Synergy of Single Atoms Pd and Oxygen Vacancies on In₂O₃ for Highly Selective C₁ Oxygenates Production from Methane under Visible Light

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Abstract

Methane (CH₄) oxidation to high value chemicals under mild conditions through photocatalysis is a sustainable and appealing pathway, nevertheless confronting the critical issues on both conversion and selectivity. Herein, under visible irradiation (420 nm), the synergy of palladium (Pd) atom cocatalyst and oxygen vacancies (OVs) on In₂O₃ nanorods enabled superior photocatalytic CH₄ activation by O₂. The optimised catalyst reached ca. 100 µmol·h⁻¹ of C1 oxygenates, with a selectivity of primary products (CH₃OH and CH₃OOH) up to 82.5 %. Mechanism investigation elucidated that such superior photocatalysis was induced by the dedicated function of Pd single atoms and oxygen vacancies on boosting hole and electron transfer pathway, respectively. O₂ was proven to be the only oxygen source for CH₃OH production, while H₂O acted as the promoter for efficient CH₄ activation through ·OH production and facilitated product desorption as indicated by DFT modelling. This work thus provides new understandings on simultaneous regulation of activity and selectivity by the significant synergy of single atom cocatalysts and oxygen vacancies.

Introduction

As the predominant constituent of natural gas, methane hydrate and shale gas resources, selective methane (CH₄) oxidation to value-added chemicals holds considerable financial and environmental prospective [1–5]. However, the inert symmetrical tetrahedral structure of CH₄ makes it rather difficult for the dissociation of the first C-H bond, which is the most important step for activation of methane. [6–8] Industrial multistep route via steam reforming and subsequent Fischer-Tropsch synthesis could efficiently activate CH₄, while it requires harsh experimental conditions (eg. > 700 °C temperature and/or high pressure), causing huge energy-consumption and safety issues [9–13]. In parallel, it is relatively difficult to achieve high selectivity due to the more reactive characteristics of the desired oxygenates against both the reactant CH₄ and stable product CO₂. [14–17] Therefore, selective CH₄ conversion to value-added chemicals under mild conditions other than CO₂ is highly attractive, while confronting considerable challenges.

Photocatalysis offers an appealing alternative to drive many tough redox reactions under mild conditions including CO₂ conversion [18, 19], N₂ reduction[20] and selective CH₄ oxidation [8]. Recently, various value-added chemicals such as methanol [1, 21–23], formaldehyde [24, 25], ethanol [26, 27], ethane and ethylene [28–33] were produced by photocatalysis. For example, we found that up to 90 % selectivity with a yield of 3.5 µmol·h⁻¹ methanol could be achieved over the optimized FeOₓ/TiO₂ photocatalyst under ambient condition using H₂O₂ as an oxidant [22]. Recently a high yield of liquid oxygenates including CH₃OH, CH₃OOH and HCHO were produced under full arc irradiation over Au supported ZnO, together with the good selectivity of primary products (CH₃OH and CH₃OOH) (< 70 %) [1]. Very recent, the yields of 18.7 µmol·h⁻¹ HCHO and 3.7 µmol·h⁻¹ CH₃OH were reported on quantum BiVO₄ with an excellent selectivity toward HCHO (87 %) and CH₃OH (99 %) under 300–400 nm or 400-780nm irradiation[25]. Given these
significant advances in photocatalytic methane conversion, the yield and/or selectivity to high value chemicals are still quite moderate, in particular it is very challenging to achieve methane activation under visible light irradiation instead of a full arc spectrum due to a narrowed bandgap with mitigated reduction or oxidation potentials.

To realize visible driven methane oxidation by O$_2$ gas on narrow bandgap photocatalysts, cocatalyst is crucial that does not only promote charge separation, more importantly manipulates the activation energy of the methane conversion and the selectivity [34–39]. Furthermore rationally regulating the production of reactive oxygen species (ROS) through cocatalyst modification is necessary as ·OH radicals have been widely regarded as the main species that induced CH$_4$ activation and over-oxidation [40, 41]. When CH$_3$OH served as the desired products, over-oxidation to HCHO or CO$_2$ would be suppressed by lowering the oxidative potential of photogenerated hole through cocatalyst modification, thus improving the selectivity. Stimulated by molecular catalysis, single atom cocatalysts promise an extremely high efficiency, where atomic dispersed species with unsaturated coordination environment could improve the catalytic performances based on the unique electronic structure [42–44]. Meanwhile, high atom utilization efficiency could be achieved [45, 46]. On the other hand, since CH$_4$ exhibited low electron and proton affinity, moderate decoration of defective sites could enhance the chemical-adsorption of non-polar molecular, then promoting the activation of CH$_4$ [47]. Therefore, the integration of both defects and single atom cocatalyst decoration could boost charge separation, weaken oxidative potential and enhance CH$_4$ activation on a photocatalyst.

