

Water-Triggered Photocatalytic Oxidative Coupling of Methane toward C₂H₆ over Au/GaN Nanoarchitecture

Yixin Li¹, Lin Yao^{2*}, Jinglin Li¹, Tianqi Yu¹, Andreas Kafizas³, Ying Li², Liang Qiu¹, Lam Jun Kay¹, Tao Wang^{4*}, Md Afjalur Rahman⁵, Nirmal Anand⁵, Sharif Md. Sadaf^{5*}, Baowen Zhou^{1*}

1. Key Laboratory for Power Machinery and Engineering of Ministry of Education, Research Center for Renewable Synthetic Fuel, School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, China.

2. China-UK Low Carbon College, Shanghai Jiao Tong University; Shanghai, 201306, China.

3. Department of Chemistry, Molecular Science Research Hub, Imperial College London, London, W12 0BZ, United Kingdom.

4. Electron Microscope Laboratory, School of Physics, Peking University, 100871, China.

5. Centre Energie, Matériaux et Télécommunications, Institut National de la Recherche Scientifique (INRS)-Université du Québec, 1650 Boulevard Lionel-Boulet, Varennes, Quebec J3X1S2, Canada

*Corresponding authors Email: zhoubw@sjtu.edu.cn; yaol@sjtu.edu.cn; cwwangtao@pku.edu.cn; sharif.sadaf@inrs.ca

Abstract: Solar-driven oxidative coupling of CH₄ offers a sustainable alternative route for value-added chemical synthesis beyond petroleum. Herein, we report solar-driven oxidative coupling of CH₄ for efficient and selective production of C₂H₆ over Au-decorated GaN nanowires using water as an ideal oxidizer. The optimized photocatalyst delivers an appreciable C₂H₆ activity of 112.6 mmol·g_{cat}⁻¹·h⁻¹ with a high selectivity of 94.9% with the only inputs of CH₄ and H₂O under concentrated white light irradiation of 6.3 W·cm⁻². Moreover, a considerable turnover number of 40824 moles C₂H₆ per mole Au is achieved over 256 hours without significant activity degradation. Notably, the proof-of-concept solar-driven oxidative coupling of CH₄ toward C₂H₆ using water as the oxidant is validated by outdoor tests under

concentrated natural sunlight illumination. Isotope kinetic experiments, *in-situ* spectroscopic characterizations, and theoretical calculations reveal that the coupling of CH₄ into C₂H₆ is considerably accelerated via an interesting H-exchange mechanism of highly active species of •OH from water oxidation by photogenerated holes trapped on Au sites with CH₄ (•OH + CH₄ → •CH₃ + H₂O), which significantly lowers the energy barrier of C₂H₆ formation. Moreover, Au cooperates with GaN to provide a kinetically and thermodynamically promoting interface that inhibits CH₄ over-oxidation, resulting in superior activity, selectivity, and stability. This work showcases an increasingly promising pathway for solar-driven fuel production through the oxidative coupling of CH₄ to C₂H₆, using the green and environmentally friendly oxidant, H₂O.

Introduction

As petroleum diminishes, methane has appeared as an ideal alternative for producing value-added chemicals due to its abundance and low cost.^{1, 2} Direct and selective transformation of methane (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 methane into ethane 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 methane (NOCM), the activity remains limited, owing to the endothermic nature of the reaction, and remains at the order of several μmoles of C₂H₆ produced per mole metal per hour.^{11, 12} By contrast, the yield of C₂H₆ can be considerably improved by photocatalytic oxidative coupling of methane (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 C_2H_6 .¹⁵ where to date, H_2O_2 and O_2 are the most frequently used oxidizers. For example, Zhai and coworkers designed an interesting photocatalyst of Au/BiO_x-TiO_2 with dual active sites.¹⁶ The activated lattice oxygen in BiO_x facilitated the cleavage of the C-H bond of CH_4 , and the consumed lattice oxygen was supplemented by suitable concentration of oxygen, thus forming a chemical looping. Nevertheless, the over-oxidation of CH_4 into CO_x is often inevitable because of its high exothermicity with O_2 as the oxidizer, thus resulting in a limited selectivity of C_2H_6 .¹⁷ In contrast with O_2 , H_2O_2 is promising for achieving high selectivity of CH_4 -to- C_2H_6 conversion, bypassing the endothermic steps of activating CH_4 . For example, Zheng and coworkers have reported H_2O_2 -triggered CH_4 coupling over Au/WO_3 , where the H_2O_2 -derived $\bullet OH$ radicals were rapidly consumed for the C-H cleavage of CH_4 into $\bullet CH_3$ exothermically.¹⁸ Despite appreciable performance, H_2O_2 is not currently considered an economically viable oxidant for promoting CH_4 -to- C_2H_6 conversion because of its comparatively high cost. Therefore, it is of great interest to achieve photocatalytic OCM to C_2H_6 with economically viable alternatives. Herein, we explore the use of H_2O as the oxidant for the photocatalytic OCM to C_2H_6 , which is an earth abundant, low cost, and eco-friendly alternative. However, to our best knowledge, there has been a lack of substantial endeavors into the use of H_2O as the oxidant in the photocatalytic OCM to C_2H_6 .

The development of high performance photocatalysts for the OCM to C_2H_6 remains a significant materials challenge.¹⁹ GaN nanowires (NWs) vertically aligned on a commercial silicon 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 $\bullet OH$ 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 CH_4 .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.

Au is a widely studied cocatalyst for decorating various semiconductors to achieve photocatalytic OCM to C₂H₆ owing to its unique plasmonic and catalytic properties.²⁸⁻³⁰ Specifically, Au can 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 photocatalysts 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 eV 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 40824 mole C₂H₆ per mole Au is achieved during 256 hours of reuse without any notable reduction of activity, far outperforming state-of-the-art OCM photocatalysts ([Table S1](#)). Combination of a range of *in-situ* spectroscopic characterizations (electron paramagnetic resonance spectroscopy, diffuse reflectance infrared Fourier transform spectroscopy, and irradiated X-ray photoelectron spectroscopy), and isotope-labeling experiments with theoretical investigations reveal that under light illumination, photoexcited holes are extracted from GaN by the decorated Au nanoparticles, followed by the formation of hydroxyl radicals (•OH) from H₂O oxidation ($\text{H}_2\text{O} + \text{h}^+ \rightarrow \bullet\text{OH} + \text{H}^+$). 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 to 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 C_2H_6 by inhibiting over-oxidation. Meanwhile, outdoor tests demonstrated the feasibility of using this photocatalyst for the synthesis of C_2H_6 from H_2O -triggered CH_4 coupling under real-world conditions. This work offers a low-carbon strategy for solar-driven production of value-added chemicals via H_2O -triggered OCM beyond fossil fuels.

