

ELECTRONIC SUPPLEMENTARY INFORMATION

High-turnover visible-light photoreduction of CO₂ by a Re(I) complex stabilized on dye-sensitized TiO₂

Eun-Gyeong Ha,^a Jeong-Ah Chang,^a Seong-Min Byeong,^a Chyongjin Pac,^b Dong-Myung Jang,^a Jeonghee Park,^a and Sang Ook Kang^a

^a Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong-city 339-700, Korea, E-mail: parkjh@korea.ac.kr; sangok@korea.ac.kr.

^b Yulchon Research Center, Korea University, Sejong-ro 2511, Sejong-city 339-700, Korea, E-mail: jpac@korea.ac.kr.

Table of Contents

Experimental details

Fig. S1 IR and diffuse-reflectance absorption spectra of H-TiO₂ and **ReC/H-TiO₂/Dye**.

Fig. S2 CO formation for the hybrids based on S-TiO₂ and D-TiO₂.

Fig. S3 CO formation by extended irradiation for **ReC/H-TiO₂/DA**.

Fig. S4 CO formation for homogeneous solution photoreactions of ReE/triethanolamine, ReE/SD and Ru(bpy)₃²⁺/ReE/SD combinations in DMF.

Fig. S5 Transmission electron microscopy images of H-TiO₂, D-TiO₂, as-prepared [001] facet-exposed TiO₂ and S-TiO₂

Fig. S6 Transmission electron microscopy images of H-TiO₂, D-TiO₂, as-prepared [001] facet-exposed TiO₂ and S-TiO₂

Fig. S7 XRD pattern of H-TiO₂, D-TiO₂ and S-TiO₂.

Fig. S8 CO formation in repetitive irradiation experiments for Dye/S-TiO₂/**ReC**, Dye/H-TiO₂/**ReC** and Dye/D-TiO₂/**ReC**.

Experimental details

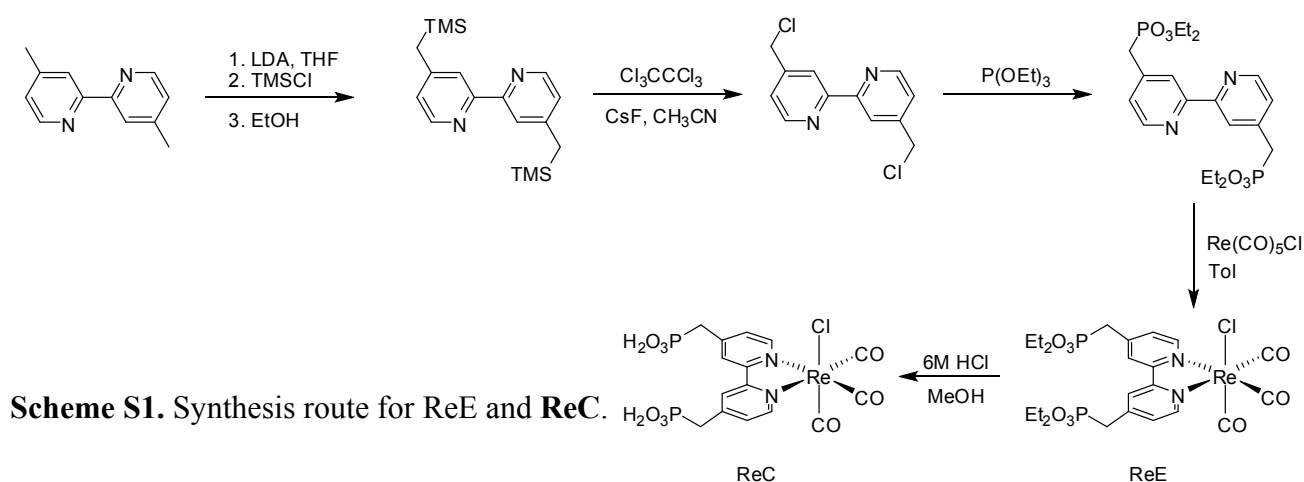
Unless stated otherwise, all reagents and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ were purchased from Aldrich and used without further purification. All manipulations were performed under a dry nitrogen or argon atmosphere using standard Schlenk techniques. *N,N*-Dimethylformamide (DMF) was distilled from calcium hydride and stored over molecular sieves. Tetrahydrofuran (THF) and toluene were refluxed over and distilled from sodium/benzophenone before use. The ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 and 75.4 MHz, respectively, for CDCl_3 or $\text{DMSO-}d_6$ solutions. Proton and carbon chemical shifts were referenced relative to the corresponding solvent signals, δ_{H} 7.24 and δ_{C} 77.0 of CHCl_3 and δ_{H} 2.49 and δ_{C} 39.5 of $\text{DMSO-}d_6$. Column chromatography was performed on silica gel (Merck 70D, 230 mesh), and TLC was done on silica-gel plates (Merck, kieselgel 60 F254, 0.20 mm). Elemental analyses and high resolution tandem mass spectrometry were performed, respectively, on a Carlo Erba Instruments CHNS-O EA 1108 analyzer and on a Jeol LTD JMS-HX 110/110A at the Korean Basic Science Institute (Ochang). The absorption and photoluminescence spectra were recorded on a Shimadzu UV-3101PC UV/Vis/NIR scanning spectrophotometer and a VARIAN Cary Eclipse fluorescence spectrophotometer, respectively. The diffuse reflectance UV-visible absorption spectra of powder samples were recorded on a Scinco spectrophotometer S-3100. The IR spectra were taken on a Cary 660 FTIR spectrometer. Cyclic voltammetry (CV) measurements were carried out for DMF solutions of the rhenium complexes or the dye (1 mM) in the presence of tetrabutylammonium hexafluorophosphate (0.1 M) at room temperature using a BAS 100B electrochemical analyzer equipped with a Pt working electrode, a platinum wire counter electrode, and an $\text{Ag}|\text{AgNO}_3$ (0.1 M) reference. All potential values were calibrated vs. a ferrocenium/ferrocene (Fc^+/Fc) redox couple (-0.63 V).

