Supplementary Information for:

Direct assembly synthesis of metal complex-semiconductor hybrid photocatalyst anchored by phosphonate for highly efficient CO₂ reduction

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SI-1. Materials

N-doped Ta₂O₅ powder

N-doped Ta₂O₅ powder (N-Ta₂O₅) was prepared by annealing Ta₂O₅ powder under NH₃ flow at 848 K for 6 h, according to a previously reported method.¹,²

Synthesis of [Ru-dpbpy]/N-Ta₂O₅ by a direct assembly method

4,4’-diphosphonate-2,2’-bipyridine ([dpbpy])³ adsorbed on N-Ta₂O₅ ([dpbpy]/N-Ta₂O₅) was prepared by shaking a mixture of N-Ta₂O₅ (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-Ta₂O₅ was calculated. [dpbpy]/N-Ta₂O₅ (400 mg) and [Ru(bpy)(CO)₂(CF₃SO₃)]²⁺ (2 equiv. vs. adsorbed [dpbpy]) were mixed in ethanol under N₂ and refluxed for 5 h. The solution was filtered, washed, and dried in vacuo to obtain [Ru-dpbpy]/N-Ta₂O₅. The [Ru(dcbpy)(bpy)(CO)₂]²⁺/N-Ta₂O₅ ([Ru-dcbpy]/N-Ta₂O₅, 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).
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$_3$SO$_3$)$_2$]$^4$ 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$_2$O$_5$**

A Hitachi FE-SEM S-5500 field-emission scanning electron microscope was used for morphological characterization of N-Ta$_2$O$_5$.

![Fig. S1 FE-SEM image of N-Ta$_2$O$_5$.](image-url)
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 x 100μm. The total ion dose in these measurements was maintained to ensure static conditions.

Fig. S2  TOF-SIMS positive spectra of (a) N-Ta$_2$O$_5$, (b) [Ru-bpy], (c) [Ru-dcbpy]/N-Ta$_2$O$_5$, (d) [Ru-dcbpy]$_{ads}$/N-Ta$_2$O$_5$, and (e) [Ru-dpbpy]/N-Ta$_2$O$_5$. 
Fig. S3 TOF-SIMS negative spectra of (a) N-Ta$_2$O$_5$, (b) [Ru-bpy], (c)dpbpy, (d) [dpbpy]/N-Ta$_2$O$_5$, and (e) [Ru-dpbpy]/N-Ta$_2$O$_5$. 
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