Results and discussion

The assembly of Au/GaN NWs on a silicon wafer is schematically shown in [Fig. S1](#). At first, GaN NWs were controllably grown on a 4-inch silicon wafer through a plasma-assisted molecule beam epitaxy (MBE) method under an N_2 -rich atmosphere.³¹ Au nanoparticles (NPs) are subsequently decorated onto GaN NWs via an established photo-deposition method. As depicted by the scanning electron microscope (SEM) image ([Fig. 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 nanoparticles were hemispherical in shape and relatively uniformly dispersed on the surface of GaN NWs with an average diameter of 6.7 nm ([Fig. 1b](#) and [Fig. S2](#)). As further characterized by the high-angle annular dark-field scanning transmission microscope (HAADF-STEM) of a single Au/GaN nanowire ([Fig. 1c](#)), the lattice spacing of 0.26 nm corresponds to the (002) plane of GaN, in line with X-ray diffraction (XRD) patterns ([Fig. S3](#)), indicating the c-axis preferential growth direction of the nanowires. Meanwhile, the 0.23 nm lattice spacing is attributed to the (111) plane of Au nanoparticles. However, the typical signals of Au were not observed in XRD patterns and Raman spectroscopy ([Fig. S4](#)), owing to the low content of $0.049 \mu\text{mol} \cdot \text{cm}^{-2}$ as measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The energy dispersive X-ray spectroscopy (EDS) elemental mapping images ([Fig. S5](#)) further validate the success in the decoration of GaN NWs with Au nanoparticles.

The differential charge density analysis was conducted to explore the electronic interaction between Au and GaN (**Fig. 1d**). Bader charge calculation reveals that an average of 0.2094 electrons are transferred from GaN to Au over a simple Au₄/GaN model (**Fig. S6**). Such an electronic interaction between Au and GaN NWs not only stabilizes the nanoparticles 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 (**Fig. 1e**). The average lifetime of GaN NWs decreased from 3.15 ns to 1.89 ns after coupling with Au nanoparticles, which indicates the fast transfer of photocarriers upon excitation from GaN NWs to Au nanoparticles, thus benefiting the reaction.

The interaction between Au and GaN was further investigated through X-ray photoelectron spectroscopy (XPS) (**Fig. S7**). The high-resolution XPS spectra of Au 4f in **Fig. 1f** suggest 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 eV (4f_{7/2}), which are significantly lower than those of standard Au species (87.7 eV and 84.0 eV).³³ Meanwhile, the upward shift of Ga 3d was observed upon decorating with Au species (**Fig. 1g**). These findings indicated that transfer of electrons from GaN to Au created a robust electronic interaction, which facilitates charge transfer during photocatalysis.³⁴

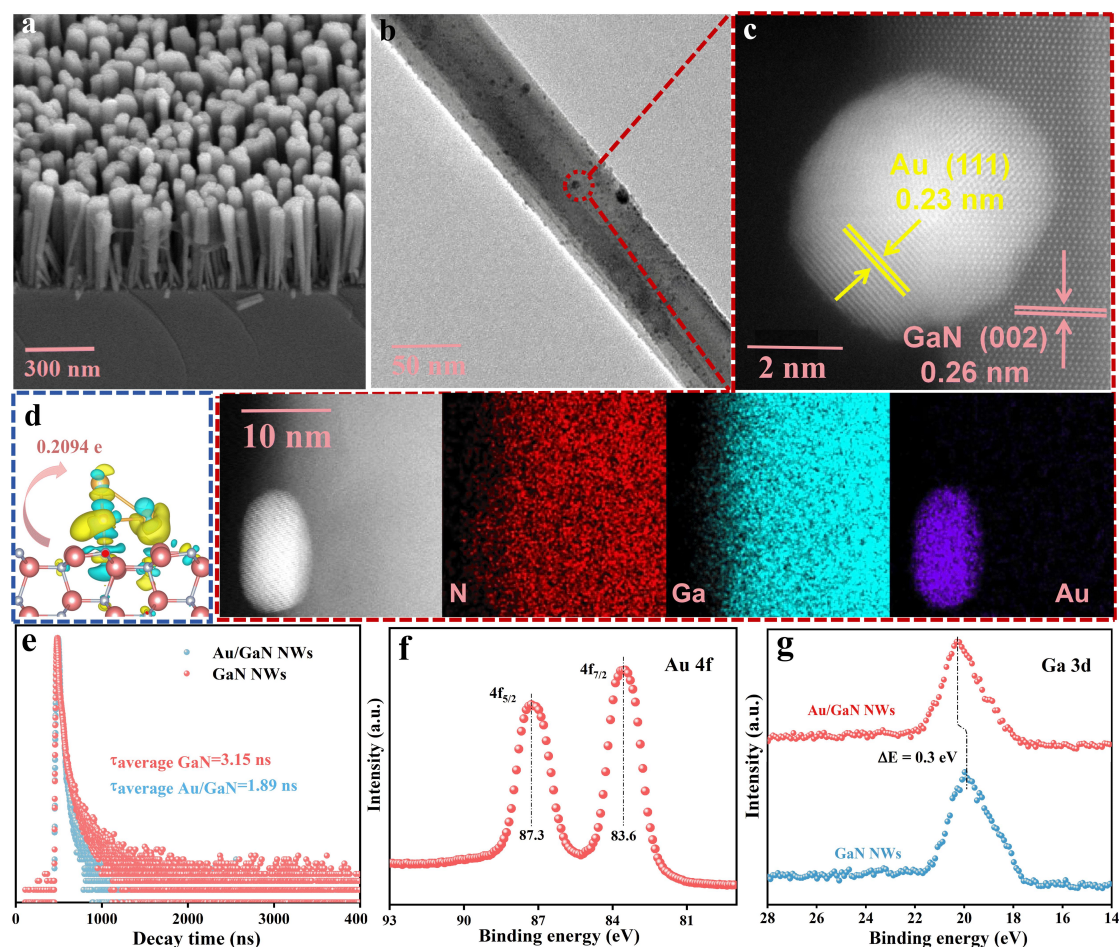


Fig. 1 | Assembly and Characterization of Au-decorated GaN NWs on a silicon wafer. (a) A 45°-tilted SEM image of Au-decorated GaN NWs; (b) TEM image of a single GaN nanowire decorated with Au nanoparticles. (c) The high-resolution HAADF-STEM and elemental mapping images of Au/GaN NWs. (d) Differential 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) TR-PL spectrum of Au/GaN NWs and GaN NWs. High-resolution (f) Au 4f and (g) Ga 3d XPS spectra of Au/GaN NWs.

