Photocatalytic selective oxidation of methane by quantum sized bismuth vanadate

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Abstract

Selective oxidation of methane to desirable C1 oxygenates has long been the major challenge in catalysis. Here we report photocatalytic oxidation of methane by using quantum-sized bismuth vanadate nanoparticles as catalyst and oxygen as mild oxidant. A high selectivity towards methanol (1.1 mmol g\(^{-1}\) yield and 96.6% selectivity) and formaldehyde (13.1 mmol g\(^{-1}\) yield and 86.7% selectivity) products is successfully realized by simply controlling the light wavelength, light energy, reaction time and the amount of water solvent. Comprehensive characterizations disclose that the radical reaction mechanism is responsible for this efficient photocatalytic methane conversion.

Introduction

Methane (CH\(_4\)), approximately occupying 70% to 90% in natural gas\(^1,2\), has been broadly recognized as an indispensable feedstock in the manufactures of fuels and chemicals with high added-values\(^3,4\). Traditional industrial technology has succeeded in implementing large-scale transformation of CH\(_4\) to liquid chemicals via an indirect mode, involving the first syngas (H\(_2\) and CO) formation and the second downstream process\(^5,6\). Obviously, the divided reaction steps and required high operation temperature (800 - 900\(^\circ\)C)\(^7\) are the formidable challenges for modern sustainable development.

Taking light illumination instead of high-temperature heating, photocatalytic CH\(_4\) oxidation holds the great promise to transform CH\(_4\) into many types of high valued liquid chemicals at room temperature\(^8,9\). Amongst the investigated liquid products, methanol (CH\(_3\)OH) and formaldehyde (HCHO) are two major targets because of their roles as the basic and widely used chemicals\(^10,11,12\). Until now, a few photocatalytic CH\(_4\) conversions with satisfied yield of CH\(_3\)OH and HCHO have been reported; for instance, photocatalytic oxidation of CH\(_4\) over 0.1 wt% Au/ZnO and 0.1 wt% Ag/ZnO achieved 41.2 \(\mu\)mol CH\(_3\)OH (15.7% selectivity) and 112.1 \(\mu\)mol HCHO (42.6% selectivity)\(^12\), respectively, under moderate reaction condition.

Noteworthily, there has been always a serious dilemma between the productivity and selectivity for CH\(_4\) oxidation, which is a complicated and energy-downhill process of \(\text{CH}_4 \rightarrow \text{CH}_3\text{OOH} \rightarrow \text{CH}_3\text{OH} \rightarrow \text{HCHO} \rightarrow \text{CO}_2\)\(^13,14,15,16,17\) (Fig. 1), and the undesired intermediates and overoxidation always exist. To be specific to the formation of CH\(_3\)OH, optimizing its selectivity needs maximizing the reduction of CH\(_3\)OOH while preventing the overoxidation to HCHO and CO\(_2\). Similarly, to promote the selectivity of HCHO, CH\(_3\)OH intermediates must be further oxidized whilst avoiding overoxidation to CO\(_2\).

Herein, we suggest a highly selective aerobic conversion of CH\(_4\) to CH\(_3\)OH and HCHO at room temperature using quantum-sized BiVO\(_4\) nanoparticles (q-BiVO\(_4\)) as photocatalyst. On the basis of the maximum yield (1.1 mmol g\(^{-1}\) CH\(_3\)OH or 13.1 mmol g\(^{-1}\) HCHO), the selectivity of CH\(_3\)OH and HCHO
reaches 96.6% and 86.7%, respectively. The q-BiVO₄ is characteristic of high kinetic energy of charge carrier and large specific surface, enabling effective conversion of CH₄ into CH₃OH and HCHO. By altering the amount of oxygen (O₂) and solvent (H₂O), reaction time, irradiation wavelength and light intensity, the selectivity towards CH₃OH and HCHO is rationally tuned. The aerobic oxidation of CH₄ is disclosed to be proceeded with a radical mechanism according to the isotopic test (¹³CH₄, H₂¹⁸O,¹⁸O₂ and CD₄), intermediate capture and rate-determining step determination.

