

# Modified Ta<sub>3</sub>N<sub>5</sub> Powder as a Photocatalyst for O<sub>2</sub> Evolution in a Two-Step Water Splitting System with an Iodate/Iodide Shuttle Redox Mediator under Visible Light

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## ***Supporting Information***

### **Experimental Details**

#### **Preparation of Catalysts**

Ta<sub>3</sub>N<sub>5</sub> powder as an O<sub>2</sub> evolution photocatalyst was prepared by heating Ta<sub>2</sub>O<sub>5</sub> powder under NH<sub>3</sub> flow (500 mL·min<sup>-1</sup>) at 1123 K for 15 h.<sup>S1</sup> ZrO<sub>2</sub>/TaON composite material as an H<sub>2</sub> evolution photocatalyst was prepared by heating ZrO<sub>2</sub>/Ta<sub>2</sub>O<sub>5</sub> composite powder under NH<sub>3</sub> flow (20 mL·min<sup>-1</sup>) at 1123 K for 15 h according to the method reported previously.<sup>S2</sup>

Ta<sub>3</sub>N<sub>5</sub> loaded with TiO<sub>2</sub>-rutile (R-TiO<sub>2</sub>/Ta<sub>3</sub>N<sub>5</sub>) was prepared in a mixture of distilled water, nitric acid, 2-propanol, and titanium isopropoxide (450/5/13/1 by molar ratio).<sup>S3</sup> Water (40 mL) and nitric acid were first mixed at room temperature, and then 2-propanol was added. After the solution was thoroughly mixed, titanium isopropoxide was gradually added by pipette. Gelatinous white precipitates formed instantly. The mixture was ultrasonically agitated, and became transparent, indicating the formation of a sol. Then, the as-prepared Ta<sub>3</sub>N<sub>5</sub> (0.25 g) was added and the mixture was heated at 323 K for 60 h **with a lid to avoid vaporization of the solvent. Similarly, TiO<sub>2</sub>-anatase (A-TiO<sub>2</sub>) can be introduced on Ta<sub>3</sub>N<sub>5</sub>. In this case, however, the aqueous mixture was dried up at 333 K without using a lid.** The powder was separated by centrifugation and dried at 343 K.

Ni, Pt, Rh (1 wt% each), Ir (1 or 5 wt%), or Ru (0.5 wt%) cocatalysts were loaded on Ta<sub>3</sub>N<sub>5</sub> (with or without TiO<sub>2</sub>-modification) by impregnation from an aqueous Ni(NO<sub>3</sub>)<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub>, Na<sub>3</sub>RhCl<sub>6</sub>, Na<sub>2</sub>IrCl<sub>6</sub>, or RuCl<sub>3</sub> solution, respectively, followed by heating at 473 K for 1 h under H<sub>2</sub> flow (20 mL·min<sup>-1</sup>). For ZrO<sub>2</sub>/TaON, 1 wt% Pt as a cocatalyst for H<sub>2</sub> evolution was loaded in the same manner.

#### **Characterization of Catalysts**

The prepared samples were studied by powder X-ray diffraction (XRD; RINT-UltimaIII, Rigaku; Cu K $\alpha$ ), X-ray photoelectron spectroscopy (XPS; JPS-9000, JEOL), scanning electron microscopy (SEM; S-4700, Hitachi), and transmission electron microscopy (TEM; JEM-2010F, JEOL). The

## ***Supporting Information***

binding energies determined by XPS were corrected in reference to the Au 4f<sub>7/2</sub> peak (83.9 eV) for each sample.

