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Highly Efficient and Selective Photocatalytic Nonoxidative Coupling of Methane to Ethylene over Pd-Zn Synergistic Catalytic Sites

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Abstract

Photocatalytic nonoxidative coupling of CH₄ to multi-carbon (C₂+) hydrocarbons (e.g., C₂H₄) and H₂ under ambient conditions provides a promising energy-conserving approach for utilization of carbon resource. However, as the methyl intermediates prefer to undergo self-coupling to produce ethane, it is a challenging task to control the selective conversion of CH₄ to higher value-added C₂H₄. Herein, we adopt a synergistic catalysis strategy by integrating Pd-Zn active sites on visible light-responsive defective WO₃ nanosheets for synergizing the adsorption, activation and dehydrogenation processes in CH₄-to-C₂H₄ conversion. Benefiting from the synergy, our model catalyst achieves a remarkable C₂+ compounds yield of 31.85 μmol·g⁻¹·h⁻¹ with an exceptionally high C₂H₄ selectivity of 75.3% and a stoichiometric H₂ evolution. In-situ spectroscopic studies reveal that the Zn sites promote the adsorption and activation of CH₄ molecules to generate methyl and methoxy intermediates with the assistance of lattice oxygen, while the Pd sites facilitate the dehydrogenation of methoxy to methylene radicals for producing C₂H₄ and suppress over-oxidation. This work demonstrates a strategy for designing efficient photocatalysts toward selective coupling of CH₄ to higher value-added chemicals, and highlights the importance of synergistic active sites to the synergy of key steps in catalytic reactions.
1. Introduction

Under the reality of insufficient coal and oil stockpiles, conversion of methane (CH₄), which is the predominant component in natural gas, biogas, shale gas and combustible ice, to value-added chemical feedstocks is an intriguing approach for sustainable development [1-4]. However, as a non-polar molecule with tetrahedral symmetry, CH₄ has a high C–H bond energy which requires high energy input (i.e., high operating temperatures and pressures) to cleave the C–H bond [5-7]. Additionally, such harsh reaction conditions commonly lead to the production of undesired but thermodynamically favorable over-oxidized products (i.e., CO and CO₂) [8-11]. Given such a circumstance, there are giant economic and environmental incentives for developing efficient sustainable approaches to achieve selective CH₄ conversion toward the target products.

Photocatalysis, employing inexhaustible solar energy instead of thermal energy, provides an attractive alternative route to sustainable CH₄ conversion under ambient reaction conditions [11-15]. Among various methane conversion schemes, nonoxidative coupling of CH₄ to ethylene (C₂H₄) along with simultaneous production of H₂ is a preferable pathway, as C₂H₄ is the high value-added key chemical feedstock while H₂ is an important clean energy carrier. Nevertheless, it is still a grand challenge to achieve efficient and selective conversion of CH₄ to C₂H₄, mainly because photocatalysts often lack efficient active sites for activation of C–H bond and the generated methyl radicals upon activation prefer to undergo self-coupling toward production of less valued ethane (C₂H₆) [16-20]. In this regard, there is an urgent need to rationally engineer active sites on the photocatalyst surface for synergizing the adsorption, activation and dehydrogenation processes to enable achieving the efficient and selective photocatalytic nonoxidative coupling of CH₄ to C₂H₄.

Among various reported active sites, the Zn⁺–O⁻ pairs in ZnO have been well recognized as efficient active sites for photocatalytic CH₄ activation and coupling, and as such, ZnO has been extensively applied to construct photocatalysts for CH₄ conversion [21-23]. However, due to the wide bandgap, ZnO can only absorb ultraviolet light, which severely restricts their catalytic efficiency in practical application under sunlight. In addition, the insufficient dehydrogenation capability for Zn⁺ sites limits the efficiency of C₂H₄ production. To achieve the goal of CH₄-to-C₂H₄ nonoxidative coupling conversion, it is greatly desired yet challenging to implement the Zn⁺–O⁻ pairs in other photosensitive semiconductor materials with the light harvesting capacity in broad spectral range and to simultaneously introduce another active site with strong dehydrogenation capability.

