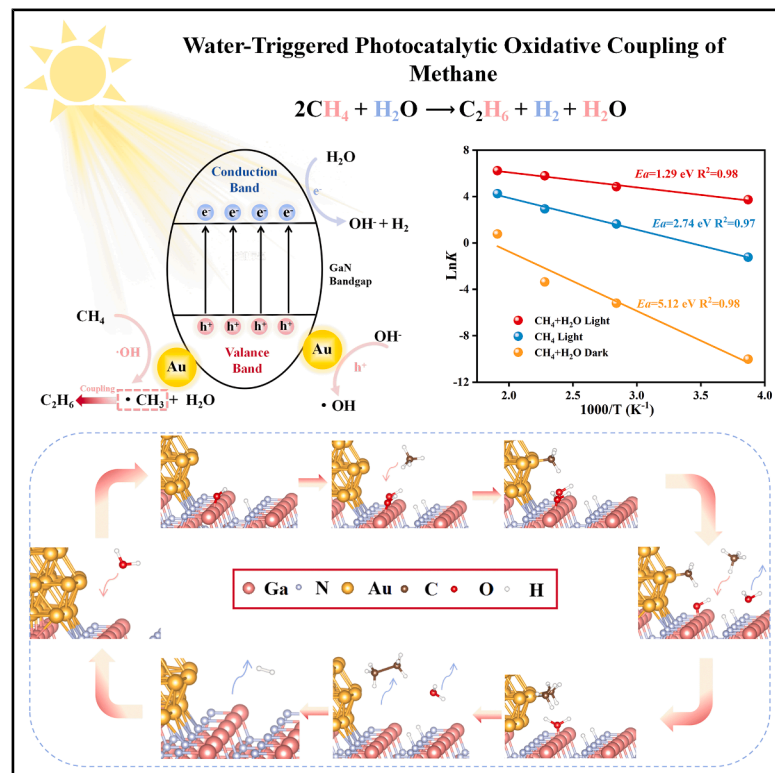


Water-triggered photocatalytic oxidative coupling of methane toward C₂H₆ over Au/GaN nanoarchitecture

Graphical abstract



Highlights

- Water replaces oxygen and hydrogen peroxide as highly selective oxidant for OCM
- The interface of Au/GaN facilitates H₂O activation to generate reactive ·OH
- Water-derived ·OH radicals accelerate C–H bond cleavage of CH₄ via H-exchange
- H₂O lowers the energy barrier of C–C coupling and prevents over-oxidation

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In brief

Upgrading abundant methane to valuable ethane typically requires immense industrial energy. This work presents a sustainable alternative using only sunlight and water. By employing an engineered nanomaterial, light generates active radicals from water that gently break methane's tough chemical bonds. This unique water-triggered pathway prevents unwanted over-oxidation, delivering ethane with exceptional selectivity and stability. This conceptual breakthrough paves a remarkably green and economically viable route for next-generation chemical manufacturing beyond fossil fuels.



Li et al., 2026, Chem 12, 103033
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<https://doi.org/10.1016/j.chempr.2026.103033>

Article

Water-triggered photocatalytic oxidative coupling of methane toward C₂H₆ over Au/GaN nanoarchitecture

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<https://doi.org/10.1016/j.chempr.2026.103033>

THE BIGGER PICTURE As society transitions away from a reliance on depleting petroleum reserves, abundant natural gas (methane) has emerged as a crucial bridge for producing value-added chemicals. However, upgrading methane to higher-order hydrocarbons like ethane conventionally requires extreme industrial temperatures and pressures, making the process both costly and highly energy intensive. While solar-driven photocatalysis offers a promising, environmentally friendly alternative, breaking the famously inert carbon–hydrogen bonds of methane typically leads to either sluggish reaction rates or undesirable over-oxidation into carbon dioxide when traditional oxidants like oxygen are used. This work introduces a paradigm-shifting strategy: utilizing earth-abundant, inexpensive water as a “green” oxidant to trigger the light-driven coupling of methane into ethane. By decorating gallium nitride nanowires with gold nanoparticles, solar energy is efficiently harvested to oxidize water into highly reactive hydroxyl radicals. Rather than over-oxidizing the methane, these transient species gently abstract hydrogen atoms via an elegant exchange mechanism, drastically lowering the energy barrier for ethane formation while simultaneously preventing carbon buildup that would otherwise deactivate the catalyst. By successfully demonstrating this concept even under natural outdoor sunlight, this research establishes a highly sustainable, economically viable, and carbon-neutral blueprint for next-generation chemical manufacturing, moving us one step closer to a sustainable energy future.

SUMMARY

Solar-driven oxidative coupling of methane (CH₄) offers a sustainable route for synthesizing value-added chemicals beyond petroleum. To address current thermodynamic and selectivity challenges, a photocatalytic system employing nano-gold-decorated GaN nanowires is developed for the efficient conversion of CH₄ into ethane (C₂H₆), using water as a green oxidant. The optimized catalyst delivers a remarkable C₂H₆ production rate of 112.6 mmol·g_{cat}^{−1}·h^{−1} with 94.9% selectivity and a turnover number of 40,824 after 256 h operation. Mechanistic investigations reveal that photogenerated holes trapped at Au sites oxidize H₂O into highly active ·OH radicals. These radicals significantly lower the energy barrier for C₂H₆ formation via an H-exchange mechanism. Ultimately, the synergistic Au/GaN interface inhibits CH₄ over-oxidation, showcasing a highly promising, environmentally friendly pathway for solar-to-chemical energy conversion.

INTRODUCTION

As petroleum diminishes, methane (CH₄) has appeared as an ideal alternative for producing value-added chemicals because of its abundance and low cost.^{1,2} Direct and selective transformation of CH₄ into ethane (C₂H₆) is of particular interest and has attracted tremendous attention.^{3–6} However, the inert C–H bond and highly symmetrical molecular structure of CH₄ pose substantial challenges for converting CH₄ into C₂H₆.^{7,8} In industry, the transformation of CH₄ into C₂H₆ requires high temperatures (>700°C) and elevated pressure (>3 MPa) and is therefore an energy-intensive and costly route.^{9,10} From the prospect of carbon neutrality and environmental accountability, it is imperative to explore a green route for the efficient and selective transformation of CH₄ into C₂H₆.

Photocatalysis provides a disruptive strategy for driving the CH₄-to-C₂H₆ conversion with solar energy via non-oxidative or oxidative coupling routes. For photocatalytic non-oxidative coupling of CH₄ (NOCM), the activity remains limited, owing to the endothermic nature of the reaction, and remains at the order of several μmol of C₂H₆ produced per mol metal per hour.^{11,12} By contrast, the yield of C₂H₆ can be considerably improved by photocatalytic oxidative coupling of CH₄ (OCM), since the oxidizer makes the conversion of CH₄-to-C₂H₆ thermodynamically favorable.^{13,14} Thus far, significant efforts have been devoted to the photocatalytic OCM into C₂H₆,¹⁵ where to date, H₂O₂ and O₂ are the most frequently used oxidizers. For example, Zhai and coworkers designed an interesting photocatalyst with dual active sites.¹⁶ The activated lattice oxygen in bismuth oxide (BiO_x) facilitated the cleavage of the C–H bond of CH₄, and the consumed lattice oxygen was supplemented by a suitable concentration of oxygen, thus forming a chemical looping. Nevertheless, the over-oxidation of CH₄ into CO_x is often inevitable because of its high exothermicity with O₂ as the oxidizer, thus resulting in a limited selectivity of C₂H₆.¹⁷ In contrast with O₂, H₂O₂ is promising for achieving high selectivity of CH₄-to-C₂H₆ conversion, bypassing the endothermic steps of activating CH₄. For example, Zheng and coworkers have reported H₂O₂-triggered CH₄ coupling over Au/WO₃, where the H₂O₂-derived hydroxyl (·OH) radicals were rapidly consumed for the C–H cleavage of CH₄ into ·CH₃ exothermically.¹⁸ Despite appreciable performance, H₂O₂ is not currently considered an economically viable oxidant for promoting CH₄-to-C₂H₆ conversion because of its comparatively high cost. Therefore, it is of great interest to achieve photocatalytic OCM to C₂H₆ with economically viable alternatives. Herein, we explore the use of H₂O as the oxidant for the photocatalytic OCM to C₂H₆, which is an earth-abundant, low-cost, and eco-friendly alternative. However, to the best of our knowledge, there has been a lack of substantial endeavors in the use of H₂O as the oxidant in the photocatalytic OCM to C₂H₆.

