Supporting Information

Accelerated Interfacial Hole Transfer over Au/TiO_2 Photocatalysts for Highly Efficient Oxidative Coupling of Methane

Shihua Zhu,[1] Yachao Wang,[1] Yu Wang,[2] Yaxiong Wei,[2] Guofeng Zhao,[1] Cong Fu,[1]*

[1] Anhui Basic Discipline Research Center for Clean Energy and Catalysis, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China

[2] Anhui Province Key Laboratory of Optoelectric Materials Science and Technology, School of Physics and Electronic Information, Anhui Normal University, Wuhu 241002, China

* Corresponding author. E-mail: fc4432@mail.ustc.edu.cn

Experimental details:

Chemicals. Nano-TiO_2 (99.8% metal basis, 60 nm) were purchased from Aladdin. $HAuCl_4 \cdot 4H_2O$, $AgNO_3$ and $H_2PtCl_6 \cdot 6H_2O$ were purchased from Macklin.Deionized water with a resistivity of 18.2 MΩ cm^{-1} was used in all experiments. All chemicals were used as received and without further purification.

Materials synthesis. Au was introduced by a photodeposition method, chemical reduction method and deposition-precipitation method. In photodeposition method, 300 mg TiO_2 was dispersed into a solution of 27 mL DI water and 3 mL methanol. Then a desired amount of $HAu(Cl)_4$ solution was dropwise added into the above solution and allowed to be bubbled with argon for 30 min. Afterwards, the suspension was stirred under irradiation with a 300W Xe lamp at 25 ℃ for 4h. The samples were collected by centrifugation, washed with DI water for three times and dried at 60 ℃ for 6 h. Ag/TiO_2 and Pt/TiO_2 photocatalysts was also prepared through photodeposition method for comparsion. In chemical reduction method, 0.2g anatase TiO_2 powder was dispersed in a 50 mL aqueous solution of metal precursor. 5 mL aqueous solution of $NaBH_4$ and NaOH (containing 100 µmol of $NaBH_4$ and 250 µmol of NaOH) was added to the suspension slowly under vigorous stir at 20 °C. After the addition of reductant, the resulted suspension was stirred for 1 h in dark. Then, the catalyst powder was separated by centrifugation, washed 3 times using DI water and dried at 60 °C for 12 h. The sample was calcined at 500 °C for 2 h before use. In deposition-precipitation method, Fine powder of anatase TiO_2 and metal precursor were dispersed in 50ml H_2O under vigorous stir to make a suspension. 2 M aqueous solution of NaOH was used as the precipitant and added dropwise into the suspension until the pH reached 9.0. The resulted suspension was further stirred for another h. Then, the catalyst powder was separated by centrifugation, washed 3 times using DI water, and dried at 60 °C for 12 h. The sample was calcined at 500 °C for 2 h before use.

Structural characterizations. The Au loadings in various Au/TiO_2 samples were determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). Powder X-ray diffraction (XRD) patterns were recorded in the 2θ range 20–80° on a Philips X'Pert Pro Super diffractometer with Cu Ka radiation (k = 0.15406 nm) operating at 40 kV and 50 mA. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were acquired with a JEOL JEM-2100F instrument at an acceleration voltage of 120 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high-performance electron spectrometer using monochromatized Al Kα (hv = 1486.7 eV) as the excitation source, and the likely charging of samples was corrected by setting the C 1s binding energy of the adventitious carbon to 284.8 eV. The UV/vis DRS of the samples were recorded on a SHIMADZU UV-3600i plus spectrophotometer. Electrochemical and photoelectrochemical analyses were conducted by the CHI760E electrochemical workstation in a threeelectrode setup. Notably, an Ag/AgCl electrode (in saturated KCl), a Pt wire electrode and a fluorine-doped tin oxide (FTO, active area of 1 cm^2) covered with the catalysts were used as reference electrode, counter electrode and working electrode, respectively.

