB shows the most negative onset shift among all the prepared samples, implying that WO<sub>3</sub>NB owns the strongest response to CH<sub>4</sub> molecules. Note that the turbulence of gas bubbles and the magnetic stirring (800 rpm) necessary for facilitating CH<sub>4</sub> mass transport in water cause noise in the photocurrent-potential profile.

Subsequently, the PEC CH<sub>4</sub> conversion is carried out at 0.7-1.5 V vs. RHE to analyze the products of CH<sub>4</sub> oxidation and their corresponding Faradaic efficiencies (FEs). The production of the liquid product (ethylene glycol and  $CH_3OH$ ) and gas products ( $C_2H_6$ , CO and trace  $CO_2$ ) in the system is confirmed via <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy and gas chromatography (Figures S13 and S14), respectively. The PEC CH<sub>4</sub> conversion performance on the prepared WO3 photoanodes is boosted with the increasing {010} facet ratio (Figure S15), affirming the key role of WO<sub>3</sub> {010} facets in optimizing 'OH reactivity. Additionally, as shown in Figure 3c and d, at applied potential of 1.3 V vs. RHE, the production rate of EG on WO<sub>3</sub>NB reaches as high as 0.47 µmol cm<sup>-2</sup>h<sup>-1</sup> and its CH<sub>4</sub>-to-EG conversion selectivity is up to 66%. Such a PEC methane conversion on WO<sub>3</sub>NB achieves 0.10 and 0.12% solar-to-fuel efficiency (STF) at 1.1 and 1.3 V vs. RHE applied potential with >90% carbon balance (Table S2 and Figure S16), respectively. The increase of the anodic potential would promote the removal of photogenerated electrons from WO<sub>3</sub> photoanode surface and suppress the surface recombination of photogenerated carriers, which boosts the production of hydroxyl radicals on WO<sub>3</sub> surface.<sup>[20-22]</sup> All three WO<sub>3</sub> photoanodes show higher EG production rate at higher bias because of more production of hydroxyl radicals. However, according to our DFT calculation, the 'OH bound on the {010} facets of WO<sub>3</sub> photoanodes shows much stronger reactivity than that on {100} and {001} facets due to the formation of hydrogen bond between spatially closed 'OH on {100} and {001} facets. Since WO<sub>3</sub>NB possesses the highest {010} facet ratio, the performance for PEC CH<sub>4</sub> activation on WO<sub>3</sub>NB would be further amplified at higher bias, which results in much higher EG production rate on WO<sub>3</sub>NB than the other two. Moreover, both yield and selectivity of EG (Figure S17) are nearly linearly related with {010} facet ratio indicating the highest 'OH reactivity on {010} facets in PEC CH<sub>4</sub> conversion toward EG. Figure S18a shows FEs for EG produced by WO<sub>3</sub> photoanodes under various applied potentials. The FE for EG on the WO<sub>3</sub>NB is 23.9 % (1.3 V vs. RHE), nearly 2.5 times higher than that on the WO<sub>3</sub>NP. The FE for oxygen evolution, the main competition reaction, is also shown in Figure S18b. Although the FE for oxygen evolution is higher than that for EG production, 23.9 % FE for PEC CH<sub>4</sub> conversion (Table S3) toward EG is acceptable considering the outrageously low solubility of hydrophobic CH<sub>4</sub>. Nevertheless, our work shows significant carbon selectivity for CH<sub>4</sub>-to-EG conversion (66 %). In addition, no significant fluctuation arises in the average photocurrent density after 12 h of PEC CH<sub>4</sub> conversion (Figure S19) using WO<sub>3</sub>NB, suggesting its superiority for long-term CH<sub>4</sub> conversion.

Notably, the PEC CH<sub>4</sub> conversion has a dependence on illumination power density. The photocurrent density of the WO<sub>3</sub>NB at the range of 0.5–1.9 V is promoted with the increasing illumination power density (Figure S20). Specifically, as the light intensity increases, the response of WO<sub>3</sub>NB to CH<sub>4</sub> becomes stronger at relatively lower applied potential range (0.7–1.2 V vs. RHE) and turns weaker at relatively higher applied potential range (1.3–1.9 V vs. RHE). This observation is an outcome of the enhanced competition of oxygen evolution under high applied potentials.<sup>[23]</sup> The FEs for products of CH<sub>4</sub> conversion (Figure S21) are in good agreement with the photocurrent density results.

