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Engineering surface lattice hydroxyl groups toward highly efficient photocatalytic methane coupling

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Experimental Methods

Synthesis of Nb₃O₇(OH) and Nb₂O₅ nanorods. Nb₃O₇(OH) nanorods (NRs) were synthesized based on a modified procedure in reported literature.¹ Typically, one gram of niobium powder (Shanghai Macklin Biochemical Technology Co., Ltd., 99.99%, 325 mesh) was dispersed into 25 mL of concentrated hydrochloric acid (Sinopharm Chemical Reagent Co.,Ltd., AR, 36-38%) and 25 mL deionized (DI) water. The mixture was transferred a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was sealed tightly and heated at 453 K for 24 h. After cooling down to room temperature naturally, the Nb₃O₇(OH) products were collected and washed thoroughly with DI water and dried in a vacuum oven at 333K for 7 h. The corresponding Nb₂O₅ was obtained by calcinating Nb₃O₇(OH) at 923 K for 4 h. The content of surface hydroxyl groups over Nb₃O₇(OH) was tuned by O₂ plasma treatment method with exposure time of 1 min and 5 min, respectively².

Loading of Au nanoparticles cocatalyst. The Au nanoparticles (NPs) as cocatalyst were loaded on Nb₃O₇(OH) and Nb₂O₅ by a photodeposition method.^{3,4} Briefly, 200 mg of Nb₃O₇(OH) or Nb₂O₅ were suspended in 20 ml of an aqueous solutions of ethanol (50 vol%) containing certain volume of AuHCl₄ (Shanghai Macklin Biochemical Technology Co., Ltd., 99%, 10 mg/ml, Au-based). The suspension was placed in a quartz reactor and irradiated for 1 h by a 300 W xenon lamp (PLS-SXE300, Perfect light). Afterwards, the resultant powder was washed repeatedly with distilled water (DI) and then dried at 333 K under vacuum. The samples were denoted as X%Au-Nb₃O₇(OH) or X%Au-Nb₂O₅, where X refers to the practical Au content in mass fraction. The actual loading of AuNPs in the composites was determined via inductively coupled plasma atomic emission spectrometry (ICP-AES) by dissolving Au with aqua regia, and the results are summarized in Table S1.

Structural characterization. Powder X-ray diffraction (XRD) patterns were carried out on a rotating-anode X-ray diffractometer with Cu-Kα radiation (SmartLab) to identify the phase of photocatalyst. UV-Vis diffuse reflectance spectroscopy (DRS) were measured in the spectral region of 300–1000 nm with a Shimadzu3700 spectrophotometer. ¹H magic angle spinning (MAS) solid-state nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 NMR spectrometer operating in the Fourier transform mode at 400 MHz. Transmission electron microscopy (TEM) images were obtained on a Hitachi Model H-7700 microscope operating at 100 kV. High-resolution TEM (HR-TEM) images and the high-angle annular dark

field (HAADF) images were measured on the JEOL ARM-200F field-emission transmission electron microscope operated at 200 kV.

Photocatalytic test. A 180 mL custom-made quartz reactor was used to evaluate the performance of photocatalytic CH₄ conversion. Typically, 2.0 mg of as-prepared photocatalyst was dispersed in 350 µL of DI water via sonication and uniformly dropped onto a pre-cleaned quartz substrate (1.5×1.5 cm). After drying at 313 K, the quartz substrate was horizontally placed in the reactor. Subsequently, the reactor was purged with Ar (99.999%) for 15 min and CH₄ (99.999%) for another 15 min, and then sealed with a butyl rubber. A 300 W xenon lamp (PLS-SXE300, Perfect light) was used to irradiate the reactor from top (see Fig.S1 for detail) with light intensity of 600 mW cm⁻². The reacted gas was analysed by a gas chromatograph (GC, 7890B, Ar carrier, Agilent) equipped with thermal conductivity detector (TCD) and flame ionization detector (FID) to quantify H₂ and hydrocarbons, respectively. Another GC (7890A, Ar carrier, Agilent) equipped with a methanizer, FID detector, and TCD detector was used to analyze CO and CO₂ products. The isotope-labelled experiments were performed by using CD₄ as the feeding gas, and the products were analysed with gas chromatography-mass spectrometry (GC–MS, 7890 A and 5975 C, He carrier, Agilent).

