Experimental Procedures

Preparation of Semiconductors

Layered oxinitrides Li$_2$LaTa$_2$O$_6$N, CaTaO$_2$N, and LaTaON$_2$ were prepared by polymerized complex (PC) method.\[^1\] For Li$_2$LaTa$_2$O$_6$N, TaCl$_5$ (≥ 99.9 %, Mitsuwa Chemical Co.) was dissolved in methanol (≥ 99.8%, Kanto Chemical Co.). Then, LiCl (≥ 99.0, Kanto Chemical Co.), La(NO$_3$)$_3$·6H$_2$O (≥ 99.0%, Kanto Chemical Co.), Ethylene glycol (EG, ≥ 99.5%, Kanto Chemical Co.) and citric acid (CA, ≥ 98.0%, Wako Pure Chemical Co.) were added to the solution at a ratio of Li : La : Ta : EG : CA = 2–2.4 : 1 : 2 : 80 : 20. An excess amount of Li was added to compensate the loss due to volatilization during a calcination step. For CaTaO$_2$N and LaTaON$_2$, TaCl$_5$, CaCO$_3$ (≥ 99.5%, Kanto Chemical Co.) or La(NO$_3$)$_3$·6H$_2$O, EG and CA were dissolved in methanol (Ca : Ta : EG : CA = 1.25 : 1 : 9 : 36 or La : Ta : EG : CA = 1 : 1 : 7.5 : 30). The resulting solution was heated on a hot plate at ca. 473 K to form a resin, followed by heating in a muffle heater at 673 K to produce grey powder. The obtained powder was heated at 873 K for 5 h on an Al$_2$O$_3$ plate in air to get white powder, then heated at 1173 K for 12 h under 20 mL min$^{-1}$ of NH$_3$ flow in the case of Li$_2$LaTa$_2$O$_6$N, and 1223 K for 20 h under 100 mL min$^{-1}$ of NH$_3$ flow in the case of CaTaO$_2$N and LaTaON$_2$.

Preparation of RuRu’/Semiconductor

A Ru(II) binuclear complex (RuRu’) was synthesized according to a method reported in our previous paper.\[^2\] 50 mg semiconductor was suspended in 25 mL of MeCN in which an appropriate amount of RuRu’ (3 µmol g$^{-1}$) was dissolved, followed by stirring overnight and filtration. The complete absorption of the Ru complex was confirmed by the absence of MLCT absorption for the Ru photosensitizer unit in the remaining filtrate. The filtrated powder was dried under vacuum at room temperature and used for photocatalytic reactions. If necessary, modification of semiconductors with Ag nanoparticles was made before adsorption of RuRu’ by an impregnation method using AgNO$_3$ (99.8%; Kanto Chemical Co.) as the precursor, followed by heating in an H$_2$ stream (20 mL min$^{-1}$) at 473 K for 1 h in a tube furnace.\[^2\]

Fabrication of Electrodes

Li$_2$LaTa$_2$O$_6$N electrodes were prepared by electrophoretic deposition on a conductive glass modified with a fluorine-doped tin oxide (FTO) layer.\[^3\] A pair of FTO glasses was immersed in parallel at a distance of 1.8 cm in 50 mL of acetone (≥ 99.5 %, Kanto Chemical Co.) containing 50 mg of Li$_2$LaTa$_2$O$_6$N and 10 mg of I$_2$ (≥ 99.8%, Wako Pure Chemical Co.). The FTO electrodes were connected to a DC power supply (GW Instek PSW 80-13.5) and a bias of 50 V was applied between the FTO glasses for 1 min. The coated area was 1.5 cm × 3.7 cm. The electrode was finally heated at 473 K for 1 h in an air.

