

Electronic Supplementary Information (ESI)

A Z-scheme photocatalyst constructed with an
yttrium-tantalum oxynitride and a binuclear Ru(II) complex
for visible-light CO₂ reduction

Kanemichi Muraoka,^a Hiromu Kumagai,^a Miharuru Eguchi,^b Osamu Ishitani,^{a} Kazuhiko Maeda^{a*}*

^a Department of Chemistry, School of Science, Tokyo Institute of Technology, 2-12-1-NE-2
Ookayama, Meguro-ku, Tokyo 152-8550, Japan.

^b Electronic Functional Materials Group, Polymer Materials Unit, National Institute for Materials
Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

*To whom corresponding author should be addressed.

TEL: +81-3-5734-2239, FAX: +81-3-5734-2284

Email: ishitani@chem.titech.ac.jp, maedak@chem.titech.ac.jp

Experimental section

Preparation of YTON

YTON powder was prepared via the conventional thermal ammonolysis of a mixed Y and Ta metal oxide, previously synthesized by the polymerized complex (PC) method first reported by Kakihana.^{S1} Briefly, 0.014 mol of TaCl₅ (90.0+%; Wako Pure Chemicals) was dissolved in 100 mL of methanol (99.8%; Kanto Chemicals). Subsequently, 0.21 mol of citric acid (CA, 98%; Wako Pure Chemicals) was added to the above methanol solution with continuous stirring at room temperature to produce a metal-CA complex. A 0.014 mol quantity of Y(NO₃)₃·6H₂O (>99.0%; Kanto Chemicals) was then added to the solution and the mixture was magnetically stirred to afford a transparent solution, after which 0.84 mol of ethylene glycol (EG, 99.5%; Kanto Chemicals) was added. The resulting clear mixture was gradually heated to approximately 573 K to remove the methanol and to accelerate the esterification reaction between the CA and the EG. Upon continued heating, the solution began to gel, eventually transitioning to a glassy, transparent, brownish resin. This resin was thermally decomposed in a heating mantle at 673 K to produce a grey solid, and carbon-based compounds were removed by calcination on an Al₂O₃ plate at 873 K for 2 h to yield a white powder. This amorphous powder, representing the Y-Ta mixed oxide, was nitrided by heating under a flow of gaseous NH₃ (40 mL min⁻¹) at 1123 K for 24 h in a tubular furnace. After nitridation, the resulting powder was washed six times with distilled water and dried at 343 K overnight.

Preparation of IrO₂/TiO₂/YTON/FTO electrodes

YTON/FTO electrodes were prepared using a conventional squeegee method. First, 100 mg of YTON powder, 30 μL of acetylacetone, 400 μL of water, and 10 μL of Triton X-100 were mixed for 10 min with a mortar and pestle. The resulting paste was painted on an FTO (fluorine-doped tin oxide, AGC Fabritech, 15 × 50 mm) substrate and then heated under a flow of N₂ (100 mL min⁻¹) at 623 K for 1 h. TiO₂ necking was then performed to improve the interparticle electron transfer by reducing the resistance between YTON particles. The as-prepared YTON/FTO electrode was subsequently soaked in a solution of 0.1 M TiCl₄ in methanol and then dried at 523 K on a hot plate according to a method previously reported in the literature.^{S2} After repeating this procedure three times, the electrode specimen was heated under a flow of N₂ (100 mL min⁻¹) at 673 K for 1 h.

