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Efficient and selective photocatalytic CH_4 conversion to CH_3OH with O_2 by controlling overoxidation on TiO_2

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The conversion of photocatalytic methane into methanol in high yield with selectivity remains a huge challenge due to unavoidable overoxidation. Here, the photocatalytic oxidation of CH₄ into CH₃OH by O₂ is carried out on Ag-decorated facet-dominated TiO₂. The {001}-dominated TiO₂ shows a durable CH₃OH yield of 4.8 mmol g⁻¹ h⁻¹ and a selectivity of approximately 80%, which represent much higher values than those reported in recent studies and are better than those obtained for {101}-dominated TiO₂. Operando Fourier transform infrared spectroscopy, electron spin resonance, and nuclear magnetic resonance techniques are used to comprehensively clarify the underlying mechanism. The straightforward generation of oxygen vacancies on {001} by photoinduced holes plays a key role in avoiding the formation of •CH₃ and •OH, which are the main factors leading to overoxidation and are generally formed on the {101} facet. The generation of oxygen vacancies on {001} results in distinct intermediates and reaction pathways (oxygen vacancy \rightarrow Ti-O₂• \rightarrow Ti-OO-Ti and Ti-(OO) \rightarrow Ti-O• pairs), thus achieving high selectivity and yield for CH₄ photooxidation into CH₃OH.

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irect conversion of CH4 into methanol (CH3OH) is one of the most promising methods for methane optimization and utilization. However, CH4 is a very stable and inert molecule due to its negligible electron affinity, low polarizability, and high bonding energy for C-H (the first dissociation energy at 439 kJ mol⁻¹). Thus, high temperatures and pressures are normally required to activate C-H bonds, which greatly increases capital investment and gives rise to operational risks and environmental problems¹. Photocatalysis is a potential way to drive CH₄ oxidation by utilizing photon energy instead of thermal energy. Upon excitation of semiconducting photocatalysts by photons, a series of highly active oxygen-containing radicals formed in photocatalytic CH₄ oxidation can readily activate the C-H bond at room temperature²⁻⁶. However, the activation energy of the C-H bond in CH₄ is much higher than that in the product $(CH_3OH)^7$. Thus, after the first C-H bond of CH_4 is activated by active free radicals to form methyl or methoxy species, these species are easier to be activated and oxidized than CH₄, eventually resulting in overoxidation of CH₃OH to produce CO and CO₂⁸. Especially for gas-phase CH₄ oxidation, the product CH₃OH can easily adsorb onto the surface of photocatalyst (such as TiO₂ and ZnO loaded with various cocatalysts) and become overoxidized to CO and CO₂⁹⁻¹¹.

Due to unavoidable overoxidation, achieving high activity along with high selectivity at the same time is barely realized in the photocatalytic oxidation of CH_4 to CH_3OH^{12-14} . The enhancement of one usually sacrifices the other. It has been found that in aqueous-phase CH₄ oxidation, water can promote the desorption of products from active sites to avoid serious overoxidation^{15,16}. Recently, Ma and Tang et al.¹⁷ reported direct photocatalysis of CH₄ into CH₃OH using a FeO_x/TiO₂ catalyst with H₂O₂ as the oxidant in an aqueous-phase system, resulting in a high CH₃OH selectivity of ~90% but a relatively low yield of ~352 μ mol g⁻¹ h⁻¹. However, the relatively high cost of H₂O₂ greatly limits its commercial application. Using O2 instead of H₂O₂ as the economically viable oxidant would represent substantial progress towards the oxidation of CH_4^{1} . In this case, Ye and coworkers² used molecular O₂ to photooxidize CH₄ on Au/ ZnO with a total organic compound selectivity of 95%. However, the CH₃OH product tends to be overoxidized by •OH radicals formed in the reaction, which results in a CH₃OH selectivity of less than 27% with a yield of 2.0 mmol $g^{-1} h^{-1}$. More recently, Ye and coworkers used a CrOx-decorated Au/TiO2 photocatalyst to reduce the formation of •OH radicals in the reaction¹⁸, which increased the selectivity of CH₃OH to ~50% with a yield of 2.5 mmol $g^{-1}h^{-1}$. As such, the overoxidation of CH₃OH should be partly attributed to the formation of •OH radicals. Furthermore, for the reported catalysts, CH₄ can react with the photoinduced holes to form •CH3 on the surface, and the •CH3 can react with O_2 and superoxide ($O_2^{\bullet-}$) to mainly form CH₃OOH rather than CH₃OH^{2,6,19}. It should be noted that CH₃OOH can readily decompose into HCHO and H₂O^{2,9}. Therefore, as long as •CH₃ and \bullet OH exist in photocatalytic CH₄ oxidation, it is difficult to improve the selectivity of CH₃OH unless a new reaction pathway is introduced to reduce the formation of •CH₃ and •OH through rational catalyst design. It has been reported that the intermediate photocatalytic species are closely related to the arrangement and coordination of the surface atoms on different crystal facets²⁰⁻²⁴.

In this work, two types of anatase TiO₂, {001} or {101}dominated TiO₂ with Ag cocatalysts, are studied for CH₄ photooxidation by O₂. The {001}-dominated TiO₂ shows a durable CH₃OH yield of 4.8 mmol/g/h and a selectivity of ~80%, which are much higher values than those obtained on {101}-dominated TiO₂. A comprehensive study by operando IR, ESR, and NMR reveals that the initial generation of oxygen vacancies on {001} by photoinduced holes can avoid the formation of •CH₃ and •OH in the following reaction steps $(Ti-O_2 \cdot \rightarrow Ti-OO-Ti \text{ and } Ti-(OO) \rightarrow Ti-O^{\bullet}$ pairs) to significantly reduce overoxidation. The scarcity of photogenerated oxygen vacancies on {101} leads to the formation of \bullet CH₃ and \bullet OH, which is the main factor for overoxidation. This study provides a strategy to avoid overoxidation in reforming CH₄ to CH₃OH using other photocatalysts by controlling the generation of photogenerated oxygen vacancies.

