Direct methane conversion to value-added chemicals through photocatalysis is promising but still has great challenges in both efficient activation of C–H bonds and suppression of over-oxidation. Herein, palladium nanoparticles and oxygen vacancies (OVs) co-modified TiO$_2$ photocatalysts are prepared and employed for photocatalytic CH$_4$ conversion at room temperature. Under optimized conditions with O$_2$ and water as the oxidants, a high yield of liquid oxygenates, e.g., 54 693 µmol g$^{-1}$ h$^{-1}$ with a nearly 100% selectivity has been achieved. Mechanism investigations reveal that Pd and OVs synergistically promote charge separation, with Pd and OVs acting as hole and electron acceptors, respectively. Isotopic experiments elucidate that both H$_2$O and O$_2$ are oxygen sources for oxygenate production, where O$_2$ is the predominant one.

### 1. Introduction

As the principal constituent of natural/shale gases, methane (CH$_4$) is a promising industrial feedstock for manufacturing value-added chemicals.[1] However, efficient CH$_4$ conversion is still of a great challenge owing to its high C–H bond energy (439 kJ mol$^{-1}$), low electron affinity (−1.9 eV), and high ionization energy (12.6 eV).[2] The current industrial CH$_4$ conversion via dry/steam-reforming[3] and subsequent Fischer–Tropsch synthesis[4] is an energy-intensive and indirect route, where high temperature (>700 °C) is required.[3] Accordingly, direct CH$_4$ conversion under mild conditions is highly desired.

Photocatalysis has emerged as the green pathway to activate CH$_4$ under mild conditions through the injection of a photo-induced charge carrier instead of thermal energy.[6] The key to efficient photocatalytic CH$_4$ conversion lies in the development of suitable photocatalysts. Recently, ZnO loaded with noble metal was reported to convert CH$_4$ into liquid oxygenates, with oxygen (O$_2$) as the oxidant.[7] Au$_x$-BP promoted CH$_4$ conversion into CH$_3$OH with the reactive hydroxyl radicals (OH), which are formed by O$_2$ with the assistance of water under light irradiation.[8] It is clear that the predominant challenge lies in simultaneous regulation of both activation of CH$_4$ and selectivity of desired products. Suitable co-catalysts like Au and Pd were reported to be the hole/electron acceptors to promote charge separation,[9] as well as accelerating H$_2$O oxidation and O$_2$ reduction to generate reactive oxygen species. Such encouraging advances then provide to some extent understanding of both charge dynamics and surface kinetics during photocatalytic CH$_4$ activation. Besides co-catalysts modification, surface engineering is the other way to promote charge dynamics.[10] It was reported that oxygen vacancies (OVs) and metastable Ti$^{3+}$ played a vital role in determining the photocatalytic performance of TiO$_2$, especially due to the n-type doping and the improved carrier density.[10c,11] Moreover, interfacial resistance could also be regulated through surface engineering.[12] In parallel, surface kinetics could also be optimized by the introduction of surface defects by providing additional chemical adsorption and reactive sites.[13] Given these aforementioned attractive potentials of co-catalyst and OVs modification, the synergy of both would largely promote charge separation and surface reactions.

Besides the design of suitable photocatalysts, reaction conditions including oxidant, solvent, pressure, and reaction time during CH$_4$ conversion are also important taking into account the reaction kinetics. Though it is difficult to gain an efficient activity due to the low solubility of CH$_4$ in H$_2$O, H$_2$O oxidation into ·OH radicals was reported to be essential in the activation of CH$_4$.[14] Meanwhile, H$_2$O could also promote the desorption of the oxygenate products and avoid over-oxidation of CO$_2$.[15] In parallel, a high pressure would increase the concentration of reactants, and a long reaction time might result in deep oxidation. Moreover, the oxidants are also important. Compared with H$_2$O$_2$, O$_2$ is much more benign and economically available, which is beneficial for future industrial application.[16] Therefore, it is critical to study the influence of the reaction conditions on CH$_4$ conversion.

