

Article

Ultrathin WO3-0.33H2O nanotubes for CO2 photoreduction to Acetate with high selectivity

Songmei Sun, Motonori Watanabe, Ji Wu, Qi An, and Tatsumi Ishihara

J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b03316 • Publication Date (Web): 30 Apr 2018

Downloaded from http://pubs.acs.org on April 30, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

 Ultrathin WO₃·0.33H₂O nanotubes for CO₂ photoreduction to acetate with high selectivity Songmei Sun^{1*}, Motonori Watanabe¹, Ji Wu¹, Qi An², Tatsumi Ishihara^{1*} 1 International Institute for Carbon-Neutral Energy Research (I²CNER), Kyushu University,

Fukuoka 819-0395, Japan

2 Department of chemical and materials engineering, University of Nevada, Reno, Nevada 89557-0388, USA

* Correspondence: <u>songmeisun@i2cner.kyushu-u.ac.jp</u>, <u>ishihara@cstf.kyushu-u.ac.jp</u>

Abstract

Artificial photosynthesis from CO₂ reduction is severely hampered by the kinetically challenging multi-electron reaction process. Oxygen vacancies (Vo) with abundant localized electrons have great potential to overcome such limitation. However, the surface Vo usually have low concentrations and easily oxidized to lose their activities. For practical application of CO₂ photoreduction, fabricating and enhancing the stability of Vo on semiconductor is indispensable. Here we report the first synthesis of ultrathin WO₃·0.33H₂O nanotubes with large amount of exposed surface Vo sites, which can realize excellent and stable CO₂ photoreduction to CH₃COOH in pure water under solar light. The selectivity for acetum generation is up to 85% with an average productivity of about 9.4 μ molg⁻¹h⁻¹. More importantly, Vo in the catalyst are sustainable and the concentration was not decreased even after 60 h reaction. Quantum chemical calculations and in-situ DRIFT studies revealed the main reaction pathway might be CO₂ \rightarrow ·COOH \rightarrow (COOH)₂ \rightarrow CH₃COOH.

Introduction

Artificial photosynthesis from CO₂ reduction has attracted particular interest because of its dual effects on both suppressing the greenhouse effect and alleviating the dependence on fossil fuels¹⁻⁷. However, the conversion of CO₂ requires high energy input because of the high dissociation energy of the C=O bond (~750 kJ/mol)⁸. Therefore, most of the studied catalysts for photochemical CO₂ reduction were wide band gap semiconductors which could provide negatively enough electrons for CO₂ reduction but only response under UV light, such as TiO_2^{9-12} , $SrTiO_3^{13}$, $ZnS^{14,15}$, $Zn_2GeO_4^{16}$, $InTaO_4^{17}$ etc. In addition, H₂ evolution was usually competed with the CO₂ reduction because the H⁺ reduction is kinetically more favorable¹⁸, severely decreasing the selectivity for CO₂ reduction.

To overcome the above mentioned limitations, a desirable photocatalyst should have a broad solar light absorption along with a highly active and selective CO_2 reduction performance. Among the various semiconductor photocatalyst, tungsten trioxide (WO₃) with a small band gap of 2.4~2.8 eV, has been demonstrated as one of the most promising candidates because of its strong solar light adsorption, stable physicochemical properties, and the relatively low conduction band edge potential for suppressing H⁺ reduction¹⁹⁻²¹. However, the low conduction band potential also suppresses the CO_2 reduction performance because of the insufficient reduction power of the photogenerated electrons. Up to the present, only C₁ products (such as CH₄, CH₃OH) were obtained from CO₂ photo-reduction with a reaction rate lower than 2.5 µmol/g.h²²⁻²⁴. Elevating the conduction band edge and increasing the CO₂ activation on WO₃ surface are indispensable to largely improve its photocatalytic activity.

Construction of atomic scale nanostructure provides unique opportunity to both improve the conduction band potential and CO_2 activation by modifying the particle size and surface microstructure of the photocatalyst. For instance, quantum sized semiconductors have been proved to possess elevated conduction band and exhibit much improved performance for water splitting²⁵⁻²⁸. In addition, when the particle size decreases to quantum size, the extremely large fraction of low-coordinated surface atoms will largely improve the molecular adsorption^{5,29}. A recent study by Zeng *et al.* reported the surface negative charge density generally determine the adsorption and

 activation of $CO_2^{30,31}$. At present, the general approach for improving the surface negative charge density is loading noble metals to improve photocatalytic CO_2 reduction performance^{9,32,33}. However, for metal oxide semiconductors, constructing surface oxygen vacancies (Vo) may be a more economical and accessible approach for increasing surface negative charge density, since the positively charged Vo can accumulate excess free electrons during the photocatalysis and play a similar role to that of noble metals^{34,35}. At present, several studies have been reported on the application of oxygen vacancy in photocatalytic CO_2 reduction^{10,22,36,37}, proving the feasibility of this approach. However, it was found the Vo is not stable and only C₁ product was obtained by these catalyst. Especially, the design principle of stable and sustainable Vo functioned photocatalyst has not been established yet.

In this work, we report a new $WO_3 \cdot 0.33H_2O$ catalyst with large amount of sustainable surface Vo site for highly efficient CO_2 reduction to CH_3COOH under solar light. It is found CH_3COOH is the main product with a high selectivity more than 80% from CO_2 photoreduction. Computational and experimental results proved that Vo active sites can be sustainably used because of an unique C-C bond formation process.

Results and discussion

Quantum sized WO₃·0.33H₂O with high concentration of Vo (H-WO₃) was synthesized by oleate assistant hydrothermal synthesis method. The XRD pattern (Figure S1) of the H-WO₃ sample can be indexed to orthorhombic WO₃·0.33 H₂O (JCPDS card, No. 87-1203). TEM images (Figure 1a,b) indicate an ultrathin tube-like structure with an uniform diameter of ~8 nm and a wall thickness of ~2 nm. The surface structure of the nanotube was further observed by a high resolution TEM (HRTEM) image from the marked area in Figure 1b. As shown in Figure 1c, the lattice spacing along the growth orientation of the nanotube was measured to be 0.37 nm which is corresponding to the d spacing of {200} plane. Besides, {040} lattice plane was also clearly observed with a d spacing of 0.31 nm. Both of the {200} and {040} planes are belong to the [001] zone axis, indicating the



Figure 1 Characterizations for the hydrothermally synthesized H-WO₃ sample. a. low-magnification TEM image of the H-WO₃ nanotube sample. b. High magnified TEM image of single one nanotube. Inset of b: Schematic atomic model of WO₃·033H₂O (Fmm2), clearly showing the atomic configuration of W/O along the [001] direction, red: oxygen, blue: tungsten, gray: hydrogen. c. HRTEM image of the nanotube from the marked area of b. d. W4f XPS spectrum of the as-prepared WO₃·033H₂O samples. e. O1s XPS spectrum of the H-WO₃ sample. f. O1s XPS spectrum of the L-WO₃ sample. g. ESR spectra of different WO₃·0.33 H₂O samples at 300 K in N₂. h. Ultraviolet-visible-near infrared absorption spectrum of the oxygen deficient WO₃·033H₂O samples.

surface plane of the WO₃·0.33 H₂O nanotube is {001} plane. The schematic crystal structure of WO₃·0.33 H₂O along the [001] direction in the inset of Figure 1b which displayed the same orientation and arrangement of {040} and {200} planes as that observed from Figure 1c. Oleate ions played an important role in the formation of this ultrathin nanotube structure (detailed illustration as shown in Figure S2). For comparative study, WO₃·0.33 H₂O (L-WO₃) sample with similar grain size (Figure S1, S3) but lower Vo concentrations was also prepared under the same conditions without

adding oleate ions.

