Supporting Information

Constructing cubic-orthorhombic surface-phase junctions of $NaNbO_3$ towards significant enhancement of CO_2 photoreduction

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SI-1 Experimental Section

Material preparation.

The $NaNbO_3$ samples were synthesized via the following method. Firstly, 1.0 g of $(C_2H_5O)_5Nb$ (Strem Chem., USA) and 0.24 g of C_2H_5ONa (Strem Chem., USA) were dissolved in 15 mL of 2-methoxyethanol (Wako Chem., Japan) and stirred for 5 min to form a clear colloid. Then, this solution was added into 50 mL of 2-methoxyethanol solution containing 12.0 g of critic acid (Wako Chem., Japan) and 2.0 mL of ethylene glycol (Wako Chem., Japan). After stirred for 30 minutes, the mixture was heated to 120°C and maintained at this temperature for 20 h to form a solid precursor. Finally, the precursor was oxidized in air at 400 – 600°C for 10 h and a white powder product was obtained.

Sample characterization.

The crystal structure of $NaNbO_3$ powder was determined with an X-ray diffractometer (X'Pert Powder, PANalytical B.V., Netherlands) with Cu-Kα radiation. Transmission electron microscopy images and high-resolution 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 $BaSO_4$ 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. Photoelectron Spectroscopy (XPS) experiments were performed in type Theta probe (Thermo Fisher Co., USA) using monochromatized Al Kα at hν= 1486.6 eV and the peak positions were internally referenced to the C 1*s* peak at 284.6 eV.

Photocatalytic H_2 evolution.

The H_2 evolution experiments were carried out in a gas-closed circulation system. The $NaNbO_3$

powder (0.25 g) was dispersed by using a magnetic stirrer in CH_3OH aqueous solution (220 mL of distilled water + 50 mL of CH_3OH) in Pyrex cell with a side window. The 0.5 wt% of Pt co-catalyst was photodeposited on the $NaNbO_3$ catalyst by adding a calculated amount of H_2PtCl_6 solution into the reaction solution. The light source was a 300 W of Xe arc lamp without filter. The H_2 evolution was measured with an on-line gas chromatograph (GC-8A, Shimadzu) with a thermal conductivity detector (TCD) according to the standard curve. After the H_2 evolution persisted for 8 h, the resulting $NaNbO_3$ powder was separated by centrifugation and washed with the distilled water for several times. Then the sample was dried at 70°C and continually heated at 400°C for 3 h to remove organic compounds adsorbed on the surface of catalyst. The obtained sample with 0.5 wt% Pt-loading was further used for the CO_2 reduction experiments.

CO_2 photoreduction.

The CO_2 photoreduction experiments were carried out in a gas-closed circulation system. The $NaNbO_3$ powder with 0.5 wt% Pt-loading (0.1 g) was dispersed on a small glass cell and then located in a Pyrex reaction cell equipped with an upside window. After that, 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 CO_2 gas. The light source was a 300 W of Xe arc lamp without filter. The 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.

