

Electronic Supporting Information

Photocatalytic CO₂ conversion over alkali modified TiO₂ without loading noble metal cocatalyst

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Sample preparation:

TiO₂ (commercial ST01, anatase form, mean particle size: 5 nm) powder was pretreated at 200 °C in air for 1 hour before loading NaOH. NaOH-TiO₂ composites were prepared by the impregnation of TiO₂ in aqueous solution (10 ml) containing quantitative NaOH (1, 3, 5, and 7 wt%). The suspensions were sonicated to fully disperse TiO₂ nanoparticles and then dried in a vacuum drying oven at 70 °C.

Reaction condition and activity evaluation:

The gas phase photoreduction reaction was carried out in a closed circulation system equipped with a vacuum line. The NaOH-TiO₂ photocatalyst (0.08 g) was dispersed uniformly on a quartz fiber filter with the area of 7 cm². The quartz fiber filter film is fixed on the stage inside the reaction cell. 2 ml of water was injected into the system as reducer. The system was vacuumed and then 80 kPa of CO₂ was introduced. A 300 W Xe lamp was employed as light source.

The contents of CO₂, CO and CH₄ in the reaction system were sampled and measured with a gas chromatograph (GC-14B, Shimadzu) equipped with a flame ionization detector (FID) according to the standard curves. The contents of H₂ were measured with an online gas chromatograph (GC-8A, Shimadzu) with a TCD detector according to the standard curve. Isotope experiments were performed by gas chromatography-mass spectrometry (GC-MS, JMS-K9, JEOL Co., Japan). The apparent quantum efficiency was calculated as following equation,

$$AQE = N(\text{CH}_4) \times 8 / N(\text{Photons}) \times 100\%$$

in which $N(\text{CH}_4)$ and $N(\text{Photons})$ signify the molecular number of generated CH₄ in unit time and the number of incident photons in unit time, respectively.

Sample characterization:

X-ray diffraction (XRD) patterns were recorded on an X-Pert diffractometer equipped with graphite monochromatized Cu-K α radiation. 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. Transmission electron microscopy (TEM) images were taken by a field emission transmission electron microscope (2100F, JEOL Co., Japan) operated at 200 kV. The diffuse reflection spectra of catalysts were measured by UV-visible spectrophotometer (UV-2500PC, Shimadzu Co., Japan). Surface chemical analysis was performed by X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM, ULVAC-PHI Inc., Japan). A Fourier transform-infrared (FT-IR) spectrophotometer (IR Prestige-21, Shimadzu Co., Japan) was utilized to obtain IR absorption spectra. In-situ FT-IR (FT-IR-6300, JASCO Inc.) measurement was carried out to investigate the mechanism of CO₂ conversion.

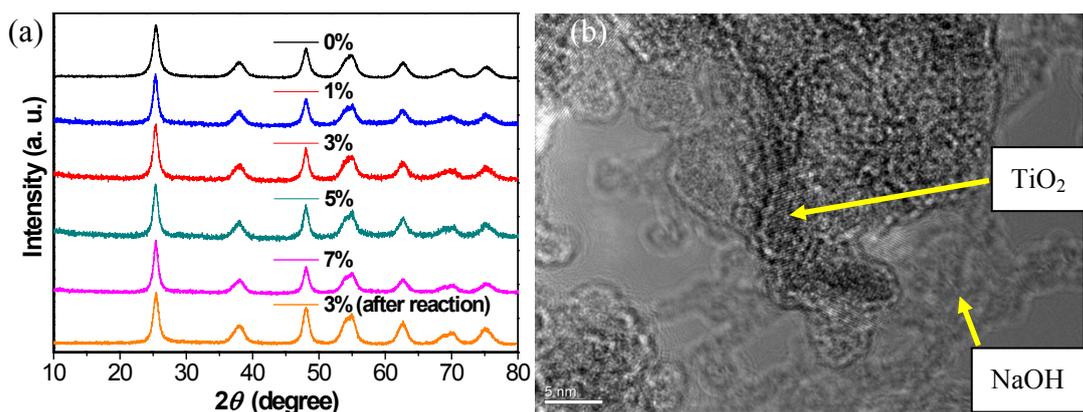


Fig. S1 (a) XRD patterns of TiO_2 and NaOH-TiO_2 composites; (b) TEM image of 3 wt% NaOH-TiO_2 composite.

