

# Zr-doped BaTaO<sub>2</sub>N photocatalyst modified with Na-Pt cocatalyst for efficient hydrogen evolution and Z-scheme water splitting

Huihui Li<sup>a,b</sup>, Junie Jhon M. Vequizo<sup>b</sup>, Takashi Hisatomi<sup>b,c</sup>, Mamiko Nakabayashi<sup>d</sup>,  
Jiadong Xiao<sup>b</sup>, Xiaoping Tao<sup>b</sup>, Zhenhua Pan<sup>b</sup>, Wenpeng Li<sup>e</sup>, Shanshan Chen<sup>f</sup>,  
Zheng Wang<sup>g</sup>, Naoya Shibata<sup>d</sup>, Akira Yamakata<sup>h</sup>, Tsuyoshi Takata<sup>b</sup>, and Kazunari  
Domen<sup>b,i,\*</sup>

<sup>a</sup> School of Materials and Energy, Lanzhou University, 222 South Tianshui Road, Lanzhou 730000, China.

<sup>b</sup> Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, Nagano-shi, Nagano 380-8553, Japan.

<sup>c</sup> PRESTO, JST, 4-17-1 Wakasato, Nagano-shi, Nagano 380-8553, Japan

<sup>d</sup> Institute of Engineering Innovation, The University of Tokyo, Tokyo 113-8656, Japan.

<sup>e</sup> Department of Science and Technology, Graduate School of Medicine, Science and Technology, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan.

<sup>f</sup> School of Materials Science and Engineering & National Institute for Advanced Materials, Nankai University, Tianjin 300-350, China

<sup>g</sup> Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

<sup>h</sup> Faculty of Natural Science and Technology, Okayama University, 3-1-1, Tsushima-naka, Kita-ku, Okayama, Japan

<sup>i</sup> Office of University Professors, The University of Tokyo, 2-11-16 Yayoi, Bunkyo-ku, Tokyo 113-8656, Japan.

\*Corresponding author.

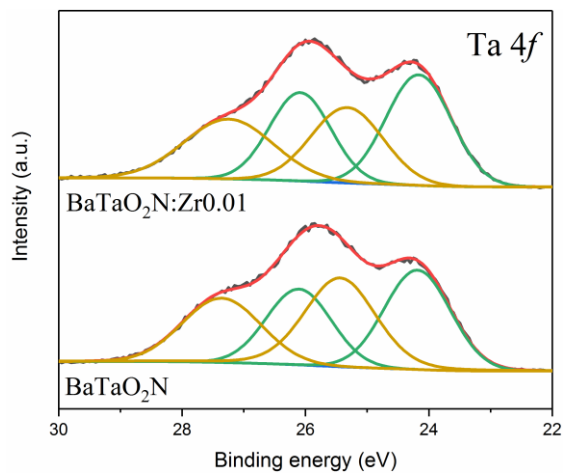
Email: [domen@shinshu-u.ac.jp](mailto:domen@shinshu-u.ac.jp)

**Table S1.** Chemical compositions of three BaTaO<sub>2</sub>N samples.

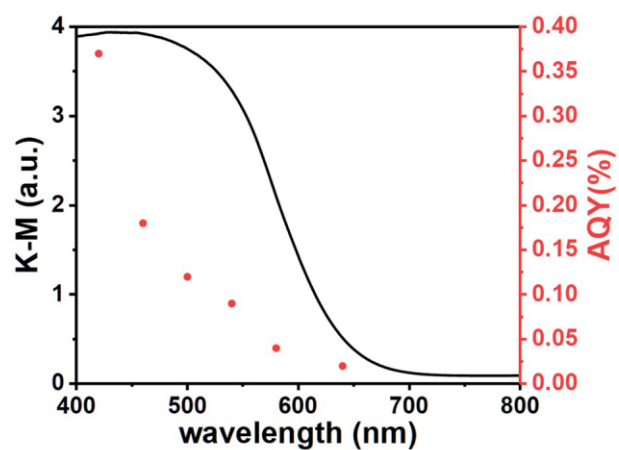
Sample	Atomic ratio (at%)				
	Ba <sup>a</sup>	Ta <sup>a</sup>	Zr <sup>a</sup>	O <sup>b</sup>	N <sup>b</sup>
BaTaO <sub>2</sub> N	20.24	20.04	-	38.88	20.84
BaTaO <sub>2</sub> N:Zr0.01	19.19	20.00	0.20	39.60	21.01
BaTaO <sub>2</sub> N:Zr0.1	18.29	18.89	1.99	40.76	20.08