Herein, we aim to adopt a synergistic catalysis strategy by integrating multiple active sites on a visible light-responsive substrate for harnessing the adsorption, activation and dehydrogenation processes to achieve highly efficient and selective CH₄-to-C₂H₄ conversion. Taking the visible light-responsive defective WO₃ as a model substrate, Zn⁺–O⁻ paired active sites are implemented into WO₃ nanosheets with large specific surface area and suitable energy band position through a doping method [24, 25]. Furthermore, considering the strong dehydrogenation capability toward C–H bond, Pd sites are introduced on WO₃ nanosheets by depositing Pd
nanoparticles via a self-reduction process. Benefiting from the synergy of two active sites, our model catalyst achieves remarkable activity and selectivity for CH₄-to-C₂H₄ conversion as well as a nearly stoichiometric H₂ evolution, benchmarked against the state-of-the-art photocatalysts. In-situ spectroscopic studies reveal that the Zn sites promote the adsorption and activation of CH₄ molecules, while the Pd sites facilitate the dehydrogenation of methoxy intermediates and suppress the over-oxidation [26-28]. Moreover, we unravel the reaction pathway for CH₄-to-C₂H₄, in which the adsorbed CH₄ is activated and dehydrogenated to in turn generate methyl, methoxy and methylene intermediates, and finally the methylene radicals undergo self-coupling reactions to produce C₂H₄. This work provides a new perspective for designing the photocatalyst through leveraging synergistic active sites, and highlights the key role of strong dehydrogenation capability in enhancing the selectivity for CH₄-to-C₂H₄ conversion.

2. Results
As illustrated in Figure 1a, the Pd-Zn co-modified WO₃ nanosheets are constructed through a two-step protocol, in which Zn is in-situ doped during hydrothermal synthesis of defective WO₃ nanosheets and subsequently Pd nanoparticles are integrated by self-reduction. The prepared model catalyst is denoted as Pd₅/Zn₀.₃₅-WO₃ (5% and 0.35% refer to the theoretical mass fractions of Pd and Zn in the composite). The actual mass fractions of Pd and Zn determined by ICP-MS results are 4.46% (10.27 mg/L) and 0.31% (0.71 mg/L) in Pd₅/Zn₀.₃₅-WO₃ (230 mg/L). The X-ray diffraction (XRD) patterns (Figure S1a) show that the prepared defective WO₃ substrate is monoclinic phase (JCPDS Card No. 83-0950), and the crystalline phase structure remains unchanged after Zn doping and Pd modification [25]. Such a result is consistent with that from UV–vis diffuse reflectance spectra (DRS, Figure S1b), showing that the samples maintain the inherent light absorption characteristics of defective WO₃ substrate after the Zn doping and Pd modification. Taken together, the results indicate that the Pd-Zn co-modification strategy has no negative effect on the basic physical properties of WO₃ substrate.

Scanning electron microscopy (SEM) images (Figure S2a and S2b) reveal that the bare WO₃ substrate has a nanosheet structure with a diameter of approximately 400 nm. Furthermore, transmission electron microscopy (TEM) also demonstrates the nanosheet morphology of the prepared Pd-Zn co-modified WO₃ (Pd₅/Zn₀.₃₅-WO₃). The clear lattice fringes with the spacings of 0.379 nm and 0.397 nm at an angle of 90° in high-resolution TEM (HRTEM) images can be assigned to the (020) and (002) crystal planes of monoclinic phase WO₃ (Figure 1b), which are consistent with the XRD results [25]. Meanwhile, such a nanosheet morphology remains unchanged after Zn doping and Pd modification (Figure S2c and S2d). Additionally, the aberration-corrected high-angle annular dark-field scanning TEM (HAADF-STEM) image of the Pd-Zn co-modified WO₃ nanosheets (Figure 1c) shows that Pd nanoparticles with an average diameter of 5 nm are highly dispersed on the WO₃ substrate surface. The lattice fringes with an interplanar distance of 0.228 nm ascribed to the (111) plane of Pd nanoparticles are clearly observed in HRTEM image (Figure 1d) [28]. The corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Figure 1e) demonstrates that Zn dopants and Pd nanoparticles are uniformly distributed on the surface of the WO₃ substrate. Moreover, X-ray photoelectron spectroscopy (XPS, Figure S3) reveals that isolated Zn²⁺ ions have been successfully
doped into the WO\textsubscript{3} lattice while the zero-valent state of Pd proves that Pd nanoparticles are indeed formed by the self-reduction method. Note that low-valence W\textsuperscript{5+} species is resolved along with the binding energy of 531.8 eV for adsorbed oxygen species at the defects in the WO\textsubscript{3} substrate by XPS, manifesting the existence of oxygen vacancies as defects [29, 30]. Taken together, the characterizations confirm that Zn sites and Pd nanoparticles have been successfully introduced onto WO\textsubscript{3} substrate, constructing the Pd-Zn co-modified WO\textsubscript{3} nanosheets.

