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

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Photocatalytic nonoxidative coupling of CH4 to multicarbon (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 overoxidation. 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 nonpolar 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 overoxidized products (i.e., CO and CO2) [8–11]. Given such 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 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 in 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 band gap, 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 substrate, constructing the Pd-Zn comodified 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 a high-resolution TEM (HRTEM) images can be assigned to the (020) and (002) crystal planes of monoclinic phase WO₃ (Figure 1(b)), which are consistent with the XRD results [25]. Meanwhile, such a nanosheet morphology remains unchanged after Zn doping and Pd modification. Taken together, the results indicate that the Pd-Zn comodification 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 comodified 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 a high-resolution TEM (HRTEM) images can be assigned to the (020) and (002) crystal planes of monoclinic phase WO₃ (Figure 1(b)), 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 comodified WO₃ nanosheets (Figure 1(c)) 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 1(d)) [28]. The corresponding energy-dispersive x-ray spectroscopy (EDS) elemental mapping (Figure 1(e)) 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 Zn⁺⁺⁺ ions have been successfully doped into the WO₃ lattice while the zero-valent state of Pd proves that Pd nanoparticles are indeed formed by the self-reduction method. Note that low-valence W⁵⁺ species is resolved along with the binding energy of 531.8 eV for adsorbed oxygen species at the defects in the WO₃ 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 WO₃ substrate, constructing the Pd-Zn comodified WO₃ nanosheets.

After confirming the formation of Pd-Zn comodified WO₃ nanosheets, we then evaluate their performance as a photocatalyst for CH₄ conversion under full-spectrum
The catalytic performance of the synthesized Pd-Zn comodified WO₃ (denoted as Pdₓ/Zny-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 2(a). 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).

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 WO$_3$, the Zn-doped WO$_3$ exhibits remarkably enhanced C$_2$ products yield and C$_2$H$_4$ selectivity, and the C$_2$H$_4$ yield increases with the amount of doped Zn within a certain range (Figure 2(a)), suggesting that the doped Zn can facilitate CH$_4$ activation and coupling. However, excessive Zn doping leads to the decrease in C$_2$ products yield, most likely due to the increased work function and reduced lattice oxygen content by excessive doped Zn [31]. The activation of CH$_4$ heavily depends on the O$^-$ centers in Zn$^{2+}$O$^-$ pairs. In the absence of Pd, the O$^-$ centers in Zn$_{0.35}$WO$_3$ serving as strong oxidants cause the serious overoxidation of activated CH$_3$ to CO$_2$ (Figure S6b). The Pd nanoparticles-modified WO$_3$ (Pd$_x$/WO$_3$) also exhibits substantially enhanced C$_2$ products yield and C$_2$H$_4$ selectivity, while a considerable amount of C$_3$H$_6$ emerges. The production of C$_3$H$_6$ indicates that the introduced Pd nanoparticles serving as

Figure 2: Photocatalytic performance for CH$_4$ conversion. (a) C$_2$+ compound yields for CH$_4$ conversion by WO$_3$, Zn$_{x}$-WO$_3$, Pd$_x$/WO$_3$, and Pd$_x$/Zn$_y$-WO$_3$ (x% and y% 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 C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_6$, as well as the C$_2$H$_4$ selectivity in C$_2$+ products, for photocatalytic CH$_4$ coupling by Pd$_{0.5}$/Zn$_{0.35}$-WO$_3$ in six successive cycling tests. (c) GC-MS data of $^{13}$C$_2$H$_6$ and $^{13}$C$_2$H$_4$ produced from photocatalytic $^{13}$CH$_4$ coupling by Pd$_{0.5}$/Zn$_{0.35}$-WO$_3$. 

![Graph A](image1.png)

![Graph B](image2.png)

![Graph C](image3.png)
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 C₂H₆. Furthermore, after modifying Zn₀.₃₅-WO₃ with Pd nanoparticles, the production yield of C₂H₄ further increases significantly with the loading amount of Pd (Figure 2(a)). 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 overoxidation of carbon intermediates to CO₂ as compared with Zn₀.₃₅-WO₃ (Figure S6b). Moreover, excessive Pd loading, such as Pd₅/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 overoxidation.