High resolution XPS spectrum revealed the surface chemical environment of the as-prepared $WO_3 \cdot 0.33 H_2O$ samples. Compared with L-WO_3 sample, the W 4f7/2 and W 4f5/2 peaks of the H-WO_3 sample (Figure 1d) are decreased from 35.85 and 37.95 eV to 35.6 and 37.65 eV respectively, indicating a lower valence state of W in the H-WO_3 sample which possesses higher Vo concentration. The surface Vo concentration was estimated from the high resolution O1s XPS spectrum. As shown in Figure 1e, the peak at 530.7 eV is ascribed to the lattice oxygen, while the other two peaks located at 531.6 eV and 533 eV are attributed to the O-atoms in the vicinity of Vo and the O-atoms in the surface OH, respectively. The relative concentration of the surface O-atoms around Vo can be calculated about 36.4% (Figure 1e) in H-WO_3 sample. The L-WO_3 sample possesses much lower surface O-atoms around Vo which is calculated about 22.3% (Figure 1f).

The presence of Vo was also evidenced by ESR (Figure 1g). A characteristic single-electron-trapped Vo signal with a g factor of 2.001 was observed for H-WO₃ and L-WO₃ sample at room temperature in N₂ gas. The higher Vo concentration of the H-WO₃ sample was also observed from the ultraviolet-visible-near infrared absorption spectrum (Figure 1h). Because of the similar grain size, the intrinsic UV-Vis absorption edge of the two different WO₃·0.33 H₂O samples are almost the same, generating a similar intrinsic band gap of about 2.85 eV. However, a higher broad absorption tail appeared in the H-WO₃ sample. A DFT calculation on band structure (Figure S4) proved this absorption tail comes from Vo associated middle band in the band gap of oxygen deficient WO₃·0.33 H₂O sample.

To assess the catalytic performance, photocatalytic CO_2 reduction was performed in pure water under solar light simulator. Before the CO_2 reduction, the catalyst powder was dispersed into 100 mL water and then irradiated under a 300 W Xe lamp for 6 h to eliminate the surface organic contaminants during the catalyst preparation process. Solid state ¹³ C NMR (Figure S5) can confirm the surface organic contaminants were eliminated by this photocatalytic oxidation process. We also conducted a control experiment by Ar-bubbling. It was found there is no organic substance existed in the reaction solution before and after light irradiation. After that, the WO₃·0.33 H₂O catalyst was

then used for the photocatalytic CO_2 reduction reaction. It was found the main product of CO_2 reduction on the as-prepared WO₃·0.33 H₂O samples was CH₃COOH under a simulated solar light irradiation, while a small amount of HCOOH and CO were also detected. H₂ as the mostly reported competitive product only exhibit trace amount in this experiment, indicating the high selectivity of the photocatalyst for CO₂ reduction. Before quantitatively evaluating the catalytic performance, control experiments showed that CH₃COOH, CO and HCOOH cannot be detected by gas chromatography and ion chromatography in the absence of the catalyst or under dark, indicating the product is come from photocatalytic reaction. To further prove the CO₂ reduction, isotopic ¹³CO₂ gas was used as the reactants and the obtained liquid products after 4 h irradiation were identified by GC-MS and NMR. In the mass spectrum extracted from GC-MS analysis (Figure 2a), the molecular ion peak appeared at an m/z value of 60, which can be ascribed to the ionic CH₃COO⁻ with one carbon labeled. According to the standard fragmentation



Figure 2 Photocatalytic CO_2 reduction performance of the as-prepared oxygen deficient $WO_3 \cdot 033H_2O$ samples under simulated solar light irradiation. a. Mass spectra extracted from GC-MS analysis of acetic acid product from $^{13}CO_2$ reduction on hydrated H-WO₃ sample in water. b. ¹H NMR spectra of the obtained acetum product in D₂O saturated water solution by using different $^{12}CO_2$ and $^{13}CO_2$ gas on H-WO₃ catalyst. c. Acetum evolution along with irradiation times in pure water, Inset of a: the acetum formation rate of the different samples. d. Photostability of the as-prepared hydrated H-WO₃ sample for CO₂ reduction under simulated solar light irradiation. e. Mott–

Schottky plot of the as-prepared H-WO₃ electrode in 0.1M Na₂SO₄. f. Mott–Schottky plot of the as-prepared L-WO₃ electrode in 0.1M Na₂SO₄.

pattern of acetic acid, the highest m/z peak appeared at 43 (Figure S6), corresponding to the fragmented CH₃CO. In the ¹³C labeled acetic hydrate product, the highest m/z peak appeared at 44 instead of 43. Besides, the m/z peak of fragmented CH₃ also shifted from 15 to 16, proved the ¹³C specie in the CH₃ fragment. Non-isotope labelled ¹²COOH fragment is come from the tightly adsorbed surface HCO₃ specie (further proved by TPD, DRIFT and DFT calculation in the following section) which could not eliminated by Ar bubbling. ¹H NMR spectrum was also used for detecting the ¹³C species in the obtained acetum product. As shown in Figure 2b, if ¹²CO₂ was used as the carbon source, only singlet was observed around 2.07 ppm which is the characteristic methyl proton peak for CH₃COOH in D₂O. However, if the carbon source was changed into ¹³CO₂ gas, the methyl proton resonance at δ 2.07 is split into two peaks, which is due to a one-bond coupling between ¹³C and ¹H. These studies clearly show that the CH₃COOH product is indeed come from CO₂ reduction.

