

Electronic Supplementary Information

Highly efficient and stable photocatalytic reduction of CO₂ to CH₄ over Ru loaded NaTaO₃ semiconductor

Mu Li,^{ab} Peng Li,^{*b} Kun Chang,^b Tao Wang,^b Lequan Liu,^c Qing Kang,^b Shuxin Ouyang^c and Jinhua Ye^{*abc}

a Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo, Japan. E-mail: Jinhua.YE@nims.go.jp

b Environmental Remediation Materials Unit and International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044 (Japan) E-mail: LI.Peng@nims.go.jp

c TU-NIMS Joint Research Center, School of Materials Science and Engineering, Tianjin University, 92 Weijin Road, Nankai District, Tianjin, P. R. China.

Experimental

Preparation of NaTaO₃ nanoparticles

The NaTaO₃ was synthesized via a typical furfural alcohol derived polymerization–oxidation (FAPO) process^{8,9}. First, 1.61 g of (C₂H₅O)₅Ta and 0.29 g of C₂H₅ONa were added into 15 mL of 2-methoxyethanol and stirred at room temperature to form a clear colloid. After that, 2.0 g of P-123 (M_w = 5800) dissolved in 30 mL of furfuryl alcohol was added. Next, the mixture was stirred for 60 min and then heated to 95°C with a rate of 1°C·min⁻¹ and maintained at this temperature for 120 h in air to form a black solid polymer. Finally, the black solid was oxidized in air at 500°C for 10 h, and a white powder product was obtained.

Loading the cocatalysts

The loading process was performed by a photocatalytic reduction method. 0.5wt % of Pt, Au, Cu, Pd and Ru co-catalysts were photodeposited on the NaTaO₃ catalyst by adding a calculated amount of H₂PtCl₆, HAuCl₄, CuNO₃, Pd(O₂CCH₃)₂ and RuCl₃ solution into the reaction solution, respectively. The NaTaO₃ powder (0.2 g) was dispersed by using a magnetic stirrer in CH₃OH aqueous solution (230 mL of distilled water + 50 mL of CH₃OH) in a Pyrex cell with a side window. The reactant solution was irradiated by a 300 W UV-enhanced Xe lamp ($\lambda > 200\text{nm}$) for 4 h. The H₂ evolution was measured with an online gas chromatograph (GC-8A, Shimadzu) with a thermal conductivity detector (TCD) according to the standard curve (Fig.S1). After H₂ evolution achieving a stable linear growth, the resulting NaTaO₃ photocatalyst with cocatalysts was collected after heating and drying in air overnight. The powder was then dried in vacuum at 300 °C for 3 h to remove organic compounds adsorbed on the surface of the catalyst. The obtained samples with different cocatalysts loaded were further tested for the photoactivity of CO₂ reduction.

Sample characterization

The crystal structure of NaTaO₃ powder was determined with an X-ray diffractometer (X'Pert Powder, PANalytical B.V., Netherlands) with Cu-K α radiation. Scanning electron microscopy images were recorded with a HITACHI S-4800 field emission scanning electron microscopy. Transmission electron microscopy images were recorded with a field emission transmission electron microscope (2100F, JEOL Co., Japan) operated at 200 kV. The diffuse reflection spectra were measured with an integrating sphere equipped UV–visible recording spectrophotometer (UV-2600, Shimadzu Co., Japan) using BaSO₄ as reference and the optical absorptions were converted from the reflection spectra according to Kubelka-Munk equation. The specific surface areas were determined with a surface-area analyzer (BEL Sorp-II mini, BEL Japan Co., Japan) by the Brunauer–Emmett–Teller (BET) method. X-ray Photoelectron Spectroscopy (XPS) experiments were performed in type Theta probe (ULVAC-PHI, Japan) using monochromatized Al K α at 1.4×0.1 mm 100 W(20 kV, 5 mA) and the peak positions were internally referenced to the C 1s peak at 285.0 eV.

CO₂ photoreduction

The CO₂ photoreduction experiments were carried out in a gas-closed circulation system. The NaTaO₃ powder as well as 0.5 wt% cocatalysts loaded samples (0.07 g) were located in a Pyrex reaction cell equipped with an upside window, respectively. In the case of using H₂O as the reducing agent, 3 mL of distilled water was added into the gas-closed reaction system. Then, the whole system was evacuated and filled with 80 kPa of pure CO₂ gas. In the case of using H₂ gas, the whole system was also firstly evacuated and then filled with 40 kPa of pure CO₂ gas and 40 kPa of pure H₂ gas. The light source was a

300 W UV-enhanced Xe lamp ($\lambda > 200\text{nm}$) without filter. The CO, CO₂ and organic products were sampled and measured with a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector (FID) according to the standard curves. The GC column is Porapak Q-methanizer for CO and CO₂ measurement (CH=1), PEG1000 for organic products measurement (CH=2). The H₂ evolution was measured with an online gas chromatograph (GC-8A, Shimadzu) with a TCD detector according to the standard curve. The GC column is 5A molecular sieve.