Results

Selective photocatalytic oxidation of CH₄ to CH₃OH. Two types of anatase TiO₂ (Supplementary Fig. S1) with predominantly exposed {001} or {101} facets were prepared, called TiO_{2 {001}} and TiO_{2 {101}}, respectively. Silver (Ag) was chosen to decorate TiO₂, which can trap photoinduced electrons to facilitate the separation and transfer of photoinduced carriers²⁵⁻²⁷. Typical oxide semiconductors, such as ZnO and TiO₂, loaded with Ag cocatalysts have been demonstrated to exhibit good photocatalytic activity for CH_4 activation^{10,28}. Bare TiO_2 (including $TiO_{2 \{001\}}$ and $TiO_{2 \{101\}}$) and that with variable Ag loading were evaluated for photocatalytic CH₄ oxidation with molecular O₂ as an oxidant ($CH_4:O_2$ ratio = 20:1). As shown in Fig. 1A, the products of CH4 photooxidation on TiO2 {001} are CH3OH, HCHO, CO, and CO₂. Among these products, the yield of CH₃OH is 950 μ mol g_{cat.}⁻¹ h⁻¹ and the selectivity of CH₃OH is 42%. However, only deep oxidation products (HCHO, CO, and CO_2) are formed on TiO_{2 {101}}, and the production of CH₃OH is invisible (Fig. 1B). This is consistent with previous reports of CH₄ photooxidation by O_2 over TiO₂ (P25) and ZnO^{2,9}. As such, the {001} facet should be favorable for the formation of CH₃OH in CH_4 photooxidation by O_2 , while the {101} facet is inclined to undergo deep oxidation.

We further studied the effect of the Ag loading amount on the catalytic performance. Clearly, a series of Ag loadings on TiO2 can effectively improve the activity of CH4 photooxidation. For TiO2 {001}, a 2.5%Ag and 3.2%Ag loading exhibited a high CH₃OH yield of 4.3 mmol $g_{cat}^{-1}h^{-1}$ with a selectivity of ~70% and a yield of 4.8 mmol $g_{cat}^{-1}h^{-1}$ with an ultrahigh selectivity of ~80%, respectively (Fig. 1A and Table 1). For TiO_{2 {101}, the 2.1%Ag loading shows an optimal CH₃OH yield of 3.3 mmol g_{cat.}⁻¹ h⁻¹ and a selectivity of ~68% (Fig. 1B and Table 1). Furthermore, with increasing irradiation time, the amounts of the total products (including CH₃OH, HCHO, CO, and CO₂) increase gradually with relatively stable CH₃OH selectivity (74-80%) in CH₄ photooxidation of 3.2%Ag/TiO_{2 {001}}. (Fig. 1C and Table 1). Similar results can also be found for 2.5%Ag/TiO_{2 {001}} (Supplementary Fig. S2). The optimal CH₃OH yield and selectivity on 3.2%Ag/TiO2 {001} are much superior to those of most reported photocatalytic systems for CH₄ oxidation to CH₃OH (Supplementary Table S1). And we believe that this is the first study to achieve a high CH₃OH yield and selectivity for CH₄ photooxidation with O₂ at room temperature. For 2.1%Ag/TiO2 {101}, although the amount of the deep oxidation product (HCHO, CO, and CO₂) still increases with increasing irradiation time, the amount of CH3OH barely increases after 2 h of irradiation, which results in a significant decrease in CH₃OH selectivity from 68% to 53% (Fig. 1D and Table 1). Therefore, it can be indicated that the mechanism for CH_4 photooxidation by O_2 on the {001} facet should be different from that on the {101} facet. The synergy between the cocatalyst Ag and the {001} facet can achieve selective and stable photocatalytic oxidation of CH_4 into CH_3OH by O_2 .

Characterization of Ag/TiO₂ nanocatalysts. To further clarify the correlation between photocatalytic performance and the crystal facet on Ag/TiO₂ nanocatalysts, high-resolution transmission electron microscopy (HRTEM, 3100FEF spectrometer) and X-ray photoelectron spectroscopy (XPS) were performed to validate the



Fig. 1 Photocatalytic CH₄ **conversion with molecular O**₂**.** CH₃OH selectivity and product yields for a series of Ag-loaded TiO₂ photocatalysts with predominantly exposed **A** {001} facets (0-5.0%Ag/TiO_{2 {001}}) and **B** {101} facets (0-3.0%Ag/TiO_{2 {101}}) under 2 h of irradiation. Time course for CH₃OH selectivity and product yields for **C** 3.2%Ag/TiO_{2 {001}} and **D** 2.1%Ag/TiO_{2 {101}} under irradiation. Reaction conditions: 10 mg Ag/TiO₂, 100 mL water, 2 MPa CH₄, 0.1 MPa O₂, 25 °C, light source: 300 W Xe lamp, light intensity of 450 mW/cm².

Photocatalysts	CH ₄ pressure (Mpa)	O ₂ pressure (Mpa)	Amount of product (μ mol)				CH₃OH	СН₃ОН	Organic compound
			CH₃OH	нсно	со	CO ₂	yield (mmol/g/h)	selectivity (%)	selectivity (%)
TiO _{2{001}}	2.0	0.1	19.0	17.5	0.2	8.6	0.95	41.9	80.5
1.0%Ag/TiO _{2{001}}	2.0	0.1	30.4	11.0	0.4	9.0	1.52	59.8	81.5
1.7%Ag/TiO _{2{001}}	2.0	0.1	47.4	11.5	0.5	12.5	2.37	65.9	82.0
2.5%Ag/TiO _{2{001}}	2.0	0.1	86.0	18.7	0.7	17.8	4.30	69.8	85.0
3.2%Ag/TiO _{2{001}}	2.0	0.1	95.4	12.8	0.7	11.3	4.77	79.4	90.0
5.0%Ag/TiO _{2{001}}	2.0	0.1	53.0	8.9	0.6	11.8	2.65	71.3	83.3
TiO _{2{101}}	2.0	0.1	0.0	26.3	0.5	11.2	0.00	0.0	69.2
1.3%Ag/TiO _{2{101}}	2.0	0.1	28.7	12.4	0.4	9.6	1.44	56.2	80.4
2.1%Ag/TiO _{2{101}}	2.0	0.1	65.6	15.1	0.7	14.0	3.28	68.7	84.6
3.0%Ag/TiO _{2{101}}	2.0	0.1	43.1	10.5	0.4	12.7	2.15	64.6	80.4

