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Supplementary Information

Band-to-band transition visible-light-responsive anatase titania photocatalyst by N,F-codoping for water splitting and CO_2 reduction

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Characterization

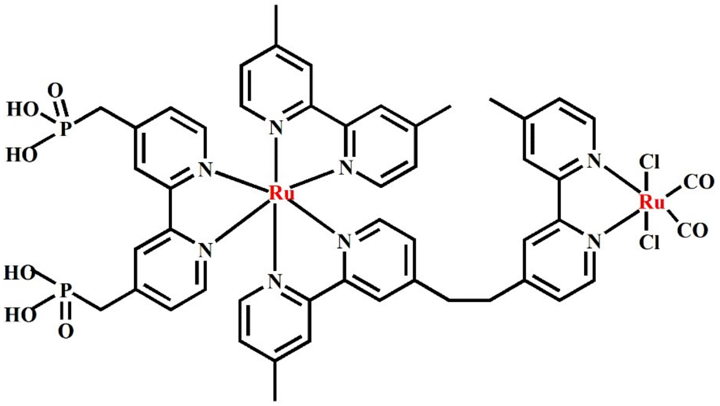
XRD measurements were carried out using a Rigaku D/Max-2500/PC powder diffractometer (Cu Kα radiation) with an operating voltage of 40 kV and current of 200 mA. The scan range and scan rate were 10-60° and 5 °/min, respectively. Ultraviolet-visible absorption spectra over the range of 200-800 nm were recorded on a UV-vis spectrophotometer (V-670, JASCO). Surface morphologies of the samples were imaged by a field emission scanning electron microscopy (FESEM, S-5500, Hitachi). Energy dispersive spectrometer (EDS, max800) elemental analysis was used to study the distribution of constituent elements in the synthesized materials. The surface elemental binding energies were recorded on an X-ray photoelectron spectrometer (XPS, Thermo Esclab 250Xi, monochromatic Al Kα X-ray source). The C1s peak (284.6 eV) was referenced to normalize the measured binding energies for each sample. Transient absorption spectroscopy was conducted with a homemade spectrometer as the previous description[1]. Specifically, an amplified Ti: sapphire laser system from Coherent (800 nm, 35 fs, 6 mJ/pulse, and 1 kHz repetition rate), nonlinear frequency mixing techniques and Femto-TA 100 spectrometer (Time-Tech Spectra) were used. For transient absorption spectroscopy, a pump pulse at 400 nm was used to excite the sample, and the induced absorption change (ΔA) as functions of wavelength was recorded.

First-principle calculations

All the calculations were performed using the Vienna Ab-initio Simulation Package (VASP)[2, 3] with projector augmented wave (PAW) method[4] based on the density functional theory. The generalized gradient approximation (GGA)[5] of Perdew-Burke-Ernzerhof (PBE) form[6] was applied to describe the exchange-correlation functional with an energy cutoff of 500 eV. The valence electron configuration including Ti ($3s^2 3p^6 3d^2 4s^2$), O ($2s^2 2p^4$), N ($2s^2 2p^3$), and F ($2s^2 2p^5$) were considered in the present work[7]. According to the Monkhorst-Pack scheme[8], the gamma-centered k-point mesh of the Brillouin zone sampling for the primitive cells of bulk TiO_2 was set at $7 \times 7 \times 3$. To investigate the effect of N,F-doping on the electronic structure of TiO_2, the TiO_2 (101) surface structure model with four-layer periodic structure (containing 32 O atoms and 16 Ti atoms) was established, and then substituted by N atoms, F-connecting with Ti atoms of the surface based on the fully optimized anatase TiO_2 unit cell.. Thus the N,F-codoped TiO_2 (101) structure model has been established (containing 28 O atoms, 16 Ti atoms, 4 N atoms and 2 F atoms). The k-point mesh of the Brillouin zone was set at 3 × 7 × 1 for the two models, and the vacuum layer is set to 15 Å. The geometries were fully optimized, and the convergence threshold was set to be 10^{-6} eV in energy and 0.01 eV $Å^{-1}$ in force. The PBE + U approach was employed to accurately describe the electronic structure with Ti 3d electron states with a U-J value of 4.5 eV according to the previous report[9].

Supplementary data

Chart 1 Structure and abbreviation of Ru complex used in this work.