Photocatalytic coupling of methane over Au-decorated GaN NWs was tested in a homemade sealed quartz reactor. A 300 W Xenon lamp equipped with a quartz lens was used as the light source, without external heating (Fig. S8). As expected, C₂H₆ was produced in low quantities over bare GaN (Fig. 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 larger size at a higher loading content (Fig. S9). Herein, the contribution of plasmonic effect of Au to the superior performance was also excluded by cooling experiments with different spectral ranges (Fig. S10-11). Further, control experiments showed that photocatalytic NOCM was limited, which is associated with both thermodynamic and kinetic restrictions (Fig. 2b and Fig. S12). In sharp contrast, the introduction of H₂O enables a significant improvement in C₂H₆ selectivity (~95%), without varying any other experimental condition. 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 (Fig. 2b). The influence of H₂O concentration in the photocatalytic OCM over Au-decorated GaN NWs was also examined (Fig. S13). It was found that both activity and selectivity of ethane increased with increasing the amount of H₂O, approaching a plateau C₂H₆ activity of 112.6 mmol·g_{cat}⁻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 silicon wafer as a control (Fig. S14). As depicted in Fig. 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 methane-water reaction significantly exceeds that without water involvement (Fig. 2c). As shown in Fig. 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 activation energy (E_a) from 5.12 eV to 1.29 eV upon light illumination. What is more, as seen from Fig. 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 (Fig. 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 nm, 420 nm, 535 nm, 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 Fig. S18 and Fig. S19, the AQE value shows a matched trend with the light absorption spectrum of the photocatalyst, showing a maximal value of 1.36% under 365 nm monochromatic light irradiation. Meanwhile, the 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 nanoparticles. The findings above demonstrate that the dominating role of photoexcited charge carriers and water in light-driven oxidative coupling of methane into ethane.

The influence of water 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 Fig. 2e, for photocatalytic NOCM of CH_4 without H_2O , the activity decreases sharply after 31 hours of operation. In stark contrast, the production rate and turnover frequency (TOF) of C_2H_6 didn't vary significantly over a 256 hour period in the presence of H_2O under the same conditions, verifying the promotion effect of H_2O on the stability of the nanohybrid photocatalyst. Consequently, a considerable turnover number (TON) of 40824 mole C_2H_6 per mole Au is achieved (Fig. 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 OCM of methane testing (Fig. S21). Moreover, SEM and XPS characterizations show that the morphology and elemental states of the NWs remained almost unchanged after the stability test (Fig. S22 and 23). These results illustrate that H_2O 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 Fig. S24, nanoparticle 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 hours. Compared with the state-of-the-art photocatalysts for light-driven CH_4 -to- C_2H_6 conversion, Au/GaN NWs have significant advantages in mass activity, selectivity and stability when H_2O is used as the oxidant, demonstrating the great promise for using H_2O to enhance the performance of photocatalysts for coupling CH_4 to C_2H_6 (Fig. 2f and Table S1).

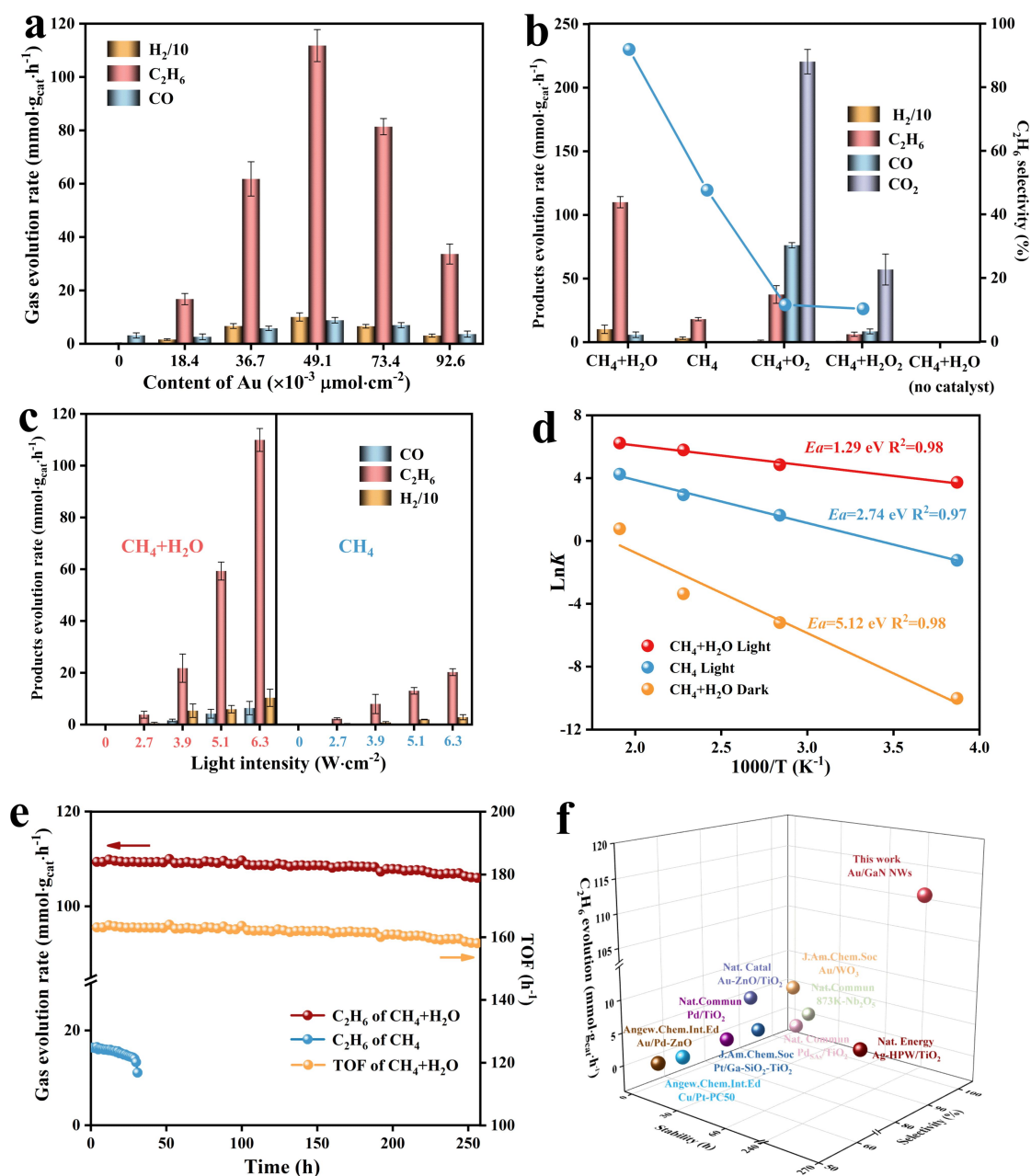


Fig. 2 | Performance of water-triggered light-driven oxidative coupling of CH_4 towards C_2H_6 . (a) Influence of Au content on C_2H_6 production rate over Au/GaN NWs. (b) Control experiment of photocatalytic oxidative coupling of CH_4 with varied oxidants over Au/GaN NWs. (c)

Performances comparison between the photocatalytic oxidative and non-oxidative coupling of CH₄ over Au/GaN NWs under various light intensities. (d) The calculated activation energy of photocatalytic (red) and thermo-catalytic (orange) oxidative coupling of CH₄ with H₂O, and photocatalytic non-oxidative (blue) coupling of methane over Au/GaN NWs. (e) Stability test of photocatalytic oxidative (red and orange) and non-oxidative (blue) coupling of methane 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 minutes.