morphology and elemental structure of 2.5%Ag/TiO_{2 {001}} and 2.1% Ag/TiO_{2 {101}}. According to the HRTEM results, TiO_{2 {001}} exhibits a uniform square morphology with an average length of 54 nm and thickness of 4.6 nm (Fig. 2A), and TiO_{2 {101}} possesses an octahedral morphology with an average size of 17 nm (Fig. 2D). The lattice spacing parallel to the lateral facets and the top is 3.56 and 2.38 Å,

corresponding to the {101} and {001} facets of anatase TiO₂, respectively (Fig. 2B–E). As such, it can be found that both TiO_{2 {001}} and TiO_{2 {101} nanoparticles coexpose {001} and {101} facets, and the percentage of dominant facets should be ~87% of the {001} facet in TiO_{2 {001}, and ~92% of the {101} facet in TiO_{2 {101}. Furthermore, HRTEM clearly shows that the Ag cocatalyst with a particle size of



Fig. 2 Photocatalyst characterization. A-C HRTEM images of 2.5%Ag/TiO_{2 {001}}. **D**, **E** HRTEM images of 2.1%Ag/TiO_{2 {101}}. **F** Ag 3*d* XPS spectra for 2.5%Ag/TiO_{2 {001}} (red line) and 2.1%Ag/TiO_{2 {101}} (black line).

~1.5 nm was selectively photodeposited onto the {101} facet of 2.5% Ag/TiO_{2 {001}} as shown in Fig. 2A, B. The chemical states for the Ag species on 2.5%Ag/TiO_{2 {001}} were characterized by XPS (Fig. 2F), and the Ag $3d_{5/2}$ peak observed at 368.0 eV can be associated with metal Ag nanoparticles. Similarly, on 2.1% Ag/TiO_{2 {101}}, the Ag cocatalyst was also selectively photodeposited onto the {101} facet. However, due to the larger {101} facet, Ag can be dispersed better and smaller (<1.0 nm) than that on 2.5%Ag/TiO_{2 {001}} (Fig. 2D, E), which is reflected redshift observed for the Ag $3d_{5/2}$ peak (0.2 eV) in the XPS spectrum, as shown in Fig. 2F. According to the XPS results in Supplementary Fig. S3, titanium atoms exist in the form of Ti⁴ $^+$ –O bonds in both TiO_{2 {101}} and TiO_{2 {001}}²⁹, as confirmed by the Ti $2p_{3/2}$ and $2p_{1/2}$ XPS peaks at 458.8 and 464.5 eV, and the O 1s XPS spectra show two peaks at 530.0 and 531.4 eV ascribed to lattice oxygen in Ti-O²⁻-Ti bonds and OH groups on the surface of TiO₂³⁰. In addition, no fluorine or chlorine atoms are present on Ag/TiO₂ catalysts. The elemental composition of Ag and Ti was studied by energy dispersive spectroscopy (EDS), as shown in Supplementary Fig. S4. In addition, according to N2 adsorption and desorption experiments (Supplementary Fig. S5), the BET surface area of TiO_{2 {101}} (100.6 m²/g) is slightly higher than that of TiO_{2 {001}} (84.5 m² g⁻¹). Due to the particle accumulation, both TiO_{2 {101}} and TiO_{2 {001}} are porous with similar pore diameters 14.3 and 14.9 nm, respectively. As such, compared with TiO2 [101], the higher photocatalytic activity and selectivity on TiO2 {001} can be mainly ascribed to crystal plane and elemental structure rather than surface area and porosity.

Reactive intermediate by operando and in situ characterization. To gain insight into the different photocatalytic mechanisms for CH_4 photooxidation on the {001} and {101} facets of TiO₂, reactive intermediates were detected by operando ATR-FTIR experiments on 2.5%Ag/TiO_{2 {001}} and 2.1% Ag/TiO_{2 {101}} in the aqueous phase. The change in the difference spectra before light irradiation was also taken as the reference and indicator. It is certain at first that all the spectra observed under different conditions showed no change before light irradiation (Supplementary Figs. S6-S9). For the 2.5%Ag/TiO2 {001} photocatalyst in the aqueous-phase saturated with Ar and O_2 (Ar + O_2) (Fig. 3A in 1st column), light irradiation led to the appearance of several peaks located at 943, 842, and 812 cm⁻¹. The peaks in the $800-1000 \text{ cm}^{-1}$ region were specifically assigned in previous reports^{31,32} to the O–O stretching of a surface peroxo species Ti– (OO) at 943 cm^{-1 32,33}, Ti–OOH at 842 cm^{-1 31}, and Ti–OO–Ti at $812 \text{ cm}^{-1} \frac{32,34-36}{5}$. To validate this assignment, operando FTIR experiments were performed for the adsorption of H2O2 on the surface of TiO2 {001} over time, and it was confirmed that the signal in the region of $800-1000 \text{ cm}^{-1}$ corresponds to free and adsorbed H₂O₂ (Supplementary Fig. S10). The intensities of the peaks at 943 and 812 cm⁻¹ increase immediately with the light irradiation time and drop down quickly after the light is turned off, suggesting that the intermediate species of Ti-(OO) and Ti-OO-Ti are photoinduced and metastable. Besides, these intermediate species show few changes with time under the light. However, when CH₄ was introduced into the aqueousphase system instead of Ar (CH₄ + O₂), both peaks at 943 and 812 cm^{-1} decreased significantly with light irradiation (Fig. 3A in 2nd column), suggesting the consumption of intermediate species (Ti-(OO) and Ti-OO-Ti) in the presence of CH₄. Instead, two new peaks appear in the region of $1000-1100 \text{ cm}^{-1}$, which can be