SI-2 TG-DTA analysis of the polymerized precursor

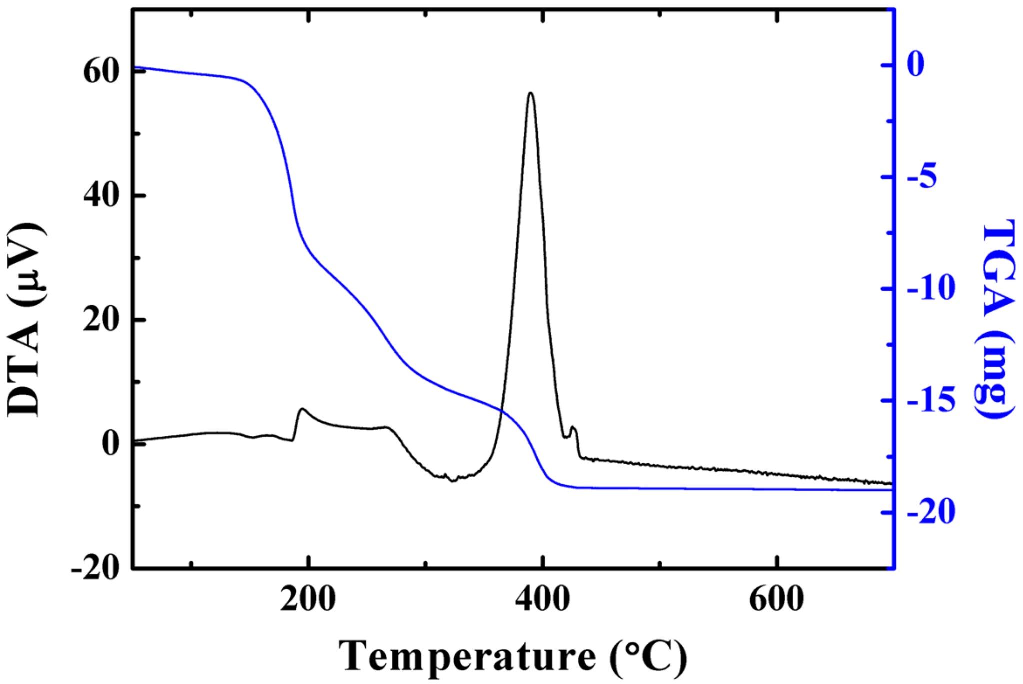

Fig. S1 TG-DTA plots of the NaNbO$_3$-poly(citric acid)-block-poly(ethylene glycol) copolymers precursor.

For the polymerized precursor, a subsequent thermogravimetric analysis (TGA) (Fig. S1) runs in air with a flow rate of 20 mL·min^{-1} shows a significant weight loss that occurs between 150 and 200°C from the evaporation of the remaining solvent. There is another weight loss between 200 and 360°C from the oxidation of low molecular weight poly(citric acid)-block-poly(ethylene glycol) copolymers to CO$_2$. The third rapid weight loss from 360 to 400°C was attributed to the decomposition of high molecular weight poly(citric acid)-block-poly(ethylene glycol) copolymers.