***In situ* transient absorption measurements.** Nanosecond time-resolved transient absorption spectra and decay kinetics were obtained using an LFP instrument (LP 980, Edinburgh Instruments Ltd). The pump laser beam and the probe beam crossed perpendicularly through the liquid sample in a quartz cuvette (10 mm × 10 mm). ACQ was excited by 355 nm laser pulses (10 Hz, 7.0 mJ per pulse) which were delivered by the third harmonic of a Nd:YAG laser (Surelite II-10, Continuum Inc.). A dynamic decay curve was recorded with a digital phosphor oscilloscope (TDS 3012C, Tektronix Inc.). The TiO_2 nanoparticles were dispersed in water and then coated on a quartz glass to form a smooth film with a thickness of ~1 µm for the TA spectra measurements. The film samples were placed in a sealed quartz cuvette and were degassed by purging with high purity nitrogen (99.99%) for about 20 minutes prior to measurements to ensure complete removal of oxygen.

***In-situ*/operando DRIFTS experiments.** *In situ*/operando DRIFTS experiments were performed on a Bruker INVENIO R Spectrometer with a MCT detector. The spectrometer was equipped with a Harrik Praying Mantis diffuse reflection accessory and a Harrick high-temperature reaction chamber with ZnSe windows. 365 LED UV light source of a 10 W point-source light (UVGO) was shed on the sample through the front window of the reaction chamber. Typically, 50 mg catalyst was loaded onto the sample stage of the reaction chamber, heated in Ar at 100 °C for 1 h, and then cooled to room temperature, whose spectrum was recorded as the background spectrum for the measurements of UV light illumination of bare sample and of CH_4 adsorption without or with UV light illumination. For CH_4 adsorption, CH_4 was admitted into the reaction cell at a flow rate of 30 mL min^{-1}. UV light was turned on after the adsorption reached the steady-state, and DRIFTS spectra were recorded in the series measurement mode with a temporal resolution of 4 s at a resolution of 4 cm^{-1}. For photocatalytic OCM, a CH_4 and O_2 mixture with a CH_4:O_2 ratio of 75 was admitted into the reaction cell at a flow rate of 30 mL min^{-1}. After the adsorption reached the steady-state, the spectrum was recorded as the background spectrum and the UV light was turned on, and DRIFTS spectra were recorded every 5 mins with 64 scans at a resolution of 4 cm^{-1}.

Photocatalytic OCM reaction. The photocatalytic OCM experiments was conducted using a flow reactor with a temperature controller. Typically, the glass fibre membrane with Au/TiO_2 sample on top was transferred to the middle of the reactor. Then, a stainless ring was installed to fix the membrane. Next, a rubber O-ring and a stainless cap were used to seal the reactor. The membrane was irradiated by a 365 nm light-emitting diode (LED) (70 W) from the quartz window of the cap. The temperature of the catalyst bed could be monitored and controlled by the temperature probe with a thermocouple at the bottom. Two gases, methane (BOC, 20%vol CH_4/N_2) and O_2 (BOC, 1%vol O_2/N_2), were supplied to the reactor at different ratios controlled by two mass flow controllers (Bronkhorst). The reaction system was purged by the gas mixture with the setting ratio for at least 1 h to reach equilibrium before photocatalytic activity evaluation. The reactor was connected to one gas chromatographs for product analysis. The gas chromatographs (GC1690) equipped with a methanizer, an FID and an TDX-01 column (TQ0135) was used to accurately quantify the concentration of CO_2, CO, CH_4, C_2H_6 and C_2H_4.

The C_2 selectivity calculation was based on the observable products (C_2H_6 and CO_2) analysed, and the formula is shown below:

$$Sel_{C2} = \frac{2 \times n_{C2H6}}{2 \times n_{C2H6} + n_{CO2}} \times 100\%$$

where n is the yield rate of different products.