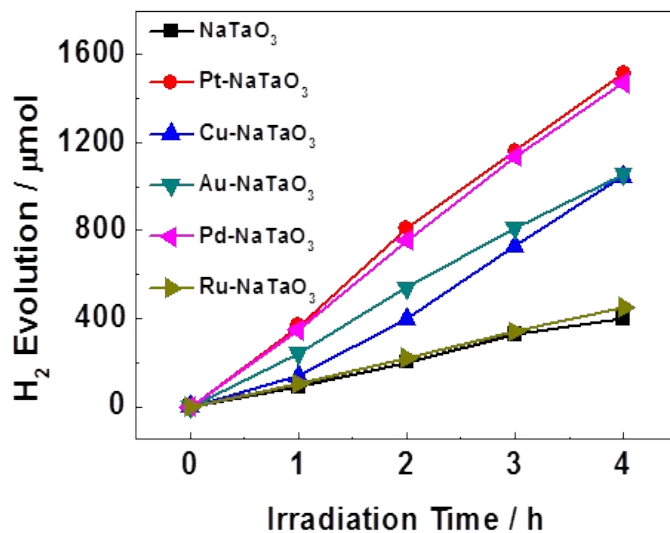
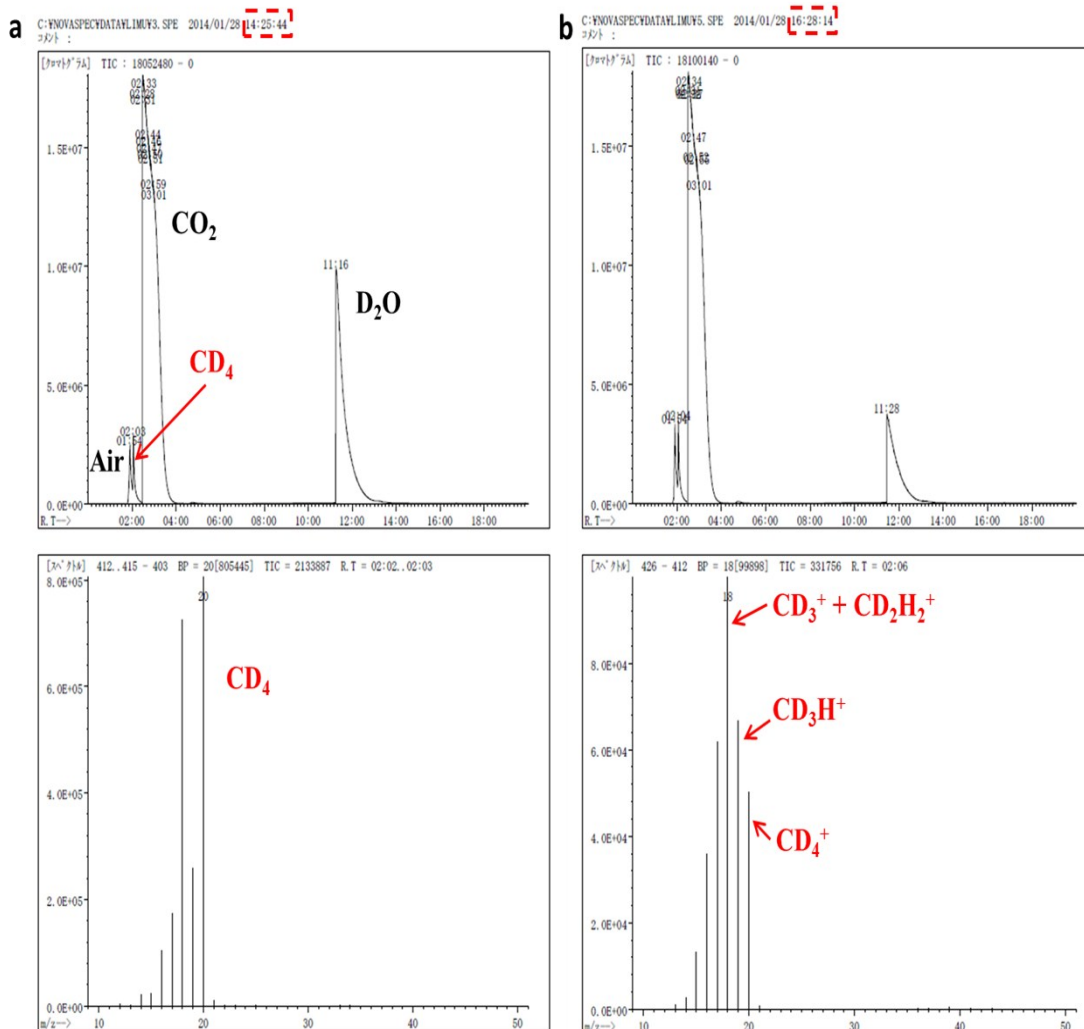
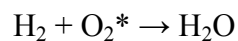


