Synergizing Inter and Intraband Transitions in Defective Tungsten Oxide for Efficient Photocatalytic Alcohol Dehydration to Alkenes

Melin Duan,‡ Canyu Hu,‡ Hao Li,‡ Yihong Chen, Ruitian Chen, Wanbing Gong, Zhou Lu,* Ning Zhang,* Ran Long,* Li Song, and Yujie Xiong*  

**ABSTRACT:** Photocatalysis under mild conditions is an intriguing avenue for organic chemical manufacturing to confront the serious fossil energy crisis. Herein, we report a direct light-driven alkene production through alcohol dehydration, using non-stoichiometric tungsten oxide of W18O49 nanowires with abundant lattice defects as a photocatalyst. A representative ethylene (C2H4) production rate of 275.5 mmol gcat⁻¹ h⁻¹ is achieved from ethanol (C2H5OH) dehydration, together with excellent selectivity up to 99.9%. The universality of our approach is further demonstrated with other alcohol dehydration. Combining ultrafast transient absorption spectroscopy with in situ X-ray photoelectron spectroscopy, we underline that the inter- and intraband transitions synergistically contribute to such excellent activity. In particular, the intraband transition excites the electrons in defect bands into an energetically “hot” state, largely alleviating the charge recombination. As a result, the C−OH bond of chemisorbed C2H5OH molecules can be effectively dissociated to furnish the formation of C=C bonds. Our work offers a fresh insight into sustainable alkene production with renewable energy input under mild conditions.

**KEYWORDS:** W18O49 nanowire, photocatalysis, defect, ethanol dehydration, intraband transition  

**INTRODUCTION**

Alkenes, a class of organic compounds containing C=\(\text{C}\) bonds, are regarded to be of vital importance in modern chemical manufacturing. Taking the simplest ethylene (C2H4) as the representative, it is one of the largest chemical products in the world and accounts for up to 75% in petrochemical products, which is widely used in the synthesis of polymer materials, pharmaceuticals, and pesticides.⁵ However, the worldwide huge demands toward alkene compounds result in excessive fossil energy consumption. Upon this dilemma, it is an urgent task to seek alternative but sustainable approaches to alkene production, among which biomass-derived alcohol is an appealing candidate to serve as the feedstock via the alcohol dehydration to alkenes.⁶⁻⁸ However, alcohol dehydration is traditionally operated at an elevated temperature using strong acids as catalysts, still facing the grand challenge related to energy and environmental issues. Therefore, a catalytic system using renewable energy input under mild reaction conditions is highly desirable for alcohol dehydration to alkenes.

Recently, sunlight-driven reactions through photocatalysis hold great promise to offer such an attractive route for the sustainable chemical synthesis in comparison with the conventional thermal-driven counterpart.⁶⁻⁸ In principle, light irradiation can induce the intrinsic interband transition of semiconductor photocatalysts (i.e., electron excitation from the valence band (VB) to conduction band (CB)).⁹ Such light harvesting can generate energetic excitons to trigger the molecular activation and bond dissociation on the catalyst surface, turning on the relative chemical reactions. To ensure effective solar-to-chemical energy conversion, two key issues deserve particular attention. The photogenerated excitons should be well maintained before the reactions, while the catalyst surface has to offer a strong chemical interaction with reactant molecules for charge and energy transfer.¹⁰,¹¹ To this end, metal oxides are promising photocatalysts whose lattice matrix can be rationally tailored via defect engineering, inducing multiple synergetic effects on the photocatalytic process in terms of both charge dynamics and molecular chemisorption.¹²,¹³ The emerged defect band can serve as a reservoir for photogenerated electron accumulation, thereby alleviating unfavorable charge recombination. Meanwhile, surface defects enable the metal center to become coordinatively unsaturated, which offers a suitable site for molecular chemisorption and thus builds up an effective channel for electronic interaction. More interestingly, some...
heavily doped semiconductors by defect engineering can also exhibit a strong intraband transition in their defect band, analogously to the localized surface plasmon resonance (LSPR) property. This photophysical property can further excite the electrons into an energetically “hot” state as well as induce a photothermal effect, both of which may fundamentally alter the catalytic activity. Given the attractive merits, defect engineering in semiconductors has received tremendous attention toward the activity improvement of photocatalytic molecular conversion, including \( \text{O}_2 \) activation, \( \text{CO}_2 \) reduction, \( \text{N}_2 \) fixation, and \( \text{CH}_4 \) conversion. Among the various metal oxide photocatalysts, tungsten oxide (WO\(_3\)) is an appealing catalyst with an LSPR-like feature delivered a \( \text{C}_2\text{H}_4 \) generation rate as high as 275.5 mmol g\(_{\text{cat}}\)\(^{-1}\) \( \text{h}^{-1}\) photocatalyzed by the defective WO\(_3\) phase. Recent studies have also reported that the alcohol dehydration can be well photocatalyzed by the defective WO\(_{3-x}\) materials, with high activity improvement through accelerating the charge dynamics. A fundamental alteration of the catalytic activity of alcohol dehydration is still largely insufficient.