Preparation of Dye-sensitized TiO_2/ReC Catalyst. The [001] facet exposed TiO_2 which had been prepared according to the published method¹ was treated with 0.1 M NaOH aqueous solution to give S- TiO_2 .² The alkaline treatment was indispensable for efficient deposition of **ReC** and Dye on the particles, because the deposition of **ReC** and Dye was poor on the fluorinated surface of the as-prep

ared [001] TiO₂. H-TiO₂ and D-TiO₂ are commercially available Hombikat UV-100 and Degussa P-25, respectively. The specific Brauner-Emmet-Teller (BET) surface areas were determined to be > 250 m²/g for H-TiO₂, 50 m²/g for D-TiO₂ and 110 m²/g for S-TiO₂. These TiO₂ materials were thoroughly washed with distilled water, ultrasonically treated in water, separated by centrifugation and then dried in an oven under N₂. The TiO₂ particles (0.1 g) were stirred overnight in an MeCN/*tert*-butanol solution of **ReC** (1 μmol) and then subjected to centrifugation. The collected solids were washed with the solvent and then dried in an oven under N₂. The Re(I) complex-deposited TiO₂ powders (0.1 g) were dispersed into an MeCN/*tert*-butanol solution of Dye (15 μmol) and allowed to stand overnight under stirring. The photocatalysts (**ReC**/TiO₂/Dye) were separated by centrifugation, washed with MeCN/*tert*-butanol, dried in an oven (70°C) and stored under N₂ in the dark. The preparation of Dye/TiO₂/**ReC** was performed by the initial loading of Dye on the TiO₂ particles followed by treatment with an MeCN/*tert*-butanol solution of **ReC**, while each procedure for Dye or **ReC** loading was identical with that described above for **ReC**/TiO₂/Dye. It was confirmed by UV-visible absorption spectroscopy that each supernatant separated after centrifugation of the Dye- and **ReC**-treated suspensions shows negligible absorption of Dye or **ReC**.

Photocatalyzed CO₂ Reduction. Suspensions of **ReC**/TiO₂/Dye or Dye/TiO₂/**ReC** particles (10 mg with 0.1 μmol **ReC** and 1.5 μmol Dye) in 3 ml DMF containing SD (0.1 M) were placed in a quartz cell (1-cm pass length; 6.0 mL total volume), bubbled with CO₂ for 30 min, sealed with a septum and then irradiated under stirring by a Xenon lamp (450 W, model 66924, Newport corporation); the incident light ($\lambda > 420$ nm) was obtained by passing the light from the Xenon lamp through a water layer of 10 cm path length and a glass light filter. Homogeneous-solution photoreactions were performed for 3 mL solutions of (a) ReE (1.0 mM) in 5:1 DMF/triethanolamine (TEOA), (b) ReE (1.0 mM) in DMF containing 0.1 M SD and (c) a mixture of [Ru(bpy)₃]Cl₂ (0.1 mM) and ReE (0.5 mM) in DMF containing 0.1 M SD. The irradiation setup was the same as that described above, but appropriate glass light filters were used to cut off the light

of ≤ 350 nm for (a), ≤ 400 nm for (b) and ≤ 420 nm for (c). The amounts of CO evolved in the overhead space of the cell were determined by gas chromatography (HP6890A GC equipped with a TCD detector) using a 5 A molecular sieve column. The liquid phase of the irradiated samples was subjected to HPLC analysis using a Waters 515 pump, a Waters 486 UV detector operated at 210 nm, a RezexTM ROA-Organic Acid H⁺ column (300 mm \times 7.8 mm) and 0.01 M H₂SO₄ aqueous solution eluent. No peak was detected at 5 min (retention time for oxalic acid) and at 9 min (retention time for formic acid).



Synthesis

The preparation method for Dye was described in a previous paper.³ ReCl(CO)₅⁴ and SD⁵ were prepared according to the published methods. Scheme S1 shows the synthetic route for ReE and ReC following literature methods,⁶ details of which are described below.