### **Electrochemical Measurements**

To study the electrochemical properties of Ta<sub>3</sub>N<sub>5</sub> photocatalysts, porous Ta<sub>3</sub>N<sub>5</sub> film electrodes (1.5×4 cm<sup>2</sup>) were prepared by electrophoretic deposition<sup>S4</sup> on conducting glass supports (F-doped SnO<sub>2</sub>). Then, TaCl<sub>5</sub> treatment was carried out to improve the inter-particle electron transfer as follows.<sup>S5</sup> TaCl<sub>5</sub> was dissolved in methanol (10 mM) and the solution was dropped on the prepared electrodes with a pipette (250 μL). The electrodes were dried and heated at 773 K for 30 min under NH<sub>3</sub> flow (10 mL·min<sup>-1</sup>). It was loaded on porous Ta<sub>3</sub>N<sub>5</sub> electrodes by impregnation from an aqueous Na<sub>2</sub>IrCl<sub>6</sub> solution, followed by heating at 473 K for 1 h under H<sub>2</sub> flow if necessary. A platinum wire and an Ag/AgCl electrode were used as a counter and reference electrode, respectively. The Pt counter electrode was separated from the as-prepared Ta<sub>3</sub>N<sub>5</sub> electrode by an ion-exchange membrane (Nafion). The potential of the Ta<sub>3</sub>N<sub>5</sub> working electrode was controlled by a potentiostat. An Na<sub>2</sub>SO<sub>4</sub> aqueous solution (0.1 M, pH = 6) was used as an electrolyte solution for electrochemical measurements. The solution was purged with argon gas before the measurements. The measurements were conducted at room temperature.

### **Photocatalytic Reactions**

Reactions were carried out in a Pyrex reaction vessel connected to a closed circulation system. The photocatalyst powder (0.05 g) was suspended in distilled water using a magnetic stirrer, and the required amount of solute (e.g., NaI, NaIO<sub>3</sub>) was added to the suspension. The suspension was then thoroughly degassed, and then exposed to argon at 5 kPa. The suspension was irradiated using a Xe lamp (300 W) fitted with a cold mirror (CM-1) and a cutoff filter to eliminate light in the UV regions

### ***Supporting Information***

for visible light irradiation ( $\lambda > 420$  nm). A high-pressure Hg lamp (450 W) with a Pyrex reaction vessel was used for UV light irradiation ( $\lambda > 300$  nm). The effective power at 420–600 nm, which is the wavelength range available for Ta<sub>3</sub>N<sub>5</sub>, was measured using a Si photodiode to be ca.  $6.7 \times 10^{18}$  photons·s<sup>-1</sup>. The evolved gases were analyzed using on-line gas chromatography.

### **References**

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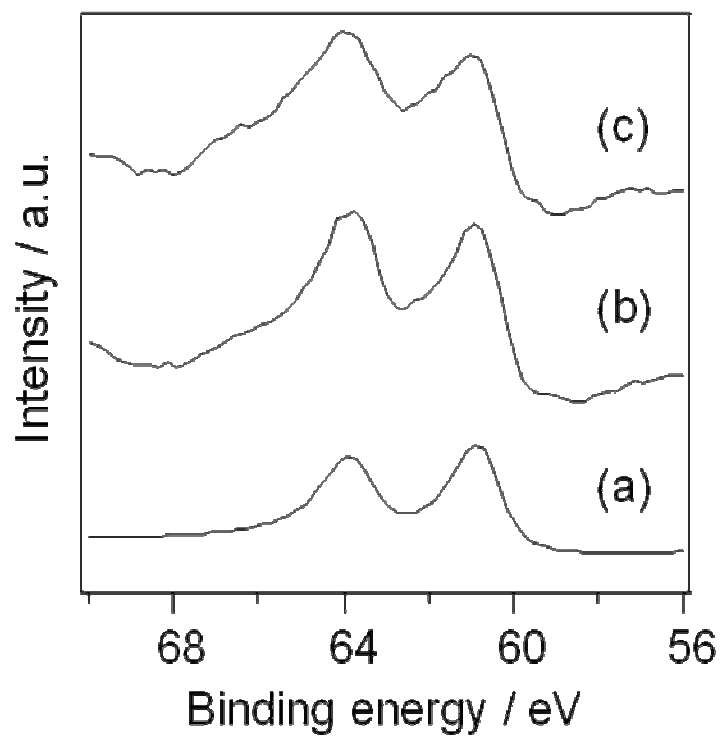
## Supporting Information

