Title: Molecular oxygen enhances H2O2 utilization for the photocatalytic conversion of methane to liquid-phase oxygenates
Reviewer #1 (Remarks to the Author):

This research uses molecular oxygen to improve H2O2 utilization efficiency for photocatalytic CH4 oxidation. The authors did provide many evidences to establish a plausible reaction mechanism. However, it is not enough to be accepted by NC, I suggest reject it. Several points have to be addressed to make it a complete work.

1. As photocatalyst, its photophysical and photoelectrical properties before and after synthesis should be studied, such as UV-vis diffuse reflectance spectra, band structures, photo-response curves, electrochemical impedance spectroscopies. The authors should give more discussions in main text.

2. In photocatalytic CH4 conversion, are all products formed at the same time? Or in particular order? It is suggested to study the change of product concentration over reaction time.

3. How about the light and chemical stabilities of catalyst after being used many times? And catalytic effect?

4. The statement “These oxygen isotope labelling experimental results suggest that O2 mainly acts as a promoter for photocatalytic CH4 conversion with H2O2, instead of as a reactant” is less rigorous. (Page 5, Paragraph 1, Last line) The conducted oxygen isotope labeling experiments only seem to prove that the oxygen in liquid products mainly comes from H2O2, rather than oxygen and water, but it cannot be inferred that oxygen promotes photocatalytic CH4 conversion.

5. Please add the decomposition rate of H2O2 into O2 by catalysts in the presence of H2O2, catalyst and/or light.

Reviewer #2 (Remarks to the Author):

In this manuscript, the author reported that the introduction of O2 could enhance the utilization efficiency of H2O2 by suppressing H2O2 adsorption on oxides and consequent photogenerated holes-mediated H2O2 dissociation into O2. Detailed characterizations and DFT study were carried out to explain the effect of Z-scheme TiO2-C3N4 heterojunctions to photocatalytic methane oxidation with H2O2. However, there are several crucial issues to be solved.

1. The lattice fringe should be re-measured and lattice spacing in TEM images must be calculated again because the yellow lines in TEM images were misplaced and ambiguous. The lattice spacing of C3N4 should be provided to explain the successful synthesis for heterojunction catalysts (Z-scheme TiO2-C3N4).

2. The light wavelength of 300 W Xe lamp should be added. Blank experiments must be made if the
wavelength of light illumination was UV range, for example, no catalysts and no CH4 with TiO2{001}-
C3N4 catalyst to exclude the carbon source on C3N4 support.
3. The authors only showed the selectivity of various oxygenates, but the yield or productivity of all
products should be exhibited especially in the manuscript to compare the change of photocatalytic
activity after adding O2.
4. For products analysis, CH2O species at 1712 cm-1 were detected on in situ DRIFTS spectra, and ·CHO
radicals were proposed in the reaction paths of TiO2 NCs and TiO2 NCs-C3N4. However, the authors did
not quantify the generation of HCHO. According to enormous references on photocatalytic methane
oxidation over TiO2 photocatalysts, HCHO can be the prominent over-oxidized products. Therefore, it
is necessary to provide analysis about HCHO.
5. We disagreed that “O2 mainly acts as a promoter for photocatalytic CH4 conversion with H2O2,
instead of as a reactant” at line 154. Firstly, ·O2-radicals were detected by in situ ESR spectra, it is easy
to form ·OOH by combination ·O2- with H+. Secondly, the authors presented O2 participated in the
generation of CH3OOH in Figure 2. Finally, CH318OH, HCO18OH, CH3HC218OH and CH3CO18OH were
detected by mass spectra when using 18O2. So the above conclusions is contradictory with “O2 mainly
acts as a promoter for photocatalytic CH4 conversion with H2O2, instead of as a reactant”.
6. If authors wanted to obtain the conclusion about “photocatalytic CH4 activation to ·CH3 radicals is
mainly mediated by h+ ”in line 179, the “DMPO-CH3” signals between the in situ ESR spectra of CH4 and
that of CH4+isopropyl alcohol mixture in Figure S12 should be compared under the same level. The
author should provide in situ ESR spectra of CH4+hole trapping agents to determine the oxidation of
methane to ·CH3 is mainly by h+.
7. The author should recheck the assignments of vibrational bands observed in the in situ DRIFTS spectra
especially about carbonates (1504 and 1592 cm-1) in methane oxidation reaction. Meanwhile, in situ
DRIFTS spectra among the 2100-2400 cm-1 should be given to exclude the generation of COx.
8. The photocatalytic reaction path of CH4 photocatalytic in Figure 2g and 2h was inadequate. For
example, the generation of ·O2- radicals should be represented on the schemes. The author proposed
the formation of CH3OH was mainly the reduction of CH3OOH, but it was easy to form CH3OH by the
coupling of ·CH3 and ·OH. In addition, authors did not explain the oxidation pathway of HCOOH from
·OH radicals or holes.

Reviewer #3 (Remarks to the Author):

Comments on the manuscript NCOMMS-22-18924-T entitled “Oxygen as a Molecular Additive to
Enhance Utilization Efficiency of H2O2 for Photocatalytic Conversion of Methane to Liquid-Phase
Oxygenates” by Weixin Huang et al.

This paper reported the photocatalytic methane (CH4) conversion by H2O2 as the oxidant over
TiO2{001})-C3N4 composite photocatalysts, in which, interestingly, O2 is used an molecular additive to
enhance the utilization efficiency of H2O2 up to 93.3%, and the selectivity of formic acid and liquid-
phase oxygenates is up to 69.8% and 97%, respectively. According to the studies of the NMR, ESR, and
in-situ FTIR techniques, the photocatalytic mechanism of CH4 is proposed. Thus, I can recommend the publication of this manuscript after a major revision:

1. An interesting discovery that O2 can enhance the utilization efficiency of H2O2 effectively was proposed, which, however, was not discussed comprehensively how O2 can improve the utilization efficiency of H2O2. It was found that the oxygen atoms in CH3OOH, CH3OH, HCOOH and CH3CH2OH are contributed majorly by H2O2 and minor by O2, but seldom by H2O, while the oxygen atoms of CH3COOH are contributed majorly by H2O, and minor by O2. (Figure 2) As such, the authors proposed that O2 mainly acts as a promoter for photocatalytic CH4 conversion with H2O2, instead of as a reactant. (Page 5, line 155) This expression is inappropriate, because O2 is clearly involved in the reaction, and the oxygen atom of O2 transfers into all the products. The low proportion of products from O2 oxidation may be due to the low amount of O2. Therefore, it is necessary to detect and discuss the activity and selectivity of photocatalytic CH4 conversion by H2O2 with the variable amount of O2.

