

Electronic Supplementary Information (ESI)

Photocatalytic Overall Water Splitting on the Perovskite-type Transition Metal Oxynitride CaTaO_2N under Visible Light Irradiation

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Experimental

1. Preparation of CaTaO_2N

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_2N with RhCrO_y mixed oxide nanoparticles

The impregnation method was used to load the as-synthesized CaTaO_2N sample with a Rh-Cr bimetallic oxide cocatalyst, RhCrO_y , which served as a H_2 evolution promoter. CaTaO_2N powder was immersed in a small amount of water containing RhCl_3 and $\text{Cr}(\text{NO}_3)_3$ 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 $\text{RhCrO}_y/\text{CaTaO}_2\text{N}$

Preparation of aqueous Ti peroxide solution

To prepare the precursor solution to be used for photodepositing Ti oxyhydroxide (1wt% TiO₂), 9 μL (25 μmol) of titanium tetraisopropoxide (TTIP, Kanto Chemical Co., Inc. 97% purity) was dissolved into 25 μL of aqueous H₂O₂ solution (ca. 250 μmol, Kanto Chemical Co., Inc., 30-35 wt% H₂O₂). 1 mL of H₂O 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 O₂ evolution was observed, indicating H₂O₂ decomposition. Irradiation was typically performed for 4-6 h until the peroxide species added were completely decomposed, which was marked by the termination of O₂ 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:

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

Here, the number of reacted electrons refers to the photogenerated electrons used to produce H₂ 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 1.9×10²⁰ photons/cm² h. The irradiated area was 18.1 cm².

5. Calculation method for band position

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

$$E_c = (\chi_{(A)}^a \cdot \chi_{(B)}^b \cdot \chi_{(C)}^c)^{1/(a+b+c)} - 1/2 E_g + E_0 \quad (1)$$

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

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).

* Y. Xu and M. A. A. Schoonen, *Am. Mineral.*, 2000, **85**, 543.

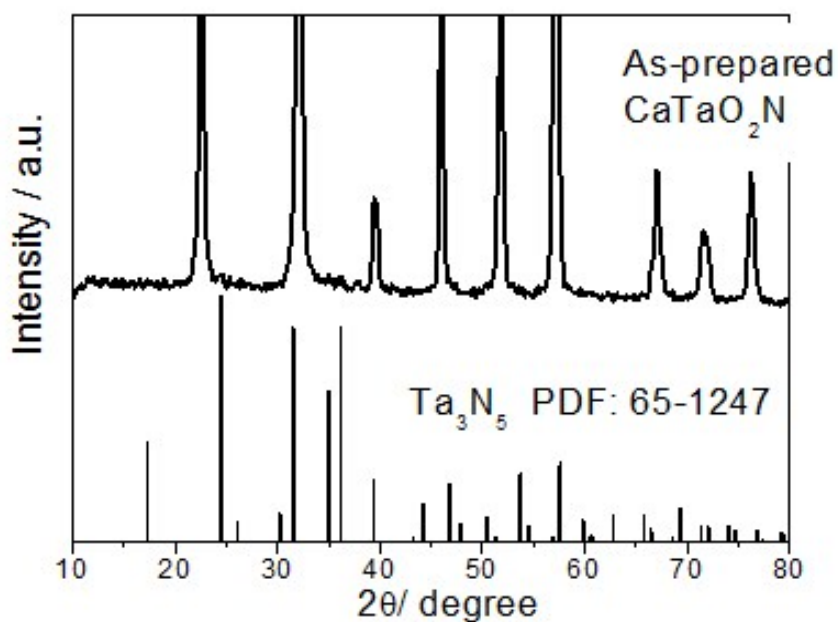


Fig. S1. Enlarged XRD pattern of as-prepared CaTaO_2N and reference data of Ta_3N_5 .

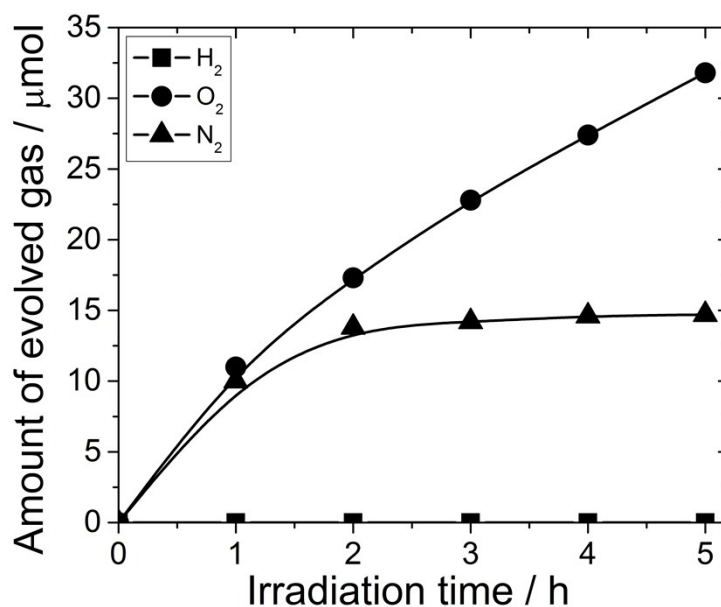


Fig. S2 Time course of gas evolution on CaTaO_2N from an aqueous AgNO_3 solution under photoirradiation. Reaction conditions: catalyst, 0.2 g; reaction solution, 250 mL 0.01M AgNO_3 aq. containing 0.1g La_2O_3 (pH ca. 8.5); light source, Xe lamp (300W, $\lambda \geq 300$ nm); side-irradiation-type reaction vessel made of Pyrex.