Herein, we propose the nonstoichiometric tungsten oxide of W\(_{18}\text{O}_{49}\) NWs with abundant oxygen defects as an attractive photocatalyst candidate toward alcohol dehydration to alkenes. Using \( \text{C}_2\text{H}_5\text{OH} \) as the feedstock, the W\(_{18}\text{O}_{49}\) NW catalyst delivers a \( \text{C}_2\text{H}_4 \) generation rate as high as 275.5 mmol g\(_{\text{cat}}\)\(^{-1}\) \( \text{h}^{-1}\), together with excellent selectivity of 94.9%. Nevertheless, a mechanistic understanding of how the defects in the lattice matrix influence or even decide the activity of alcohol dehydration is still largely insufficient.

RESULTS AND DISCUSSION

Catalyst Characterization

The W\(_{18}\text{O}_{49}\) NW sample was synthesized through a mild solvothermal method using WCl\(_6\) as the precursor. The X-ray diffraction pattern (Figure S1) is well indexed to the monoclinic W\(_{18}\text{O}_{49}\) NW phase with JCPDS No. 71-2450. The morphology of the W\(_{18}\text{O}_{49}\) NW sample was characterized by electron microscopy. Transmission electron microscopy (TEM) images show a one-dimensional ultralong NW feature with the length up to several micrometers, as displayed in Figures 1a and S2. The diameter of NWs is further confirmed to be less than 20 nm by the corresponding high-resolution TEM (HRTEM) image (Figure 1b). Such an ultrahigh length-to-diameter ratio can deliver a large lattice surface, beneficial to exposing metallic active sites. The observed lattice fringe with a spacing of 3.8 Å can be indexed to the \( \{010\} \) plane, indicating the \( \{010\} \) growth direction of W\(_{18}\text{O}_{49}\) NWs. In addition, owing to the absence of any surfactant or capping agent during the synthesis process, the surface of the as-obtained W\(_{18}\text{O}_{49}\) NWs contains no significant contaminants, which is confirmed by XPS (Figure S3).