The origin of the superior performance of Au/GaN NWs was then studied. At first, temperature-dependent photoluminescence (TD-PL) spectroscopy characterizations were conducted to study the carriers' behavior upon concentrated light illumination. As shown in **Fig. 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, 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 eV and 83.18 eV to 86.98 eV and 83.28 eV, respectively (**Fig. 3b**). By contrast, the N 1s peak was shifted from 397.28 eV downward to 396.68 eV (**Fig. S25**). It is indicative that under light illumination, Au species acts as hole-trapping sites, in line with the recent discovery for photocatalytic OCM of CH₄ over Au/TiO₂.²⁹ Transient absorption spectra (fs-TAS) was further measured to reveal the dynamics of photogenerated carriers after excitation. The fs-TAS spectra of bare GaN NWs was composed of a broad positive peak at around 400-700 nm, which is attributed to the excited-state absorption (ESA) of photo-generated holes (**Fig. S26**). As revealed by the fs-TAS spectra of Au/GaN NWs in **Fig. 3c**, it's dominated by photo-carrier absorption at 400 nm, strong excited-state absorption (ESA), ground-state bleaching (GSB), and Au surface plasmon resonance (SPR) at ~550 nm. It suggests the migration of photogenerated electrons and holes towards the surface of Au/GaN NWs

after separation. Notably, combined with the results [Fig. S11](#) and [Fig. S19](#), it can be concluded that the contribution of the SPR effect to water-triggered methane coupling towards ethane over Au/GaN NWs is negligible. Moreover, transient absorption spectroscopy (TAS) kinetics reveal that Au nanoparticles significantly prolong electron decay times on picosecond-to-nanosecond timescales ([Fig. 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 nanoparticles significantly enhances photogenerated charge separation efficiency.

The kinetic isotope effect was also studied to reveal the reaction mechanism. As shown in [Fig. 3d](#), the reaction kinetic ratio of $(\text{CH}_4+\text{H}_2\text{O})/(\text{CH}_4+\text{D}_2\text{O})$ does not vary substantially compared with $(\text{CH}_4+\text{H}_2\text{O})/(\text{CD}_4+\text{H}_2\text{O})$, suggesting the activation of H_2O and CH_4 are both pivotal for the synthesis of C_2H_6 . Moreover, as characterized by the liquid chromatography-mass spectrometer (LC-MS), HDO was detected with the input reactants of $\text{CH}_4+\text{D}_2\text{O}$, validating the H-D exchange between CH_4 and D_2O ([Fig. 3e](#)). Additionally, gas chromatography-mass spectroscopy (GC-MS) measurements demonstrated that during photocatalytic OCM of CH_4 with D_2O , D_2 rather than H_2 was primarily detected ([Fig. S28](#)). Based on the results above, it is rationalized that the introduction of H_2O enables suppressing the continuous dehydrogenation of CH_4 , thus favoring C_2H_6 production while inhibiting coke deposition.

To better understand the reaction mechanism at the molecular level, *in-situ* electron paramagnetic resonance (EPR) was used to detect the key intermediates during the reaction. As illustrated in [Fig. 3f](#), an apparent $\cdot\text{CH}_3$ signal was observed from photocatalytic OCM with H_2O , whose intensity was superior to that of photocatalytic NOCM by only feeding CH_4 ([Fig. S29](#)). It thus offers direct spectroscopic evidence that the incorporation of H_2O facilitates the cleavage of the first C-H of CH_4 to yield $\cdot\text{CH}_3$, which is critical for the subsequent formation of C_2H_6 . *In-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization was further performed to study the evolving track of CH_4 to C_2H_6

(Fig. 3g). The typical peaks at 1304 cm⁻¹ and 3016 cm⁻¹ are indexed to the adsorbed CH₄. During photocatalytic OCM, a rising peak of extensional vibration of O-H appears at 3352-3568 cm⁻¹,³⁷ which can be attributed to the O-H dissociation of water by photo-excited holes ($\text{H}_2\text{O} + \text{h}^+ \rightarrow \bullet\text{OH} + \text{H}$), being well matched with the EPR characterization above. Meanwhile, the characteristic peak of scissoring vibration and extensional vibration of C-H is observed at 1343 cm⁻¹ and 2800-3000 cm⁻¹, which is apparently intensified by the introduction of H₂O compared to 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 Fig. S30, when O₂ or H₂O₂ was used as the oxidizer, CH₄ was more readily over-oxidized into CO_x products (CO: ~2340 cm⁻¹; CO₂: ~2360 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 (Fig. 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.

