Supplementary Information (SI) for Journal of Materials Chemistry A.

Solar Hydrogen Production via Z-Scheme Water Splitting System Based Solely on Perovskite-type Tantalum Oxynitrides

Wenpeng Li,[a] Akio Hirako,[b] Shuji Sekimori,[b] Rhauane Almeida Galvão,[a] Mamiko Nakabayashi,[c] Faze Wang,[d] Takashi Hisatomi,*[e] Kazunari Domen*[e,f,g]

[a] *Graduate School of Medicine, Science and Technology, Shinshu University, Nagano, Japan*

[b] *Graduate School of Science and Technology, Shinshu University*

[c] *Institute of Engineering Innovation, School of Engineering, The University of Tokyo, Tokyo, Japan*

[d] *Research Initiative for Supra-Materials, Shinshu University, Nagano, Japan*

[e] *Institute for Aqua Regeneration, Shinshu University, Nagano, Japan*

[f] *Office of University Professors, The University of Tokyo, Japan*

[g] *Department of Chemistry, Kyung Hee University, Republic of Korea*

*Corresponding author

Kazunari Domen: domen@chemsys.t.u-tokyo.ac.jp

Takashi Hisatomi: hisatomi@shinshu-u.ac.jp

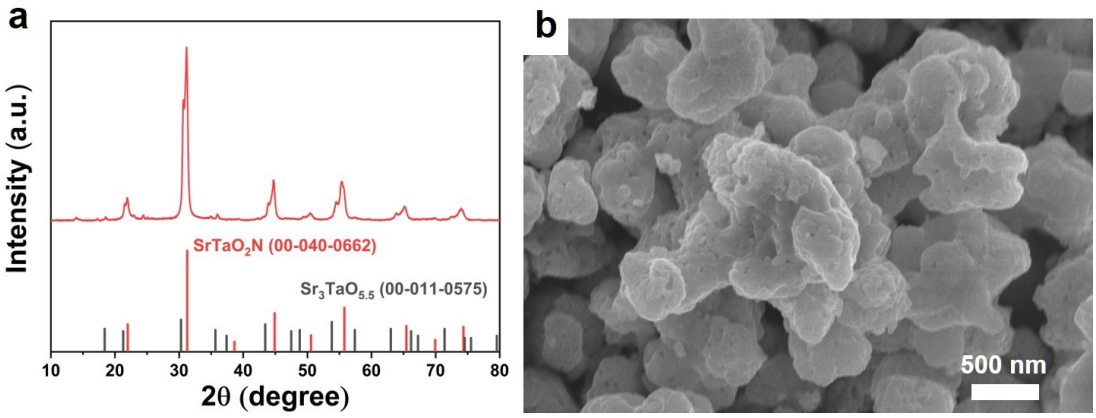

Figure S1. (a) XRD pattern and (b) SEM image for $SrTaO_2N$(SSR).

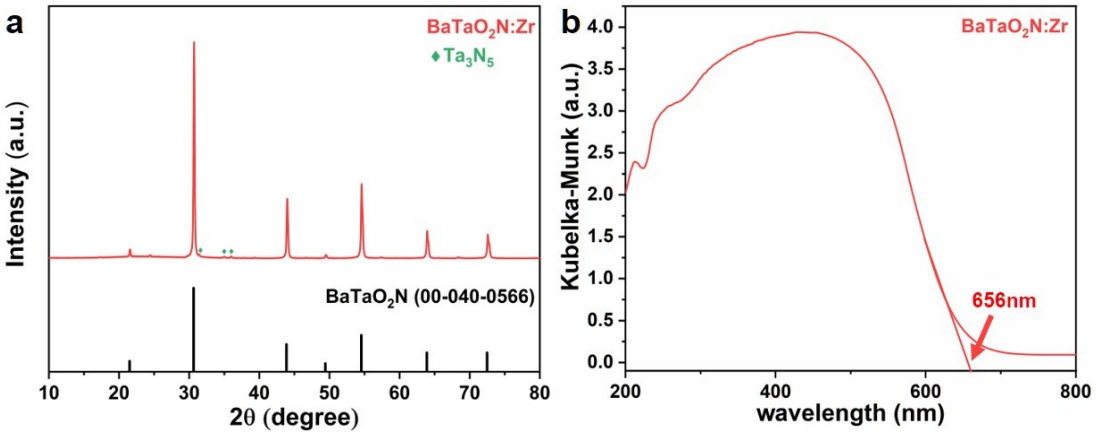

Figure S2. (a) XRD pattern and (b) UV-vis DRS spectrum for $BaTaO_2N$:Zr.