To improve the water oxidation reaction activity, colloidal IrO₂ was adsorbed onto these electrodes as a cocatalyst. To do so, a colloidal IrO₂ solution was prepared by hydrolysis of Na₂IrCl₆.^{S3} This was accomplished by dissolving 0.016 g of Na₂IrCl₆·6H₂O (97.0%; Kanto Chemical) in 50 mL H₂O, then adjusting the pH of the solution to 12. The solution was heated at 343 K with stirring for 30 min, at which point it was transparent, and then cooled to room temperature by immersion in an ice water bath. The pH of the solution was adjusted to 9. Subsequent heating and stirring at 348 K for 20 min followed by cooling to room temperature resulted in a blue solution containing colloidal IrO₂, which was diluted to a total volume of 50 mL by adding distilled water. In each procedure, the pH of the diluted solution was adjusted using either aqueous NaOH (95.0% Kanto Chemical) or HNO₃ (70% Kanto Chemical) solutions previously diluted to the appropriate concentrations. The as-prepared colloidal IrO₂ was adsorbed onto the TiO₂/YTON/FTO electrodes by soaking each electrode overnight in 1.2 mL of the IrO₂ solution previously diluted by the addition of 30 mL of distilled water. Finally, the electrodes were rinsed with water prior to electrochemical measurements. The successful adsorption of the IrO₂ was confirmed by the observation of reduced intensity of the IrO₂ peak in UV-vis spectra before and after soaking.

Modification of YTON with Ag nanoparticles

The as-prepared YTON powder was modified with Ag nanoparticles using an impregnation method.^{S4} In this process, 10 mL of an aqueous AgNO₃ (99.8%; Kanto Chemical) solution (containing the desired amount of AgNO₃) was slowly added dropwise into 10 mL of H₂O in which 100 mg of YTON was suspended, with continuous stirring. H₂O was subsequently removed from

Electronic Supplementary Information (ESI)

the mixture by distillation under reduced pressure in a rotary evaporator. Finally, the as-obtained powder was placed in an alumina boat and heated under a flow of H₂ (20 mL min⁻¹) at 473 K for 1 h in a tube furnace.

Adsorption of Ru complexes on Ag/YTON

The as-prepared Ag/YTON powder (30 mg) was dispersed in 15 mL of acetonitrile containing **RuRu'** or in 15 mL of methanol containing **Ru(Cat)**. The suspension was stirred at room temperature in the dark overnight to allow for adsorption/desorption equilibration. The resulting powders were collected by filtration and washed with 5 mL of acetonitrile or methanol. The filtrate was collected and adjusted to a total volume of 15 mL. The amount of the complex that had adsorbed was estimated using Eq. 1, where A_{before} and A_{after} are the absorbance values of the **RuRu'** complex at 465 nm before and after the adsorption procedure, and C is the initial concentration of the complex.

$$\text{adsorbed amount (mol/g)} = \frac{A_{\text{before}} - A_{\text{after}}}{A_{\text{before}}} \times \frac{C(\text{mol/L}) \times 15 \times 10^{-3}(\text{L})}{30 \times 10^{-3}(\text{g})} \quad (\text{Eq. 1})$$

After washing, the powders were dried at room temperature for 3 h under reduced pressure. The as-obtained hybrid material was employed as the photocatalyst for the photocatalytic CO₂ reduction reaction.

Characterization of the as-prepared materials

The prepared materials were characterized by X-ray diffraction (XRD; Model MiniFlex600, Rigaku; Cu K α radiation), UV-visible diffuse reflectance spectroscopy (DRS; Model V-565, Jasco), energy-dispersive X-ray spectroscopy (EDX; Model EMAX-7000, Horiba), transmission electron microscopy (TEM; Model JEM-2010F, JEOL), and Fourier-transform infrared spectroscopy (FT-IR; Model FT-IR-610, Jasco). The Brunauer-Emmett-Teller (BET) surface areas of samples were also determined, using a BELSORP-mini apparatus (BEL Japan) at liquid nitrogen temperature. Thermogravimetric (TG) analysis was performed using a thermogravimetric analyser (TG/DTA 6200, Seiko Instruments Co.) under a flow of air (70 mL min⁻¹) at a heating rate of 10 K min⁻¹.