4,4'-Bis[(trimethylsilyl)methyl]-2,2'-bipyridine. To a THF solution (16 mL) of diisopropylamine (1.75 mL, 12.5 mmol) cooled to -78 °C was added a 1.6 M hexane solution of butyllithium (n-BuLi) (6.9 mL, 11 mmol). The solution was stirred at -78 °C for 10 min, warmed to 0 °C, stirred for 10 min at this temperature and then cooled to -78 °C. To this solution kept at -78 °C was added a solution of 4,4'-dimethyl-2,2'-bipyridine (0.921 g, 5 mmol) in THF (22 mL) via cannula. The resulting reaction mixture was stirred at -78 °C for 20 min, warmed to -10 °C, stirred for 25 min and then cool

ed to $-78\text{ }^{\circ}\text{C}$. To this cold solution was added chlorotrimethylsilane (1.65 mL, 12.5 mmol) via syringe. After the solution became pale blue-green, the reaction was quenched by rapid addition of absolute ethanol (3 mL). The yellow cold reaction mixture was poured into aqueous saturated sodium bicarbonate ($\approx 60\text{ mL}$) and extracted with EtOAc; the combined organic fractions were shaken with brine ($\approx 200\text{ mL}$) and dried over Na_2SO_4 . Filtration and concentration on a rotary evaporator afforded 1.6 g (40 %) of 4,4'-bis[(trimethylsilyl)methyl]-2,2'-bipyridine. mp $90\text{--}92\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ : 0.04 (s, 18 H), 2.21 (s, 4 H), 6.94 (d, 2 H), 8.05 (br s, 2 H), 8.46 (d, 2 H). HRMS(FAB) calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{Si}_2$: 328.60. Found: 328.65 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{Si}_2$: C, 65.79; H, 8.59; N, 8.53. Found: C, 65.78; H, 8.43; N, 8.76.

4,4'-Bis(chloromethyl)-2,2'-bipyridine. A mixture of 4,4'-bis[(trimethylsilyl)methyl]-2,2'-bipyridine (1.0 g, 3.0 mmol), hexachloroethane (2.9 g, 12.2 mmol) and cesium fluoride (1.8 g, 12.2 mmol) in 20 mL acetonitrile was stirred at $60\text{ }^{\circ}\text{C}$ for 3.5 h under a nitrogen atmosphere, cooled to $25\text{ }^{\circ}\text{C}$ and then poured into a separate flask containing ethyl acetate and water (20 mL each). The product was extracted with EtOAc ($3 \times 20\text{ mL}$); the combined organic fractions were shaken with brine (40 mL) and dried over Na_2SO_4 . After filtration and concentration on a rotary evaporator, the residue was subjected to flash chromatography on silica gel (6:4 ethyl acetate:hexanes) to give 0.7 g (91%) of bis(chloromethyl)bipyridine as a white solid. mp $98\text{--}100\text{ }^{\circ}\text{C}$; $^1\text{H NMR}$ (CDCl_3 , 300 MHz) δ : 4.63 (s, 4 H), 7.38 (dd, 2 H), 8.43 (s, 2 H), 8.70 (d, 2 H). HRMS(FAB) calcd for $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2$: 253.13. Found: 253.19 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{N}_2$: C, 56.94; H, 3.98; N, 11.07. Found: C, 56.82; H, 4.04; N, 11.01.

4,4'-Bis(diethoxyphosphorylmethyl)-2,2'-bipyridine.⁷ A 50-mL three-neck round bottom flask containing 1.0 g of 4,4'-bis(chloromethyl)-2,2'-bipyridine (4.0 mmol) was purged and evacuated under argon ($\times 3$), and then triethyl phosphite (6.96 mL, 40 mmol) was added. The solution was refluxed overnight with stirring and cooled to room temperature. After removal of volatile materials under reduced pressure, the residue was subjected to column chromatography on silica gel using a 4:4:1 toluene:hexanes:triethylamine eluent to yield the phosphonated bipyridine 88% (1.23 g, 3.55

mmol); ^1H NMR (CDCl_3 , 300 MHz) δ : 1.27 (t, 12 H), 3.19 (s, 2 H), 3.26 (s, 2 H), 4.07 (m, 8 H), 7.32 (d, 2 H), 8.33 (s, 2 H), 8.60 (d, 2 H). HRMS(FAB) calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_2$: 456.16. Found: 456.41 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_6\text{P}_2$: C, 52.63; H, 6.63; N, 6.14. Found: C, 52.61; H, 6.66; N, 6.19.

***fac*-[Re(4,4'-Bis(diethoxyphosphorylmethyl)-2,2'-bipyridine)(CO)₃Cl] (ReE).** A toluene solution (5 mL) containing a mixture of 4,4'-bis(diethoxyphosphorylmethyl)-2,2'-bipyridine (0.13 g, 0.29 mmol) and $\text{Re}(\text{CO})_5\text{Cl}$ (0.1 g, 0.28 mmol) was refluxed for 5 h and then cooled to room temperature. After evaporation of solvent, the remaining solid was recrystallized from methanol to give the product as a yellow solid. Yield : 0.19 g (90 %) ; ^1H NMR (CDCl_3 , 300 MHz) δ : 1.32 (t, 12 H), 3.25 (s, 2 H), 3.32 (s, 2 H), 4.13 (m, 8 H), 7.45 (d, 2 H), 8.20 (s, 2 H), 8.94 (d, 2 H). HRMS(FAB) calcd for $\text{C}_{23}\text{H}_{30}\text{ClN}_2\text{O}_9\text{P}_2\text{Re}$: 762.07. Found: 762.10 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{ClN}_2\text{O}_9\text{P}_2\text{Re}$: C, 36.25; H, 3.97; N, 3.68. Found: C, 36.23; H, 3.99; N, 3.65.