<sup>a</sup>Measured by ICP-OES

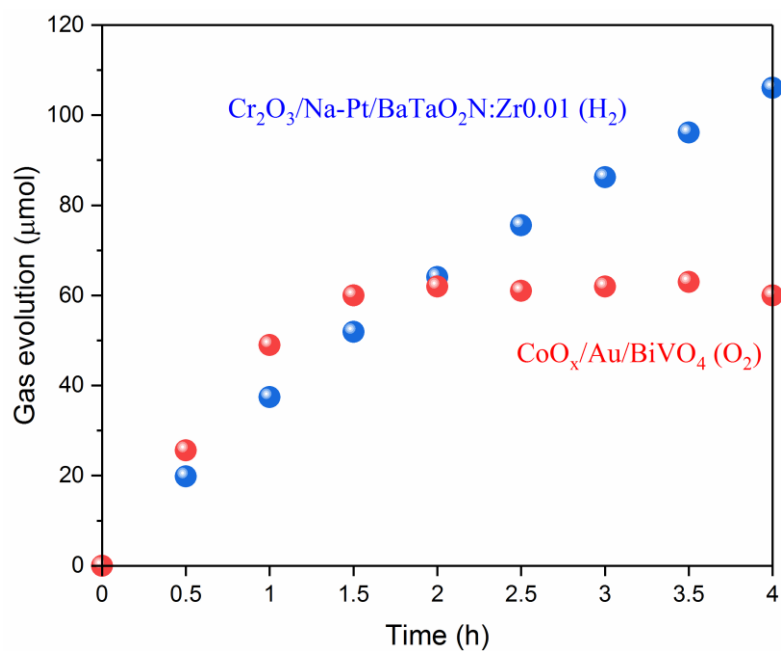
<sup>b</sup>Measured by the N-O combustion analyzer



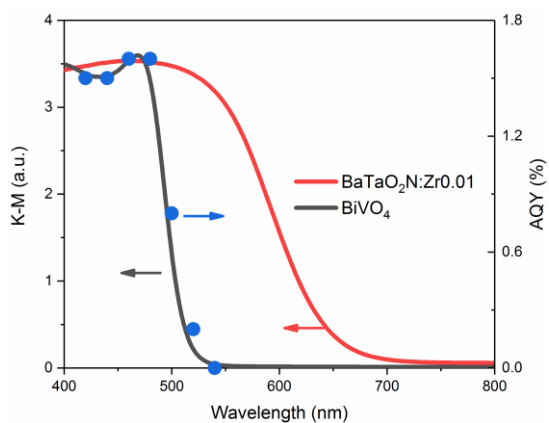
**Figure S1.** Ta 4f XPS spectra of BaTaO<sub>2</sub>N and BaTaO<sub>2</sub>N:Zr0.01.



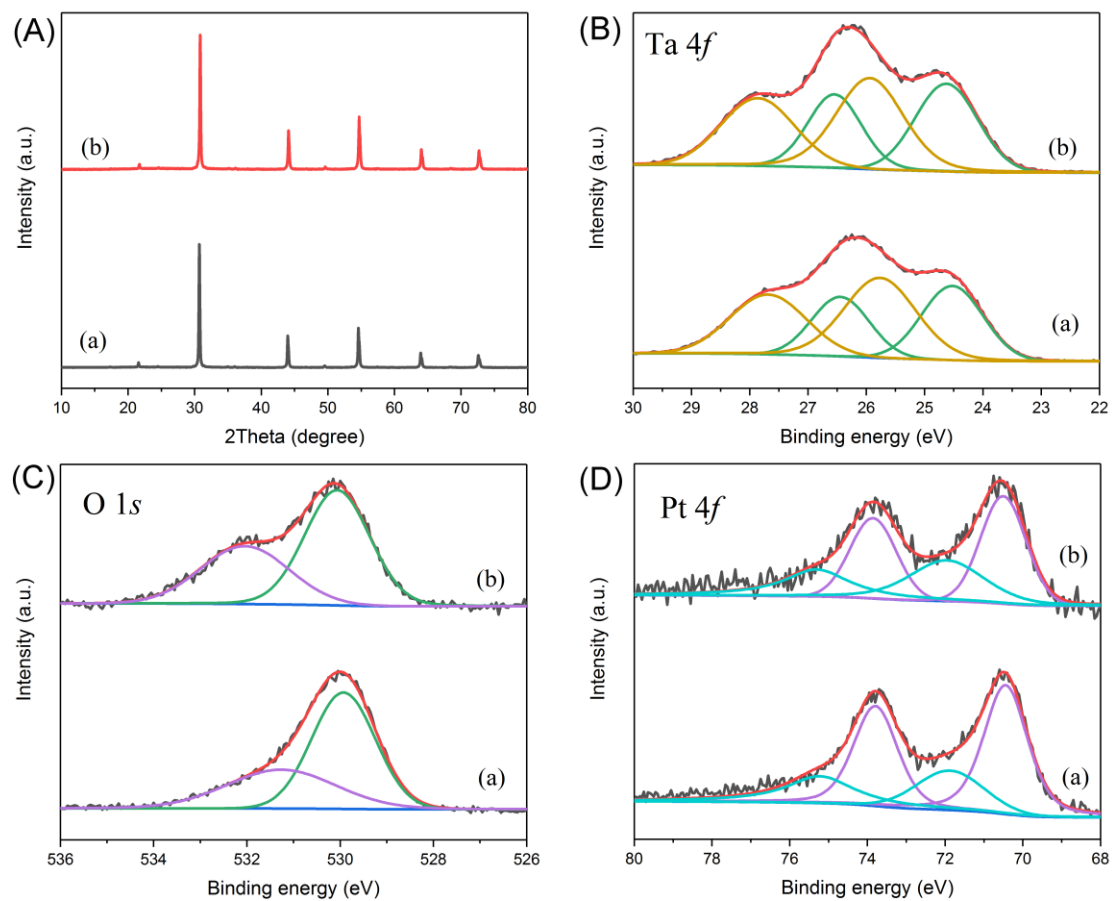
**Figure S2.** The action spectrum of  $\text{Cr}_2\text{O}_3$  (0.9 wt% Cr)/0.23 wt% Na-0.3 wt% Pt/BaTaO<sub>2</sub>N:Zr0.01 (100 mg) for photocatalytic water reduction in an aqueous 50 mM sodium phosphate buffer solution at pH 6 (150 mL) containing 6 mM  $\text{K}_4[\text{Fe}(\text{CN})_6]$  under 300 W xenon lamp ( $420 \text{ nm} < \lambda < 800 \text{ nm}$ ) equipped with various band-pass filters.



