


 Cite this: *Chem. Commun.*, 2024, 60, 14276

 Received 29th September 2024,
 Accepted 5th November 2024

DOI: 10.1039/d4cc05090h

rsc.li/chemcomm

Anatase/TiO₂(B) homojunction nanosheets with a gold cocatalyst for direct photocatalytic coupling of methane to ethane†

 Xuanzhao Lu,^{‡,b} Huanhuan Luo,^{‡,b} Biyang Xu,^{‡,b} Zhuo Liu,^{‡,b} Yue Cao,^a Kai Li,^c Xiaohan Yang,^b Liangyiqun Xie,^b Tao Guan,^b Wenlei Zhu^{*,b} and Yang Zhou^{*,a}

An anatase/TiO₂(B) homojunction loaded with Au nanoparticles was synthesized, achieving a C₂H₆ yield rate of 170 μmol g⁻¹ h⁻¹ in a flow photoreactor. The homojunction reduces TiO₂(B)'s strong oxidative ability, offering a more moderate environment for methane dehydrogenation, while Au aids in charge mitigation and methyl radical coupling. The catalyst highlights homojunction engineering and a ternary synergistic effect in photocatalytic CH₄ coupling.

The efficient conversion of methane (CH₄) into valuable products can help mitigate the greenhouse effect while generating useful chemicals.^{1–6} The non-oxidative coupling of methane (NOCM) can convert CH₄ to C₂ hydrocarbons (such as ethane (C₂H₆)) directly. However, this reaction is thermodynamically unfavorable owing to the high C–H bond energy, low polarizability, and poor electron affinity of CH₄, which requires a huge energy input and harsh reaction conditions for the first C–H bond breakage.⁷ Therefore, developing sustainable strategies for cleaner and more cost-effective NOCM routes is essential.

Photocatalysts can reduce the activation energy of CH₄ dehydrogenation more easily than thermal catalysts, thereby enabling CH₄ coupling under mild conditions.^{8–10} Noble metals are considered as promising co-catalysts for promoting CH₄ coupling, and Au is the most effective owing to its relatively higher C₂H₆ selectivity.^{11,12} However, small-sized unsupported Au nanoparticles (NPs) are thermodynamically unstable and prone to agglomeration

due to their high surface energy. Hence, appropriate supports are required to achieve a balance between the dispersion and stability of the Au NPs.

Bulk TiO₂ is a well-studied photocatalyst for NOCM, but it struggles with poor photogenerated electron-hole pair separation capacity and scarce CH₄ adsorption sites, reducing its photocatalytic performance.^{13–15} Two-dimensional TiO₂ provides sufficient sites for CH₄ adsorption, and its atomic-level thickness facilitates the efficient short-distance diffusion of carriers to the catalyst surface.^{16,17} TiO₂(B) is a polymorph of TiO₂. Recently, TiO₂(B) nanosheets (NSs) have attracted attention in photocatalysis because of their relatively high specific surface area and inherent defect-rich surface properties. These features provide an ideal platform for the surface nucleation of noble metals, enabling dispersed cocatalyst loading or heterogeneous structure modification.^{18,19}

In this work, a TiO₂(B)-anatase homojunction catalyst loaded with Au NPs was synthesized and the optimal C₂H₆ yield rate reached 170 μmol g⁻¹ h⁻¹ in a flow-cell photocatalytic system. We found that the photocatalyst composed of Au, TiO₂(B), and anatase exhibited a ternary synergistic effect, which enhanced the overall photocatalytic activity. The *in situ* conversion of TiO₂(B) to anatase TiO₂ allows the formation of closely contacted TiO₂ type-II homojunctions, creating a more moderate environment for CH₄ dehydrogenation and coupling compared to the initial TiO₂(B) NSs. In addition, the participation of Au not only further improves the separation of electron-hole pairs but also helps to capture some methyl intermediates, alleviating the excessive oxidation of CH₄ to CO₂, thus resulting in improved C₂H₆ production.