Results

Preparation and characterizations of BiVO₄ photocatalysts. We hypothesize that the low photocatalytic activity of commonly-used submicro-sized BiVO₄ particles (s-BiVO₄) originates from their rather narrow bandgap and small surface-to-volume ratio. Therefore, a hard-template method was developed for preparing q-BiVO₄ with shrunk size, which would have an increased bandgap and larger surface-to-volume ratio. As shown in Fig. 2a, homogeneous blending of silica gels with Bi(NO₃)₃ and NH₄VO₃ precursors followed by calcination resulted in a composite structure with silica template encapsulated by BiVO₄ (Fig. S1). Subsequent high-pressure hydrothermal reaction made silica template fully dissolve, which broke BiVO₄ shell into quantum sized particles. Transmission electron microscopy (TEM) images reveal that the spherical aggregates (Fig. 2b, c) are composed of point-like q-BiVO₄ with an average particle size of ~ 4.5 nm (Fig. 2d, e). It is known that the Bohr radius of BiVO₄ is about 2 nm¹⁸,¹⁹ which is close to the radius of q-BiVO₄ (2.25 nm). Thus, q-BiVO₄ should exhibit a strong quantum confinement effect. X-ray diffraction (XRD) pattern indicates that as-synthesized q-BiVO₄ is of monoclinic scheelite structure without any impurity crystal phase (Fig. 2g and Fig. S2). Note that the absence of broad XRD shoulder corresponding to amorphous silica manifests the successful removal of template (Fig. S2). The characteristic XRD peaks are also used to analyze the average aggregation size of q-BiVO₄ (10.5 nm) within Debye-Scherrer method (Fig. S3). The clear lattice fringe in high-resolution TEM (HRTEM, Fig. 2f) and the selected area electron diffraction (SAED) pattern both confirm the high crystalline nature of q-BiVO₄. Element mapping images based on high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM, Fig. S4) display that all the Bi, V and O elements are homogeneously distributed over q-BiVO₄, and the quantitative estimation by energy dispersive X-ray (EDX) spectroscopy presents the stoichiometric composition of Bi, V and O elements in q-BiVO₄ (Fig. S5).

Photocatalytic performance. The photocatalytic CH₄ oxidation was investigated in a high-pressure stainless-steel vessel with a transmittance quartz glass window on the top plate (Fig. S6). The adoption of high-pressure reactor is based on below two considerations. One is to economically utilize the available pressure energy from the practical transportation and storage condition of natural gas, where the pressure is as high as 70-200 bar in main pipelines and tanks²⁰,²¹. The specific analysis is briefly summarized in supplementary information (Fig. S7). The other is to promote the yield of desired products through dissolving more CH₄ reactants in the solvent at high pressure. In a typical reaction, 10 mg q-
BiVO$_4$ photocatalysts were dispersed in certain amount of H$_2$O, while the total pressure of CH$_4$ and O$_2$ mixed gas was fixed to be 20 bar. After irradiation with Hg lamp (excitation wavelength of 300-600 nm) at room temperature (surface temperature of catalyst = 28.5±0.5°C, Fig. S8), the yield of liquid organic products such as CH$_3$OH and C$_2$H$_5$OH was evaluated by nuclear magnetic resonance spectroscopy (NMR) and gas chromatography (GC) with flame ionization detector. Note that liquid HCHO is known to exist in the form of methanediol (HOCH$_2$OH) in aqueous solution, which $^1$H NMR signal overlaps with the broad peak of water solvent. So, the quantity of HCHO was determined by acetylacetone color-developing method (Fig. S9, S10, S11). Other gaseous products (CO$_2$, C$_2$H$_6$, O$_2$ and H$_2$) were monitored by GC spectra with flame ionization and thermal conductivity detectors.

The effect of photocatalyst type, O$_2$ and H$_2$O amount, reaction time, irradiation wavelength as well as light intensity on CH$_4$ conversion performance is investigated in detail. First of all, photocatalytic activity of q-BiVO$_4$ (4.5 nm) is compared with conventional s-BiVO$_4$ (454.3 nm, Fig. S12). As shown in Fig. 3a, about 4 folds in the oxygenated products by q-BiVO$_4$ (2.3 mmol g$^{-1}$ CH$_3$OH, 1.9 mmol g$^{-1}$ HCHO and 0.3 mmol g$^{-1}$ CO$_2$) are acquired with respect to s-BiVO$_4$ (0.5 mmol g$^{-1}$ CH$_3$OH, 0.5 mmol g$^{-1}$ HCHO and 0.1 mmol g$^{-1}$ CO$_2$). The corresponding increment is also distinguished in conversion of CH$_4$ and O$_2$ reactants (Fig. S13a). These enhancements by q-BiVO$_4$ are ascribed to both the raised charge carrier kinetics (Fig. S14) and the improved Brunauer-Emmett-Teller (BET) specific surface area (226.9 m$^2$ g$^{-1}$, Fig. S15). This deduction is supported by comparing the BET surface area normalized CH$_4$ oxidation activity (Table S1), and q-BiVO$_4$ still exhibits higher performance than s-BiVO$_4$. Except for s-BiVO$_4$, commercial TiO$_2$ nanoparticle (P25) is also employed as the contrast sample and tested under the same reaction condition, and only HCHO (48.9 µmol g$^{-1}$) and CO$_2$ (48.9 µmol g$^{-1}$) are found in the products (Fig. S16).