Herein, atomically dispersed palladium (Pd) supported on defective In$_2$O$_3$ was prepared and served as the visible-light responsive photocatalyst for CH$_4$ conversion to high value chemicals. Under 420 nm irradiation, the optimized production of oxygenates reached up to ca. 300 µmol in 3 h, with a very high selectivity of 82.5 % of the primary products. In-situ XPS and EPR spectra were conducted to investigate the charge transfer dynamics. The results indicated the dedicated roles of Pd atoms and oxygen vacancies (OVs) in promoting the transfer of photo-induced holes and electrons, respectively. DFT calculation results indicated H$_2$O could also promoted the desorption of the oxygenate products, thus suppressing over-oxidation and facilitate high selectivity of primary products. The introduction of atomic Pd and oxygen vacancies further enhanced this effect on suppressing over-oxidation. Isotopic labelled experiments further proved the methane conversion pathway.

**Results And Discussion**

Visible-light photocatalytic CH$_4$ oxidation by O$_2$

Atomic Pd cocatalyst was prepared by the in-situ photo-deposition method with K$_2$PdCl$_4$ and (NH$_4$)$_2$PdCl$_4$ as the precursors on the visible driven In$_2$O$_3$ nanorod photocatalyst. Two types of photocatalysts were synthesized as the defect-rich and defect-lean materials, denoted as Pd-def-In$_2$O$_3$ and Pd-In$_2$O$_3$, respectively. For comparison, other noble metals including Pt and Au modified photocatalysts were also
prepared with the same dosage, denoted as M-(def)-In$_2$O$_3$ (M = Pt and Au). With different K$_2$PdCl$_4$ dosage, the as-prepared samples were denoted as Pd$_x$-def-In$_2$O$_3$, where x % represented the weight percentage of Pd to In$_2$O$_3$. In the following discussion, the best sample Pd-def-In$_2$O$_3$ and the reference Pd-In$_2$O$_3$ referred to Pd$_{0.1}$-def-In$_2$O$_3$ and Pd$_{0.1}$-In$_2$O$_3$ unless otherwise specified.

Typical noble metal cocatalysts (Pt, Pd, Au) loaded on In$_2$O$_3$ nanorods were first tested via photocatalytic CH$_4$ conversion with O$_2$ as the oxidant (Figure 1a). Under 420 nm irradiation, the products including CH$_3$OH, CH$_3$OOH and HCHO over Pd-In$_2$O$_3$ reaches 13.4, 32.3 and 27.5 μmol in 3 h reaction, respectively. The selectivity of the primary products (CH$_3$OH and CH$_3$OOH) was 62.1 % and the selectivity to the overoxidation products (HCHO and CO$_2$) was 37.9 %. In comparison, Au-In$_2$O$_3$ and Pt-In$_2$O$_3$ performed almost 100 % over-oxidized products (HCHO), with the trace yields of 1.4 and 0.9 μmol HCHO, respectively. Such differences suggested Pd cocatalyst was more suitable than Pt and Au for CH$_4$ activation to produce these primary products. The yield of oxygenates for Pd- In$_2$O$_3$ was improved further to 179.7 μmol by the introduction of defective sites to form Pd-def-In$_2$O$_3$, 2.5 times higher than that of Pd-In$_2$O$_3$ (73.2 μmol). Meanwhile, the selectivity of the primary products was improved from 62.1 % to 80.4 %, suggesting that deep-oxidation to HCHO and CO$_2$ was greatly suppressed under the synergy of Pd single atoms and oxygen vacancies (OVs). In the case of Au-def-In$_2$O$_3$ and Pt-def-In$_2$O$_3$, defect modification exhibited the similar phenomenon on promoting CH$_4$ conversion although the yield was much lower than that achieved on the Pd modified photocatalyst.

The effect of Pd single atoms was explored over Pd$_x$-def-In$_2$O$_3$. As shown in Figure 1b, Pd$_x$-def-In$_2$O$_3$ photocatalysts exhibited much higher oxygenates production than that of the pristine In$_2$O$_3$. With the raising of K$_2$PdCl$_4$ dosage, the production of the liquid oxygenates exhibited the volcanic trend, increasing from 48.7 μmol on Pd$_{0.01}$-def-In$_2$O$_3$ to 179.7 μmol on Pd$_{0.1}$-def-In$_2$O$_3$. Furthermore, the increasing K$_2$PdCl$_4$ dosage resulted in the decreased photocatalytic performance. Notably, the selectivity exhibited slight improvement from 76.5 % to 82.8 %. With a close look at the above results, OVs and Pd cocatalyst played the synergistic role in optimizing the activity and selectivity for photocatalytic CH$_4$ conversion.