**Figure 1. Schematic synthetic process and morphology characterization.** (a) Schematic illustration for the synthetic protocol of the Pd-Zn co-modified WO\textsubscript{3} nanosheets. (b) HRTEM image of WO\textsubscript{3}. (c and d) HRTEM and (d) HAADF-STEM images of Pd\textsubscript{5}/Zn\textsubscript{0.35}-WO\textsubscript{3}. (e) The corresponding EDS elemental mapping of W (yellow), O (red), Zn (green) and Pd (purple) for Pd\textsubscript{5}/Zn\textsubscript{0.35}-WO\textsubscript{3}.
After confirming the formation of Pd-Zn co-modified WO₃ nanosheets, we then evaluate their performance as a photocatalyst for CH₄ conversion under full-spectrum illumination. The catalytic performance of the synthesized Pd-Zn co-modified WO₃ (denoted as Pdₓ/Znᵧ-WO₃, x% and y% refer to the mass fractions of Pd and Zn in the composite) in reference to control samples are summarized in Figure 2a. The CH₄ coupling products of the optimized Pd₅/Zn₀.₃₅-WO₃ are C₂H₆, C₂H₄ and C₃H₆ (Figure S4, S5), in which the C₂⁺ compounds yield reaches 31.85 μmol·g⁻¹·h⁻¹ with a C₂H₄ selectivity of 75.3% (57% in total carbonaceous products). The control experiments demonstrate that there is no thermal-catalytic contribution (Figure S6a), indicating that the coupling of CH₄ is a photocatalytic reaction rather than a photothermal catalytic reaction. Furthermore, the Pd₅/Zn₀.₃₅-WO₃ catalyst can still effectively realize selective photocatalytic nonoxidative coupling of CH₄ to C₂H₄ outside the laboratory under condensed sunlight (Figure S6a), indicating its great potential for practical application. Such performance well exceeds the activity and selectivity of the state-of-the-art catalysts for photocatalytic nonoxidative coupling of CH₄ to C₂H₄ (Table S1). The yields of C₂H₄ and C₂H₆ for Pd₅/Zn₀.₃₅-WO₃ are 19-fold and 5.5-fold higher than that of bare WO₃, confirming that the introduced Zn and Pd give a boost to the activation and coupling of CH₄. More notably, the yields of H₂ and carbon-containing products almost conform to the stoichiometric ratio during the CH₄ conversion process, indicating that the hydrogen atoms are derived from CH₄ with high atom economy (Figure S6b and Table S2).

![Figure 2. Photocatalytic performance for CH₄ conversion.](image-url)
refer to the mass fraction of Pd and Zn in the composite) photocatalysts under light irradiation of 2 h. “ND” stands for “not detected.” (b) Production rates of C2H4, C2H6, and C3H6, as well as the C2H4 selectivity in C2+ products, for photocatalytic CH4 coupling by Pd5/Zn0.35-WO3 in six successive cycling tests. (c) GC-MS data of 13C2H6 and 13C2H4 produced from photocatalytic 13CH4 coupling by Pd5/Zn0.35-WO3.

Upon recognizing the significantly enhanced catalytic performance, the individual roles of Zn dopants and Pd nanoparticles are explored by investigating the catalytic performance for the control samples with only Zn doping and Pd loading, as well as assessing the effects of their loading amounts on the performance. Compared to bare WO3, the Zn-doped WO3 exhibits remarkably enhanced C2 products yield and C2H4 selectivity, and the C2H4 yield increases with the amount of doped Zn within a certain range (Figure 2a), suggesting that the doped Zn can facilitate CH4 activation and coupling. However, excessive Zn doping leads to the decrease in C2 products yield, most likely due to the increased work function and reduced lattice oxygen content by excessive doped Zn [31]. The activation of CH4 heavily depends on the O– centers in Zn2–O– pairs. In the absence of Pd, the O– centers in Zn0.35-WO3 serving as strong oxidants cause the serious over-oxidation of activated ·CH3 to CO2 (Figure S6b). The Pd nanoparticles-modified WO3 (Pd5/WO3) also exhibits substantially enhanced C2 products yield and C2H4 selectivity, while a considerable amount of C3H6 emerges. The production of C3H6 indicates that the introduced Pd nanoparticles serving as active sites have a strong dehydrogenation capability to further dehydrogenate methyl intermediates to generate methylene and methyne radicals, which undergo cross-coupling reaction to produce C3H6. Furthermore, after modifying Zn0.35-WO3 with Pd nanoparticles, the production yield of C2H4 further increases significantly with the loading amount of Pd (Figure 2a). This verifies that the modified Pd nanoparticles are conducive to dehydrogenating methyl radicals and further promoting the generated radicals to undergo self- and cross-coupling reactions, which eventually dramatically suppresses the over-oxidation of carbon intermediates to CO2 as compared with Zn0.35-WO3 (Figure S6b). Moreover, excessive Pd loading, such as Pd7/Zn0.35-WO3, leads to the reduced yields of C2H6 and C2H4 without production of C3H6, most likely because the agglomeration of small Pd nanoparticles weakens their dehydrogenation effect. The results above demonstrate the significant roles of synergistic Pd and Zn on WO3 in promoting the CH4 coupling and C2H4 production as well as suppressing the over-oxidation.