The synthesis processes of Au-Ti300 are illustrated in Fig. 1(a). The anatase phase was introduced into the TiO₂(B) phase by calcining the TiO₂(B) NSs at 300 °C, resulting in the sample designated as Ti300. Scanning electron microscopy (SEM) images (Fig. S1 and S2, ESI[†]) reveal that the nanosheet morphology of Au_{1.0}-Ti300 remains largely unchanged after heat treatment. UV-Vis diffuse reflectance spectroscopy (DRS; Fig. S3, ESI[†]) indicates enhanced visible light absorbance for Ti300 due to the TiO₂(B)-anatase junction and confirms the presence of Au NPs through an absorption peak at ~560 nm.²⁰

^a State Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing University of Posts & Telecommunications, Nanjing 210023, China. E-mail: iamyangzhou@njupt.edu.cn

^b State Key Laboratory of Pollution Control and Resource Reuse, State Key Laboratory of Analytical Chemistry for Life Science, Frontiers Science Center for Critical Earth Material Cycling, School of Chemistry and Chemical Engineering, School of the Environment, Nanjing University, Nanjing 210023, China. E-mail: wenleizhu@nju.edu.cn

^c School of Science, Wuhan University of Science and Technology, Wuhan 430065, China

† Electronic supplementary information (ESI) available. See DOI: <https://doi.org/10.1039/d4cc05090h>

‡ These authors contributed equally to this work.

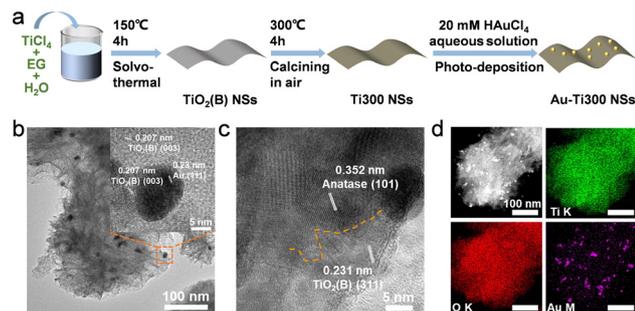


Fig. 1 (a) Schematic illustration of the preparation of Au–Ti300. (b) TEM image of Au_{1.0}–Ti300. The enlarged image of the selected area (inset). (c) HRTEM image of Au_{1.0}–Ti300. (d) STEM image of Au_{1.0}–Ti300 and corresponding element mapping (Ti, O, and Au).

Transmission electron microscopy (TEM) images reveal the wrinkled ultrathin morphology of TiO₂ NSs (Fig. S4, ESI[†]), which remains unchanged after calcination (Fig. 1(b)). Au NPs were evenly distributed on Ti300, averaging 9.77 nm in diameter (Fig. S5, ESI[†]). The actual loading of Au on the TiO₂ samples was quantified using inductively coupled plasma–optical emission spectroscopy (ICP–OES; Table S1, ESI[†]). The high-resolution TEM (HRTEM) image (Fig. 1(c)) shows lattice spacings of 0.352 and 0.231 nm, corresponding to the anatase TiO₂ (101) and TiO₂(B) (311) planes, respectively. A close-contact interface (marked by the orange dashed line) between the two phases suggests the formation of a homojunction between the anatase and TiO₂(B) phase, potentially enhancing charge transfer over the phase interfaces. Another HRTEM image (Fig. 1(b), inset) shows lattice spacings of 0.207 and 0.230 nm, corresponding to TiO₂(B) (003) and Au (111), respectively. Scanning TEM (STEM) and the corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Fig. 1(d)) reveal that Ti, O, and Au are homogeneously distributed throughout Au_{1.0}–Ti300.