**Table S1.** Initial rate of O<sub>2</sub> evolution on Ta<sub>3</sub>N<sub>5</sub> loaded with various cocatalysts from an aqueous NaIO<sub>3</sub> solution (4 mM) under visible light ( $\lambda > 420$  nm).<sup>a</sup>

Entry	Cocatalyst	Rate of O <sub>2</sub> evolution / $\mu\text{mol}\cdot\text{h}^{-1}$
1	None	0
2	Ni 1 wt %	0
3	Pt 1 wt %	0
4	Ru 0.5 wt %	3.1
5	Rh 1 wt %	3.3
6	Ir 1 wt %	34.0

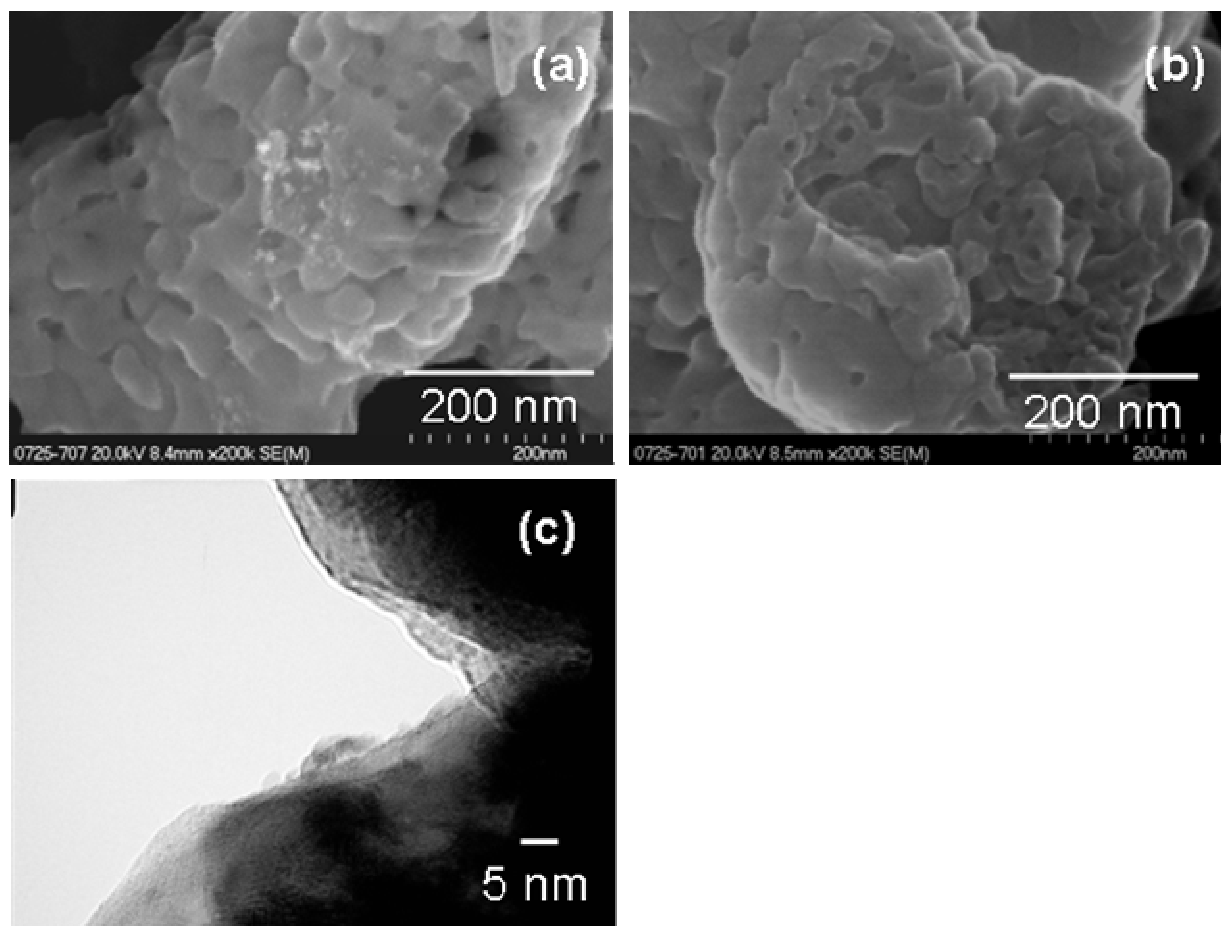
<sup>a</sup> Reaction conditions: catalyst, 0.05 g; aqueous solution, 250 mL; light source, xenon lamp (300 W) fitted with a cutoff filter; reaction vessel, Pyrex side-irradiation type.

