Electronic Supplementary Information (ESI)

Photocatalytic Overall Water Splitting on the Perovskite-type Transition Metal Oxynitride CaTaO$_2$N under Visible Light Irradiation

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Experimental

1. Preparation of CaTaO$_2$N
The oxide precursor was prepared via a solution route called the citric acid method. In a typical experiment, TaCl$_5$ (4 mmol) and citric acid (30 mmol) were added to MeOH (30 mL), followed by the addition of CaCO$_3$ (4 mmol) and water (30 mL) under stirring, yielding a transparent solution. This solution was heated at 473 K to evaporate the MeOH and initiate gelation, and subsequently heated at 623 K, yielding a carbonized black-brown powder. The carbonized powder was heated in air at 1073 K for 4 h to completely remove carbon and to generate an oxide precursor. The as-synthesized oxide precursor was subjected to nitridation in a tubular furnace under flowing dry ammonia (100 mL min$^{-1}$) at 1123 K for 6 h. Finally, the resulting nitrided sample was stirred in EtOH for 3 days to obtain well-dispersed particles.

2. Modification of CaTaO$_2$N with RhCrO$_y$ mixed oxide nanoparticles
The impregnation method was used to load the as-synthesized CaTaO$_2$N sample with a Rh-Cr bimetallic oxide cocatalyst, RhCrO$_y$, which served as a H$_2$ evolution promoter. CaTaO$_2$N powder was immersed in a small amount of water containing RhCl$_3$ and Cr(NO$_3$)$_3$ and then dried on a hot water bath. After that, the sample was heated under N$_2$ flow at 623 K for 1 h in a tubular furnace.

3. Photodeposition of Ti oxyhydroxide on RhCrO$_y$/CaTaO$_2$N

Preparation of aqueous Ti peroxide solution
To prepare the precursor solution to be used for photodepositing Ti oxyhydroxide (1wt% TiO$_2$), 9 μL (25 μmol) of titanium tetraisopropoxide (TTIP, Kanto Chemical Co., Inc. 97% purity) was dissolved into 25 μL of aqueous H$_2$O$_2$ solution (ca. 250 μmol, Kanto Chemical Co., Inc., 30-35 wt% H$_2$O$_2$). 1 mL of H$_2$O was added therein. The resulting suspension was subjected to several times of sonication for a few min, yielding a transparent solution.

**Photodeposition method**

The as-prepared Ti-peroxide solution was added into the photocatalytic reaction solution containing 0.2 g of photocatalyst powder and 250 mL of distilled water. The pH of the solution was not adjusted (pH = 7.2). Photodeposition was carried out *in situ* using our conventional photocatalytic reaction system. After evacuation, the solution was exposed to UV irradiation (300 W Xe lamp, $\lambda \geq$ 300 nm) to decompose the peroxide species. During irradiation, a large amount of O$_2$ evolution was observed, indicating H$_2$O$_2$ decomposition. Irradiation was typically performed for 4-6 h until the peroxide species added were completely decomposed, which was marked by the termination of O$_2$ evolution. The reaction solution was maintained at room temperature by a flow of cooling water.

4. **Photocatalytic reaction**

The photocatalytic reaction was carried out in a side-irradiation-type reaction vessel made of Pyrex connected to a closed gas circulation system. The air in the gas phase and the air dissolved in the solution were removed completely by evacuation. The system was then photoirradiated by a Xe lamp (300 W) directly ($\lambda \geq$ 300 nm) or through a cutoff filter ($\lambda \geq$ 420 nm) for the UV and visible light irradiation, respectively. To prevent heating up of the reaction solution during irradiation, the reaction vessel was placed into an outer vessel through which cooling water was flown. The evolved gases were analyzed by gas chromatography (thermal conductivity detector, Ar carrier gas, molecular sieve 5A column).

The apparent quantum efficiency (AQE) was calculated on the basis of the number of incident photons via the following equation:

$$\text{AQE}(\%) = \frac{\text{Number of reacted electrons}}{\text{Number of incident photons}} \times 100$$

Here, the number of reacted electrons refers to the photogenerated electrons used to produce H$_2$ during overall water splitting. The number of incident photons, adjusted with respect to the wavelength region by a bandpass filter, was measured with a spectroradiometer (LS-100, EKO Instruments Co., Ltd.). The intensity of the incident light in the wavelength region of 440±30 nm was 1.9×10$^{20}$ photons/cm$^2$ h. The irradiated area was 18.1 cm$^2$.

5. **Calculation method for band position**

The bandgap position was estimated from theoretical calculations by Xu et al.* For compounds $A_nB_mB_c$, band edge positions are given by the following equations:

$$E_c = \left(\chi(A)^a \cdot \chi(B)^b \cdot \chi(C)^c\right)^{1/(a+b+c)} \cdot (1/2)E_g + E_0$$ (1)

$$E_v = E_c + E_g$$ (2)

Here, $\chi(A)$, $\chi(B)$, and $\chi(C)$ are the absolute electronegativities of the constituent atoms A, B, and C, respectively; $E_C$, $E_V$, and $E_g$ are respectively the energy levels of the conduction band minimum
(CBM), valence band maximum (VBM), and the bandgap energy of the semiconductor, as determined by optical measurements; and $E_0$ is the scale factor relating the reference electrode redox level to the vacuum level ($E_0 = -4.5$ eV for a normal hydrogen electrode; NHE).

Fig. S1. Enlarged XRD pattern of as-prepared CaTaO$_2$N and reference data of Ta$_3$N$_5$.

Fig. S2 Time course of gas evolution on CaTaO$_2$N from an aqueous AgNO$_3$ solution under photoirradiation. Reaction conditions: catalyst, 0.2 g; reaction solution, 250 mL 0.01M AgNO$_3$ aq. containing 0.1g La$_2$O$_3$ (pH ca. 8.5); light source, Xe lamp (300W, $\lambda \geq 300$ nm); side-irradiation-type reaction vessel made of Pyrex.