X-ray diffraction (XRD) was employed to investigate the phase transformations of the crystals (Fig. 2(a) and Fig. S6, ESI[†]). The diffraction peaks of the pristine TiO₂(B) NSs match well with those of the pure TiO₂(B) phase (JCPDS no. 46-1238). Phase transformations of TiO₂ crystals occurred during calcination;²¹ notably, an anatase (101) peak at 25.3° appeared in Ti400 (Fig. S6, ESI[†]), accompanied by the gradual disappearance of the TiO₂(B) phase and the aggregation of the NSs into larger particles. By Ti500 and Ti600, TiO₂(B) was completely converted into pure anatase. With the further increase of the calcination temperature above 700 °C, the anatase phase is further converted to the rutile phase (JCPDS no. 21-1276). For Ti300, characteristic peaks of the anatase phase (JCPDS no. 21-1272) were observed, and the red-shift of the peak from 24.9° to 25.1° indicated the existence of mixed TiO₂ crystal phases on Ti300, consistent with the HRTEM results. Because of the low crystallinity and adjacent diffraction peaks of anatase and TiO₂(B), it was difficult to obtain the exact anatase/TiO₂(B) phase ratio for Ti300. However, the TiO₂(B) phase was still the dominant component of Ti300 based on the existence of a peak assigned to TiO₂(B) (003) at 43.5° after calcination. XRD analysis also shows Au peaks but no incorporation of Au into the TiO₂ lattice.

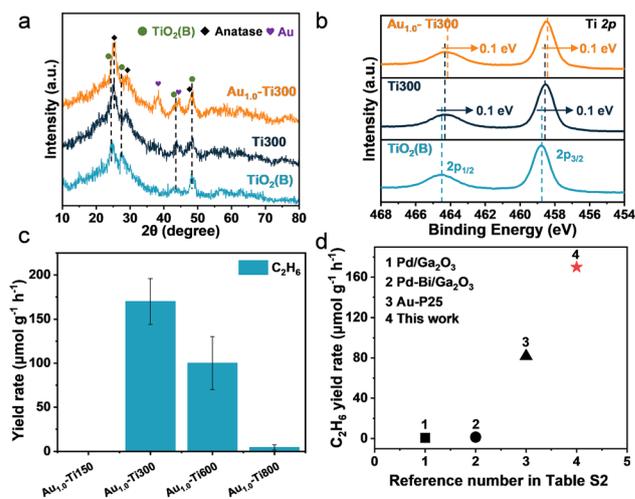


Fig. 2 (a) XRD patterns of TiO₂(B) NSs, Ti300, and Au_{1.0}–Ti300. (b) Ti 2p high-resolution XPS spectra of related samples. (c) The production rate of C₂H₆ for photocatalytic CH₄ coupling over Au_{1.0}–Ti with different calcination temperatures. (d) The comparison of C₂H₆ yield rate of recently published references using flow reactors.

X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical states. Ti, O, and C were detected in all samples (Fig. S7, ESI[†]); the peak of Au was not obvious owing to its low content. XPS confirmed the existence of Ti⁴⁺ in all samples.²² The lower binding energy of the Ti 2p peaks for Ti300 suggests a lower oxidation state of Ti, indicating the self-doping of Ti³⁺ arising from phase contact (Fig. 2(b)).²³ With Au loading, the binding energies of the Ti 2p peaks decreased by ~0.1 eV, suggesting that more electrons moved into the Ti sites. O 1s spectra revealed different oxygen species (Fig. S8a, ESI[†]),^{21,24} and a decrease in hydroxyl groups after heat treatment indicates an increase in available adsorption sites. Au 4f peaks confirmed the presence of metallic Au NPs (Fig. S8b, ESI[†]).²⁵