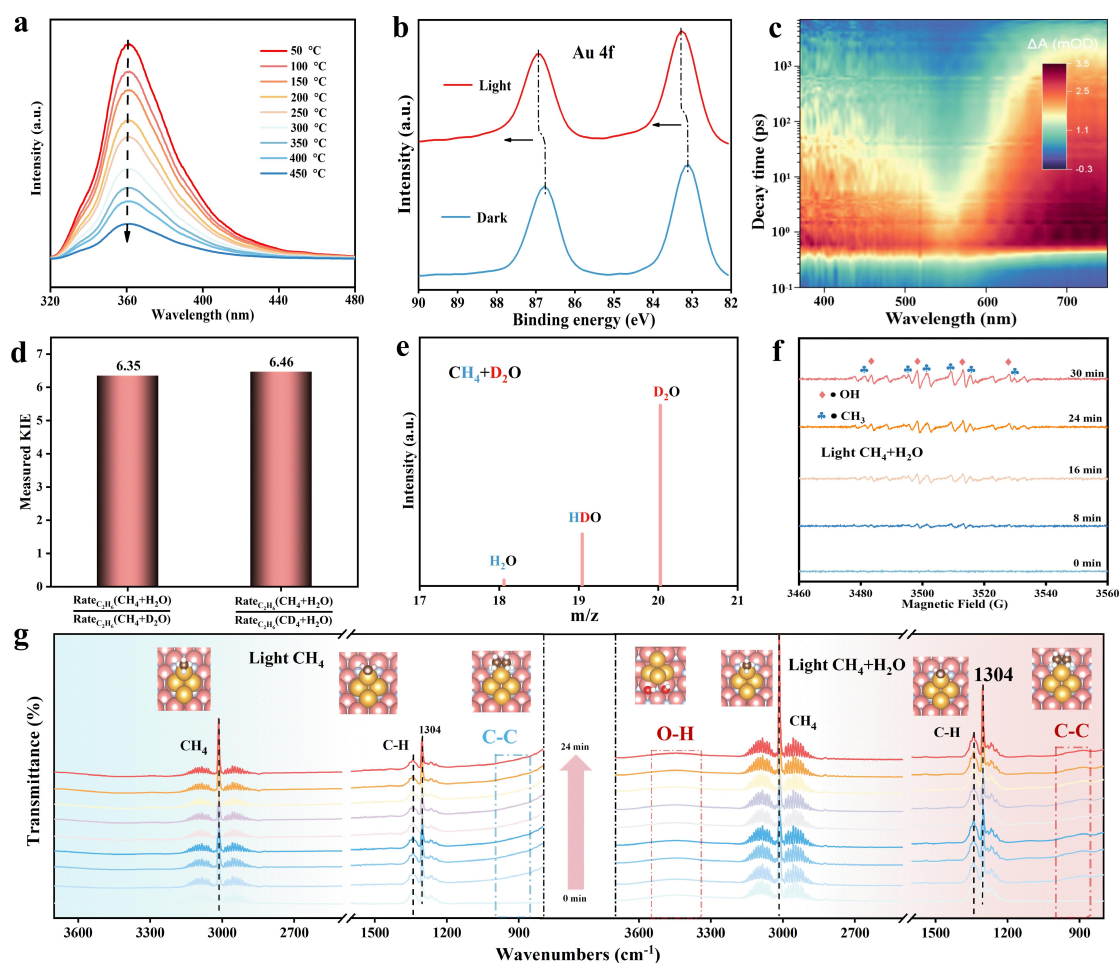


Fig. 3 | *In-situ* spectroscopic characterizations and isotope-related experiments for water-triggered oxidative coupling of CH₄. (a) TD-PL spectra of Au/GaN NWs under various temperatures. (b) *In-situ* illumination XPS measurement of Au 4f of Au/GaN NWs under dark and light irradiation. (c) The fs-TAS 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 oxidative coupling of CH₄ with D₂O. (f) *In-situ* EPR spectra of photocatalytic oxidative of CH₄ with H₂O over Au/GaN NWs under light irradiation 6.3 W·cm⁻². DMPO was used as the radical trapping agent. (g) *In-situ* DRIFT spectra of photocatalytic oxidative and non-oxidative coupling of CH₄ over Au/GaN NWs.

Ground-state theoretical simulations were performed to gain deeper insights into the thermodynamics and kinetics of the reaction mechanism, without accounting for photoexcitation (**Fig. 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 [Fig. S32](#), Au exhibits a higher work function (5.049 eV) relative to GaN (4.715 eV). This difference drives electrons migration from GaN to Au at ground state, establishing a built-in electric field oriented from the GaN bulk toward the Au nanoparticle. Under light irradiation, the photogenerated holes are driven toward the Au nanoparticles by the built-in electric field. Combined with with ISI-XPS findings illustrated in [Fig. 3b](#), it could be concluded that Au nanoparticles 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 eV to -0.924 eV by decorating with Au ([Fig. S33](#) and [Table S2](#)). Combined with the result of temperature-programmed desorption (TPD) measurements in [Fig. S34](#), it can be concluded that Au plays an efficient site for CH₄ adsorption. The activation of water over Au₄/GaN is further simulated. As illustrated in [Fig. 4a](#), H₂O is facilely 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 suggests 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 [Fig. 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 [Fig. 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 eV and -2.46 eV, respectively ([Table S3](#)). Furthermore, combined with the differential charge density analysis in [Fig. 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 Fig. 4c and Fig. S37-38, the H-exchange step between •OH and CH₄ to form •CH₃ is thermodynamically more favorable with H₂O compared to the direct C-H cleavage without it. 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 facilely adsorbed/activated on GaN surface. Water is facilely 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 to NOCM, the introduction of H₂O enables the reduction of the energy barrier of 2•CH₃ → C₂H₆ from 2.43 eV 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 under both with and without H₂O. As shown in Fig. 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 forfor 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 oxidative coupling of CH₄ over Au/GaN NWs is proposed (Fig. 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 hydroxyl radicals (•OH) 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) (Fig. 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 overoxidation and coke deposition with water, thus enabling the achievement of efficient, selective, and stable photocatalytic oxidative coupling of methane into ethane.

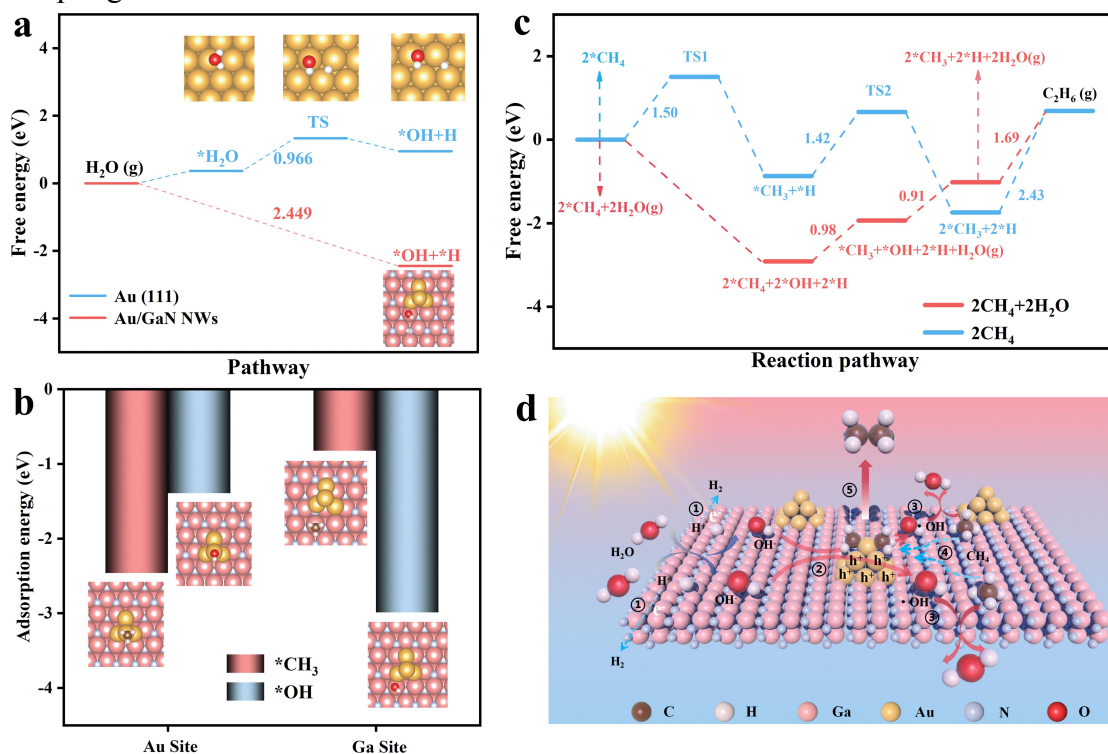


Fig. 4 | Computational investigations of the mechanism of H₂O-triggered CH₄ coupling into C₂H₆ over Au-decorated GaN. (a) The calculated free energy diagrams for H₂O activation over Au (111) and Au₄/GaN NWs. Ga, pink; N, gray; Au, yellow; O, red; H, white. (b) Adsorption energy of CH₃ and OH over Au₄/GaN 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 towards C₂H₆ reaction over Au/GaN NWs. Ga, pink; N, gray; Au, yellow; C, brown; O, red; H, white.