The valence states of the W element were confirmed by XPS measurements. In detail, high-resolution W 4f core-level spectra (Figure 1c) can be deconvoluted into a mixture of W\(^{6+}\) (binding energy (BE) at 36.0 and 38.2 eV), W\(^{5+}\) (BE at 35.6 and 37.8 eV), and W\(^{4+}\) (BE at 34.7 and 36.9 eV) species, respectively. The atomic ratio of W\(^{6+}\):W\(^{5+}\):W\(^{4+}\) is determined to be 0.4:0.49:0.11. The existence of low-valence W\(^{5/4+}\) species can be rationalized by the nonstoichiometric W/O ratio of 1/2.72. In principle, these low-valence W\(^{5/4+}\) species give rise to the formation of lattice defects with numerous oxygen vacancies in the lattice matrix of W\(_{18}\text{O}_{49}\) NWs, which can contribute to a defect band near the CB in the band alignment (Figure S4). This sub-band induced by lattice defects is partially occupied by the electrons in the valence band (\( \text{V}_{\text{CB}} \)) as well as induce a photothermal effect also acts as a promoter through elevating local reaction temperature. As a result, through monitoring the evolution of reaction intermediates by the in situ ambient-pressure XPS (NAP-XPS) technique, we uncover that the effective exciton preservation can well turn on the rate-determining step (RDS) of alcohol dehydration (i.e., C–OH bond cleavage), then effectively achieving the following \( \beta\)-H elimination to form C≡C bonds.
by coupling the energy in visible and near-infrared (vis−NIR) light. To corroborate this physical property, we collected the UV−vis−NIR light adsorption of our as-synthesized W18O49 NW sample. As shown in Figure 1d, apart from the intrinsic interband transition for a semiconductor below 450 nm, a strong adsorption tail in the NIR region is also clearly observable for W18O49 NWs, derived from the energy resonance of the intraband transition in the defect band. The optical inter- and intraband transitions observed from our W18O49 NW sample coincide with previous reports about optical inter- and intraband transitions observed from our W18O49 NW sample, we are now in a position to examine the catalyst. As a comparison, a stoichiometric WO3 sample (Figure S5) shows a substantially weaker intraband transition owing to the absence of lattice defects.

**Catalytic Performance**

Given the confirmed structure of the as-synthesized W18O49 NW sample, we are now in a position to examine the photocatalytic performance toward alcohol dehydration to alkenes using C2H5OH as the model substrate for C2H4 production. The catalytic experiments were carried out in the gas−solid phase in a sealed reactor (see Figure S6) under Xe lamp irradiation (see details in the Experimental Section in the Supporting Information). Ethanol evaporated into the vapor phase, directly taking part in the reaction with the catalyst. The gas−solid phase system can not only improve the molecular exchange on the catalyst surface, but also avoid the shielding light absorption by solution, thereby benefiting the proceeding of the photocatalytic reaction.36,37 As shown in Figure 2a, a stoichiometric WO3 catalyst is sluggish for C2H5OH dehydration under the full-spectrum illumination, only delivering a low C2H4 generation rate of 35.4 mmol gcat−1 h−1. In sharp contrast, the W18O49 NW catalyst with a strong intraband transition can well trigger the C2H5OH conversion under the same experimental conditions with a 7.8-fold higher C2H4 generation rate (i.e., 275.5 mmol gcat−1 h−1) than the WO3 catalyst. Given that water does not influence the catalytic activity (Figure S7), the significantly improved C2H4 generation rate for the W18O49 NW catalyst can be attributed to the strong intraband transition. Product quantification implies that the desired C2H4 product has an excellent selectivity up to 99.9% only with a trace amount of ethane (C2H6) and carbon monoxide (CO) as byproducts. The control experiment without adding the C2H5OH source cannot obtain any products (for both C2H4 and byproducts), suggesting that no possible surface contaminants impact the catalytic results. To further exclude the influence of the lattice structure difference, we further annealed the W18O49 NW catalyst at 400 °C under an Ar atmosphere to obtain a control sample with low intraband transition (named W18O49-400A, see the structural characterization in Figure S8) to evaluate the catalytic performance. As a result, the C2H4 generation rate of the W18O49-400A catalyst is dramatically reduced to 39.8 mmol gcat−1 h−1 (Figure 2a). This activity decrement consolidates the argument that the intraband transition derived from lattice defects plays a decisive role in boosting C2H5OH dehydration. To ascertain the origin of the C2H4 product, an isotope labeling experiment was performed using C2D5OD as the reactant. As expected, the product of C2D4 with m/z = 32 is readily detected by mass spectroscopy (MS, see Figure S9).

In addition, we employed 1-propanol (C3H7OH) as another feedstock for propylene (C3H6) production. The W18O49 NW catalyst can also well photocatalyze the C2H5OH conversion to C3H6 with a generation rate of 210.8 mmol gcat−1 h−1 (Figure 2b), underlining its universality toward alcohol dehydration. The selectivity of the C3H6 product can reach as high as 99.5% with a trace amount of C2H4, C2H6, and CO as byproducts.