Molar ratio of CH$_4$ to O$_2$ was tuned over Pd-def-In$_2$O$_3$ (Figure 1c). The production of oxygenates demonstrated the volcanic trend again, with the highest oxygenate production and selectivity achieved at 1 bar O$_2$ pressure. Reducing molar ratio of CH$_4$ to O$_2$ caused the decreased production to 116.0 μmol of primary products when CH$_4$/O$_2$ = 10/10, mainly ascribed to the decrease of CH$_4$ concentration. In parallel, the increased concentration of O$_2$ induced over-oxidation and decreased selectivity of the primary products from 80.4 % to 67.6 %. With the increase of H$_2$O dosage (Figure 1d), the production of oxygenates gradually increased, reaching the highest value with 100 mL H$_2$O dosage. The highest oxygenates achieved 299.0 μmol, 2.3 times improvement than that of 25 mL dosage (128.0 μmol) over Pd-def-In$_2$O$_3$. Moreover, the selectivity of the primary products improved from 74.2 to 82.5 % with H$_2$O
dosage increasing from 25 to 100 mL, which could be attributed to the enhanced desorption of the products from the surface of the photocatalyst when more water was used as discussed later. Notably, in the absence of H$_2$O dosage, CO$_2$ (8.5 μmol) was produced as the only product, suggesting the critical role of H$_2$O in promoting CH$_4$ activation as well suppressing over-oxidation, probably ascribed to the production of ·OH radical and promotion desorption of oxygenates by H$_2$O [48]. While increasing the total pressure of the gaseous reactants, CH$_4$ dissolved increased and the oxygenate production gradually increased (Figure 1e), e.g. only trace amount of HCHO (4.1 μmol) produced at 1 bar and reaching the highest yield of 179.7 μmol when the pressure was 20 bar. To investigate the stability of the optimized photocatalyst, we carried out the cycling test experiment over Pd-def-In$_2$O$_3$ photocatalyst. No obvious decrease of oxygenates was observed under 15 hours reaction (Figure 1f), demonstrating the good stability of Pd-def-In$_2$O$_3$.

Structural identification

X-ray diffraction (XRD) patterns were recorded to probe the crystalline structure of the representative photocatalysts (In$_2$O$_3$, Pd-In$_2$O$_3$ and Pd-def-In$_2$O$_3$) (Figure S1). The diffraction peaks on all three samples at 30.7°, 35.5°, 51.0° and 60.7° were well matched with the standard phase of In$_2$O$_3$ (PDF#71-2194). While no Pd and PdO$_x$ diffraction peaks were observed on Pd-In$_2$O$_3$ and Pd-def-In$_2$O$_3$, indicating the high dispersion of Pd species. The slightly weakened relative intensity from 100 % of In$_2$O$_3$ to 97 % and 93 % of Pd-In$_2$O$_3$ and Pd-def-In$_2$O$_3$ could be probably ascribed to the introduction of defects. Raman spectra (Figure 2a) further supported the well-established In$_2$O$_3$ phase. The typical Raman peaks for In$_2$O$_3$ were clearly observed at 130.6, 305.1 and 494.8 cm$^{-1}$ [49]. For Pd-In$_2$O$_3$ and Pd-def-In$_2$O$_3$, the dominant peak exhibited a slight left-shift from 130.6 to 129.9 cm$^{-1}$, attributed to the surface stain effect induced by the Pd cocatalyst deposition [50].

Electron paramagnetic resonance (EPR) spectra were conducted to evaluate the spin-electrons including oxygen vacancies (Figure 2b). For the pristine In$_2$O$_3$ and Pd-In$_2$O$_3$, a single Lorentz peak at g = 1.882 was observed, ascribed to the electrons on the conduction band (CB) [51, 52]. In the case of Pd-def-In$_2$O$_3$, the signal of this peak exhibited much stronger intensity than the others, suggesting the higher electron density on CB. Meanwhile, an additional Lorentz peak was observed at g = 2.001, which could be attributed to the free-electrons trapped by the oxygen vacancies [52], thus suggesting the existence of oxygen vacancies in Pd-def-In$_2$O$_3$. The introduction of oxygen vacancies might contribute to the stronger EPR peak at g = 1.882.