Optimizing the yield of both CH$_3$OH and HCHO is carried out through varying O$_2$ amount (Fig. 3b). The highest productivity of CH$_3$OH and HCHO is 2.3 and 1.9 mmol g$^{-1}$ at the O$_2$ pressure of 10 bar, respectively, and the corresponding conversion percentage of O$_2$ is 0.23% (Fig. S13b). The gradual increase of oxygenates at the O$_2$ partial pressure of less than 10 bar implies that O$_2$ involves the rate-determining step of CH$_4$ oxidation. When the O$_2$ pressure surpasses 10 bar, the reduced productivity of CH$_3$OH and HCHO is ascribed to the lowered CH$_4$ partial pressure and their overoxidation to CO$_2$. Hence, the partial pressure of O$_2$ is controlled to be 10 bar.

The inspection of reaction time discloses that 3 h is the best for the yield of CH$_3$OH (2.3 mmol g$^{-1}$) though its selectivity continuously decreases (Fig. 3c). It is noticed that when the reaction time arrives 7 h, the productivity of HCHO ascends to 5.6 mmol g$^{-1}$ with 69.8% selectivity, demonstrating that the prolonged reaction promotes oxidation of both CH$_4$ reactants and CH$_3$OH intermediates. The corresponding conversion percentage of CH$_4$ at 7 h is 0.40% (Fig. S13c) with turnover number (TON) of 2.6. Evidently, extending the reaction time enables improving the HCHO selectivity simultaneously ensuring its output.
The balance between the consumption rate of feed gas (CH$_4$ and O$_2$) and the formation rate of products (CH$_3$OH, HCHO and CO$_2$) is explored by Fig. S17 and S18.

H$_2$O acts as the solvent for CH$_4$ oxidation. Fig. 3d shows that with the H$_2$O volume increase from 10 to 80 mL, conversion of CH$_4$ and O$_2$ synchronously improves from 0.23% (TON = 1.5) to 0.54% (TON = 3.5) (Fig. S13d), while the yield of CH$_3$OH and HCHO gets to 6.8 and 4.0 mmol g$^{-1}$, respectively. More CH$_4$ molecules are dissolved in aqueous solution with H$_2$O amount increasing, leading to the rise of CH$_3$OH product. Moreover, the concentration of CH$_3$OH is diluted in a large volume of H$_2$O, alleviating overoxidation to HCHO and CO$_2$ and causing enhancement of the selectivity towards CH$_3$OH. It is noted that owing to the possible test error in low concentration of CH$_3$OH solution (Fig. S19), further increase of H$_2$O volume is not tried. Nevertheless, augmenting the solvent volume is an efficient method to boost the selectivity of CH$_3$OH with high yield.

The relationship between photocatalytic performance and input photon number or light energy is also examined. As indicated in Fig. 3e, along with the increase of light intensity of Hg lamp, the yield of CH$_3$OH, HCHO and CO$_2$ all raises from 1.0 (CH$_3$OH, 100 mW cm$^{-2}$), 0.5 (HCHO, 100 mW cm$^{-2}$) and 0.2 (CO$_2$, 100 mW cm$^{-2}$) to 2.3 (CH$_3$OH, 170 mW cm$^{-2}$), 1.9 (HCHO, 170 mW cm$^{-2}$) and 0.3 mmol g$^{-1}$ (CO$_2$, 170 mW cm$^{-2}$), respectively. This result manifests that the photocatalytic CH$_4$ conversion largely depends on the inputted photon number. Fig. 3f and Table S2 further summarize the photocatalytic efficiency under irradiation of monochromatic light with different energy. In good agreement with change in the diffuse reflectance spectrum, the quantum efficiency (Q.E.) value of q-BiVO$_4$ (0, 0, 0.47, 0.82 and 3.07%) increases with the reduction of irradiation light wavelength (630, 535, 470, 420 and 365 nm). The prominent photon utilization efficiency of 3.07% at 365 nm demonstrates that irradiation with the short-wavelength and high-energy light would promote the oxidation conversion of CH$_4$. The quantitative conversion percentage of CH$_4$ and O$_2$ is outlined in Fig. S13e and S13f.