Photocatalytic performance was tested using a homemade flow-cell system (Fig. S9, ESI[†]). Pure TiO₂(B) loaded with Au (*i.e.* Au_{1.0}–Ti150) produced almost no C₂H₆ (Fig. 2(c)), highlighting the essential role of anatase in regulating the strong over-oxidative ability of Au–TiO₂(B). Au_{1.0}–Ti300 exhibited the highest photocatalytic C₂H₆ yield rate (170 μmol g^{−1} h^{−1}). Au_{1.0}–Ti600 did not have better catalytic performance for C₂H₆ production, probably due to the weaker oxidation ability of pure anatase compared to the homojunction, which diminished its capacity to activate CH₄. An increase in the rutile ratio further reduced the photocatalyst activity, with no C₂H₆ produced from Au_{1.0}–Ti800. The optimal Au loading on Ti300 was 1.0 wt% (Fig. S10, ESI[†]). Notably, the Au_{1.0}–Ti300 catalyst exhibited the highest C₂H₆ yield rate among state-of-the-art photocatalytic NOCM reactions using flow-cell reactors (Fig. 2(c) and Table S2, ESI[†]).

No H₂ was detected in this photocatalytic system, probably because of the consumption of lattice oxygen on the surface of TiO₂, which led to the production of surface-adsorbed oxygen species or water. Additionally, the reaction involving lattice oxygen produces CO and CO₂ as by-products of CH₄ overoxidation (Fig. S11, ESI[†]), resulting in a C₂H₆ selectivity (carbon

balance selectivity) of 45%. Fig. S12 (ESI[†]) illustrates the photocatalytic performance of Au_{1.0}-Ti300 over 2 h. The C₂H₆ yield rate became stable at 90 min and the CO₂ yield rate gradually declined after 30 min of irradiation, suggesting possible consumption of surface lattice oxygen. The cycling stability test of Au_{1.0}-Ti300 is shown in Fig. S13 (ESI[†]). To regenerate the lost lattice oxygen,²⁶ the catalyst was exposed to air for 2 h in each cycle. The performance of Au_{1.0}-Ti300 did not decrease significantly after four cycles, suggesting rapid lattice oxygen regeneration capability and good stability of the TiO₂(B)-anatase homojunction. TEM images reveal that the NS morphology of the catalyst remained unchanged after the reaction (Fig. S14, ESI[†]), and the average size of the Au NPs increased to ~14 nm, possibly owing to the heating agglomeration from long-term illumination.

Control experiments were conducted to gain a better understanding of the structure–activity relationship of the components in Au_{1.0}-Ti300 (Fig. S15, ESI[†]). With no CH₄ source, no products were detected, confirming that carbon products originated from CH₄ rather than organic residues. Under visible-light illumination, only a small amount of CO₂ was produced, indicating that the localized surface plasmon resonance effect of Au did not influence this reaction, and that the dehydrogenation of CH₄ to methyl radicals (CH₃•) mainly occurred on the TiO₂ surface rather than on Au. Au_{1.0}-Ti150 had significantly higher activity than Ti150, showing Au's role in enhancing electron–hole pair separation. No C₂H₆ was produced without Au, highlighting its necessity for coupling methyl radicals. The ternary system of Au_{1.0}-Ti300, with a balanced anatase/TiO₂(B) ratio, showed enhanced performance by suppressing over-oxidation and facilitating C₂H₆ production, outperforming commercial P25 TiO₂ by a factor of 1.6.

Photoluminescence (PL), transient photocurrent, and electrochemical impedance spectroscopy (EIS) were used to assess electron–hole separation in the catalysts. PL spectra (Fig. S16a, ESI[†]) revealed that Au_{1.0}-Ti300 had weaker PL intensity than Ti300, indicating longer carrier lifetimes. Ti300 has a higher photocurrent density than pristine TiO₂(B) (Fig. S16b, ESI[†]), demonstrating effective electron–hole separation due to the homojunction structure. Au further promotes charge transfer between TiO₂(B) and anatase, which is in agreement with the XPS results. The EIS results also exhibited a trend consistent with the transient photocurrent response (Fig. S16c and Table S3, ESI[†]), in which the Au and homojunction decreased the transfer resistance of the photogenerated charges.