2. According to the previous reports, HCHO should be formed in the photocatalytic reaction over TiO2 photocatalysts. It should be discussed why the HCHO is not produced in the CH4 oxidation herein.

3. The 13CH4 was used to demonstrate that all products exclusively form from CH4. However, if the C of the products is originated from CH4, why are not the splitting peaks due to 1H–13C J coupling (~140 Hz) for 13CH3OH, 13CH313CH2OH, and 13CH3COOH observed in these 1H NMR spectra (Figure S3)? Furthermore, all the 1H NMR signals of the 13CH4 and its oxidation products shift to high field in relation to the 1H NMR signals of the natural CH4, which should be because the magnetic field is unstable during the NMR experiment. Thus, it is necessary to redo the 1H NMR experiments with stable magnetic field.

4. The ESR experiments were performed in the presence of DMPO at low temperature (130K), rather than under approximate reaction conditions. Thus, it should be ex-situ experiment, rather than in-situ experiment.
**Author reply to Reviewer 1’s comments**

This research uses molecular oxygen to improve H$_2$O$_2$ utilization efficiency for photocatalytic CH$_4$ oxidation. The authors did provide many evidences to establish a plausible reaction mechanism. However, it is not enough to be accepted by NC, I suggest reject it. Several points have to be addressed to make it a complete work.

**Author reply:** We appreciate the reviewer’s insightful comments very much. In our submission, we report for the first time O$_2$-suppressed H$_2$O$_2$ adsorption on oxides and consequent photogenerated holes-mediated H$_2$O$_2$ dissociation into O$_2$, which provides a promising new strategy to achieve high H$_2$O$_2$ utilization efficiency and excellent photocatalytic performance for photocatalytic oxidation reactions over oxide-based photocatalysts via co-use of H$_2$O$_2$ and O$_2$. In the photocatalytic aqueous-phase methane conversion over an optimized TiO$_2$(001)-C$_3$N$_4$ composite photocatalyst during our study, O$_2$ additive significantly enhances the utilization efficiency of H$_2$O$_2$ unprecedentedly up to 93.3%, giving formic acid and liquid-phase oxygenates selectivity respectively of 69.8% and 97% and formic acid yield of 486 μmol·HCOOH·g$_{\text{catalyst}}$·h$^{-1}$. Since H$_2$O$_2$ production is well known as an environment-unfriendly and economic-costly process, in addition to excellent photocatalytic performance, high H$_2$O$_2$ utilization efficiency is also very desirable in photocatalytic selective conversion of methane over oxide-based photocatalysts widely using H$_2$O$_2$. Therefore, we believe that our results truly represent a breakthrough and will attract great attention and exert profound influences. Meanwhile, we have seriously considered the reviewer’s comments and revised the manuscript accordingly. We hope that the revised manuscript will be suitable for the publication in *Nature Communications*.

1 As photocatalyst, its photophysical and photoelectrical properties before and after synthesis should be studied, such as UV-vis diffuse reflectance spectra, band structures, photo-response curves, electrochemical impedance spectroscopies. The authors should give more discussions in main text.

**Author reply:** We appreciate the reviewer’s kind suggestions and accept them. We have added a paragraph to describe photophysical and photoelectrical properties of various TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$ composite photocatalysts in the revised manuscript as the following:

“The band structures of various TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$-0.1 photocatalysts were determined using UV–vis spectra and valence band XPS spectra (Supplementary Fig. 21). TiO$_2$ NCs-C$_3$N$_4$-0.1 exhibits smaller band gaps than corresponding the TiO$_2$ NCs, suggesting stronger capacity for light absorption and charge generation. The conduction band edges of TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$ composites were measured to be -0.14~0.34 and -0.41~0.47 vs RHE, respectively, consistent with the experimental observations that H$_2$O$_2$ undergoes the e$^-$-mediated activation into -OH radicals over TiO$_2$ NCs and -OOH radicals over TiO$_2$ NCs-C$_3$N$_4$-0.1 composites. ESR spectra (Supplementary Fig. 22a) show that TiO$_2$ NCs-C$_3$N$_4$-0.1 exhibit much lower densities of F$^+$ and Ti$^{3+}$ defects than TiO$_2$ NCs and the defect density follows an order of TiO$_2$[101] > TiO$_2$[100] > TiO$_2$[001] > TiO$_2$[101]-C$_3$N$_4$-0.1 > TiO$_2$[100]-C$_3$N$_4$-0.1 > TiO$_2$[001]-C$_3$N$_4$-0.1. Accordingly, PL spectra (Supplementary Fig. 22b) show that the PL peak arising from the recombination of photoexcited electrons and holes displays an intensity order of TiO$_2$[101] > TiO$_2$[100] > TiO$_2$[001] > TiO$_2$[101]-C$_3$N$_4$-0.1 > TiO$_2$[100]-C$_3$N$_4$-0.1 > TiO$_2$[001]-C$_3$N$_4$-0.1. EIS spectra of various TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$-0.1 photocatalysts were also measured, in which a smaller radius...
represents a low charge transfer resistance. All photocatalysts exhibit semicircle EIS spectra (Supplementary Fig. 22c), and the semicircle radius and consequently the charge transfer resistance follow an order of TiO$_2$\{101\} > TiO$_2$\{100\} > TiO$_2$\{001\} > TiO$_2$\{101\} - C$_3$N$_4$-0.1 > TiO$_2$\{100\} - C$_3$N$_4$-0.1 > TiO$_2$\{001\} - C$_3$N$_4$-0.1. ESR, PL and EIS are all bulk-sensitive characterization techniques, and their characterization results show that TiO$_2$ NCs-C$_3$N$_4$-0.1 exhibit higher charge separation and transfer efficiencies than corresponding TiO$_2$ NCs and that TiO$_2$\{001\} is the best of various TiO$_2$ NCs while TiO$_2$\{001\} - C$_3$N$_4$-0.1 is the best of TiO$_2$ NCs-C$_3$N$_4$-0.1 composite photocatalysts, consistent with the photocatalytic activity results.” (Please see Lines 259-281).

2 In photocatalytic CH$_4$ conversion, are all products formed at the same time? Or in particular order? It is suggested to study the change of product concentration over reaction time.