To test the proof-of-concept solar-driven oxidative coupling of CH₄ towards C₂H₆ with H₂O as the oxidizer, an outdoor test was conducted under natural concentrated sunlight illumination. As illustrated in **Fig. 5a**, the home-made outdoor test equipment mainly constitutes 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 outdoor test, an independently movable light intensity meter is positioned at the center of the light spot to measure irradiance before the test is performed. The C₂H₆ rate reached up

to $20.5 \text{ mmol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ during 2:00-3:00 pm, then decreased (Fig. 5b). The fluctuating trend in C_2H_6 production rate matches the variable light intensity during the measurement period (Fig. S41). In total, 211 moles C_2H_6 per mole Au was achieved after 16 h's operation under the concentrated natural sunlight (Fig. 5c). The aforementioned results validate the potential of value-added chemical synthesis from CH_4 using H_2O as a green oxidizer and sunlight as the energy input.

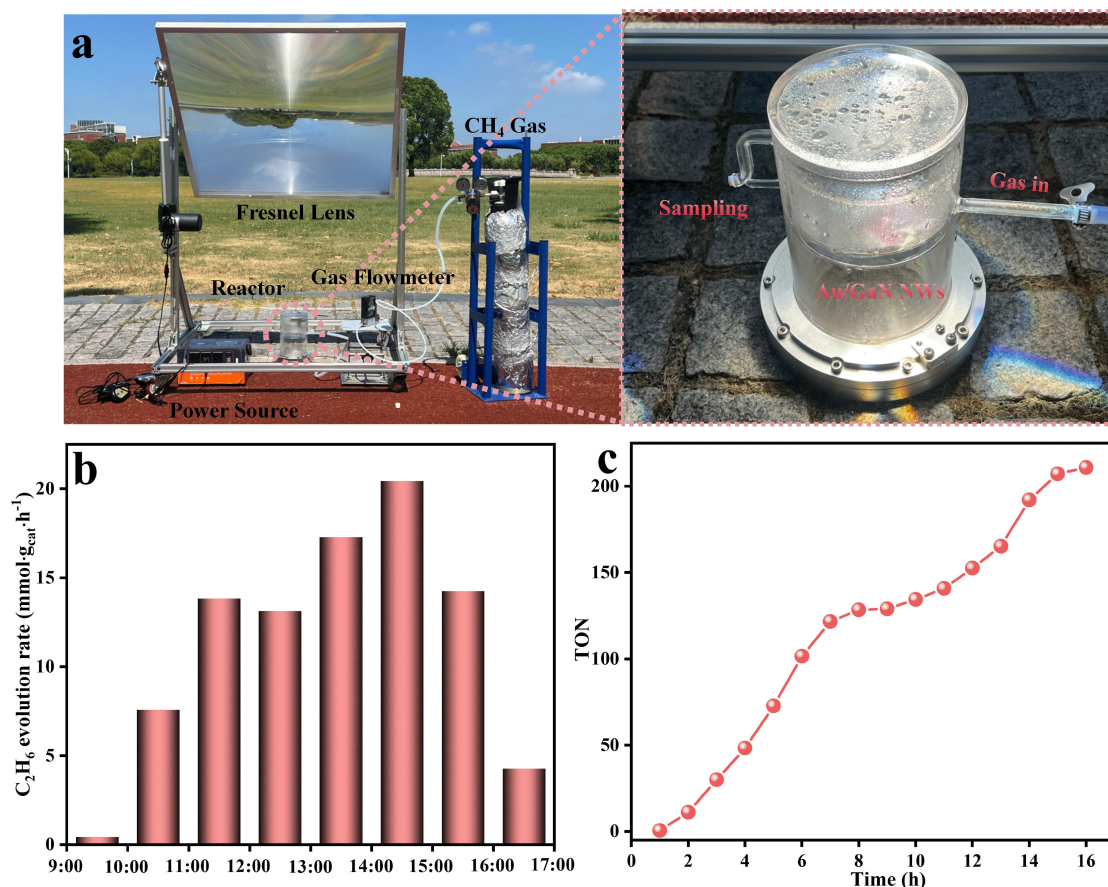


Fig. 5 | Water-promoted coupling of CH_4 towards C_2H_6 under outdoor concentrated sunlight irradiation. (a) Image illustration of the designed outdoor equipment under natural concentrated sunlight irradiation. (b) C_2H_6 evolution rate and (c) TON of Au/GaN NWs for coupling of CH_4 towards C_2H_6 under natural concentrated sunlight. Location: ($121^\circ 25' 31.70''\text{E}$, $31^\circ 01' 41.83''\text{N}$), Environment Conditions: 6-Aug-2024: Temperature: 28-39 °C; air humidity: 55%; weather: sunny. 7-Aug-2024: temperature: 28-37 °C; air humidity: 65%; weather: cloudy to sunny.

Conclusion

In summary, water has been successfully utilized as a green oxidizer for solar-driven coupling of CH₄ to C₂H₆ by using Au nanoparticle decorated GaN nanowires 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 40824 mole C₂H₆ per mole Au was obtained after 256 h's 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

(i) **MBE growth of GaN NWs arrays supported on a 4-inch Si wafer.** The p-type doped GaN nanowires were grown on Si substrate by Veeco Gen 930 plasma-assisted molecular beam epitaxy. 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 nanowires were grown in N-rich growth conditions. The details of the growth condition can be found in the previous publication.^{42, 43}

(ii) **Integration of Au nanoparticles with GaN NWs on a silicon wafer.** The deposition was carried out in a sealed chamber with a quartz lid using a 300 W Xenon 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 Xenon lamp at a light intensity of 2 W·cm⁻² for 30 minutes to immobilize Au NPs over the surface of GaN NWs. Au was also loaded on a bare silicon wafer without GaN through the same method for comparison.

Characterization. Scanning electron microscopy (SEM) images were measured by using a Quattro ESEM (ESCALAB, America). X-ray diffraction (XRD) patterns were measured by a Bruker D8 Advance diffractometer (with Cu K α , at 60 kV and 80 mA). Transmission electron microscopy images were collected using a JEOL 2100F microscope (JEOL, Japan). High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) images were obtained by a JEM-ARM300F2 (GRAND ARM(TM)2), equipped with 158mm² dual Si drift detector (SDD) system and operated at 300 kV. A 250xi non-monochromatic (ESCALAB, America) Al anode was employed for X-ray photoelectron spectroscopy (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 measurements were performed using an ICP-OES 730 (AGILENT, America). *In-situ* diffuse reflection infrared Fourier transform spectroscopy was carried out using a Frontier FT-IR Spectrometer (PerkinElmer, America), which was equipped with an MCT detector and 10-cm Demountable Gas Cell. Gas chromatography-mass spectrometry measurement was performed for isotope labeling experiments by TRACE 1300, ISQ 7000, Thermo Scientific. PL and TR-PL 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 (1030 nm) of the ultrafast TAS spectra was from the Yb:KGW laser (Pharos, Light Conversion Ltd.), which was divided into two beams. The transmitted probe light is 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 Xenon lamp equipped with a quartz lens for the desired time. The stability was assessed by performing 256 consecutive 1-hour 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 silicon wafer was estimated as follows (S6): The fill factor of the epitaxial GaN NWs grown on Si wafer is estimated to be about 81% (Fig. S42). The nanowires illustrated an average length of 850 nm as measured by the SEM technique (Fig. 1a). Since the density of GaN is 6.1 g·cm⁻³, the weight of GaN per unit area is calculated to be 0.420 mg·cm⁻² (±5% analytical error). The Au loading was determined to be 0.049 μmol·cm⁻² by ICP-AES measurement (±1% analytical error).