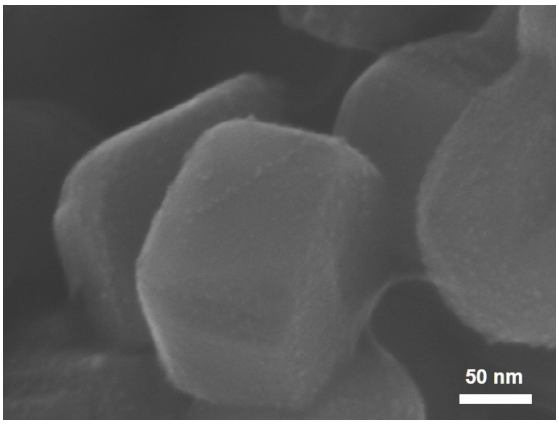

Figure S3. SEM image of Cr_2O_3/Pt/$BaTaO_2N$:Zr.

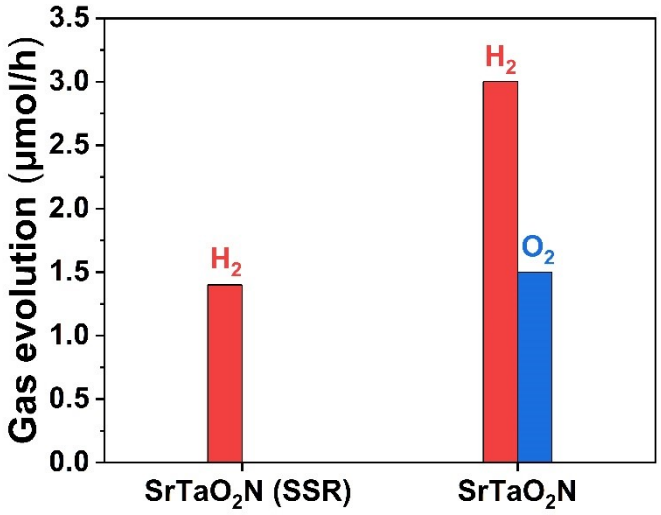

Figure S4. Photocatalytic activities for ZOWS systems based on different $SrTaO_2N$ samples, as reflected by gas evolution rates. Reaction conditions: 50 mg HEP (Cr_2O_3/Pt/$BaTaO_2N$:Zr, 0.9 wt% Cr and 0.3 wt% Pt) and 100 mg OEP (Pt(PD)/CoO_x/$SrTaO_2N$, 0.2 wt% Co and 0.2 wt% Pt); 150 mL of a 25 mM sodium phosphate buffer solution (pH 8) containing 1 mM $[Co(bpy)_3]^{3+/2+}$ ions; 300 W Xe lamp ($\lambda \geq 420$ nm). The gas evolution rates represent the average values over a span of 10 h.