Herein, Pd nanoparticles and OVs co-modified TiO$_2$ photocatalyst were designed to drive CH$_4$ conversion with O$_2$ as the
oxidant in an aqueous solution. The optimized production rate of C1 oxygenate products reached 54,693 μmol g⁻¹ h⁻¹ with ≈98.6% selectivity. Mechanism investigations proved that Pd and OVs acted as the hole and electron acceptors, respectively, making a synergetic contribution to inhibit charge recombination and activate both methane and oxygen gas. Furthermore, the reaction pathway and the oxygen source including O₂ and H₂O were discussed according to the isotopic experiments.

2. Results and Discussion

2.1. Structural Identification

X-ray diffraction (XRD) patterns were conducted to study the phase of crystals. As shown in Figure 1a, XRD patterns displayed the anatase TiO₂ structure (PDF#21-1272) of TiO₂, def-TiO₂, and Pd₀.₅-def-TiO₂. The characteristic diffraction peaks remained the same for all samples. No Pd-associated diffraction peak was observed, indicating the low loading amount or uniform distribution of Pd species. Electron paramagnetic resonance (EPR) spectra were applied to study the unpaired electrons of the catalysts. In Figure 1b, both TiO₂ and def-TiO₂ exhibited a similar EPR signal at g = 2.003, which was attributed to OVs. The improved EPR intensity on def-TiO₂ indicated the successful introduction of OVs into def-TiO₂ during calcination with urea. In addition, Pd₀.₅-def-TiO₂ showed the largest intensity of OVs, which implied that the Pd species loading might be beneficial to more OVs formation by reducing the formation energy of OVs. As shown in Figure S1, Supporting Information, the corresponding low-magnification transmission electron microscope (TEM) images of TiO₂ and def-TiO₂ exhibited that the pristine TiO₂ and def-TiO₂ photocatalysts were nanoparticles. The lattice fringe of d = 0.36 nm was indexed to the (101) facet of anatase TiO₂. Moreover, the high-resolution TEM (HRTEM) image of def-TiO₂ showed an amorphous layer, indicating the successful introduction of OVs. HRTEM image of Pd₀.₅-def-TiO₂ (Figure 1c) showed a 3 nm amorphous layer, which was consistent with the existence of OVs as proven by EPR spectra. The lattice fringe of d = 0.36 nm was indexed to the (101) facet of anatase TiO₂. Figure 1d displayed the fast Fourier transform (FFT) image of Pd₀.₅-def-TiO₂, in which the diffraction rings could be indexed as (101), (200) facet of TiO₂, and (111) facet of Pd. Energy dispersive spectroscopy (EDS)-mapping images showed the elemental distribution of O, Pd, and Ti (Figure 1e), which further proved the successful introduction of Pd nanoparticles. Moreover, specific surface area (S_BET) was measured by the nitrogen adsorption–desorption isotherms (Figure S2, Supporting Information).

Figure 1. a) X-ray diffraction (XRD) patterns and b) electron paramagnetic resonance (EPR) spectra of TiO₂, def-TiO₂, and Pd₀.₅-def-TiO₂ samples. c) High-resolution transmission electron microscope (HRTEM) image, d) fast Fourier transform (FFT) image, and e) EDS-mapping images of Pd₀.₅-def-TiO₂. Red, purple, and green color represent O, Pd, and Ti elements, respectively.
No obvious difference in $S_{BET}$ was detected, implying that surface area would not be the main factor for the improvement of catalytic CH$_4$ conversion investigated later.