To evaluate the stability of the model photocatalyst, the physicochemical properties of Pd5/Zn0.35-WO3 after reaction are investigated. After the reaction, the Pd5/Zn0.35-WO3 sample exhibits slight changes in color, crystallinity and light absorption properties, but no obvious change on morphology can be observed (Figure S7a-d). Such changes are related to the consumption of a small amount of lattice oxygen in the sample during the reaction, as evidenced by O 1s XPS spectra (Figure S7e). The production of CO2 (Figure S6b) under oxygen-free reaction conditions also proves that the lattice oxygen could be consumed in the process of CH4 over-oxidation. Nevertheless, such lattice oxygen consumption would not limit the long-term application of photocatalyst; the consumed lattice oxygen can be effectively replenished after photooxidation treatment under air conditions by seizing oxygen atoms from the environment. The color, crystallinity and light absorption properties are almost restored to the state of fresh sample after the
treatment (Figure S7). These results suggest that the model photocatalyst can maintain the recyclability through the batch reaction mode. To further assess the recoverability and recyclability of our model photocatalyst, the cycling tests are performed on the Pd$_5$/Zn$_{0.35}$-WO$_3$ catalyst, during which a photooxidation pretreatment of 30 min is performed on the recycled catalyst under air conditions before each cycle (Figure 2b). After the six cycles, the recycled catalyst well retains the activity and selectivity for photocatalytic coupling of CH$_4$ to C$_2$H$_4$, manifesting the eminent recyclability and practicability of our model photocatalyst.

To further verify the carbon source of produced C$_2$H$_4$ and C$_2$H$_6$ in photocatalytic CH$_4$ conversion, isotope labeling experiment is performed by using $^{13}$CH$_4$ as the reactant. The $^{13}$C$_2$H$_4$, $^{13}$C$_2$H$_6$ and $^3$CO$_2$ products as well as various intermediates derived from isotopic $^{13}$CH$_4$ can be observed by gas chromatography-mass spectrometry (GC-MS, Figure 2c, S8). Additionally, no products are detected during the control experiments without catalyst or under dark condition (Figure 2a). These results confirm that all coupling products are derived from CH$_4$, rather than the release of any residual organic matters in raw materials during the preparation process.

**Figure 3. Charge dynamics and CH$_4$ adsorption behavior.** (a) TR-SPV responses of WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. (b) TS-PL spectra of WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. (c) In-situ EPR signals of Pd$_5$/Zn$_{0.35}$-WO$_3$ collected under different conditions. (d) CH$_4$-TPD curves of WO$_3$, Zn$_{0.35}$-WO$_3$, Pd$_5$/WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. 
To elucidate the origin of the superior activity by our designed photocatalyst, we further survey its charge dynamics behavior, which is a key factor to the photocatalytic efficiency. The time-resolved surface photovoltage (TR-SPV), as an advanced characterization method to comprehend the behavior of charge separation and transfer, can qualitatively estimate the charge separation efficiency and photogenerated carrier lifetime by analyzing the signal intensity and duration. To put it simply, the stronger TS-SPV signal, the better charge separation; the wider TS-SPV signal, the longer charge lifetime. For the Pd5/Zn0.35-WO3 with Zn doping and subsequent Pd modification on WO3, both the intensity and duration of the TS-SPV signal gradually increase (Figure 3a), suggesting the enhanced charge separation efficiency and photogenerated carrier lifetime by introducing Zn and Pd. Such a positive effect on charge dynamics is also confirmed by the steady-state surface photovoltage spectroscopy (Figure S9). Moreover, the transient-state photoluminescence (TS-PL) spectroscopy (Figure 3b and Table S3) is further employed to reveal the dynamic charge behavior by fluorescence lifetimes. The fluorescence lifetime for Pd5/Zn0.35-WO3 (τ = 1.86 ns) is the shortest among the samples (WO3, τ = 2.54 ns; Zn0.35-WO3, τ = 2.28 ns). This indicates that the photogenerated charges in Pd5/Zn0.35-WO3 are favorably captured by doped Zn and modified Pd during the charge migration process, thus achieving the promoted charge separation. Overall, the results above confirm the role of Pd-Zn co-modification in facilitating charge separation and transfer, which consequently promotes CH4 conversion reaction.