Fig. S1 Photocatalytic H₂ evolution from the aqueous methanol solution over NaTaO₃ samples with 0.5 wt% cocatalysts loading under the irradiation of a 300 W UV-enhanced Xe lamp (0.20 g catalyst).



Initial period (Fig.S2a): $\text{CO}_2 + \text{D}_2\text{O} \rightarrow \text{CD}_4 + \text{O}_2^*$



After several hours (Fig.S2b): $\text{CO}_2 + \text{D}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CD}_3\text{H} + \text{CD}_2\text{H}_2 + \text{O}_2^*$

O₂*: peroxide intermediates

Fig. S2 Original data of GC-MS spectra of photocatalytic CO₂ reduction products over Ru/NaTaO₃ under H₂ atmosphere in the present of D₂O: (a) Sampling at the initial period of the reaction, (b) sampling several hours after the reaction start.

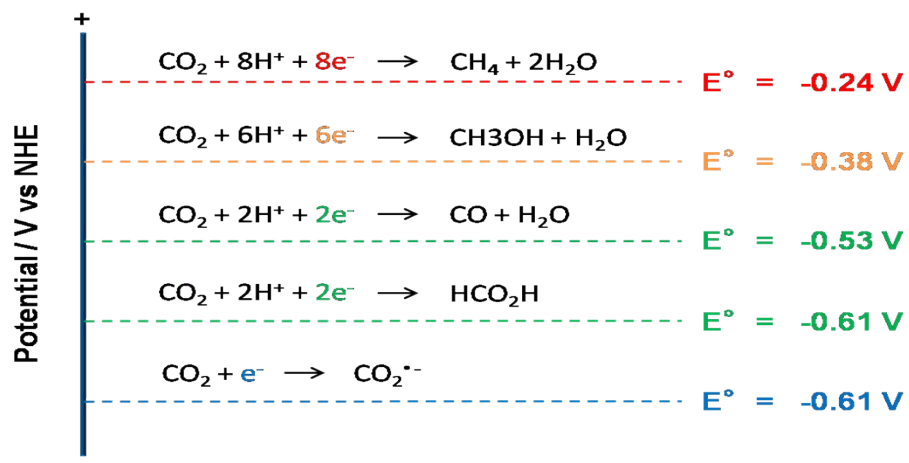


Fig. S3 Thermodynamic potentials for various CO₂ reduction products. (pH 7 vs NHE, 25 °C, 1 atm gas pressure.)