Photocatalytic reactions

8 mg of photocatalyst powder was dispersed in 4 mL of a 20 vol% TEOA solution in DMA within an 8 mL test tube. The suspension was subsequently purged with gaseous CO₂ (Taiyo Nippon Sanso Co., >99.9995%) for 20 min prior to irradiation. The light source employed in this work was a 400 W high pressure Hg lamp (SEN) with an aqueous NaNO₂ solution filter to allow for visible light irradiation ($\lambda > 400$ nm). The liquid phase of the reaction mixture was analysed using a capillary electrophoresis system (Otsuka Electronics Co. CAPI-3300) and the gaseous phase of the reaction cell was analysed with a gas chromatograph (GL science, GC323) employing a thermal conductivity detector (TCD), an activated carbon column and argon as the carrier gas.

Photoelectrochemical measurements

Photoelectrochemical measurements were carried out with a potentiostat (Model HSV-110, Hokuto Denko) at room temperature. The electrochemical cell was made of Pyrex glass with a three electrode-type system consisting of a Pt wire as the counter electrode and Ag/AgCl as the reference electrode. An aqueous Na₂SO₄ solution (0.1 M) was used as the electrolyte and was purged with Ar gas for 15 min prior to measurements. To obtain pH-dependent flat-band potential measurements, the pH of the electrolyte solution was adjusted to the desired values using either NaOH or H₂SO₄ solutions. The cell was irradiated with visible light from the backside of the working electrode, using a xenon lamp (300 W) with cut-off filters (L42 and Y50) to allow for visible light ($\lambda > 500$ nm) irradiation, where only the YTON component undergoes photoexcitation.

Emission decay measurements

The measurements were conducted in a similar manner to that reported previously.^{S4} Emission decay profiles were recorded using the single photon counting method, employing a FluoroCube spectrometer (emission decay; excitation light source: nanoLED-440 ($\lambda_{\text{ex}} = 444$ nm), detector:

Electronic Supplementary Information (ESI)

TBX-04, HORIBA ($\lambda_{\text{ob}} = 630 \text{ nm}$). The spectra were acquired at room temperature in 4.0 mL of an acetonitrile solution containing 3.0 mg of Ag/YTON on which **Ru(PS)** had been adsorbed at $1.4 \mu\text{mol g}^{-1}$. The suspension was bubbled with Ar gas for 20 min prior to each measurement.

Isotope-tracer experiments

Gaseous $^{13}\text{CO}_2$ (^{13}C , 99%, Aldrich Co.) was introduced into 2 mL of a 20 vol% TEOA solution mixed with $\text{MeCN-}d_3$ (4:1 v/v) containing 8.0 mg of the photocatalyst powder after the reaction cell was degassed by freeze-pump-thaw cycling. ^1H NMR spectra of the reaction solutions were acquired using a JEOL Model JNM-ECA 400 spectrometer, employing the $\text{MeCN-}d_3$ as an internal standard. Prior to obtaining spectra, the reacted suspensions were filtered to remove solids.

References

- S1. M. Kakihana, *J. Sol-Gel. Sci. Technol.*, 1996, **6**, 7–55.
- S2. K. Maeda, and K. Domen, *J. Catal.*, 2014, **310** 67–74.
- S3. A. Harriman, I. J. Pickering, J.M. Thomas, and P. A. Christensen, *J. Chem. Soc. Faraday Trans.*, 1988, **1**, 2795–2806.
- S4. F. Yoshitomi, K. Sekizawa, K. Maeda, and O. Ishitani, *ACS Appl. Mater. Interfaces*, 2015, **7**, 13092–13097.