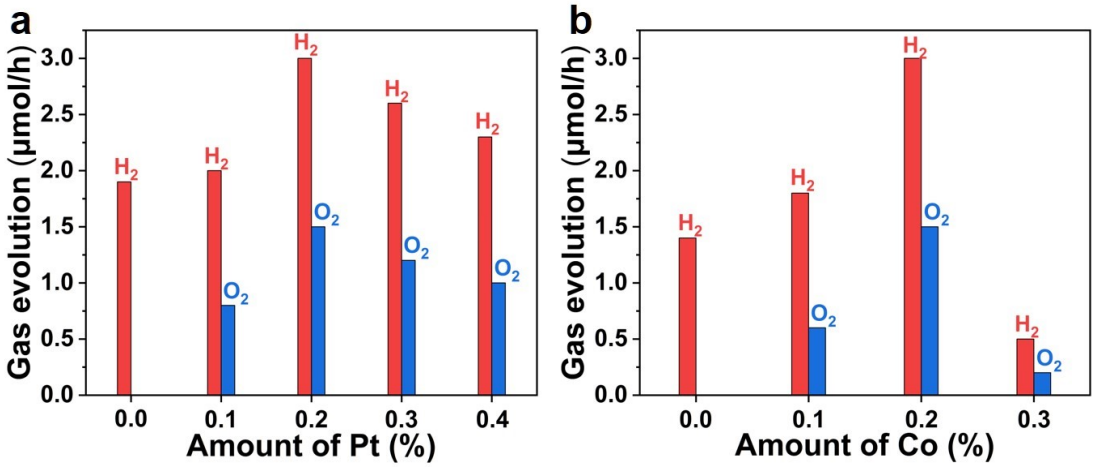

Figure S5. Effect of amount of (a) Pt(PD) and (b) CoO_x loaded onto $SrTaO_2N$ on photocatalytic ZOWS activity for $BaTaO_2N$:Zr-$[Co(bpy)_3]^{3+/2+}$-$SrTaO_2N$ system. Reaction conditions: 50 mg HEP (Cr_2O_3/Pt/$BaTaO_2N$:Zr, 0.9 wt% Cr and 0.3 wt% Pt) and 100 mg OEP (Pt(PD)/CoO_x/$SrTaO_2N$, 0.2 wt% Co and 0.2 wt% Pt); 150 mL of a 25 mM sodium phosphate buffer solution (pH 8) containing 1 mM $[Co(bpy)_3]^{3+/2+}$ ions; 300 W Xe lamp ($\lambda \geq 420$ nm).

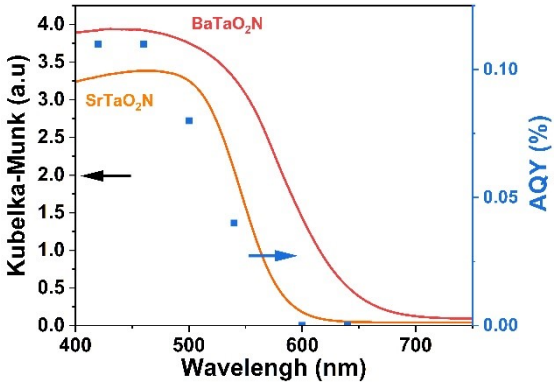

Figure S6. AQY as function of incident-light wavelength during ZOWS using $BaTaO_2N$:Zr-$[Co(bpy)_3]^{3+/2+}$-$SrTaO_2N$ system. Reaction conditions: 50 mg HEP (Cr_2O_3/Pt/$BaTaO_2N$:Zr, 0.9 wt% Cr and 0.3 wt% Pt) and 100 mg OEP (Pt(PD)/CoO_x/$SrTaO_2N$, 0.2 wt% Co and 0.2 wt% Pt); 150 mL of a 25 mM sodium phosphate buffer solution (pH 8) containing 1 mM $[Co(bpy)_3]^{3+/2+}$ ions; 300 W Xe lamp with various bandpass filters.

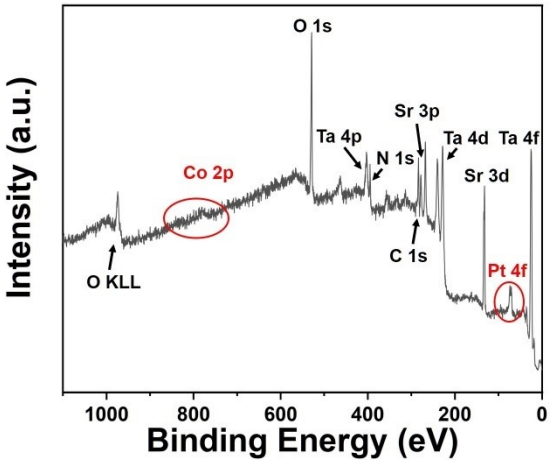

Figure S7. XPS spectrum of Pt(PD)/CoO_x/$SrTaO_2N$.