According to the UV-vis DRS and the corresponding Tauc plot (Fig. S3, ESI[†]), the energy band gaps (E_g) of TiO₂(B) and anatase were calculated to be 3.69 eV and 3.38 eV, respectively. The valence band maxima (VBM) of TiO₂(B) and anatase are located at 2.97 eV and 2.49 eV, respectively (Fig. 3). Consequently, the estimated conductive band minimum (CBM) of TiO₂(B) and anatase are calculated to be -0.72 and -0.89 eV, which are consistent with the flat band potentials of TiO₂(B) and anatase determined through Mott–Schottky measurements (Fig. S17, ESI[†]). Through combining the band structure analysis and XPS results, possible type-II and Z-scheme band structures were proposed (Fig. 3(c)). Interestingly, the introduction of water vapor

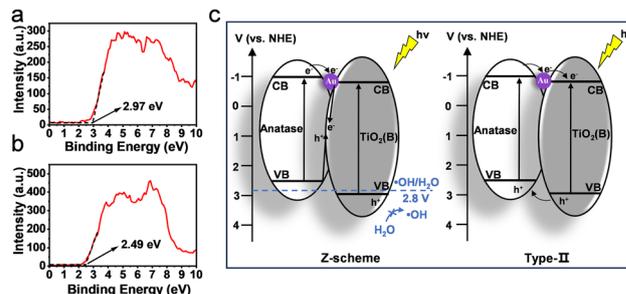


Fig. 3 Energy band structure. (a) VB-XPS spectrum of TiO₂(B). (b) VB-XPS spectrum of anatase TiO₂. (c) Schematic illustration of the energy band structure of Au_{1.0}-Ti300.

into the photocatalytic system did not alter product distributions or yield rates (Fig. S18, ESI[†]). This proves that water cannot be oxidized to hydroxyl radicals ($E^0(^{\bullet}\text{OH}/\text{H}_2\text{O}) = 2.8 \text{ V}$) over the TiO₂ homojunction structure.²⁷ Thus, the type-II structure is preferred over the Z-scheme structure, which retains the undesirably strong oxidation capacity of TiO₂(B).

In situ diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) was employed to detect the reaction intermediates and reveal the reaction pathway. Peaks at 1536 cm⁻¹, corresponding to the symmetric stretching vibrations of CH₄, emerged upon light irradiation, indicating enhanced CH₄ adsorption on the TiO₂ surface.^{11,28} Vibration modes related to CH₃/CH₂ deformation at 1475 cm⁻¹, 1465 cm⁻¹, and 1448 cm⁻¹ (Fig. S19, ESI[†]) suggest that adsorbed CH₄ undergoes dehydrogenation on the TiO₂ surface.^{29,30} These signals become stronger for Au_{1.0}-Ti300 (Fig. 3(b)), indicating that the loading of Au NPs improves overall CH₄ activity. Additionally, C–O stretching vibrational modes at 1016 and 1009 cm⁻¹, assigned to CO₂ formation, appeared in both catalysts, demonstrating the over-oxidation of CH₄ on the TiO₂ catalyst surface. Furthermore, a small signal at 865 cm⁻¹ assigned to the C–C stretching mode of C₂H₆ was only in Au_{1.0}-Ti300.^{30,31} This shows that Au dominates the coupling stage of CH₄, which is consistent with the results of the control experiments.