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 overoxidation. Nevertheless, such lattice oxygen consumption would not limit the long-term application of photocatalyst; the consumed lattice oxygen can be effectively replenished after photo-oxidation 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 Pd₅/Zn₀.₃₅-WO₃ catalyst, during which a photo-oxidation pretreatment of 30 min is performed on the recycled catalyst under air conditions before each cycle (Figure 2(b)). After the six cycles, the recycled catalyst well retains the activity and selectivity for photocatalytic coupling of CH₄ to C₂H₄, manifesting the eminent recyclability and practicability of our model photocatalyst.

To further verify the carbon source of produced C₂H₄ and C₂H₆ in photocatalytic CH₄ conversion, isotope labeling experiment is performed by using ¹³C₂H₄ as the reactant. The ¹³C₂H₄, ¹³C₂H₆, and ¹³CO₂ products as well as various intermediates derived from isotopic ¹³CH₄ can be observed by gas chromatography-mass spectrometry (GC-MS, Figure 2(c) and S8). Additionally, no products are detected during the control experiments without catalyst or under dark condition (Figure 2(a)). These results confirm that all coupling products are derived from CH₄, rather than the release of any residual organic matters in raw materials during the preparation process.

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 TR-SPV signal, the better charge separation; the wider TR-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 3(a)), 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 3(b) 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 comodification in facilitating charge separation and transfer, which consequently promotes CH₄ conversion reaction.

Since the promoting effect of Pd-Zn comodification 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 3(c) 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 Zn⁺ to produce Zn⁺⁺ sites [32]. In addition, the signals at g = 2.005 attributed to unpaired electrons trapped in surface defects (V₀⁺ or O⁻) become stronger for both WO₃ and Pd₅/Zn₀.₃₅-WO₃ upon light irradiation. Considering that Zn⁺ and O⁻ 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 (O⁻ 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 O⁻ centers at g = 2.005 slightly decreases for Pd₅/Zn₀.₃₅-WO₃ under light irradiation, indicating that the O⁻ 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\(^{+}\)--O\(^{-}\) pairs (which have been well recognized as efficient active sites for CH\(_4\) activation [21–23]) for achieving efficient catalytic CH\(_4\) conversion. In contrast, the signal intensity at \(g = 2.005\) does not obviously change for WO\(_3\) upon introducing CH\(_4\) under light irradiation, which is consistent with the poor activity for photocatalytic CH\(_4\) conversion. This reveals that WO\(_3\) lacks sufficient O\(^{-}\) centers to activate CH\(_4\) without Zn doping. The in situ EPR results confirm the specific electrons/holes migration path from WO\(_3\) to doped Zn\(^{2+}\)/lattice O and the emergence of Zn\(^{+}\)--O\(^{-}\) paired sites, which play an important role in adsorbing and activating the CH\(_4\) molecules.

Upon ascertaining the charge dynamics behavior, we further examine the role of introduced Zn and Pd in CH\(_4\) activation and coupling process. The CH\(_4\) temperature programmed desorption (CH\(_4\)-TPD) measurements are first performed to explore the CH\(_4\) adsorption behavior, which is the essential prerequisite for activation process. As shown by the CH\(_4\)-TPD curves (Figure 3(d)), 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 WO\(_3\). After doping Zn sites, Zn\(_{0.35}\)–WO\(_3\) shows similar physical adsorption peak in low temperature range, while the chemical desorption peak area in middle temperature range increases significantly as compared with WO\(_3\), indicating that more CH\(_4\) is firmly adsorbed on the catalyst surface by chemisorption. More importantly, a new CH\(_4\) chemical desorption peak appears around 325°C after Zn doping, suggesting that the doped Zn sites can promote the CH\(_4\) adsorption capacity, thereby contributing to the enhanced CH\(_4\) conversion performance. When the Pd nanoparticles are incorporated into the catalyst, the CH\(_4\) chemical desorption temperature for Pd\(_5\)/WO\(_3\) and Pd\(_5\)/Zn\(_{0.35}\)–WO\(_3\) 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 CH\(_4\) adsorption capacity through increasing the binding strength for CH\(_4\). Combined with mass spectra (MS), the CH\(_4\) 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 comodification 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 (Figures 4(a)–4(c)), when the photocatalysts are fully immersed in the CH₄ atmosphere for 40 min under dark conditions (Figure 4(a)), 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.