The development of high-performance photocatalysts for the OCM to C₂H₆ remains a significant materials challenge.¹⁹ Gallium nitride (GaN) nanowires (NWs) vertically aligned on a commercial silicon (Si) wafer offer an attractive semiconductor platform for photocatalysis.²⁰ In the past few years, it has demonstrated numerous advances in water splitting,²¹ artificial photosynthesis,²² biomass valorization,^{23,24} and organic transformations.²⁵ It is worth noting that the unique N-rich [10-10] wurtzite surface of

GaN NWs is efficient for the *in situ* formation of active ·OH species with high oxidation potential from water splitting.²⁶ In our recent work, it is noted that GaN could work in synergy with appropriate metal sites to activate the inert C–H bond of CH₄.²⁷ Together, 1-D nanostructured GaN photocatalysts exhibit significant potential for the H₂O-triggered OCM to C₂H₆ using sunlight, which to our knowledge has not been investigated to date.

Gold (Au) is a widely studied co-catalyst for decorating various semiconductors to achieve photocatalytic OCM to C₂H₆, owing to its unique plasmonic and catalytic properties.^{28–30} Specifically, Au species not only serve as hole-trapping sites to accelerate the separation of photoexcited carriers but also facilitate the desorption of ·CH₃ for the formation of C₂H₆. The integration of Au with a suitable semiconductor photocatalyst thus holds significant promise for the photocatalytic OCM to C₂H₆.

Herein, 1-D nanostructured GaN is coupled with Au co-catalysts and investigated for the photocatalytic OCM to C₂H₆. Owing to the unique catalytic properties, the Au-decorated GaN NWs are capable of utilizing H₂O as a green and inexpensive oxidant to trigger OCM into C₂H₆. The incorporation of H₂O molecules enables a substantial reduction in apparent activation energy (*E_a*) of the CH₄-to-C₂H₆ conversion from 5.12 to 1.29 eV. Under concentrated white light illumination of 6.3 W·cm^{–2}, the photocatalyst affords a considerable C₂H₆ evolution rate of 112.6 mmol·g_{cat}^{–1}·h^{–1} with a high selectivity of 94.9%, with the only inputs being CH₄ and H₂O, which is nearly 6.5 times higher than that of photocatalytic NOCM. More critically, a record-high turnover number (TON) of 40,824 mol C₂H₆ per mol Au is achieved during 256 h of reuse without any notable reduction of activity, far outperforming state-of-the-art OCM photocatalysts (Table S1). A combination of a range of *in situ* spectroscopic characterizations (electron paramagnetic resonance [EPR] spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy [DRIFTS], and irradiated X-ray photoelectron spectroscopy [XPS]) and isotope-labeling experiments with theoretical investigations reveal that under light illumination, photoexcited holes are extracted from GaN by the decorated Au nanoparticles (NPs), followed by the formation of ·OH radicals from H₂O oxidation (H₂O + h⁺ → ·OH + H⁺). The coupling of CH₄ into C₂H₆ is accelerated by the highly active ·OH species via H-exchange with CH₄, concurrently regenerating H₂O and forming ·CH₃. C₂H₆ is then produced through the facile self-coupling of ·CH₃ radicals, with a significantly lowered energy barrier, compared with the process without H₂O. More importantly, the *in situ* formation of ·OH enables the stabilization of ·CH₃ intermediates, which not only contributes to suppressing coke deposition (which can arise from continued dehydrogenation) but also improves the selectivity of C₂H₆ by inhibiting over-oxidation. Meanwhile, outdoor tests demonstrated the feasibility of using this photocatalyst for the synthesis of C₂H₆ from H₂O-triggered CH₄ coupling under real-world conditions. This work offers a low-carbon strategy for solar-driven production of value-added chemicals via H₂O-triggered OCM beyond fossil fuels.

RESULTS

The assembly of Au/GaN NWs on an Si wafer is schematically shown in Figure S1. At first, GaN NWs were controllably grown

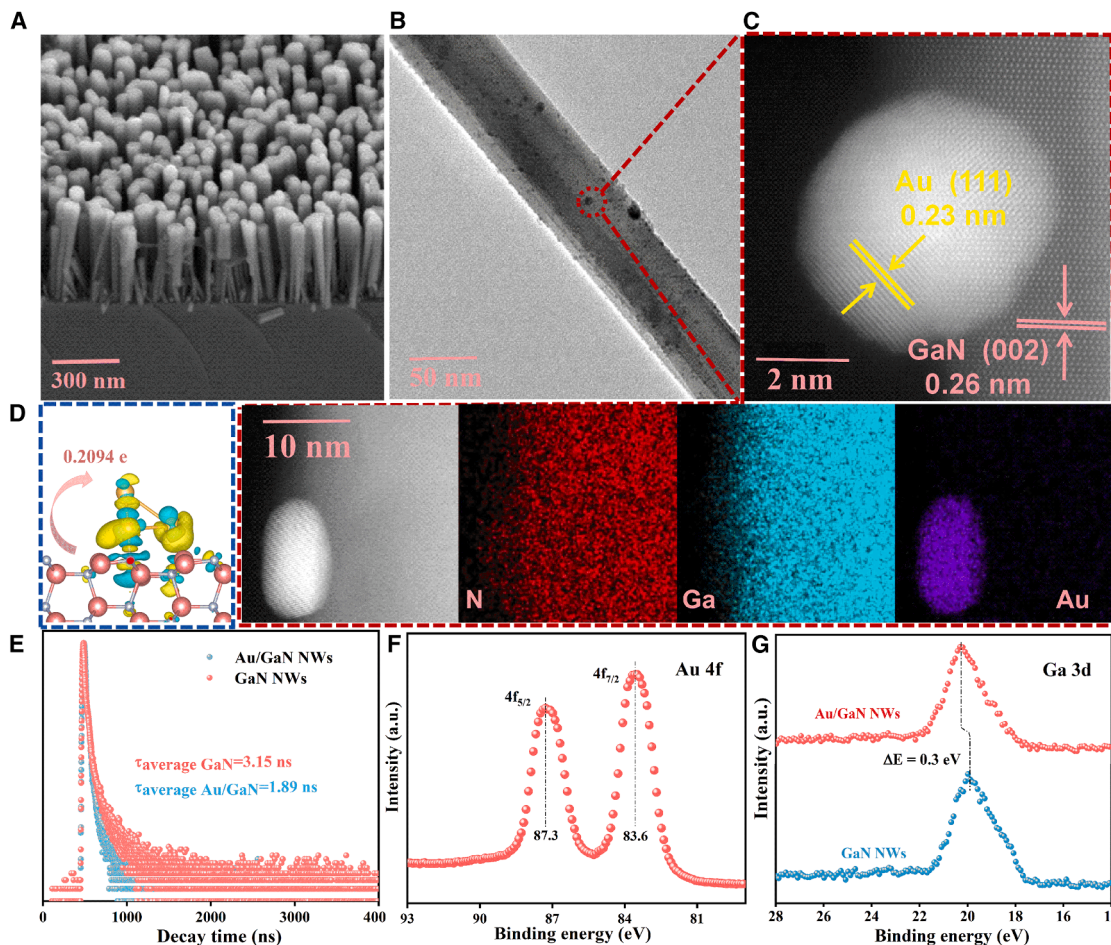


Figure 1. Assembly and characterization of Au-decorated GaN NWs on an Si wafer

(A) A 45°-tilted SEM image of Au-decorated GaN NWs.