Figure 2c summarizes the photocatalytic CO₂ reduction activity of the as-prepared WO₃·0.33 H₂O samples. As shown in Figure 2c, the acetum yield gradually increased with the photocatalytic time, and the total yield of acetum obtained by the H-WO₃ sample was about 94 µmol/g after 10 h, corresponding to an CH₃COOH generation rate of 9.4 µmol/g h (Figure 2c). The flat stage for acetum generation before 4h may be ascribed to the low concentration of the dissolved CO₂ (HCO₃⁻) at initial. After the surface pre-adsorbed HCO₃ specie (proved by in-situ DRIFT in the following section) was transformed into the final product, the acetate generation rate may depend on the HCO₃⁻ concentration in the reaction solution. This phenomenon has been observed in electrochemical CO₂ reduction experiment³⁸. For the H-WO₃ sample, the HCO₃⁻ concentration can only be largely increased under light irradiation. An obvious HCO₃⁻ peak at δ 160.4 was observed in ¹³C NMR spectrum after 5h irradiation (Figure S7) and this peak rapidly increased along with the irradiation time. Without light irradiation, there is no peak observed in the ¹³C NMR spectrum within 5h. This finding demonstrates the HCO₃⁻ may be an important intermediate for acetum generation by the H-WO₃ catalyst. There is no O₂ evolved in the reaction system during the CO₂ reduction

experiment. After the photocatalytic reaction for 10 h, a total amount of 17.6 μ mol H₂O₂ was detected by the titanium sulfate spectrophotometric method in the reaction solution, indicating H₂O provide the protons for acetum generation.

Besides the acetum product, a small amount of CO and formic acid were also detected in the reaction system. After 10 h, the total amount of CO (Figure S7a) and HCOOH (Figure S7b) produced by H-WO₃ catalyst is 1.12 µmol/g and 15 µmol/g respectively, indicating the high selectivity (85%) for acetum production. The L-WO₃ sample with lower Vo concentration exhibits an obvious decreased activity for CH₃COOH production but a much increased CO production when comparing with the H-WO₃ sample (Figure S8). The higher photocatalytic activity of L-WO₃ sample for CO production is ascribed to its higher conduction band potential (detailed discussed in the following section).

To further confirm the important role of Vo for the CH₃COOH production, the H-WO₃ sample was oxidized with 30 % hydrogen peroxide (H₂O₂) for five hours to eliminate the surface Vo. After that, the color of the sample was changed from medium blue to light yellow. The CO₂ reduction experiment by the H₂O₂ treated H-WO₃ (H₂O₂-WO₃) sample indicates there is no acetum generated in the final reaction solution, which is similar as the performance of commercial WO₃ (C-WO₃).

To evaluate the photocatalytic stability of the as-prepared H-WO₃ sample, the used catalysts were re-collected, washed and freeze dried for recycling tests. As demonstrated in Figure 2d, after 6 consecutive runs (60 h), the photocatalytic activity of the H-WO₃ nanotube for acetum production was well-maintained. The total amount of the obtained acetum is 562 µmol/g within 60 h, which is equivalent to a turnover number of 1.07 for the consumed photo-generated electrons for acetum generation. This suggests that acetum evolution under these conditions is catalytic. The XRD pattern (Figure S9) of the spent H-WO₃ is almost the same as that of the initial sample. In addition, XPS analysis (Figure S10) revealed the relative concentration of the surface O atoms around Vo were also well maintained (38%) after photocatalytic reaction, further proving the high stability of Vo.

To investigate the thermodynamic feasibility of the as-prepared $WO_3 \cdot 0.33$ H₂O samples for acetum generation, the conduction band potential of the catalysts were studied by electrochemical

measurements. Figures 2e-f show the Mott–Schottky spectrum of the as-prepared WO₃·0.33 H₂O samples, which is usually used for the analysis of the flat band potential (E_{fb}) of semiconductor electrodes³⁹. The E_{fb} value calculated from the intercept of the axis with potential values was at -0.62 and -0.67 V vs. SCE for H-WO₃ and L-WO₃, respectively. For many n-type semiconductors, E_{fb} is considered to be about 0.1 V below the conduction band (E_{cb})⁴⁰. Based on this, the estimated E_{cb} value of the H-WO₃ and L-WO₃ samples were -0.48 and -0.53 V vs. NHE at pH 7. Although the E_{cb} value decreased in H-WO₃ along with the increase of Vo concentration, the photo-generated electrons in the H-WO₃ sample are still energetically enough for CO₂ reduction to acetum, because the CO₂/CH₃COO⁻ redox potential (-0.29 V vs. NHE at pH 7) is much lower than the E_{cb} value of the catalyst. Besides E_{cb} , the conductivity of the H-WO₃ is found slightly decreased because of the increased Vo concentration when comparing with L-WO₃ sample (Figure S11). Although both of the decreased E_{cb} and conductivity may lower the CO₂ reduction activity, the H-WO₃ sample still exhibit a much improved photocatalytic performance, which may be ascribed to its higher Vo concentration and larger BET surface area of the nanotube structure.

An interesting question raised in the experiment is why the as-prepared WO₃ \cdot 0.33 H₂O samples exhibited highly efficient and sustainable photocatalytic activity for acetum production which is an eight electron transfer reduction process. Kinetically, CO is the most possible product from CO₂ reduction because this process only needs two electrons. However, this process is thermodynamically difficult, because the redox potential of CO₂/CO is as high as -0.53 V vs. NHE at pH 7. From the electrochemical measurement, the conduction band electron of the as-prepared WO₃ \cdot 0.33 H₂O samples are not energetically enough for efficient CO₂ reduction to CO. A multi-electron reduction process which possesses a relative low thermodynamic barrier is more possible to realize on these WO₃ \cdot 0.33 H₂O catalyst. For multi-electron reduction, an activation process is necessary for promoting the reaction rate.

To investigate the CO₂ activation, quantum chemical calculations were conducted to explore the adsorption property of CO₂ on the surface of WO₃ \cdot 0.33 H₂O. For the defect-free surface, we

expected that the CO₂ will be on top of surface W atoms, as shown in Figure 3a. The calculated binding energy is 0.08 eV and the C=O bond length is only prolonged from 1.169 Å to 1.177 Å, suggesting a weak activation of CO₂ by perfect {001} surface. For the oxygen deficient {001} surface, there are two possible Vo sites, as shown in Figure 3 b. The O1 site has the longest O-W bond distance (1.972 Å) among these two sites, suggesting this is most plausible Vo site. Thus, we removed the O atom in the O1 site and added one CO₂ molecule to this site. The calculated binding energy of CO₂ on O1 site is 1.32 eV, much larger than that in the defect free surface. The energetically stable configurations of CO₂ are shown in Figure 3c. It was found the C=O bond close to the Vo was prolonged from 1.169 Å to 1.4589 Å, which is similar as the single C-O bond length, indicating the potential advantage of oxygen deficient surface for CO₂ activation.