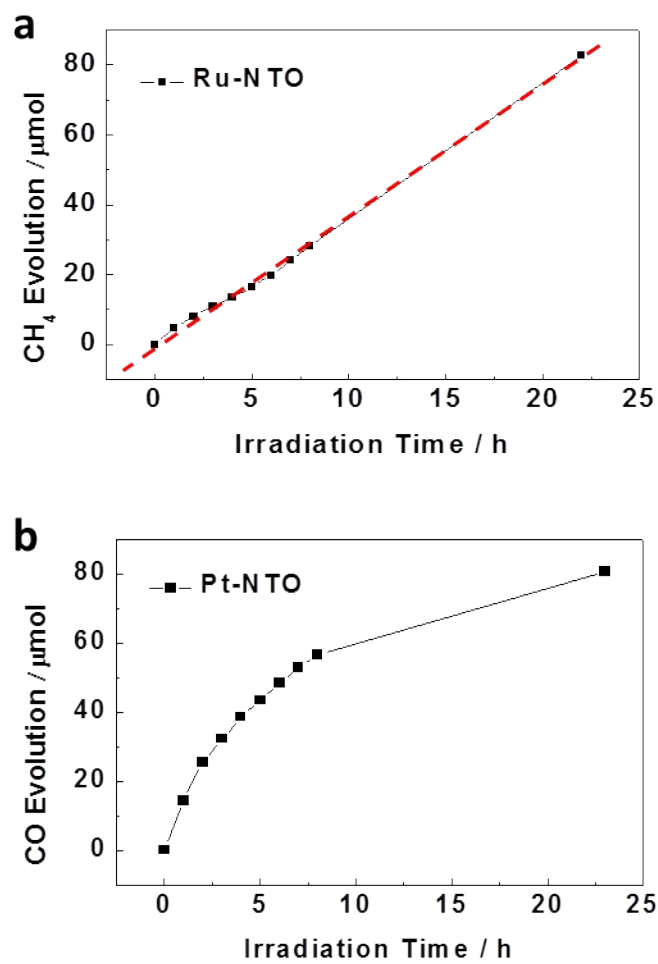


Fig. S4 An overnight prolonging text under the irradiation of a 300W UV-enhanced Xe lamp within H₂ atmosphere: (a) CH₄ evolution over Ru/NaTaO₃, (b) CO evolution over Pt/NaTaO₃.

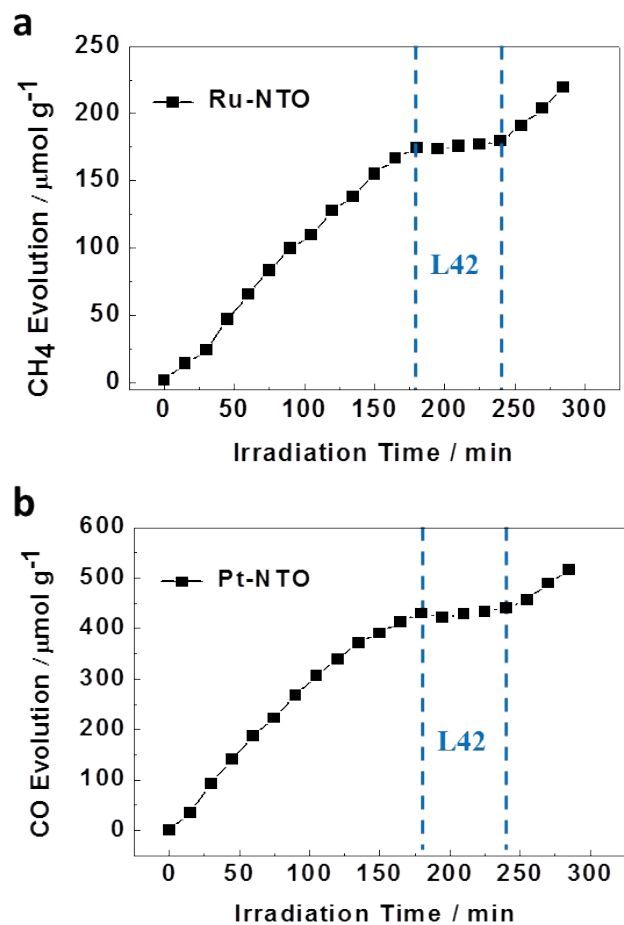


Fig. S5 UV-light responds text by inserting a cutoff 420 nm filter (L42) under the irradiation of a300W UV-enhanced Xe lamp within H₂ atmosphere: (a) CH₄ evolution over Ru/NaTaO₃, (b) CO evolution over Pt/NaTaO₃.