SI-3 Morphology of the as-prepared samples

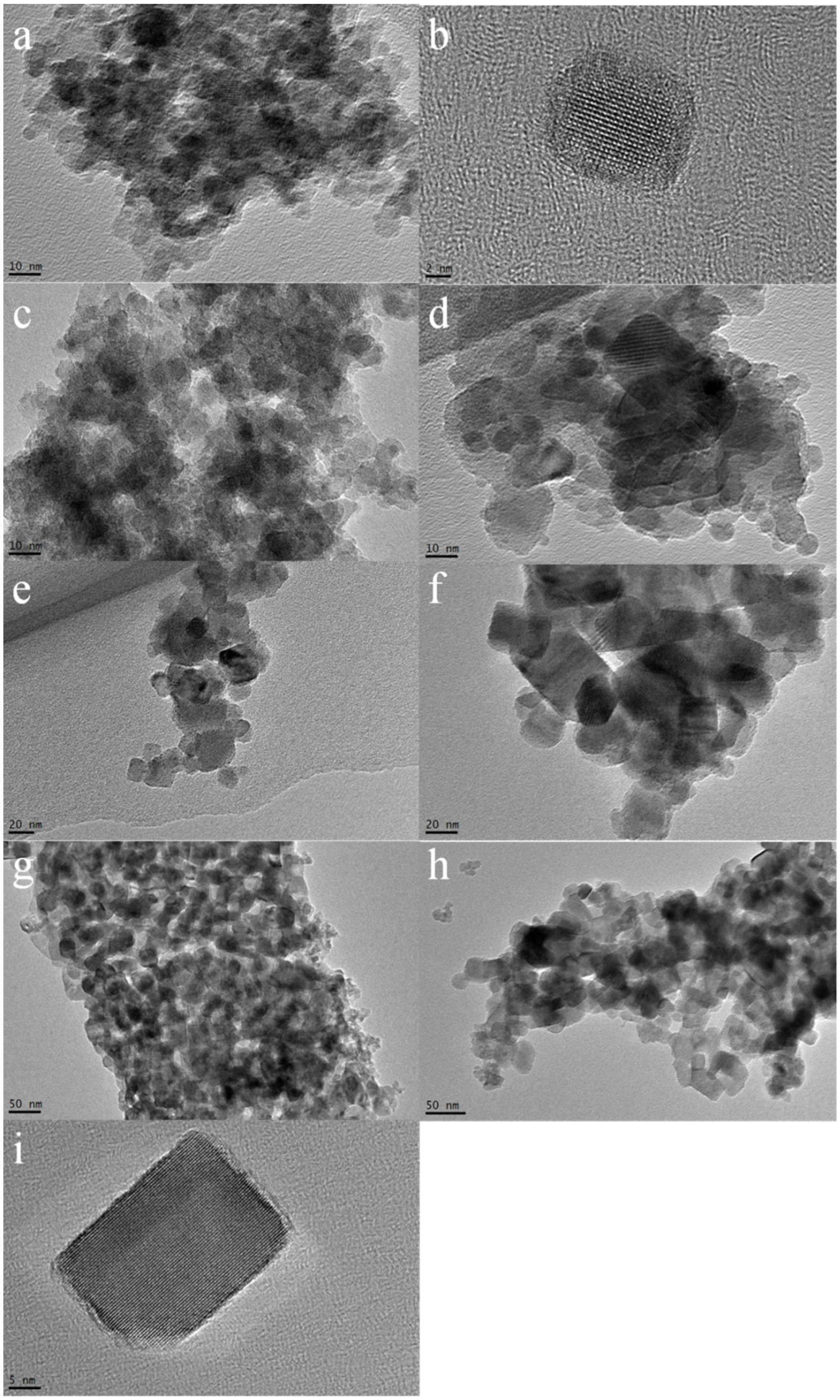

Fig. S2 TEM images of the $NaNbO_3$ samples oxidized at (a) 400°C, (c) 450°C, (d) 475°C, (e) 500°C, (f) 525°C, (g) 550°C, (h) 600°C, and HR-TEM images of the $NaNbO_3$ samples oxidized at (b) 400°C and (i) 600°C.

SI-4 Photocatalytic H_2 evolution performances of the as-prepared samples

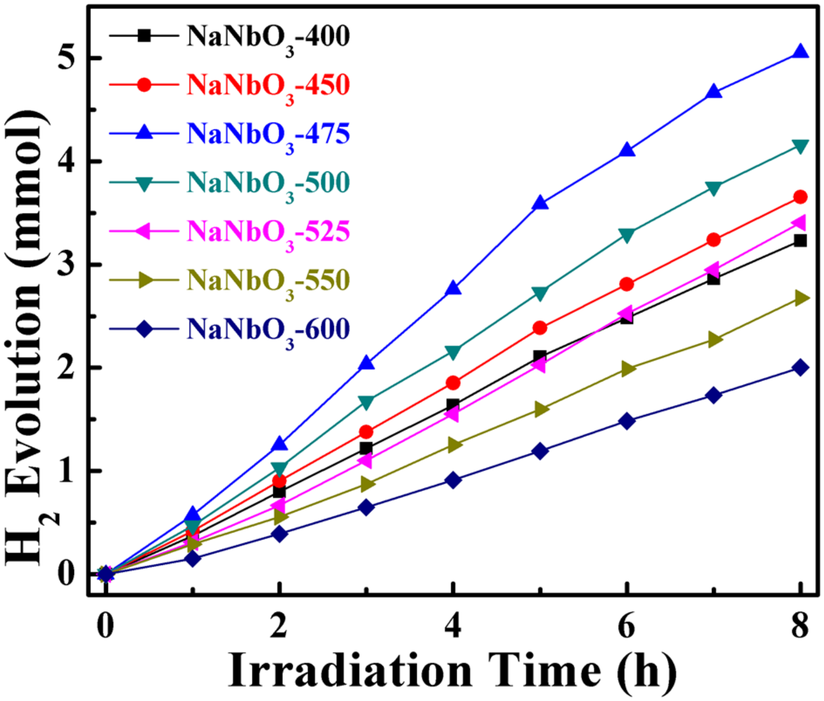

Fig. S3 Photocatalytic H_2 evolution from the aqueous methanol solution over the as-prepared $NaNbO_3$ samples with 0.5wt% Pt loading under the irradiation of 300 W Xe lamp (0.25 g catalyst, $\lambda > 300$ nm).

