Supplementary Information for:

Direct assembly synthesis of metal complex-semiconductor hybrid photocatalyst anchored by phosphonate for highly efficient CO_2 reduction

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SI-1. Materials

N-doped Ta_2O_5 powder

N-doped Ta_2O_5 powder (N-Ta_2O_5) was prepared by annealing Ta_2O_5 powder under NH_3 flow at 848 K for 6 h, according to a previously reported method.[1,2]

Synthesis of [Ru-dpbpy]/N-Ta_2O_5 by a direct assembly method

4,4'-diphosphonate-2,2'-bipyridine ([dpbpy])[3] adsorbed on N-Ta_2O_5 ([dpbpy]/N-Ta_2O_5) was prepared by shaking a mixture of N-Ta_2O_5 (500 mg) and 1.5 mM [dpbpy] solution in DMSO (10 mL) overnight. The solution was centrifuged, washed, and dried *in vacuo* at 313 K. The adsorption spectra of the supernatants were measured using a UV/vis spectrophotometer (Shimadzu UV-3600) and the amount of adsorbed ligand ([dpbpy]) on N-Ta_2O_5 was calculated. [dpbpy]/N-Ta_2O_5 (400 mg) and $[Ru(bpy)(CO)_2(CF_3SO_3)_2]$[4] (2 equiv. vs. adsorbed [dpbpy]) were mixed in ethanol under N_2 and refluxed for 5 h. The solution was filtered, washed, and dried i*n vacuo* to obtain [Ru-dpbpy]/N-Ta_2O_5. The $[Ru(dcbpy)(bpy)(CO)_2]^{2+}$/N-$Ta_2O_5$ ([Ru-dcbpy]/N-Ta_2O_5, anchoring group: carboxylate) hybrid photocatalysts were also synthesized by a similar method. The chemical structures of the composites were characterized using Fourier transform infrared (FTIR) spectroscopy (VERTEX 80, Bruker Optics) combined with an attenuated total reflectance (ATR) accessory (Dura Sample IR, Smiths Detection). The

Ru content in the samples was determined by inductively-coupled plasma (ICP) analysis (Rigaku CIROUS 120 EOP).

Synthesis of [Ru-dpbpy]/TiO_2 by a direct assembly method

Ru-complex immobilized using phosphonate groups on TiO_2 powder (particle size 20 nm)-coated fluorine-doped tin dioxide (FTO) glass were fabricated by the direct assembly method (abbreviated as [Ru-dpbpy]/TiO_2).

4,4'-diphosphonate-2,2'-bipyridine ([dpbpy])[3] adsorbed on TiO_2/FTO electrode ([dpbpy]/TiO_2) was prepared by shaking a mixture of TiO_2/FTO electrode (0.8 cm x 1 cm) and 1 mM [dpbpy] solution in DMSO (5 mL) overnight. The electrode was washed and dried *in vacuo* at 313 K. [dpbpy]/TiO_2 and $[Ru(bpy)(CO)_2(CF_3SO_3)_2]$[4] were mixed in ethanol under N_2 and refluxed for 5 h. The solution was filtered, washed, and dried *in vacuo* to obtain [Ru-dpbpy]/TiO_2. The [Ru-dcbpy]/TiO_2 electrode (anchoring group: carboxylate) was also synthesized by a similar method.

SI-2. FE-SEM image of N-Ta_2O_5

A Hitachi FE-SEM S-5500 field-emission scanning electron microscope was used for morphological characterization of N-Ta_2O_5.

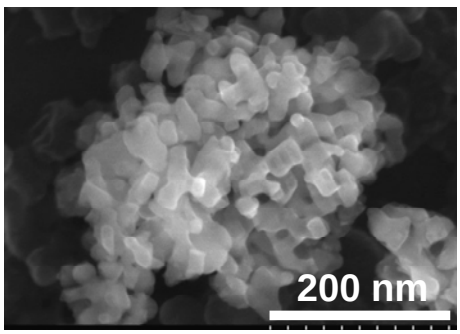

Fig. S1 FE-SEM image of N-Ta_2O_5.