**Author reply:** We appreciate the reviewer’s insightful comments very much. Following the reviewer’s comments, we examined initial evolutions of reaction products as a function of reaction time over TiO$_2$\{001\} - C$_3$N$_4$-0.1. The results have been added in the revised manuscript as the following:

“Initial evolutions of reaction products as a function of reaction time were examined over TiO$_2$\{001\} - C$_3$N$_4$-0.1 (Supplementary Table 11). At a reaction time of 10 min, CH$_3$OOH, CH$_3$OH and HCHO were detected, and CH$_3$OOH was the major product. The CH$_3$OOH, CH$_3$OH and HCHO productions increased at a reaction time of 30 min, meanwhile, HCOOH and CH$_3$CH$_2$OH appeared. As a reaction time of 1 h, the CH$_3$OOH production decreased and HCHO was not detected, whereas the CH$_3$OH and HCOOH productions increased greatly and the CH$_3$CH$_2$OH production increased slightly, meanwhile, CH$_3$COOH emerged. These observations suggest CH$_3$OOH as the primary product and CH$_3$OH, HCHO, HCOOH, CH$_3$CH$_2$OH and CH$_3$COOH as the secondary products that are produced sequentially. Moreover, the reaction rate of HCHO seems to be faster than the formation rate.” (please see Lines 145-155)

3 How about the light and chemical stabilities of catalyst after being used many times? And catalytic effect?

**Author reply:** We appreciate the reviewer’s insightful comments very much. Following the reviewer’s comments, we evaluated the stability of TiO$_2$\{001\} - C$_3$N$_4$-0.1 photocatalyst and found that TiO$_2$\{001\} - C$_3$N$_4$-0.1 is stable and its performance maintains well within six cycles of photocatalytic activity evaluations. Routine structural characterization results, including XPS, XPS, UV-Vis spectra and photocurrent measurements, show few difference between the as-synthesized and used TiO$_2$\{001\} - C$_3$N$_4$-0.1 catalysts. The results have been added in the revised manuscript as the following:

“TiO$_2$\{001\} - C$_3$N$_4$-0.1 is stable and its performance maintains well within six cycles of photocatalytic activity evaluations (Supplementary Fig. 4). Routine structural characterization results (Supplementary Fig. 5), including XPS, VB-XPS, UV-Vis spectra and photocurrent measurements, show few difference between the as-synthesized and used TiO$_2$\{001\} - C$_3$N$_4$-0.1 catalysts.” (please see Lines 135-139)

4 The statement “These oxygen isotope labelling experimental results suggest that O$_2$ mainly acts as a promoter for photocatalytic CH$_4$ conversion with H$_2$O$_2$, instead of as a reactant” is less rigorous.

(Page 5, Paragraph 1, Last line) The conducted oxygen isotope labeling experiments only seem to
prove that the oxygen in liquid products mainly comes from H₂O₂, rather than oxygen and water, but it cannot be inferred that oxygen promotes photocatalytic CH₄ conversion.

Author reply: We appreciate the reviewer’s insightful comments very much. We have rewritten the commented sentence more rigorously in the revised manuscript as the following:

“Therefore, during photocatalytic aqueous-phase CH₄ conversion in the presence of H₂O₂ and O₂, CH₄ preferentially reacts with H₂O₂ to produce liquid-phase oxygenates, while O₂ acts mainly as a promoter to enhance H₂O₂ utilization efficiency and consequently CH₄ conversion, and minorly as a reactant.” (please see Lines 207-210)

5 Please add the decomposition rate of H₂O₂ into O₂ by catalysts in the presence of H₂O₂, catalyst and/or light.

Author reply: We appreciate the reviewer’s kind suggestions very much. We have added the decomposition rate of H₂O₂ under different conditions in Fig. 1e and Supplementary Tables 2 and 3, and described the results in the revised manuscript as the following:

“As shown in Fig. 1e, the H₂O₂ decomposition percentage/H₂O₂ decomposition rate/O₂ selectivity are 31.2%/610.9 μmol·h⁻¹/93.0% over TiO₂{001} NCs in the Ar atmosphere and decrease to 15.4%/301.5 μmol·h⁻¹/91.8% in the 10% O₂/Ar atmosphere, while they are 20.4%/399.4 μmol·h⁻¹/89.0% over TiO₂{001}-C₃N₄-0.1 in the Ar atmosphere and decrease to 8.26%/161.7 μmol·h⁻¹/86.4% in the 10% O₂/Ar atmosphere.” (please see Lines 88-93)

We appreciate the reviewer’s effort on reviewing our manuscript very much, and we hope that the revised manuscript will be suitable for the publication in Nature Communications.
**Author reply to Reviewer 2’s comments**

In this manuscript, the author reported that the introduction of O\(_2\) could enhance the utilization efficiency of H\(_2\)O\(_2\) by suppressing H\(_2\)O\(_2\) adsorption on oxides and consequent photogenerated holes-mediated H\(_2\)O\(_2\) dissociation into O\(_2\). Detailed characterizations and DFT study were carried out to explain the effect of Z-scheme TiO\(_2\)-C\(_3\)N\(_4\) heterojunctions to photocatalytic methane oxidation with H\(_2\)O\(_2\). However, there are several crucial issues to be solved.

**Author reply:** We appreciate the reviewer’s positive recommendation and insightful comments very much. We have seriously considered the reviewer’s comments and revised the manuscript accordingly. We hope that the revised manuscript will be suitable for the publication in *Nature Communications*.

1. The lattice fringe should be re-measured and lattice spacing in TEM images must be calculated again because the yellow lines in TEM images were misplaced and ambiguous. The lattice spacing of C\(_3\)N\(_4\) should be provided to explain the successful synthesis for heterojunction catalysts (Z-scheme TiO\(_2\)-C\(_3\)N\(_4\)).

**Author reply:** We appreciate the reviewer’s insightful comments very much. We have re-measured lattice fringes and clearly marked the values and assigned crystal planes in HRTEM images shown in Supplementary Figs. 1 and 3. We are sure that the lattice fringes of 0.24 and 0.35 nm arise from anatase TiO\(_2\) \{001\} and \{101\} crystal planes, respectively. We also re-took the HRTEM and elementary mapping images of our samples with higher qualities. Unfortunately, we failed to observe clear lattice fringes of g-C\(_3\)N\(_4\) in the HRTEM images (Supplementary Fig. 3d), which is rather well known due to the strong damage effect of high-energy electron beam on the structure of g-C\(_3\)N\(_4\), but its presence in the TiO\(_2\) NCs-C\(_3\)N\(_4\) composites is identified by XRD patterns (Supplementary Fig. 3e) and XPS spectra (Supplementary Fig. 3f).