***fac*-[Re(4,4'-Bis(dihydroxyphosphorylmethyl)-2,2'-bipyridine)(CO)₃Cl] (ReC).** A methanol solution (12 mL) containing a mixture of ReE (0.1 g, 0.16 mmol) and 6N HCl (6mL) was refluxed for 12 h. To this solution were added methanol (2 mL) and 1M NaHCO_3 (2 mL), and then yellow solid precipitated was collected by filtration. The solid was recrystallized from methanol. Yield : 0.08 g (80 %) ; ^1H NMR (CDCl_3 , 300 MHz) δ : 3.25 (s, 2 H), 3.33 (s, 2 H), 3.67 (br s, 4 H), 7.61 (d, 2 H), 8.54 (s, 2 H), 8.90 (d, 2 H). HRMS(FAB) calcd for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{O}_9\text{P}_2\text{Re}$: 649.94. Found: 649.89 $[\text{M}]^+$. Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{O}_9\text{P}_2\text{Re}$: C, 27.72; H, 2.17; N, 4.31. Found: C, 27.75; H, 2.11; N, 4.29.

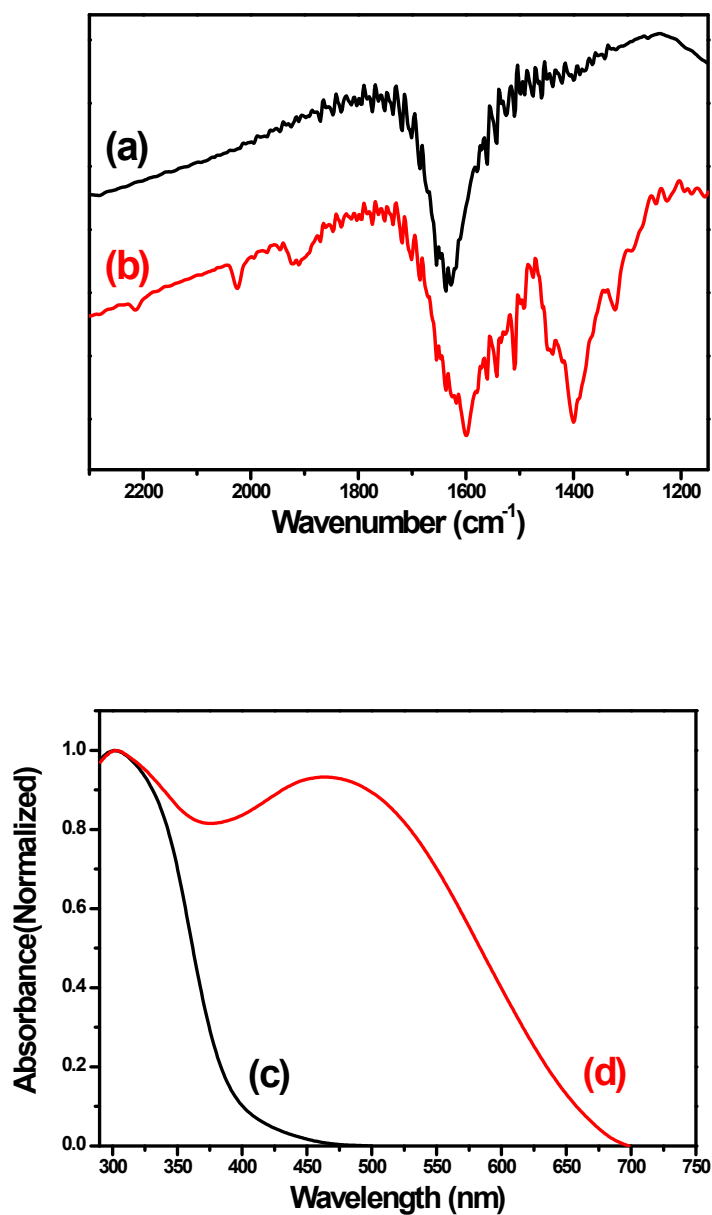


Fig. S1 IR spectra of H-TiO₂ (a) and **ReC**/H-TiO₂/Dye (b) in KBr disc (top) and normalized diffuse-reflectance absorption spectra of H-TiO₂ (c) and **ReC**/H-TiO₂/Dye (d) (bottom). The IR spectrum (b) show absorptions at 2030 and 1890 – 1920 cm⁻¹ due to the CO ligands of **ReC**, at 2210 cm⁻¹ for the CN group of Dye and at 1300 – 1700 cm⁻¹ mainly attributable to the C=O, P=O and C=C bonds.