2.2. Photocatalytic CH$_4$ Conversion

Photocatalytic activity was evaluated by CH$_4$ conversion conducted in a stainless-steel autoclave reactor with the top irradiation. The detailed oxygenate production was summarized in Table S2, Supporting Information. The targeted C1 products included CH$_3$OH, CH$_3$OOH, and HCHO, while CO$_2$ was regarded as the overoxidation product. The effect of noble metal species was studied by loading Pt, Au, Ag, and Pd (0.5 wt%) on def-TiO$_2$ (Figure 2a). Under the same reaction condition, Pt$_{0.5}$-def-TiO$_2$, Au$_{0.5}$-def-TiO$_2$, and Ag$_{0.5}$-def-TiO$_2$ exhibited a similar yield of C1 products at 10 664, 11 705, and 14 885 μmol g$^{-1}$ h$^{-1}$, respectively. While a much higher performance was observed over Pd$_{0.5}$-def-TiO$_2$ (54 693 μmol g$^{-1}$ h$^{-1}$).

Figure 2. Photocatalytic direct methane conversion over a) different cocatalyst-def-TiO$_2$ for photocatalytic activity. b) Pd$_x$-def-TiO$_2$ for Pd loading content optimization. Investigations on: c) the reaction time, d) the molar ratio of CH$_4$ to O$_2$, e) the total pressure, and f) dosage of H$_2$O over Pd$_{0.5}$-def-TiO$_2$. Reaction conditions: 10 mg catalyst, 100 mL H$_2$O, 2 MPa CH$_4$ and 0.1 MPa O$_2$ for 20 min irradiation with 365 nm light emitting diode (LED) light and maintained at 25 °C.
For the other noble-metal modification including Au, Pt, and Ag, no significant improvements were observed, which is because they were reported as electron acceptors and could not efficiently trap holes for CH₄ oxidation.[19] Such results indicated that Pd was a more suitable cocatalyst compared with other noble metals to drive CH₄ conversion.

The effect of OVs and the loading amount of Pd on CH₄ conversion were then studied. As observed from Figure 2b, in the absence of OVs, pristine TiO₂ presented a low C1 yield of 3994 μmol g⁻¹ h⁻¹. The relatively low activity was attributed to the severe charge recombination of pristine TiO₂. After modifying with OVs, the yield of C1 products improved to 13 765 μmol g⁻¹ h⁻¹ for def-TiO₂, 3.4 times higher than that of pristine TiO₂, indicating the critical role of OVs in promoting CH₄ conversion. Further modification with Pd cocatalyst resulted in a dramatic enhancement of CH₄ conversion. The C1 yield increased from 21 951 to 54 693 μmol g⁻¹ h⁻¹ as the Pd loading varied from 0.1 to 0.5 wt%. The highest yield of C1 products reached 54 693 μmol g⁻¹ h⁻¹ over the optimal photocatalyst Pd₀.₅-def-TiO₂, almost 14 and 4 times that of pristine TiO₂ and def-TiO₂. Further increasing Pd content led to the declined yield of C1 products, which might be caused by the enlarged particle size of Pd cocatalysts.[20] Thus, OVs and the appropriate amount of Pd modification played a vital role in promoting the CH₄ conversion synergistically.[11æ] Reaction conditions including reaction time, the molar ratio of CH₄ to O₂, total pressure, and dosage of H₂O were then investigated on Pd₀.₅-def-TiO₂. As prolonging reaction time, oxygenates produced and gradually occupied the adsorption sites of CH₄. Therefore, further prolonging the reaction time contributed little to the formation of oxygenates while the improved concentration of oxygenates on the surface easily led to the overoxidation of CO₂, and exhibited the improved production rate of CO₂ from 525 to 1172 μmol g⁻¹ h⁻¹ (Figure 2c). Therefore, the short reaction time was beneficial to obtain higher C1 products. The molar ratio of CH₄ to O₂ was optimized on Pd₀.₅-def-TiO₂ at a total pressure of 2.1 MPa (Figure 2d). At CH₄/O₂ = 6/15, a relatively low yield of C1 products reaches only 15 483 μmol g⁻¹ h⁻¹. A higher ratio at CH₄/O₂ = 11/10 led to the increased yield to 27 247 μmol g⁻¹ h⁻¹. The yield of C1 products increased to the highest (54 693 μmol g⁻¹ h⁻¹) at CH₄/O₂ = 20/1. Besides, the yield of CO₂ increased from 311 to 768 μmol g⁻¹ h⁻¹ with the gradually increased molar ratio of CH₄ to O₂. Compared with CH₄, the solubility of O₂ in H₂O is higher,[21] and when the partial pressure of CH₄ increased, the dissolved CH₄ in water increased as well. Therefore, with the increase of dissolved CH₄ in H₂O, the yield of oxygenates generated also increased. Maintaining a constant molar ratio of CH₄ to O₂ (20:1) and lowering the amount of CH₄ and O₂ by lowering the total pressure, the yield of C1 products decreased from 54 693 μmol g⁻¹ h⁻¹ at 2.1 MPa to 3290 μmol g⁻¹ h⁻¹ at 0.6 MPa (Figure 2e). It is clear that the solubility of CH₄ and O₂ plays a crucial role in CH₄ conversion. The dosage of H₂O was then investigated and exhibited in Figure 2f. Along with the increase in H₂O dosage, the yield of C1 products increased from 22 466 to 54 693 μmol g⁻¹ h⁻¹, which is probably attributed to the enhanced mass transfer by water.[22] The wavelength-dependent AQY of C1 oxygenate products was then measured as 1.05% at 365 nm for Pd₀.₅-def-TiO₂ (Table S3, Supporting Information).