High-resolution transmission electron microscope (HRTEM) images further proved the defective structure of Pd-def-In$_2$O$_3$ (Figure 2c-d). Pd-def-In$_2$O$_3$ reserved the nanorod morphology with dimension of 203 nm in diameter and 1450 nm in length (insert of Figure 2c) as that of the In$_2$O$_3$ substrate and Pd-In$_2$O$_3$ (Figure S2). In addition, a thin amorphous/defective layer of ca. 4 nm was observed on the edge (Figure
The bulk crystal plane distance of 0.415 nm was indexed to the (211) facet of In$_2$O$_3$. On the contrary, there is not such defective layer as indicated in Figure S2b. Elemental distribution of the corresponding area was analysed by the EDS-mapping images (Figure 2e). Obviously, Pd-def-In$_2$O$_3$ exhibited uniform palladium distribution with indium and oxygen elements. The aberration corrected HAADF-STEM image in Figure 2f clearly indicated the atomic distribution of Pd, where the weak intensity spots cycled by the yellow corresponded to Pd atoms. The x-y line scan along the yellow rectangle of Figure 2f clearly presents the atomic dispersion of Pd as shown in Figure 2g. Therefore the best sample was composed of single atom Pd and oxygen vacancies on In$_2$O$_3$ nanorods.

Mechanism investigation

UV-vis diffuse reflection spectra (UV-DRS) were conducted to evaluate the photoabsorption ability of the representative photocatalysts (In$_2$O$_3$, Pd-In$_2$O$_3$ and Pd-def-In$_2$O$_3$) (Figure 3a). All the three photocatalysts exhibited the similar photoabsorption onset at ca. 450 nm, indicating that the modification of single atom Pd and OVs has little influence on bandgap energy and bandgap energy was not the decisive reason that induced improvement of photocatalysis.

In-situ high-resolution Pd$_{3d}$ X-ray photoelectric spectra (XPS) in dark and under light were conducted to study the charge transfer direction of Pd-def-In$_2$O$_3$ (Figure 3b and Figure S3). In dark, the Pd$_{3d5/2}$ XPS peak could be deconvoluted into two binding peaks at 336.55 and 335.38 eV, which were assigned to the Pd$^{2+}$ and Pd$^{0}$ species, respectively [53]. Under light irradiation, the peak exhibited a left-shift to higher binding energy (Figure S3). Further deconvoluted results (Figure 3b) suggested that Pd$^{2+}$ content increased to 26.3 %, much higher than 6.9 % in dark. Such increased Pd$^{2+}$ content suggested Pd served as the hole acceptors upon excitation. In-situ EPR spectra under light were conducted to evaluate the role of OVs. As shown in Figure 3c, the signal at g = 2.0009 was attributed to the electrons trapped by the oxygen vacancies, which performed gradually increasing intensity from 100 % to 226 % with the prolonged irradiation to 360 seconds. This stronger EPR intensity suggested a higher concentration of spin-electrons and thus demonstrated OVs served as the electron acceptor [54]. Therefore, single atom Pd and OVs separately acted as the hole and electron acceptors under light irradiation, which would greatly contribute to the enhanced charge separation.

Photocurrent responses (Figure S4) were tested to evaluate the charge separation efficiency. Pristine In$_2$O$_3$ exhibited a relatively low photocurrent density of 61.8 μA·cm$^{-2}$. After photo-depositing high dispersed Pd cocatalyst, Pd-In$_2$O$_3$ nearly doubled photocurrent density to 120.6 μA·cm$^{-2}$. The photocurrent density was further improved to 168.1 μA·cm$^{-2}$ on Pd-def-In$_2$O$_3$, almost 2.7 and 1.4 times enhancement than that of In$_2$O$_3$ and Pd-In$_2$O$_3$, respectively. Such highest photocurrent density on Pd-def-In$_2$O$_3$ attributed to the most efficient charge separation, indicating the defects and single atom Pd could greatly enhance charge transfer, which is consistent with the analysis mentioned above. Steady-state
fluorescence (PL) spectra further evidenced the enhanced charge separation efficiency. As shown in Figure 3d, a relatively strong PL emission peak was observed for the pristine In$_2$O$_3$, attributed to the severe charge recombination. In comparison, the PL intensity for Pd-In$_2$O$_3$ was greatly weakened, indicating the suppressed charge recombination. For Pd-def-In$_2$O$_3$ photocatalyst, the most weakened PL peak were observed, ascribed to the most enhanced charge separation efficiency, which was corresponding with the photocurrent analysis. Time-decay PL spectra were conducted to evaluate the PL lifetime. As shown in Figure S5, Pd-def-In$_2$O$_3$ photocatalyst exhibited the slowest PL decay kinetics. The fitting results (Table S1) showed that Pd-def-In$_2$O$_3$ exhibited the average PL lifetime at 4.99 ns, longer than that of In$_2$O$_3$ (3.60 ns) and Pd-In$_2$O$_3$ (4.28 ns), which would be beneficial to the efficient utilization of separated charge carriers.