The apparent quantum efficiency (AQE) of $Au_{5\%}/TiO_2$ at 365 nm was measured (10 mg catalyst, 365 nm LED 70W, 353K, 75 ml/min of CH_4 (20%vol CH_4/N_2) + 1 ml/min of O_2 (1%vol O_2/N_2))) and calculated as the following:

$$AQE(\%) = \frac{8 \times \text{amount of CO2 generated} + 2 \times \text{amount of C2H6 generated}}{\text{Total photons incident } (N)} \times 100\%$$

$$N = IA\frac{\lambda}{hc}$$

Light intensity (I) = 74 mW·cm^{-2}

Irradiation area (A) = 8 cm^2

Wavelength of the LED light source (λ) = 356 nm

Planck constant (h) = 6.63 $\times 10^{-34}$ J·s

Speed of light (c) = 3 $\times 10^{8}$ m·s^{-1}

Thus,

$$AQE = \frac{8 \times 1.74\ \mu\text{mol} \cdot \text{h}^{-1} \times 10^{-6} \div 3600 \times 6.02 \times 10^{23} + 2 \times 33.13\ \mu\text{mol} \cdot \text{h}^{-1} \times 10^{-6}}{74\text{mW·cm}^{-2} \times 10^{-3} \times 8\ \text{cm}^2 \times \frac{365\ \text{nm} \times 10^{-9}}{6.63 \times 10^{-34}\text{J} \cdot s \times 3 \times 10^{8}\text{m} \cdot}} \times 100\% \approx 1.2\%$$

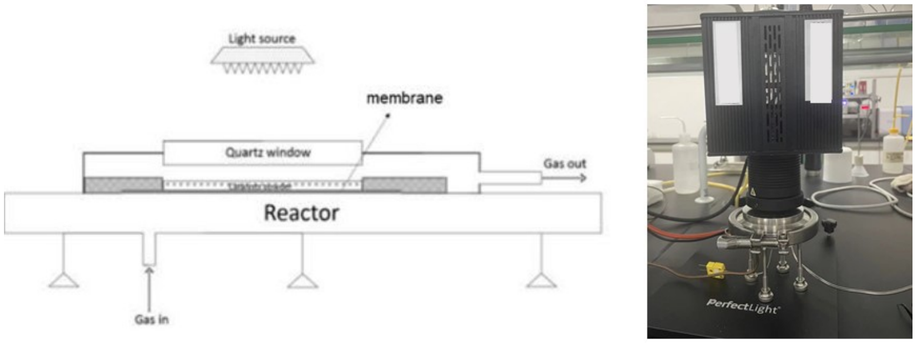

Figure S1. (left) Schematic illustration of customer-designed photocatalytic flow reactor and (right) photograph of the working apparatus. The apparatus was manufactured by Beijing Perfect Light Ltd.

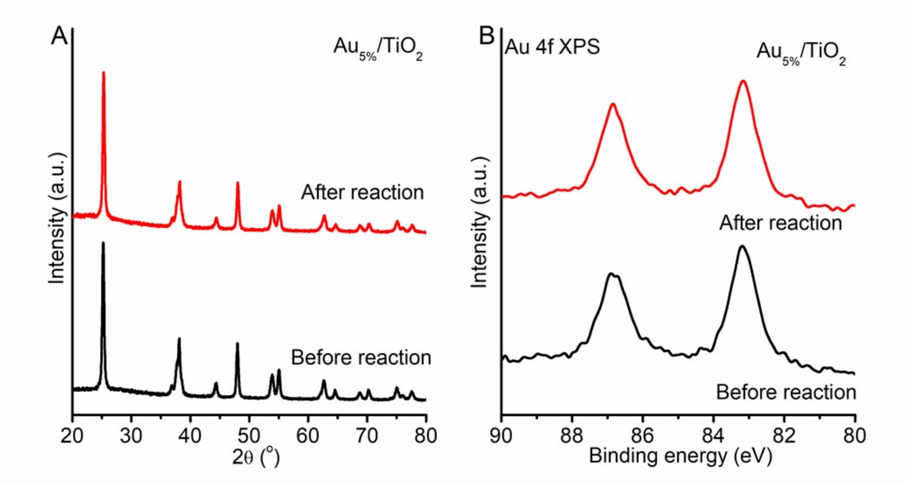

Figure S2. XRD (A) and Au 4f XPS spectra (B) of $Au_{5\%}/TiO_2$ before and after the reaction.