Based on the above results, we conclude the favorable reaction condition for production of HCHO and CH$_3$OH, respectively. Since HCHO is the further oxidation product of CH$_3$OH, increasing the oxidation capacity would be an efficient strategy to elevate the selectivity of HCHO. As demonstrated in Fig. 4a, utilization of short-wavelength UV irradiation (300-400 nm) with high intensity (170 mW cm$^{-2}$) not only promotes the CH$_4$ conversion but also accelerates the oxidation of CH$_3$OH to HCHO. Significantly, upon a long time oxidation of 7 h, HCHO product is achieved with a good selectivity and yield of 86.7% and 13.1 mmol g$^{-1}$ (TON = 4.7), respectively. The corresponding conversion of both CH$_4$ and O$_2$ reaches 0.73% (Fig. S13g). On the contrary, reducing the oxidation degree of reaction system could be conducive to production of CH$_3$OH. Using visible Xenon lamp irradiation (400-780 nm), a remarkable 92.8% selectivity of CH$_3$OH is achieved in 10 mL H$_2$O. It needs to be pointed out that the weak oxidation capacity under visible light inevitably results in low productivity of oxygenates. Therefore, by increasing the dissolved CH$_4$ in 80 mL H$_2$O, the yield of CH$_3$OH is promoted to 1.1 mmol g$^{-1}$ with an exceptional selectivity of...
96.6% (TON = 0.4, Fig. 4b, S20). The corresponding conversion of both CH\textsubscript{4} and O\textsubscript{2} is 0.06% (Fig. S13h). Evidently, the diluted concentration of CH\textsubscript{3}OH generated in large solvent volume gives rise to the enhanced selectivity from 92.8% to 96.6% through depressing the overoxidation (Fig. S21). The contrast experiments with absence of catalyst, CH\textsubscript{4}, O\textsubscript{2} or H\textsubscript{2}O show no production of oxygenates under visible light irradiation (Table S3). To preclude the influence of temperature, thermocatalytic reaction (30\degree C) under similar condition is also conducted and no products is observed (Fig. S22). It deserves to be stressed that the highly selective generation of CH\textsubscript{3}OH or HCHO from CH\textsubscript{4} oxidation over the single photocatalyst is unattained in previous works (Table S4).

**Photocatalytic mechanism.** Fig. 5A illustrates the proposed radical mechanism for CH\textsubscript{4} oxidation on q-BiVO\textsubscript{4} (Fig. 5). Under light irradiation, q-BiVO\textsubscript{4} is excited to induce \textsuperscript{•}OH generation via two routes: oxidation of H\textsubscript{2}O by valence band holes and reduction of O\textsubscript{2} by conduction band electrons (step 1). The \textsuperscript{•}OH cleaves C-H bond for producing the methyl radical (\textsuperscript{•}CH\textsubscript{3}) (step 2), which is a rate-determining step. Also as an oxidant, O\textsubscript{2} rapidly binds to \textsuperscript{•}CH\textsubscript{3} and then reacts with as-formed H\textsuperscript{+} and electron to generate methylhydroperoxide (CH\textsubscript{3}OOH, step 3), which will be reduced by electrons\textsuperscript{23,24} or decomposed under UV irradiation to form CH\textsubscript{3}OH (step 4)\textsuperscript{25,26}. Upon oxidation by holes from valence band of q-BiVO\textsubscript{4}, as-formed CH\textsubscript{3}OH is further activated to \textsuperscript{•}CH\textsubscript{2}OH that is combined with \textsuperscript{•}OH to produce HCHO in the form of HOCH\textsubscript{2}OH (step 5). In the following parts, we validate this reaction mechanism step by step.

To solidly prove that the oxygenated products results from the conversion of CH\textsubscript{4}, \textsuperscript{13}CH\textsubscript{4} was used as reactant instead of \textsuperscript{12}CH\textsubscript{4}. Gas chromatography-mass spectrometry (GC-MS) with isotopically labelled \textsuperscript{13}CH\textsubscript{4} discloses that CH\textsubscript{4} is the carbon source of CH\textsubscript{3}OH with the appearance of \textsuperscript{13}CH\textsubscript{3}OH peak at m/z = 33 (red curve in Fig. 6a). The obvious \textsuperscript{13}C NMR peaks of CH\textsubscript{3}OH and HOCH\textsubscript{2}OH (HCHO) also verify that the C1 oxygenated products are derived from CH\textsubscript{4} (black curve in Fig. S23a). The carbon type of C1 oxygenated products is identified from the \textsuperscript{13}C DEPT-135 (distortionless enhancement by polarization transfer) spectrum, where up and down signals represent -CH\textsubscript{3} and -CH\textsubscript{2} groups from CH\textsubscript{3}OH and HOCH\textsubscript{2}OH (HCHO), respectively (red curve in Fig. S23a). Furthermore, as displayed in Fig. S23b, satellite peaks of \textsuperscript{13}CH\textsubscript{3}OH (δ = 3.12 and 3.40 ppm) are discerned in \textsuperscript{1}H NMR spectrum without \textsuperscript{12}CH\textsubscript{3}OH (δ = 3.28 ppm) signal\textsuperscript{23}, indicating that CH\textsubscript{4} is the 100% carbon source for CH\textsubscript{3}OH product. Similarly, 2D \textsuperscript{1}H-\textsuperscript{13}C HMQC (heteronuclear multiple-quantum correlation, Fig. S24) and 2D \textsuperscript{1}H-\textsuperscript{13}C HMBC (heteronuclear multiple-bond correlation, Fig. S25) spectra indicate that \textsuperscript{13}CH\textsubscript{4} is the feedstock for HCHO (HOCH\textsubscript{2}OH) generation.

