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Supporting information

Na-containing Pt cocatalyst for efficient visible-light-induced hydrogen evolution on $BaTaO_2N$

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Experimental Section

Preparation of photocatalysts: $BaTaO_2N$ powder was prepared by one-pot flux-assisted nitridation.[s1] In this process, $BaCO_3$ and Ta_2O_5 were combined in a Ba/Ta atomic ratio of 1:1 and RbCl was employed as the flux agent, with a solute concentration of 10 mol.%. A 2 g quantity of this mixture was thoroughly blended and then heated at 1223 K for 8 h under a flow of ammonia (200 mL min^{-1}). The resulting $BaTaO_2N$ was washed with water and dried to give the final product. All chemicals were used directly as received.

Modification of $BaTaO_2N$ with Na-containing Pt nanoparticulate cocatalyst: The Na-containing Pt cocatalyst was loaded using an impregnation method, employing NaOH and H_2PtCl_6 in aqueous solution as the precursors. In a typical process, $BaTaO_2N$ powder (100 mg) was immersed in an aqueous solution containing these precursors at loading amounts of 0.28 wt% as Pt and 0.23 wt% as Na with respect to the photocatalyst, after which the solution was heated in a boiling water bath. The product was completely dried and then heated at 523 K for 1 h in a flow of 10% H_2 in N_2. For comparison, the reduction temperature was also varied from 473-623 K. To investigate the possibility of Na doping into $BaTaO_2N$, $BaTaO_2N$ was first impregnated with NaOH followed by hydrogen reduction. After washing by water and drying, the obtained $BaTaO_2N$ was loaded with Pt by impregnation and subsequent hydrogen reduction. Then, the hydrogen evolution reaction was carried out using this photocatalyst.

Modification of PtO_x/WO_3 for O_2 evolution: The as-purchased WO_3 was loaded with PtO_x using an impregnation method, followed by calcination in air at 773 K for 1 h.[s2] The resulting PtO_x/WO_3 was then loaded with 1 at% Cs^+ ions via impregnation using an aqueous cesium carbonate solution, followed by calcination in air at 773 K for 0.5 h. Following this, the modified PtO_x/WO_3 was stirred in 35 ml of a 1 M aqueous H_2SO_4 solution, with subsequent washing and drying to obtain the final product, which is denoted as $H^+\text{-}Cs^+/PtO_x/WO_3$.

Characterization: The as-prepared $BaTaO_2N$ was analyzed by powder X-ray diffraction (XRD; Rigaku MiniFlex 300; Cu-K_α), ultraviolet/visible diffuse reflectance spectroscopy (UV/vis-DRS; JASCO V-670), X-ray photoelectron spectroscopy (XPS; PHI Quantera II (Ulvac-PHI, Inc.) and scanning transmission electron microscopy (STEM; JEOL JEM-2800). Transient absorption (TA) spectroscopic measurement was carried out using a Nd:YAG laser system (Continuum, Surelite I; duration: 6 nm) equipped with custom-built spectrometers.[S3] The photocarriers were monitored at 649 nm. The probe beam (coming from the halogen lamp) was focused on the sample and was reflected from the sample and entered the monochromatic grating spectrometer. The monochromated light was then detected by Si photodetectors. The output electric signal was amplified with an AC-coupled amplifier (Stanford Research Systems, SR560, 1 MHz). The time resolution of the spectrometer was limited to 1 μs by the response of photodetectors. One thousand responses were accumulated to obtain the transient profile (decay curve) at 649 nm. The pristine $BaTaO_2N$, Pt/$BaTaO_2N$, and Na-containing Pt/$BaTaO_2N$ photocatalysts were photoexcited using the 470 nm pump pulses with a fluence of 3 mJ $pulse^{-1}$. Each powder sample was fixed on circular CaF_2 substrate by drop-casting with a density of 1.24 mg cm^{-2}. The TAS experiment was carried out in a vacuum at room temperature. The elemental analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Shimadzu, ICPS-8100).