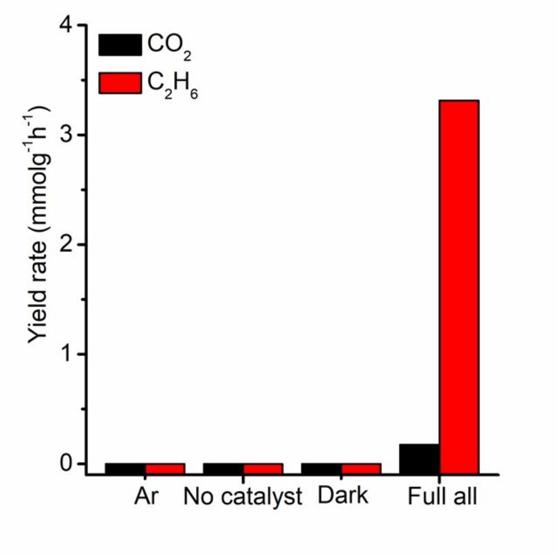

Figure S3. Gas yield rates under different conditions over $Au_{5\%}/TiO_2$ photocatalysts.

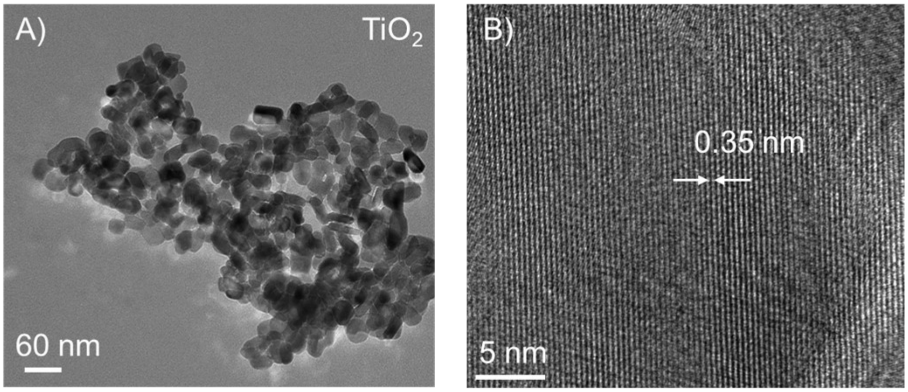

Figure S4. Representative TEM images (A) and HRTEM images (B) of TiO_2 samples.

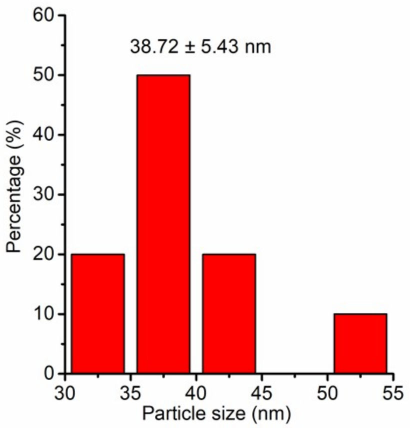

Figure S5. Au particle size distributions of of $Au_{5\%}/TiO_2$ samples.