EPR spectra measurements. The samples were placed in a slender tube and the tube was vacuumized or purged with CH_4 for in situ electron paramagnetic resonance (EPR) measurements. The experiments were performed on a JEOL JES-FA200 spectrometer equipped with a 500 W Xe lamp (USHIO Optical Modulex SXU1501XQ) as light source. The electronic g-factor was calculated by the formula $g = hv/\beta H$, where h is the Planck constant, v is the scanning microwave frequency (9.09 GHz), β is the Bohr magneton, and H is the magnetic field (mT). To assess the relative production quantity of hydroxy radicals, the samples were prepared by mixing the photocatalysts in a 50 mM DMPO (5, 5'-dimethyl-1-pyrroline N-oxide, Aladdin, 97%) aqueous solution.

DRIFTS for in Situ CH₄ adsorption and conversion. The in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) experiments were carried out on a Bruker IFS 66v Fourier-transform spectrometer equipped with a Harrick diffuse reflectance accessory at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) in National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.⁵ A custom-made IR reaction chamber with two ZnSe windows was used to load the photocatalysts enabling examine highly scattering powder

samples in the diffuse reflection mode. All spectrums were recorded by averaging 128 scans at a resolution of 2 cm⁻¹. Pure Ar (99.999%) was flushed into the reactor for background spectra collection after loading the samples. Subsequently, CH₄ gas (99.999%) was introduced into the system under dark condition. The spectra were then collected at certain time in the CH₄ atmosphere under dark condition. After 30 min of CH₄ adsorption, the light irradiation was turned on from an optical fiber through the front window of the chamber. The spectra were then collected at certain time in the CH₄ atmosphere under dark certain time in the CH₄ atmosphere under dark certain time in the CH₄ atmosphere under light illumination.



Fig. S1 XRD patterns of pristine Nb₃O₇(OH) and X%Au-Nb₃O₇(OH) samples.



Fig. S2 XRD patterns of pristine Nb_2O_5 and $0.5\%Au-Nb_2O_5$.



Fig. S3 UV–Vis DRS spectra of pristine $Nb_3O_7(OH)$, Nb_2O_5 and their Au-decorated counterparts.



Fig. S4 (a) TEM image of as-prepared Nb₃O₇(OH). (b) HAADF image of Au-Nb₃O₇(OH). (c) HR-TEM image of Au-Nb₂O₅.



Fig. S5 O 1s (a), Nb 3d (b) and Au 4f (c) XPS spectra of Au-Nb₃O₇(OH) and Au-Nb₂O₅ photocatalyst.

The O 1s XPS spectra of Au-Nb₃O₇(OH) and Au-Nb₂O₅ are mainly consist of the peaks from lattice O at ca. 530.6 eV and OH group at ca. 532.1 eV (the Fig. S5a). The O 1s XPS spectra indicate that the proportion of OH/lattice O for Au-Nb₃O₇(OH) was ca. 29.09%, which is significantly higher than that of Au-Nb₂O₅ (22.12%).



Fig. S6 Schematic diagram of the batch reactor system.



Fig. S7 Typical GC traces of photocatalytic CH_4 conversion.



Fig. S8 O 1s XPS spectra of Au-Nb₃O₇(OH) and Au-Nb₃O₇(OH) treated with O₂ plasma exposure for 1 min and 5 min, respectively. The corresponding proportion of OH/lattice O is ca. 28.72%, 29.52% and 34.43%, respectively.

The content of surface hydroxyl groups was tuned by O_2 plasma treatment method.² The highresolution O 1s XPS spectra reveal that the relative content of surface hydroxyl groups is increased with a longer O_2 plasma exposure time (Fig. S8), and the higher content of surface hydroxyl groups gives a higher C_2H_6 yield rate (Fig. S9). But an excessive content of surface hydroxyl groups gives more overoxidation product CO_2 .