Figure 3 CO₂ adsorption and activation on different WO₃ \cdot 0.33H₂O samples revealed by DFT calculation (a-c) and in-situ DRIFT observation (d,e). a. CO₂ adsorption on perfect {001} surface, b. the possible V₀ sites on {001} surface, c. CO₂ adsorption on oxygen deficient WO₃ \cdot 0.33H₂O {001} surface, red: oxygen, grey: tungsten, white:

hydrogen, sienna: carbon. d. In-situ DRIFT spectrum of the H-WO₃ sample after ambient temperature adsorption of CO_2 under solar light irradiation. e. In-situ DRIFT spectrum of the L-WO₃ sample after ambient temperature adsorption of CO_2 under solar light irradiation.

To further investigate the role of Vo on the adsorption and activation of CO₂, in-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) study was performed on the as-prepared catalysts. Before introducing CO₂, we analyze the DRIFT spectrum of WO₃·0.33H₂O catalyst in vacuum under dark (Figure S12). The H-WO₃ surface was dominated by strongly adsorbed OH and CO₂ although in vacuum state. The absorption band at ~1420 cm⁻¹ 1620 cm⁻¹ are ascribed to the symmetric and asymmetric OCO stretching vibration of surface bicarbonate HCO₃ specie, which is formed by interaction of Vo adsorbed CO₂ with surface hydroxyl^{9,41}. The slight absorption bands around ~1550 cm⁻¹ are bidentate or monodentate carbonates (b-CO₃²⁻, m-CO₃²⁻) species^{42,43}. The strong absorption bands around 3538 cm⁻¹ are attributed to the stretching vibration of the surface W-OH groups. Another strong absorption band around 2350 cm⁻¹ is ascribed to the asymmetric stretching vibration of linear adsorbed CO₂.

In situ DRIFT spectra of CO₂ with H₂O vapor during photo-irradiation were further recorded for studying the adsorption and activation process. The DRIFT absorption spectra were obtained by subtracting the WO₃·0.33H₂O background in vacuum. Both of the H-WO₃ and L-WO₃ exhibited a similar behavior on the DRIFT under light irradiation. As shown in Figure 3d-e, after introducing CO₂, a distinct linearly absorbed CO₂ was observed at ~2350 cm⁻¹. In situ solar light irradiation of the H-WO₃ sample for 5 min resulted in the appearance of three obvious negative absorption bands at ~1400 cm⁻¹, 1600 cm⁻¹ and 3540 cm⁻¹ along with a new positive absorption peak at ~980 cm⁻¹. The negative absorption bands at ~1400 and 1600 cm⁻¹ are assigned to the decreased concentration of surface bicarbonate under light irradiation. Besides, it was found the absorption bands of bicarbonate species are red shift by -20 cm⁻¹, indicating the HCO₃ specie further adsorbed on the catalyst surface after light irradiation which is consistent with the theoretical simulation result which will be discussed in the following section. The negative absorption band around 3540 cm⁻¹ is relevant to the decreasing of surface hydroxyl OH. The new appeared positive absorption band

around 980 cm⁻¹ is most probably the C-O stretching band of the new formed C-OH from surface HCO₃ reduction. There is no decreased absorption band about bidentate or monodentate carbonate, indicating that these carbonate ($CO_3^{2^-}$) species are not active for further photo-reduction. From the above, the in situ DRIFT study suggests a reaction between the surface bicarbonate specie and hydroxyl to produce the COOH intermediate which has been proved as the kinetically dominant key intermediate leading to CO₂ reduction^{44,45}.

 CO_2 TPD of the H-WO₃ and L-WO₃ samples are provided in Figure S13. Based on the above DRIFT data, the TPD profiles were deconvoluted in four desorption peaks: a low temperature peak at 66 °C assigned to the liner adsorbed CO_2 by surface OH, a middle-temperature peak around 280 °C and 320 °C attributed to bidentate or monodentate carbonate (b- CO_3^{2-} , m- CO_3^{2-}) species, and a high-temperature peak after 350 °C assigned to CO_2 desorption from Vo⁴⁶. From the TPD spectrum, it was found the H-WO₃ sample has much higher Vo adsorbed CO_2 but lower linear adsorbed CO_2 than L-WO₃ sample, further proving the improved CH₃COOH generation in H-WO₃ sample is closely related to the higher Vo adsorbed bicarbonate specie.

The above experimental studies have confirmed the HCO₃ species is a vitally important intermediate for the final acetum production, which is transformed into COOH intermediate under light irradiation. In order to further investigate the hydrogenation mechanism, quantum chemical simulations based on density functional theory (DFT) were conducted on the oxygen deficient H-WO₃ sample. From the DFT simulation, it was found that protonating of the V₀ site adsorbed CO₂ will result in a tightly attached HCO₃ intermediate on the WO₃ surface, because this process further buried the O atom in C–O bond to the Vo site and the protonated H atom can form a hydrogen bond with adjacent oxygen atom, as shown in the initial stage of Figure 4a. This result can explain why desorption of HCO₃ species is difficult during TPD measurement. Further calculation found that once another protonated CO₂ (O= \dot{C} –OH) approaching the HCO₃ intermediate. During this process, the Vo adsorbed O atom in the C–O bond depart from the Vo site because of the formation of adjacent C-C bond (as shown in the final stage Figure 4a). This simulation result coincides with the experimental

observation that the oxygen atom did not fill in the Vo site after photocatalytic reaction, making the Vo is sustainable. The reaction barrier was calculated by searching the transition state of this reaction using the CI-NEB method, which was found to be 0.96 eV as shown in Figure 4a. This energy barrier is much smaller than the band gap of the $WO_3 \cdot 0.33H_2O$ sample, indicating the photogenerated electrons are energetically enough to drive the spontaneous reaction for C₂ species production.

At present, there are mainly two pathways about the photocatalytic CO₂ reduction, depending on whether the hydrogenation or the deoxygenation process is faster^{47,48}. Quantum chemical calculations and in situ DRIFT spectrum revealed the CO₂ reduction pathway on the as-prepared catalyst might be CO₂ \rightarrow ·COOH \rightarrow (COOH)₂ \rightarrow CH₃COOH via a hydrogenation process, as



Figure 4 The possible CO_2 activation and hydrogenation process on oxygen deficient $WO_3 \cdot 0.33H_2O$ {001} surface. a. A summary of the transition state analysis and the energy changes along the reaction pathway of the C₂ product formation by DFT calculation. The reference energy state is selected to be the oxygen defective $WO_3 \cdot 0.33H_2O$ {001} surface with one Vo adsorbed CO_2 and one free CO_2 . b. Schematic illustration of possible reaction pathway for CH_3COOH production.

shown in Figure 4b. Specifically, upon light irradiation, the unsaturated C=O bond in the linear absorbed CO_2 which coordinated with surface W-OH group are attacked by the photo-generated