For the sake of future scalable production and practical application, the CH<sub>4</sub> conversion needs to be associated with economic viability, which is generally determined by market prices and production rate of the resultant products. Benefiting from the sublime reactivity of 'OH on {010} facet, the high-value EG can be obtained in an impressive production rate (the unit is converted into mmolh<sup>-1</sup>g<sup>-1</sup> for comparison), substantially higher than many reported products from solar-energy-mediated CH<sub>4</sub> conversion under mild conditions (Figure S22 and Table S4).<sup>[5,7,24-31]</sup> Such a result once again highlights the commercial-ready PEC CH<sub>4</sub> conversion performance of the optimized WO<sub>3</sub> photoanode.

To fundamentally elucidate the mechanism of PEC  $CH_4$  conversion into EG on WO<sub>3</sub>NB, in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) is employed to monitor reaction intermediates.<sup>[32]</sup> Four distinct DRIFTS peaks are gradually evolved during the PEC  $CH_4$  conversion under an applied potential of 1.3 V vs. RHE and 365 nm LED light irradiation (Figures 4a and S23). The



**Figure 4.** a) In situ DRIFTS for PEC CH<sub>4</sub> conversion on WO<sub>3</sub>NB. b) Schematic illustration of the proposed reaction mechanism for PEC CH<sub>4</sub> conversion into EG.

Angew. Chem. Int. Ed. 2021, 60, 9357-9361

prominent peaks at 2853 and 2924 cm<sup>-1</sup> exhibit an obvious dependence on PEC duration, which can be attributed to methylene (CH<sub>2</sub>) symmetric C–H stretching and antisymmetric C–H stretching of EG,<sup>[33,34]</sup> suggesting the stable production of EG with the PEC duration. In addition, the peaks around 2879 and 2957 cm<sup>-1</sup>, which can be assigned to methyl (CH<sub>3</sub>) symmetric C–H stretching and antisymmetric C–H stretching of CH<sub>3</sub>OH,<sup>[33,34]</sup> gradually increase at the initial PEC stage and become stable after 10 min of PEC. This suggests the transformation of the CH<sub>3</sub>OH into EG during the PEC process. Clearly, the CH<sub>3</sub>OH can be produced by the reaction between the highly reactive OH and methyl radicals ('CH<sub>3</sub>) adsorbed on WO<sub>3</sub>, and act as an intermediate for subsequent formation of EG.

Thus a working mechanism for the PEC CH<sub>4</sub> conversion on the WO<sub>3</sub>NB can be proposed (Figure 4b). According to our DFT calculation results, the reactivity of the 'OH attached on {010} facets is optimized, which can abstract H atom from C-H bond of CH<sub>4</sub>, forming CH<sub>3</sub>.<sup>[30, 35]</sup> Some of these produced ·CH<sub>3</sub> subsequently react with ·OH or ·CH<sub>3</sub> to produce CH<sub>3</sub>OH or C<sub>2</sub>H<sub>6</sub>. Further, the produced CH<sub>3</sub>OH can be further attacked by highly reactive 'OH forming hydroxymethyl radicals (Figure S24). Benefiting from the twinning characteristic of the W atoms on the {010} facets of WO<sub>3</sub>NB, these hydroxymethyl radicals can easily couple to form C-C bonds, yielding high-value EG.<sup>[25,36]</sup> When the surface-bound 'OH is not sufficiently active like the case of WO<sub>3</sub>NF, the CH<sub>3</sub>OH would be preserved as a product. In the meantime, other oxidative species (e.g., photogenerated holes) that often easily lead to over-oxidation of  $CH_4^{[11,29,37]}$  would take the role in oxidizing CH4 to produce CO as observed for WO3NF and NP. Thus 'OH is the key to tuning the production and selectivity of EG.

In summary, we present an effective strategy for selective PEC CH<sub>4</sub> conversion into EG using monoclinic WO<sub>3</sub>. Based on DFT simulation and radicals trapping test, we reveal that the OH bound on the {010} facets of WO<sub>3</sub> photoanodes shows much stronger reactivity, thereby providing highly efficient reactive oxygen species for CH<sub>4</sub> conversion under ambient condition. The in situ DRIFTS confirms that the methanol. which can be attacked by highly reactive 'OH on surface to form hydroxymethyl radicals, is the main intermediate for the production of EG on WO<sub>3</sub>. Furthermore, the C-C coupling active sites provided by the twinning W atoms on {010} facets allow the formation of high-value C2+ oxygenated products. As a result, the prepared  $WO_3NB$  with an optimized  $\{010\}$ facet ratio demonstrates a superior PEC CH<sub>4</sub> conversion performance (EG production rate of 0.47  $\mu$ mol cm<sup>-2</sup>h<sup>-1</sup>) and EG selectivity of 66%. The insights gleaned in this work manifest the key role of reactive oxygen species to enhancing PEC CH<sub>4</sub> conversion efficiency and guide further development in catalyst design for PEC CH<sub>4</sub> conversion.

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### Conflict of interest

The authors declare no conflict of interest.

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