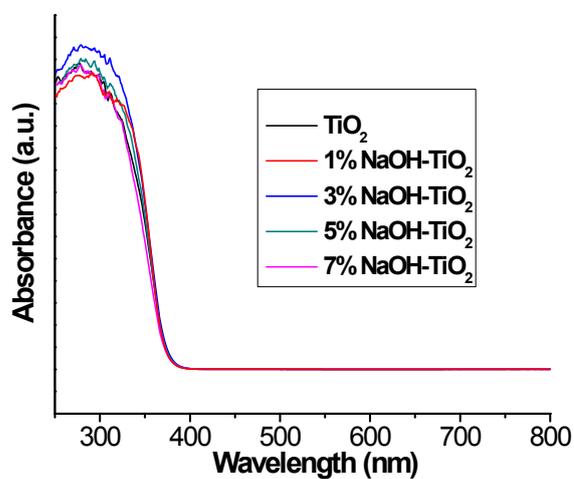


Fig. S2 UV-Vis diffused reflectance spectra of TiO_2 and NaOH-TiO_2 composites.

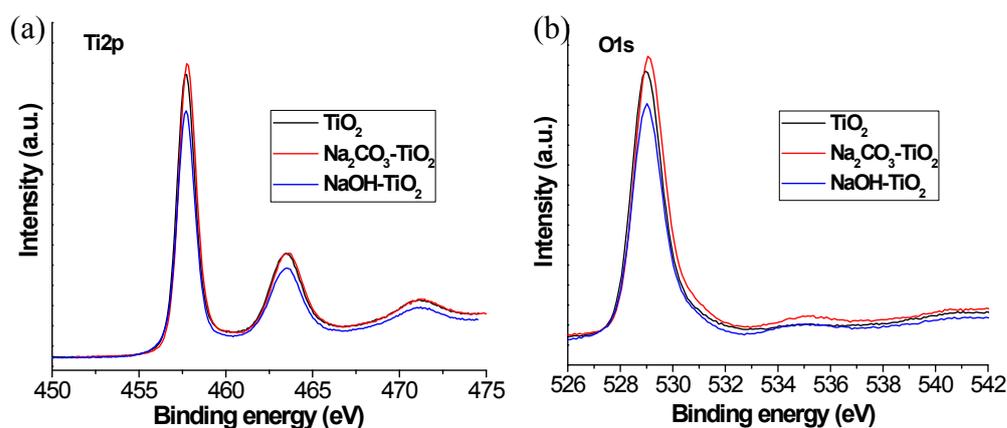


Fig. S3 XPS spectra of TiO_2 , 3.975wt% $\text{Na}_2\text{CO}_3\text{-TiO}_2$, and 3 wt% NaOH-TiO_2 composites. (a) $\text{Ti}2p$ and (b) $\text{O}1s$.

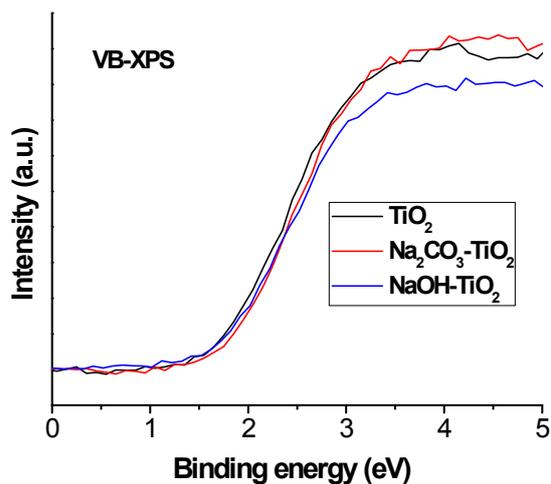


Fig. S4 Valence band-XPS of TiO_2 , 3.975 wt% $\text{Na}_2\text{CO}_3\text{-TiO}_2$, and 3 wt% NaOH-TiO_2 composites.