For in-situ illumination (ISI) XPS measurement, the sample was placed in the XPS chamber, and a full-arc 300 W Xenon 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 μL aliquot of this dispersion was mixed with 100 μL of 100 mM DMPO (5,5-Dimethyl-1-pyrroline-N-oxide) solution in a quartz capillary tube to form a homogeneous suspension. The tube was

purged with CH₄ gas for 5 minutes 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 was recorded at 298 K with 19.23 mW microwave power, 100 kHz modulation frequency, and signal accumulation over 2-3 scans.

The in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) 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 minutes) under continuous illumination.

The apparent quantum efficiency (AQE) was estimated as **Eqs. (S7) and (S8)**. Where the 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 (420, 535, 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 3600 s.

The time-resolved photoluminescence (TRPL) curves was fitted by using the **Eqs. (S9)**. 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, turnover frequency, selectivity, mass density of photocatalyst, AQE and average lifetimes.

$$\text{Products evolution rate} = \frac{\text{products yield per unit area of catalyst per hour}}{\text{Mass of catalyst per unit area}} \quad (\text{S1})$$

$$\text{TOF} = \frac{\text{C}_2\text{H}_6 \text{ yield per unit area of catalyst per hour}}{\text{Content of Au nanoparticles per unit area of catalyst}} \quad (\text{S2})$$

$$\text{TON} = \frac{\text{C}_2\text{H}_6 \text{ yield per unit area of catalyst}}{\text{Content of Au nanoparticles per unit area of catalyst}} \quad (\text{S4})$$

$$\text{Selectivity of C}_2\text{H}_6 = \frac{\text{Yield of C}_2\text{H}_6}{\text{Yield of CO} + \text{Yield of CO}_2 + \text{Yield of C}_2\text{H}_6} \quad (\text{S5})$$

$$\text{Mass of catalyst per unit area} = \text{FF} \times \text{L} \times \rho \quad (\text{S6})$$

$$\text{AQE} = \frac{nR}{I} \quad (\text{S7})$$

$$I = \frac{E\lambda}{hc} \times S = \frac{P\tau\lambda}{hc} \times S \quad (\text{S8})$$

$$\tau_{\text{average}} = \frac{I_1\tau_1^2 + I_2\tau_2^2}{I_1\tau_1 + I_2\tau_2} \quad (\text{S9})$$

Computational methods. DFT calculations were performed employing the Vienna Ab Initio Simulation Package (VASP).^{44, 45} The interaction between valence electrons and ions were 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 constructed 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 [Fig. 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 nanoparticles. 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 via the:

$$\Delta G = E_{\text{ad}} + \Delta \text{ZPE} - T\Delta S \quad (\text{S9})$$

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

$$E_{ad} = E_{ad} - E_{surface} - E_{adsorbate} \quad (S10)$$

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

Data availability

The data of this research are available in the manuscript and Supporting Information.

Acknowledgments

The work is supported by Shanghai Pilot Program for Basic Research-Shanghai Jiao Tong University (No. 21TQ1400211), the National Key Research and Development 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). The work is 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.

Declaration of interests

The authors declare no competing interests.

References

1. Pham, C., et al. (2022) Production of hydrogen and value-added carbon materials by catalytic methane decomposition: a review. *Environ. Chem. Lett.* *20*, 2339-2359.
2. Reddy, P., Kim, K., Song, H (2013). Emerging green chemical technologies for the conversion of CH_4 to value added products. *Renew. Sust. Energ. Rev.* *24*, 578-585.
3. Schwach, P., Pan, X., Bao, X. (2017) Direct conversion of methane to value-added chemicals over heterogeneous catalysts: challenges and prospects. *Chem. Rev* *117*, 8497-8520.

4. Meng, X., Cui, X., Rajan, N. P., Yu, L., Deng, D., Bao, X. (2019) Direct methane conversion under mild condition by thermo-, electro-, or photocatalysis. *Chem* 5, 2296-2325.
5. Hu, A., Guo, J., Pan, H., Zuo, Z. (2018) Selective functionalization of methane, ethane, and higher alkanes by cerium photocatalysis. *Science* 361, 668-672.
6. Dai, Y., Gao, X., Wang, Q., Wan, X., Zhou, C., Yang, Y. (2021) Recent progress in heterogeneous metal and metal oxide catalysts for direct dehydrogenation of ethane and propane. *Chem. Soc. Rev* 50, 5590-5630.
7. He, C., et al. (2024) Single-Atom Alloys Materials for CO₂ and CH₄ Catalytic Conversion. *Adv. Mater* 36, 2311628.
8. Caballero, A., et al. (2011) Silver-catalyzed C-C bond formation between methane and ethyl diazoacetate in supercritical CO₂. *Science* 332, 835-838.
9. Chen, R., Weng, G. (2023) Sustainable energy resources for driving methane conversion. *Adv. Energy Mater* 13, 2301734.
10. Li, Q., Ouyang, Y., Li, H., Wang, L., Zeng, J. (2022) Photocatalytic conversion of methane: recent advancements and prospects. *Angew. Chem. Int. Ed.* 134, e202108069.
11. Wu, S., Tan, X., Lei, J., Chen, H., Wang, L., Zhang, J. (2019) Ga-doped and Pt-loaded porous TiO₂-SiO₂ for photocatalytic nonoxidative coupling of methane. *J. Am. Chem. Soc.* 141, 6592-6600.
12. Li, L., et al. (2011) Efficient sunlight-driven dehydrogenative coupling of methane to ethane over a Zn⁺-modified zeolite. *Angew. Chem. Int. Ed.* 50, 8299-8303.
13. Li, X., et al. (2023) PdCu nanoalloy decorated photocatalysts for efficient and selective oxidative coupling of methane in flow reactors. *Nat. Commun* 14, 6343 .
14. Zhou, Q., et al. (2021) CH₃•-generating capability as a reactivity descriptor for metal oxides in oxidative coupling of methane. *ACS Catal.* 11, 14651-14659 .
15. Li, X., Wang, C., Tang, J. (2022) Methane transformation by photocatalysis. *Nat. Mater. Rev* 7, 617-632.