In the revised manuscript, we have included a separate paragraph to describe synthesis and routine spectroscopic and microscopic characterization results of our TiO\(_2\) NCs and TiO\(_2\) NCs-C\(_3\)N\(_4\) composite photocatalysts as the following:

**“Synthesis and structural characterizations.** Anatase TiO\(_2\) nanocrystals (NCs) predominantly enclosed by the \{001\} facets (denoted as TiO\(_2\)\{001\}), the \{100\} facets (denoted as TiO\(_2\)\{100\}) and the \{101\} facets (denoted as TiO\(_2\)\{101\}) were prepared following well-established recipes\(^{27}\). XRD patterns, TEM and HRETM images of as-synthesized various TiO\(_2\) NCs (Fig. 1a, Supplementary Fig. 1) agree with those reported previously\(^{27}\). TiO\(_2\) NCs-C\(_3\)N\(_4\) composites were prepared by calcination of mixture of calculated amounts of dicyandiamide (C\(_2\)H\(_4\)N\(_4\)) and TiO\(_2\) NCs in Ar at 550 °C and denoted as TiO\(_2\) NCs-C\(_3\)N\(_4\)-x, in which x was the actual TiO\(_2\):C\(_3\)N\(_4\) mole ratio acquired by TGA analysis (Supplementary Fig. 2 and Table 1). TEM, HRTEM and element mapping images (Figs. 1 b-d, Supplementary Fig. 3 a-c) show that various TiO\(_2\) NCs preserve their original morphologies and form smooth anatase TiO\(_2\)-g-C\(_3\)N\(_4\) interfaces. We failed to observe clear lattice fringes of g-C\(_3\)N\(_4\) in the HRTEM images (Supplementary Fig. 3d) likely due to the strong damage effect of high-energy electron beam on the structure of g-C\(_3\)N\(_4\), but its presence in the TiO\(_2\) NCs-C\(_3\)N\(_4\) composites is identified by XRD patterns (Supplementary Fig. 3e) and XPS spectra (Supplementary Fig. 3f).” (please see Lines 62-75)

2. The light wavelength of 300 W Xe lamp should be added. Blank experiments must be made if the
wavelength of light illumination was UV range, for example, no catalysts and no CH₄ with TiO₂{001}-C₃N₄ catalyst to exclude the carbon source on C₃N₄ support.

**Author reply:** We appreciate the reviewer’s kind suggestions very much. We have added the spectrum of used Xe light in the revised Supplementary Information (please see Page S3).

We also did blank photocatalytic experiment of photocatalytic reaction in the presence of TiO₂{001}-C₃N₄-0.1 but absence of CH₄ in the reactant and did not detected any C-contained products. The results, together with the ¹³CH₄ experimental results, demonstrate that all C-contained products exclusively form from CH₄. We have described these results in the revised manuscript as the following:

“Blank photocatalytic experiment of photocatalytic reaction in the presence of TiO₂{001}-C₃N₄-0.1 but absence of CH₄ in the reactant did not produce detectable C-contained products; meanwhile, using ¹³CH₄, all C-contained products only contained ¹³C (Supplementary Fig. 6). Thus, all C-contained products exclusively form from CH₄.” (please see Lines 142-145)

3. The authors only showed the selectivity of various oxygenates, but the yield or productivity of all products should be exhibited especially in the manuscript to compare the change of photocatalytic activity after adding O₂.

**Author reply:** We appreciate the reviewer’s kind suggestions very much. We have added the yields of all products in Fig. 1 f and g and Supplementary Tables 5-10, and described the results in the revised manuscript as the following:

“the HCOOH yield from 12.0 to 37.6 μmol·g⁻¹·h⁻¹,” (please see Line 118)

“the HCOOH yield from 202.2 to 486 μmol·g⁻¹·h⁻¹,” (please see Lines 125 and 126)

4. For products analysis, CH₂O species at 1712 cm⁻¹ were detected on in situ DRIFTS spectra, and -CHO radicals were proposed in the reaction paths of TiO₂ NCs and TiO₂ NCs-C₃N₄. However, the authors did not quantify the generation of HCHO. According to enormous references on photocatalytic methane oxidation over TiO₂ photocatalysts, HCHO can be the prominent over-oxidized products. Therefore, it is necessary to provide analysis about HCHO.

**Author reply:** We appreciate the reviewer’s insightful comments very much. Our in situ DRIFTS spectra demonstrate the formation of adsorbed HCHO as a surface intermediate during photocatalytic aqueous-phase CH₄ conversion to HCOOH using H₂O₂ and O₂. We analyzed all likely products but did not detect the formation of HCHO under the studied reaction conditions. As suggested by the reviewer 1, we examined initial evolutions of reaction products as a function of reaction time over TiO₂{001}-C₃N₄-0.1. The HCHO formation appears at a reaction time of 10 min, increases at a reaction time of 30 min, but disappears at a reaction time of 1 h. These observations suggest that the reaction rate of HCHO seems to be faster than the formation rate, which makes HCHO undetectable. We have added these results in the revised manuscript as the following:

“Initial evolutions of reaction products as a function of reaction time were examined over TiO₂{001}-C₃N₄-0.1 (Supplementary Table 11). At a reaction time of 10 min, CH₃OOH, CH₃OH and HCHO were detected, and CH₃OOH was the major product. The CH₃OOH, CH₃OH and HCHO productions increased at a reaction time of 30 min, meanwhile, HCOOH and CH₃CH₂OH appeared.
As a reaction time of 1 h, the CH$_3$OOH production decreased and HCHO was not detected, whereas the CH$_3$OH and HCOOH productions increased greatly and the CH$_3$CH$_2$OH production increased slightly, meanwhile, CH$_3$COOH emerged. These observations suggest CH$_3$OOH as the primary product and CH$_3$OH, HCHO, HCOOH, CH$_3$CH$_2$OH and CH$_3$COOH as the secondary products that are produced sequentially. Moreover, the reaction rate of HCHO seems to be faster than the formation rate. (please see Lines 145-155)

5. We disagreed that “O$_2$ mainly acts as a promoter for photocatalytic CH$_4$ conversion with H$_2$O$_2$, instead of as a reactant” at line 154. Firstly, ∙O$_2$- radicals were detected by in situ ESR spectra, it is easy to form ∙OOH by combination ∙O$_2$- with H$.+$ Secondly, the authors presented O$_2$ participated in the generation of CH$_3$OOH in Figure 2. Finally, CH$_3$H$_2$O$_{18}$, HCO$^{18}$OH, CH$_3$HC$_2$O$_{18}$OH and CH$_3$CO$^{18}$OH were detected by mass spectra when using $^{18}$O$_2$. So the above conclusions is contradictory with “O$_2$ mainly acts as a promoter for photocatalytic CH$_4$ conversion with H$_2$O$_2$, instead of as a reactant”.