(B) TEM image of a single GaN NW decorated with Au NPs.

(C) The high-resolution HAADF-STEM and elemental mapping images of Au/GaN NWs.

(D) Differential charge density analysis of Au/GaN NWs. The yellow and cyan regions indicate the gain and loss of electrons, respectively, with an isosurface of 0.0023 e/Å³. Ga, green; N, gray; Au, yellow.

(E) TRPL spectrum of Au/GaN NWs and GaN NWs.

(F and G) High-resolution (F) Au 4f and (G) Ga 3d XPS spectra of Au/GaN NWs.

on a 4-inch Si wafer through a plasma-assisted molecular-beam epitaxy (MBE) method under an N₂-rich atmosphere.³¹ Au NPs are subsequently decorated onto GaN NWs via an established photo-deposition method. As depicted by the scanning electron microscope (SEM) image (Figure 1A), the morphology of the GaN NWs—featuring an average length of about 850 nm with a diameter of about 60 nm—was not altered upon decoration with Au NPs. The well-defined 1-D nanoarchitecture is favorable for decoupling photon absorption, carrier separation, and surface chemical reactions.³² Transmission electron microscope (TEM) characterizations illustrate that Au NPs were hemispherical in shape and relatively uniformly dispersed on the surface of GaN NWs, with an average diameter of 6.7 nm (Figures 1B and S2). As further characterized by high-angle annular dark-field scanning transmission microscopy (HAADF-STEM) imaging of a single Au/GaN NW (Figure 1C), the lattice spacing of 0.26 nm corre-

sponds to the (002) plane of GaN, in line with X-ray diffraction (XRD) patterns (Figure S3), indicating the c-axis preferential growth direction of the NWs. Meanwhile, the 0.23-nm lattice spacing is attributed to the (111) plane of Au NPs. However, the typical signals of Au were not observed in XRD patterns and Raman spectroscopy (Figure S4), owing to the low content of 0.049 μmol·cm⁻² as measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The energy dispersive X-ray spectroscopy (EDS) elemental mapping images (Figure S5) further validate the success in the decoration of GaN NWs with Au NPs.

A differential charge density analysis was conducted to explore the electronic interaction between Au and GaN (Figure 1D). Bader charge calculation reveals that an average of 0.2094 electrons is transferred from GaN to Au over a simple Au₄/GaN model (Figure S6). Such an electronic interaction

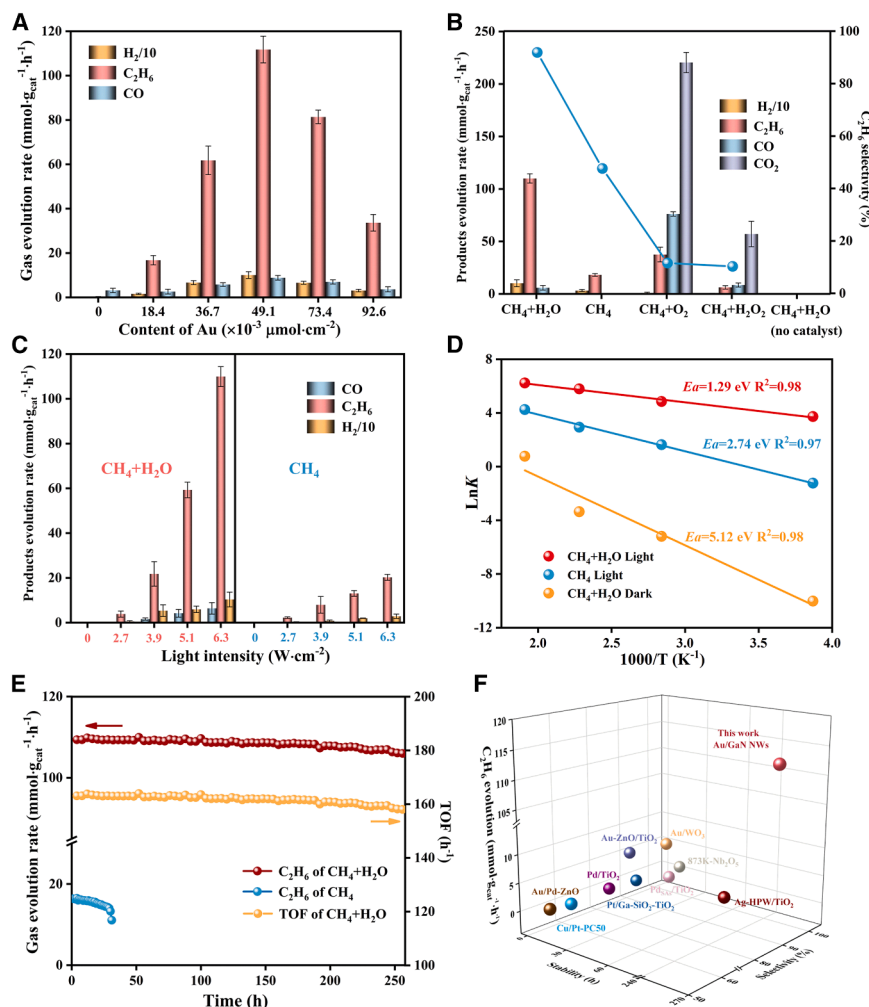


Figure 2. Performance of H₂O-triggered light-driven coupling of CH₄ toward C₂H₆

(A) Influence of Au content on C₂H₆ production rate over Au/GaN NWs. (B) Control experiment of photocatalytic OCM with varied oxidants over Au/GaN NWs. (C) Performance comparison between the photocatalytic OCM and NOCM over Au/GaN NWs under various light intensities. (D) The calculated E_a of photocatalytic (red) and thermocatalytic (orange) OCM with H₂O and photocatalytic (blue) NOCM over Au/GaN NWs. (E) Stability test of photocatalytic OCM (red and orange) and NOCM (blue) over Au/GaN NWs. (F) Performance comparison of the activity, selectivity, and stability of state-of-the-art photocatalysts for light-driven CH₄-to-C₂H₆ conversion. Experimental condition: light intensity, 6.3 W·cm⁻²; the effective light irradiation area (S) is ~0.5 cm², which is the geometric area of the Au/GaN NWs photocatalyst; chamber volume, 440 mL; CH₄: H₂O = 40:2 (volume ratio); Ar, atmosphere; reaction time, 30 min.

between Au and GaN NWs not only stabilizes the NPs against agglomeration but also promotes the separation of photo-carriers. The behavior of photo-carriers is subsequently studied by employing time-resolved photoluminescence (TRPL) spectra (Figure 1E). The average lifetime of GaN NWs decreased from 3.15 to 1.89 ns after coupling with Au NPs, which indicates the fast transfer of photo-carriers upon excitation from GaN NWs to Au NPs, thus benefiting the reaction.