### 2.3. Mechanism Investigation

UV-vis diffuse reflectance spectra (UV-DRS) spectra were conducted to determine the light absorbance of the photocatalysts. Compared to TiO₂, def-TiO₂ exhibited a slight improvement in absorbance between 395 nm and 540 nm due to oxygen vacancies (Figure 3a). In addition, TiO₂, def-TiO₂, and Pd₀.₅-def-TiO₂ showed a similar adsorption edge at 380-390 nm, indicating the identical structure of the as-prepared TiO₂-based photocatalysts.

To study the charge transfer of the as-prepared photocatalysts, in situ XPS under light were conducted. Pd₃d XPS spectrum of Pd₀.₅-def-TiO₂ displayed two main peaks located at 340.02 and 334.78 eV, and two minor peaks at 340.87 and 335.82 eV (Figure 3b). The former and the latter were assigned to Pd⁰ and Pd²⁺ species, respectively.[18a] The content of Pd²⁺ species increased from 18.8% in the dark to 31.5% under irradiation, meanwhile, the content of Pd⁰ species decreased from 81.2% to 68.5%, indicating the role of Pd cocatalyst as the hole acceptor.

The band structure of photocatalysts was measured to figure out whether the catalysts can generate reactive oxygen species (ROS). The bandgap energy (Eᵥ) was calculated to be 3.10 eV of TiO₂, 3.04 eV of def-TiO₂, and 3.00 eV of Pd₀.₅-def-TiO₂ by the Tauc plots (Figure S3, Supporting Information). As shown in Figure S4, Supporting Information, Mott–Schottky plots were used to measure the flat band potential, which is located below the conduction band (CB) by 0.1 V for n-type semiconductor.[23] The positive slopes of the three samples indicated that three samples were n-type semiconductors. The correlative CB position worked out at −0.97 V of TiO₂, −0.88 V of def-TiO₂, and −1.05 V of Pd₀.₅-def-TiO₂ vs Ag/AgCl (pH = 7). Accordingly, the energy level of the valence band (Eᵥ) was attained by Eᵥ = Eᵦ + Eᵦᵣ (Eᵦ, Eᵦᵣ, and Eᵦ are the energy level of the valence band, bandgap, and CB, respectively). Therefore, the corresponding valence band worked out at 2.74 V of TiO₂, 2.77 V of def-TiO₂, and 2.56 V of Pd₀.₅-def-TiO₂ vs RHE (pH = 0). The band positions with respect to RHE at pH = 0 are shown in Figure S5, Supporting Information. It suggested the band potentials of the catalysts are theoretically sufficient for the generation of ROS.