Author reply: We appreciate the reviewer’s insightful comments very much. We have rewritten the commented sentence more rigorously in the revised manuscript as the following:

“Therefore, during photocatalytic aqueous-phase CH$_4$ conversion in the presence of H$_2$O$_2$ and O$_2$, CH$_4$ preferentially reacts with H$_2$O$_2$ to produce liquid-phase oxygenates, while O$_2$ acts mainly as a promoter to enhance H$_2$O$_2$ utilization efficiency and consequently CH$_4$ conversion, and minorly as a reactant.” (please see Lines 207-210)

6. If authors wanted to obtain the conclusion about “photocatalytic CH$_4$ activation to ∙CH$_3$ radicals is mainly mediated by h$^+$” in line 179, the “DMPO-CH$_3$” signals between the in situ ESR spectra of CH$_4$ and that of CH$_4$+isopropyl alcohol mixture in Figure S12 should be compared under the same level. The author should provide in situ ESR spectra of CH$_4$+hole trapping agents to determine the oxidation of methane to ∙CH$_3$ is mainly by h$^+$.

Author reply: We appreciate the reviewer’s insightful comments very much. We have compared the in situ ESR spectra of CH$_4$+H$_2$O and CH$_4$+ isopropyl alcohol+H$_2$O under UV light illumination in the presence of DMPO over TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$-0.1 composites at 298 K in Supplementary Fig. 17 of revised manuscript.∙CH$_3$ radicals greatly grew when isopropanol was added to quench ∙OH radicals, supporting that the formation of ∙CH$_3$ radicals is not related to ∙OH radicals. This also suggests the likely reaction between co-existing∙CH$_3$ and ∙OH radicals. Meanwhile, ∙CH$_3$ radicals were not observed in the in situ ESR spectra of CH$_4$+methanol mixture (CH$_4$ +5 mL CH$_3$OH+3µL DMPO) + H$_2$O$_2$ + O$_2$ under UV light illumination in the presence of DMPO over TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$-0.1 composites at 298 K (Supplementary Fig. 18) due to the quench of h$^+$ by methanol, but ∙O$_2$- radicals appear. Thus, photocatalytic CH$_4$ activation to ∙CH$_3$ radicals is mainly mediated by h$^+$, instead of by-OOH, ∙OH and ∙O$_2$- radicals.

The relevant results are described in the revised manuscript as the following:

“When CH$_4$ was introduced to the aqueous solutions containing TiO$_2$ NCs or TiO$_2$ NCs-C$_3$N$_4$-0.1 composites under UV light illumination (Fig. 2f), ∙CH$_3$ radicals$^{22,26}$, in addition to ∙OH radicals, were detected. They greatly grew when isopropanol was added to quench ∙OH radicals (Supplementary Fig. 17), but could not be detected in the presence of H$_2$O$_2$ and O$_2$ when h$^+$ was quenched using methanol (Supplementary Fig. 18). Thus, photocatalytic CH$_4$ activation to ∙CH$_3$
radicals is mainly mediated by $h^+$, instead of by OOH, $\cdot$OH and $\cdot$O$_2^-$ radicals.” (please see Lines 227-233)

7. The author should recheck the assignments of vibrational bands observed in the in situ DRIFTS spectra especially about carbonates (1504 and 1592 cm$^{-1}$) in methane oxidation reaction. Meanwhile, in situ DRIFTS spectra among the 2100-2400 cm$^{-1}$ should be given to exclude the generation of CO$_x$.

**Author reply:** We appreciate the reviewer’s insightful comments very much. As discussed in our manuscript, the observed vibrational bands (Supplementary Table 14) were assigned based on in situ DRIFTS spectra of CH$_3$OH and HCOOH adsorption on various TiO$_2$ NCs (Supplementary Fig. 28) and previous reports$^{34-36}$ (please see Lines 355-358). The assignments of carbonates on TiO$_2$ have been ambiguous due to the presence of different types of carbonates. According to our own work [Ref. 34, *J. Phys. Chem. C* 120, 21472–21485 (2016) and *ACS Catal.* 12, 6457-6463 (2022)], the peak at 1592 cm$^{-1}$ can be assigned to bidentate carbonate while that at 1504 cm$^{-1}$ can be assigned to monodentate carbonate. We believe that our assignments are reliable.

In the revised manuscript, we have added the papers *J. Phys. Chem. C* 120, 21472–21485 (2016) and *ACS Catal.* 12, 6457-6463 (2022) as Ref. 35 and 36 to further support our assignments. We have also re-ordered all references accordingly.

Meanwhile, we have included the in situ DRIFTS spectra among the 2100-2400 cm$^{-1}$ to Figure 4a in the revised manuscript, in which no CO$_x$ signal could be seen.

8. The photocatalytic reaction path of CH$_4$ photocatalytic in Figure 2g and 2h was inadequate. For example, the generation of $\cdot$O$_2^-$ radicals should be represented on the schemes. The author proposed the formation of CH$_3$OH was mainly the reduction of CH$_3$OOH, but it was easy to form CH$_3$OH by the coupling of $\cdot$CH$_3$ and $\cdot$OH. In addition, authors did not explain the oxidation pathway of HCOOH from $\cdot$OH radicals or holes.

**Author reply:** We appreciate the reviewer’s insightful comments very much. It is unlikely to schematically show the while reaction network of our photocatalytic reactions in Fig. 2 g and h due to the complexity. The contents of Fig. 2 g and h are to schematically show the proposed dominant photocatalytic aqueous-phase CH$_4$ reaction paths to liquid-phase oxygenates in the presence of H$_2$O$_2$ and O$_2$ over TiO$_2$ NCs and TiO$_2$ NCs-C$_3$N$_4$ based on the photocatalytic reaction data, ESR results, isotope-labelling results, in situ DRIFTS results, and the literature’s reports. The description and discussion of Fig. 2 g and h can be found at Lines 231-255, 259-263, 362-365.