SI-5 The reference experiment using D_2O in photocatalytic CO_2 reduction over $NaNbO_3$-organic.

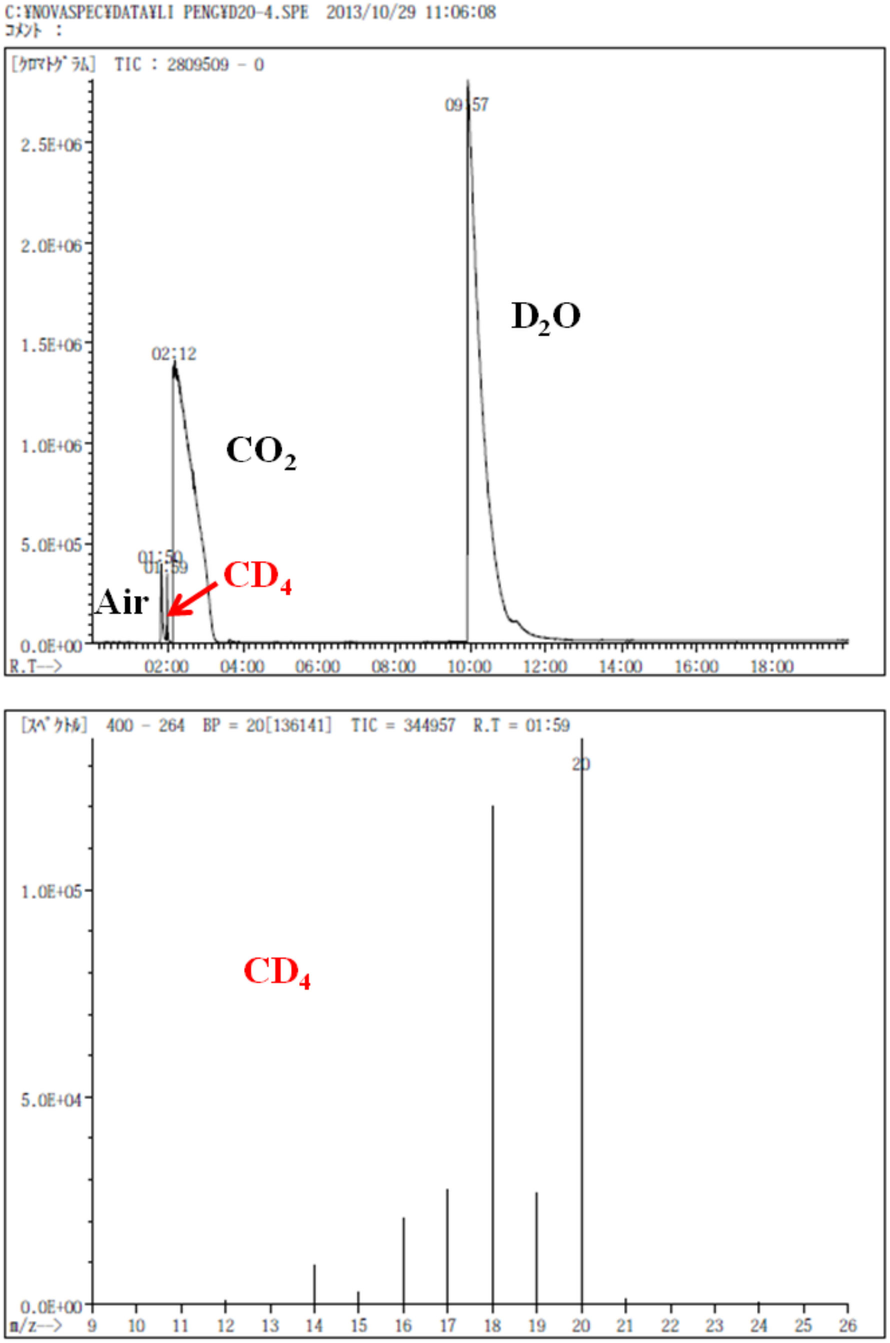

Fig. S4 GC-MS spectra of the products of photocatalytic CO_2 reduction over $NaNbO_3$-500 in the present of D_2O.

SI-6 Product evolutions over non-loaded $NaNbO_3$-500 in CO_2 reduction experiment.