According to the mechanism illustration, \textsuperscript{•}OH is responsible for removing the H atom from CH\textsubscript{4} molecule, which is the key step for CH\textsubscript{4} activation. To explore the ability of q-BiVO\textsubscript{4} towards the generation of \textsuperscript{•}OH in step 1, its band structure is established through UV-Vis diffuse reflectance spectrum\textsuperscript{27} (Fig. S26a), transformed Kubelka-Munk function plot (Fig. S26b)\textsuperscript{28}, Mott-Schottky plot (Fig. S26c, S27)\textsuperscript{29} and
ultraviolet photoelectron spectroscopy (Fig. S28). As shown in Fig. 6b, the conduction and valence bands of q-BiVO$_4$ are tested to be 0.075 and 2.555 V vs. normal hydrogen electrode (NHE) at pH=0, respectively. Therefore, the \(^\cdot\)OH can be produced through two approaches: H$_2$O oxidation (\(^\cdot\)OH/H$_2$O: 2.380 eV vs. NHE at pH=0)$^{30}$ and two-electron O$_2$ reduction (O$_2$/\(^\cdot\)OH: 0.695 eV vs. NHE at pH=0)$^{31}$. In order to assess the generation of \(^\cdot\)OH from both hole oxidation and electron reduction of q-BiVO$_4$, we carried out the fluorescence detection of coumarin solution without or with O$_2$ (Fig. S29). In the absence of O$_2$ (Fig. S29a), an enhanced fluorescence signal is achieved with q-BiVO$_4$ photocatalyst under visible light, indicating that the holes from valence band can successfully oxidize H$_2$O into \(^\cdot\)OH. After the solution is saturated with O$_2$ (Fig. S29b), the fluorescence intensity with q-BiVO$_4$ exhibits 2.3 times increase than that in absence of O$_2$, confirming that O$_2$ also greatly contributes to the generation of \(^\cdot\)OH. Note that the quantity of O$_2$ solely generated from H$_2$O decomposition by q-BiVO$_4$ is too low to make a detectable yield of oxygenates (Fig. S30). Moreover, the energy band structure of s-BiVO$_4$ is likewise constructed (Fig. S31 and S32) with the conduction and valence bands at 0.084 and 2.474 V vs. NHE at pH=0, respectively. With respect to the energy band structure of s-BiVO$_4$, the more negative conduction band and positive valence band of q-BiVO$_4$ lead to more \(^\cdot\)OH species for CH$_4$ oxidation (Fig. S33). We notice that such fluorescence signal comes from 7-hydroxycoumarin that is the \(^\cdot\)OH trapping product of coumarin (Fig. S34 and S35).

Step 2 refers to the activation step of CH$_4$ by \(^\cdot\)OH, which is recognized as the rate-determining step in this work. To verify that \(^\cdot\)OH is the initiator for CH$_4$ activation on the surface of q-BiVO$_4$ rather than the photoinduced hole, we performed a thermocatalytic reaction containing 10 mg q-BiVO$_4$, 5 mL H$_2$O$_2$, 5 mL H$_2$O, 10 bar O$_2$ and 10 bar CH$_4$ at 60$^\circ$C in absence of light irradiation. The H$_2$O$_2$ is decomposed to provide \(^\cdot\)OH at 60$^\circ$C, and the dark condition prevents the hole formation on the surface of q-BiVO$_4$. After reaction, CH$_4$ is found to be oxidized to CH$_3$OOH, which is not further reduced to CH$_3$OH due to the lack of photogenerated electrons under dark condition (Fig. 6c). In absence of H$_2$O$_2$ (Fig. S36) or q-BiVO$_4$ (Fig. 6d), no oxygenated product is distinguished. Thus, we deduce that \(^\cdot\)OH activates CH$_4$ for oxygenate generation on the surface of q-BiVO$_4$. Besides, the solid evidence that CH$_4$ is not directly oxidized by photoinduced holes from q-BiVO$_4$ is supported by electron spin resonance (ESR) spectroscopy (Fig. 6e). Under Xenon lamp irradiation in argon (Ar) atmosphere, the ESR spectrum of q-BiVO$_4$ shows a g value of 2.006$^{32}$, corresponding to the active hole center O$^-$ (Fig. 6e, blue curve); subsequently, atmosphere is switched from Ar to CH$_4$, no distinct intensity decrease is discerned on O$^-$ signal (Fig. 6e, green curve), indicating no occurrence of reaction between O$^-$ hole and CH$_4$ molecule$^{33}$; on the contrary, upon continuous irradiation for 15 min in CH$_4$ atmosphere, the intensity of O$^-$ signal increases (Fig. 6e, red curve), again denying that the O$^-$ hole can directly oxidize CH$_4$. The fact that C-H bond breakage is rate-determining step of CH$_4$ oxidation was verified through kinetic isotope effect (KIE)$^{34}$. Taking 420 nm monochromatic light for irradiation, the KIE value is estimated to be 8.3 (larger than 6)$^{35}$ based on the
reaction rate ratio \( (k_H / k_D) \) using CH\(_4\) or CD\(_4\) as reactants, respectively (Fig. 6f and S37). This large value reveals the C-H bond cleavage in the rate-determining step.