The interaction between Au and GaN was further investigated through XPS (Figure S7). The high-resolution XPS spectra of Au 4f in Figure 1F suggest that Au resides in the metallic state. It is worth noting that the featured peaks of Au 4f in the architecture appeared at 87.3 (4f_{5/2}) and 83.6 (4f_{7/2}) eV, which are significantly lower than those of standard Au species (87.7 and 84.0 eV).³³ Meanwhile, the upward shift of Ga 3d was observed upon decorating with Au species (Figure 1G). These findings indicated that transfer of electrons from GaN to Au created a robust electronic interaction, which facilitates charge transfer during photocatalysis.³⁴

Photocatalytic coupling of CH₄ over Au-decorated GaN NWs was tested in a homemade sealed quartz reactor. A 300 W Xenon (Xe) lamp equipped with a quartz lens was used as the

light source, without external heating (Figure S8). As expected, C₂H₆ was produced in low quantities over bare GaN (Figure 2A). However, the activity was considerably improved by incorporating Au species, illustrating an increasing trend as the deposited amount of Au increased. Au/GaN NWs reached a maximum value of 112.6 mmol·gcat⁻¹·h⁻¹ at an optimal Au loading of 0.049 μmol·cm⁻² with an impressive CH₄ conversion of 1.75%. Then, the activity decreased sharply with

further increasing the Au content. As measured by TEM, the reduced activity may be ascribed to both light shielding effect and lowered intrinsic activity of Au NPs with a larger size at a higher loading content (Figure S9). Herein, the contribution of plasmonic effect of Au to the superior performance was also excluded by cooling experiments with different spectral ranges (Figures S10 and S11). Further, control experiments showed that photocatalytic NOCM was limited, which is associated with both thermodynamic and kinetic restrictions (Figures 2B and S12). In sharp contrast, the introduction of H₂O enables a significant improvement in C₂H₆ selectivity (~95%), without varying any other experimental conditions. Although the overall rate of product formation was higher when the more popular oxidants of O₂ and H₂O₂ were employed, selectivity for C₂H₆ formation was in the region of 10% (with CO and CO₂ the more dominant products), and therefore, overall C₂H₆ production was significantly faster when H₂O was used as the oxidant (Figure 2B). The influence of H₂O concentration in the photocatalytic OCM over Au-decorated GaN NWs was also examined (Figure S13). It was found that both activity and selectivity of C₂H₆ increased with increasing the amount of H₂O, approaching a plateau C₂H₆ activity of 112.6 mmol·gcat⁻¹·h⁻¹ with a record-high selectivity of 94.8% at

a CH₄:H₂O ratio of 40:2. In addition, to verify the vital role of GaN NWs, Au was directly deposited on the Si wafer as a control (Figure S14). As depicted in Figure S15, the Au/Si hybrid did not show any significant conversion of CH₄ to C₂H₆. This finding verifies the critical role of 1-D GaN NWs by providing photoexcited carriers and cooperating with Au for mediating surface chemical reactions.

Notably, as the light intensity increases, the growth rate of C₂H₆ activity from the CH₄-water reaction significantly exceeds that without water involvement (Figure 2C). As shown in Figure 2D, the kinetics of C₂H₆ formation from CH₄ over Au-decorated GaN NWs was significantly improved by the incorporation of H₂O, without varying other experimental conditions, as indicated by the reduced apparent E_a from 5.12 to 1.29 eV upon light illumination. What is more, as seen from Figure S16, the C₂H₆ activity under various light intensities is nearly 22 times higher than that of pure thermal catalysis under the corresponding equivalent temperatures. The photocatalyst surface temperature was evaluated by an infrared camera, while the thermocatalytic reaction temperature was controlled by an external heater (Figures S17 and S18). The wavelength-dependence experiments were measured using a 0.05-L stainless steel cell equipped with a top sapphire window under different monochromatic light (365, 420 535, and 730 nm) irradiation. During the reaction process, an external heating system was employed to maintain the stainless steel cell at 290°C monitored by a thermocouple. As illustrated in Figures S18 and S19, the apparent quantum efficiency (AQE) value shows a matched trend with the light absorption spectrum of the photocatalyst, showing a maximal value of 1.76% under 365 nm monochromatic light irradiation. Meanwhile, the ultraviolet-visible (UV-vis) spectrum exhibits no discernible absorption peak within the visible region, which can be attributed to the insufficient loading (0.049 $\mu\text{mol}\cdot\text{cm}^{-2}$) of Au NPs. The findings above demonstrate that the dominating role of photoexcited charge carriers and H₂O in light-driven OCM into C₂H₆.

The influence of H₂O on the stability of the photocatalyst was also measured. After 1 h of reaction, the reactor was emptied and then refilled with reactants prior to next cycle. As described in Figure 2E, for photocatalytic non-oxidative coupling of CH₄ without H₂O, the activity decreases sharply after 31 h of operation. In stark contrast, the production rate and turnover frequency (TOF) of C₂H₆ didn't vary significantly over a 256-h period in the presence of H₂O under the same conditions, verifying the promotion effect of H₂O on the stability of the nanohybrid photocatalyst. Consequently, a considerable TON of 40,824 mol C₂H₆ per mole Au is achieved (Figure S20). As expected, the typical peak of defective carbon (D) and graphite carbon (G) appears in Raman spectra after NOCM testing, whereas there are no apparent coke-related peaks after photocatalytic oxidative coupling of CH₄ testing (Figure S21). Moreover, SEM and XPS characterizations show that the morphology and elemental states of the NWs remained almost unchanged after the stability test (Figures S22 and S23). These results illustrate that H₂O plays a crucial role in the stability of the catalyst, preventing coke formation during photocatalysis that may lead to catalyst inactivation. However, as described in Figure S24, NP sintering with the average particle size of 42.6 nm was observed

because of the local high temperature arising from the photo-thermal effect of concentrated light illumination, which could explain the partial activity loss seen after 256 h. Compared with the state-of-the-art photocatalysts for light-driven CH₄-to-C₂H₆ conversion, Au/GaN NWs have significant advantages in mass activity, selectivity, and stability when H₂O is used as the oxidant, demonstrating the great promise for using H₂O to enhance the performance of photocatalysts for coupling CH₄ to C₂H₆ (Figure 2F; Table S1).

The origin of the superior performance of Au/GaN NWs was then studied. At first, temperature-dependent PL (TD-PL) spectroscopy characterizations were conducted to study the carriers' behavior upon concentrated light illumination. As shown in Figure 3A, the intensity of radiative recombination of photogenerated carriers decreases with increasing temperature from 50°C to 450°C, corresponding to the suppression of radiative recombination. Furthermore, when *in situ* illumination XPS characterization was conducted in the absence of CH₄ and CO₂, the Au 4f peak exhibited an upward binding for the 4f_{5/2} and 4f_{7/2} environments from 86.78 and 83.18 eV to 86.98 and 83.28 eV, respectively (Figure 3B). By contrast, the N 1s peak was shifted from 397.28 eV downward to 396.68 eV (Figure S25). It is indicative that under light illumination, Au species acts as hole-trapping sites, in line with the recent discovery for photocatalytic oxidative coupling of CH₄ over Au/TiO₂.²⁹ Transient absorption spectra (fs-TAS) were further measured to reveal the dynamics of photogenerated carriers after excitation. The fs-TAS spectra of bare GaN NWs were composed of a broad positive peak at around 400–700 nm, which is attributed to the excited-state absorption (ESA) of photogenerated holes (Figure S26). Figure 3C reveals that the fs-TAS spectra of Au/GaN NWs are dominated by photo-carrier absorption at 400 nm, strong ESA, ground-state bleaching (GSB), and Au surface plasmon resonance (SPR) at ~550 nm. This suggests the migration of photogenerated electrons and holes toward the surface of Au/GaN NWs after separation. Notably, combined with the results shown in Figures S11 and S19, it can be concluded that the contribution of the SPR effect to water-triggered CH₄ coupling toward C₂H₆ over Au/GaN NWs is negligible. Moreover, TAS kinetics reveal that Au NPs significantly prolong electron decay times on picosecond-to-nanosecond timescales (Figure S27). Critically, the prolonged decay time observed in fs-TAS reveals an obvious delay in the recombination of separated electron-hole pairs.³⁵ Correspondingly, the decrease of the average TRPL lifetime reflects an accelerated transfer of carriers from GaN to Au.³⁶ Collectively, these results demonstrate that the introduction of Au NPs significantly enhances photogenerated charge separation efficiency.