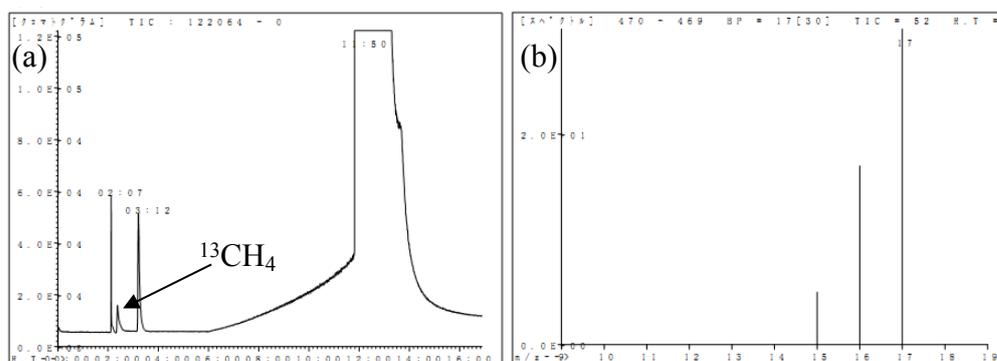


Fig. S5 (a) Gas chromatogram and (b) mass spectrum of $^{13}\text{CH}_4$ produced over 3 wt% NaOH-TiO_2 photocatalyst. Carbon dioxide $^{13}\text{CO}_2$ was used.

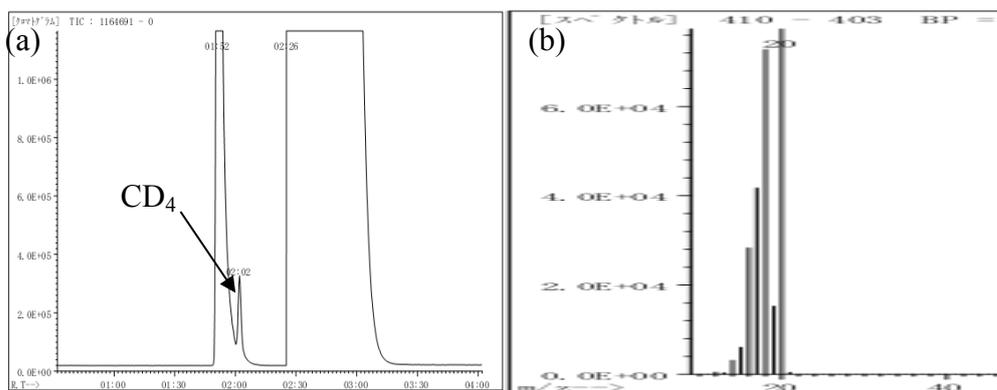


Fig. S6 (a) Gas chromatogram and (b) mass spectrum of CD_4 produced over 3 wt% NaOH-TiO_2 photocatalyst. D_2O water (purity 99.9%) was used.

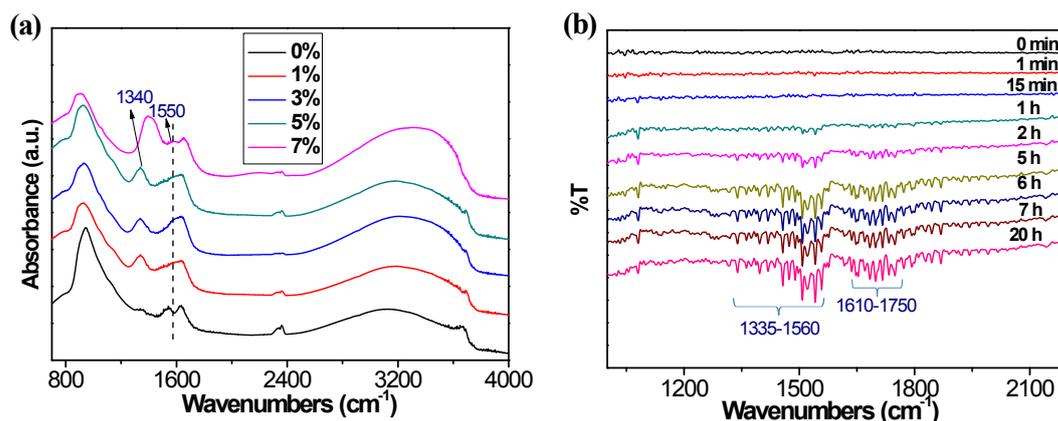


Fig. S7 (a) FT-IR spectra of NaOH-TiO₂ composites with different NaOH loading amount and (b) in-situ FT-IR spectra of CO₂ photoreduction over 3 wt% NaOH-TiO₂ photocatalyst at different irradiation times. The in-situ FT-IR spectra were measured in the presence of H₂O and CO₂ atmosphere under the irradiation from a 300W Xe lamp.