Fig. 3 Reactive intermediates on the {001} and {101} facets. A Operando ATR-FTIR matrix for 2.5%Ag/TiO_{2 {001}} and 2.1% Ag/TiO_{2 {101}} with a 4 mL aqueous phase in a (Ar + O₂) and (CH₄ + O₂) atmospheres before, during, and after light irradiation. **B** In situ ESR spectra for 2.5%Ag/TiO_{2 {001}} (left) and 2.1% Ag/TiO_{2 {101}} (right) with 300 µmol H₂O loading in O₂ (bottom) and (CH₄ + O₂) (upper) atmospheres before and during light irradiation. We fit the ESR data with the easyspin programs. **C** Ex situ ¹⁷O NMR spectra for 2.5%Ag/TiO_{2 {001}} (upper) and 2.1% Ag/TiO_{2 {101}} (lower) in a (CH₄ + ¹⁷O₂) atmosphere before and after light irradiation. The signals marked by asterisks are spinning sidebands. We fit the ¹⁷O NMR data with the Dimfit programs.

assigned to the C–O stretching modes of $\rm CH_3OH$ and $\rm Ti–O–CH_3{}^{37}.$

Compared with the 2.5%Ag/TiO2 {001} photocatalyst, no peak appears in the 800–1000 cm⁻¹ region for the 2.1%Ag/TiO_{2 {101}} photocatalyst in the aqueous phase with $Ar + O_2$ during light irradiation (Fig. 3A in 3rd column). It is suggested that the intermediates of Ti-(OO) and Ti-OO-Ti are not photoinduced on 2.1%Ag/TiO2 {101}. A similar change in spectral behavior is observed for 2.1%Ag/TiO_{2 {101}} in the aqueous phase with $CH_4 +$ O2 during light irradiation (Fig. 3A in 4th column), except for the presence of the peaks in the region of $1000-1100 \text{ cm}^{-1}$ due to CH₃OH and Ti-O-CH₃ formation during light irradiation. Notably, the peaks in the region of $1000-1100 \text{ cm}^{-1}$ on 2.1% Ag/TiO_{2 {101}} are much weaker than those on 2.5%Ag/TiO_{2 {001}} (Fig. 3A in 2nd and 4th columns) indicating that CH₄ activation on the {001} facet should make it easier to form CH₃OH and Ti–OCH₃. In addition, a new peak located at 966 cm⁻¹ can be assigned to the O-O stretching mode of CH₃OOH (Fig. 3A in 4th column)38.

We used in situ ESR spectroscopy to follow the formation of paramagnetic intermediates on the {001} and {101} facets (Fig. 3B). For 2.5%Ag/TiO₂ {001} with 300 µmol H₂O loading in a 24 µmol O₂ atmosphere, two sets of ESR signals appeared upon light irradiation (Fig. 3B, left). The strong signal at g = 1.9996 is associated with oxygen vacancies arising from trapped photo-induced holes at surface oxygen. According to previous reports^{39,40}, the signal for orthorhombic symmetry at $g_{zz} = 2.023$, $g_{yy} = 2.007$, and $g_{xx} = 2.000$ is ascribed to surface

superoxide (Ti-O₂•) sites. O₂•- is usually stabilized on a metallic cationic site so that the electrostatic interaction splits the $2\pi^*$ antibonding orbitals by a certain amount (δ) due to the local cationic crystal field. The g_{zz} value can be measured by the equation $g_{zz} = g_e + 2\lambda/\delta$, where λ is the spin-orbit coupling constant of oxygen⁴⁰. As such, $g_{zz} = 2.023$ indicates that $O_2^{\bullet-}$ is stabilized at the Ti sites for the oxygen vacancies. Combined with the operando FTIR results, the surface superoxide can be converted into surface peroxo species by the reduction of photoinduced electrons. However, when 30 µmol CH4 was introduced into the O_2 -Ag/TiO_{2 {001}} system ((CH₄ + O₂)-Ag/ TiO_{2 {001}}), both ESR signals decreased obviously upon light irradiation, indicating the consumption of paramagnetic intermediates (oxygen vacancies and Ti-O2) in the presence of CH4. Compared with 2.5%Ag/TiO_{2 {001}}, no surface superoxide appears for 2.1%Ag/TiO2 {101} with a 300 µmol H2O loading in a 24 µmol O₂ atmosphere during light irradiation (Fig. 3B, right), except for a small number of oxygen vacancies associated with the signal at g = 1.9996. Furthermore, the amount of oxygen vacancies does not change in the presence of 30 µmol CH₄, indicating that oxygen vacancies are not involved in CH4 photooxidation by O2 on 2.1%Ag/TiO_{2 {101}}. In addition, the pair of signals at g = 2.03and 1.96 should be assigned to the background signal of in situ ESR tube (Supplementary Fig. S11).

Ex-situ ¹⁷O MAS NMR experiments were used to follow the transfer and evolution of oxygen in CH₄ photooxidation by ¹⁷O₂ on TiO₂ photocatalysts (Fig. 3C). For 2.5%Ag/TiO₂ {001} in a 24 μ mol ¹⁷O₂ and 30 μ mol CH₄ atmosphere, three NMR signals