Fig. S9 The production rate and selectivity of C_2H_6 over Au-Nb₃O₇(OH) and Au-Nb₃O₇(OH) treated with O₂ plasma exposure for 1 min and 5 min, respectively.



Fig. S10 EPR signals of DMPO-•OH over $Au-Nb_2O_5$ and $Au-Nb_3O_7(OH)$ in aqueous suspension under dark and light irradiation conditions.

The electron paramagnetic resonance (EPR) was further employed to assess the relative production quantity of hydroxy radicals by using 5, 5'-dimethyl-1-pyrroline N-oxide (DMPO) as spin trapping reagent. As shown in Fig.S10, Au-Nb₃O₇(OH) exhibited stronger characteristic 1:2:2:1 quadruple peak of the DMPO–•OH adduct than that of Au-Nb₂O₅ under light irradiation, indicating the enhanced production of hydroxy radicals in Au-Nb₃O₇(OH) contributed to the higher photocatalytic capacity.



Fig. S11 The O 1s XPS spectra of Au-Nb₃O₇(OH) before (bottom panel) and after (top panel) photocatalytic CH₄ conversion reaction. The corresponding proportion of OH/lattice O is ca. 29.09% and 30.85%, respectively

The O 1s XPS spectra indicate that the surface -OH groups and lattice O can be regenerated and the relative content of OH group with lattice O can be well kept over Au-Nb₃O₇(OH) after photocatalytic CH_4 conversion reaction.



Fig. S12 The in situ EPR spectra collected over the (a) $Au-Nb_2O_5$ and (b) $Au-Nb_3O_7(OH)$ samples under various conditions.



Fig. S13 The in situ EPR spectra collected over the (a) Nb_2O_5 and (b) $Nb_3O_7(OH)$ samples under various conditions.



Fig. S14 In situ DRIFTS spectra for adsorption of CH_4 over (a) Nb_2O_5 , (b)Au-Nb₂O₅, (c) $Nb_3O_7(OH)$ and (d) Au-Nb₃O₇(OH) at different time under dark condition.



Fig. S15 (a) Full range in situ DRIFTS spectra for adsorption of CH_4 over Au-Nb₃O₇(OH) at different time under dark condition. (b, c) The absorbance intensity at the wavenumber of ca. 998 cm⁻¹ over different adsorption time for (b) Au-Nb₂O₅ and (c) Au-Nb₃O₇(OH) under dark condition.



Fig. S16 In situ DRIFTS spectra for photocatalytic conversion of CH_4 over (a) Nb_2O_5 , (b)Au-Nb₂O₅, (c) $Nb_3O_7(OH)$ and (d) Au-Nb₃O₇(OH) at different time under light irradiation.



Fig. S17 (a) In situ high-resolution C1s XPS spectra showing intensity over Au-Nb₃O₇(OH) under ultrahigh vacuum, upon exposure to 0.45 mbar of CH₄ under dark and under light irradiation. (b) C 1s XPS intensity (background subtracted) at the binding energy of ca. 286.1 eV over time.



Fig. S18 (a) In situ high-resolution O1s XPS spectra showing intensity over Au-Nb₃O₇(OH) under ultrahigh vacuum, upon exposure to 0.45 mbar of CH₄ under dark and under light irradiation. (b) O 1s XPS intensity (background subtracted) at the binding energy of ca. 532.1 eV over time. The decrease of signal intensity upon CH₄ injection is (inherently) caused by scattering losses in the gas atmosphere.

Table S1. The actual mass fractions of Au in various samples determined by ICP-AES.

Sample	Actual Au% (wt)
Nb ₃ O ₇ (OH)	null
0.1%Au-Nb ₃ O ₇ (OH)	0.12
0.2%Au-Nb ₃ O ₇ (OH)	0.23
0.5%Au-Nb ₃ O ₇ (OH)	0.53
0.8%Au-Nb ₃ O ₇ (OH)	0.84
1.1%Au-Nb ₃ O ₇ (OH)	1.12
Nb ₂ O ₅	null
0.5%Au-Nb ₂ O ₅	0.52

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