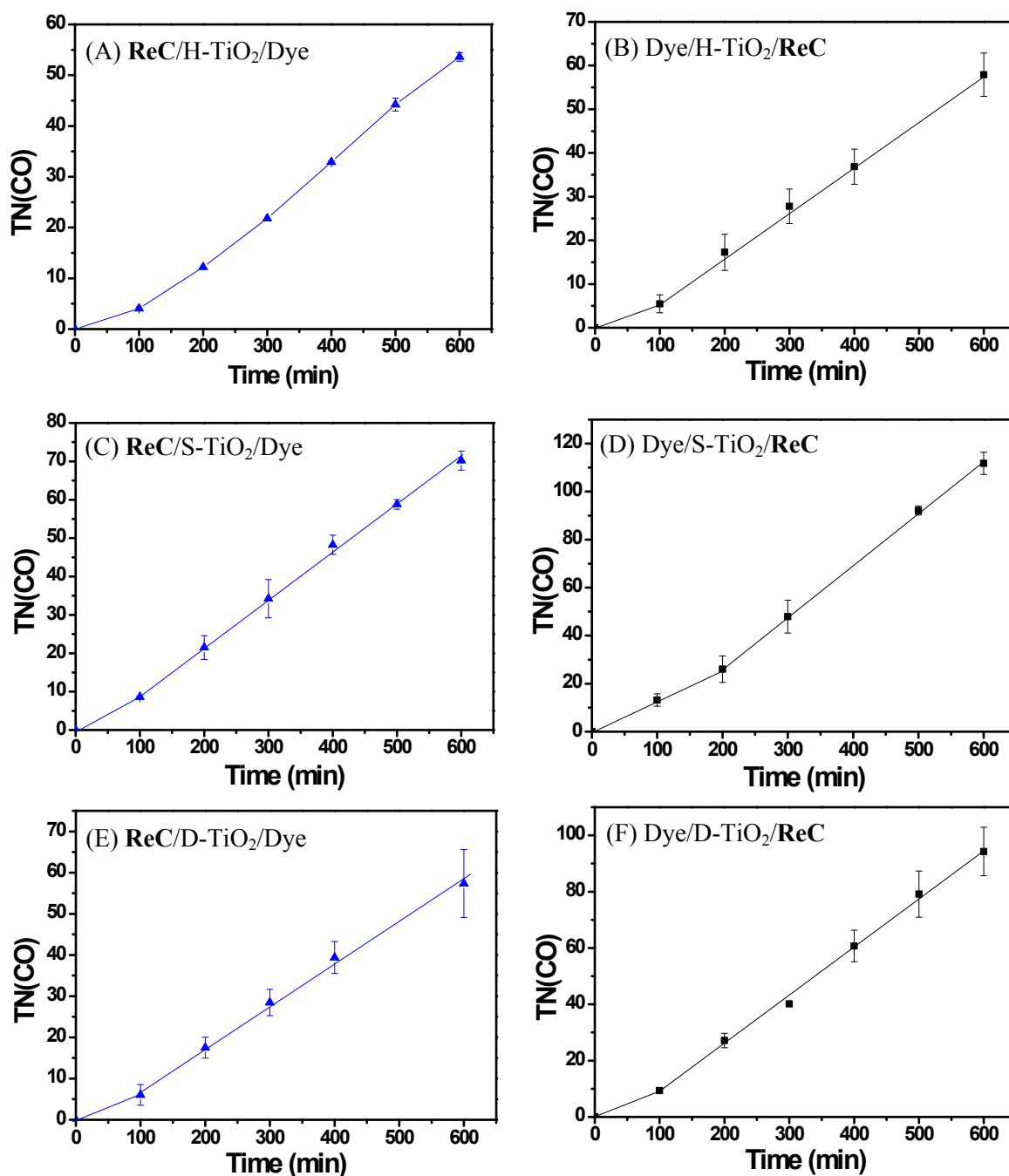


Fig. S2 Time courses of CO formation during irradiation at > 420 nm for 10 h. The left and right panels show the plots for **ReC/TiO₂/Dye** and for **Dye/TiO₂/ReC**, respectively (TiO₂ = H-TiO₂ (A, B), S-TiO₂ (C, D) and D-TiO₂ (E, F)); 10 mg of the hybrids with 0.1 μ mol **ReC** and 1.5 μ mol **Dye** in 3 mL DMF in the presence of 0.1 M SD.

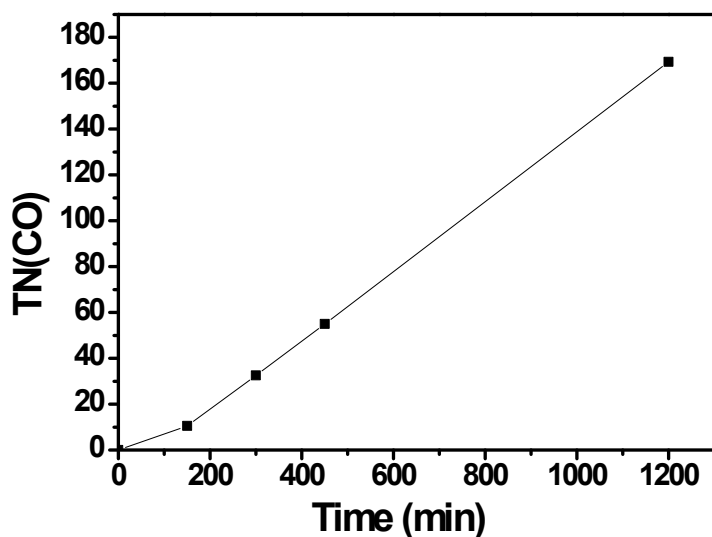


Fig. S3 Formation of CO during irradiation for 20 h at > 420 nm; 10 mg of **ReC**/H-TiO₂/Dye with 0.1 μ mol **ReC** and 1.5 μ mol Dye in 3 mL DMF in the presence of 0.1 M SD.