Furthermore, the light irradiation is introduced to examine the CH₄ coupling reaction process (Figures 4(b) and 4(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 4(c)). 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 C₂H₆ [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 1 s XPS spectrum of Pd₅/Zn₀.₃⁵-WO₃ displays a peak at 284.8 eV under vacuum condition (Figure 4(d)), 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 4(e)), 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].

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 O²⁻ centers, while the photogenerated electrons are transferred to the nearby doped Zn²⁺ sites via W⁶⁺, forming Zn²⁺–O⁻ pairs. The formed Zn²⁺ sites are available for capturing the CH₄ molecules through donating the single electron to the empty C–H σ *-antibonding orbital of CH₄ molecule, while the O²⁻ centers have a strongly attractive force to abstract the H atoms from CH₄ [22, 23]. Subsequently, the adsorbed CH₄ is activated by Zn²⁺–O⁻ pairs to generate methyl intermediates, which are then stabilized by the Zn²⁺ centers. The formed methyl intermediates can either follow the C₂H₆ pathway after desorbing from the catalyst to generate O²⁻ and Zn²⁺ centers have a strongly attractive force to abstract the H atoms from CH₄ [22, 23]. Subsequently, the adsorbed CH₄ is activated by Zn²⁺–O⁻ pairs to generate methyl intermediates, which are then stabilized by the Zn²⁺ centers. The formed methyl intermediates can either follow the C₂H₆ pathway after desorbing from the catalyst to generate O²⁻ and Zn²⁺ pairs to generate methyl radicals, or undergo the C₂H₄ pathway by diffusing onto the adjacent O²⁻ 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 C₂H₄ and C₂H₆. Simultaneously, the H atoms dissociated from the activated CH₄ can couple with each other to produce H₂. The holes enriched at O²⁻ centers can recombine with the electrons trapped at Zn²⁺ sites to generate O²⁻ and Zn²⁺. It should be noted that the lattice oxygen participates in the photocatalytic CH₄ conversion in two different pathways. One is producing O²⁻ centers as active sites to activate CH₄ molecules for photocatalytic nonoxidative coupling of CH₄ with a stoichiometric H₂ evolution, during which the lattice oxygen will not be consumed. The other is serving as strong oxidants leading to the over oxidation of CH₄ to CO₂, during which the lattice oxygen will be consumed similarly to the Mars-van Krevelen mechanism [42].
Nevertheless, the consumed lattice oxygen during the overoxidation process can be effectively supplemented by the photo-oxidation 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 comodified 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 CH₄ molecules, while the Pd sites play a dominant role in facilitating the dehydrogenation of the intermediates and suppressing overoxidation. The synergistic functions dramatically increase the selectivity toward C₂H₄ and efficiently suppress the CH₄ overoxidation to CO₂. This work provides insights for designing highly efficient photocatalyst for selective photocatalytic nonoxidative coupling of CH₄ toward the 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 WO₃ 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 WCl₆ 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 WO₃ nanosheets with a yellow color.

4.2. Synthesis of Zn-Doped WO₃ Nanosheets. The Zn-doped WO₃ nanosheets were synthesized by following the same procedure for WO₃ nanosheets except that various mass (0.005, 0.010, and 0.020 g) of Zn (Ac)₂ were added into the solution A with WCl₆ at the same time. The prepared Zn-doped WO₃ nanosheets with various mass fraction of Zn are denoted as Znₓ-WO₃, where x refers to the theoretical mass fraction of Zn in the sample.