Incorporation of O\(_2\) with \(^{1}\)CH\(_3\) to form CH\(_3\)OH in step 3 was proved by \(^{18}\)O\(_2\) and H\(_2\)^{18}O isotope tests as well as the reusability of q-BiVO\(_4\) photocatalyst, considering that these three oxygen sources possibly involved the catalytic reaction. GC-MS analyses (Fig. 6g) demonstrate that CH\(_3\)^{18}OH fragment occupies 100\% intensity by using \(^{18}\)O\(_2\) and H\(_2\)^{16}O, whereas the CH\(_3\)^{16}OH fragment contains 100\% intensity by using \(^{16}\)O\(_2\) and H\(_2\)^{18}O. Therefore, one can deduce that the O element in H\(_2\)O is not incorporated into CH\(_3\)OH formation during the photocatalytic CH\(_4\) oxidation. To exclude the possibility of lattice O in q-BiVO\(_4\) as oxygen source, its stability was evaluated. After five photocatalytic cycles, q-BiVO\(_4\) almost preserves its initial catalytic activity (Fig. S38). Therefore, O\(_2\) is the mere oxygen source for CH\(_3\)OH formation (step 3). TEM images (Fig. S39), XRD patterns (Fig. S40), XPS (Fig. S41), Raman (Fig. S42a), UV-Vis diffuse reflectance spectra (Fig. S42b) and inductively coupled plasma optical emission spectrometer tests (Fig. S43) were carried out to prove only slight change in the morphologies and chemical states of q-BiVO\(_4\) before and after photocatalytic reaction.

According to step 4, CH\(_3\)OOH is first formed and then reduced to CH\(_3\)OH. Since this reduction process easily happens under high photoinduced electron density\(^{36}\), the NMR signal of CH\(_3\)OOH is difficult to be detected. Therefore, we increased the amount of q-BiVO\(_4\) (50 mg) and reduced the amount of H\(_2\)O solvent (0.5 mL) in order to increase the concentration of CH\(_3\)OOH intermediates. By prolonging the reaction time to 7 h, a weak CH\(_3\)OOH peak appeared at 3.78 ppm, providing the clear evidence on CH\(_3\)OOH production (Fig. 6h). As-formed CH\(_3\)OH would be further oxidized to HCHO (HOCH\(_2\)OH) in step 5. Based on the Gibbs free energy values (Fig. 1)\(^{22,37,38}\), oxidation of CH\(_3\)OH to HCHO is thermodynamically favorable. To confirm this transformation process from the experimental aspect, CH\(_3\)OH was taken as reactants in a similar photocatalytic system with argon (Ar) replacing CH\(_4\). The \(^{13}\)C NMR spectrum of CH\(_3\)OH oxidation products verifies that CH\(_3\)OH can be oxidized to HOCH\(_2\)OH using q-BiVO\(_4\) as catalysts under light illumination (Fig. S6i).

**Summary**

Through regulation of reaction time, irradiation wavelength, light intensity and the adding amount of O\(_2\) as well as H\(_2\)O, selective oxidation of CH\(_4\) into CH\(_3\)OH and HCHO with satisfied yield is successfully realized over q-BiVO\(_4\) photocatalyst at room temperature under the aerobic condition. The quantum sized q-BiVO\(_4\) with an appropriate energy band structure enables simultaneous H\(_2\)O oxidation via photogenerated holes and O\(_2\) reduction via photogenerated electrons, greatly promoting the production of \(^{1}\)OH. As-formed \(^{1}\)OH causes the cleavage of C-H bond in CH\(_4\) and gives to the generation of \(^{1}\)CH\(_3\), which is proved to be a rate-determining step. Except for participating into \(^{1}\)OH production, O\(_2\) is found to incorporate with \(^{1}\)CH\(_3\), resulting in the oxygenated products. This work not only provides a comprehensive
analysis for CH₄ oxidation, but also broadens the avenue toward selective conversion of CH₄ into valuable products in sustainable way.

**Methods**

**Chemicals.** Bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O), ammonium metavanadate (NH₄VO₃), coumarin, deuteroxide (D₂O), water-¹⁸O (H₂¹⁸O), barium sulfate (BaSO₄) and dimethyl sulfoxide (DMSO) were all purchased from Innochem in Beijing. LUDOX® HS-40 colloidal silica 40 wt.% suspension in water was bought from Sigma-Aldrich. Gases of CH₄ and O₂ were achieved from KODI corporation in Foshan. Isotopic gases of ¹⁸O₂, ¹³CH₄ and CD₄ were obtained from LION biology corporation in Shanghai. All the chemicals were used as received without further purification. Deionized water with a resistivity of 18.2 MΩ cm⁻¹ was used in all experiments.