SI-3. TOF-SIMS measurements of hybrid photocatalysts

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were performed using a TOF-SIMS V instrument (ION-TOF GmbH) equipped with a Bi liquid metal ion gun. Mass spectra were acquired with a pulsed 30keV, 1.6pA Bi^+ primary ion beam in high current bunched mode from an area of 100μm×100μm. The total ion dose in these measurements was maintained to ensure static conditions.

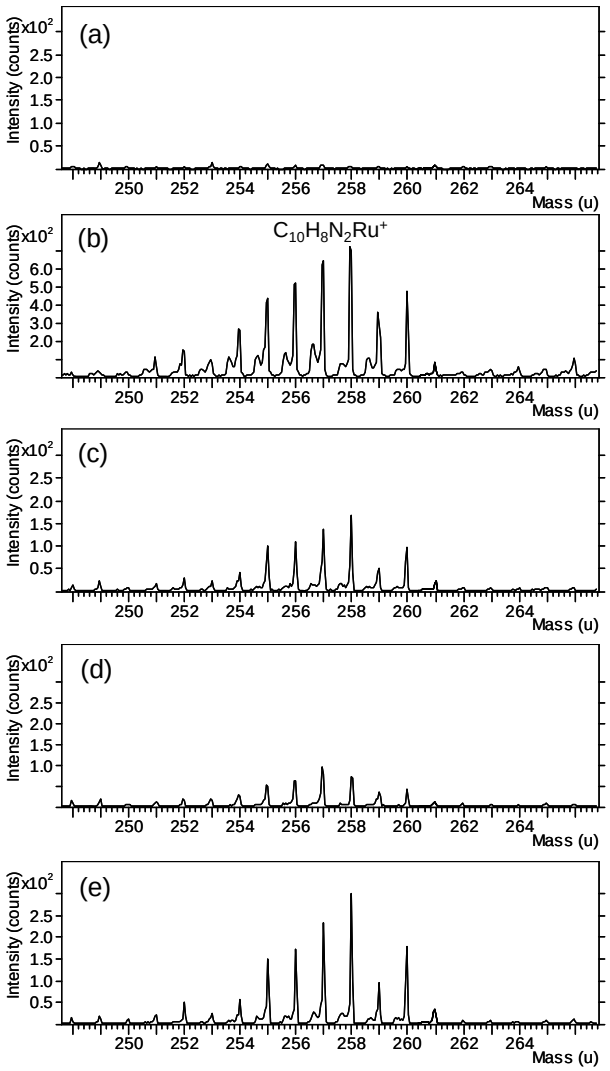

Fig. S2 TOF-SIMS positive spectra of (a) N-Ta_2O_5, (b) [Ru-bpy], (c) [Ru-dcbpy]/N-Ta_2O_5, (d) $[Ru\text{-}dcbpy]_{ads}$/N-Ta_2O_5, and (e) [Ru-dpbpy]/N-Ta_2O_5.