4.3. Synthesis of Pd-Zn Comodified WO₃ Nanosheets. 1.000 g optimized Zn₀.₃₅-WO₃ and different amount (0.063, 0.105, and 0.147 g) of Pd (Ac)₂ were dispersed in 50 mL of CH₂Cl₂ under stirring for 24 h at room temperature [43]. After separation, washing, and drying, the powder of Pd-Zn comodified WO₃ nanosheets was obtained and denoted as Pdₓ/Zn₀.₃₅-WO₃, where x refers to the mass fraction of Pd in the sample.

Figure 5: Schematic diagram illustrating the pathway for photocatalytic coupling conversion of CH₄ to C₂H₄ and C₂H₆ on the designed Pdₓ/Zn₀.₃₅-WO₃ catalyst.
4.4. Evaluation of Photocatalytic Performance for CH4 Conversion. In the photocatalytic CH4 conversion test, the dispersion (2 mg photocatalyst, and 500 μL H2O) was evenly daubed on a FTO conductive glass (1 cm x 4 cm). After the photocatalyst was dried, the FTO conductive glass was put into a 67 mL quartz reaction tube (99.999%). Subsequently, the reactor was irradiated vertically with a 300 W xenon lamp for 2 h with a light intensity of 500 mW/cm2 and a irradiation area of 2 cm². A gas chromatography (GC) of GC-7890B (Agilent) with TCD and flame ionization detector (FID) was used to detect H2 and other hydrocarbon products (C2H6 and C2H4). Other overoxidation products (CO and CO2) were analyzed by GC-7890A gas chromatography (Agilent) with TCD and FID detectors. Using the same method, isotope labelling experiments were performed with 13CH4 as the reactant and gas chromatography-mass spectrometry (GC-MS, 7890A-5975C, Agilent) as the detection instrument.

Data Availability

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

Conflicts of Interest

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

Authors’ Contributions

Y.L. designed and performed the experiments, analyzed and discussed the experimental results, and drafted the manuscript. Y.C. performed the 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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Supplementary Materials

Figure S1. (a) XRD patterns and (b) UV-vis DRS spectra of WO3, Zn0.35-WO3, and Pd5/Zn0.35-WO3 samples. Figure S2. SEM images of (a) WO3, (c) Zn0.35-WO3, and (d) Pd5/Zn0.35-WO3. Figure S3. (a) W 4f and (b) O 1 s XPS spectra of WO3, Zn0.35-WO3, and Pd5/Zn0.35-WO3. (c) Zn 2p XPS spectra of Zn0.35-WO3 and Pd5/Zn0.35-WO3. (d) Pd 3d XPS spectra of Pd5/Zn0.35-WO3. Figure S4. GC data for photocatalytic CH4 conversion over (a) WO3, (b) Zn0.35-WO3, and (c) Pd5/Zn0.35-WO3. Figure S5. Time-dependent production yield of C2H6, C2H4, and CH3 in photocatalytic CH4 conversion over Pd5/Zn0.35-WO3 photocatalysts under light irradiation of 2 h. Figure S6. Products yields and theoretical H2 yield for CH4 conversion over WO3, Zn0.35-WO3, and Pd5/Zn0.35-WO3 photocatalysts under light irradiation of 2 h. Figure S7. (a) Photographs of the Pd5/Zn0.35-WO3 sample before reaction, after reaction and after photo-oxidation treatment. (b) SEM image of Pd5/Zn0.35-WO3 after photo-oxidation treatment. (c) XRD patterns, (d) UV-vis DRS spectra, and (e) O 1 s XPS spectra of Pd5/Zn0.35-WO3 before reaction, after reaction, and after photo-oxidation treatment. Figure S8. GC-MS data of 13CO2 produced in photocatalytic 13CH4 coupling by Pd5/Zn0.35-WO3. Figure S9. SS-SPS responses of WO3, Zn0.35-WO3, and Pd5/Zn0.35-WO3. Figure S10. In situ EPR signals of WO3 collected under different conditions. Figure S11. TPD-MS profiles of H2 over WO3, Zn0.35-WO3, and Pd5/Zn0.35-WO3. Figure S12. Illustration of the band structures of WO3 and the redox potentials for oxidizing CH4 to CH3. 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. (Supplementary Materials)