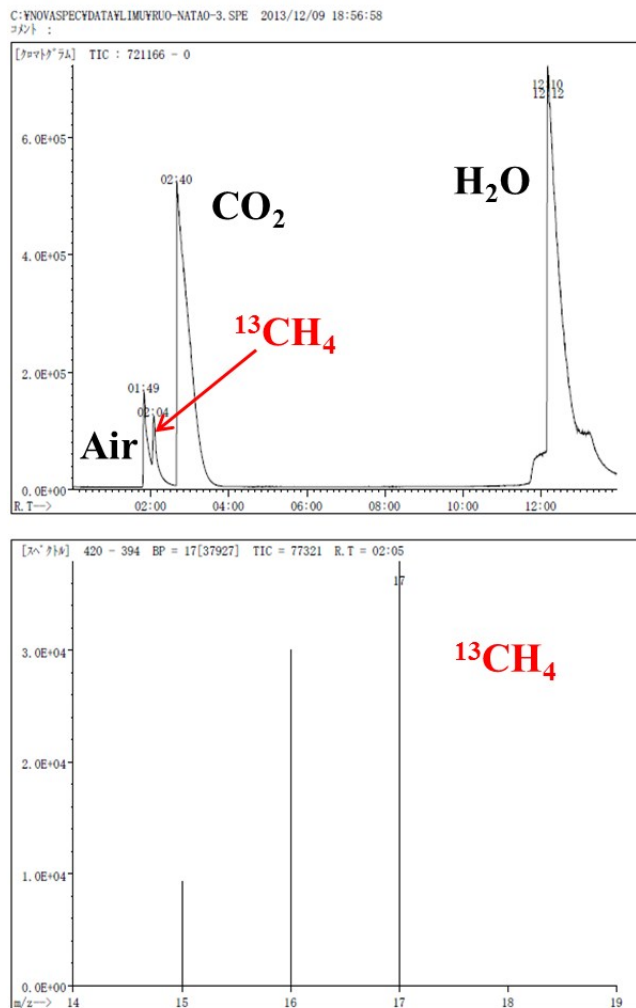


Fig. S6 Original data of GC-MS spectra of photocatalytic CO₂ reduction products over Ru/NaTaO₃ under H₂ atmosphere in the present of ¹³CO₂.

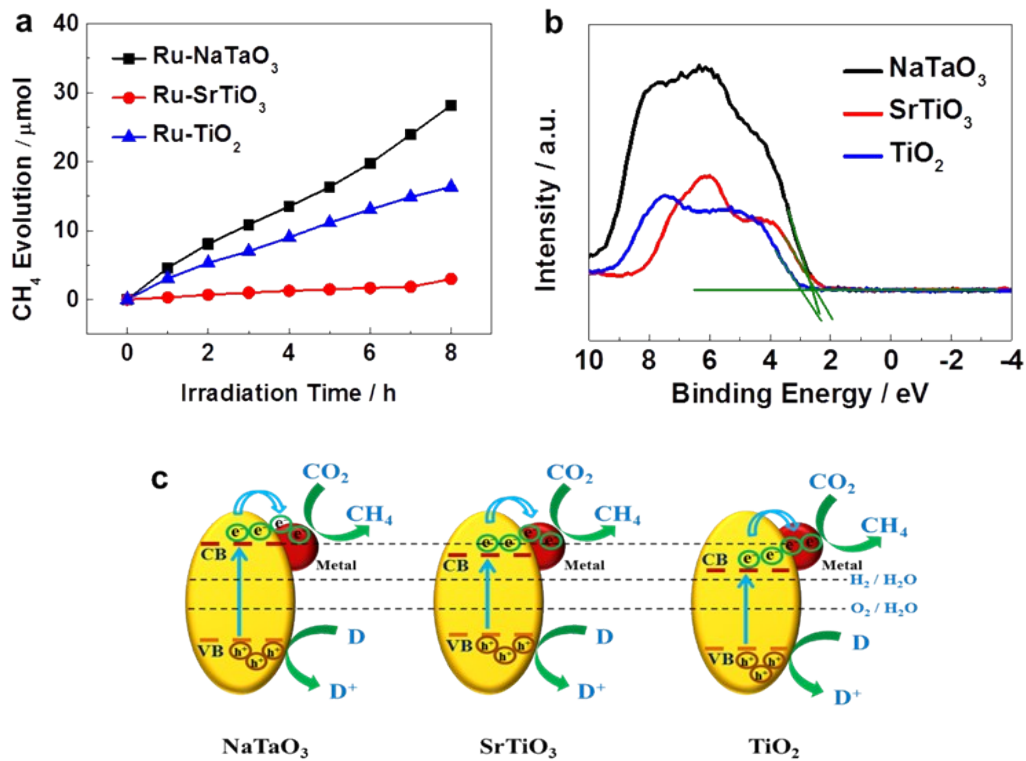


Fig. S7 (a) CH₄ evolution comparison of Ru loaded NaTaO₃, commercial SrTiO₃ (Nano-sized, Wako Pure Chemical Industries, Japan) and TiO₂ (ST01, ISHIHARA SANGYO KAISHA, Japan) under the irradiation of a 300W UV-enhanced Xe lamp within H₂ atmosphere. (b) Valence band XPS of NaTaO₃, SrTiO₃ and TiO₂. (c) Schematic model of energy levels of NaTaO₃, SrTiO₃ and TiO₂ under UV irradiation.