In the revised manuscript, we have re-written the caption of Fig. 2 g and h to clarify their contents as the following:

“Schematic diagrams of proposed dominant photocatalytic aqueous-phase CH$_4$ reaction paths to liquid-phase oxygenates in the presence of H$_2$O$_2$ and O$_2$ over (g) TiO$_2$ NCs and (h) TiO$_2$ NCs-C$_3$N$_4$.” (please see Lines 169 and 170)

We appreciate the reviewer’s effort on reviewing our manuscript very much, and we hope that the revised manuscript will be suitable for the publication in *Nature Communications*. 
Author reply to Reviewer 3’s comments

This paper reported the photocatalytic methane (CH₄) conversion by H₂O₂ as the oxidant over TiO₂(001)-C₃N₄ composite photocatalysts, in which, interestingly, O₂ is used a molecular additive to enhance the utilization efficiency of H₂O₂ up to 93.3%, and the selectivity of formic acid and liquid-phase oxygenates is up to 69.8% and 97%, respectively. According to the studies of the NMR, ESR, and in-situ FTIR techniques, the photocatalytic mechanism of CH₄ is proposed. Thus, I can recommend the publication of this manuscript after a major revision:

Author reply: We appreciate the reviewer’s positive recommendation and insightful comments very much. We have seriously considered the reviewer’s comments and revised the manuscript accordingly. We hope that the revised manuscript will be suitable for the publication in Nature Communications.

1. An interesting discovery that O₂ can enhance the utilization efficiency of H₂O₂ effectively was proposed, which, however, was not discussed comprehensively how O₂ can improve the utilization efficiency of H₂O₂. It was found that the oxygen atoms in CH₃OOH, CH₃OH, HCOOH and CH₃CH₂OH are contributed majorly by H₂O₂ and minor by O₂, but seldom by H₂O, while the oxygen atoms of CH₃COOH are contributed majorly by H₂O, and minor by O₂. (Figure 2) As such, the authors proposed that O₂ mainly acts as a promoter for photocatalytic CH₄ conversion with H₂O₂, instead of as a reactant. (Page 5, line 155) This expression is inappropriate, because O₂ is clearly involved in the reaction, and the oxygen atom of O₂ transfers into all the products. The low proportion of products from O₂ oxidation may be due to the low amount of O₂. Therefore, it is necessary to detect and discuss the activity and selectivity of photocatalytic CH₄ conversion by H₂O₂ with the variable amount of O₂.

Author reply: We appreciate the reviewer’s insightful comments very much. Following the reviewer’s comments, we the O₂ concentration in the reactant was increased from 4% (8%CH₄+4%O₂+88%Ar+165μL H₂O₂+20mL H₂O) to 12% (8%CH₄+12%O₂+80%Ar+165μL H₂O₂+20mL H₂O), and the photocatalytic reaction was studied over TiO₂(001)-C₃N₄-0.1 comparatively with ¹⁶O₂ or ¹⁸O₂ in order to further clarify the role of O₂. The results show that using ¹⁶O₂ or ¹⁸O₂ gave similar H₂O₂ utilization efficiencies of around 94% and slightly different CH₄ conversion rates and product selectivity. Using ¹⁸O₂, the CH₃¹⁸OH/CH₃¹⁶OH, HC¹⁶O¹⁸OH/HC¹⁶O¹⁶OH and CH₃CH₂¹⁸OH/CH₃CH₂¹⁶OH ratios in the liquid-phase products were measured respectively as around 0.19, 0.17 and 0.22, similar to the case of the reactant with 4% O₂; however, C¹⁸O and C¹⁸O₂ were detected and the fraction of C¹⁸O¹⁸O in CO₂ is much larger than that of C¹⁶O¹⁸O, different from the case of the reactant with 4% O₂. These results prove that, during photocatalytic aqueous-phase CH₄ conversion in the presence of H₂O₂ and O₂, CH₄ preferentially reacts with H₂O₂ to produce liquid-phase oxygenates, while O₂ acts mainly as a promoter to enhance H₂O₂ utilization efficiency and consequently CH₄ conversion, and minorly as a reactant.

We have included these results in the revised manuscript as the following:

*In order to further clarify the role of O₂, the O₂ concentration in the reactant was increased from 4% (8%CH₄+4%O₂+88%Ar+165μL H₂O₂+20mL H₂O) to 12% (8%CH₄+12%O₂+80%Ar+165μL H₂O₂+20mL H₂O), and the photocatalytic reaction was studied over TiO₂(001)-C₃N₄-0.1 comparatively with ¹⁶O₂ or ¹⁸O₂. Using ¹⁶O₂ or ¹⁸O₂ gave similar H₂O₂ utilization efficiencies of
around 94% and slightly different CH4 conversion rates and product selectivity (Supplementary Table 13). Using 18O2, the CH318OH/CH316OH, HC16O18OH/HC16O16OH and CH3CH318OH/CH3CH316OH ratios in the liquid-phase products were measured respectively as around 0.19, 0.17 and 0.22 (Supplementary Figs. 12-14), similar to the case of the reactant with 4% O2; however, C18O and C18O2 were detected and the fraction of C16O18O in CO2 is much larger than that of C16O16O, different from the case of the reactant with 4% O2. Therefore, during photocatalytic aqueous-phase CH4 conversion in the presence of H2O2 and O2, CH4 preferentially reacts with H2O2 to produce liquid-phase oxygenates, while O2 acts mainly as a promoter to enhance H2O2 utilization efficiency and consequently CH4 conversion, and minorly as a reactant.” (please see Lines 197-210)

2. According to the previous reports, HCHO should be formed in the photocatalytic reaction over TiO2 photocatalysts. It should be discussed why the HCHO is not produced in the CH4 oxidation herein.