References

[1] BP statistical review of world energy, 2018.
[2] H. Song, X. G. Meng, Z. J. Wang, H. Liu, and J. Ye, “Solar-energy-mediated methane conversion,” Joule, vol. 3, no. 7, pp. 1606–1636, 2019.
[3] M. A. Newton, A. J. Knorpp, V. L. Sushkevich, D. Palagin, and J. A. van Bokhoven, “Active sites and mechanisms in the direct conversion of methane to methanol using Cu in zeolitic hosts: a critical examination,” Chemical Society Reviews, vol. 49, no. 5, pp. 1449–1486, 2020.
[4] X. G. Meng, X. J. Cui, N. P. Rajan, L. Yu, D. Deng, and X. Bao, “Direct methane conversion under mild condition by thermo-, electro-, or photocatalysis,” Chem, vol. 5, no. 9, pp. 2296–2325, 2019.
[5] M. Ravi, M. Ranocchiari, and J. A. Bokhoven, “The direct catalytic oxidation of methane to methanol—a critical assessment,” Angewandte Chemie International Edition, vol. 56, no. 52, pp. 16464–16483, 2017.
[6] A. M. Arinaga, M. C. Ziegels, and T. J. Marks, “Alternative oxidants for the catalytic oxidative coupling of methane,” Energy & Fuels, vol. 32, no. 7, pp. 7059–7067, 2018.
X. Chen, Y. Li, X. Pan, D. Cortie, X. Huang, and Z. Yi, "Photo-catalytic oxidation of methane over silver decorated zinc oxide nanocatalysts," *Nature Communications*, vol. 7, no. 1, p. 12273, 2016.

L. Li, G. D. Li, C. Yan et al., "Efficient sunlight-driven dehydrogenative coupling of methane to ethane over a Zn+ modified zeolite," *Angewandte Chemie International Edition*, vol. 50, no. 36, pp. 8299–8303, 2011.

Z. Sun, T. Liao, Y. Dou et al., "Generalized self-assembly of scalable two-dimensional transition metal oxide nanosheets," *Nature Communications*, vol. 5, no. 1, p. 3813, 2014.

B. Li, L. Q. Sun, J. Bian et al., "Controlled synthesis of novel Z-scheme iron phthalocyanine/porous WO3 nanocomposites as efficient photocatalysts for CO2 reduction," *Applied Catalysis B: Environmental*, vol. 270, article 118849, 2020.

B. B. Zhu, W. B. Ye, Z. T. He, S. S. Zhang, C. G. Feng, and G. Q. Lin, "Regioselective tandem C–H alkylation/coupling reaction of ortho-iodophenylethylenes via C–C-palladium(II)cycles," *ACS Catalysis*, vol. 11, no. 19, pp. 12123–12132, 2021.

R. Zhang, H. Wang, S. Tang et al., "Photocatalytic oxidative dehydrogenation of ethane using CO2 as a soft oxidant over Pd/TiO2Catalysts to C2H4and syngas," *ACS Catalysis*, vol. 8, no. 10, pp. 9280–9286, 2018.

W. B. Jiang, J. X. Low, K. K. Mao et al., "Pd-modified ZnO–au enabling alkyo intermediates formation and dehydrogenation for photocatalytic conversion of methane to ethylene," *Journal of the American Chemical Society*, vol. 143, no. 1, pp. 269–278, 2021.

J. Song, Z. F. Huang, L. Pan, J. J. Zou, X. Zhang, and L. Wang, "Oxygen-deficient tungsten oxide as versatile and efficient hydrogenation catalyst," *ACS Catalysis*, vol. 5, no. 11, pp. 6594–6599, 2015.

N. Zhang, A. Jalil, D. Wu et al., "Refining defect states in W18O49by Mo doping: a strategy for tuning N2Activation towards solar-driven nitrogen fixation," *Journal of the American Chemical Society*, vol. 140, no. 30, pp. 9434–9443, 2018.