Reactive oxygen species including ·OOH and ·OH radicals were widely regarded as the main active species for CH$_4$ activation [55] and monitored by in-situ EPR spectra with 5, 5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin-electron trapping agents. As shown in Figure 4a, the DMPO-OOH adduct was detected under light over different photocatalysts and ascribed to the presence of ·OOH, which came from the reduction of O$_2$ molecule with photo-induced electrons and H$^+$. A stronger intensity of DMPO-OOH was observed for Pd-def-In$_2$O$_3$, suggesting the production of ·OOH radical was enhanced by the integration of single atom Pd and OVs. On the other hand, in-situ EPR spectra under light was used to monitor the generation of ·OH radical with DMPO as the trapping agent in H$_2$O. The 1:2:2:1 quartet signals were observed and assigned to the DMPO-OH adduct, suggesting the generation of ·OH radical (Figure 4b). It was obvious that Pd-def-In$_2$O$_3$ produced much more ·OH under identical conditions than Pd-In$_2$O$_3$ and In$_2$O$_3$ was the worse. It is believed that ·OH initially activates CH$_4$ to methyl radical (·CH$_3$), thus Pd-def-In$_2$O$_3$ performed CH$_4$ activation best followed by Pd-In$_2$O$_3$, which is consistent with the step by step enhanced photocatalytic performances by Pd and then both Pd and oxygen vacancies, indicating that oxygen vacancies could promote charge separation and also facilitate water oxidation reaction on Pd. Coumarin was used as the probe for ·OH radical detection due to the easy reaction between coumarin and ·OH to produce 7-hydroxycoumain (7-HC) that could be detected by UV-vis spectra at 412 nm (Figure 4c). The results further supported that Pd-def-In$_2$O$_3$ held the strongest ability for ·OH production, which facilitated CH$_4$ activation. Therefore, single atom Pd worked as the hole acceptor, which then catalysed ·OH radical production from water oxidation. Simultaneously, OVs acted as the electron acceptor, which then catalysed O$_2$ reduction to generate ·OOH radical.

The reaction pathway was investigated by isotopic labelled experiments, including using H$_2^{18}$O and $^{18}$O$_2$. In the presence of 3 mL H$_2^{18}$O, 1 bar $^{16}$O$_2$ and 19 bar CH$_4$, no isotopic labelled CH$_3^{18}$OH (m/z = 33 and 34) was detected by GCMS (Figure 4d), suggesting H$_2$O was not the oxygen source that directly participated the formation of oxygenates. In parallel, when using 3 mL H$_2^{16}$O, 1 bar $^{18}$O$_2$ and 19 bar CH$_4$, the signals at m/z = 34 and 33 were attributed to the isotopic labelled CH$_3^{18}$OH and its fragment (Figure 4d), suggesting O$_2$ was the only oxygen source for CH$_3$OH formation. Carbon source for methanol
production were also studied in the presence of 5 bar isotopic labelled $^{13}$CH$_4$ (**Figure 4e**), where the signal of mass spectra (MS) at m/z = 33 was ascribed to $^{13}$CH$_3$OH, demonstrating that CH$_4$ was the carbon source for oxygenates production.

DFT calculations (**Figure 5**) were conducted to explain the improved selectivity of primary products. It should be noted that timely desorption of the primary products on the active sites could efficiently avoid its deep-oxidation to HCHO and CO$_2$. As ·OH radical was regarded as the main species that induced oxidation on single atom Pd cocatalyst, it was accordingly considered that the efficient desorption of primary products like CH$_3$OH on Pd is critical to suppress further oxidation. Thus, the adsorption energies of H$_2$O and CH$_3$OH were calculated since the stronger adsorption of H$_2$O might promote the desorption of CH$_3$OH. H$_2$O and CH$_3$OH adsorption on In$_2$O$_3$ and on Pd/In$_2$O$_3$ were modelled and optimized by the density functional theory (DFT) calculations. As shown in **Figure 5a** and **b**, the adsorption energies of H$_2$O on In$_2$O$_3$, Pd-In$_2$O$_3$ and Pd-def-In$_2$O$_3$ were -0.76, -1.57 and -2.14 eV, respectively, much larger than the CH$_3$OH adsorption energy of -0.47, -1.38 and -1.50 eV on the specified model. Such larger adsorption energies indicate CH$_3$OH could be easily replaced by H$_2$O on In$_2$O$_3$ or Pd atoms, promoting the desorption of CH$_3$OH. Moreover, adsorption energies further increased with the introduction of both Pd atom and oxygen vacancy, demonstrating such co-modification of Pd atoms and OVs could promote the adsorption of H$_2$O most efficiently, which is consistent with the increased production of ·OH radicals as analyzed by the in-situ EPR and coumarin experiments. Though the adsorption of CH$_3$OH was also enhanced due to the introduction of Pd atoms and OVs, H$_2$O adsorption energy was enhanced much more, thus water could facilitate the desorption of primary products and avoid overoxidation as indicated in **Figure 1d**.