In situ solid-state EPR spectra were conducted to further elucidate the photogenerated charge dynamics of def-TiO₂ under light (Figure 3c). Under dark condition, the signal at g = 2.004 was observed, which was attributed to the OVs.[24] Under light illumination for 30 s, the signal intensity of OVs enhanced significantly, indicating that after excitation by light, OVs played a vital role in capturing the migrated photo-generated electrons.[25] However, after illumination for 120 and 240 s, the signal intensity of OVs decreased, which might be the recombination of photogenerated electrons and holes.[26]

Steady-state PL spectra were conducted to study charge separation behavior (Figure 3d). Pristine TiO₂ exhibited a strong PL emission peak at 475 nm, which was corresponding with the severe charge recombination.[24] After introducing OVs, the PL emission peak was relatively quenched, indicating that OVs could promote charge separation.[11æ] The weakest PL peak intensity of Pd₀.₅-def-TiO₂ showed the highest carrier separation efficiency, which was ascribed to the synergistic effect of the OVs and Pd nanoparticles loading. Photocurrent density further
confirmed the charge separation efficiency of the photocatalyst (Figure S6, Supporting Information). A low photocurrent density of 113 μA cm⁻² was observed over pristine TiO₂. After OVs decoration, the photocurrent density for def-TiO₂ showed 1.4 times improvement compared with pristine TiO₂. The highest photocurrent intensity was found to be 227 μA cm⁻² for Pd₀.₅-def-TiO₂, nearly 2.0 times that of pristine TiO₂, indicating the most efficient charge separation efficiency, consistent with the PL analysis. Electrochemical impedance spectroscopy (EIS) showed the smallest radius of the Pd₀.₅-def-TiO₂ compared with others, representing the lowest polarization resistance, which was more favorable for interfacial charge transfer (Figure S7, Supporting Information).

In situ EPR spectra were used to study the ROS under light over Pd₀.₅-def-TiO₂ with DMPO as the radical trapping agent. Figure 4a exhibited DMPO-OH and DMPO-OOH signals in the presence of Pd₀.₅-def-TiO₂ under light irradiation, which indicated ·OH and ·OOH were the ROS during the CH₄ conversion.[27] ROS generation was further evaluated by using COU and NBT as the ·OH and ·OOH radicals probes, respectively. Figure 4b exhibited the fitted kinetic curves of NBT photodegradation, which were used to evaluate the production rate of ·OOH radicals.[28] Pristine TiO₂ showed a low kinetic constant at 0.036 min⁻¹, and the constant of def-TiO₂ was improved to 0.10 min⁻¹. The highest constant was 0.18 min⁻¹ for Pd₀.₅-def-TiO₂. Such results demonstrated that Pd₀.₅-def-TiO₂ exhibited the strongest ability for ·OOH radicals generation. As shown in Figure 4c, TiO₂ and def-TiO₂ showed the similar intensity of 7HC after 10 min irradiation, and the relatively low intensity indicated the moderate ability of TiO₂ and def-TiO₂ to generate ·OH radicals. The strongest PL intensity of 7HC was observed over Pd₀.₅-def-TiO₂, indicating its strongest ability to form the ·OH radicals after 10 min irradiation.