Based on the aforementioned photocatalytic CH₄ performance, energy band structure analysis, and DRIFTS results, we propose a schematic of the possible reaction routes for the photocatalytic NOCM to C₂H₆ on Au_{1.0}-Ti300 (Fig. 4). First, CH₄ is adsorbed onto the surface of TiO₂ in the dark. Upon irradiation, electron–hole pairs are generated within TiO₂. Subsequently, dehydrogenation of CH₄ occurs on the TiO₂ surface, and lattice oxygen is converted to O⁻ by hole induction, trapping protons from adjacent adsorbed CH₄ to form methyl radicals attached to the Ti sites. The O⁻ sites tend to trap methyl radicals to form intermediate species such as *CH₃O or *CH₂O, which can further be overoxidized to CO and CO₂. In addition, surface O sites that trap one proton can subsequently trap a second proton from CH₄, resulting in water generation. Consequently, lattice oxygen is removed along with water or over-oxidative products when they are dissociated from the catalyst surface to leave oxygen vacancies. In this process, the homogeneous heterojunction enables TiO₂(B) to exhibit a more moderate oxidation ability, reducing the CO₂ generation.

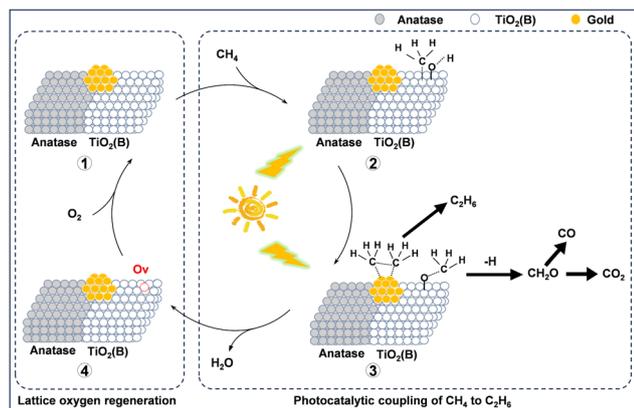


Fig. 4 Schematic illustration for photocatalytic CH_4 conversion in the case of $\text{Au}_{1.0}\text{-Ti}_{300}$.

Besides, during the charge-transfer process, some electrons that avoid charge recombination pass through the Au NPs, resulting in the negatively charged Au surface capturing dissociative methyl radicals and protecting them from overoxidation. Finally, the coupling of the methyl radicals results in the formation and desorption of free C_2H_6 into the gas flow. The lost lattice oxygen can be easily regenerated in an oxygen-rich atmosphere for another catalytic cycle.

In summary, the TiO_2 -based hybrid photocatalyst achieves efficient conversion of CH_4 to C_2H_6 at a rate of $170.0 \mu\text{mol g}^{-1} \text{h}^{-1}$ in a flow reactor. The dehydrogenation of CH_4 occurs over TiO_2 with a relatively moderate oxidative ability owing to the formation of type-II homojunctions between the $\text{TiO}_2(\text{B})$ and anatase phases. Au plays a critical role not only in promoting charge mitigation but also in coupling methyl radicals. The catalyst highlights the ternary synergistic effect in photocatalytic CH_4 coupling, providing insights for future catalyst design and industrial CH_4 conversion.

X. L., H. L., B. X., and Z. L. designed and conducted the experiments, analyzed the results, and drafted the manuscript. Y. C., K. L., X. Y., L. X., and T. G. contributed to the discussion of the results. Y. Z. and W. Z. supervised the project, engaged in discussions, and revised the manuscript.

Y. Z. would like to acknowledge the support from the National Natural Science Foundation of China (22276100), Natural Science Foundation of Jiangsu Province (BK20220405), Research Fund for Jiangsu Distinguished Professor (RK030STP22001), and Key Laboratory for Organic Electronics & Information Displays (GZR2024010003). W. Z. would like to acknowledge the support from the National Natural Science Foundation of China (22176086), Research Funds for Jiangsu Distinguished Professor, Carbon Peaking and Carbon Neutrality Technological Innovation Foundation of Jiangsu Province (BE2022861), the Research Funds from Frontiers Science Center for Critical Earth Material Cycling of Nanjing University, State Key Laboratory of Pollution Control and Resource Reuse, and the Fundamental Research Funds for the Central Universities (021114380214, 021114380222).

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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