Upon the collected UV−vis−NIR diffuse reflectance spectra (Figure 1d), we can recognize that the W18O49 NW catalyst exhibits both interband and intraband transitions, mainly located in the UV and vis−NIR light region, respectively. To investigate their contribution to catalytic activity, we carried
considering di−irradiation, we further normalized the C2H4 generation rate by intraband transitions for photocatalytic alcohol dehydration to alkenes. Slightly different light intensities of various light pumps.38,39 In particular, 310 or 800 nm pumps (pulse energy of 100 nJ) were selected to excite the inter/intraband transitions, respectively, and the white-light continuum probe was used to detect transient absorption (TA) signals. As depicted in Figure S14, the positive TA signals correspond to the highest C2H4 yield (Figure S11), coinciding with the conclusion normalized by the catalyst.

Durability is also a key parameter for photocatalysis. It is common sense that the defect site is too chemically active to be well retained during catalysis. Impressively, the W18O49 NW catalyst exhibits good catalytic durability in eight cycling tests for C2H5OH dehydration with comparable C2H4 generation rates (Figure 2d). Structural characterization of the catalyst after cycling tests (Figure S12) indicates the well-maintained phase and structure in the W18O49 NW lattice matrix. Furthermore, considering the potential practical application, we assembled a continuous flow reactor (see Figure S6) for the long-term catalytic evaluation over the W18O49 NW catalyst, using Ar flow to introduce C2H5OH gas into the reactor. The passed C2H5OH amount is determined in Figure S13. A 10-h test was carried out, and the generated C2H4 product was monitored simultaneously. As shown in Figure 2e, the C2H4 amount steadily increases with prolonging the reaction time (orange dots), together with the high C2H5OH conversion up to 90% after reacting for 5 h (violet dots). The C2H4 generation rate was also calculated according to the different reaction times, which well remains at more than 200 mmol gcat−1 h−1 during the long-term test (indigo dots). Such remarkable performance shows the great advantage of the W18O49 NW photocatalyst toward coupling solar energy into chemical molecular synthesis.

Charge Dynamics

The activity evaluation inspires us to decipher the intrinsic origin why W18O49 NWs can offer such high catalytic performance. As a photocatalyst, charge dynamics is considered as a vital knob in terms of chemical reactions. We therefore resorted to the ultrafast TAS technique to analyze the transient electron behavior of the W18O49 NW sample under different light pumps.38,39 In particular, 310 or 800 nm pumps were used to detect the excited-state absorption mode for both 310 and 800 nm pumps (pulse energy of 100 nJ) to excite the inter/intraband transitions, respectively, and the white-light continuum probe was used to detect transient absorption (TA) signals. As depicted in Figure S14, the positive TA signals demonstrate the excited-state absorption mode for both 310 and 800 nm pumps. To be of great interest, the probe decay using the 800 nm pump is apparently alleviated at least one order of magnitude, relative to the ones using the 310 nm pump. The slower TA signal decay pumped at 800 nm implies the prolonged preservation of excited electrons through
intraband transition in the defect band of the W₁₈O₄₉ NW sample. To acquire the deep understanding of charge dynamics, we specifically exacted the pertinent time constants from the probe decays at a wavelength of 500 nm through an exponential decay function, as drawn in Figure 3a. The fast relaxation within a few picoseconds (lifetime of τ) is attributed to the electron–phonon scattering process.⁴¹–⁴³ Meanwhile, the eventual recovery of the TA bleach on a longer timescale is indexed to the charge recombination process, whose time constant (τᵣ) relates to the relaxation time of excited electrons to the ground state.⁴⁴–⁴⁶ As we attempt to study the charge dynamics matter, we specifically emphasize the longer relaxation. When pumped at 310 nm for interband transition, τᵣ is determined to be 11.4 ± 1.4 ps. Such a short lifetime indicates that the excited electrons tend to quickly recombine with holes.⁴⁷–⁴⁹ Notably, the lifetime can be substantially prolonged up to 55.9 ± 5.1 ps for 800 nm pumped intraband transition, which manifests the fact that energetically "hot" electrons excited in the defect band can be well preserved to avoid the bleach into the ground state.