appeared after 0.5 h of light irradiation. According to the previous reports⁴¹, the resonances at 480–570 ppm should arise from three coordinated oxygen species in the bulk of TiO₂; the peaks at higher frequencies (600-750 ppm) can be assigned to two coordinated oxygen species on the surface of TiO₂; the signals at much lower frequencies (100-300 ppm) can be attributed to hydroxyl groups (Ti-OH); the signals at -100-10 ppm can be attributed to adsorbed H₂O. As such, the signals observed at -24and 180 ppm are associated with $H_2^{17}O$ and surface terminal hydroxyl (Ti-¹⁷OH), respectively (Fig. 3C, upper). Due to the deshielding effect of CH₃, the ¹⁷O NMR signal of Ti-OCH₃ should shift to a lower field than that of Ti-OH. Accordingly, we assign the ¹⁷O NMR signal at 263 ppm to Ti-OCH₃ (Fig. 3C, upper), which is in good agreement with the formation of -OCH₃ in the operando IR experiment for CH₄ oxidation. Similar results are obtained on 2.1%Ag/TiO_2 $_{\{101\}}$ in a 24 μmol $^{17}O_2$ and 30 μmol CH₄ atmosphere before and after light irradiation (Fig. 3C, lower). However, the ¹⁷O signals at 180 ppm and 263 ppm are much lower than those for 2.5%Ag/TiO2 {001}, indicating that the O transfer efficiency from O₂ to Ti-OCH₃ and Ti-OH on the {001} facet in the photoreaction is much higher than that on the {101} facet. Combined with the operando FTIR and in situ ESR results, this can be attributed to the difference in the photocatalytic mechanism between the {001} and {101} facets, rather than the difference in the catalytic activity, because of the difference in reactivity (Fig. 1) is far from matching the difference in the O transfer efficiency.

Distinct photocatalytic mechanism of CH₄ oxidation by O₂ on the $\{001\}$ facet. To detect the direct participation of CH₄ and O₂ in the formation of CH₃OH, isotope labeling NMR experiments using ${}^{13}CH_4$ and ${}^{17}O_2$ were conducted under 80 kPa ${}^{13}CH_4$ mixed with 20 kPa ¹⁷O₂ on 2.5%Ag/TiO_{2 {001}} and 2.1% Ag/TiO₂ {101} in 50 mL water for 4 h. Figure 4A shows the ¹H NMR spectra for the product obtained from photocatalytic CH₄ oxidation in various atmospheres. For 2.5%Ag/TiO_{2 {001}} in a ¹²CH₄ and ¹⁶O₂ atmosphere, the strong peak at 3.26 ppm corresponds to ¹²CH₃OH, and the weak peak at 3.77 ppm corresponds to trace ¹²CH₃OOH. Using ¹³CH₄ instead of ¹²CH₄, both peaks split into two peaks due to ¹H-¹³C J coupling (~140 Hz) for the methyl groups in the formed ¹³CH₃OH (3.40 and 3.12 ppm) and ¹³CH₃OOH (3.62 and 3.91 ppm) (Fig. 4A, upper). Similar results are also obtained on 2.1%Ag/TiO_{2 {101}} (Fig. 4A, lower). It can be indicated that the product CH₃OH indeed originates from CH₄ conversion on both 2.5%Ag/TiO_{2 {001}} and 2.1% Ag/TiO_{2 {101}}. Interestingly, when the reaction was carried out on 2.5%Ag/TiO₂ $_{\{001\}}$ in a 13 CH₄ and 17 O₂ atmosphere, the FWHM (full width at half maximum) for the 13 CH₃OH signal obviously increased (Fig. 4A, upper). It should be noted that the FWHM of the signal for dissolved ${}^{13}CH_4$ (0.20 and -0.04 ppm) in the ${}^{13}CH_4$ and ${}^{17}O_2$ atmosphere is consistent with that of dissolved ${}^{13}CH_4$ in the ¹³CH₄ and ¹⁶O₂ atmosphere (Fig. 4A, upper). Thus, the widening of the ¹³CH₃OH signal is due to weak J coupling (1.96 Hz) between the methyl proton and ¹⁷O, rather than any error related to the spectrometer and operation. On the other hand, when the reaction was carried out on 2.1% Ag/TiO_{2 {101}} in a ¹³CH₄ and ¹⁷O₂ atmosphere, the FWHM for the signal for the product ¹³CH₃OH barely increased compared with that of the product ¹³CH₃OH in a ¹³CH₄ and ¹⁶O₂ atmosphere (Fig. 4A, lower). Similar results were also found from the ¹³C NMR spectra (Fig. 4B). For Ag/TiO₂ in the ¹³CH₄ and ¹⁶O₂ atmosphere, the two ¹³C NMR signals at 48.97 and 65.03 ppm can be attributed to ¹³CH₃OH and ¹³CH₃OOH, respectively, which further proves that the product CH₃OH indeed originated from CH₄ conversion

on both 2.5%Ag/TiO₂ {001} and 2.1% Ag/TiO₂ {101}. When the reaction was carried out on Ag/TiO₂ in a ¹³CH₄ and ¹⁷O₂ atmosphere, the obvious peak broadening, originating from ¹³C-¹⁷O J coupling only occurred for the signal for ¹³CH₃OH generated by 2.5%Ag/TiO₂ {001} (Fig. 4B, upper) but was barely observed for the signal for ¹³CH₃OH generated by 2.1% Ag/TiO₂ {101} (Fig. 4B, lower). Combined with the results from ¹H NMR experiments, it can be indicated that the oxygen in the CH₃OH product mainly originates from the O₂ in the photocatalytic CH₄ oxidation on the {001} facet, while the oxygen in the CH₃OH product should mainly originate from H₂O and the surface oxygen of TiO₂ in the photocatalytic CH₄ oxidation on the {101} facet.

As in the previous reports^{2,7,9,42}, the primary step of CH₄ activation on typical oxide semiconductors should involve a reaction with surface O⁻ radical ions. When a TiO_{2 {101}} sample is illuminated under UV irradiation, the surface oxygen (Ti–O–Ti) captures one photoinduced hole to form Ti–O^{•2–4}. As O⁻ is present on typical TiO₂ and ZnO^{2,9}, Ti–O[•] can easily react with CH₄ and H₂O to form •CH₃ and •OH:

$$\mathrm{Ti} - \mathrm{O}^{\bullet} + \mathrm{CH}_4 \to \mathrm{Ti} - \mathrm{OH} + \bullet \mathrm{CH}_3, \tag{1}$$

$$Ti - O^{\bullet} + {}^{-}OH \rightarrow Ti - OH + \bullet OH,$$
 (2)

which was proven by ESR for 2.1% Ag/TiO₂ {101} in an aqueous solution (Supplementary Fig. S12). The active •CH₃ can couple with the surface O⁻ and •OH to form Ti-OCH₃ and CH₃OH, as evidenced in the IR range of 1000–1100 cm⁻¹ (Fig. 3A in 4th column). This is the reason why the oxygen in the CH₃OH product mainly originates from H₂O and Ti-O-Ti rather than O₂ in the photocatalytic CH₄ oxidation on 2.1% Ag/TiO₂ {101} (Fig. 4A, B). The O₂ can be reduced by photoinduced electrons to form superoxide anion radicals (O₂•⁻), which can easily react with •CH₃ to form CH₃OOH associated with the IR signal at 966 cm⁻¹ (Fig. 3A in 4th column)^{2,9,42}:

$$O_2 + e \to O_2^{\bullet-},$$
 (3)

$$\bullet CH_3 + O_2^{\bullet -} + H^+ \to CH_3OOH \bullet$$
(4)