Characterization

X-ray diffraction (XRD) patterns were measured by a Rigaku MiniFlex600 powder diffractometer employing monochromatic Cu $K\alpha$ radiation. For Rietveld analysis, XRD data were measured by a laboratory-based X-ray powder diffractometer (Rigaku Co. Ltd. RINT-2500, Cu $K\alpha$), and the data were analyzed using a computer program Z-code.\[^4\] UV-visible diffuse reflectance spectra were obtained using a spectrophotometer (V-565, JASCO) with an integration sphere and BaSO$_4$ as a reference. Nitrogen adsorption measurements were conducted using a BELSORP-mini (MicrotracBEL) apparatus at liquid nitrogen temperature (77 K). SEM observations were performed using a Keyence VE-8800 microscope or a Jeol JSM-IT100LA microscope equipped with an EDS apparatus. For the STEM observations, a Titan Cubed microscope (FEI) equipped with spherical aberration correctors (CEOS) was used at an acceleration voltage of 80 kV to reduce electron irradiation damages. The convergence semiangle of the incident probe was 25 mrad. The inner and outer
detection semiangles of the ADF detector were 77 and 200 mrad, respectively. The incident probe current was set to 20 pA. The magnified image was processed for noise reduction using a Wiener filter implemented as FiltersPro plug-in (HREM Research) for DigitalMicrograph (Gatan).

XAFS measurements were conducted on the BL01B1 beamline of the SPring-8 synchrotron facility (Hyogo, Japan) using a ring energy of 8 GeV and a stored current of 100 mA in the top-up mode (Proposal No. 2017B1040 and 2017B1438) to acquire Ag-K edge spectra. XAFS spectra were acquired at room temperature in the transmittance mode using a Si(311) double-crystal-monochromator. A pair of Rh-coated mirrors was used to eliminate higher harmonics. The XANES spectra were processed using the Athena software package.[5]

Mott-Schottky Analysis
Mott-Schottky plots were measured in MeCN solution containing 0.1 M Et₄NBF₄ solution as an electrolyte at room temperature with a potentiostat (BAS ALS/CHI-760e) and a three-electrode-system. Li₂LaTa₂O₆N/FTO electrode, Pt wire and Ag/AgNO₃ electrode were used as working, counter and reference electrodes, respectively. Electrolyte was thoroughly bubbled with Ar prior to electrochemical measurement.

Transient Absorption Spectroscopy
Measurements were obtained using a homemade spectrometer described previously. Powders of Li₂LaTa₂O₆N, CaTaO₂N, and LaTaON₂ were applied to a CaF₂ plate at a density of 1.5 mg cm⁻² and placed into an IR cell for measurements. The samples were photoexcited using a 480 nm VIS pulse from an Nd:YAG laser (Continuum Surelite I; duration, 6 ns; power, 5 mJ; repetition rate, 5–0.1 Hz), and transient absorptions in the visible to mid-IR region were measured in vacuum. The time resolution of this spectrometer was limited to 1–2 µs by the bandwidth of the amplifier (Stanford Research Systems, SR560, 1 MHz).

Density Functional Theory (DFT) Simulations
To obtain total and partial density of states for Li₂LaTa₂O₆N, we performed DFT simulations with the GGA/PBE exchange-correlation functional. All the ionic cores were replaced with ultrasoft pseudopotentials. Kohn-Sham orbitals were expanded in terms of plane wave with cutoff energy of 340 eV. The Monkhorst-Pack k-point separation was set to be 0.07 Å⁻¹. The lattice parameters were fixed to the experimental ones, while atomic positions were optimized using the BFGS algorithm with convergence criteria for energy tolerance of 1.0×10⁻⁵ eV/atom, maximum force tolerance of 0.01 eV/Å, and maximum stress tolerance of 0.01 GPa. All the DFT simulations were performed using the CASTEP software.[9]

CO₂ Reduction
Reactions were performed at room temperature using an 8 mL test tube that contained 4 mL of solution and 4 mg of photocatalyst powder. Prior to irradiation, the suspension was purged with CO₂ (Taiyo Nippon Sanso Co., >99.995%) for 20 min. A 400 W high-pressure Hg lamp (SEN) was employed as a light source, in combination with an aqueous NaNO₂ solution to allow for visible light irradiation (λ > 400 nm). The formate generated in the liquid phase was analyzed using a capillary electrophoresis system (Otsuka Electronics Co., model CA-3300). The gaseous reaction products were analyzed using a gas chromatograph with a thermal conductivity detector (TCD) (GL Science, model GC323), an activated carbon column, and argon carrier gas.