To further ascertain the influence of intraband transition on charge dynamics, we implemented in situ XPS experiments under UHV conditions with different light illumination to monitor the electronic states of W species. The spectra under dark conditions were collected as a reference (Figure S15). As displayed in Figure 3b, under UV light irradiation, the shoulder peaks of low-valence W⁴⁺ species become more distinct in comparison with the counterpart under dark conditions. According to the deconvolution results, we quantitatively determined the atomic percentages of various W species (Figure 3c). UV light irradiation can apparently give rise to the increasing ratio of W⁴⁺ species from 15 to 31%. As UV light can only excite the interband transition from the VB to CB, we interpret that the increasing ratio of low-valence W⁴⁺ species is ascribed to the photogenerated electrons localized in W 5d orbitals. To be sharply different, under vis–NIR light irradiation, the valence of W species is only slightly disturbed by the energetically "hot" electron effect, but no extra electrons are excited to fill into W 5d orbitals. Interestingly, when we integrated UV and vis–NIR light (i.e., full spectrum) to illuminate the sample, the evolution of W 4f XPS spectra turns to be much more intense, namely, more apparent increment of W⁴⁺ species (as high as 43%, see Figure 3c). Given that intraband transition dominantly excites the "hot" electrons in the defect band alone, we surmise that such a valence decrease of W species is derived from the robust alleviation of charge recombination by intraband transition, which coincides with the argument from TAS spectra results. The electron excitation and charge dynamics matter are further consolidated by in situ VB spectra. Figure S16 depicts the more decrement of the VB population irradiated by the full spectrum. Concomitantly, the intensity of the defect band sublevel near Eᵢ increases more obviously (see insets in Figure S16). The variation of VB spectra demonstrates the fact that more electrons are excited from the VB and aggregated into the defect band. Related to UV light irradiation, such promotion can be interpreted by the alleviation of charge recombination under the contribution of vis–NIR light-induced intraband transition. Taken together, we propose a photoexcitation process to rationalize the high catalytic activity of the defective W₁₈O₄₉ NW catalyst toward alcohol dehydration to alkenes, involving the synergy of inter- and intraband transitions, as illustrated in Figure 3c. The intraband transition can excite electrons from the VB to CB and finally localize them into the defect band. However, this photoexcitation can only give a very low catalytic activity because the unfavorable charge recombination seriously impedes the electron transfer from adsorbed C–OH bonds to the catalytic site. When the intraband transition occurs under the vis–NIR light irradiation, it can further excite and preserve the electrons in the defect band into a "hot" state,²⁻¹⁹ significantly alleviating the charge recombination to ensure the charge transfer. Meanwhile, a photothermal effect also acts as a promoter for activity improvement.

**Mechanism Study**

Mechanistically, the alcohol dehydration to alkenes is a single-molecule elimination reaction (E1 reaction), involving the initial C–O bond cleavage (RDS) and the subsequent β-H elimination to form C═C bonds.⁴⁴ To fundamentally understand the photocatalytic process toward C₂H₅OH dehydration to C₂H₄ over the W₁₈O₄₉ NW catalyst at the molecular level, we employed in situ NAP-XPS to monitor the evolution of different reaction intermediates about C–O bond cleavage through O 1s and C 1s core-level spectra, respectively, as shown in Figure 4a,b. To avoid the spectrum difference derived from XPS facilities and offer a fairer comparison, we first collected the XPS spectra under UHV conditions to ascertain the surface states of W₁₈O₄₉ NWs, which further served as reference spectra for the following tests under NAP conditions. In particular, the peaks at BEs of 529.9 and 531.6 eV in O 1s spectra (Figure 4a) are ascribed to lattice oxygen and oxygen vacancies in the W₁₈O₄₉ NW lattice matrix, respectively,⁴⁸ while the peak at a BE of 284.8 eV in C 1s spectra (Figure 4b) indicates the existence of adventitious carbon species derived from external environmental contaminants.⁴⁵–⁴⁷ To investigate the adsorption of C₂H₅OH, we introduced a 0.15 mbar of C₂H₅OH gas into the chamber and collected the related XPS spectra after adsorption equilibrium. The peak intensities apparently decrease for both O 1s and C 1s spectra under NAP conditions owing to the negative scattering and absorption effects by the introduced reactant gas in the XPS chamber.⁴⁸ Therefore, we mainly focus on the spectrum changes under NAP conditions. Several assignable peaks about the adsorbed C₂H₅OH molecule on the W₁₈O₄₉ NW surface emerge in both O 1s and C 1s spectra, including the adsorbed hydroxyl (at a BE of 533.1 eV) and carbon elements (i.e., α-C in the CH₃− group and β-C in the −CH₂− group at BEs of 285.8 and 287.1 eV, respectively).⁴⁹–⁵₀ The substantial adsorption can offer a robust electronic interaction between the active site and chemisorbed C₂H₅OH molecules, benefiting the bond activation and cleavage. In this case, the strong C₂H₅OH adsorption can be interpreted by the fact that the lattice defects of the W₁₈O₄₉ NW catalyst can expose the coordinatively unsaturated W atoms on the surface, serving as the suitable site for molecular adsorption.¹²