CH₃OOH can readily decompose into formaldehyde (HCHO) and H₂O^{2,9}, and HCHO and CH₃OH can be overoxidized to CO₂ and H₂O by •OH radicals. Thus, as long as •CH₃ and •OH radicals occur in photocatalytic CH₄ oxidation, overoxidation should be unavoidable.

It has been found that the Ti-O-Ti bond angles of the {001} facets are more distorted than those of the {101} facets²¹, and there are much more pentacoordinated Ti4+ sites present on the {001} facets than that on the {101} facet^{21,24}. All this leads to a higher surface energy (0.90 Jm^{-2}) on $\{001\}$ facets than that (0.44) $J m^{-2}$) on {101} facets²³. In order to further prove the difference of the activity of oxygen sites and the formation of intermediates (oxygen (O) vacancy and surface peroxide species) on {001} and $\{101\}$ facet of TiO₂, the theoretical calculation has been performed (Supplementary Fig. S13). The energy (E_f) required for the formation of O vacancy on {001} facet is much lower than that on the {101} facet, and the energy (E_{ads}) released by O_2 adsorption on O vacancy of {001} facet is much higher than that on O vacancy of {101} facet. In one word, the energy (2.717 eV) required for the formation of peroxide intermediate by O2 adsorption on {001} facet is much lower than that (3.983 eV) on {101} facet. Therefore, it can be concluded that, firstly, the O centers of the {001} facet are more active than those of the {101} facet, which is favorable for the formation of O vacancies on the {001} facet upon light irradiation, as confirmed by the ESR signal at g = 1.9996 in Fig. 3B; secondly, it should be easier to form



Fig. 4 Photocatalytic mechanism. A ¹H and **B** ¹³C NMR spectra for the product obtained from photocatalytic CH₄ oxidation at a 4 h reaction time using 50 mL water, 80 kPa CH₄, 20 kPa O₂, and 10 mg Ag/TiO₂. **C** Proposed photocatalytic mechanism for CH₄ oxidation by O₂ on the {01} facets of TiO₂.

peroxide intermediates by O_2 adsorption on {001} facet, as confirmed by the operando FTIR experiment in Fig. 3A.

irradiation⁴³:

$$Ti - OO - Ti + hv \rightarrow Ti - O^{\bullet \bullet}O - Ti.$$
 (8)

Thus, unlike CH_4 activation on the {101} facet, the primary step of CH_4 activation on the {001} facet should be the oxidation of surface oxygen by photoinduced holes to form oxygen vacancies:

$$Ti - O - Ti + 2h \rightarrow TiTi,$$
 (5)

which results in a distinct catalytic mechanism appearing on the {001} facet (Fig. 4C). The oxygen vacancy can stabilize the superoxide radical $(O_2^{\bullet-})$, which should be formed by O_2 reduction by photoinduced electrons, as in reaction 3, to form surface superoxide (Ti– O_2^{\bullet}):

$$\operatorname{Ti}\operatorname{Ti} + \operatorname{O}_{2}^{\bullet-} \to \operatorname{Ti} - \operatorname{OO}^{\bullet}\operatorname{Ti}$$
 (6)

which is associated with the ESR signals at $g_{zz} = 2.023$, $g_{yy} = 2.007$, and $g_{xx} = 2.000$ (Fig. 3B). The surface superoxide can capture photoinduced electrons to form two types of surface peroxides (Ti–OO–Ti and Ti–(OO)):

$$Ti - OO^{\bullet} Ti + e \rightarrow Ti - OO - Ti,$$
 (7)

which corresponds to the appearance of O–O stretching bands at 812 and 943 cm⁻¹ that show increased intensity with light irradiation time in the operando FTIR experiment, respectively (Fig. 3A in 1st column). With the presence of CH₄, both Ti–OO–Ti and Ti–(OO) decrease significantly upon light irradiation (Fig. 3A in 2nd column). Theoretically, the dissociation barrier for the surface peroxides into Ti–O• pairs on the {001} facet of anatase TiO₂ is 1.0–1.4 eV, which can be overcome by the photon energy available from UV and visible light

The Ti–O[•] pairs can split CH_4 to generate adjacent surface methoxyl and hydroxyl groups (Ti–OCH₃ HO–Ti), which are associated with the NMR signals observed 263 and 180 ppm, respectively (Fig. 3C), subsequently releasing CH_3OH :

$$Ti - O^{\bullet \bullet}O - Ti + CH_4 \rightarrow Ti - OCH_3HO - Ti \rightarrow Ti - O - Ti + CH_3OH.$$
(9)

This should be the reason why the oxygen in the CH₃OH product mainly originates from O2 rather than H2O and Ti-O-Ti on 2.5% Ag/TiO_{2 {001}} (Fig. 4A, B), with almost no \bullet CH₃ and \bullet OH generated in the photocatalytic CH₄ oxidation on 2.5% Ag/TiO₂ {001} (Supplementary Fig. S12). Obviously, this reaction path can effectively hinder the formation of CH₃OOH. According to the ESR spectra (Supplementary Fig. S12), there are no •OH species present in the photocatalytic CH₄ oxidation on 2.5% Ag/TiO₂ {001}, which can greatly reduce the overoxidation of CH₃OH by •OH². In addition, the presence of water in the reactions could promote the desorption of methoxyl/methanol from the surface of catalysts into an aqueous solution to avoid overoxidation of methanol to CO and CO₂¹⁵⁻¹⁷, since the product CH₃OH can physically or chemically adsorb onto the photocatalyst surface⁴, and can be further oxidized with the surface-active species (such as Ti–O[•], peroxides, and superoxide) to form CO and $CO_2^{9,10}$. Thus, the aqueous phase is important to improve CH₃OH selectivity in a photocatalytic CH₄ oxidation reaction.