Based on the above results, aerobic photocatalytic CH$_4$ conversion mechanism over Pd-def-In$_2$O$_3$ was proposed (**Scheme 1**). Generally, under 420 nm irradiation, electrons (e$^-$) were excited to the conduction band of In$_2$O$_3$ nanorod photocatalyst, while leaving holes (h$^+$) on the valence band. Then the photo-induced electrons were trapped by the oxygen vacancies, activating O$_2$ with H$^+$ to produced ·OOH radicals as detected by the in-situ EPR spectra. In parallel, Pd atoms served as the hole acceptors (Pd + h$^+$ → Pd$^{5+}$), and then reacted with the adsorbed H$_2$O to produced ·OH (Pd$^{5+}$ + H$_2$O → Pd$^0$ + ·OH + H$^+$). CH$_4$ molecules were next activated by the as-produced ·OH to ·CH$_3$. The coupling reaction between ·CH$_3$ and ·OOH then generated the primary products (CH$_3$OOH), and subsequently transferred to CH$_3$OH as indicated in **Scheme 1b**. Compared with the pristine In$_2$O$_3$, the incorporation of Pd single atoms significantly promoted charge separation and facilitated the generation of reactive species, thus promoting CH$_4$ conversion to oxygenates. Pd atoms loading also moderated the oxidation ability of photoinduced holes on In$_2$O$_3$ as indicated in **Scheme 1a**, reducing the overoxidation of the primary products. Further decoration of oxygen vacancies could strengthen the promoted charge separation efficiency, which eventually resulted in the superior photocatalytic CH$_4$ conversion activity and selectivity. In order to suppress over-oxidation, it was also critical to enhance the desorption of primary oxygenate products by H$_2$O, as supported by the DFT calculation.
In summary, visible-light-driven CH$_4$ conversion at ambient temperature was reported over the In$_2$O$_3$ nanorod photocatalyst with loading of Pd single atoms cocatalysts and oxygen vacancies. Under 420 nm irradiation, superior yield (99.7 $\mu$mol·h$^{-1}$) and selectivity (82.5 %) of the primary products were achieved on Pd-def-In$_2$O$_3$ photocatalyst under optimized reaction conditions. In-situ XPS and EPR spectra under visible light irradiation indicated that Pd and oxygen vacancies acted as the hole and electron acceptors, respectively, thus synergistically boosted charge separation and transfer. Isotopic labelled experiment proved that O$_2$ was the only oxygen source for oxygenates production, while H$_2$O was the promoter of CH$_4$ activation through the production of ·OH radical as monitored by the in-situ EPR spectra with DMPO as the spin-trapping agent. DFT calculation results suggested that H$_2$O performed much larger adsorption energies than CH$_3$OH on either In$_2$O$_3$, def-In$_2$O$_3$ or Pd-def-In$_2$O$_3$, suggesting the stronger adsorption of H$_2$O than CH$_3$OH, which was beneficial to the timely desorption of the produced CH$_3$OH, thus avoiding further over-oxidation. The introduction of Pd and oxygen vacancies could further improve the selectivity of primary oxygenates mainly through the greatly enhanced adsorption of H$_2$O and the reduced oxidation potential of photoinduced holes. This work provided an useful avenue on co-modification by oxidative single atom cocatalyst and oxygen vacancies for simultaneous regulation of both activity and selectivity through enhancing charge separation, moderated photohole oxidation ability and timely promoted desorption of primary products by a solvent.

**Methods**

**Synthesis of In$_2$O$_3$ nanorods**

In$_2$O$_3$ nanorods were prepared according to the previous study [56]. Typically, 12.0 g urea and 1.5 g InCl$_3$ were dissolved in 135 g H$_2$O, followed by stirring at 80 °C for 14 h. After naturally cooling down, the reactant was centrifuged and washed with H$_2$O for several times. The white powder was then dried in vacuum at 60 °C overnight. After thermal-treating in air at 700 °C for 5 h at a ramping rate of 5 °C·min$^{-1}$, yellow powder was obtained and denoted as In$_2$O$_3$.