Photocatalytic H_2 evolution reaction: Hydrogen evolution reactions over Na-containing Pt/$BaTaO_2N$ photocatalysts were performed at room temperature in a Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system. In each trial, a quantity of the Na-containing Pt/$BaTaO_2N$ (100 mg) was dispersed in an aqueous methanol solution (15 vol%, 150 mL) using a magnetic stirrer. The vessel was subsequently evacuated several times to ensure complete air removal. The activity of a photocatalyst can depend on the pressure in the reaction system.[S4] To minimize the change of the pressure by gas evolution and heating of the reaction solution by lamp irradiation, Ar was introduced to the reaction system prior to the reaction to a pressure of approximately 10 kPa. The reaction was initiated by irradiation with a 300 W Xe lamp fitted with a cutoff filter and a dichroic mirror (420 nm < λ < 800 nm), and a flow of cooling water was used to keep the suspension at approximately 284 K. The evolved gases were analyzed by gas chromatography (GC; Shimadzu, GC-8A with a thermal conductivity detector, MS-5 A column, Ar as the carrier gas). The apparent quantum yield (AQY) for photocatalytic reaction over Na-containing Pt/$BaTaO_2N$ at 420 nm was measured similarly as in our previous paper.[s4] The same light source equipped with a 420 nm band-pass filter was used. The number of incident photons illuminating the reaction cell was measured using a grating spectroradiometer.

Photocatalytic overall water splitting: Reactions were carried out using the same reactor and system described above. In each experiment, Na-containing Pt/$BaTaO_2N$, acting as the H_2 evolution photocatalyst (100 mg), and modified H^+-Cs^+/PtO_x/WO_3, acting as the O_2 evolution photocatalyst (200 mg), were suspended in 150 ml of an aqueous NaI solution (2 mM) without pH adjustment. After complete degassing, Ar gas was introduced to the reaction system to an initial pressure of 10 kPa. Following this, the suspension was irradiated with the Xe lamp and cooling water system (at 284 K) as described above. The evolved gases were also analyzed by the same gas chromatography instrumentation.

Reference

s1 Y. Luo, S. Suzuki, Z. Wang, K. Yubuta, J. Vequizo, A. Yamakata, H. Shiiba, T. Hisatomi, K. Domen, K. Teshima, *ACS Appl. Mater. Interfaces* 2019, **11**, 22264-22271.

s2 Y. Miseki, S. Fujiyoshi, T. Gunji, K. Sayama, *Catal. Sci. Technol.* 2013, **3**, 1750-1756.

S3. A. Yamakata, M. Kawaguchi, N. Nishimura, T. Minegishi, J. Kubota, K. Domen, *J. Phys. Chem. C*. 2014, **118**, 23897-23906.

S4. Z. Wang, Y. Luo, T. Hisatomi, J. Vequizo, S. Suzuki, S. Chen, M. Nakabayashi, L. Lin, Z. Pan, N. Kariya, A. Yamakata, N. Shibata, T. Takata, K. Teshima, K. Domen, *Nature Comm*. 2021, **12**, 1005.

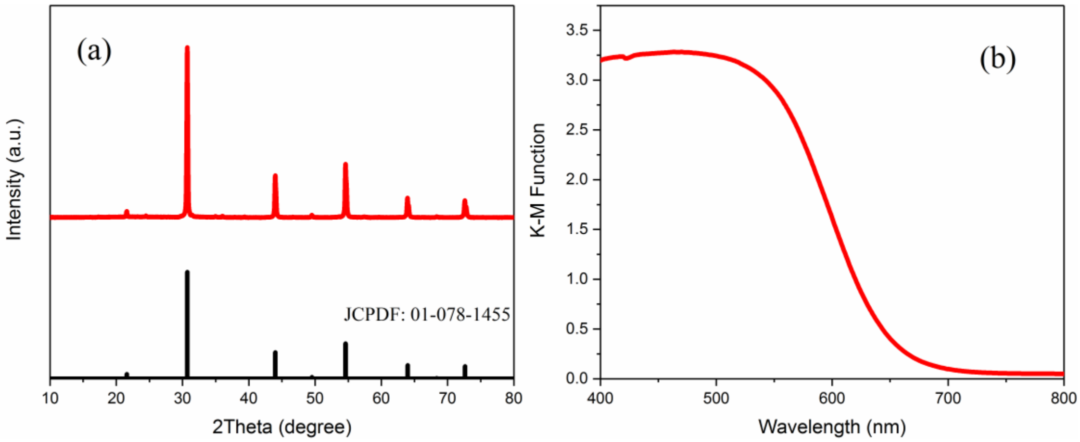

Fig. S1. (a) XRD pattern and (b) DRS spectrum for $BaTaO_2N$. The small impurity peaks in the XRD pattern at 24.5°, 31.5°, 36.0° were ascribed to Ta_3N_5.