The proposed mechanism can further shed light on the results obtained for the photocatalytic activity and selectivity relative to the Ag loading amount on both TiO_{2} [001] and TiO_{2} [101]. As

observed in Fig. 1A, B, the initial increase in Ag loading can increase the photocatalytic activity and selectivity for both TiO_{2 {001}} and TiO_{2 {101}}. To get insight into the role of Ag, the operando ATR-FTIR experiments on TiO₂ {001} and TiO₂ {101} have been performed (Supplementary Fig. S14). Similar to 2.5% Ag/ TiO₂ (001), light irradiation also led to two types of surface peroxo intermediates (Ti-OO-Ti and Ti-(OO)) for the TiO_{2 {001}} in the aqueous phase saturated with Ar and O_2 (Ar + O_2). On the other hand, similar to 2.1%Ag/TiO2 {101}, almost no peak appears in the 800-1000 cm⁻¹ region for the $TiO_{2 \{101\}}$ in the aqueous phase with $Ar + O_2$ during light irradiation. It can be indicated that the formation of surface peroxo intermediates mainly occurred on the {001} facet of TiO₂. The in situ ESR experiments were used to follow the formation of paramagnetic intermediates on TiO_{2 {001}} and TiO_{2 {101}} (Supplementary Fig. S15). Different from 2.5%Ag/ TiO_{2 {001}}, no surface superoxide (Ti-O₂•) was observed on both TiO_{2 {001}} and TiO_{2 {101}} in the presence of 300 µmol H₂O and 24 µmol O₂ during light irradiation, while a small number of oxygen vacancies was formed on TiO_{2 {001}}. It can be indicated that Ag loading contributes to the formation of Ti-O2. on TiO_{2 {001}}. This may have two reasons: firstly, Ag as a cocatalyst can trap the photogenerated electrons to reduce molecular O_2 to form O_2^- species; secondly, the electron trapping on cocatalyst Ag can effectively improve the separation of photogenerated electrons and holes, which can lead to the increase of O vacancy formation arisen from the oxidation of surface oxygen by photogenerated hole on the {001} facet of TiO₂ (Fig. 3B). As a result, the observable O_2^- species is stabilized at the O vacancy on the $\{001\}$ facet of TiO_2 loaded with Ag (Fig. 3B). In addition to the role of Ag in separating the electronhole pairs to increase the activity, more Ag loading can reduce the exposed area of the {101} facet since the Ag is mainly photodeposited on the {101} facet. Instead, the {001} facet will continue to be exposed to the solution, resulting in superior selectivity. However, excessive loading of Ag will decrease the activity because of the intrinsic light absorption by Ag, while the selectivity can remain high since the {001} facet can still be exposed to the solution.

Discussion

In summary, we report the photocatalytic oxidation of CH₄ into CH₃OH by molecular O₂ on anatase TiO₂. To compare the microstructure and catalytic mechanism on the {001} and {101} facets of TiO₂, two types of TiO₂ with predominantly exposed {001} or {101} facets were prepared. By selectively photodepositing a Ag cocatalyst onto the {101} facet of TiO₂ to facilitate the separation and transfer of photoinduced carriers, the CH₃OH yield can be promoted significantly. According to studies based on operando FTIR, in situ ESR, and NMR techniques, completely different catalytic mechanisms exist for CH₄ photooxidation by O_2 on the {001} and {101} facets. It was found that oxygen vacancies on {001} facets are generated in a straightforward manner by photoinduced holes and that these photogenerated oxygen vacancies can stabilize superoxide radicals (Ti-O2). Ti-O2 can capture photoinduced electrons to form surface peroxides (Ti-OO-Ti and Ti-(OO)), and the surface peroxides dissociate into Ti-O• pairs, which can split CH4 to release CH₃OH directly. This distinct catalytic mechanism effectively avoids the formation of •CH₃ and •OH, which are the main factors leading to overoxidation and are generally formed on the {101} facet. Thus, the optimized {001} facet-dominated TiO₂ sample shows an impressively high CH₃OH yield of 4.8 mmol $g^{-1}h^{-1}$ with high CH₃OH selectivity of ~80%. This study will provide a strategy to avoid overoxidation in CH₄

reforming to CH₃OH in other photocatalysts by controlling the generation of photoinduced oxygen vacancies.

Methods

Sample preparation. The anatase TiO_2 with predominantly exposed {001} facets ($\text{TiO}_2_{(001)}$) were prepared according to the previous report⁴⁴. 25 mL of $\text{Ti(OBu})_4$ and 4 mL of hydrofluoric acid solution were mixed in a dried Teflon autoclave with a capacity of 100 mL, and then kept at 180 °C for 24 h. After being cooled to room temperature, the white powder was separated by high-speed centrifugation and washed with ethanol, 0.1 M NaOH aqueous solution, and deionized water several times to remove F^- on the surface.

The anatase TiO₂ with predominantly exposed {101} facets (TiO_{2 {101}}) were prepared according to the previous report⁴⁵. Firstly, for the preparation of Ti(OH)₄ precursor, 6.6 mL of TiCl₄ was added to aqueous HCl (0.4 mol L⁻¹) drop by drop under strong stirring in an ice bath to obtain an aqueous TiCl₄. This TiCl₄ aqueous was then added to aqueous NH₃·H₂O (5.5 wt.%) drop by drop under stirring. White Ti(OH)₄ precipitate could be formed during the process. Afterward, the aqueous NH₃·H₂O (4.0 wt.%) was added to adjust the pH value to 6–7. After aging at room temperature for 2 h, the suspension was centrifuged, and the precipitate was washed with ethanol, 0.1 M NaOH aqueous solution, and deionized water several times to remove Cl⁻ on the surface.