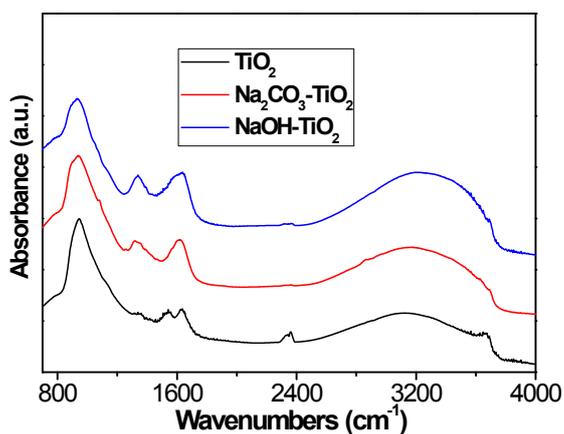


Fig. S8 FT-IR spectra of 3 wt% NaOH-TiO₂ and 3.975 wt% Na₂CO₃-TiO₂ composites (OH stretch region 2800-3500 cm⁻¹).

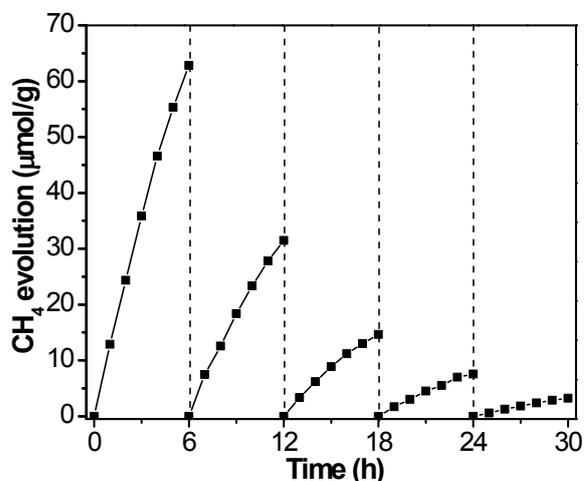


Fig. S9 cycle performance of 3 wt% NaOH-TiO₂ photocatalyst.

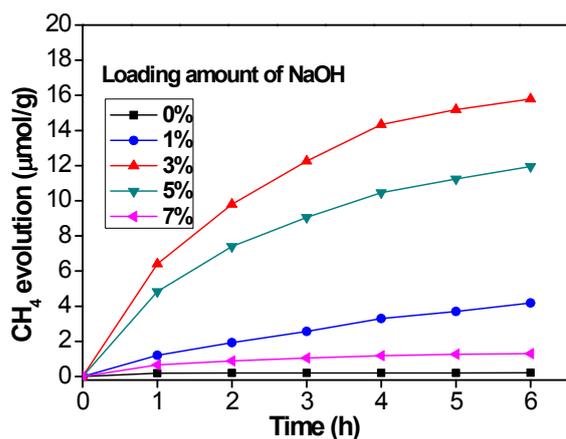


Fig. S10 Time course of CH₄ evolution over 1 wt% Pt-NaOH-TiO₂ photocatalysts.

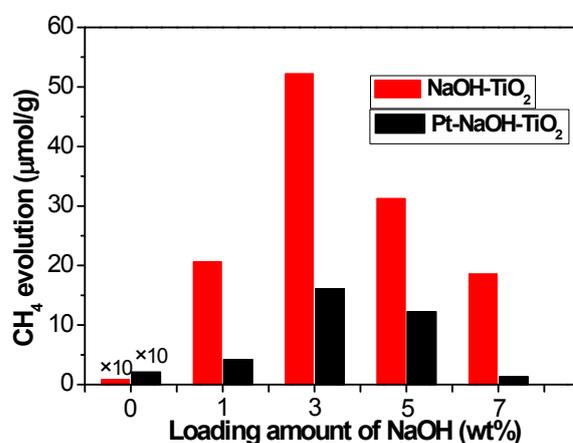


Fig. S11 Evolution amounts of CH₄ over NaOH-TiO₂ and 1 wt% Pt-NaOH-TiO₂ in the first 6 hours' irradiation from photocatalytic CO₂ conversion. The loading of 1 wt% Pt on TiO₂ was prepared by photodeposition method in aqueous solution containing H₂PtCl₆ and methanol. The obtained Pt-TiO₂ was heated at 200°C in air for 1 hour to remove the methanol. Finally, Pt-TiO₂ was impregnated in NaOH solutions.