**Photocatalyst preparation.** The q-BiVO₄ was prepared through a template method. 0.48 g Bi(NO₃)₃·5H₂O was dissolved in 10 mL 1 M HNO₃, meanwhile 0.12 g NH₄VO₃ was added into another 15 mL HNO₃ solution, giving two precursor solutions with concentration of 1 mM, respectively. Under vigorous stirring, two precursor solutions were mixed with silica gel (12 nm in diameter) added as the template. After rotary evaporation drying, the prepared powder was calcinated at 400°C to obtain BiVO₄-silica composite. As for silica template removal, 70 mg BiVO₄-silica composite was dispersed in 70 mL deionized water by ultrasonication. Then, the suspension was transferred into a 100 mL Teflon-lined stainless-steel autoclave, which was treated under hydrothermal reaction at 180°C for 24 h. Finally, q-BiVO₄ was obtained by centrifugation and dried at 60°C for 12 h.

The s-BiVO₄ with an average size of 454.3 nm was synthesized by a standard precipitation method. Typically, 2.9 g Bi(NO₃)₃·5H₂O and 0.69 g NH₄VO₃ were dissolved in 25 mL 2 mM HNO₃ solution, and the solution was stirred until clear. Then, 5 g urea was added into the mixed solution followed by heating at 90°C for 24 h under continuous stirring. The product was washed thoroughly with pure water and drying at 60°C overnight.

**Characterization.** Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), high-angle annular darkfield scanning transmission electron microscopy (HAADF-STEM), elemental mapping and energy dispersive X-ray (EDX) spectroscopy were carried out on a FEI Tecnai G2 F20 electron microscope operated at 200 kV. Scanning electron microscopy (SEM) was performed on a Hitachi S8220 scanning electron microscope. The crystal structures were characterized through power X-ray diffraction patterns (XRD), which were carried out on D/MAX-TTRIII (CBO) and Xeuss SAXS/WAXS system with Cu Kα radiation (λ = 1.542 Å) operating at 50 kV and 300 mA. UV-Vis diffuse reflectance spectra taking BaSO₄ as internal reference sample were recorded on a Hitachi U-3010 UV-Vis spectrometer. A Mott-Schottky plot was performed on CHI 760E electrochemical workstation in 1 M Na₂SO₄ solution under frequencies of 500, 700 and 900 Hz, respectively.
**Photocatalytic oxidation of CH$_4$.** Photocatalytic oxidation of CH$_4$ was performed in a stainless-steel autoclave with a quartz glass window on the top (Supplementary Fig. S5). Photocatalysis experiments were carried out at a fixed pressure of 20 bar and room temperature along with 25°C cooling water unless otherwise stated. 10 mg photocatalyst sample was placed at the center inside reactor, and then certain amount of deionized water was added. The mixed CH$_4$ and O$_2$ at different ratio (8:12, 10:10, 12:8, 14:6) were filled, and high-pressure mercury lamp (excitation wavelength of 300-600 nm, CEAUlioHT), Xenon lamp (excitation wavelength of 400-780 nm and irradiation intensity of 170 mW cm$^{-2}$, Perfect Light) or LED monochromatic light source (Perfect Light) was used the light source for photocatalytic reactions.

**Thermocatalytic oxidation of CH$_4$ in presence of H$_2$O$_2$.** To verify that •OH activated CH$_4$ for CH$_3$OH formation on the surface of q-BiVO$_4$, a free radical based thermocatalytic reaction was performed at 60°C. 10 mg q-BiVO$_4$ was dispersed in the mixture of 5 mL H$_2$O$_2$ and 5 mL H$_2$O. 10 bar O$_2$ and 10 bar CH$_4$ were charged to make a total gas pressure to be 20 bar. Under dark condition, the reaction system was heated to 60°C.

**Product analysis.** Analysis of the C1 oxygenated liquid product (CH$_3$OOH, CH$_3$OH, HCHO) was carried out using GC, GC-MS, and NMR spectroscopy. GC equipped with a flame ionization detector was performed on Shimadzu GC-2014C to analyze and quantify the product of CH$_3$OH. A Shimadzu GC-MS QP2010 Ultra was applied to monitor generation of $^{13}$CH$_3$OH. The $^1$H-NMR, $^{13}$C-NMR, $^{13}$C DEPT-135, 2D $^1$H-$^{13}$C HMQC and 2D $^1$H-$^{13}$C HMBC were recorded on Bruker AVANCE III HD 400 MHz nuclear magnetic resonance spectrometer. The amount of HCHO was quantified with acetylacetone color-developing method.

**Acetylacetone color-developing method.** 3 mL product solution was mixed with 2 mL as-prepared 0.25% (V/V) acetylacetone solution, and then heated for 3 min in boiling water. Afterward, the mixed solution became yellow-color. Through absorbance detection at 413 nm, the HCHO content was obtained. Specific reaction mechanism was shown in Fig. S6.