NaTaO₃ possess the most negative CB energy level, thus it could provide the most energetic photogenerated electrons to overcome the activation barrier and fulfill the 8e⁻ reaction during the CO₂ reduction process.

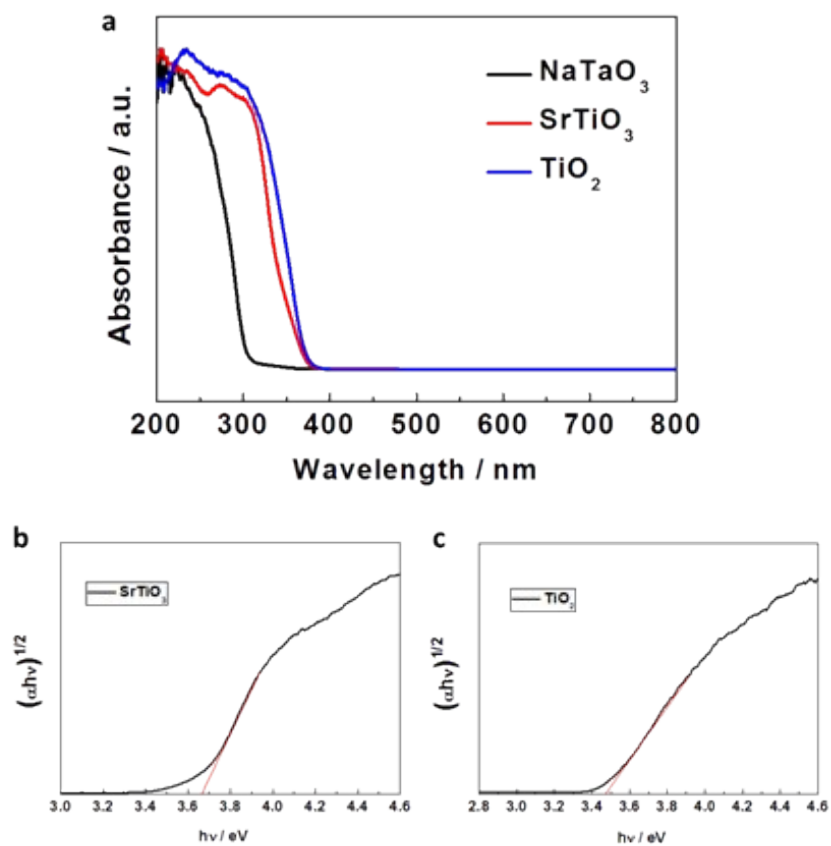


Fig. S8 (a) UV-vis absorption spectra comparison of NaTaO₃, SrTiO₃ and TiO₂; (b) the corresponding band gap obtained from $(\alpha h\nu)^{1/2} - h\nu$ curves: (b) SrTiO₃, (c) TiO₂.

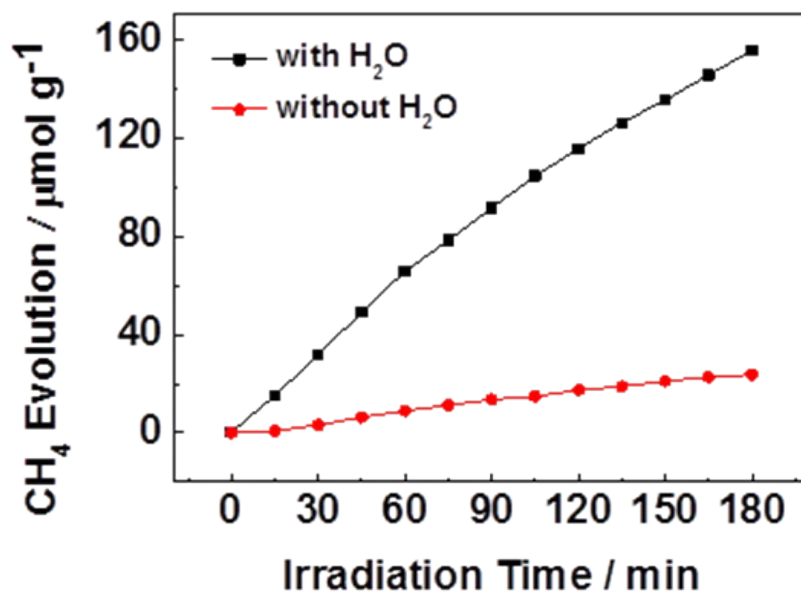


Fig. S9 CH₄ evolution comparison of Ru/NaTaO₃ with and without H₂O in presence of electron donor H₂.