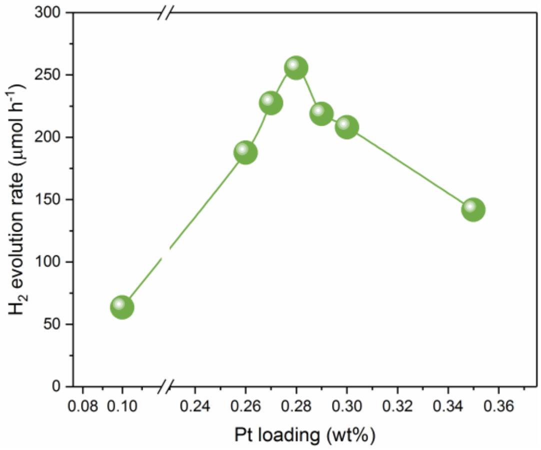

Fig. S2. Effect of Pt loading amount (with constant Na ion level of 0.23 wt%) on photocatalytic H_2 production rate.

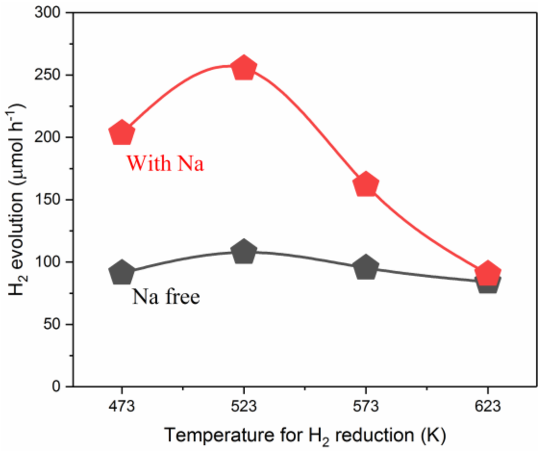

Fig. S3. Effect of hydrogen reduction temperature on photocatalytic H_2 production rate.

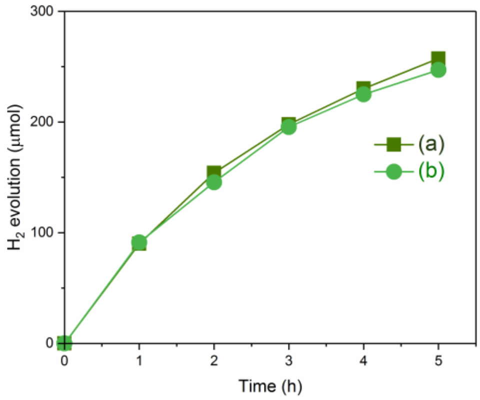

Fig. S4. Time courses of H_2 evolution over (a) $BaTaO_2N$ treated with NaOH (0.23 wt% Na) and subsequently loaded with 0.28 wt% Pt, and (b) $BaTaO_2N$ loaded with 0.28 wt% Pt directly. Reaction conditions: 100 mg of photocatalyst; 150 mL aqueous methanol solution (15 vol.%); light source, Xe lamp (420 nm < λ < 800 nm).