Isotopic labeling experiments over Pd₀.₅-def-TiO₂ were applied to investigate the oxygen sources for oxygenating production. In the presence of H₂¹⁸O and ¹⁶O₂ (Figure 4d), both CH₃¹⁶OH (m/z = 31, 32) and CH₃¹⁸OH (m/z = 33, 34) were detected suggesting that CH₃OH was formed with both O₂ and H₂O as the oxygen sources. Meanwhile, CH₃¹⁶OH was found as the predominant products, thus demonstrating that O₂ was the main oxygen source for CH₃OH production. Further evidence came from the usage of H₂¹⁸O and ¹⁸O₂ system for CH₄ conversion, where CH₃¹⁸OH was the majority one. It was further confirmed that O₂ was the main oxygen source.
Based on the aforementioned analysis, the mechanism of photocatalytic CH$_4$ conversion over the Pd$_{0.5}$-def-TiO$_2$ was proposed in Scheme 1. Electrons were excited to the CB and holes settled on the valence band of Pd$_{0.5}$-def-TiO$_2$ under light irradiation (Equation 1). Then, the holes transferred to the Pd nanoparticle which was confirmed by the in situ XPS spectra and in situ solid-state EPR spectra, activating H$_2$O to form ·OH radicals (Equation 2 and 3). The existence of ·OH radicals was proved by the in situ EPR spectra and COU probe detected by PL spectra. In parallel, electrons transferred to the oxygen vacancies and then reduced the adsorbed O$_2$ to produce ·OOH (Equation 5). The as-formed ·OH radicals next activated CH$_4$ into ·CH$_3$ radicals (Equation 4). As the oxygen source for CH$_3$OH came from both H$_2$O and O$_2$, it was accordingly concluded that ·CH$_3$ radicals reacted with both ·OH radicals and ·OOH radicals (Equation 6 and 7), which were generated from H$_2$O oxidation and O$_2$.
reduction, respectively. The generation of HCHO in the presence of CH₄, formed by oxidation of CH₂OH and CH₃OH, can be described by a reaction where 100% of HCHO is formed from CH₂OH. Consequently, the enhanced charge separation efficiency is achieved over the optimized Pd₀.₅-def-TiO₂ catalyst. In addition, both O₂ and H₂O₂ provide the oxygen sources for CH₂OH formation through H₂O oxidation and O₂ reduction, respectively. This work thus provides effective guidance for the synergistic effect of metal cocatalysts and OVs on direct CH₄ conversion under mild conditions.

4. Experimental Section

Chemicals: Commercial TiO₂ (anatase phase, 60 nm), potassium hexachloroplatinate (IV) (K₂PtCl₆), chloroauric acid (HAuCl₄), chloroplatinate acid (H₂PtCl₆), silver nitrate (AgNO₃), methanol (CH₃OH), barium sulfate (BaSO₄), sodium sulfate (Na₂SO₄), nitrotetrazolium blue chloride (NBT), 15-dimethyl-1-pyrroline-N-oxide (DMPO), and Nafion solution (5 wt%) were purchased from Adamas-Beta. All chemicals were utilized as received without further purification.

Synthesis of OVs-Modified TiO₂: OVs-modified TiO₂ photocatalyst was prepared through the two-step thermal calcination of the mixture of urea and anatase.[11] Typically, a certain amount of urea and anatase TiO₂ were uniformly ground in a mortar, and then underwent calcination under a flow of nitrogen at 550 °C for 4 h in a tubular furnace (99.999 vol%) with a heating rate of 2 °C/min. Afterward, the obtained yellow powder was further calcined in air at 550 °C for 2 h with a ramp rate of 5 °C/min. The as-prepared yellow product was named as def-TiO₂.

Synthesis of Pd and OVs Co-Modified TiO₂ Photocatalyst: Pd and OVs co-modified TiO₂ photocatalysts were synthesized by photodeposition method with def-TiO₂ as the substrate.[12] In a typical experiment, 250 mg def-TiO₂ was suspended in a 30 mL methanol aqueous solution (10 vol%). After being stirred for 5 min, a certain amount of Pd₂Cl₆·6H₂O was added, followed by ultrasonication, then the reactor was sealed and purged with ultrapure argon (99.999 vol%) for 20 min. Afterward, 2.0 MPa CH₄ (99.999 vol%) and 0.1 MPa O₂ (99.999 vol%) were injected into the reactor. The reaction was conducted for 20 min at 25 °C with a circulating cooling device. Gaseous products, as well as CH₃OH in the reactant, were detected by gas chromatography (GC-2014, Shimadzu Co., Ltd.) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID). CH₃OOH was measured by the 1H nuclear magnetic resonance (1H NMR) spectroscopy (Avance III JEOL Ltd.). CH₃OOH and CH₃OH have the same amount of methyl, the molar ratio of CH₃OOH/CH₃OH should be regarded as the area ratio in 1H NMR results. HCHO was quantified by the colorimetric method.[13] Typically, 100 mL color reagent was first prepared by the mixture of 15.0 g ammonium, 0.3 mL acetic acid, and 0.2 mL diacetylmethane. Then, 1.0 mL liquid product was mixed with 4.0 mL distilled water and 1 mL of the above color reagent, which was then maintained at 35 °C for 1 h. The absorbance of the solution was then measured by UV-vis absorption spectroscopy (UV-3600 plus, Shimadzu Co., Ltd.) and used for the quantification of HCHO.