Isotope Tracer Experiments
¹³CO₂ (13C, 99%) was purchased from Aldrich Co. No contamination of H¹3COOH in the ¹³CO₂ gas was detected using ¹H NMR spectroscopy. The ¹³CO₂ gas was introduced into a MeCN/TEOA mixed solution (4:1 (v/v), 2.0 mL) containing 4.0 mg of the photocatalyst powder,
after the solution was degassed by freeze–pump–thaw cycling. The no-deuterium proton NMR (No-D NMR) spectra for reaction solutions were obtained using a JEOL JNM-ECA 400 spectrometer. Solids were removed before measurements by filtration.

References

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**Figure S1.** (Left) Structure of binuclear Ru(II) complex (RuRu') and (right) the absorption spectrum.

**Figure S2.** Schematic illustration of CO₂ reduction over a RuRu'/semiconductor hybrid photocatalyst.
Figure S3. XRD patterns of Li$_2$LaTa$_2$O$_6$N prepared in different conditions.

Figure S4. XRD patterns of as-prepared materials with different amounts of Li supplied to the precursor. The reference pattern of Li$_2$LaTa$_2$O$_6$N (ICPDS #181960) is shown at the bottom.

Figure S5. Rietveld pattern of the Li$_2$LaTa$_2$O$_6$N. The experimental pattern (red dots), calculated pattern (green solid line) and difference profile (blue solid line) are shown. The triangle marks indicate the peak positions. Structure analysis was carried out with tetragonal crystal system (space group: $I4/mmm$). The final reliability factor was $R_{wp} = 0.1076$, with lattice parameters of $a$, $b = 3.9533(4)$ Å, $c = 18.452 (3)$ Å, and lattice volume of $V = 288.38(6)$ Å$^3$. 
**Figure S6.** SEM image of Li$_2$LaTa$_2$O$_6$N heated at 1173 K for 12 h under 20 mL min$^{-1}$ of NH$_3$ flow.

**Figure S7.** Mott-Schottky plots of Li$_2$LaTa$_2$O$_6$N with different frequencies in a MeCN solution containing 0.1 M Et$_4$NBF$_4$. Red: 100 Hz, blue: 500 Hz and green: 1000 Hz.

**Figure S8.** Schematic illustration of the band structure of Li$_2$LaTa$_2$O$_6$N determined by Mott-Schottky analysis and UV-visible diffuse reflectance spectroscopy. Data for CaTa$_2$O$_2$N and LaTaON$_2$ are also shown. Ag/AgNO$_3$ = 0.56 V vs. NHE at pH 7.
Figure S9. Total and partial DOS of Li$_2$LaTa$_2$O$_6$N with different N$^{3-}$ positions, where O atoms located at Wyckoff positions of 8g, 2a, or 4e are replaced with N atoms, respectively. Note that 2a and 4e cases have higher energies by 1.0 and 0.3 eV/f.u., respectively, compared to 8g one.

Figure S10. (a) XRD patterns and (b) DRS of RuRu$/\text{Li}_2\text{LaTa}_2\text{O}_6\text{N}$ before and after the photocatalytic CO$_2$ reduction reaction.
Figure S11. (a) Ag K-edge EXAFS spectra of Ag(1.5 wt%)-loaded Li$_2$LaTa$_2$O$_6$N, along with bulk Ag$_2$O and Ag foil for comparison. (b) FT of the $k^3$-weighted EXAFS spectra of the same samples.

Figure S12. TEM images of Ag(1.5 wt%)/Li$_2$LaTa$_2$O$_6$N.

Figure S13. No-D NMR spectra of filtered reaction solution [2.0 mL of 4:1 (v/v) MeCN/TEOA] containing 4.0 mg of RuRu'(3.0 µmol g$^{-1}$)/Ag(1.5 wt%)/Li$_2$LaTa$_2$O$_6$N. The photocatalyst suspension was subjected to visible light irradiation from a 400 W high-pressure mercury lamp with a NaNO$_2$ solution filter for 15 h under $^{13}$CO$_2$ (498 Torr) and saturated unlabeled CO$_2$. 
Figure S14. (a) XRD patterns of reference materials of CaTaO$_2$N and LaTaON$_2$, which were prepared by nitridation at 1223 K for 20 h and at 1223 K for 15 h, respectively, under NH$_3$ flow (100 mL min$^{-1}$). (b) DRS of the same samples.