Author reply: We appreciate the reviewer’s insightful comments very much. We analyzed all likely products but did not detect the formation of HCHO under the studied reaction conditions. As suggested by the reviewer 1, we examined initial evolutions of reaction products as a function of reaction time over TiO2[001]-C3N4-0.1. The HCHO formation appears at a reaction time of 10 min, increases at a reaction time of 30 min, but disappears at a reaction time of 1 h. These observations suggest that the reaction rate of HCHO seems to be faster than the formation rate, which makes HCHO undetectable. We have added these results in the revised manuscript as the following:

“Initial evolutions of reaction products as a function of reaction time were examined over TiO2[001]-C3N4-0.1 (Supplementary Table 11). At a reaction time of 10 min, CH3OOH, CH3OH and HCHO were detected, and CH3OOH was the major product. The CH3OOH, CH3OH and HCHO productions increased at a reaction time of 30 min, meanwhile, HCOOH and CH3CH2OH appeared. As a reaction time of 1 h, the CH3OOH production decreased and HCHO was not detected, whereas the CH3OH and HCOOH productions increased greatly and the CH3CH2OH production increased slightly, meanwhile, CH3COOH emerged. These observations suggest CH3OOH as the primary product and CH3OH, HCHO, HCOOH, CH3CH2OH and CH3COOH as the secondary products that are produced sequentially. Moreover, the reaction rate of HCHO seems to be faster than the formation rate.” (please see Lines 145-155)

3. The 13CH4 was used to demonstrate that all products exclusively form from CH4. However, if the C of the products is originated from CH4, why are not the splitting peaks due to 1H–13C J coupling (~140 Hz) for 13CH3OH, 13CH313CH2OH, and 13CH3COOH observed in these 1H NMR spectra (Figure S3)? Furthermore, all the 1H NMR signals of the 13CH4 and its oxidation products shift to high field in relation to the 1H NMR signals of the natural CH4, which should be because the magnetic field is unstable during the NMR experiment. Thus, it is necessary to redo the 1H NMR experiments with stable magnetic field.

Author reply: We appreciate the reviewer’s insightful comments very much. We have inquired our colleague in charge of the NMR facility on which our 1H NMR spectra were acquired, an expert on NMR. We were told that the frequency of the used NMR facility (Nuclear magnetic resonance spectrometer, AVANCE III HD400) is ~400 Hz, which is not able to induce the 1H–13C J coupling (~140 Hz). Meanwhile, we measured the mass spectra of the products using 13CH4, whose results only show 13C-contained products, furthering confirming that all products are from CH4.
In the revised manuscript, the mass spectra of the products using $^{13}$CH$_4$ are added to Supplementary Fig. 6.

4. The ESR experiments were performed in the presence of DMPO at low temperature (130 K), rather than under approximate reaction conditions. Thus, it should be ex-situ experiment, rather than in-situ experiment.

Author reply: We appreciate the reviewer’s insightful comments very much. All ESR spectra in the presence of DMPO were measured at 298 K under UV light illumination, and thus can be referred as in situ ESR. We have added the temperature to the figure captions in the revised manuscript as the following:

“(e) In situ ESR spectra of H$_2$O, H$_2$O+O$_2$, H$_2$O+H$_2$O$_2$ and H$_2$O+O$_2$+H$_2$O$_2$ solutions under UV light illumination at 298 K in the presence of DMPO over TiO$_2${001} NCs and TiO$_2${001}-C$_3$N$_4$-0.1. (f) In situ ESR spectra of CH$_4$+H$_2$O mixture under UV light illumination at 298 K in the presence of DMPO over TiO$_2${101}, TiO$_2${100} and TiO$_2${001} NCs, TiO$_2${101}-C$_3$N$_4$-0.1, TiO$_2${100}-C$_3$N$_4$-0.1 and TiO$_2${001}-C$_3$N$_4$-0.1 composites.” (please see Lines 165-169)

We appreciate the reviewer’s effort on reviewing our manuscript very much, and we hope that the revised manuscript will be suitable for the publication in *Nature Communications*.
Reviewer #1 (Remarks to the Author):

The authors answered all the issues from reviewers, it can be accepted by NC.

Reviewer #2 (Remarks to the Author):

The concerns have been well addressed in the revised manuscript. I recommend the publication of this manuscript in Nature Communications.

Reviewer #3 (Remarks to the Author):

Reviewer 3’s comments 3: The 13CH4 was used to demonstrate that all products exclusively form from CH4. However, if the C of the products is originated from CH4, why are not the splitting peaks due to 1H–13C J coupling (~140 Hz) for 13CH3OH, 13CH313CH2OH, and 13CH3COOH observed in these 1H NMR spectra (Figure S3)? Furthermore, all the 1H NMR signals of the 13CH4 and its oxidation products shift to high field in relation to the 1H NMR signals of the natural CH4, which should be because the magnetic field is unstable during the NMR experiment. Thus, it is necessary to redo the 1H NMR experiments with stable magnetic field.

Author reply: We appreciate the reviewer’s insightful comments very much. We have inquired our colleague in charge of the NMR facility on which our 1H NMR spectra were acquired, an expert on NMR. We were told that the frequency of the used NMR facility (Nuclear magnetic resonance spectrometer, AVA VCE III HD400) is ~400 Hz, which is not able to induce the 1H–13C J coupling (~140 Hz). Meanwhile, we measured the mass spectra of the products using 13CH4, whose results only show 13C-contained products, furthering confirming that all products are from CH4.

According to the reply for the question 3 of Reviewer 3’s comments, it is reasonable to believe that the author did not realize the seriousness of the question. Since the catalysts used by the author contain carbon, the sufficient evidence should be provided to prove that the product (such as CH3OH, CH3CH2OH, CH3COOH, and HCOOH) originates from the reactant (CH4) rather than the organic substance contained in the catalyst. In the manuscript, the CH4 was labeled by 13C, and then the 1H NMR technique was used to study the products of CH4 oxidation. If the C of the products is originated from the 13CH4, the splitting peaks due to 1H–13C J coupling (~140 Hz) for 13CH3OH, 13CH313CH2OH, 13CH3COOH, and HCOOH should be observed definitely in the 1H NMR spectra. However, the splitting peaks of these products do not occur, which proves that the product does not originate from the 13CH4. To reply the comments, the authors inquired an expert on NMR, and were told that “the frequency of the used NMR facility (Nuclear magnetic resonance spectrometer, AVA VCE III HD400) is ~400 Hz, which is not able to induce the 1H–13C J coupling (~140 Hz)”’. We doubt the professionalism of this expert.
First, the magnetic field of the nuclear magnetic resonance spectrometer (AVANCE III HD400) should be ~400 MHz, rather than ~400 Hz. Second, the ~140 Hz of 1H–13C J coupling corresponding to ~0.35 ppm can occur definitely in the spectra. Additionally, the authors do not explain why all the 1H NMR signals of the 13CH₄ and its oxidation products shift to high field in relation to the 1H NMR signals of the natural CH₄.
Author reply to Reviewer 3’s comments

Reviewer 3’s comments 3: The $^{13}$CH$_4$ was used to demonstrate that all products exclusively form from CH$_4$. However, if the C of the products is originated from CH$_4$, why are not the splitting peaks due to $^1$H–$^{13}$C J coupling (~140 Hz) for $^{13}$CH$_3$OH, $^{13}$CH$_3$CH$_2$OH, and $^{13}$CH$_3$COOH observed in these $^1$H NMR spectra (Figure S3)? Furthermore, all the $^1$H NMR signals of the $^{13}$CH$_4$ and its oxidation products shift to high field in relation to the $^1$H NMR signals of the natural CH$_4$, which should be because the magnetic field is unstable during the NMR experiment. Thus, it is necessary to redo the $^1$H NMR experiments with stable magnetic field.