Furthermore, we carried out continuous full-spectrum irradiation to monitor the changes of XPS peaks. The sample temperature in the XPS chamber was determined to reach about 200 °C, which can well simulate the reaction environments. Quantitative determination about peak intensity is shown in Figure S17 and Tables S1 and S2. As a result, as long as the light was introduced (i.e., "Light + Ethanol" in Figure 4a,b), the relative peak intensity of hydroxyl and α-C difference evidently decreases. Given that both of them involve C–O bonds, we conclude that the light irradiation effectively enables the cleavage of C–O bonds. Along with the
illuminated for 10 min, the peaks undergo dramatic changes. The signals assigned to C₂H₅OH molecules can hardly be recognized, suggesting the effective molecular reaction through C–O bond dissociation. Concomitantly, some new peaks further appear. In O 1s spectra, the peaks at the BEs of 532.6 and 533.9 eV can be indexed to the *OH species from dissociated C–O bonds and adsorbed H₂O* molecules generated through C₂H₅OH dehydration, respectively.⁵¹ Meanwhile, the peaks of α-C and β-C species in C₅H₅OH* groups in C 1s spectra are aggregated into one peak at a BE of 286.5 eV sp² C in the generated C₂H₄ product.⁵² More specifically, a strong peak at a slightly lower BE of 285.5 eV is clearly observed, which can be ascribed to sp² C in the generated C₂H₄ product.⁵³ An affiliated peak at a BE of 287.7 eV can be responsible for the oxidized C≡O group, which evolves to the trace CO byproduct.⁵⁴ Prolonging the illumination for 20 min, the peaks for dehydration products (i.e., H₂O* in O 1s spectra and sp² C₂H₄ in C 1s spectra) are further boosted, together with the consumed intermediate species (i.e., HO* in O 1s spectra and sp² C₂H₅ in C 1s spectra) (see Figure S17), indicating that the reaction can proceed well under light irradiation on the W₁₈O₄₉ NW surface. We would also like to point out that the observed NAP-XPS may only provide a qualitative discussion owing to the intrinsic energy resolution limitation of current XPS measurements. Nevertheless, by virtue of development of synchrotron radiation-based techniques, we highly expect that the related NAP-XPS technique is competent to provide more distinct and convincing results for mechanism studies at the atomic/molecular level.⁵⁴⁵⁵