Since the promoting effect of Pd-Zn co-modification on charge separation and transfer is clarified, in-situ electron paramagnetic resonance (EPR) technology is used to understand the specific charge migration process. As shown in the EPR spectra (Figure 3c and S10), the intensity of Zn* signal at g = 1.968 for Pd5/Zn0.35-WO3 increases upon light irradiation, manifesting that the photogenerated electrons are transferred from WO3 to doped Zn2+ to produce Zn* sites [32]. In addition, the signals at g = 2.005 attributed to unpaired electrons trapped in surface defects (Vo* or O2-) become stronger for both WO3 and Pd5/Zn0.35-WO3 upon light irradiation. Considering that Zn* and O2- are always generated in pairs, the enhanced signals at g = 2.005 for Pd5/Zn0.35-WO3 suggest the emergence of photogenerated holes-enriched lattice oxygen sites (O2- centers) [22, 28]. Meanwhile, the enhanced signals at g = 2.005 for WO3 can be attributed to the unpaired photogenerated electrons trapped in oxygen vacancies, as there is no obvious signal for lattice electron trapping sites. Upon introducing CH4, the signal intensity of O2- centers at g = 2.005 slightly decreases for Pd5/Zn0.35-WO3 under light irradiation, indicating that the O2- centers play a vital role for CH4 activation and the free electrons and holes are continually supplied under light irradiation to maintain the content of Zn*-O2- pairs (which have been well recognized as efficient active sites for CH4 activation [21-23]) for achieving efficient catalytic CH4 conversion. In contrast, the signal intensity at g = 2.005 does not obviously change for WO3 upon introducing CH4 under light irradiation, which is consistent with the poor activity for photocatalytic CH4 conversion. This reveals that WO3 lacks sufficient O2- centers to activate CH4 without Zn doping. The in-situ EPR results confirm the specific electrons/holes migration path from WO3 to doped Zn2+/lattice O and the emergence of Zn*-O2- paired sites, which play an important role in adsorbing and activating the CH4 molecules.
Upon ascertaining the charge dynamics behavior, we further examine the role of introduced Zn and Pd in CH₄ activation and coupling process. The CH₄ temperature programmed desorption (CH₄-TPD) measurements are first performed to explore the CH₄ adsorption behavior, which is the essential prerequisite for activation process. As shown by the CH₄-TPD curves (Figure 3d), two wide gas desorption peaks, corresponding to physical adsorption and chemical adsorption, appear respectively in the low temperature range (100-150 °C) and the middle temperature range (200-400 °C) for WO₃. After doping Zn sites, Zn₀.35-WO₃ shows similar physical adsorption peak in low temperature range, while the chemical desorption peak area in middle temperature range increases significantly as compared with WO₃, indicating that more CH₄ is firmly adsorbed on the catalyst surface by chemisorption. More importantly, a new CH₄ chemical desorption peak appears around 325 °C after Zn doping, suggesting that the doped Zn sites can promote the CH₄ adsorption capacity, thereby contributing to the enhanced CH₄ conversion performance. When the Pd nanoparticles are incorporated into the catalyst, the CH₄ chemical desorption temperature for Pd₅/WO₃ and Pd₅/Zn₀.35-WO₃ shifts toward higher temperature by about 25 °C, and the peak area further increases. This indicates that the additional Pd nanoparticles can further enhance the CH₄ adsorption capacity through increasing the binding strength for CH₄. Combined with mass spectra (MS), the CH₄ TPD-MS technique is further used to analyze the related species derived from CH₄ dissociation. As the essential product in CH₄ conversion, the peak area for H₂ is significantly enhanced after Zn doping (Figure S11), especially after Pd-Zn co-modification as compared with WO₃, demonstrating that the modified Pd nanoparticles exhibit a stronger effect on dehydrogenation of the intermediates, contributing to the increased H₂ production. The results above indicate that the doped Zn plays a major role in promoting the CH₄ adsorption, while the modified Pd nanoparticles play a dominant role in facilitating the dehydrogenation of the intermediates.

To further decode the reaction mechanism, in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) and in situ near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) are employed to track the evolution of intermediates during the CH₄ activation and coupling process. As shown in the in-situ DRIFTS spectra for WO₃, Zn₀.35-WO₃ and Pd₅/Zn₀.35-WO₃ (Figure 4a-c), when the photocatalysts are fully immersed in the CH₄ atmosphere for 40 min under dark conditions (Figure 4a), the absorption peaks at 1428, 1473 and 3015 cm⁻¹, corresponding to the symmetrical and asymmetrical deformation vibration of the C−H bond in CH₄ molecules, emerge and increase with the adsorption time [21, 27, 33-35]. This implies that the CH₄ molecules are increasingly adsorbed on the photocatalyst surface. After modification of Zn and Pd, the intensity of each CH₄-related absorption peak for Zn₀.35-WO₃ and Pd₅/Zn₀.35-WO₃ in the same adsorption time period is significantly promoted as compared with WO₃. This observation is particularly emphasized on the peak for the symmetric vibration of the C−H bond in CH₄ molecules (1541 cm⁻¹), proving that more CH₄ molecules are captured on photocatalyst surface attributed to the modified Zn and Pd. In addition, when the adsorption time exceeds 30 min, the peak intensity for CH₄ has no obvious increase, suggesting that a saturated adsorption has been achieved.
Figure 4. In situ spectroscopic measurements for tracking the evolution of intermediates during photocatalytic CH₄ conversion. (a) In-situ DRIFTS spectra of CH₄ adsorption in dark for different times over WO₃, Zn₀.₃₅-WO₃ and Pd₅/Zn₀.₃₅-WO₃. (b and C) In-situ DRIFTS spectra of CH₄ conversion under light irradiation for different times over WO₃ and Pd₅/Zn₀.₃₅-WO₃. (d and e) In-situ NAP-XPS spectra of C 1s over Pd₅/Zn₀.₃₅-WO₃ upon exposure to 0.45 mbar of CH₄ in dark and under light irradiation for different times.