ACS Paragon Plus Environment

electrons to form one O=C-OH radical intermediate. Meanwhile, a considerable proportion of the photo-generated electrons are trapped in the middle sub-band of the Vo and a proton coupled electron transfer take place on the Vo adsorbed HCO₃ bicarbonate specie to form another $O=\dot{C}-OH$ intermediate radical. The photo-generated electron transfer to Vo can be proved by ESR of the light irradiated catalyst in CO_2 gas (Figure S14), from which one can see the single electron trapped Vo signal was slightly decreased and shifted to lower magnetic field under light irradiation. If there are not sufficient H radical around these new formed COOH intermediates, the adjacent COOH radicals can form C-C bond simultaneously. During this process, the Vo absorbed O atom in the O=C-OH radical gradually departs from the oxygen vacancy (observed from quantum chemical simulation). Different from the deoxygenation process where the Vo adsorbed CO₂ usually leaving one oxygen on the Vo to form CO, this hydrogenation process can refrain the deactivation of Vo from oxygen filling. After the C₂ intermediate formed, the Vo absorbed O atom completely detached from Vo site and then form a HOOC-COOH intermediate. Under light irradiation, proton coupled electron transfer will proceed on the hydrogen bond connected -COOH until the -COOH is reduced to -CH3 and then the acetum product formed. This reaction pathway is very similar as the electrochemical CO₂ reduction to acetate process which has been proved via a CO₂ \rightarrow CO₂⁻⁻ \rightarrow $(COO)_2$ \rightarrow CH₃COO⁻ pathway ³⁸.

From the above reaction pathway, it can be concluded the acetum product is originated from the reaction of Vo adsorbed HCO_3 specie and the surface OH adsorbed CO_2 . Different from the previously reported C_1 product which only needs one active site for reduction of one CO_2 molecule, the acetum product in our experiment is obtained by cooperation of two active sites (Vo and OH) for simultaneously reduction of two CO_2 molecule and then to form a C_2 intermediate (COOH)₂ at initial. In this process, the Vo adsorbed CO_2 is easily detached from Vo after the formation of C-C bond, realizing the sustainable use of the Vo sites. Although CO_2 activation by Vo is widely reported in the previous studies, the deactivation of Vo after photocatalytic reaction is also a general problem. In this study, the phenomenon that the collaboration of surface Vo and OH sites to co-activate two CO_2

molecules to form C_2 intermediate specie can suppress the deactivation of Vo is completely new, which may stimulate other studies on how to increase the selectivity for C_2 species production and how to maintain the activity of Vo active sites.

Conclusion

Ultrathin WO₃·0.33 H₂O nanotubes with large amount of sustainable Vo are firstly explored for photocatalytic CO₂ reduction to CH₃COOH under solar light with a high selectivity up to 85%. After systemically experimental studies and quantum chemical calculations, an innovative hydrogenation mechanism for CO₂ reduction was revealed that the collaboration of surface Vo and hydroxyl group as the main reactive sites are responsible for the highly selective CH₃COOH generation. This innovative hydrogenated mechanism refrains the surface Vo from O-atom filling during the photocatalytic process. Therefore, the catalytic activity of the oxygen deficient WO₃·0.33 H₂O nanotube does not show obvious deactivation even after six repetitive photocatalytic reactions. This study not only puts forward a new strategy for developing high-performance heterogeneous photocatalyst through the atomic scale nanostructure control, but also gives deeper insight into understanding the mechanism of CO₂ activation and then enables us to establish a strategy to design better photocatalysts.

Experimental Section

Preparation. For the H-WO₃ sample, sodium oleate (4.4 mmol) and Na₂WO₄·2H₂O (3 mmol) were successively added to distilled water (50 mL). After vigorous stirring for 2 h, the pH value was adjusted to 1 by dilute HNO₃. Before the suspension was transferred to a 100 mL Teflon-lined autoclave, the volume of the precursor suspension was adjusted to 80 mL by adding additional distilled water. The sealed reaction system was heated at 180 °C for 16 h. The system was then allowed to cool down to room temperature. The obtained solid products were collected by centrifugation, washed with absolute ethanol and dilute HNO₃ (10 μ L in 20 mL ethanol) more than three times, and then freeze-dried for further characterization. For comparison, L-WO₃ sample was prepared without adding sodium oleate in the reaction system. The obtained precursor suspension with pH value of 1 was sealed in a 100 mL Teflon-lined autoclave up to 80% of the total volume and

then heated at 180 °C for 12 h.

Characterization. The purity and the crystallinity of the as-prepared samples were characterized by powder X-ray diffraction (XRD) on a Japan Rigaku X-ray diffractmeter/RINT2500HLR+ using Cu Kα radiation while the voltage and electric current were held at 40 kV and 80 mA. The transmission electron microscope (TEM) analyses were performed by a JEOL JEM-2100F field emission electron microscope. X-ray photoelectron spectroscopy (XPS) was carried out by irradiating the sample with a 320 µm diameter spot of monochromated aluminum Ka X-rays at 1486.6 eV under ultrahigh vacuum conditions (performed on PHI5000VersaProbe). UV-VIS-NIR Spectrophotometer diffuse reflectance spectrum (DRS) of the sample was measured using a Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer. The surface adsorbed organic contaminants were analyzed by solid state ¹³C NMR on a Bruker AscendTM 400 spectrometer by using 2 g sample. The in-situ DRIFT measurement was performed on a Nicolet 8700 DRIFT spectrometer using KBr window. Before measurement, the catalyst powder was placed in the cell and evacuated at room temperature for 5 min. Temperature programmed desorption of CO₂ was performed with commercial one (TPD, Micotrac Bel Japan) under vacuum condition with quadrupole mass spectrometric detector (Anerva AOA-100). Typically, 30 mg of the sample, placed in a glass tube, was pretreated by a He gas flow at 150 °C for 2 h, and then cooled down to 50 °C. The adsorption of CO₂ was performed in a 99.99% CO₂ gas flow (0.1MPa, 100 ml/min) at 50 °C for 2 h. After evacuated with vacuum pump at 50 °C for 15 min, the sample was heated from 50 °C to 500 °C at a rate of 5 °C /min. The TPD signal was recorded by a thermal conductivity detector. Further to identify if the product was formed from CO_2 , labeled experiments were done using ${}^{13}CO_2$ and the products were analyzed with gas chromatograph mass (GC-MS) by Shimadzu GCMS-QP2010 with thermal conductivity detector (TCD). Electron spin resonance (ESR) spectra were recorded at 300K on a Bruker EMX 8/2.7 X-band spectrometer operating under 100 kHz modulation frequency. NMR spectra were acquired on a Bruker AVANCE III 600 spectrometer.