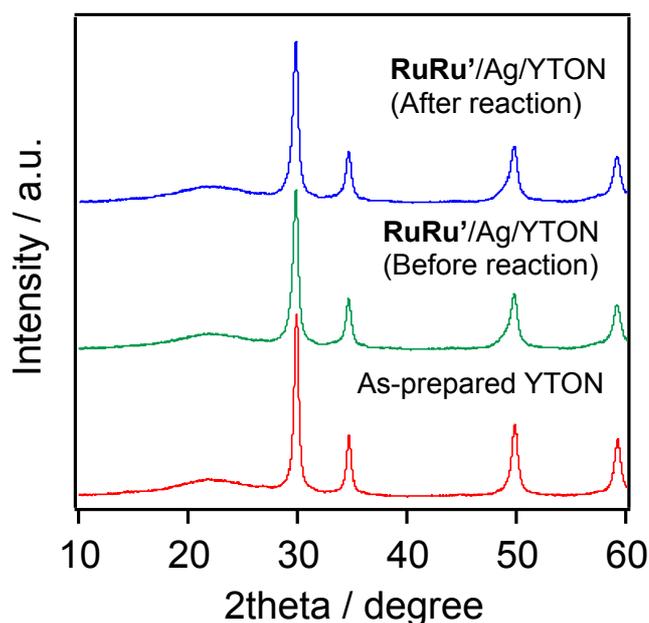


Fig. S1. XRD pattern of the as-prepared YTON. Data for **RuRu'**($4.5 \mu\text{mol g}^{-1}$)/Ag(1.5 wt%)/YTON before and after 24 h of reaction are also shown.

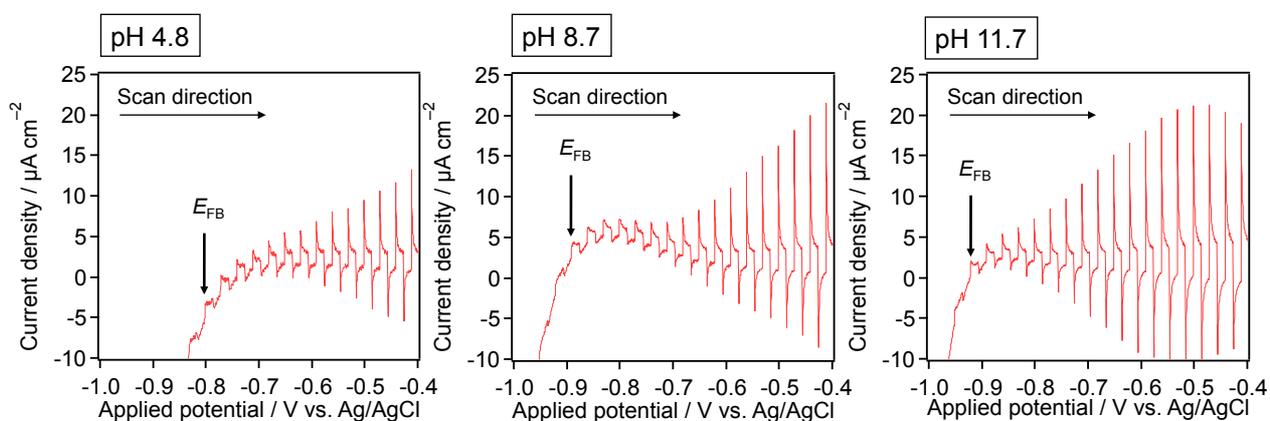


Fig. S2. Current–voltage curves acquired in a 0.1 M aqueous Na₂SO₄ solution at various pH values under intermittent visible light irradiation ($\lambda > 500$ nm) from IrO₂/TiO₂/YTON/FTO electrodes (5.25 cm²). Scan rate: 5 mV s⁻¹.

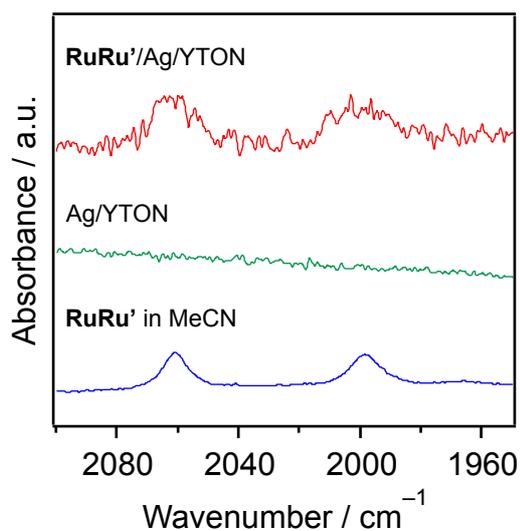


Fig. S3. FT-IR spectra of Ag/YTON with and without **RuRu'** modification (4.5 μmol g⁻¹) acquired using KBr pellets. The FT-IR spectrum of **RuRu'** in MeCN (11.5 μM) is also shown.