The CO₂ reduction over Ru/NaTaO₃ without specifically adding the distilled water into the reaction system was compared with the water-using sample. The activity decreased obviously without water, but there is still a little amount of CH₄ could be detected. It is could be considered that these CH₄ was comes from the water remained in the system as well as the gas atmosphere, because we cannot make it an extreme anhydrous condition in our reaction system.

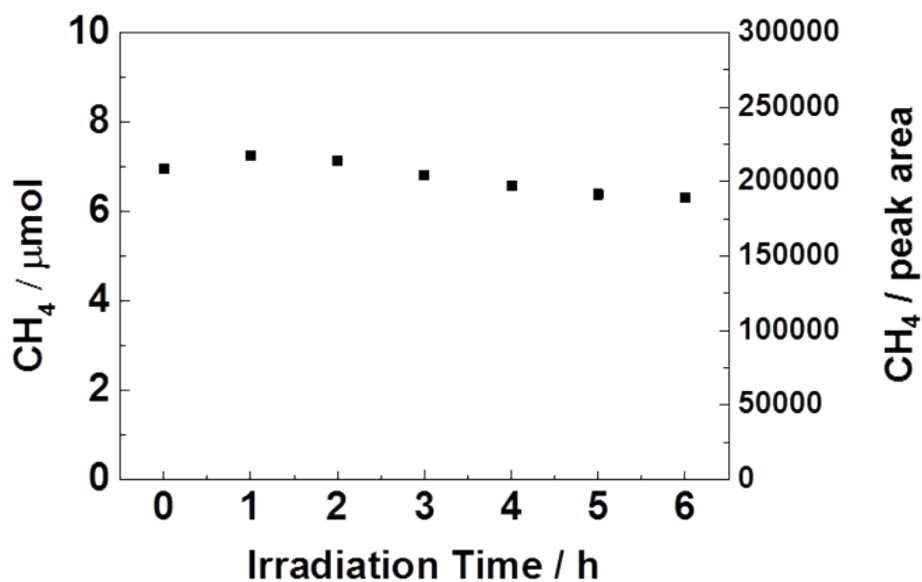


Fig. S10 Back reaction of CH₄ over Ru/NaTaO₃ under illumination.

The amount of CH₄ exhibited a fluctuation under illumination. Besides the disturbance of sampling and circulated cooling water system, there was a slightly decrease of the CH₄ amount. It can be deduced that there was a small amount of back reaction took place. Because there were large amounts of CO₂, H₂O and H₂ as electron donor in our system to carry out the CO₂ reduction, the reaction equilibrium should be mainly driven to the positive direction. Thus, this small amount of back reaction could be depressed and neglected reasonably.