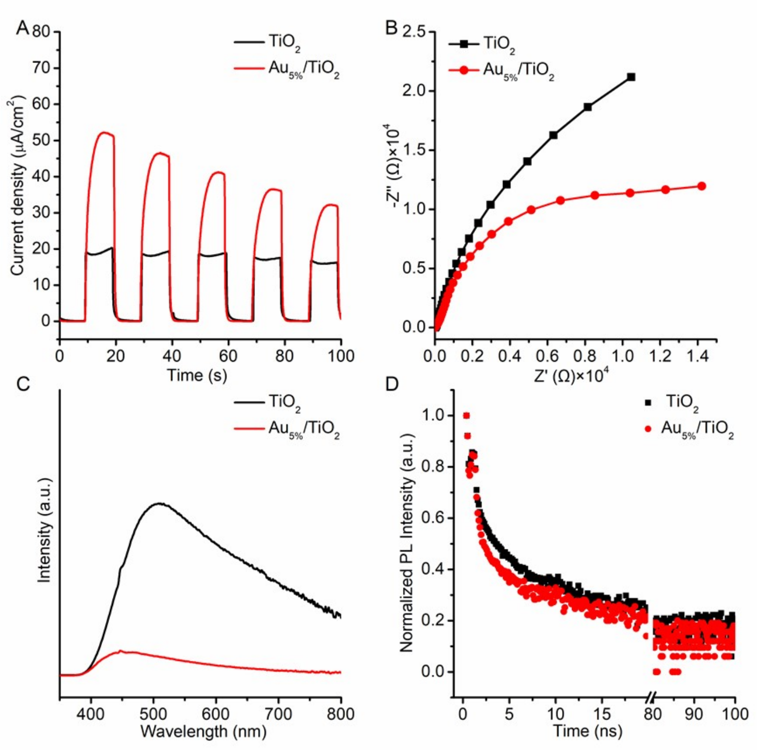

Figure S6. Transient photocurrent responses (A) and electrochemical impedance spectra plot (B) under light irriadation, PL spectra (C) and time-resolved PL (D) for TiO$_2$ and Au$_{5\%}$/TiO$_2$ samples.

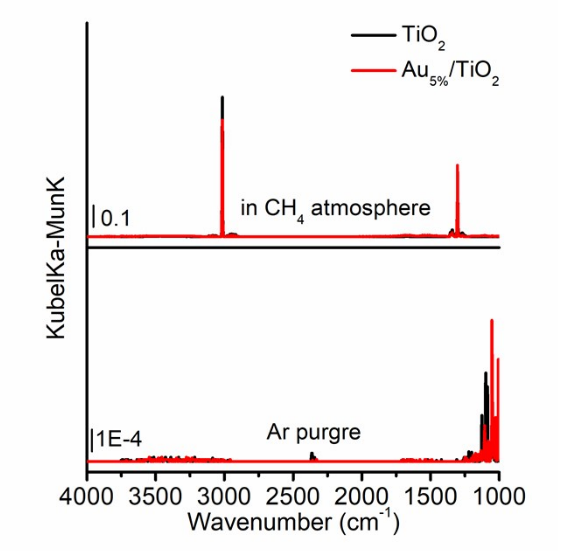

Figure S7. DRIFTS spectra of TiO_2 and $Au_{5\%}/TiO_2$ samples in CH_4 atmosphere under dark condition and followed by Ar purging at 353K. DRIFTS spectra of corresponding samples under Ar atmosphere in the dark were used as the background spectra. The features observed in the DRIFTS spectrum in CH_4 atmosphere arise from gaseous CH4, and no feature could be observed after Ar purging.

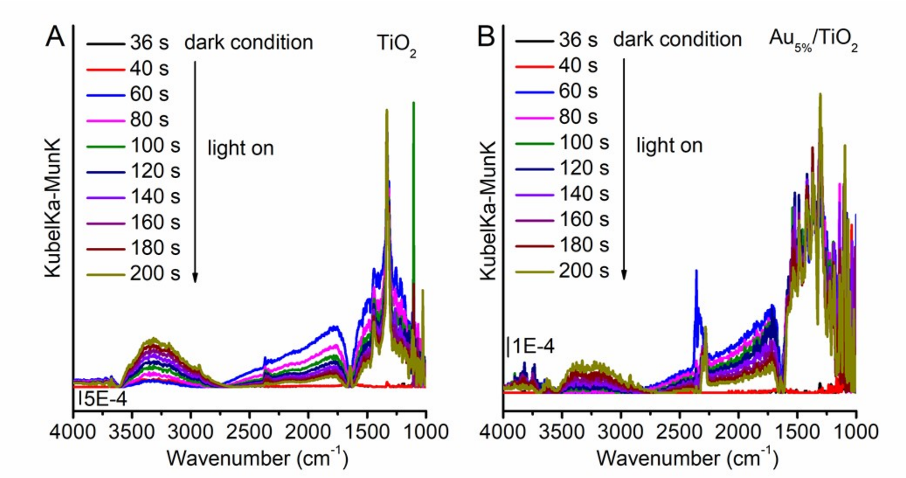

Figure S8. DRIFTS spectra of (A) TiO_2 and (B) $Au_{5\%}/TiO_2$ samples under Ar atmosphere upon UV light irradiation at different times. DRIFTS spectra of corresponding samples under Ar atmosphere in the dark were used as the background spectra.