*Supporting Information*

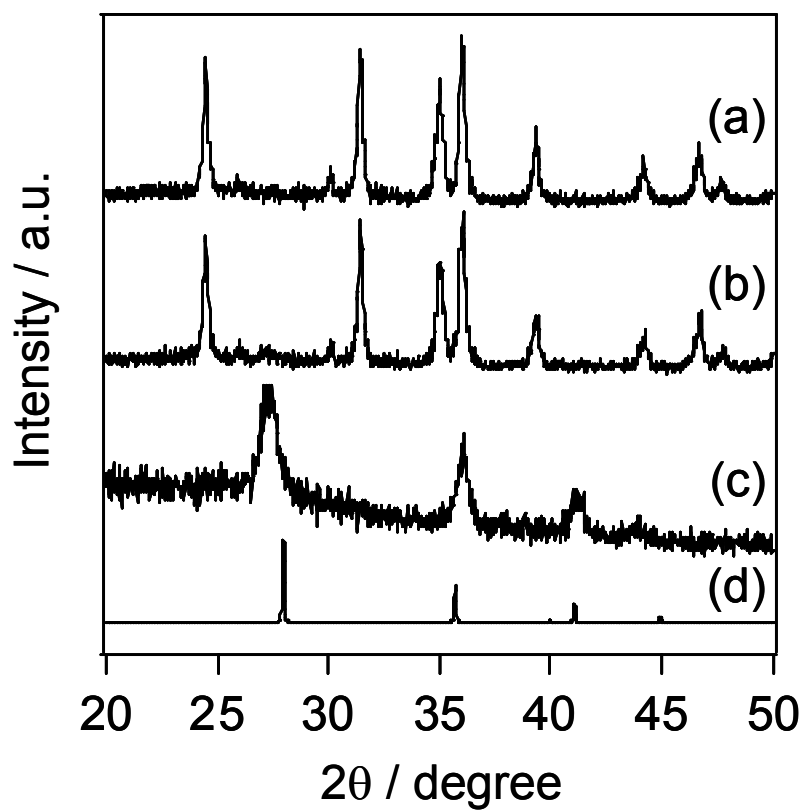


**Figure S1.** XPS spectra for Ir 4f in (a) Ir (commercially available powder, purchased from Wako Pure Chemical Industries, Ltd.), (b) Ir/Ta<sub>3</sub>N<sub>5</sub> before reaction and (c) Ir/Ta<sub>3</sub>N<sub>5</sub> reacted in aqueous NaIO<sub>3</sub> solution (4 mM) after 9 h.

*Supporting Information*



**Figure S2.** SEM images of (a) Ir/Ta<sub>3</sub>N<sub>5</sub> and (b) Ta<sub>3</sub>N<sub>5</sub> and (c) a TEM image of Ir/Ta<sub>3</sub>N<sub>5</sub>.



**Figure S3.** XRD patterns of (a)  $Ta_3N_5$ , (b) R- $TiO_2/Ta_3N_5$ , (c) R- $TiO_2$  prepared without adding  $Ta_3N_5$ , and (d) R- $TiO_2$  (reference).