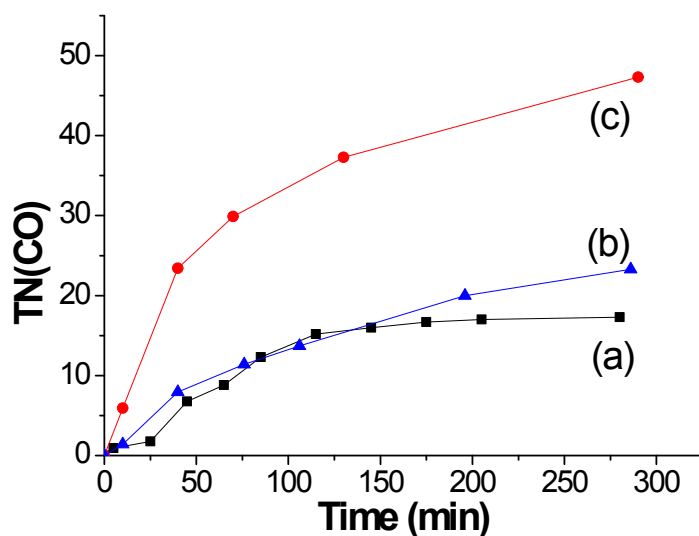


Fig. S4 Formation of CO in CO₂-saturated homogeneous solution (3 mL); irradiation of (a) ReE (1.0 mM) in 5:1 DMF:TEOA at > 350 nm (—■—), (b) ReE (1.0 mM) in the presence of SD (0.1 M) in DMF at > 400 nm (—●—) and (c) Ru(bpy)₃²⁺ (0.1 mM) in the presence of ReE (0.5 mM) and SD (0.2 M) in DMF at > 420 nm (—▲—).