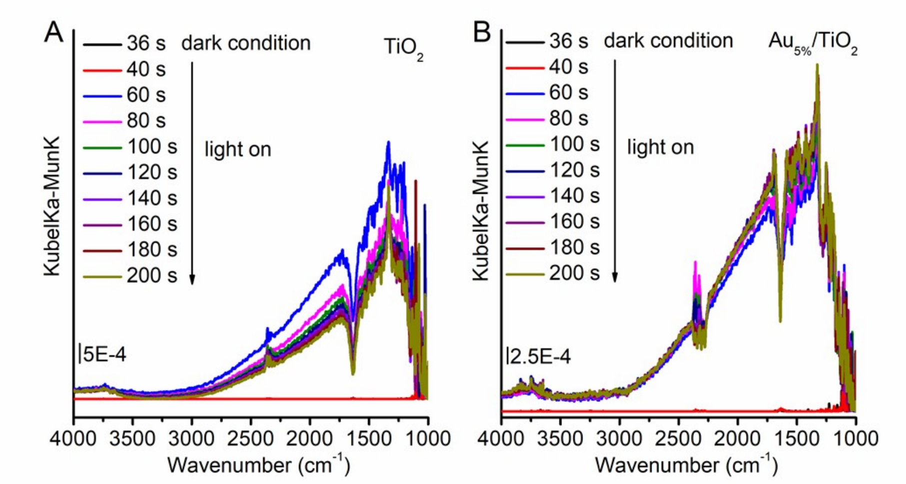

Figure S9. DRIFTS spectra of (A) TiO_2 and (B) $Au_{5\%}/TiO_2$ samples under CH_4 atmosphere upon UV light irradiation at different times. DRIFTS spectra of corresponding samples under CH_4 atmosphere in the dark were used as the background spectra.