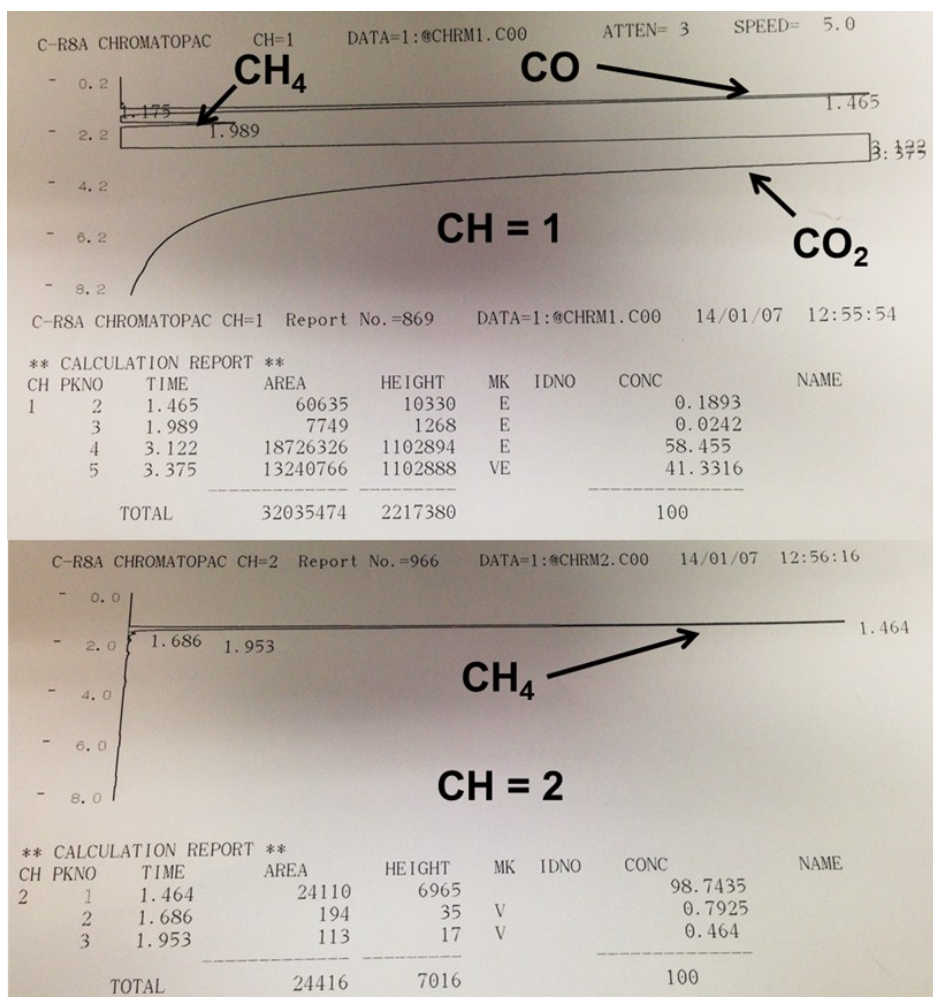


Fig. S11 An example of the original sampling data for the CO₂ reduction products over Ru-NaTaO₃, CH=1 for CO measurement; CH=2 for CH₄ measurement.

The long chain organic molecules were generated via photocatalytic reforming of CH₄, and CH₄ was the source of this reaction.^{1,2} Thus, these trace amount of organic compounds could be reasonably neglected as the products of CO₂ reduction.

(1) Yuliati, L.; Hattori, T.; Itoh, H.; Yoshida, H. *J. Catal.* 2008, 257, 396.

(2) Yuliati, L.; Hattori, T.; Yoshida, H. *Phys. Chem. Chem. Phys.* 2005, 7, 195.

Table S1. Comparison of the band gaps, BET surface areas and productivities among NaTaO₃, SrTiO₃ and TiO₂.

Materials	Band gap / eV ^a	VB / V ^b	CB / V ^c	Surface area / m ² g ⁻¹ ^d	CH ₄ productivity / μmol g ⁻¹ h ⁻¹ ^e	Normalized productivity / μmol h ⁻¹ m ⁻² ^f
NaTaO ₃	4.2	2.7	-1.5	29.2	51.8	1.72
SrTiO ₃	3.7	2.6	-1.1	14.4	5.4	0.38
TiO ₂	3.5	3.0	-0.5	302.2	29.2	0.10

^aThe band gap were obtained from UV-vis absorption spectra and the corresponding $(\alpha h\nu)^{1/2} - h\nu$ curves as shown in Fig.1c and Fig. S8. ^bThe valence band positions were obtained from valence band XPS as shown in Fig. S7. ^cThe conduction band positions were calculated from the data of band gap (E_g) and valence band by using the equation $CB = VB - E_g$. ^dThe surface area were determined by the Brunauer–Emmett–Teller (BET) method. ^eThe apparent productivity within 8 hours. ^fCalculated from dividing the apparent productivity by BET surface area.

Table S2. Productivities of the series of NaTaO₃ with and without the electron donor H₂.

Materials	CH ₄ productivity / $\mu\text{mol g}^{-1}\text{h}^{-1}$		CO productivity / $\mu\text{mol g}^{-1}\text{h}^{-1}$		H ₂ productivity / $\mu\text{mol g}^{-1}\text{h}^{-1}$	
	CO ₂ +H ₂ O	CO ₂ +H ₂ O+H ₂	CO ₂ +H ₂ O	CO ₂ +H ₂ O+H ₂	CO ₂ +H ₂ O	CO ₂ +H ₂ O+H ₂
NaTaO ₃	1.39	2.07	6.49	10.10	1.36	N/A
Pt-NaTaO ₃	0.70	1.13	5.95	139.1	80.23	N/A
Cu-NaTaO ₃	1.07	3.71	4.95	16.23	38.94	N/A
Au-NaTaO ₃	1.43	2.44	7.43	14.47	53.10	N/A
Pd-NaTaO ₃	1.73	8.61	7.56	9.71	76.43	N/A
Ru-NaTaO ₃	0.11	51.8	0.07	2.16	6.82	N/A