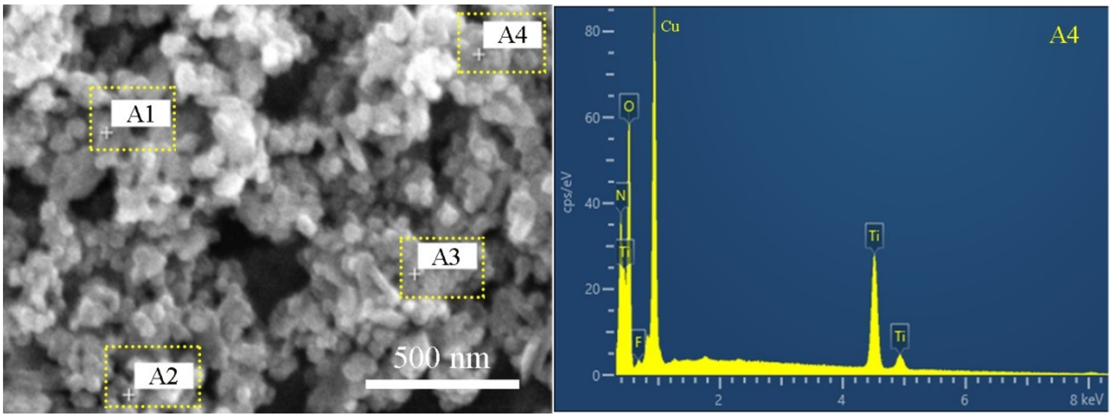


Fig. S1 SEM image of TNOF-0 sample and the selected regions for EDS analysis.

Table S1 Ti, O, N, F elements content in different selected regions (Fig. S1) of TNOF-0 sample.

Area	Ti (wt%)	O (wt%)	N (wt%)	F (wt%)
A1	46.59	47.43	4.86	1.13
A2	49.20	44.77	5.09	0.94
A3	47.26	42.83	5.05	1.06
A4	51.9	42.83	4.39	0.89

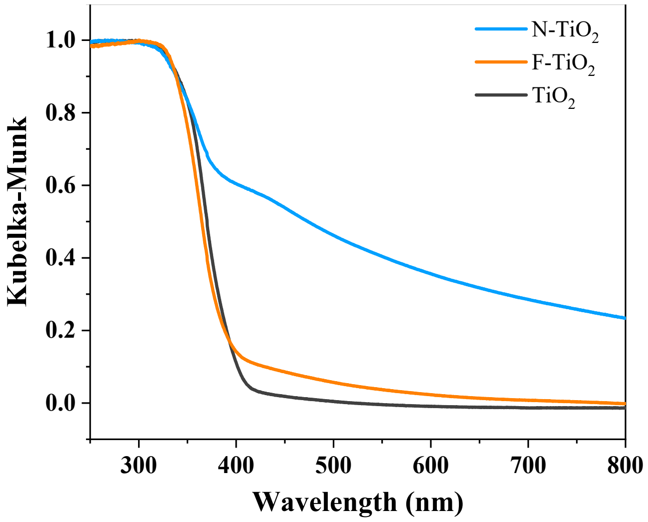


Fig. S2 UV-vis spectra of TiO_2, N-TiO_2, and F-TiO_2 samples.