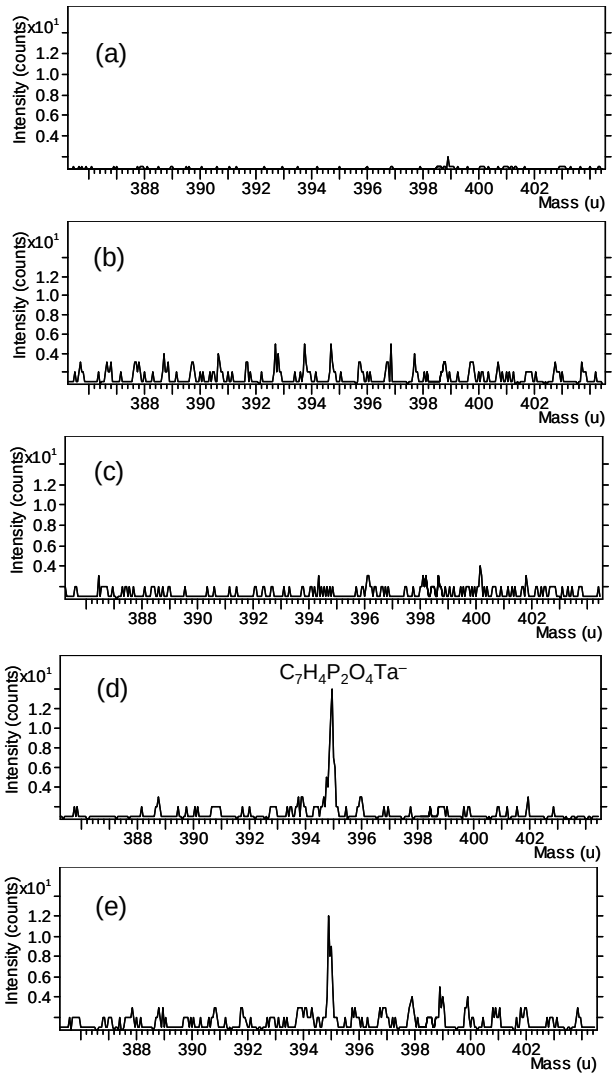

Fig. S3 TOF-SIMS negative spectra of (a) N-Ta_2O_5, (b) [Ru-bpy], (c)dpbpy, (d) [dpbpy]/N-Ta_2O_5, and (e) [Ru-dpbpy]/N-Ta_2O_5.

SI-4. Cyclic voltammograms of Ru-complex on electrode

The redox potentials of the complexes were measured in an MeCN solution containing tetraethylammonium tetrafluoroborate (0.1 M) under Ar or CO_2 atmosphere. The cyclic voltammetry was performed using an ALS2323 (ALS CO., Ltd.) electrochemical analyzer with a glassy carbon disk working electrode and I_2/I_3^- (0.1 M) reference electrode, and a Pt counter electrode.

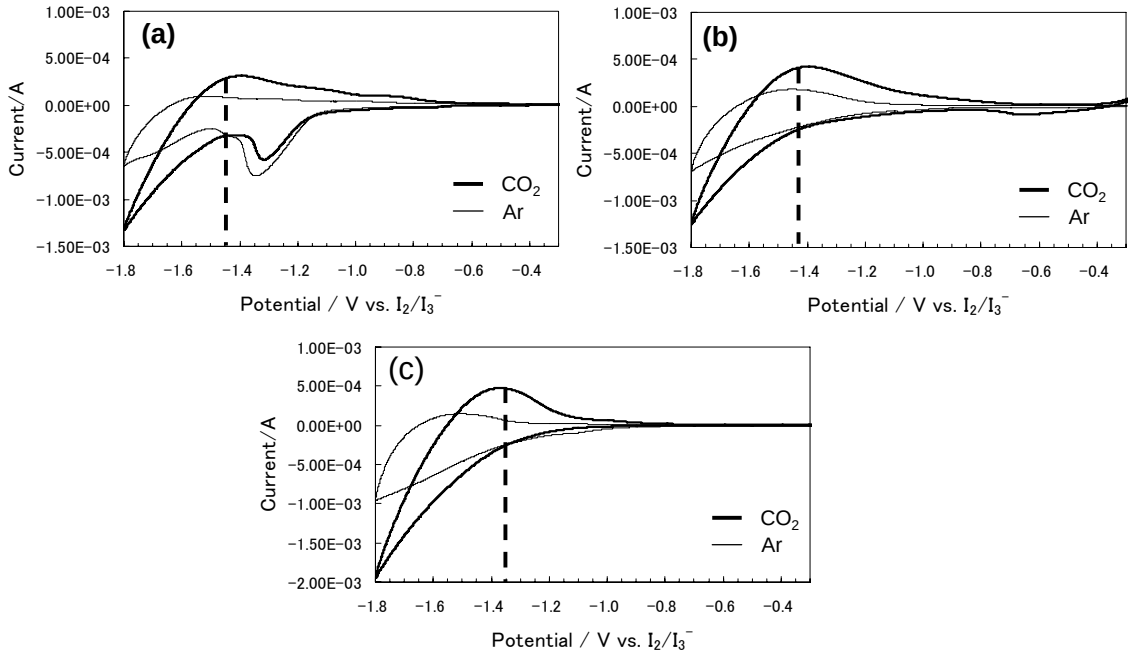

Fig. S4 Cyclic voltammograms of (a) a mixture of Ru-bpy solution and FTO-TiO_2, (b) [Ru-dcbpy]/TiO_2, and (c) [Ru-dpbpy]/TiO_2 in acetnitrile solutions containing tetraethyammonium tetrafluoroborate (0.1 M) under Ar or CO_2 atmosphere.

References

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