Supplementary Information for

Organic-inorganic hybrid photocatalyst for carbon dioxide reduction

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Experimental details

Materials and Methods

Unless stated otherwise, all chemicals were purchased from Aldrich and used without further purification commercial suppliers. Chemicals for analytical measurements were of the highest available purity. Hombikat UV-100 TiO₂ particles (100% anatase) were purchased from Huntsman P&A GmbH. Degussa P-25 (ca. 25% rutile and 75% anatase, d-TiO₂), and homemade TiO₂ nanosheets (s-TiO₂) obtained by treatment of [001] facet-exposed TiO₂ with 0.1 M NaOH aqueous solution. The [001] facet exposed TiO₂ which had been prepared according to the published method^[1] was treated with 0.1 M NaOH aqueous solution to give s-TiO₂.^[2] (*E*)-2-cyano-3-(5'-(5"-(p-(diphenylamino)phenyl)thiophen-2"-yl)thiophen-2''-yl)-acrylic acid (Dye), and *fac*-[Re(4,4'-bis(diethoxyphosphorylmethyl)-2,2'-bipyridine)(CO)₃Cl] (**ReP**) were synthesized according to literature procedures.^[3,4] 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.

Preparation of Dye-sensitized TiO₂ Catalyst

The alkaline treatment was indispensable for efficient deposition of ReP and Dye on the particles, because the deposition of **ReP** and Dye was poor on the fluorinated surface of the as-prepared [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 Acetonitrile/tert-butanol solution of Dye (15 μ mol) and then subjected to centrifugation. The collected solids were washed with the solvent and then dried in an oven under N₂. For the preparation of Dye/TiO₂/ReP sample, the Dye-sensitized TiO₂ powders (0.1 g) were dispersed into an acetonitrile/tert-butanol solution of **ReP** (1 μ mol) and allowed to stand overnight under stirring. The collected solids were separated by centrifugation, washed with the solvent and then dried in an oven (70 °C) and stored under N₂ in the dark. The complete loading of Dye and catalysts was confirmed by absorbance comparison before and after each adsorption step of Dye and catalysts: each supernatant, which is separated after centrifugation of the Dye, and **ReP** treated suspensions, showed the negligible absorption intensity of Dye, or ReP.

	h-TiO ₂	s-TiO ₂	d-TiO ₂
BET surface areas (m^2/g)	>250 m ² /g	110 m ² /g	50 m²/g



Figure: Schematic description of sequential adsorption process for immobilization of **ReP** on TiO₂ particles.

Photocatalytic CO and H₂ production

Suspensions of Dye/TiO₂/**ReP** particles (10 mg with 1.5 μ mol dye and 0.1 μ mol **ReP**) in 3 mL DMF/water (0–20 vol%) containing ED (0.1 M) were placed in a Pyrex cell (1 cm pass length; 6.0 mL total volume), bubbled with CO₂ for 30 min, and sealed with a septum. A series of samples were set on a homemade merry-go-round apparatus (see Scheme below) and then irradiated by three LED lamps ($\lambda >$ 400 nm, 60 W, model Fc-6051, Cree Inc.). The amounts of CO and H₂ evolved in the overhead space of the cell were determined by gas chromatography (HP6890A GC equipped with a TCD detector) using a SUPELCO CarboxenTM 1010 PLOT Fused Silica Capillary column.



Figure: Photo-image (side) and schematic description (center) of the homemade merry-goround irradiation apparatus.

The determination of Dye and catalysts coverage on TiO_2

The degree of coverage of Dye and catalyst on TiO_2 surface is calculated using the following method: the area of Dye or catalysts adsorbed on 10 mg of TiO_2 /2.5 m² (surface area of 10 mg of TiO_2) = coverage.

	Area of components loaded on 10 mg $TiO_2[m^2]$	Coverage (area of components/2.5 m ²)
Dye	$5.1 imes 10^{-1}$	0.20
ReP	$4.0 imes 10^{-2}$	0.016



Figure S1. TEM images for h-TiO₂ (a), d-TiO₂ (b), and s-TiO₂ (c). The insets in figure show each SEAD pattern of TiO₂ particles. Average sizes are 5 nm for h-TiO₂, 18 nm for d-TiO₂, and 20 nm (length) \times 5 nm (thickness) for square-shaped nanosheet s-TiO₂ with \approx 90% [001] facets.



Figure S2. Diffuse-reflectance spectra (DRS) of 1.5 μ mol dye and 0.1 μ mol **ReP** on 10 mg of TiO₂ particles for Dye.



Figure S3. Comparison of absorption spectra of catalyst solution before and after each adsorption process of ReP with TiO₂ particles.



Figure S4. Plot of H_2 formation versus time for Dye/h-TiO₂/ReP in the presence of additives in CO₂-saturated DMF containing 0.1 M BIH.

	HC1	HCla	HClO ₄	$BIH + HCl^{a,b}$
Concentration [M]	0.543	0.543	0.386	0.543
H ₂ (µmol)	11	12	7	14

Table S1. Additive effects on photocatalytic reaction by $Dye/h-TiO_2/ReP$.

^{*a*}In the dark. ^{*b*}In the absence of the hybrid particles (Dye/h-TiO₂/**ReP**).



Figure S5. UV-vis absorption spectra and photoluminescence spectra of Dye.



Figure S6. IR spectra of **ReP** and TiO₂/**ReP** in KBr discs (sample: KBr \approx 1:100). The IR spectrum shows the distinct absorption bands at 2030 and 1890–1920 cm⁻¹, which is derived from the presence of CO ligands of **ReP**.



Figure S7. Light intensity dependence of CO formation with different number of LED lamp.

Components	Oxidation [V]			 Reduction [V]				E_{0-0}	$E_{\rm ox}$ *
	$E_{\rm pa}$	$E_{\rm pc}$	E^{ox}	$E_{\rm pc}$	$E_{\rm pa}$	E^{red}	[[eV]	$[V]^a$
Dye ^[1]	0.9	0.84	0.87	-1.72	-1.62	-1.67	2	2.48	-1.61
RePE ^[2]	-	-	-	-1.45	-1.24	-1.34		-	-
ED	-	-	0.25	-	-	-		-	-

Table S2. Electrochemical properties of compounds used in this study (V vs. SCE).

^{*a*}The oxidation potential in the excited singlet state is determined from the following equation: $E_{ox}^* = E_{ox} - E_{0.0}$.



Figure S8. Spectrum of the LED lamp (Cree. 60 W) used as a light source in this study.



Figure S9. Energy level comparison of components (Dye, **ReP**, and BIH) with reference chemicals (i.e., Ru(bpy)₃²⁺, TEA, TEOA, and BNAH).

Reference

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