Taken together, we propose an elimination reaction pathway for photocatalytic C₂H₅OH dehydration to C₂H₄, as illustrated in Figure 4c. The C₂H₅OH molecule is first chemisorbed at the surface defect site through the −OH group (Step I). Under the light irradiation, the electron excitation induces electron transfer from C−O bonds to the W catalytic site to turn on the C−O bond cleavage (Step II). The "hot" electrons excited by inraband transition in the defect band facilitate the charge dynamics to alleviate the unfavorable charge recombination, ensuing the effective bond cleavage. Meanwhile, the photo-thermal effect further promotes this process. As alcohol dehydration is typically regarded to undergo an E1 elimination process, the loss of the leaving group (i.e., −OH group in C₂H₅OH) is the RDS.⁴⁴ We regard that such effectively photoassisted C−O cleavage contributes to the good catalytic performance for the following C₂H₄ generation. A carboxonium intermediate (C₂H₅⁺) is also proposed after C−O bond dissociation based on the mechanism of E1 elimination. Subsequently, the β-H in the −CH₂ group is further attacked by neighboring lattice oxygen with a Lewis base feature, leading to the cleavage of β−C−H bonds (Step III). The loss of protons fast impels electrons in β−C to form C≡C bonds, achieving the C₂H₄ production (Step IV). Finally, the retained OH and H species couple to form H₂O molecules which desorb from the catalytic site (Step V).

**CONCLUSIONS**

In conclusion, we have demonstrated that the defect-rich W₁₈O₄₉ NW photocatalyst can efficiently turn on the alcohol dehydration for alkene production under mild conditions. Apart from the intrinsic interband transition for exciton generation, an inraband transition derived from the defect band decisively contributes to significant activity improvement. Our comprehensive spectroscopic investigations manifest that the energetically "hot" electrons excited by inraband transition can effectively modulate the charge dynamics, preserving the charge separation. As a result, the RDS of C−OH bond cleavage can be well triggered to achieve the following C≡C bond formation. A concomitant photothermal effect supplies a local elevated reaction temperature to further promote the process of alcohol dehydration. Taken together, using C₂H₅OH as the representative, the W₁₈O₄₉ NW photocatalyst delivers a C₂H₄ generation rate of 275.5 mmol gcat⁻¹ h⁻¹ with excellent selectivity up to 99.9%. This work provides the new guideline for sustainable alkene production and demonstrates the multiple roles of defect engineering in photocatalysts for activity improvement.

**EXPERIMENTAL SECTION**

**Photocatalytic Activity Evaluation**

In the typical test, 3 mg of catalyst was dispersed in a 1 mL mixed solution of ethanol and water with a volume ratio of 1:1. Then the dispersion was uniformly coated onto a 1.5 × 3 cm² glass and dried on
a heating table at 50 °C to form a catalyst film. The photocatalytic reactions were carried out in a sealed quartz tube reactor under atmospheric pressure and at room temperature, as illustrated in Figure S6a. A 300 W Xe arc lamp (PLS-SXE300, Perfect light) was employed as the light source with full spectrum. During the reaction, the applied light irradiation conditions were maintained without changes. The UV light (λ < 420 nm) and vis—NIR light (λ > 420 nm) were obtained using a UV reflection filter and a 420 nm cutoff filter, respectively. Prior to photocatalytic tests, the glass coated with the catalyst was placed on a small platform against the inner wall of the quartz tube. Subsequently, 5 mL of ethanol was introduced into the bottom of the quartz tube reactor. After 10 min of argon (99.999%) purge, the reactor was sealed and irradiated for a certain time. The light intensities at the catalyst position were detected using a light irradiance meter to be 1.67, 0.22, and 1.38 W cm⁻² for the full spectrum, UV light, and vis—NIR light, respectively. The local reaction temperatures were determined using an infrared thermometer. After irradiation, the reacted gas was syringed from the reactor and analyzed using a gas chromatograph (GC). The possible hydrocarbon products were detected using a 7890B GC (Ag carrier, Agilent) with a flame ionization detector (FID) and a thermal conductivity detector (TCD), while the possible generated CO and CO₂ were checked using a 7890B GC (Ar carrier, Agilent) with a methanizer, an FID, and a TCD.