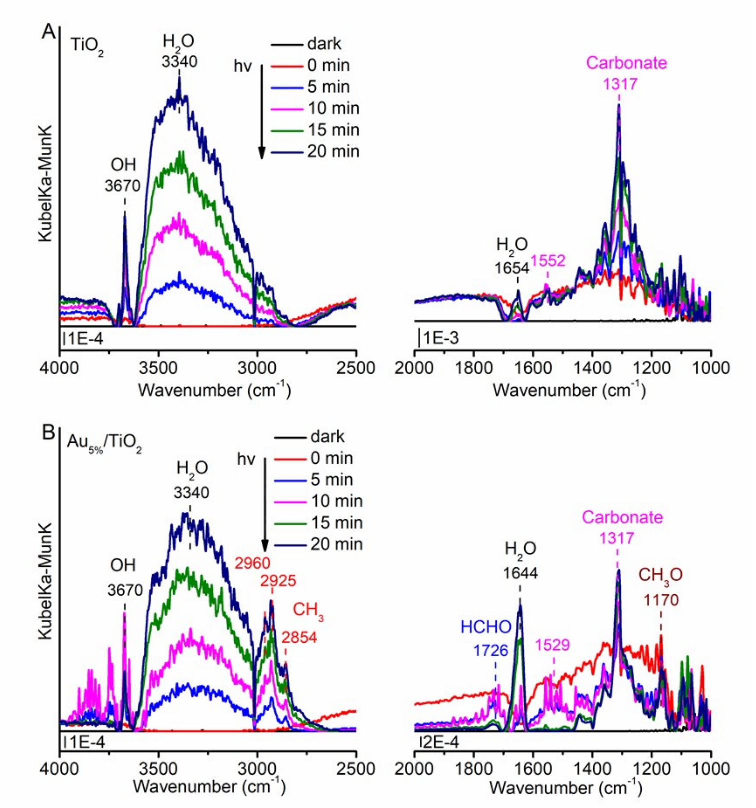

Figure S10. Operando DRIFTS spectra of photocatalytic OCM over TiO_2 and $Au_{5\%}/TiO_2$ samples. DRIFTS spectra prior to UV light irradiation were used as the background spectra). Reaction conditions: 50mg, 365 nm LED 70W, 353K, 75 ml/min of CH_4 (20%vol CH_4/N_2) + 1 ml/min of O_2 (1%vol O_2/N_2).

Table S1. Comparison of the performance of photocatalytic OCM

Catalysts	C_{2+} yield rate (μmol h^{-1} g^{-1})	C_{2+} selectivity (%)	Ref.
PtCu/TiO_2	68	60	S1
PdCu/TiO_2	1240	75	S2
Au/TiO_2	110000	90	S3
Ag-AgBr/TiO_2	354	79	S4
Pd/TiO_2	818	80.4	S5
Au/ZnO-TiO_2	5000	90	S6
Au/ZnO	683	83	S7
Au/ZnSn-LDH	2666	76.8	S8
Au/TiO_2	3300	97	This work

References

(S1) Li, X.; Xie, J.; Rao, H.; Wang, C.; Tang, J., Platinum- and CuOx-Decorated TiO_2 Photocatalyst for Oxidative Coupling of Methane to C_2 Hydrocarbons in a Flow Reactor. *Angewandte Chemie International Edition* **2020**, *59*, 19702-19707.

(S2) Li, X., et al., Pdcu Nanoalloy Decorated Photocatalysts for Efficient and Selective Oxidative Coupling of Methane in Flow Reactors. *Nature Communications* **2023**, *14*, 6343.

(S3). Li, X.; Li, C.; Xu, Y.; Liu, Q.; Bahri, M.; Zhang, L.; Browning, N. D.; Cowan, A. J.; Tang, J., Efficient Hole Abstraction for Highly Selective Oxidative Coupling of Methane by Au-Sputtered Tio2 Photocatalysts. *Nature Energy* **2023**, *8*, 1013-1022.

(S4) Wang, C.; Li, X.; Ren, Y.; Jiao, H.; Wang, F. R.; Tang, J., Synergy of Ag and AgBr in a Pressurized Flow Reactor for Selective Photocatalytic Oxidative Coupling of Methane. *ACS Catalysis* **2023**, *13*, 3768-3774.

(S5) Yang, J.; Wang, C.; Xing, J.; Tang, J., Palladium Decorated Anatase for Photocatalytic Partial Oxidation of Methane to Ethane. *Surfaces and Interfaces* **2023**, *40*, 103108.

(S6) Song, S.; Song, H.; Li, L.; Wang, S.; Chu, W.; Peng, K.; Meng, X.; Wang, Q.; Deng, B.; Liu, Q., A Selective Au-Zno/TiO_2 Hybrid Photocatalyst for Oxidative Coupling of Methane to Ethane with Dioxygen. *Nature Catalysis* **2021**, *4*, 1032-1042.

(S7) Wang, P.; Shi, R.; Zhao, Y.; Li, Z.; Zhao, J.; Zhao, J.; Waterhouse, G. I. N.; Wu, L.-Z.; Zhang, T., Selective Photocatalytic Oxidative Coupling of Methane Via Regulating Methyl Intermediates over Metal/ZnO Nanoparticles. *Angewandte Chemie International Edition* **2023**, *62*, e202304301.

(S8) Zhang, J.; Feng, X.; Li, L.; Wang, P.; Liang, J., Selective Photocatalytic Oxidative Coupling of Methane Via Directional Activation of Oxygen over Au-Loaded ZnSn-LDH with Defect Structure. *Applied Catalysis B: Environment and Energy* **2025**, *361*, 124670.