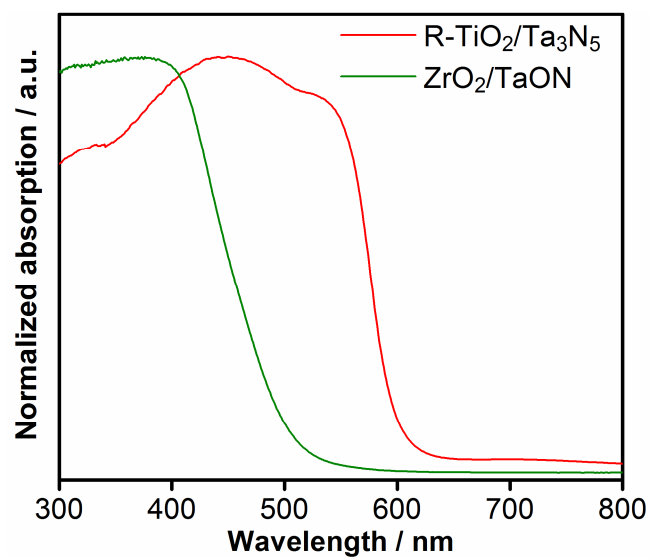


Figure S4. UV-visible diffuse reflectance spectra for ZrO<sub>2</sub>/TaON and R-TiO<sub>2</sub>/Ta<sub>3</sub>N<sub>5</sub>.

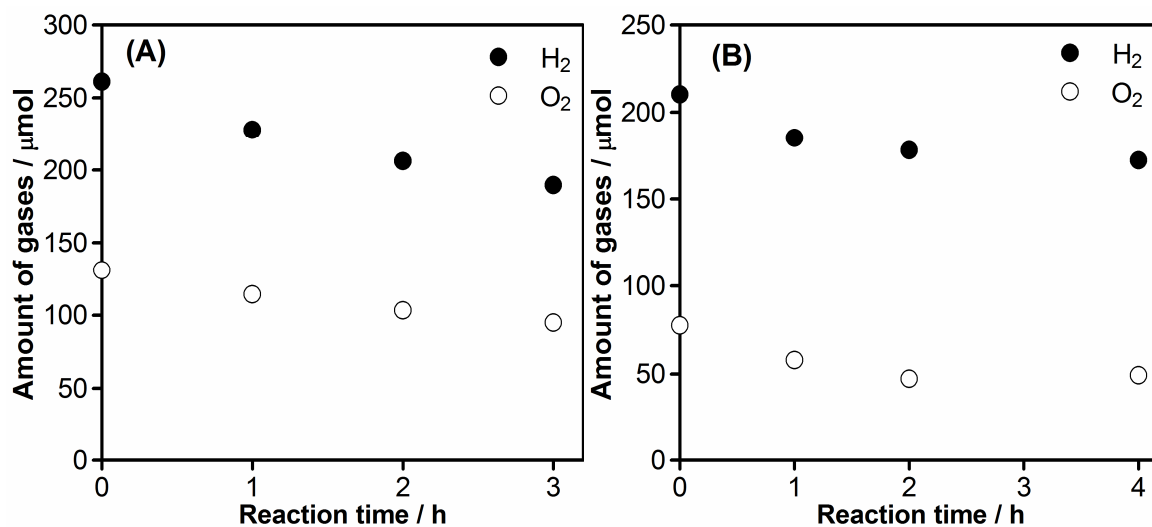


Figure S5. Water formation from H<sub>2</sub> and O<sub>2</sub> in the dark on (A) Pt/ZrO<sub>2</sub>/TaON (0.05 g) and (B) Ir/R-TiO<sub>2</sub>/Ta<sub>3</sub>N<sub>5</sub> (0.05 g). This experiment was carried out in an aqueous NaI solution (0.1 mM, 250 mL) using a closed-gas circulation system containing a stoichiometric mixture of H<sub>2</sub> and O<sub>2</sub> gases.