**Preparation of 0.25% (V/V) acetylacetone solution.** 25 g ammonium acetate was dissolved in 10 mL water, and then 3 mL acetic acid and 0.25 mL acetylacetone were added in sequence. Afterward, the solution volume was diluted to 100 mL. With pH adjusted to 6, the solution was stored at 2°C - 5°C, which could stay stable for one month.

**Band structure establishment of q-BiVO$_4$.** Taking BaSO$_4$ as internal reference sample, the UV-Vis diffuse reflectance spectrum of q-BiVO$_4$ was recorded on a Hitachi U-3010 UV-Vis spectrometer. For Mott-Schottky test, 5 mg q-BiVO$_4$ was ultrasonically dispersed in 1 mL mixed solution (0.2 mL ethanol + 0.8 mL water), and then dropped onto three 1 cm × 1 cm sized indium tin oxide (ITO) substrates as electrodes. Taking Ag/AgCl as reference electrode and Pt wire mesh as counter electrode, the Mott-Schottky plots were tested on CHI 760E electrochemical workstation in 1 M Na$_2$SO$_4$ solution under frequencies of 500, 700 and 900 Hz, respectively. The valence band of q-BiVO$_4$ was tested through ultraviolet photoelectron spectroscopy (UPS). The UPS spectrum was carried out on an EscaLab 250Xi.
The sample was pressed into film and bonded to the surface of conductive tape, while the other surface of conductive tape was fixed on the stage. Electrical contact between the stage and sample was made using a copper tape. Subsequently, the sample was stored within a vacuum chamber for further test. During the UPS measurement, He(I) emission line provided an illumination at 21.22 eV from a helium discharge lamp, and the partial gas pressure of He was adjusted to $2 \times 10^{-8}$ mbar. The stage was biased at -10.0 eV in order to accurately guarantee the low-kinetic energy cutoff and the collection of electron emission at 0° from normal. Cutoff energy was measured from the intersection between the linear extrapolation of the cutoff region and the baseline.

**Hydroxyl radical detection.** Coumarin was taken as a probe to detect production of •OH through monitoring formation of 7-OH-coumarin. Typically, 8 mg photocatalyst was dispersed in 15 mL 1 mM coumarin aqueous solution under stirring, and then either argon gas was injected to evacuate the air to produce an anaerobic environment or O$_2$ was bubbled to create a saturated O$_2$ condition under the sealed condition. After irradiation for 1 h, a certain amount of reaction solution was taken out and centrifuged to examine the fluorescence spectrum.

**Plasma optical emission spectrometer tests (ICP-OES).** In order to investigate the dissolved amount of catalysts, ICP-OES test on Bi element was conducted on the solution before and after photocatalytic reaction. 10 mg q-BiVO$_4$ was dispersed into 10 mL H$_2$O with stirring for 3 h under dark condition. Through centrifugation, the aqueous solution was collected as sample 1. Meanwhile, the other 10 mg q-BiVO$_4$ was dispersed into 10 mL H$_2$O, following by charging with 10 bar CH$_4$ and 10 bar O$_2$. After photocatalytic reaction for 3 h with stirring, the aqueous solution was obtained through centrifugation, denoted as sample 2. Both samples were tested by ICP-OES to check the dissolved catalyst during reaction. The corresponding ICP-OES test was carried out on Thermo Scientific iCAP6300 with CID detector.

**Electron spin resonance (ESR).** ESR spectroscopy was used to determine if CH$_4$ was directly oxidized by photoinduced holes from q-BiVO$_4$. Under Xenon lamp irradiation, the ESR spectra of q-BiVO$_4$ were recorded at 9.43 GHz and a liquid nitrogen temperature (77 K) using a Bruker EMX spectrometer under Ar or CH$_4$ atmosphere.

**Kinetic isotope effect (KIE) test.** Typically, 10 mg q-BiVO$_4$ was dispersed in 10 mL H$_2$O, and then 10 bar CH$_4$ (or CD$_4$) and 10 bar O$_2$ were charged into vessel. The monochromatic 420 nm light (100 mW cm$^{-2}$) was employed for irradiation, while 25°C cooling water was used to keep the reaction at room temperature. After reaction for 3, 5 or 7 h, the yield of oxygenates (CH$_3$OH, HCHO and CO$_2$) was tested from CH$_4$ and CD$_4$ reactant systems, respectively. According to the corresponding yield under different reaction time, we calculated the product formation rate constant in CH$_4$ ($k_H$) and CD$_4$ ($k_D$) systems, respectively. As a result, the rate-determining step was verified through KIE = $k_H / k_D$.

**Date availability.** The data that support the findings within this study are available upon request.
Declarations

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Author contributions

Y.F. and Z.T. conceived the idea, developed the outline, designed the experiment and compiled the manuscript. Y.F. conducted all the experiments and tests with the assistance of W.Z., X.Q., H.L. Y.J. and Z.S. D.H. coordinated the project and provided critical feedback. L.N. and Z.T. supervised the whole project.

Competing interests

The authors declare no competing interests.

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