**Synthesis of Pd$_x$-In$_2$O$_3$ and Pd$_x$-def-In$_2$O$_3$ nanorods**

Pd$_x$-In$_2$O$_3$ and Pd$_x$-def-In$_2$O$_3$ nanorods were prepared through photo-deposition with ammonium tetrachloropalladate(II) ((NH$_4$)$_2$PdCl$_4$) and potassium tetrachloropalladate(II) (K$_2$PdCl$_4$) as the precursors, respectively. The synthesis was conducted in the multichannel reactor (Beijing Perfectlight Technology Co., Ltd). For Pd$_x$-def-In$_2$O$_3$ preparation, 200 mg In$_2$O$_3$ was first dispersed through sonication with the aqueous solution containing 10 vol.% methanol. Then certain amount of K$_2$PdCl$_4$ solution was added. After sealing and purging with ultrapure argon (99.999 vol.%) for 30 min, the reactor was bottom-irradiated for 3 h to facilitate Pd photo-deposition. The suspension was then centrifuged, washed with H$_2$O for several times and dried under vacuum at 60 °C overnight. The as-prepared samples were denoted as Pd$_x$-def-In$_2$O$_3$, where x % represented the mass percentage of palladium to In$_2$O$_3$ substrates.
with no oxygen vacancies was prepared under identical conditions except the usage of (NH$_4$)$_2$PdCl$_4$ instead of K$_2$PdCl$_4$.

**Characterizations**

XRD were measured to obtain the crystalline structure on the D8 ADVANCE diffractometer (Bruker Co., Ltd). Palladium and potassium contents were measured through inductively coupled plasma atomic emission spectrometry (ICP-AES) on the Agilent 7900 ICP-MS instrument. Raman spectra were collected on the DXR 2DXR2 instrument (Thermo Fisher Scientific, Co., Ltd). HRTEM images were captured on the Talos F200X instrument (FEI Co., Ltd). UV-DRS spectra were measured on the UV-3600 plus spectrophotometer (Shimadzu Co., Ltd). Photocurrent test was conducted on the electronic workstation (CHI660E) on the three-electrode system. Ag/AgCl electrode, platinum sheet electrode and Na$_2$SO$_4$ solution (0.1 M) were used as the reference electrode, counter electrode and electrolyte, respectively. The mixtures of photocatalyst, ethanol and Nion solution (Shanghai Adams Reagent Co., Ltd) were suspended and sonicated to prepare the working electrode. In-situ XPS in dark and under light were measured on the Thermo ESCALAB 250Xi instrument with an Al Kα radiation source. In-situ solid-state EPR spectra in dark and under light were measured with 20 mg photocatalyst on the ELEXSYS II EPR instrument.

**Photocatalytic CH$_4$ conversion**

Photocatalytic CH$_4$ conversion was conducted in a top-irradiated high-pressure reactor with 200 mL volume. LED lamp (420 nm, PLS-LED100C, Beijing Perfectlight Technology Co., Ltd) was used as the light source. Typically, 20 mg photocatalyst was dispersed in 50 mL distilled water. After sealing and purging with ultrapure O$_2$ (99.999 vol.%) for 20 min, 1 bar O$_2$ and 19 bar CH$_4$ (99.999 vol.%) were flowed into the reactor. The temperature of the reactor was maintained at 25 °C by the cold-water bath. After reacting for 3 h, the gaseous and liquid products like methanol were measured by the gas chromatography (GC2014, Shimadzu Co., Ltd) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID). CH$_3$OOH and CH$_3$OH were measured through $^1$H nuclear magnetic resonance (NMR) (AVANCE III, JEOL Ltd). As CH$_3$OOH and CH$_3$OH have the same number of methyl, the area ratio of CH$_3$OOH to CH$_3$OH in $^1$H NMR should be the molar ratio of CH$_3$OOH to CH$_3$OH. Thus, CH$_3$OOH could be quantified. HCHO was measured through the colorimetric method [57] on the UV-3600 Plus spectrometer (Shimadzu Co., Ltd).

**Isotope labelling experiments**

For carbon source investigation: 20 mg Pd-def-In$_2$O$_3$ photocatalyst was dispersed in 3 mL H$_2$O. After the reactor being degassed for 30 min, 1 bar O$_2$ and 5 bar $^{13}$CH$_4$ were injected into the reactor. After reacting for 6 h, the suspension was filtered and then the solvent was analysed by GC-MS (QP2010, Shimadzu Co., Ltd) equipped with the Cap WAX column.
For oxygen source investigation: 20 mg Pd-def-In$_2$O$_3$ photocatalyst was dispersed in 3 mL H$_2^{16}$O or H$_2^{18}$O. After the reactor being degassed for 30 min, 1 bar $^{18}$O$_2$ or $^{16}$O$_2$ and 5 bar CH$_4$ were injected into the reactor. After reacting for 6 h, the suspension was filtered and then the solvent was analysed by GC-MS (QP2010, Shimadzu Co., Ltd).