Furthermore, the light irradiation is introduced to examine the CH₄ coupling reaction process (Figure 4b, c). With the increased light irradiation time, the in-situ DRIFTS spectra for Pd₅/Zn₀.₃₅-WO₃ show that the intensities of various CH₄-related peaks have no obvious change, indicating that the adsorption sites can continuously capture CH₄ from the environment to maintain the adsorption saturation state during the CH₄ coupling process (Figure 4c). In stark contrast, multiple peaks at 870, 890 cm⁻¹ and in the range of 3200-3600 cm⁻¹ corresponding to the C–C bond and –OH groups of intermediates appear upon light irradiation, and their intensities gradually increase with the light irradiation time, indicating that the adsorbed CH₄ has undergone a cleavage and coupling process to generate C₂H₆[36]. Remarkably, the peak at 1641 cm⁻¹ in the in-situ DRIFTS spectra for Pd₅/Zn₀.₃₅-WO₃, assigned to C=C of methylene radicals, suggests the process that the adsorbed CH₄ is dehydrogenated and coupled to produce C₂H₄[37].

In-situ NAP-XPS studies are further performed to supplement the information for the evolution of intermediates during the CH₄ coupling reaction. The corresponding
high-resolution C 1s XPS spectrum of Pd₅/Zn₀.₃₅-WO₃ displays a peak at 284.8 eV under vacuum condition (Figure 4d), due to the exogenous residual carbon on photocatalyst surface [21, 37]. Although such residual carbon cannot be completely purged by the Ar flow, the peak intensity basically maintains unchanged and thus has no interference to the subsequent measurement. With the continuous CH₄ adsorption and accumulation, the intensity of the peak at 286.3 eV assigned to methoxy intermediates increases significantly, indicating that the generated methyl intermediates are adsorbed on lattice oxygen sites. The peak intensity for the methoxy intermediates significantly decreases upon light irradiation (Figure 4e), suggesting that the methoxy intermediates are consumed by participating in the following reaction. With the continuous light irradiation, the peak intensities for the methoxy intermediates are recovered, indicating that the methoxy intermediates can be continuously supplemented for maintaining the CH₄ coupling reaction [38-40].

**Figure 5.** Schematic diagram illustrating the pathway for photocatalytic coupling conversion of CH₄ to C₂H₄ and C₂H₆ on the designed Pd₅/Zn₀.₃₅-WO₃ catalyst.

Based on the information gleaned above, the roles of modified Zn and Pd on charge dynamics and reaction intermediates evolution have been elucidated. In addition, the photogenerated holes in the valence band maximum of WO₃ are thermodynamically feasible for driving the oxidation of CH₄ to methyl radical (Figure S12) [41]. As such, a reasonable reaction pathway including the photogenerated charge transfer path can be proposed as illustrated in Figure 5. Upon light irradiation, the photogenerated holes are enriched at lattice oxygen (O²⁻) sites to form O⁻ centers, while the photogenerated electrons are transferred to the nearby doped Zn²⁺ sites via W⁶⁺, forming Zn⁺–O⁻ pairs. The formed Zn⁺ sites are available for...
capturing the CH$_4$ molecules through donating the single electron to the empty C–H o*-antibonding orbital of CH$_4$ molecule, while the O$^-$ centers have a strongly attractive force to abstract the H atoms from CH$_4$ [22, 23]. Subsequently, the adsorbed CH$_4$ is activated by Zn$^+$-O$^-$ pairs to generate methyl intermediates, which are then stabilized by the Zn$^+$ sites. The formed methyl intermediates can either follow the C$_2$H$_6$ pathway after desorbing from the catalyst to generate methyl radicals, or undergo the C$_2$H$_4$ pathway by diffusing onto the adjacent O$^{2-}$ sites and being further dehydrogenated by Pd nanoparticles to generate methylene radicals. Finally, the produced free methyl radicals and methylene radicals undergo self-coupling reactions to produce the products of C$_2$H$_4$ and C$_2$H$_6$. Simultaneously, the H atoms dissociated from the activated CH$_4$ can couple with each other to produce H$_2$. The holes enriched at O$^-$ centers can recombine with the electrons trapped at Zn$^+$ sites to generate O$_2$ and Zn$^{2+}$. It should be noted that the lattice oxygen participates in the photocatalytic CH$_4$ conversion in two different pathways. One is producing O$^-$ centers as active sites to activate CH$_4$ molecules for photocatalytic nonoxidative coupling of CH$_4$ with a stoichiometric H$_2$ evolution, during which the lattice oxygen will not be consumed. The other is serving as strong oxidants leading to the over-oxidation of CH$_4$ to CO$_2$, during which the lattice oxygen will be consumed similarly to the Mars-van-Krevelen mechanism [42]. Nevertheless, the consumed lattice oxygen during the over-oxidation process can be effectively supplemented by the photooxidation treatment under air conditions, realizing the recycling of the model Pd$_5$/Zn$_{0.35}$-WO$_3$ photocatalyst.