4.0 g the fresh Ti(OH)₄ precursor was first dispersed in the mixture of 30 mL deionized water and 30 ml isopropanol. After stirring and ultrasonic treatment, the suspension was transferred to a 100 mL Teflon-lined autoclave and heated for 24 h at 180 °C. The products were collected by centrifugation and washed with deionized ethanol one time and water three times. According to the EDX of TiO_{2 (101)} and TiO_{2 (001)} (Supplementary Fig. S16), there is no fluorine or chlorine atoms present on these TiO₂.

The Ag-loaded TiO₂ catalyst was prepared by in situ photodeposited reactions of AgNO₃ with TiO₂. Briefly, 0.4 g of the prepared TiO₂ was suspended in an anaerobic aqueous solution containing deionized water (20.0 mL), CH₃OH (5.0 mL), and a certain number of AgNO₃. After 0.5 h irradiation under 300 W Xe lamp, the products were collected via centrifugation, then washed by water and dried at 60 °C.

Characterization. A homemade spectral cell for attenuated total reflectance (ATR) Fourier transform infrared spectroscopy (FTIR) experiments is shown in Supplementary Fig. S17³². An internal reflection element (IRE) made of ZnSe (size: 50 mm \times 20 mm \times 3 mm, incident angle: 60°) was obtained from Pier Optics Co., Ltd. Japan. 20 mL TiO₂ suspensions of 5 mg mL⁻¹ in ethanol were drop casted on the IRE surface and dried in air. The IRE with TiO₂ coating was then set into the homemade spectral cell. 4 mL of water was purged by the gas for different purposes and was then injected into the cell. Before the Operando ATR-FTIR experiments, the cell was kept in dark for 5 min.

An FTIR spectrometer (FT/IR-6300, Jasco Inc.) with liquid nitrogen cooled MCT detector was used and purged by dry nitrogen before ATR-FTIR experiments. The absorbance spectra ranged from 4000 to 500 cm⁻¹ were obtained by repeated 32 scans with a resolution of 4 cm⁻¹ and a processing time of 30 s. The background was monitored and recorded in every minute of 5 min before the light illumination. Thereafter, the spectra were obtained at every minute of 10 min with light illumination and after light illumination.

 ^{17}O solid-state NMR spectra were acquired at 18.8 T on the Bruker Avance III spectrometers, equipped with a 4 mm double-resonance probe. The Larmor resonance frequencies for the ^{1}H and ^{17}O resonances were 800.4 and 108.5 MHz, respectively. ^{17}O MAS NMR spectra were acquired using a typical $\pi/2$ pulse length of 2.5 µs, with a recycle delay of 1.0 s and a ^{1}H decoupling field strength of 130 kHz. The experiments were carried out with a MAS frequency of 13.5 kHz. 120,000 scans were accumulated to acquire each spectrum. The chemical shifts of ^{17}O resonance signals were referred to as liquid H $_2^{17}\text{O}$. Prior to ex-situ ^{17}O NMR measurements, CH₄ (30 µmol) and $^{17}\text{O}_2$ (20µmol) were introduced into a glass ampule containing 0.05 g TiO₂ catalyst under vacuum at the liquid N₂ temperature, and then the glass ampule was sealed off. The photoreaction was performed in the sealed ampule under successive irradiation by a 300 W Xe lamp, and then the ampule was transferred into the rotor for the ex situ NMR measurements.

A homemade spectral cell for in situ electron spin resonance (ESR) experiments is shown in Supplementary Fig. S18. In situ ESR experiments were carried at X-band using a JOEL FA 2000 spectrometer. The microwave frequency was 9.1 GHz, the modulation amplitude was 0.1 mT, the microwave power was 5 mW and the experimental temperature was 25 °C. The g values of the radical species were referenced to Mn-marker. The Mn-marker is Mn^{2+} in the CaO with g = 2.0009.

Photocatalytic measurements. The photocatalytic methane oxidation reaction tests were conducted in a 230 mL batch reactor equipped with a quartz window to allow light irradiation. 10 mg catalyst was dispersed in 100 mL water by ultrasonication for 10 min. Then, the mixture was added into a glass cell with a volume of 30 mL, and the glass cell was placed in the batch reactor. The actual working volume decreased to 100 mL. The batch reactor was purged with O₂ (purity,

99.99995%) for 15 min to exhaust air. After that, the reactor vessel was pressurized with 0.1 MPa O₂ and 2 MPa CH₄ (purity, 99.9995%). Subsequently, the reactor was loaded into a cold-water bath, and the solution was stirred at 1200 rpm. 300 W Xe lamp was used as the light source with wavelength ranging from 300 to 500 nm and the light intensity of 450 mW cm⁻². A thermocouple was inserted into the solution to directly detect the temperature of the liquid solution. During the reaction process, the temperature of the liquid solution was maintained at 25 °C. After the reaction, the reactor was cooled in an ice bath to a temperature below 10 °C. Then the gas product was collected, and the concentrations of gas products were analyzed by gas chromatograph (GC, Shimadzu) equipped with methanizer and flame ionization detector. The liquid phase of the reaction mixture product was collected by centrifugation. The liquid product was analyzed by nuclear magnetic resonance spectroscopy (NMR) and the colorimetric method.

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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ARTICLE

Author contributions

J.Y. and N.F. conceived the project. N.F. designed the studies and synthesized the $\rm TiO_2$ photocatalysts. N.F. and H.S. performed photocatalytic activity experiments. H.L. performed the in situ FTIR experiments. N.F., L.Y., and F.D. performed in situ ESR and NMR experiments. D.T. performed HRTEM experiments. N.F. and H.L. analyzed all the experimental data. N.F. and H.L. wrote the first draft of the manuscript. All authors interpreted the data and contributed to the preparation of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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