16. Zhai, G., et al. (2024) Highly efficient, selective, and stable photocatalytic methane coupling to ethane enabled by lattice oxygen looping. *Sci. Adv.* *10*, eado4390.
17. Arinaga, A, M., Ziegelski, M, C., Marks, T, J. (2021) Alternative Oxidants for the Catalytic Oxidative Coupling of Methane. *Angew. Chem. Int. Ed.* *60*, 10502-10515.
18. Zheng, K., et al. (2024) Breaking the Activity-Selectivity Trade-off for CH₄-to-C₂H₆ Photoconversion. *J. Am. Chem. Soc.* *146*, 12233-12242.
19. Jiang, Y., Li, S., Fan, X., Tang, Z. (2023) Recent advances on aerobic photocatalytic methane conversion under mild conditions. *Nano Res.* *16*, 12558-12571.
20. Hoang, S., Gao, P. (2016) Nanowire Array Structures for Photocatalytic Energy Conversion and Utilization: A Review of Design Concepts, Assembly and Integration, and Function Enabling. *Adv. Energy Mater* *6*, 1600683 (2016).
21. Li, Y., Sadaf, S, M., Zhou, B. (2024) Ga(X)N/Si nanoarchitecture: an emerging semiconductor platform for sunlight-powered water splitting toward hydrogen. *Front. Energy* *18*, 56-79 (2024).
22. Zhou, B., Li, J., Dong, X., Yao, L. (2023) GaN nanowires/Si photocathodes for CO₂ reduction towards solar fuels and chemicals: advances, challenges, and prospects. *Sci. Chi. Chem.* *66*, 739-754.
23. Wang, Z., et al. (2024) Air-Promoted Light-Driven Hydrogen Production from Bioethanol over Core/Shell Cr₂O₃@GaN Nanoarchitecture. *Angew. Chem. Int. Ed.* *136*, e202400011.
24. Wang, Z., et al. (2023) Photocatalytic syngas production from bio-derived glycerol and water on AuIn-decorated GaN nanowires supported by Si wafer. *Green Chem* *25*, 288-295.
25. Liu, M., Tan, L., Zhou, B., Li, L., Mi, Z., Li, C, J. (2021) Group-III nitrides catalyzed transformations of organic molecules. *Chem* *7*, 64-92.
26. Yu, T., et al. (2024) Green Syngas Production from Natural Lignin, Sunlight, and Water over Pt-Decorated InGaN Nanowires. *Angew. Chem. Int. Ed.*, e202405904.

27. Li, Y., et al. (2024) Rh/InGa $N_{1-x}O_x$ nanoarchitecture for light-driven methane reforming with carbon dioxide toward syngas. *Sci. Bull.* *69*, 1400-1409.
28. Song, S., et al. (2021) A selective Au-ZnO/TiO₂ hybrid photocatalyst for oxidative coupling of methane to ethane with dioxygen. *Nat. Catal* *4*, 1032-1042.
29. Li, X., et al. (2023) Efficient hole abstraction for highly selective oxidative coupling of methane by Au-sputtered TiO₂ photocatalysts. *Nat. Energy* *8*, 1013-1022.
30. Huang, Q., et al. (2024) Selective oxidative coupling of methane to ethane with oxygen using an Au/Zn₂Ti₃O₈ photocatalyst under mild conditions. *J. Mater. Chem. A.* *12*, 21334-21340.
31. Li, J., et al. (2024) Utilizing full-spectrum sunlight for ammonia decomposition to hydrogen over GaN nanowires-supported Ru nanoparticles on silicon. *Nat. Commun* *15*, 7393.
32. Xia, Y., et al. (2003) One-dimensional nanostructures: synthesis, characterization, and applications. *Adv. Mater.* *15*, 353-389.
33. Chen, Y., et al. (2024) Continuous Flow System for Highly Efficient and Durable Photocatalytic Oxidative Coupling of Methane. *J. Am. Chem. Soc.* *146*, 2465-2473.
34. Zhou, B., et al. Gallium nitride nanowire as a linker of molybdenum sulfides and silicon for photoelectrocatalytic water splitting. *Nat. Commun* *9*, 3856 (2018).
35. Ma, J., et al. (2022) Charge carrier dynamics and reaction intermediates in heterogeneous photocatalysis by time-resolved spectroscopies. *Chem. Soc. Rev.* *51*, 5777-5794.
36. Wang, J., et al. (2025) Transfer dynamics of photo-generated carriers in catalysis. *Chem. Soc. Rev.* *54*, 6553-6596.
37. Jiang, W., et al. (2020) Pd-modified ZnO-Au enabling alkoxy intermediates formation and dehydrogenation for photocatalytic conversion of methane to ethylene. *J. Am. Chem. Soc.* *143*, 269-278 (2020).
38. Bu, K., et al. (2019) Methane dry reforming over boron nitride interface-confined and LDHs-derived Ni catalysts. *Appl. Catal. B-Environ.* *252*, 86-97.

39. Zhang, W., et al. (2022) High-performance photocatalytic nonoxidative conversion of methane to ethane and hydrogen by heteroatoms-engineered TiO₂. *Nat. Commun* *13*, 2806.
40. Yao, Y., et al. (2023) Highly Efficient Solar-Driven Dry Reforming of Methane on a Rh/LaNiO₃ Catalyst through a Light-induced Metal-To-Metal Charge Transfer Process. *Adv. Mater.* *35*, 2303654.
41. Menzel, J., Dong, W., Gruszecki, E., Yang, K., Mi, Z., Batista, VS. (2024) Photoinduced Surface Oxidation of GaN Nanowires Facilitates Hydrogen Evolution. *ACS Catal.* *14*, 13314-13323.
42. Sadaf, S., Ra, Y., Nguyen, H., Djavid, M., Mi, Z. (2015) Alternating-current InGa_{0.5}N/GaN tunnel junction nanowire white-light emitting diodes. *Nano. Lett.* *15*, 6696-6701.
43. Hasan, S., You, W., Ghosh, A., Sadaf, S., Arafin, S. (2023) Selective area epitaxy of GaN nanostructures: MBE growth and morphological analysis. *Cryst. Growth Des.* *23*, 4098-4104.
44. Kresse, G., Joubert, D. (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* *59*, 1758.
45. Kresse, G., Furthmüller, J. (1996) Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* *54*, 11169.
46. Blöchl, P, E. (1994) Projector augmented-wave method. *Phys. Rev. B* *50*, 17953.
47. Perdew, J, P., Burke, K., Ernzerhof, M. (1996) Generalized gradient approximation made simple. *Phys. Rev. B* *77*, 3865.
48. Perdew, J, P, et al. (1992) Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* *46*, 6671 (1992).
49. Monkhorst, H, J, Pack, J, D. (1976) Special points for Brillouin-zone integrations. *Phys. Rev. B* *13*, 5188.