3. Discussion

In summary, we have designed Pd-Zn co-modified WO$_3$ nanosheets as advanced photocatalysts for efficient CH$_4$ nonoxidative coupling to C$_2$H$_4$ with high selectivity under ambient conditions and moderate light irradiation. The optimized Pd$_5$/Zn$_{0.35}$-WO$_3$ nanostructure, featuring the Zn and Pd as synergistic active sites, achieves superior catalytic performance as compared to the state-of-the-art catalysts for photocatalytic nonoxidative coupling of CH$_4$ to C$_2$H$_4$. Importantly, a nearly stoichiometric yield of valuable H$_2$ also has been obtained, suggesting the giant economic incentives. Based on structural characterization and in-situ spectroscopic analysis, the remarkable performance of our model photocatalyst is ascribed to the synergized adsorption, activation and dehydrogenation of CH$_4$ by the synergistic O$^-$, Zn$^+$ and Pd$^0$ sites. Specifically, the doped Zn sites play a major role in promoting the adsorption and activation of CH$_4$ molecules, while the Pd sites play a dominant role in facilitating the dehydrogenation of the intermediates and suppressing over-oxidation. The synergistic functions dramatically increase the selectivity toward C$_2$H$_4$ and efficiently suppress the CH$_4$ over-oxidation to CO$_2$. This work provides insights for designing highly efficient photocatalyst for selective photocatalytic nonoxidative coupling of CH$_4$ toward high-value-added hydrocarbon products, through leveraging synergistic catalytic sites to synergize the adsorption, activation and dehydrogenation processes.

4. Materials and Methods
4.1. Synthesis of WO$_3$ nanosheets: 0.222 g of polyethylene oxide-polypropylene oxide-polyethylene (P123) (Pluronic, M = 5800) was dissolved in 14.444 g of absolute ethanol, and this mixture was stirred continuously for 1 h. After that, deionized water was added into the mixture and stirred for another 1 h. Subsequently, 1.5 mL of ethylene glycol was added to the above mixture and stirred for another 2 h to form a clear solution. The obtained solution was sealed and kept in a brown reagent bottle at least 48 h before further use (denoted as solution A). Subsequently, 0.444 g of WCl$_6$ was added into 16.833 g solution A, and stirred for 20 min to obtain a yellow solution. The solution was then transferred to a 50 mL Teflon-lined stainless autoclave. The sealed autoclave was kept under 110 °C for 3 h, and naturally cooled to room temperature. After the solvothermal treatment, the blue precipitate was washed with absolute ethanol, and dried in a vacuum oven at 80 °C for 12 h. Then the precipitate was ground to obtain powder. Finally, the powder was placed in a muffle furnace and calcinated at 400 °C for 1 h to obtain the WO$_3$ nanosheets with a yellow color.

4.2. Synthesis of Zn-doped WO$_3$ nanosheets: The Zn-doped WO$_3$ nanosheets were synthesized by following the same procedure for WO$_3$ nanosheets except that various mass (0.005, 0.010, and 0.020 g) of Zn(Ac)$_2$ were added into the solution A with WCl$_6$ at the same time. The prepared Zn-doped WO$_3$ nanosheets with various mass fraction of Zn are denoted as Zn$_X$-WO$_3$, where X refers to the theoretical mass fraction of Zn in the sample.