Monitor of the reactive species

DMPO was used as the spin-trapping agent for monitor of the reactive species including ·OOH and ·OH radicals. For ·OOH radical detection, 10 mg Pd-def-In$_2$O$_3$ photocatalyst was dispersed into 5 mL DMPO/methanol solution. After purging with ultrapure O$_2$ (99.999 vol.%) for 20 min, in-situ EPR spectra in dark and under light irradiation were collected. For ·OH radical detection, 10 mg Pd-def-In$_2$O$_3$ photocatalyst was dispersed in 5 mL aqueous DMPO solution. After purging with ultrapure O$_2$ (99.999 vol.%) for 20 min, in-situ EPR spectra in dark and under light were collected.

Analysis of hydroxyl radical (·OH)

Coumarin was used as the probe for the quantication of ·OH via the production of 7-HC [40]. Typically, 20 mg photocatalyst was dispersed in 100 mL aqueous coumarin solution (5×10$^{-4}$ M). After stirring for 30 min in dark, the suspension was irradiated with the LED light source (420 nm, PLS-LED100C, Beijing Perfectlight Technology Co., Ltd). Certain amount of suspension was sampled and filtered in the 10 min intervals. PL intensity of the produced 7-HC in the solution was then measured on the F4500 spectrofluorometer.

DFT calculation of adsorption energies

The first-principles were employed to perform all the density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the PBE formulation. The projected augmented wave (PAW) potentials have been chosen to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10$^{-4}$ eV. A geometry optimization was considered convergent when the force change was smaller than 0.05 eV/Å. Grimme's DFT-D3 methodology was applied to describe the dispersion interactions. Three models including In$_2$O$_3$ with (111) facet, def-In$_2$O$_3$ with one oxygen vacancy and Pd-def-In$_2$O$_3$ with both one oxygen vacancy and single atom Pd modification were conducted. During structural optimizations, the 2×2×1 Monkhorst-Pack k-point grid for Brillouin zone was used for k-point sampling for structures. Finally, the adsorption energies ($E_{ads}$) were calculated as $E_{ads} = E_{ad/sub} - E_{ad} - E_{sub}$, where $E_{ad/sub}$, $E_{ad}$, and $E_{sub}$ were the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively.
Data availability

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

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Declarations

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Author contributions

J.T. conceived and supervised the entire project. L. L., L. F. and H. L. conducted the material synthesis, characterizations and photocatalytic methane conversion tests. L. L. drafted the manuscript under the guidance of J. T. Y. X. helped to discuss the catalytic results and improve the manuscript. All authors discussed and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Scheme

Scheme 1 is in the supplementary files section.

Figures
Figure 1

Photocatalytic CH4 conversion performance under 420 nm irradiation. Investigations on (a) diverse noble metal species, (b) K2PdCl4 dosage during synthesis, (c) molar ratio of CH4/O2, (d) H2O dosage, (e) total pressure and (f) cycling tests over the best sample Pd-def-In2O3. Standard reaction conditions: 20 mg photocatalyst, 50 mL distilled H2O, 19 bar CH4, 1 bar O2, 3 h. For reaction condition investigation, only the specified parameter was changed.
Figure 2

(a) Raman and (b) EPR spectra of In2O3, Pd-In2O3 and Pd-def-In2O3. (c, d) HRTEM and (e) HAADF and EDS-mapping images of Pd-def-In2O3. Blue, red and green colors represent indium, oxygen and palladium elements, respectively. (f) Aberration corrected HAADF-STEM image of Pd-def-In2O3, where Pd single atoms with a weak intensity are indicated by yellow circles. (g) Line scan measured along the x-y rectangle region marked in f.
Figure 3

(a) UV-DRS spectra of In2O3, Pd-In2O3 and Pd-def-In2O3. (b) In-situ Pd3d XPS spectra and (c) in-situ EPR spectra of Pd-def-In2O3 in dark and under light. (d) Steady-state PL spectra of In2O3, Pd-In2O3 and Pd-def-In2O3.
Figure 4

In-situ EPR spectra of (a) DMPO-OOH and (b) DMPO-OH for the monitor of reactive ·OOH and ·OH radicals over different photocatalysts. (c) PL intensity of 7-HC versus time over different photocatalysts for the quantification of ·OH. Isotopic labelled experiments (d) oxygen source and (e) carbon source for methanol production in the presence of isotopic labelled H218O, 18O2 or 13CH4.
Figure 5

DFT calculation of optimized geometries and adsorption energies of (a) H2O and (b) CH3OH on In2O3, single atom Pd-In2O3 and Pd-def-In2O3.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Scheme1.png
- supportinginformation.docx