Photocatalytic Test. Photocatalytic CO₂ reduction experiments were performed under a solar

Journal of the American Chemical Society

simulator (PEC-L11) located approximately 10 cm from the sample. The reaction cell (capacity 600 mL) was made of Pyrex glass with a quartz window on top. Typically, 0.05 g of the as-prepared photocatalyst powder was dispersed in 150 mL deionized water and then stirring under the simulated solar light irradiation. Before illumination, CO_2 (50% in Ar) gas was slowly bubbled through the reaction vessel for 30 min. Then the reaction vessel was sealed and irradiated under the solar simulator. During the photocatalytic tests, the temperature of the reaction vessel was maintained at 4 °C by providing a flow of cooling water. For ¹³CO₂ isotopic labelling experiment, pure Ar gas was slowly bubbled through the reaction vessel for 30 min. Then 200 mL of Ar gas was pumped out from the sealed reaction cell and 200 mL of ¹³CO₂ gas was injected. The concentration of acetic acid and formic acid products in the reactor solution were measured using Ion Chromatography System (Dionex, ICS-1000) equipped with an ICE-AS6 column. The concentration of CO was determined with online gas chromatography equipped with a flame ionization detector (Ar carrier) and the catalytic conversion furnace. The amount of H₂O₂ in solution was determined by the titanium sulfate spectrophotometric method via a UV-VIS-NIR Spectrophotometer (Shimadzu UV-3600).

Electrochemical measurements. Electrochemical measurements were performed on an IVIUM electrochemical workstation using a standard three-electrode cell with a working electrode, a platinum mesh as counter electrode, and a standard saturated calomel electrode (SCE) in saturated KCl as reference electrode. The working electrodes were prepared by dip-coating: Briefly, 5 mg of photocatalyst was suspended in 0.1 mL of ethanol in the presence of 1% Nafion to produce slurry, which was then dipcoated onto a 2 cm \times 1.5 cm FTO glass electrode and drying at 25 °C.

Computational Methods. Periodic density functional theory (DFT) calculations with spin-polarization were performed using the Vienna Ab Initio Simulation Package (VASP)⁴⁹⁻⁵². We used the plane wave projector augmented wave (PAW) method for description of the ionic cores. The energy cutoff for the plane wave expansion was 500 eV and the $4\times4\times4$ Γ -centered symmetry reduced Monkhorst-Pack meshes was used, adequate for geometry optimization. For the CO₂ adsorption energy calculation, the Perdew–Burke–Ernzerhof (PBE) functional form of the generalized gradient approximation was used to describe the non-local exchange and correlation.

Convergence is reached if the consecutive energy and force differences are within 10^{-5} eV for electronic iterations and 10^{-2} eV/Å for ionic relaxations, respectively. Three layers of WO₃·0.33H₂O were constructed with the bottom layer fixed. A 10 Å vacuum is applied along the [001] direction to avoid the interaction between periodic images. Dipole corrections and spin-polarization were allowed in all calculations considering the polar nature of the surface. To achieve a better description of the electronic structure of the bulk phase, the band gaps and densities of states of both the ideal and oxygen deficient $WO_3 \cdot 0.33H_2O$ are calculated using the hybrid B3LYP functional with 20% mixing of the Fock exchange. The oxygen deficient $WO_3 \cdot 0.33H_2O$ lattice was created by removing one atomic oxygen from a stoichiometric unit cell of W₃O₉·H₂O so that charge neutrality was maintained. Each of the possible symmetrically unique oxygen vacancy positions was tested. The most energetically stable oxygen defect case was then selected for the band gap and density of states calculations. To evaluate the reaction barrier for the formation of the C₂ product on the WO₃ 0.33H₂O surface, a transition state search utilizing the climbing image nudged elastic band (CI-NEB) method was carried out. Five intermediate configuration images were linearly interpolated between the stable start and end configurations for the CI-NEB calculations. The two start and end configurations are pre-evaluated to be energetically stable and are corresponding to the adsorbed and reacted double CO₂ state. During the CI-NEB calculations, the atomic positions are fully relaxed with the lattice constants held fixed.

Acknowledgements

This work received financial support from the World Premier International Research Center Initiative (WPI Initiative) on Carbon-Neutral Energy Research (I²CNER), MEXT (Japan), National Natural Science Foundation of China (No. 21671197), and the research grant (No. 16ZR1440800) from Shanghai Science and Technology Commission and Grant-in-Aid for Specially Promoted Research (No.16H06293) from MEXT, Japan. JW thanks the funding support from the JSPS, Japan and the NSF, US, under the JSPS-NSF Partnerships for International Research and Education (PIRE). The authors would also like to thank Aleksandar Staykov for performing the calculations.

Supporting Information

 Other sample preparation details, additional TEM images, X-ray diffraction patterns (XRD), calculated density of states, solid state ¹³C NMR, ¹³C NMR of intermediate, EIS Nyquist plots, CO₂-TPD, ESR spectra under light, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

Competing financial interests

The authors declare no competing financial interests.

References

1. Halmann, M. Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells. *Nature* **1978**, *275*, 115–116.

2. Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature* **1979**, *277*, 637–638.

3. Richardson, R. D.; Holland, E. J.; Carpenter, B. K. A renewable amine for photochemical reduction of CO₂. *Nat. Chem.* **2011**, *3*, 301–303.

4. Zhao, Y.; Chen, G.; Bian, T.; Zhou, C.; Waterhouse, G. I. N.; Wu, L.-Z.; Tung, C.-H.; Smith, L. J.;

O'Hare, D.; Zhang, T. Defect-Rich Ultrathin ZnAl-Layered Double Hydroxide Nanosheets for Efficient Photoreduction of CO₂ to CO with Water. *Adv. Mater.* **2015**, *27*, 7824-7831.

5. Liang, L.; Lei, F.; Gao, S.; Sun, Y.; Jiao, X.; Wu, J.; Qamar, S.; Xie, Y. Single Unit Cell Bismuth Tungstate Layers Realizing Robust Solar CO₂ Reduction to Methanol. *Angew. Chem. Int. Ed.* **2015**, *54*, 13971-13974.

6. Gao, C.; Meng, Q.; Zhao, K.; Yin, H.; Wang, D.; Guo, J.; Zhao, S.; Chang, L.; He, M.; Li, Q.; Zhao, H.; Huang, X.; Gao, Y.; Tang, Z. Co₃O₄ Hexagonal Platelets with Controllable Facets Enabling Highly Efficient Visible-Light Photocatalytic Reduction of CO₂. *Adv. Mater.* **2016**, *28*, 6485–6490.

7. Ghuman, K. K.; Hoch, L. B.; Szymanski, Paul.; Loh, J. Y. Y.; Kherani, N. P.; El-Sayed, M. A.; Ozin, G. A.; Singh, C. V. Photoexcited Surface Frustrated Lewis Pairs for Heterogeneous

Photocatalytic CO₂ Reduction. J. Am. Chem. Soc. 2016, 138, 1206–1214.