The kinetic isotope effect (KIE) was also studied to reveal the reaction mechanism. As shown in Figure 3D, the reaction kinetic ratio of (CH₄ + H₂O)/(CH₄ + D₂O) does not vary substantially compared with (CH₄ + H₂O)/(CD₄ + H₂O), suggesting that the activation of H₂O and CH₄ are both pivotal for the synthesis of C₂H₆. Moreover, as characterized by the liquid chromatography-mass spectrometry (LC-MS), hydrogen deuterium oxide (HDO) was detected with the input reactants of CH₄ + D₂O, validating the H-D exchange between CH₄ and D₂O (Figure 3E). Additionally, gas chromatography-mass spectrometry (GC-MS) measurements demonstrated that

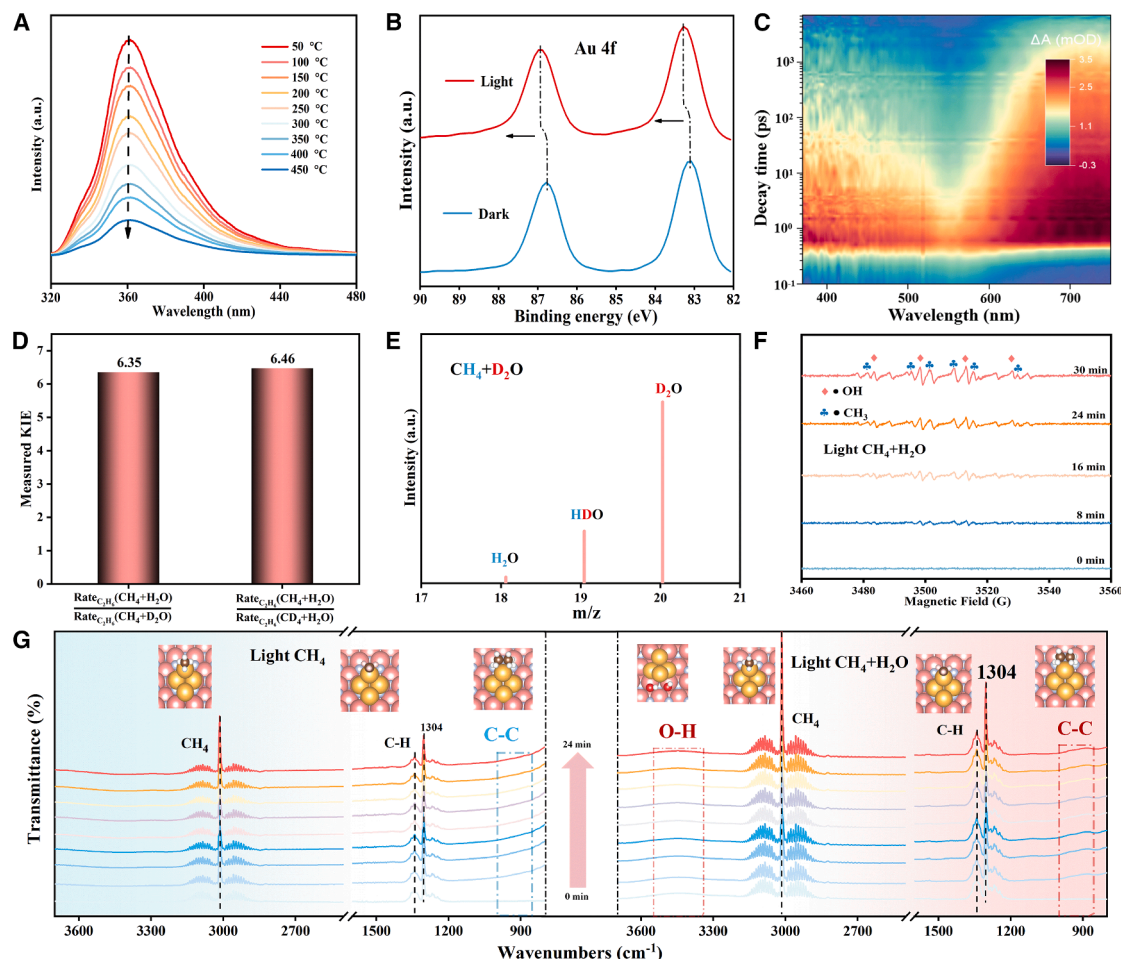


Figure 3. *In situ* spectroscopic characterizations and isotope-related experiments for H₂O-triggered OCM

- (A) TD-PL spectra of Au/GaN NWs under various temperatures.
 (B) *In situ* illumination XPS measurement of Au 4f of Au/GaN NWs under dark and light irradiation.
 (C) The fs-TAS data map of Au/GaN NWs under 400 nm excitation.
 (D) KIE ratio of (CH₄ + H₂O rate/CH₄ + D₂O rate) and (CH₄ + H₂O rate/CD₄ + H₂O rate) over Au/GaN NWs under the light intensity of 6 W·cm⁻².
 (E) LC-MS characterization of the liquid reaction mixture of photocatalytic OCM with D₂O.
 (F) *In situ* EPR spectra of photocatalytic OCM with H₂O over Au/GaN NWs under light irradiation of 6.3 W·cm⁻². DMPO was used as the radical trapping agent.
 (G) *In situ* DRIFT spectra of photocatalytic OCM and NOCM over Au/GaN NWs.

during photocatalytic oxidative coupling of CH₄ with D₂O, D₂ rather than H₂ was primarily detected (Figure S28). Based on the results above, it is rationalized that the introduction of H₂O enables suppressing the continuous dehydrogenation of CH₄, thus favoring C₂H₆ production while inhibiting coke deposition.

To better understand the reaction mechanism at the molecular level, *in situ* EPR was used to detect the key intermediates during the reaction. As illustrated in Figure 3F, an apparent ·CH₃ signal was observed from photocatalytic OCM with H₂O, whose intensity was superior to that of photocatalytic NOCM by only feeding CH₄ (Figure S29). It thus offers direct spectroscopic evidence that the incorporation of H₂O facilitates the cleavage of the first C–H of CH₄ to yield ·CH₃, which is critical for the subsequent formation of C₂H₆. *In situ* DRIFTS characterization was further performed to study the evolving track of CH₄ to C₂H₆ (Figure 3G).

The typical peaks at 1,304 and 3,016 cm⁻¹ are indexed to the adsorbed CH₄. During photocatalytic OCM, a rising peak of extensional vibration of O–H appears at 3,352–3,568 cm⁻¹,³⁷ which can be attributed to the O–H dissociation of water by photoexcited holes (H₂O + h⁺ → ·OH + H), being well matched with the EPR characterization above. Meanwhile, the characteristic peak of scissoring vibration and extensional vibration of C–H is observed at 1,343 and 2,800–3,000 cm⁻¹, which is apparently intensified by the introduction of H₂O, compared with photocatalytic NOCM.³⁸ These findings further indicate the promotion effect of H₂O on the C–H bond cleavage of CH₄ over Au/GaN NWs. C–C coupling was subsequently enhanced, as indicated by the strengthened peak at 887 cm⁻¹, thus facilitating the formation of C₂H₆.³⁹ To further verify the superiority of H₂O as an oxidizer, *in situ* DRIFT spectra of photocatalytic OCM with both O₂ and H₂O₂ over Au/GaN NW were also examined. As seen from