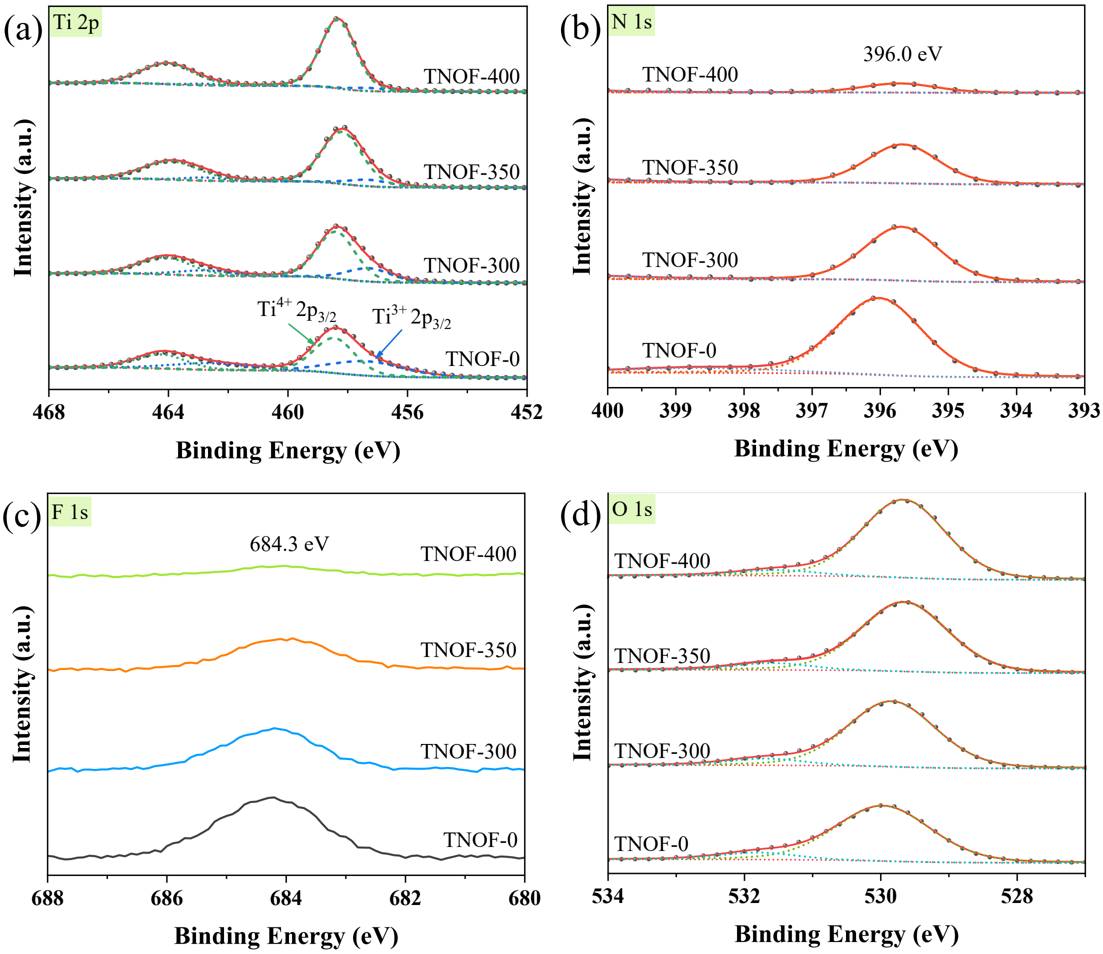


Fig. S3 XPS spectra of (a) Ti 2p, (b) N 1s, (c) F 1s, and (d) O 1s for TNOF samples obtained at different temperatures.

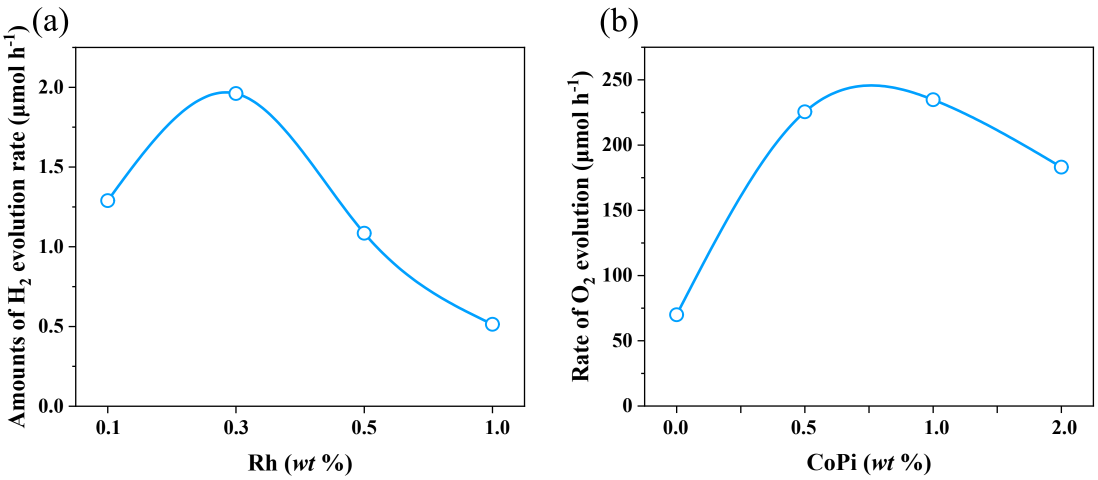


Fig. S4 (a) Optimization of Rh cocatalyst with TNOF-400, (b) Optimization of CoPi cocatalyst with TNOF-350. H_2 evolution reaction conditions: 150 mg catalyst, 100 mL 10 *vol*% triethanolamine aqueous solution; O_2 evolution reaction conditions: 100 mg photocatalysts, 150 mg La_2O_3, 150 mL 10 mM $AgNO_3$ aqueous solution. Pyrex top irradiation type, 300 W xenon lamp ($\lambda > 420$ nm).