8. Seo, H.; Katcher, M. H.; Jamison, Photoredox activation of carbon dioxide for amino acid synthesis in continuous flow. *Nat. Chem.* **2017**, *9*, 453–456.

9. Neatų, Ş.; Maciá-Agulló, J. A.; Concepción, P.; Garcia, H. Gold–Copper Nanoalloys Supported on TiO₂ as Photocatalysts for CO₂ Reduction by Water. *J. Am. Chem. Soc.* **2014**, *136*, 15969–15976.

10. Liu, L.; Zhao, H.; Andino, J. M.; Li, Y. Photocatalytic CO₂ Reduction with H₂O on TiO₂ Nanocrystals: Comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry. *ACS Catal.* **2012**, *2*, 1817–1828.

11. Mori, K.; Yamashita, H.; Anpo, M. Photocatalytic reduction of CO₂ with H₂O on various titanium oxide photocatalysts. *RSC Advances* **2012**, *2*, 3165–3172.

12. Tu, W.; Zhou, Y.; Liu, Q.; Yan, S.; Bao, S.; Wang, X.; Xiao, M.; Zou, Z. An In Situ Simultaneous Reduction-Hydrolysis Technique for Fabrication of TiO₂-Graphene 2D Sandwich-Like Hybrid Nanosheets: Graphene-Promoted Selectivity of Photocatalytic-Driven Hydrogenation and Coupling of CO₂ into Methane and Ethane. *Adv. Funct. Mater.* **2013**, *23*, 1743–1749.

13. Arai, T.; Sato, S.; Kajino, T.; Morikawa, T. Solar CO₂ reduction using H₂O by a semiconductor/metal-complex hybrid photocatalyst: enhanced efficiency and demonstration of a wireless system using SrTiO₃ photoanodes. *Energy Environ. Sci.* **2013**, *6*, 1274–1282.

14. Fujiwara, H.; Hosokawa, H.; Murakoshi, K.; Wada, Y.; Yanagida, S. Surface Characteristics of ZnS Nanocrystallites Relating to Their Photocatalysis for CO₂ Reduction¹. *Langmuir* **1998**, *14*, 5154-5159.

Zhou, R.; Guzman, M. I. CO₂ Reduction under Periodic Illumination of ZnS. J. Phys. Chem. C
 2014, 118, 11649–11656.

16. Liu, Q.; Zhou, Y.; Kou, J.; Chen, X.; Tian, Z.; Gao, J.; Yan, S.; Zou, Z. High-Yield Synthesis of Ultralong and Ultrathin Zn₂GeO₄ Nanoribbons toward Improved Photocatalytic Reduction of CO₂ into Renewable Hydrocarbon Fuel. *J. Am. Chem. Soc.* **2010**, *132*, 14385–14387.

17. Tsai, C.W.; Chen, H. M.; Liu, R.S.; Asakura, K.; Chan, T. S. Ni@NiO Core-Shell Structure-Modified Nitrogen-Doped InTaO₄ for Solar-Driven Highly Efficient CO₂ Reduction to

Methanol. J. Phys. Chem. C 2011, 115, 10180–10186.

White, J. L.; Baruch, M. F.; Pander III, J. E.; Hu, Y.; Fortmeyer, I. C.; Park, J. E.; Zhang, T.; Liao,
 K.; Gu, J.; Yan, Y.; Shaw, T. W.; Abelev, E.; Bocarsly, A. B. Light-Driven Heterogeneous Reduction
 of Carbon Dioxide: Photocatalysts and Photoelectrodes. *Chem. Rev.* 2015, *115*, 12888–12935.

19. Klepser, B. M.; Bartlett, B. M. Anchoring a Molecular Iron Catalyst to Solar-Responsive WO₃ Improves the Rate and Selectivity of Photoelectrochemical Water Oxidation. *J. Am. Chem. Soc.* **2014**, *136*, 1694–1697.

20. Tomita, O.; Otsubo, T.; Higashi, M.; Ohtani, B.; Abe, R. Partial Oxidation of Alcohols on Visible-Light-Responsive WO₃ Photocatalysts Loaded with Palladium Oxide Cocatalyst. *ACS Catal.*2016, 6, 1134–1144.

21. Zhang, N.; Li, X.; Ye, H.; Chen, S.; Ju, H.; Liu, D.; Lin, Y.; Ye, W.; Wang, C.; Xu, Q.; Zhu, J.; Song, L.; Jiang, J.; Xiong, Y. Oxide Defect Engineering Enables to Couple Solar Energy into Oxygen Activation. *J. Am. Chem. Soc.* **2016**, *138*, 8928–8935.

22. Wang, L.; Wang, Y.; Cheng, Y.; Liu, Z.; Guo, Q.; Ha, M. N.; Zhao, Z. Hydrogen-treated mesoporous WO₃ as a reducing agent of CO₂ to fuels (CH₄ and CH₃OH) with enhanced photothermal catalytic performance. *J. Mater. Chem. A* **2016**, *4*, 5314–5322.

23. Chen, X.; Zhou, Y.; Liu, Q.; Li, Z.; Liu, J.; Zou, Z. Ultrathin, Single-Crystal WO₃ Nanosheets by Two-Dimensional Oriented Attachment toward Enhanced Photocatalystic Reduction of CO₂ into Hydrocarbon Fuels under Visible Light. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3372–3377.

24. Xie, Y. P.; Liu, G.; Yin, L.; Cheng, H. M. Crystal facet-dependent photocatalytic oxidation and reduction reactivity of monoclinic WO₃ for solar energy conversion. *J. Mater. Chem.* **2012**, *22*, 6746-6751.

25. Liao, L.; Zhang, Q.; Su, Z.; Zhao, Z.; Wang, Y.; Li, Y.; Lu, X.; Wei, D.; Feng, G.; Yu, Q.; Cai, X.; Zhao, J.; Ren, Z.; Fang, H.; Robles-Hernandez, F.; Baldelli. S.; Bao, J. Efficient solar water-splitting using a nanocrystalline CoO photocatalyst. *Nature Nanotech.* **2014**, *9*, 69–73.

26. Zhang, N.; Shi, J.; Maoab, S. S.; Guo, L. Co₃O₄ quantum dots: reverse micelle synthesis and visible-light-driven photocatalytic overall water splitting. *Chem. Commun.* **2014**, *50*, 2002-2004.

27. Zhao, J.; Holmes, M. A.; Osterloh, F. E. Quantum Confinement Controls Photocatalysis: A Free Energy Analysis for Photocatalytic Proton Reduction at CdSe Nanocrystals. *ACS Nano* **2013**, *7*, 4316–4325.