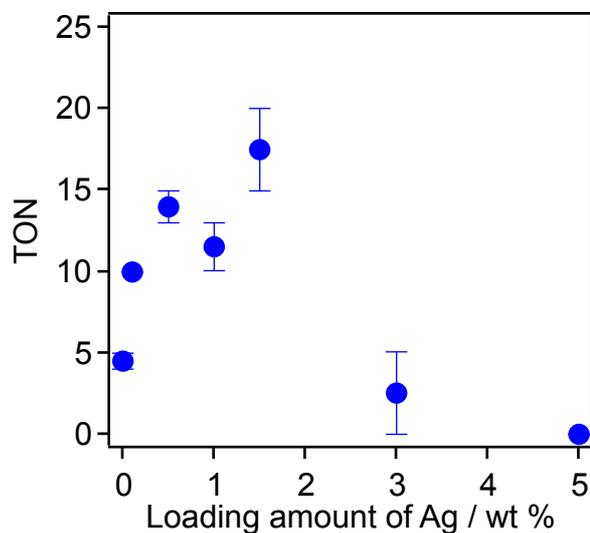


Fig. S4. Photocatalytic performance during CO₂ reduction to HCOOH over **RuRu'**(4.5 μmol g⁻¹)/Ag/YTON as a function of the loading amount of Ag. Reaction conditions: 8.0 mg photocatalyst; 4.0 mL 4:1 (v/v) DMA/TEOA; reaction time of 24 h.

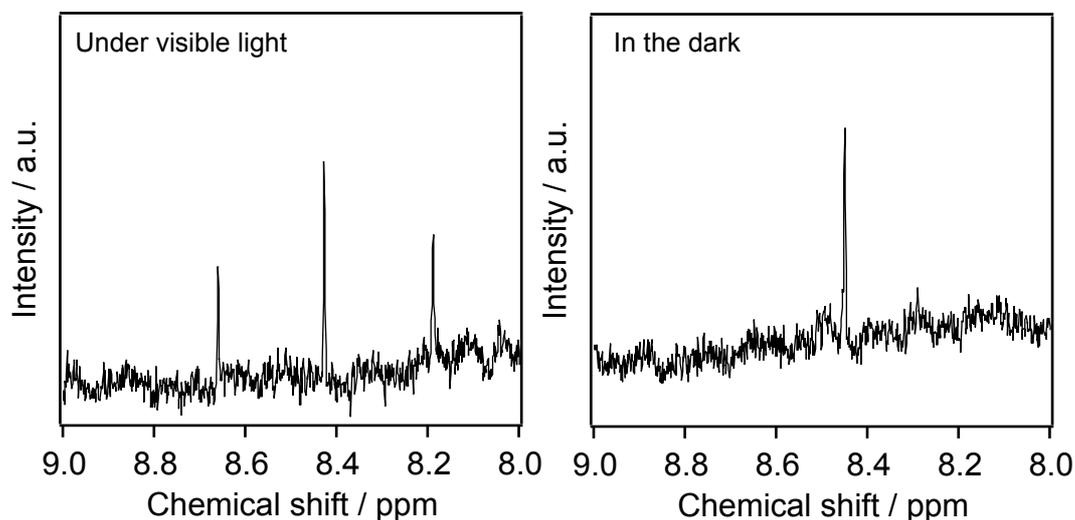


Fig. S5. ¹H-NMR spectra of a solution (MeCN/TEOA, 4:1 v/v, 2 mL) containing 8.0 mg of 1.5 wt% Ag-loaded YTON combined with **RuRu'** (11.8 μmol g⁻¹) after reaction and following filtration. The photocatalyst suspension was irradiated with visible light from a 400 W high pressure Hg lamp with a NaNO₂ solution filter for 60 h under ¹³CO₂ (640 Torr). As a control, the same procedure was performed in the dark (that is, without irradiation).