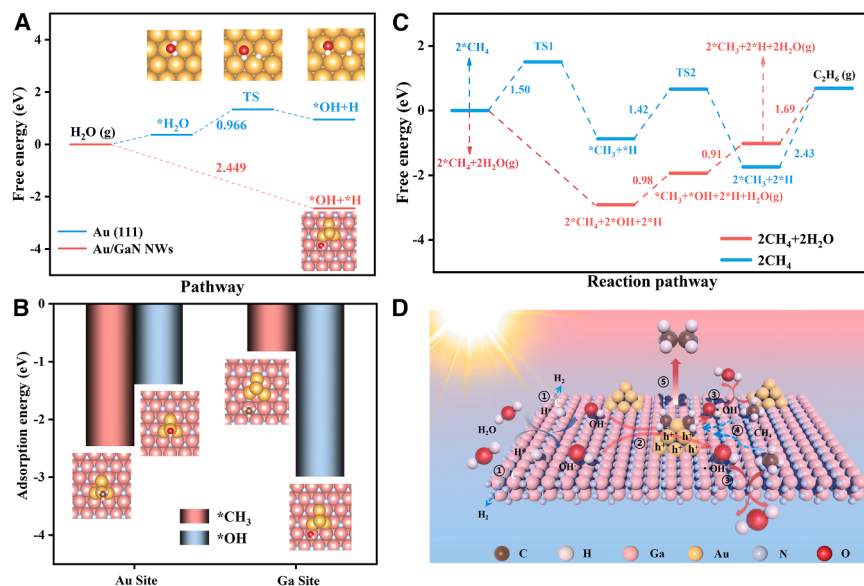


Figure 4. Computational investigations of the mechanism of H₂O-triggered CH₄ coupling into C₂H₆ over Au-decorated GaN (A) The calculated free energy diagrams for H₂O activation over Au (111) and Au₄/GaN NWs. Ga, pink; N, gray; Au, yellow; O, red; H, white. (B) Adsorption energy of CH₃ and OH over Au₄/GaN NWs with different sites, respectively. (C) The calculated free energy diagrams for H₂O-promoted CH₄-to-C₂H₆ conversion over Au₄/GaN NWs. (D) The mechanism diagram of H₂O-induced CH₄ coupling toward C₂H₆ reaction over Au/GaN NWs. Ga, pink; N, gray; Au, yellow; C, brown; O, red; H, white.

Figure S30, when O₂ or H₂O₂ was used as the oxidizer, CH₄ was more readily over-oxidized into CO_x products (CO: ~2,340 cm⁻¹; CO₂: ~2,360 cm⁻¹),⁴⁰ which is distinct from the H₂O-triggered photocatalytic OCM process and explains the limited selectivity of C₂H₆ of photocatalytic OCM with O₂ or H₂O₂ (Figure 2B). The aforementioned results validate the superiority of H₂O as a green and inexpensive oxidizer for efficient and selective OCM into C₂H₆, which will be further studied by theoretical calculations below.

Ground-state theoretical simulations were performed to gain deeper insights into the thermodynamics and kinetics of the reaction mechanism, without accounting for photoexcitation (Figure S31). To further investigate the mechanistic contribution of Au in the photocatalytic process, the work functions for GaN and Au were calculated via density functional theory (DFT) simulations. As shown in Figure S32, Au exhibits a higher work function (5.049 eV) relative to GaN (4.715 eV). This difference drives electron migration from GaN to Au at ground state, establishing a built-in electric field oriented from the GaN bulk toward the Au NP. Under light irradiation, the photogenerated holes are driven toward the Au NPs by the built-in electric field. Combined with ISI-XPS findings illustrated in Figure 3B, it could be concluded that Au NPs serve as the spatial trapping sites for photogenerated holes during the photocatalysis process, thus effectively facilitating charge carrier separation. In addition, it can be observed that the adsorption energy of CH₄ over bare GaN was considerably increased from -0.035 to -0.924 eV by decorating with Au (Figure S33; Table S2). Combined with the result of temperature-programmed desorption (TPD) measurements in Figure S34, it can be concluded that Au acts an efficient site for CH₄ adsorption. The activation of water over Au₄/GaN is further simulated. As illustrated in Figure 4A, H₂O is readily split into *OH and *H via a thermodynamically favorable process once it is adsorbed on the wurtzite GaN surface, which is consistent with some previous studies.⁴¹ This result sug-

gests that owing to the unique surface property of photocatalytic interface, the Au₄/GaN NWs is promising for producing active species of ·OH from water splitting to trigger the coupling of CH₄ into C₂H₆ by activating the inert C–H bond of CH₄ via an H-exchange mechanism. The projected density of states (PDOS) comparison of pure GaN and Au/GaN NWs in Figure S35 reveals that decoration of Au leads to hybridization with Ga and N orbitals, significantly enhancing the dominant electron density near the Fermi level. This effect provides unique advantages for H₂O activation at the Au/GaN NWs catalytic interface. As illustrated in Figure 4B, *OH is inclined to be adsorbed on the Ga sites, while *CH₃ prefers to be adsorbed on the Au sites with the adsorption energies of -2.99 and -2.46 eV, respectively (Table S3). Furthermore, combined with the differential charge density analysis in Figure S36, it can be seen that the strong interaction with the catalytic interface resulted in the firm stabilization of *CH₃ and *OH, which inhibits excessive oxidation and coke deposition, thus improving both stability and selectivity of the CH₄-to-C₂H₆ conversion.

The free energy diagram of the coupling of CH₄ into C₂H₆ was evaluated. As seen from Figures 4C, S37, and S38, the formation of *CH₃ from the C–H bond cleavage of CH₄ is energetically favored in the presence of H₂O, compared with the direct C–H cleavage without H₂O, validating the H₂O-assisted C–H activation. For photocatalytic NOCM, the potential-determining step of 2*CH₃ → C₂H₆ shows a considerable energy barrier of 2.43 eV, which is a clear indicator of the sluggish NOCM. The energy diagram was significantly varied upon the introduction of H₂O. As discussed above, water molecules are readily adsorbed/activated on GaN surface. Water is readily reproduced from the recombination of *OH_{water} with CH₄ via H-exchange, with a moderate energy barrier of 0.98 eV, in the concurrent generation of *CH₃ (*OH_{water} + CH₄ → (*OH_{water} + *H_{methane}) + *CH₃ → H₂O + *CH₃). C₂H₆ is subsequently formed via *CH₃ self-coupling. Compared with NOCM, the introduction of H₂O enables the reduction of the energy barrier of 2*CH₃ → C₂H₆ from 2.43 to 1.69 eV. To investigate the effects of cluster size and metal coordination environment on the reaction, we further performed reaction energy calculations for Au₃₀/GaN NWs

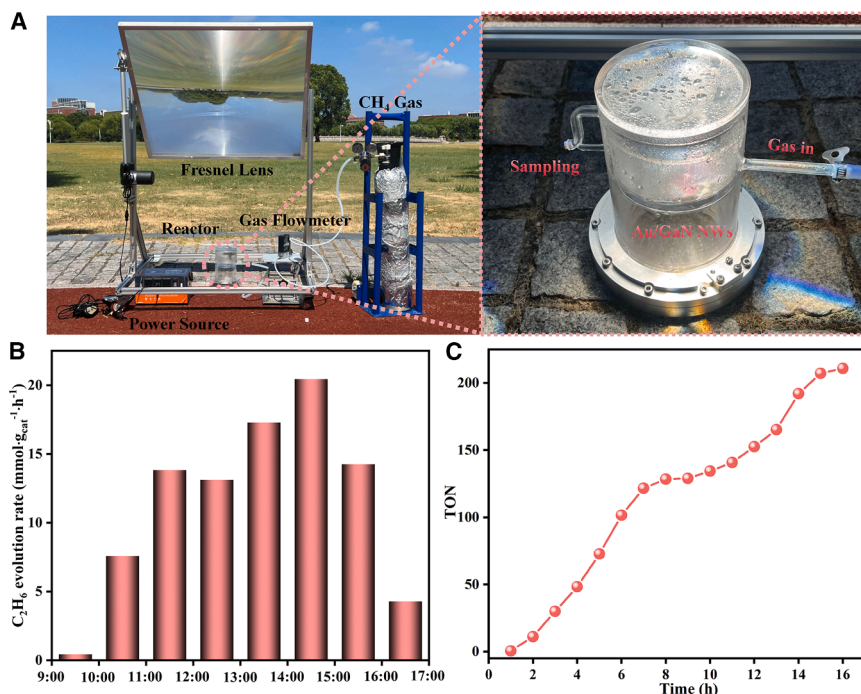


Figure 5. H₂O-promoted coupling of CH₄ toward C₂H₆ under outdoor concentrated sunlight irradiation

(A) Image illustration of the designed outdoor equipment under natural concentrated sunlight irradiation.

(B) C₂H₆ evolution rate.

(C) TON of Au/GaN NWs for coupling of CH₄ toward C₂H₆ under natural concentrated sunlight.