Q. Q. Meng, C. D. Lv, J. X. Sun et al., "High-efficiency Fe-mediated Bi2MoO6 nitrogen-fixing photocatalyst: reduced surface work function and ameliorated surface reaction," *Applied Catalysis B: Environmental*, vol. 256, article 117781, 2019.

J. Bian, J. Feng, Z. Zhang et al., "Dimension-matched zinc phthalocyanine/BiVO4 ultrathin nanocomposites for CO2 reduction as efficient wide-visible-light-driven photocatalysts via a cascade charge transfer," *Angewandte Chemie International Edition*, vol. 131, pp. 10980–10994, 2019.

C. Li and Q. Xin, "FT-IR spectroscopic investigation of methane adsorption on cerium oxide," *The Journal of Physical Chemistry*, vol. 96, no. 19, pp. 7714–7718, 1992.

A. Yee, S. J. Morrison, and H. Idriss, "A study of the reactions of ethanol on CeO2 and Pd/CeO2 by steady state reactions, temperature programmed desorption, and in situ FT-IR," *Journal of Catalysis*, vol. 186, no. 2, pp. 279–295, 1999.

D. Scarano, S. Bertarione, G. Spoto, A. Zecchina, and C. Otero Areán, "FTIR spectroscopy of hydrogen, carbon monoxide, and methane adsorbed and co-adsorbed on zinc oxide," *Thin Solid Films*, vol. 400, no. 1–2, pp. 50–55, 2001.

K. Kaehler, M. C. Holz, M. Rohe, J. Strunk, and M. Muhler, "Probing the reactivity of ZnO and Au/ZnO nanoparticles by methanol adsorption: a TPD and DRIFTS study," *ChemPhysChem*, vol. 11, no. 12, pp. 2521–2529, 2010.

F. F. Tao, J. Y. Shan, L. Nguyen et al., "Understanding complete oxidation of methane on spinel oxides at a molecular level," *Nature Communications*, vol. 6, no. 1, p. 7798, 2015.
[38] H. Li, C. Rameshan, A. V. Bukhtiyarov, I. P. Prosvirin, V. I. Bukhtiyarov, and G. Rupprechter, “CO$_2$ activation on ultra-thin ZrO$_2$ film by H$_2$O co-adsorption: in situ NAP-XPS and IRAS studies,” *Surface Science*, vol. 679, pp. 139–146, 2019.

[39] Z. Liu, E. Huang, I. Orozco et al., “Water-promoted interfacial pathways in methane oxidation to methanol on a CeO$_2$-Cu$_2$O catalyst,” *Science*, vol. 368, no. 6490, pp. 513–517, 2020.

[40] C. C. Yang, Y. H. Yu, B. van der Linden, J. C. S. Wu, and G. Mul, “Artificial photosynthesis over crystalline TiO$_2$-based catalysts: fact or fiction?,” *Journal of the American Chemical Society*, vol. 132, no. 24, pp. 8398–8406, 2010.

[41] Q. Li, Y. X. Ouyang, H. L. Li, L. Wang, and J. Zeng, “Photocatalytic conversion of methane: recent advancements and prospects,” *Angewandte Chemie International Edition*, vol. 61, no. 2, article e202108069, 2022.

[42] F. Zasada, J. Janas, W. Piskorz, M. Gorczyńska, and Z. Sojka, “Total oxidation of lean methane over cobalt spinel nanocubes controlled by the self-adjusted redox state of the catalyst: experimental and theoretical account for interplay between the Langmuir-Hinshelwood and Mars-Van Krevelen mechanisms,” *ACS Catalysis*, vol. 7, no. 4, pp. 2853–2867, 2017.

[43] G. X. Wang, S. D. Xu, L. Wang et al., “Fish-in-hole: rationally positioning palladium into traps of zeolite crystals for sinter-resistant catalysts,” *Chemical Communications*, vol. 54, no. 26, pp. 3274–3277, 2018.