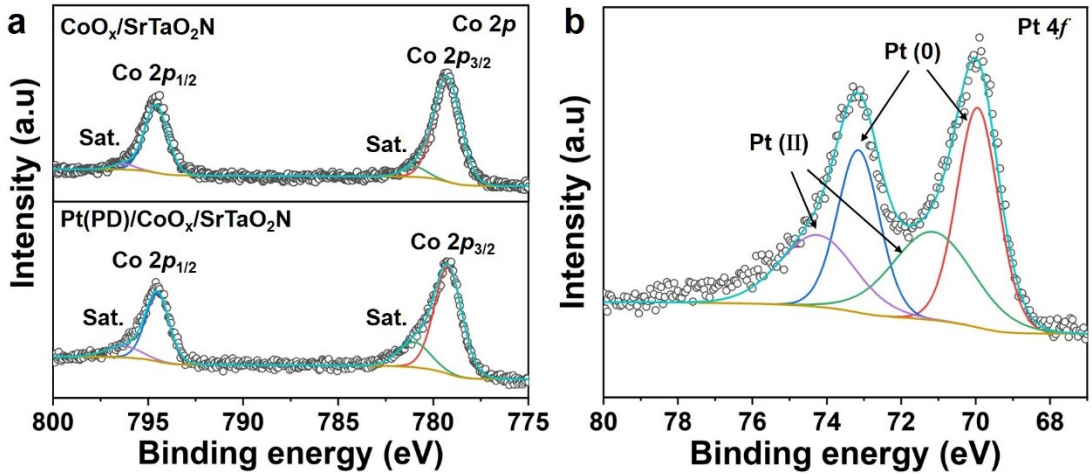

Figure S8. (a) Co 2*p* XPS spectra of Pt(PD)/CoO_x/$SrTaO_2N$ before and after Pt(PD) loading and (b) Pt 4*f* XPS spectrum of same material.

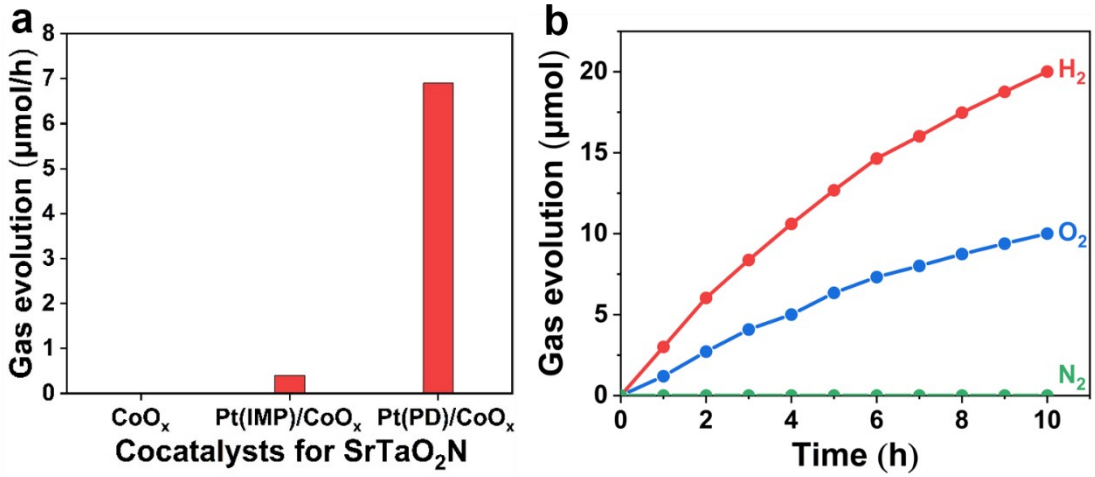

Figure S9. (a) Photocatalytic O_2 evolution activity for $SrTaO_2N$ with various cocatalysts in 150 mL of aqueous 50 mM sodium phosphate buffer solution (pH 8) containing 5 mM $K_3[Fe(CN)_6]$. (b) Time course of gas evolution during the ZOWS reaction under visible light. Reaction conditions: 50 mg HEP (Cr_2O_3(0.9 wt%)/Pt(0.3

wt%)/$BaTaO_2N$:Zr) and 100 mg OEP (Pt(PD)/CoO_x/$SrTaO_2N$, 0.2 wt% Co and 0.2 wt% Pt); 150 mL of 25 mM sodium phosphate buffer solution (pH 8) containing 1 mM $K_4Fe(CN)_6$ ions; 300 W Xe lamp ($\lambda \geq 420$ nm).