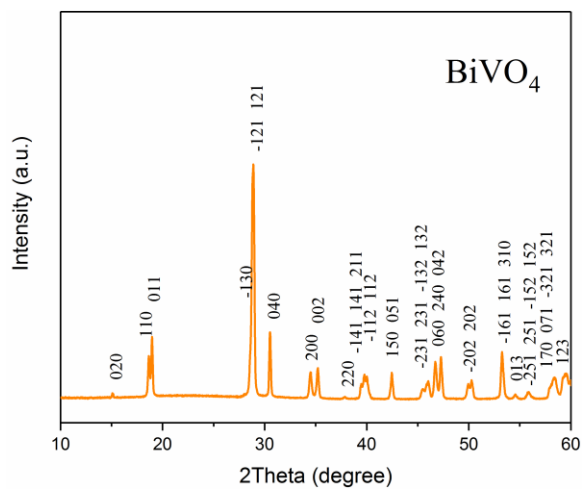
**Figure S3.** Time courses of H<sub>2</sub> evolution over Cr<sub>2</sub>O<sub>3</sub> (0.9 wt% Cr)/0.23 wt% Na-0.3 wt% Pt/BaTaO<sub>2</sub>N:Zr0.01 (100 mg) in an aqueous 50 mM sodium phosphate buffer solution at pH 6 (150 mL) containing 6 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] and O<sub>2</sub> evolution over CoO<sub>x</sub> (0.5 wt% Co)/0.2 wt% Au/BiVO<sub>4</sub> (100 mg) in the same sodium phosphate buffer solution but containing 6 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>]. Light source: 300 W xenon lamp (420 nm < λ < 800 nm).



**Figure S4.** Dependence curve of AQY as a function of irradiation wavelength and diffuse reflectance spectra of the HEP and OEP. The gas evolution over ZOWS consisted of 0.9 wt% Cr<sub>2</sub>O<sub>3</sub>/0.23 wt% Na-0.3 wt% Pt/BaTaO<sub>2</sub>N:Zr0.01 (70 mg), 0.5 wt% CoO<sub>x</sub>/0.2 wt% Au/BiVO<sub>4</sub> (100 mg), and 150 mL 25 mM sodium phosphate buffer solution (pH 6.0) containing K<sub>4</sub>[Fe(CN)<sub>6</sub>] (6 mM) was performed under 300 W xenon lamp (420 nm <  $\lambda$  < 800 nm) equipped with various band-pass filters.



**Figure S5.** (A) XRD pattern and (B) Ta 4f, (C) O 1s, and (D) Pt 4f XPS spectra of BaTaO<sub>2</sub>N:Zr<sub>0.01</sub> (a) before and (b) after a HER reaction in an aqueous 50 mM sodium phosphate buffer solution at pH 6 (150 mL) containing 6 mM K<sub>4</sub>[Fe(CN)<sub>6</sub>] under visible light irradiation.



**Figure S6.** XRD pattern of as-prepared BiVO<sub>4</sub>.