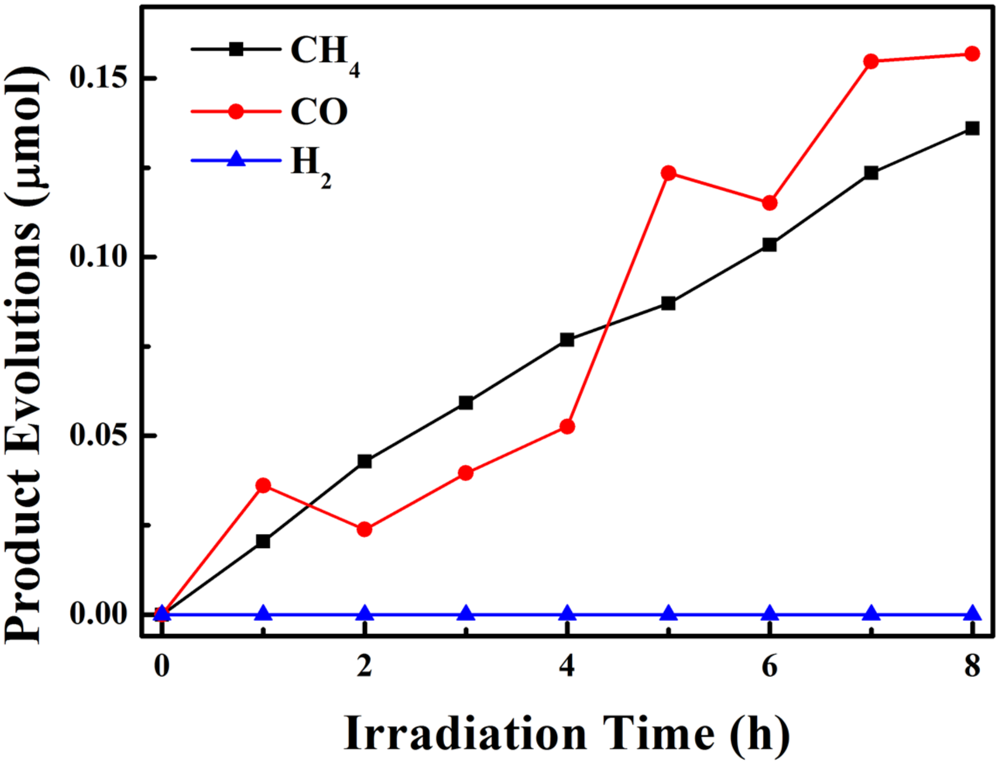

Fig. S5 CH_4, H_2 and CO evolutions over $NaNbO_3$-500 without Pt-loading.

SI-7 Products besides CH_4 generated over $NaNbO_3$ in CO_2 reduction experiments.