Location: (121°25'31.70"E, 31°01'41.83"N); environment conditions: August 6, 2024: temperature, 28°C–39°C; air humidity, 55%; weather, sunny. August 7, 2024: temperature, 28°C–37°C; air humidity, 65%; weather, cloudy to sunny.

under both with and without H₂O. As shown in Figure S39, the reaction energetics on Au₃₀/GaN NWs are comparable to those over Au₄/GaN NWs, which reinforces that the presence of H₂O is the primary factor for the improved thermodynamic feasibility of the reaction.

Based on the results of *in situ* spectroscopic characterizations, KIE investigation, and theoretical calculations, a reaction mechanism of H₂O-triggered OCM over Au/GaN NWs is proposed (Figure 4E). Upon light irradiation, the electrons of GaN are pumped from the valence band of GaN into the conduction band, while the photogenerated holes are trapped by Au. Hydrogen evolution from water splitting takes place on the surface of GaN (2H⁺ + 2e⁻ → H₂↑) (steps ①). OH⁻ is then oxidized to ·OH radicals by the holes trapped on Au sites (2OH⁻ + 2h⁺ → 2·OH) (steps ②). As the adsorption sites of CH₄, Au NPs further work in synergy with ·OH to break the first inert C–H bond in CH₄ to generate methyl radicals via an interesting H-exchange mechanism (CH₄ + ·OH → ·CH₃ + H₂O) (steps ③ and ④) (Figure S40). C₂H₆ is eventually produced by the self-coupling of ·CH₃ (·CH₃ + ·CH₃ → C₂H₆) with a considerably lowered energy barrier (steps ⑤). Meanwhile, Au is cooperative with GaN to provide a kinetically and thermodynamically friendly interface for inhibiting CH₄ over-oxidation and coke deposition with water, thus enabling the achievement of efficient, selective, and stable photocatalytic OCM into C₂H₆.

To test the proof-of-concept solar-driven OCM toward C₂H₆ with H₂O as the oxidizer, an outdoor test was conducted under natural concentrated sunlight illumination. As illustrated in Figure 5A, the homemade outdoor test equipment mainly consists of a Fresnel lens that can be adjusted for tilt angle, a support frame, a quartz chamber, a power source, and a gas flowmeter. For the outdoor test, an independently movable light intensity me-

ter is positioned at the center of the light spot to measure irradiance before the test is performed. The C₂H₆ rate reached up to 20.5 mmol·g_{cat}⁻¹·h⁻¹ during 2:00–3:00 pm, then it decreased (Figure 5B). The fluctuating trend in C₂H₆ production rate matches the variable light intensity during the measurement period (Figure S41). In total, 211 mol C₂H₆ per mol Au was achieved after 16-h operation under the concentrated natural sunlight

(Figure 5C). The aforementioned results validate the potential of value-added chemical synthesis from CH₄ using H₂O as a green oxidizer and sunlight as the energy input.

DISCUSSION

In summary, water has been successfully utilized as a green oxidizer for solar-driven coupling of CH₄ to C₂H₆ by using Au NP-decorated GaN NWs as a photocatalyst. A considerable C₂H₆ evolution rate of 112.6 mmol·g_{cat}⁻¹·h⁻¹ was achieved with an impressive selectivity of 94.9% for forming C₂H₆ under concentrated light illumination, without external energy input. Meanwhile, a marked TON of 40,824 mol C₂H₆ per mol Au was obtained after 256-h operation without obvious activity degradation. The corroborative experimental and theoretical investigations reveal that H₂O plays a vital role in accelerating the coupling of CH₄ into C₂H₆ via a H-exchange mechanism with CH₄ via the formation of highly active ·OH species from H₂O oxidation by photogenerated holes. What is more, Au is cooperative with GaN, providing a kinetically and thermodynamically friendly interface for inhibiting CH₄ over-oxidation and coke deposition with H₂O, thereby enabling the superior selectivity and stability. Together, with outdoor testing, this work showcases an attractive route for producing higher-value chemicals from CH₄, H₂O, and sunlight beyond petroleum.

METHODS

MBE growth of GaN NW arrays supported on a 4-in Si wafer

The p-type doped GaN NWs were grown on Si substrate by Veeco Gen 930 plasma-assisted MBE. The doping densities of

p-type dopant in the p-GaN were controllably tuned by controlling the Mg cell temperatures. During the growth, the plasma power was kept at 350 W, and NWs were grown in N-rich growth conditions. The details of the growth condition can be found in the previous publication.^{42,43}

Integration of Au NPs with GaN NWs on an Si wafer

The deposition was carried out in a sealed chamber with a quartz lid, using a 300 W Xe lamp as the light source. In a typical process, the Si wafer deposited with GaN NWs was cut into small pieces with a geometric surface of circa 0.5 cm². The deposition was conducted in a methanol aqueous solution with a CH₃OH/H₂O volume ratio of 1:5 (Sinopharm Chemical Reagent Company, China, Ar). A certain amount of Au precursor (HAuCl₄, Sinopharm Chemical Reagent Company, China, 99.99%) aqueous solution (0.2 mol/L) was then added into the chamber, followed by vacuum treatment. The chamber was further filled with Ar and irradiated with the Xe lamp at a light intensity of 2 W·cm⁻² for 30 min to immobilize Au NPs over the surface of GaN NWs. Au was also loaded on a bare Si wafer without GaN through the same method for comparison.

Characterization

SEM images were measured by using a Quattro ESEM (ESCALAB, USA). XRD patterns were measured by a Bruker D8 Advance diffractometer (with Cu K α , at 60 kV and 80 mA). TEM images were collected using a JEOL 2100F microscope (JEOL, Japan). HAADF-STEM images were obtained by a JEM-ARM300F2 (GRAND ARM(TM)2), equipped with 158-mm² dual Si drift detector (SDD) system and operated at 300 kV. A 250-xi non-monochromatic (ESCALAB, USA) Al anode was employed for XPS characterization. The binding energy was calibrated by using C 1s peak at 284.8 eV as the internal standard. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) measurements were performed using an ICP-OES 730 (AGILENT, USA). *In situ* DRIFTS was carried out using a Frontier FT-IR Spectrometer (PerkinElmer, USA), which was equipped with a mercury cadmium telluride (MCT) detector and 10-cm demountable gas cell. GC-MS measurement was performed for isotope-labeling experiments by TRACE 1300, ISQ 7000, Thermo Scientific. PL and TRPL spectroscopies were measured using an FLS980 (Edinburgh Instruments). TD-PL were measured using an FLS980 (Edinburgh Instruments) equipped with advanced research systems (ARS) LT4 series standard continuous flow thermostats. *In situ* EPR measurement was conducted on a Bruker A300 (Germany) using 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) as a spin trap. The fundamental beam (1,030 nm) of the ultrafast TAS spectra was from the Yb:KGW laser (Pharos, Light Conversion), which was divided into two beams. The transmitted probe light was collected by liquid nitrogen cooled detectors (PyLon 100B, Princeton Instrument), and the TAS signal was calculated by normalizing the probe spectra of pumped ones to that of unpumped ones.

Performance evaluation

The reactions were conducted in a 0.44-L homemade quartz chamber. The photocatalysts were thoroughly washed with deionized water before being fixed at the bottom of the Pyrex chamber, followed by vacuum. The chamber was then filled

with atmospheric Ar. Subsequently, 150 ml of Ar gas was extracted, followed by introducing 40 mL of CH₄ and 2 mL of H₂O. The reaction system was illuminated by a 300 W Xe lamp equipped with a quartz lens for the desired time (CEL-HXF300-S, Beijing China Education Au-light Co., Ltd, China). The stability was assessed by performing 256 consecutive 1-h cycles under an irradiance of 6.3 W·cm⁻² and a CH₄:H₂O molar ratio of 1:47. After each cycle, average activity was measured, and the reactor was then purged and replenished with fresh reactants for the next cycle. The gaseous products were analyzed by a gas chromatograph (GC-9080, Sun) equipped with a flame ionization detector (FID) detector and a thermal conductivity detector (TCD), respectively. The weight of GaN NWs onto Si wafer was estimated as follows (Equation 5). The fill factor (FF) of the epitaxial GaN NWs grown on Si wafer is estimated to be about 81% (Figure S42). The NWs illustrated an average length of 850 nm as measured by the SEM technique (Figure 1A). Since the density (ρ) of GaN is 6.1 g·cm⁻³, the weight of GaN per unit area (L) is calculated to be 0.420 mg·cm⁻² ($\pm$ 5% analytical error). The Au loading was determined to be 0.049 μ mol·cm⁻² by ICP-AES measurement ($\pm$ 1% analytical error).