In terms of the activity test in the continuous flow reactor (see Figure S6b), the same glass loaded with the catalyst (i.e., 3 mg catalyst on 1.5 × 3 cm² glass) was used and placed in a quartz tube as the reactor with one gas inlet at the bottom and one gas outlet at the top. The argon gas with a rate of ca. 2 mL min⁻¹ was first flowed through a vial containing ethanol and then carried the ethanol vapor into the reactor. The gas passing through the reactor was collected by a gas bag and quantified by GC. To determine the amount of passed ethanol, we weighed the vial containing ethanol by an analytical balance before reaction and after reaction for a certain time, respectively. The weight loss in the first vial can be ascribed to the passed ethanol for reaction.

**In Situ XPS Measurements**

In situ XPS measurements for monitoring the valence states of the W element under UVH conditions were performed at Chemistry Experiment Teaching Center in University of Science and Technology of China. The light with different wavelength cutoffs was shed on the sample (i.e., full spectrum, UV light, and vis—NIR light, respectively) through a sapphire window, using a 300 W Xe arc lamp as the light source. The spectra were collected after light irradiation for 20 min. In situ NAP-XPS measurements for monitoring the reactant species evolution were performed at the beamline of TSL-24A1 in NSRRC. The catalyst was loaded on a silicon sheet and fixed on the sample holder. After the sample chamber was evacuated to the UHV level (up to 10⁻¹⁰ mbar), we collected the XPS spectra as the background. Then 0.15 mbar of ethanol was added into the chamber and held for 20 min for adsorption equilibrium. The high-resolution XPS spectra for ethanol molecule adsorption (O 1s and C 1s) were collected. Finally, the full-spectrum light was shed on the sample through a sapphire window. The spectra were collected again under the light irradiation for 0, 10, and 20 min, respectively. The spectra were calibrated according to the C 1s peak of adventitious carbon species at 284.8 eV.

**Ultrafast TAS Measurements**

All the ultrafast TAS measurements were carried out with a typical transmission pump–probe (UV/vis pump-broadband supercontinuum probe) instrument. In this arrangement, a Ti: sapphire regenerative amplifier (Spitfire Ace, Spectra Physics, Inc.) was employed to produce laser pulses. The output laser was split into several laser beams, one of which was used to generate wavelength-tunable light serving as the pump laser for TAS via a downstream TOPAS instrument. The pump laser was further chopped with a 500 Hz mechanical chopper. Another laser beam propagated through an optical delay line (0–8 ns) and was then focused into a CaF₂ crystal to produce white-light continuum, which served as the probe light in the fs-TA.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacsau.2c00146.

Additional experimental section, additional material characterization, and supplementary photocatalytic test results (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Zhou Lu − Anhui Province Key Laboratory of Optoelectronic Material Science and Technology, School of Physics and Electronic Information, Anhui Engineering Research Center of Carbon Neutrality, Anhui Normal University, Wuhu, Anhui 241002, China; orcid.org/0000-0001-8527-0381; Email: zhoulu@ahnu.edu.cn

Ning Zhang − Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong 999077, China; Email: nzh818@mail.ustc.edu.cn

Ran Long − School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China; orcid.org/0000-0003-4845-9120; Email: longran@ustc.edu.cn

Yujie Xiong − School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China; Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui 230031, China; Anhui Province Key Laboratory of Optoelectronic Material Science and Technology, School of Physics and Electronic Information, Anhui Engineering Research Center of Carbon Neutrality, Anhui Normal University, Wuhu, Anhui 241002, China; orcid.org/0000-0002-1995-8257; Email: yjxiong@ustc.edu.cn

**Authors**

Melin Duan − School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China; Institute of Energy, Hefei Comprehensive National Science Center, Hefei, Anhui 230031, China

Canyu Hu − School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China

Hao Li − Anhui Province Key Laboratory of Optoelectronic Material Science and Technology, School of Physics and Electronic Information, Anhui Engineering Research Center of Carbon Neutrality, Anhui Normal University, Wuhu, Anhui 241002, China

Yihong Chen − School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China

Ruitian Chen − School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China
Wanbing Gong — School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China

Li Song — School of Chemistry and Materials Science, and National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230026, China

Complete contact information is available at: https://pubs.acs.org/10.1021/jacsau.2c00146

Author Contributions

‡M.D., C.H., and H.L. contributed equally.

Notes

The authors declare no competing financial interest.

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