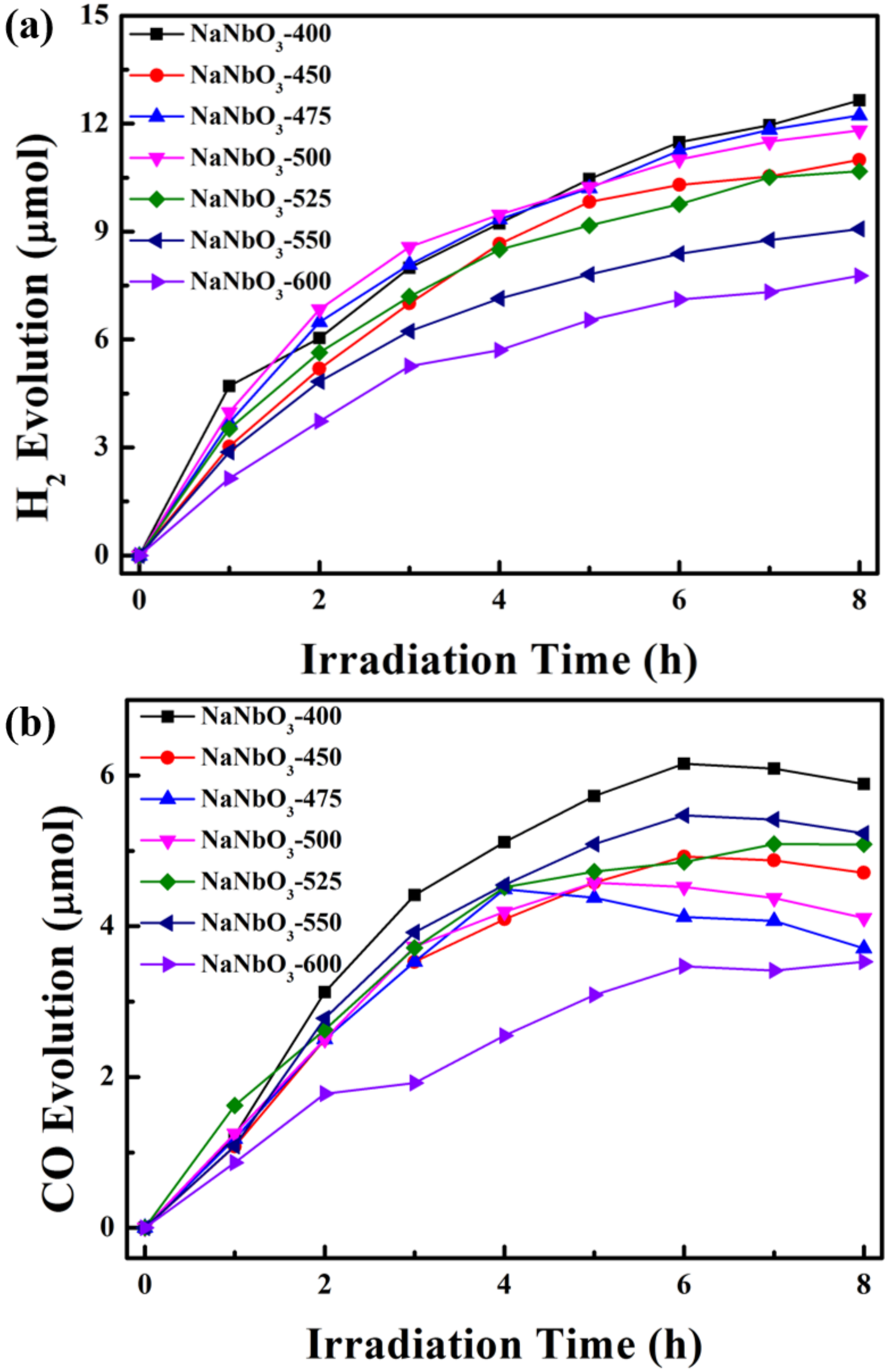

Fig. S6 H_2 and CO evolutions over the as-prepared $NaNbO_3$ samples in CO_2 reduction experiments.

SI-8 Phase contents, surface areas and photocatalytic performances of the as-prepared $NaNbO_3$ samples

Tab. S1 Calculated phase contents and crystal sizes of the as-prepared $NaNbO_3$ samples.

Photocatalyst	Cubic phase content (%)	Cubic crystal size (nm)	Orthorhombic phase content (%)	Orthorhombic crystal size (nm)
$NaNbO_3$-400	98.2	8.2	1.83	48
$NaNbO_3$-450	83.9	6.8	16.1	32
$NaNbO_3$-475	68.8	8.7	31.2	36
$NaNbO_3$-500	46.8	15	53.2	59
$NaNbO_3$-525	28.7	13	71.3	65
$NaNbO_3$-550	11.1	22	88.9	80
$NaNbO_3$-600	0		100	140

Tab. S2 Surface areas and photocatalytic performances of the as-prepared $NaNbO_3$ samples.

Photocatalyst	Surface area ($m^2 \cdot g^{-1}$)	H_2 evolution rate ($\mu mol \cdot h^{-1}$)	CH_4 evolution rate ($\mu mol \cdot h^{-1}$)
$NaNbO_3$-400	71.2	419	0.491
$NaNbO_3$-450	64.4	457	0.546
$NaNbO_3$-475	58.2	631	0.586
$NaNbO_3$-500	50.2	475	0.575
$NaNbO_3$-525	43.1	426	0.496
$NaNbO_3$-550	34.5	335	0.339
$NaNbO_3$-600	28.3	249	0.219