Author reply: We appreciate the reviewer’s insightful comments very much. We have inquired our colleague in charge of the NMR facility on which our $^1$H NMR spectra were acquired, an expert on NMR. We were told that the frequency of the used NMR facility (Nuclear magnetic resonance spectrometer, AVAVCE III HD400) is ~400 Hz, which is not able to induce the $^1$H–$^{13}$C J coupling (~140 Hz). Meanwhile, we measured the mass spectra of the products using $^{13}$CH$_4$, whose results only show $^{13}$C-contained products, furthering confirming that all products are from CH$_4$.

According to the reply for the question 3 of Reviewer 3’s comments, it is reasonable to believe that the author did not realize the seriousness of the question. Since the catalysts used by the author contain carbon, the sufficient evidence should be provided to prove that the product (such as CH$_3$OH, CH$_3$CH$_2$OH, CH$_3$COOH, and HCOOH) originates from the reactant (CH$_4$) rather than the organic substance contained in the catalyst. In the manuscript, the CH$_4$ was labeled by $^{13}$C, and then the $^1$H NMR technique was used to study the products of CH$_4$ oxidation. If the C of the products is originated from the $^{13}$CH$_4$, the splitting peaks due to $^1$H–$^{13}$C J coupling (~140 Hz) for $^{13}$CH$_3$OH, $^{13}$CH$_3$CH$_2$OH, $^{13}$CH$_3$COOH, and HCOOH should be observed definitely in the $^1$H NMR spectra. However, the splitting peaks of these products do not occur, which proves that the product does not originate from the $^{13}$CH$_4$. To reply the comments, the authors inquired an expert on NMR, and were told that “the frequency of the used NMR facility (Nuclear magnetic resonance spectrometer, AVAVCE III HD400) is ~400 Hz, which is not able to induce the $^1$H–$^{13}$C J coupling (~140 Hz)”. We doubt the professionalism of this expert. First, the magnetic field of the nuclear magnetic resonance spectrometer (AVAVCE III HD400) should be ~400 MHz, rather than ~400 Hz. Second, the ~140 Hz of $^1$H–$^{13}$C J coupling corresponding to ~0.35 ppm can occur definitely in the spectra. Additionally, the authors do not explain why all the $^1$H NMR signals of the $^{13}$CH$_4$ and its oxidation products shift to high field in relation to the $^1$H NMR signals of the natural CH$_4$.

Author reply: We appreciate the reviewer’s insightful comments very much. We fully agreed with these comments and discussed with the faculty in charge of NMR facility in detail. After careful examinations of our previous $^1$H NMR measurement, we found that the parameter of NMR was accidently set as “$^1$H experiment with decoupling”, resulting the failure to give the $^1$H–$^{13}$C coupling features.
During the course of revision, we re-measured the $^{13}$C with decoupling NMR and $^1$H NMR spectra of liquid-phase products of aqueous-phase photocatalytic conversion of methane over TiO$_2$(001)-C$_3$N$_4$-0.1 under the reaction condition of 4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O and of 8%CH$_4$+4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O at 298 K using CH$_4$ or $^{13}$CH$_4$ at 298 K. The acquired $^1$H NMR spectra show the $^1$H-$^{13}$C coupling features, consistent with those expected by the reviewer. These results, together with the MS results, confirm that all the products exclusively form from CH$_4$.

We have revised Supplementary Figure 6 shown below in the revised Supplementary Materials and updated the file “Source data” accordingly.

**Supplementary Figure 6.** (a,b) $^1$H NMR spectra of liquid-phase products of aqueous-phase photocatalytic conversion of methane over TiO$_2$(001)-C$_3$N$_4$-0.1 under the
reaction condition of 4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O and of 8%CH$_4$+4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O at 298 K using CH$_4$ or $^{13}$CH$_4$ at 298 K. The splitting peaks due to $^1$H-$^{13}$C J coupling for $^{13}$CH$_3$OH, $^{13}$CH$_3$OOH, $^{13}$HCOOH, $^{13}$CH$_4$$^{13}$CH$_2$OH, and $^{13}$CH$_3$$^{13}$COOH observed in these $^1$H NMR spectra. (c) $^{13}$C with decoupling NMR spectra of liquid-phase products of aqueous-phase photocatalytic conversion of methane over TiO$_2$-{001}-C$_3$N$_4$-0.1 under the reaction condition of 4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O and of 8%CH$_4$+4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O at 298 K using CH$_4$ or $^{13}$CH$_4$ at 298 K. (d) As-measured mass spectra of liquid-phase products of aqueous-phase photocatalytic conversion of methane over TiO$_2$-{001}-C$_3$N$_4$-0.1 under the reaction condition of 8%CH$_4$+4%O$_2$+88%Ar+165 µL H$_2$O+20 mL H$_2$O at 298 K using $^{13}$CH$_4$ (top panel) or CH$_4$ (bottom panel) at 298 K. Photocatalyst amount: 20 mg; reaction time: 8 hours; stirring speed: 500 rpm.

We appreciate the reviewer’s effort on reviewing our manuscript very much. We hope that the revised manuscript will be suitable for the publication in *Nature Communications*. 
REVIEWERS’ COMMENTS

Reviewer #3 (Remarks to the Author):

The authors answered all the issues from reviewers, it can be accepted by NC.
Author reply to Reviewer 3’s comments

Reviewer 3’s comments 3: The authors answered all the issues from reviewers, it can be accepted by NC.

Author reply: We appreciate the reviewer’s positive recommendation very much. We also appreciate the reviewer’s valuable comments very much which have greatly helped to improve the quality of our submission.