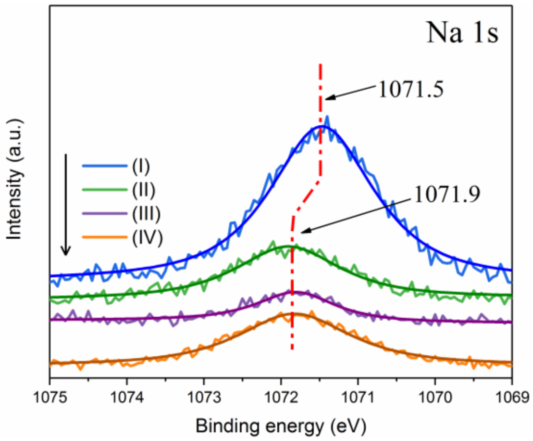

Fig. S5. Na 1s XPS spectra obtained from (I) Na-loaded $BaTaO_2N$, (II) fresh Na-containing Pt/$BaTaO_2N$ before a reaction, and (III) Na-containing Pt/$BaTaO_2N$ after a hydrogen evolution reaction for 5 h, and (IV) Na-containing Pt/$BaTaO_2N$ dispersed in methanol aqueous solution without irradiation for 5 h.

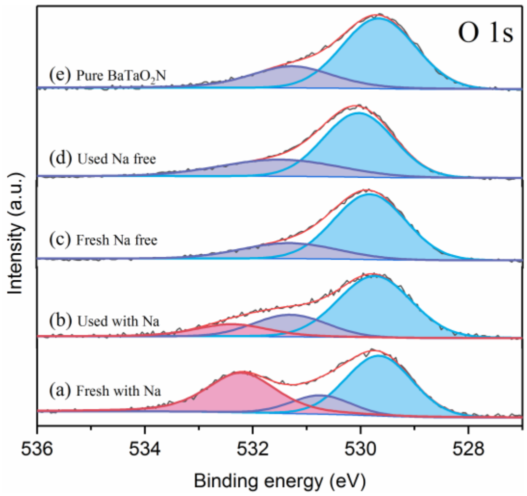

Fig. S6. O 1s XPS spectra obtained from (a,b) Na-containing and (c,d) Na-free Pt/$BaTaO_2N$ (a,c) before and (b,d) after 5 h H_2 evolution reactions, and (e) spectrum for pure $BaTaO_2N$.

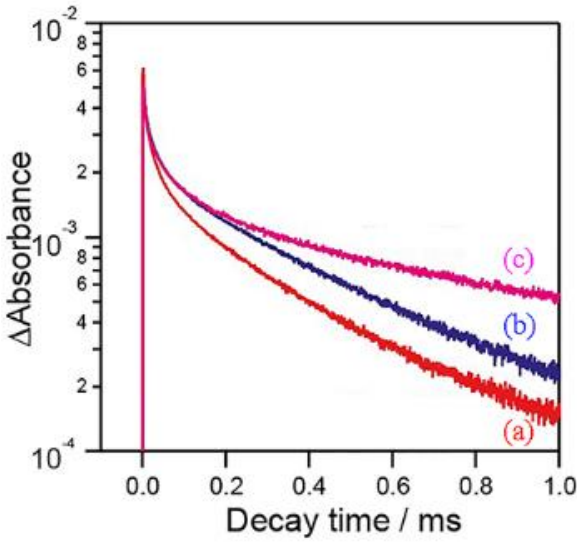

Fig. S7. Transient absorption profiles of photoinduced holes probed at 15400 cm^{-1} (649 nm, 1.91 eV) for (a) bare $BaTaO_2N$, (b) Na-free Pt/$BaTaO_2N$, and (c) Na-containing Pt/$BaTaO_2N$.

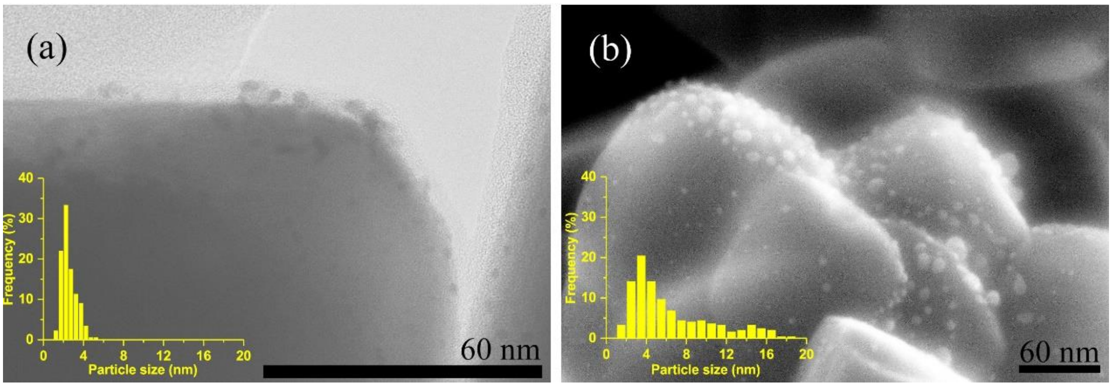

Fig. S8. STEM images and particle size distributions (insets, 300 particles counted) obtained for (a) Na-containing and (b) Na-free Pt/$BaTaO_2N$ after 5 h water splitting reactions.