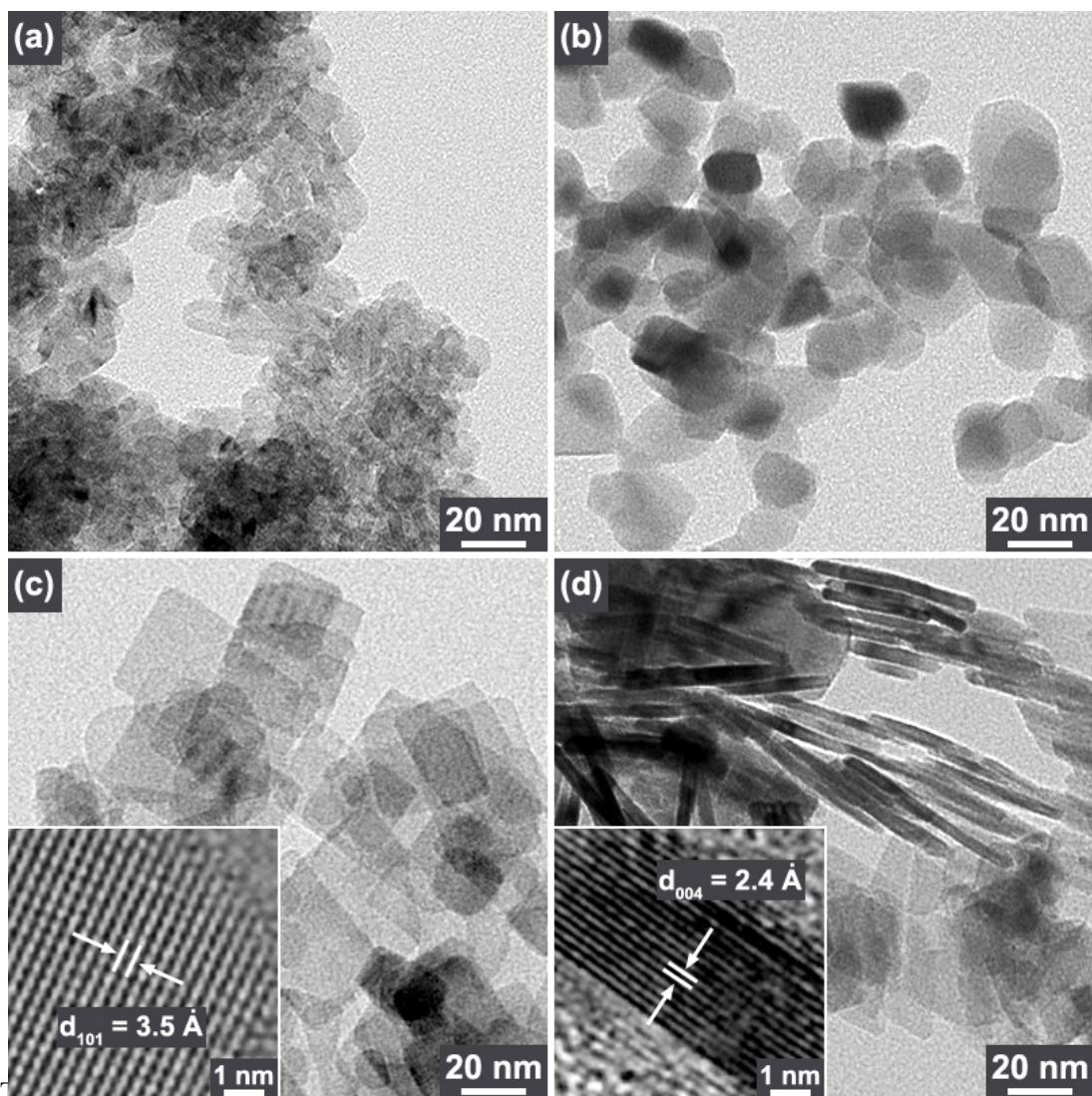


Fig. S5 Transmission electron microscopy images of H-TiO₂ (a), D-TiO₂ (b), as prepared [001] face t-exposed TiO₂ (c) and S-TiO₂ (d). Average sizes are 3.5 nm for H-TiO₂, 18 nm for D-TiO₂ and 20 nm (length)×5 nm (thickness) for square-shaped nanosheet S-TiO₂ with ≈ 90 % [001] facets. Insets in (c) and (d) show the *d*-spacing of the (101) and (004) planes which is 3.5 and 2.3 Å, respectively, consistent with the values of the anatase phase bulk (JCPDS No. 21-1272; tetragonal $a = 3.785 \text{ \AA}$ and $c = 9.513 \text{ \AA}$).

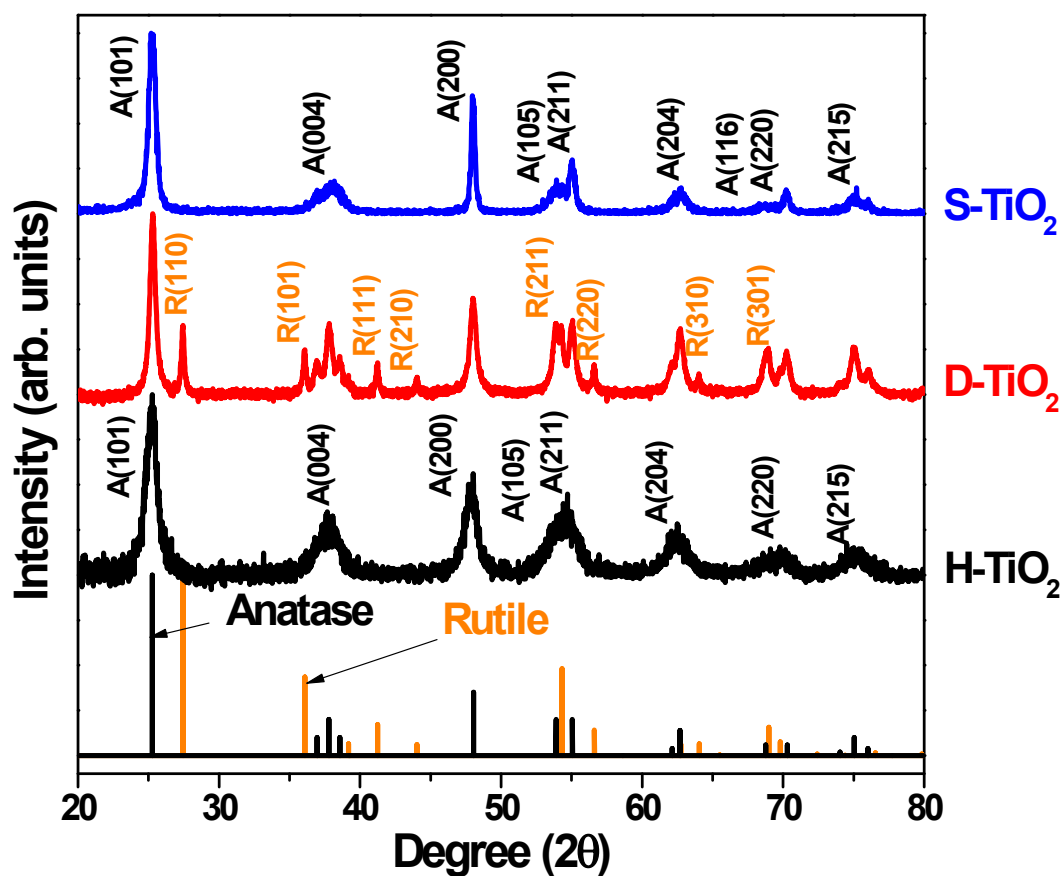


Fig. S6 XRD pattern of H-TiO₂, D-TiO₂ and S-TiO₂. The H-TiO₂ and S-TiO₂ are in almost pure anatase phase, while the D-TiO₂ consists of anatase (denoted as A) and rutile (denoted as R) tetragonal phase mixture. The peaks of A and R phases are assigned using those of the anatase phase (JCPDS No. 21-1272; tetragonal $a = 3.785 \text{ \AA}$ and $c = 9.513 \text{ \AA}$) and the rutile phase (JCPDS No. 87-0920; tetragonal $a = 4.594 \text{ \AA}$ and $c = 2.958 \text{ \AA}$), respectively.