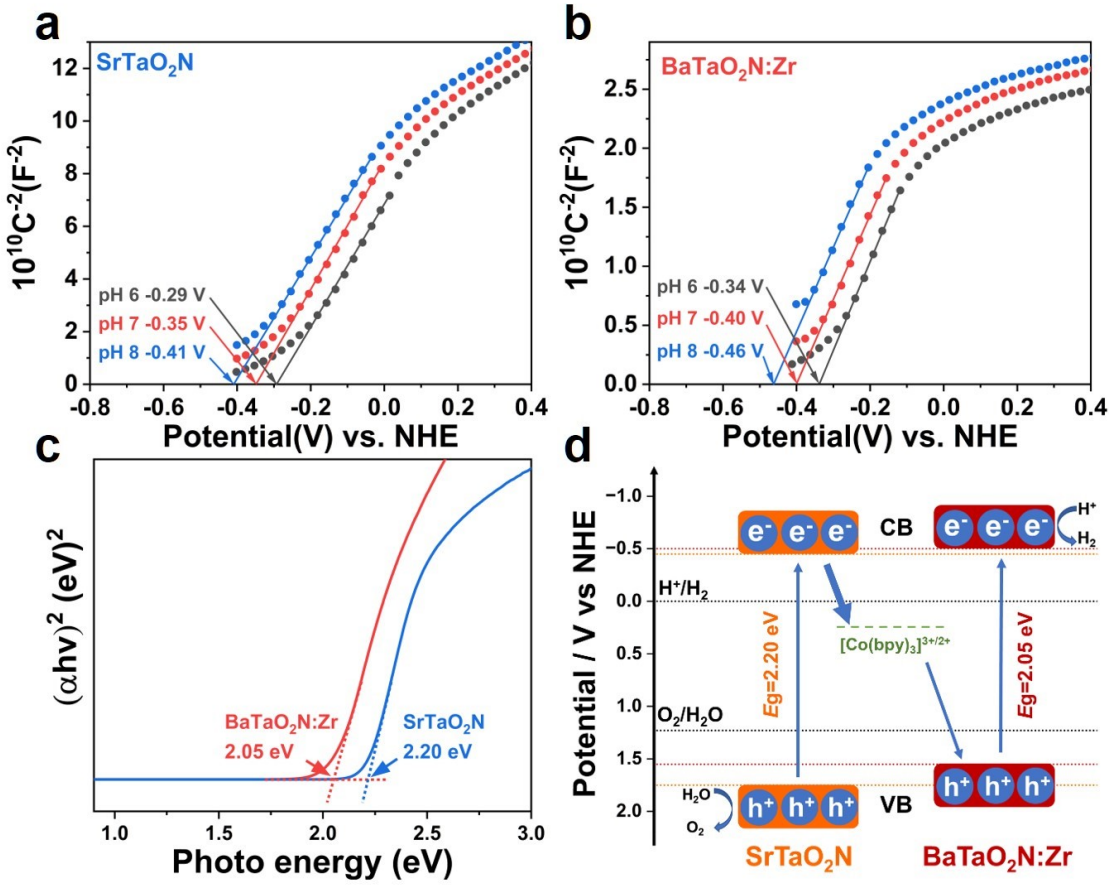

Figure S10 Mott-Schottky (MS) plots of (a) $SrTaO_2N$ and (b) $BaTaO_2N$:Zr at a fixed frequency of 1000 Hz, with the flat band potentials determined by extrapolating the MS curves to the energy axis. (c) Bandgap of $SrTaO_2N$ and $BaTaO_2N$:Zr calculated from the DRS data. (d) Energy diagram of the Z-scheme system ($BaTaO_2N$:Zr-$[Co(bpy)_3]^{3+/2+}$-$SrTaO_2N$), including water redox potentials at pH 7. CB and VB indicate conduction band and valence band, respectively.

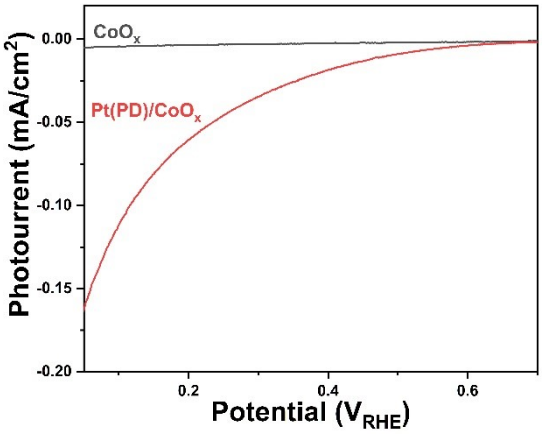

Figure S11. O_2 reduction current density for $CoO_x/SrTaO_2N/Ti$ and $Pt(PD)/CoO_x/SrTaO_2N/Ti$ photoanodes under dark conditions as functions of applied potential. Reaction conditions: 0.1 M sodium phosphate buffer solution (pH 8) saturated with O_2.