4.3. Synthesis of Pd-Zn co-modified WO$_3$ nanosheets: 1.000 g optimized Zn$_{0.35}$-WO$_3$ and different amount (0.063, 0.105, and 0.147 g) of Pd(Ac)$_2$ were dispersed in 50 mL of CH$_2$Cl$_2$ under stirring for 24 h at room temperature [43]. After separation, washing and drying, the powder of Pd-Zn co-modified WO$_3$ nanosheets was obtained and denoted as Pd$_Y$/Zn$_{0.35}$-WO$_3$, where Y refers to the mass fraction of Pd in the sample.

4.4. Evaluation of photocatalytic performance for CH$_4$ conversion: In the photocatalytic CH$_4$ conversion test, the dispersion (2 mg photocatalyst, and 500 μL H$_2$O) was evenly daubed on a FTO conductive glass (1 cm × 4 cm). After the photocatalyst was dried, the FTO conductive glass was put into a 67 mL quartz reaction tube filled with CH$_4$ (99.999%). Subsequently, the reactor was irradiated vertically with a 300 W xenon lamp for 2 h with a light intensity of 500 mW/cm$^2$ and a irradiation area of 2 cm$^2$. A gas chromatography (GC) of GC-7890B (Agilent) with TCD and flame ionization detector (FID) was used to detect H$_2$ and other hydrocarbon products (C$_2$H$_6$, and C$_2$H$_4$). Other over-oxidation products (CO, and CO$_2$) were analyzed by GC-7890A gas chromatography (Agilent) with TCD and FID detectors. Using the same method, isotope labelling experiments were performed with $^{13}$CH$_4$ as the reactant and gas chromatography-mass spectrometry (GC-MS, 7890A-5975C, Agilent) as the detection instrument.

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NAP-XPS characterizations and analyzed the results. W.J., T.K. and P.H.C.C. joined the discussion of experiment results. C.G. and Y.X. proposed the research direction, supervised the project, analyzed and discussed the experimental results, and revised the manuscript.

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**Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this article.

**Data Availability**

All data needed to evaluate the conclusions in the paper are present in the paper and the Supplementary Materials. Additional data related to this paper may be requested from the authors.

**Supplementary Materials**

Figure S1. (a) XRD patterns and (b) UV-vis DRS spectra of WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$ samples. Figure S2. SEM images of (a, b) WO$_3$, (c) Zn$_{0.35}$-WO$_3$ and (d) Pd$_5$/Zn$_{0.35}$-WO$_3$. Figure S3. (a) W 4f and (b) O 1s XPS spectra of WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. (c) Zn 2p XPS spectra of Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. (d) Pd 3d XPS spectra of Pd$_5$/Zn$_{0.35}$-WO$_3$. Figure S4. GC data for photocatalytic CH$_4$ conversion over (a) WO$_3$, (b) Zn$_{0.35}$-WO$_3$ and (c) Pd$_5$/Zn$_{0.35}$-WO$_3$. Figure S5. Time-dependent production yield of C$_2$H$_4$, C$_2$H$_6$ and C$_3$H$_6$ in photocatalytic CH$_4$ conversion over Pd$_5$/Zn$_{0.35}$-WO$_3$ photocatalysts under light irradiation of 2 h. Figure S6. Products yields and theoretical H$_2$ yield for CH$_4$ conversion over WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$ photocatalysts under light irradiation of 2 h. Figure S7. (a) Photographs of the Pd$_5$/Zn$_{0.35}$-WO$_3$ sample before reaction, after reaction and after photooxidation treatment. (b) SEM image of Pd$_5$/Zn$_{0.35}$-WO$_3$ after photooxidation treatment. (c) XRD patterns, (d) UV-vis DRS spectra and (e) O 1s XPS spectra of Pd$_5$/Zn$_{0.35}$-WO$_3$ before reaction, after reaction and after photooxidation treatment. Figure S8. GC-MS data of $^{13}$CO$_2$ produced in photocatalytic $^{13}$CH$_4$ coupling by Pd$_5$/Zn$_{0.35}$-WO$_3$. Figure S9. SS-SPS responses of WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. Figure S10. In-situ EPR signals of WO$_3$ collected under different conditions. Figure S11. TPD-MS profiles of H$_2$ over WO$_3$, Zn$_{0.35}$-WO$_3$ and Pd$_5$/Zn$_{0.35}$-WO$_3$. Figure S12. Illustration of the band structures of WO$_3$ and the redox potentials for oxidizing CH$_4$ to ·CH$_3$. Table S1. The comparison of catalytic performance with representative state-
of-the-art photocatalysts for photocatalytic coupling of CH₄ to C₂ compounds. Table S2. The yields of products in photocatalytic CH₄ conversion over Pd₅/Zn₀.₃₅-WO₃. Table S3. Fluorescence lifetimes related to the TS-PL spectra of WO₃, Zn₀.₃₅-WO₃ and Pd₅/Zn₀.₃₅-WO₃.

References