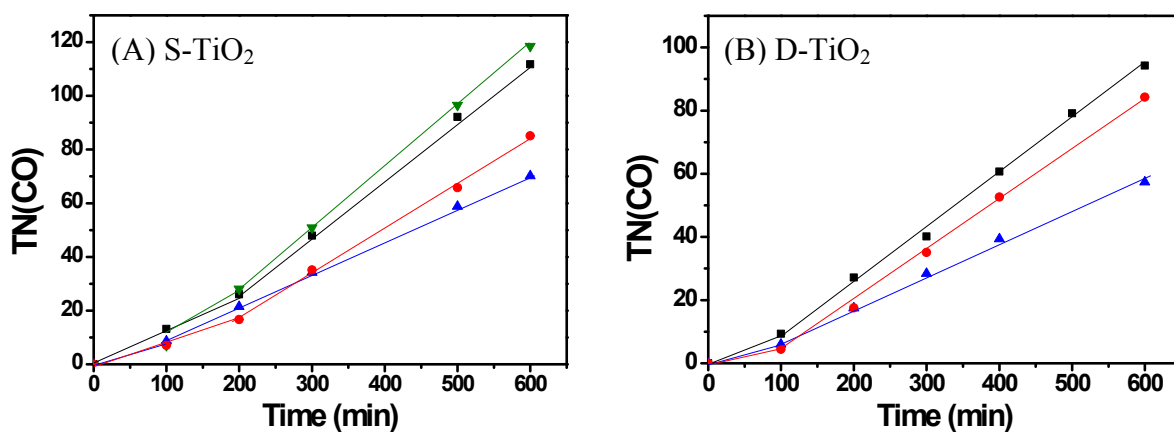


Fig. S7 Formation of CO in dry DMF (—▲—, —■—) compared with that in the presence of 10%(v/v) H₂O (—●—, —▼—): (A) **ReC/S-TiO₂/Dye** (—▲—, —●—) and **Dye/S-TiO₂/ReC** (—■—, —▼—) and (B) **ReC/D-TiO₂/Dye** (—▲—, —●—) and **Dye/D-TiO₂/ReC** (—■—); irradiation at > 420 nm for 10 mg of the hybrids with 0.1 μmol **ReC** and 1.5 μmol **Dye** in 3 mL DMF containing 0.1 M SD.

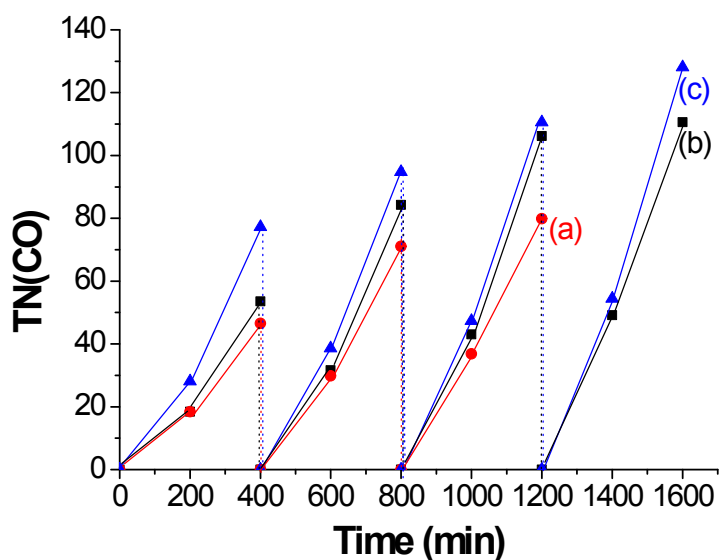


Fig. S8 Formation of CO in repetitive irradiation experiments for Dye/D-TiO₂/ReC (a) (-●-) and Dye/S-TiO₂/ReC (b) (-■-) in the presence of 1.5 M 2,2,2-trifluoroethanol and Dye/H-TiO₂/ReC in the presence of 10%(v/v) H₂O (c) (-▲-). Each run involves 30-min CO₂ bubbling in the dark followed by 400-min irradiation at > 420 nm for 10 mg of the hybrids with 0.1 μmol ReC and 1.5 μmol Dye in 3 mL DMF containing 0.1 M SD.

References

1. X. Han, Q. Kuang, M. Jin, Z. Xie and L. Zheng, *J. Am. Chem. Soc.* **2009**, *131*, 3152-3153.
2. Q. Wang, C. Chen, D. Zhao, W. Ma and J. Zhao, *Langmuir*, **2008**, *24*, 7338-7345.
3. W.-S. Han, K.-R. Wee, H.-Y. Kim, C. Pac, Y. Nabetani, D. Yamamoto, T. Shimada, H. Inoue, H. Choi, K. Cho and S. O. Kang, *Chem. Eur. J.*, **2012**, *18*, 15368-15381.
4. R. J. Angelici and A. E. Kruse, *J. Organomet. Chem.* **1970**, *22*, 461-471.
5. X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang and J.-P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501-2516.
6. X. Yi, J. Zhao, J. Sun, S. Guo and H. Zhang, *Dalton Trans.* **2013**, *42*, 2062-2074.
7. T. Chatterjee, M. Sarma and S. K. Das, *Tetrahedron Lett.* **2010**, *51*, 1985-1988.