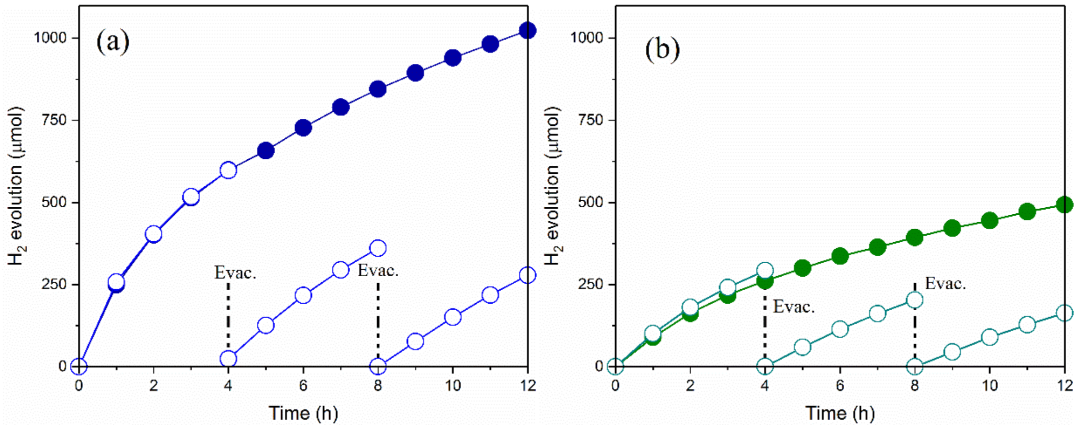

Fig. S9. Time courses of H_2 evolution over (a) Na-containing and (b) Na-free Pt/$BaTaO_2N$ photocatalysts with and without intermittent evacuation. Closed and open symbols represent measurements without and with intermittent evacuation, respectively.

Table S1. Bulk elemental compositions for Na-Pt/$BaTaO_2N$ and Pt/$BaTaO_2N$ photocatalysts before and after 5-h reaction.

Photocatalyst		Weight ratio[a] (%)		
		Ba	Ta	Na
Na-Pt/$BaTaO_2N$	Before	38.01	49.76	0.22
	After	37.16	49.73	0.03
Pt/$BaTaO_2N$	Before	38.21	49.55	0
	After	37.72	49.47	0

[a] Determined by ICP-OES analysis.

Table S2. Fitting results for Pt 4f and O 1s XPS spectra for Na-containing and Na-free $BaTaO_2N$ before and after 5 h reactions.

Photocatalyst[a]	Pt $4f_{7/2}$			O 1s		
	Peak Position (eV)	FWHM (eV)	Fraction	Peak Position (eV)	FWHM (eV)	Fraction
With Na	70.9 72.1	1.7 2.3	0.5 0.5	529.7 530.7 532.2	1.5 1.3 1.5	0.5 0.1 0.4
Na free	70.9 72.6	1.6 1.8	0.6 0.4	529.8 531.3	1.6 2.1	0.8 0.2
Used with Na	70.7 72.3	1.7 1.8	0.8 0.2	529.7 531.3 532.4	1.6 1.6 1.6	0.6 0.2 0.2
Used Na free	70.6 72.1	1.4 1.7	0.7 0.3	530.0 531.5	1.5 2.6	0.7 0.3
Pure $BaTaO_2N$	-	-	-	529.7 531.3	1.6 1.8	0.7 0.3

[a] Used catalysts analysed after testing in 150 mL of methanol aqueous solution (15 vol%) under visible light irradiation for 5 h.