28. Sun, S.; Wang, W.; Li, D.; Zhang, L.; Jiang, D. Solar Light Driven Pure Water Splitting on Quantum Sized BiVO₄ without any Cocatalyst. *ACS Catal.* **2014**, *4*, 3498–3503.

29. Sun, Y. F.; Liu, Q.; Gao, S.; Cheng, H.; Lei, F.; Sun, Z.; Jiang, Y.; Su, H.; Wei, S.; Xie, Y. Pits confined in ultrathin cerium (IV) oxide for studying catalytic centers in carbon monoxide oxidation. *Nat. Commun.* **2013**, *4*, 2899.

30. Zhang, W.; Wang, L.; Liu, H.; Hao, Y.; Li, H.; Khan, M. U.; Zeng, J. Integration of Quantum Confinement and Alloy Effect to Modulate Electronic Properties of RhW Nanocrystals for Improved Catalytic Performance toward CO₂ Hydrogenation. *Nano Lett.* **2017**, *17*, 788–793.

31. Khan, M. U.; Wang, L.; Liu, Z.; Gao, Z.; Wang, S.; Li, H.; Zhang, W.; Wang, M.; Wang, Z.; Ma, C.; Zeng, J. Pt₃Co Octapods as Superior Catalysts of CO₂ Hydrogenation. *Angew. Chem., Int. Ed.*2016, 55, 9548–9552.

32. Xie, S.; Wang, Y.; Zhang, Q.; Deng, W.; Wang, Y. MgO- and Pt-Promoted TiO₂ as an Efficient Photocatalyst for the Preferential Reduction of Carbon Dioxide in the Presence of Water. *ACS Catal.* **2014**, *4*, 3644–3653.

33. Zhai, Q.; Xie, S.; Fan, W.; Zhang, Q.; Wang, Y; Deng, W.; Wang, Y. Photocatalytic Conversion of Carbon Dioxide with Water into Methane: Platinum and Copper (I) Oxide Co-catalysts with a Core–Shell Structure. *Angew. Chem. Int. Ed.* **2013**, *52*, 5776–5779.

34. Cheng, H.;Wen, M.; Ma, X.; Kuwahara, Y.; Mori, K.; Dai, Y.; Huang, B.; Yamashita, H. Hydrogen Doped Metal Oxide Semiconductors with Exceptional and Tunable Localized Surface Plasmon Resonances. *J. Am. Chem. Soc.* **2016**, *138*, 9316–9324.

35. Yin, H.; Kuwahara, Y.; Mori, K.; Cheng, H.; Wen, M.; Huo, Y.; Yamashita, H. Localized Surface Plasmon Resonances in Plasmonic Molybdenum Tungsten Oxide Hybrid for Visible-Light-Enhanced Catalytic Reaction. *J. Phys. Chem. C* **2017**, *121*, 23531–23540.

36. Ji, Y.; Luo, Y. ZnTaO₂N: Stabilized High-Temperature LiNbO₃-type Structure. J. Am. Chem. Soc.

, *138*, 15896–15902.

37. Xi, G.; Ouyang, S.; Li, P.; Ye, J.; Ma, Q.; Su, N.; Bai, H.; Wang, C. Ultrathin W₁₈O₄₉ Nanowires with Diameters below 1 nm: Synthesis, Near-Infrared Absorption, Photoluminescence, and Photochemical Reduction of Carbon Dioxide. *Angew. Chem. Int. Ed.* **2012**, *51*, 2395–2399.

38. Liu, Y.; Chen, S.; Quan, X.; Yu, H. Efficient Electrochemical Reduction of Carbon Dioxide to Acetate on Nitrogen-Doped Nanodiamond. *J. Am. Chem. Soc.* **2015**, *137*, 11631–11636.

39. Xu, P.; Milstein, T. J.; Mallouk, T. E. Flat-Band Potentials of Molecularly Thin Metal Oxide Nanosheets. *ACS Appl. Mater. Interfaces* **2016**, *8*, 11539–11547.

40. Matsumoto, Y. Energy Positions of Oxide Semiconductors and Photocatalysis with Iron Complex Oxides. *J. Solid State Chem.* **1996**, *126*, 227–234.

41. Philippt, R.; Fujimoto, K. DRIFT spectroscopic study of carbon dioxide adsorption/desorption on magnesia/calcium oxide catalysts. *J. Phys. Chem.* **1992**, *96*, 9035-9038.

42. Yang, C. C.; Yu, Y. H.; van der Linden, B.; Wu, J. C. S; Mul, G. Artificial Photosynthesis over Crystalline TiO₂-Based Catalysts: Fact or Fiction? *J. Am. Chem. Soc.* **2010**, *132*, 8398–8406.

43. Su, W. G.; Zhang, J.; Feng, Z.; Chen, T.; Ying, P.; Li, C. Surface Phases of TiO₂ Nanoparticles Studied by UV Raman Spectroscopy and FT-IR Spectroscopy. *J. Phys. Chem. C* **2008**, *112*, 7710–7716.

44. Nie, X.; Esopi, M. R.; Janik, M. J.; Asthagiri, A. Selectivity of CO₂ reduction on copper electrodes: the role of the kinetics of elementary steps. *Angew. Chem., Int. Ed.* 2013, *52*, 2459-2462.
45. Xiao, H.; Cheng, T.; Goddard, III, W. A. Atomistic Mechanisms Underlying Selectivities in C1 and C2 Products from Electrochemical Reduction of CO on Cu(111). *J. Am. Chem. Soc.* 2017, *139*, 130–136.

46. Lin, X.; Yoon, Y.; Petrik, N. G.; Li, Z.; Wang, Z.-T.; Glezakou, V.-A.; Kay, B. D.; Lyubinetsky, I.; Kimmel, G. A.; Rousseau, R.; Dohnálek, Z. Structure and Dynamics of CO₂ on Rutile TiO₂(110)-1×1. *J. Phys. Chem. C* **2012**, *116*, 26322–26334.

47. Liu, L.; Zhao, C.; Li, Y. Spontaneous Dissociation of CO2 to CO on Defective Surface of

Cu(I)/TiO_{2-x} Nanoparticles at Room Temperature. J. Phys. Chem. C 2012, 116, 7904–7912.

48. Habisreutinger, S. N.; Schmidt-Mende, L.; Stolarczyk, J. K. Photocatalytic reduction of CO₂ on

TiO₂ and other semiconductors. Angew. Chem., Int. Ed. 2013, 52, 7372–7408.

49. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B: Condens Matter*: **1993**, 47, 558–561.

50. Kresse, G.; Furthmuller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6*, 15–50.

51. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169–11186.

52. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758–1775.

TOC

CO2

(COOH)

CH3COOH