For *in situ* illumination (ISI) XPS measurement, the sample was placed in the XPS chamber, and a full-arc 300 W Xe lamp was introduced to irradiate the sample at 6.3 W·cm⁻² under vacuum in the absence of CH₄ and H₂O. Neither CH₄ nor H₂O was introduced in the XPS chamber.

In situ EPR experiments were conducted using a Bruker A300 spectrometer (Germany). In a typical procedure, Au/GaN NWs were dispersed in 5 mL of deionized water via sonication for ·OH detection. A 200- μ L aliquot of this dispersion was mixed with 100 μ L of 100 mM DMPO solution in a quartz capillary tube to form a homogeneous suspension. The tube was purged with CH₄ gas for 5 min to ensure reactant saturation, then sealed and placed in the EPR sample cavity under continuous light irradiation using a 300 W Xe lamp with a quartz lens at 6.3 W·cm⁻². Spectra were recorded at 298 K with 19.23 mW microwave power, 100 kHz modulation frequency, and signal accumulation over 2–3 scans.

The *in situ* DRIFTS were conducted using a Bruker INVENIO S spectrometer equipped with an MCT detector, and a 300 W Xe lamp was employed as the light source. All spectra were recorded by background subtraction of the gas-phase CH₄. The spectral data were collected at regular intervals (0, 3, 6, 9,..., 30 min) under continuous illumination.

The AQE was estimated as Equations 6 and 7, where n represents the number of involved electrons, R is the evolution rate of total products, I is the amount of incident photons, h is the Planck constant, and c is the speed of light. All AQE experiments were conducted under different monochromatic light sources (365, 420, 535, and 730 nm), with supplementary external heating at 290°C to provide additional energy required for C–H cleavage. As a control, the catalytic activity of C₂H₆ was measured under dark conditions to assess the thermal catalysis contribution without light irradiation. The light intensities (P) of various wavelengths (λ) (365, 420, 535, and 730 nm) are 112.6, 201.5, 162.1, and 134.8 mW·cm⁻², respectively. The light irradiation area (S) is 0.50 cm², which is the area of the Au/GaN NWs photocatalyst. The irradiation time (T) of the monochromatic light was 3,600 s.

The TRPL curves were fitted by using Equation 8, where I_1 and I_2 are the initial intensities of the two decay components; τ_1 and τ_2 represent the characteristic lifetimes of the fast and slow decay components, respectively.

The equations for calculating products evolution rate, TOF, TON, selectivity, mass density of photocatalyst, AQE, and average lifetimes are as follows:

$$\text{Products evolution rate} = \frac{\text{products yield per unit area of catalyst per hour}}{\text{Mass of catalyst per unit area}}, \quad (\text{Equation 1})$$

$$\text{TOF} = \frac{\text{C}_2\text{H}_6 \text{ yield per unit area of catalyst per hour}}{\text{Content of Au nanoparticles per unit area of catalyst}}, \quad (\text{Equation 2})$$

$$\text{TON} = \frac{\text{C}_2\text{H}_6 \text{ yield per unit area of catalyst}}{\text{Content of Au nanoparticles per unit area of catalyst}}, \quad (\text{Equation 3})$$

$$\text{Selectivity of C}_2\text{H}_6 = \frac{\text{Yield of C}_2\text{H}_6}{\text{Yield of CO} + \text{Yield of CO}_2 + \text{Yield of C}_2\text{H}_6}, \quad (\text{Equation 4})$$

$$\text{Mass of catalyst per unit area} = \text{FF} \times \text{L} \times \rho, \quad (\text{Equation 5})$$

$$\text{AQE} = \frac{nR}{I}, \quad (\text{Equation 6})$$

$$I = \frac{E\lambda}{hc} \times S = \frac{PT\lambda}{hc} \times S, \quad (\text{Equation 7})$$

$$\tau_{\text{average}} = \frac{I_1\tau_1^2 + I_2\tau_2^2}{I_1\tau_1 + I_2\tau_2}. \quad (\text{Equation 8})$$

Computational methods

DFT calculations were performed employing the Vienna Ab Initio Simulation Package (VASP).^{44,45} The interaction between valence electrons and ions was described by the projector-augmented wave (PAW) method.⁴⁶ The exchange correlation of the Kohn-Sham equation was presented by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional.^{47,48} A plane-wave basic set was used to expand the wavefunctions with the kinetic cutoff energy set to 450 eV. For the calculations of slabs, a $2 \times 1 \times 1$ Monkhorst-Pack k-point grid was implemented to sample the Brillouin zone.⁴⁹ During the geometry optimization, the convergence

criteria for the atomic forces and the total energies were set to 0.02 eV/Å and 10^{-4} eV, respectively.

As the m-plane of GaN was observed in experiments, we constructed GaN (100) surface with a 4×3 supercell containing 6 layers to represent the pristine GaN. Besides, Au/GaN NWs were conducted by depositing a small Au₄ cluster of metal atoms on GaN [10–10]. The top view and side view of optimized

geometries models of the calculated model are represented in Figure S27. To avoid image interaction, a vacuum spacing of at least 15 Å was set along the normal direction to the surface for all slab models and along all three directions for NPs. Moreover, for all slab models, the bottom three layers of GaN were fixed in their bulk positions during structural relaxation. The Gibbs free energy of adsorption ΔG was calculated as follows:

$$\Delta G = E_{\text{ad}} + \Delta ZPE - T\Delta S, \quad (\text{Equation 9})$$

where E_{ad} is the adsorption energy defined by:

$$E_{\text{ad}} = E_{\text{ad}} - E_{\text{surface}} - E_{\text{adsorbate}}, \quad (\text{Equation 10})$$

ΔZPE and ΔS are the changes in zero-point energy and entropy during adsorption.

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Professor Baowen Zhou (zhoubw@sjtu.edu.cn).

Materials availability

All materials generated in this study are available from the lead contact.

Data and code availability

All data supporting this study are available in the article and supplemental information.

ACKNOWLEDGMENTS

This work is supported by Shanghai Pilot Program for Basic Research-Shanghai Jiao Tong University (no. 21TQ1400211), the National Key R&D Program of China (2023YFB4004900), the National Natural Science Foundation of China (no. 22109095), and the Oceanic Interdisciplinary Program of Shanghai Jiao Tong University (no. SL2022MS007). This work is also funded by the

Foundation of State Key Laboratory of Low Carbon Catalysis and Carbon Dioxide Utilization (LCCU-KF-2025B-07). This work is supported by the Natural Sciences and Engineering Research Council of Canada (NSERC)- RGPIN-2021- 04250 and Centre Energie, Matériaux et Télécommunications, Institut National de la Recherche Scientifique (INRS)-Université du Québec.

AUTHOR CONTRIBUTIONS

Yixin Li, L.Y., and B.Z. conceived the project and provided the platform for the experiment. Yixin Li, J.L., T.Y., and L.J.K. conducted the experiments. Yixin Li and L.Q. conducted the theory calculation. Ying Li, A.K., and T.W. participated in the result discussion and data analysis. M.A.R., N.A., and S.M.S. conducted the growth of the materials. Yixin Li, L.Y., and B.Z. wrote the paper with the contributions of all co-authors.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.chempr.2026.103033>.

Received: December 1, 2025

Revised: February 9, 2026

Accepted: March 19, 2026

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