Isotope Labeling Experiment: For the detection of oxygen-source in the products using isotopically labeled H₂:O₂: 20 mg Pd₀.₅-def-TiO₂ photocatalyst was dispersed in 2 mL H₂:O₂ (99%). The reactor was then degassed for 30 min to completely remove air, and then was refilled with 2.0 MPa CH₄ (99.999 vol%) and 0.1 MPa O₂ (99.999 vol%). The reaction was carried out at 25 °C for 6 h. The products were measured by gas chromatography-mass spectrometer (GC-MS) (QP2020, Shimadzu Co., Ltd) equipped with a capillary column.

For the detection of oxygen-source in the products using isotopically labeled H₂:O₂: 20 mg Pd₀.₅-def-TiO₂ photocatalyst was dispersed in 2 mL H₂:O₂. The reactor was then degassed for 30 min to completely remove air, and then was refilled with 2.0 MPa CH₄ (99.999 vol%) and 0.1 MPa O₂ (98%). The reaction was carried out at 25 °C for 6 h. The products were measured by GC-MS (QP2020, Shimadzu Co., Ltd) equipped with a capillary column.

Measurement of Apparent Quantum Yield: The apparent quantum yield (AQY) was measured over def-TiO₂, def-TiO₂, and def-TiO₂ under 365 nm irradiation with the Xe lamp equipped with a band-pass filter as the light source. Light intensity was measured as 74.0 mW cm⁻² by the light intensity meter (PL-MW2000, Beijing Perfectlight Technology Co., Ltd). As the formations of CH₂OH, CH₃OH, and HCHO need 1, 3, and 5 photogenerated charges, respectively,[7] AQY was calculated by the following equation.

\[
AQY = \left( \frac{N(CH₃OOH) + N(CH₃OH) \times 3 + N(HCHO) \times 5}{N(photons)} \right) \times 100\% \tag{1}
\]
N(CH$_2$OOH), N(CH$_3$OH), and N(HCHO) represented the number of CH$_2$OOH, CH$_3$OH, and HCHO. N(photons) represented the number of incident photons.

Monitoring of Hydroxyl Radicals (OH) and Hydroperoxyl Radicals (OOH): In situ EPR was applied to monitor the generation of OH and OOH radicals under light irradiation.$^{13b,34}$ For the detection of OH radicals, 10 mg catalyst was suspended in 5 mL water, with DMPO as the trapping agent. For detecting the OOH radicals, 10 mg catalyst was suspended in 5 mL methanol, with DMPO as the trapping agent as well.

NBT photodegradation method was applied to measure the OOH radicals.$^{32a,33}$ Briefly, 25 mg photocatalyst was first dispersed in the 100 mL NBT aqueous solution (0.02 mM) in dark for 30 min to achieve adsorption–desorption equilibrium. Then the suspension was irradiated with a 365 nm LED lamp and sampled every five minutes, which was measured on the UV-3600 Plus spectrometer after being filtered.

The PL technique was applied to measure the OH radicals according to the reaction between OH and coumarin (COU) to generate 7-hydroxycoumarine (7HC), which could be detected by PL spectra at 450 nm.$^{36}$ Briefly, 25 mg catalyst was dispersed in the 100 mL COU aqueous solution (0.5 mM). Before illumination, the mixture was stirred in dark for 30 min to achieve the adsorption–desorption equilibrium. During light illumination, the suspension was sampled, and filtered at 5 min intervals. Then, the solution was detected by the F4500 spectrofluorometer.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
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