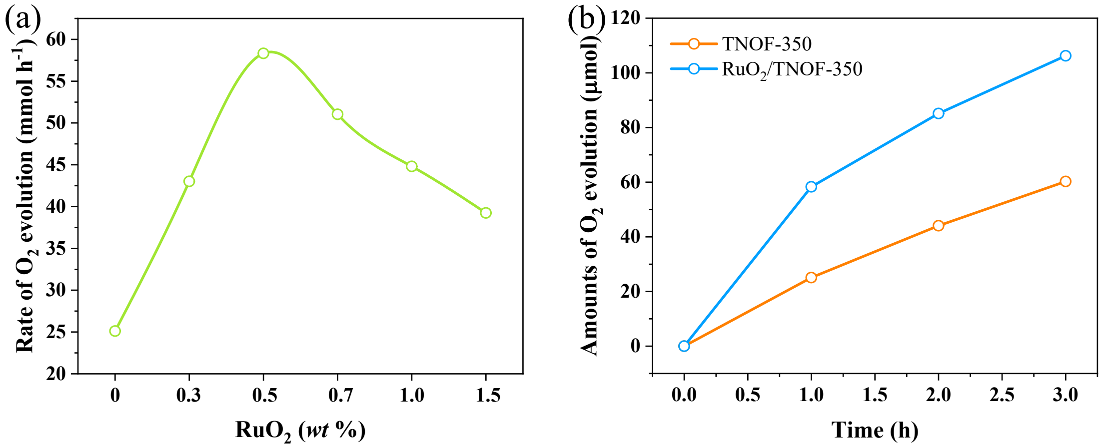


Fig. S5 (a) Optimization of RuO_2 cocatalyst with TNOF-350 and (b) time course curve of the photocatalytic O_2 evolution on TNOF-350 and 0.5 *wt*%-RuO_2/TNOF-350. Reaction conditions: 100 mg catalyst; 100 mL 5 mM $Fe(NO_3)_3$ aqueous solution; 300 W Xe lamp ($\lambda > 420$ nm).

Table S2 The photocatalytic activities of water reduction and/or oxidation over other reported N,*X*-codoped (*X* = F, B, or C) TiO_2 photocatalysts.

Sample	Bandgap	Band-to-band transition	Light source	cocatalyst	Reaction solution	HER/OER activity (μmol/h)	ref
TNOF	2.16	yes	300 W Xe lamp (λ > 420 nm)	Rh	triethanolamine/H_2O (10 vol%)	2.9	**This work**
				——	$AgNO_3$ (10 mM)	69.9	
				CoPi		234.8	
$TiN_xO_yF_z$	2.34	yes	300 W Xe lamp (λ > 450 nm)	Pt	CH_3OH/H_2O (10 vol%)	0.1	*J. Phys. Chem. C*, **2007**, 111, 18264-18270
			300 W Xe lamp (λ > 400 nm)	——	$AgNO_3$ (10 mM)	43.0	
TiOFN	2.20	yes	300 W Xe lamp (λ > 420 nm)	——	——	——	*Chem. Commun.*, **2011**, 47, 11742-11744
				——	$AgNO_3$ (10 mM)	50.0	
R-TiO_2:N,F	2.20	yes	300 W Xe lamp (λ > 420 nm)	——	——	——	*Sustain. Energy Fuels*, **2018**, 2, 2025-2035
				——	$AgNO_3$ (10 mM)	11.5	

B,N-TiO_2	1.97	yes	300 W Xe lamp (λ > 420 nm)	Pt	CH_3OH/H_2O (10 vol%)	0.69	*Chem. Eur. J.*, **2019**, 25, 1787-1794
				——	$AgNO_3$ (10 mM)	3.60	
				RuO_2		8.16	
$TiO_{2-x}(CN)_y$	2.48	yes	300 W Xe lamp (λ > 420 nm)	——	——	——	*Adv. Funct. Mater.*, **2019**, 29, 1901943
				CoO_x	$AgNO_3$ (20 mM)	4.25	

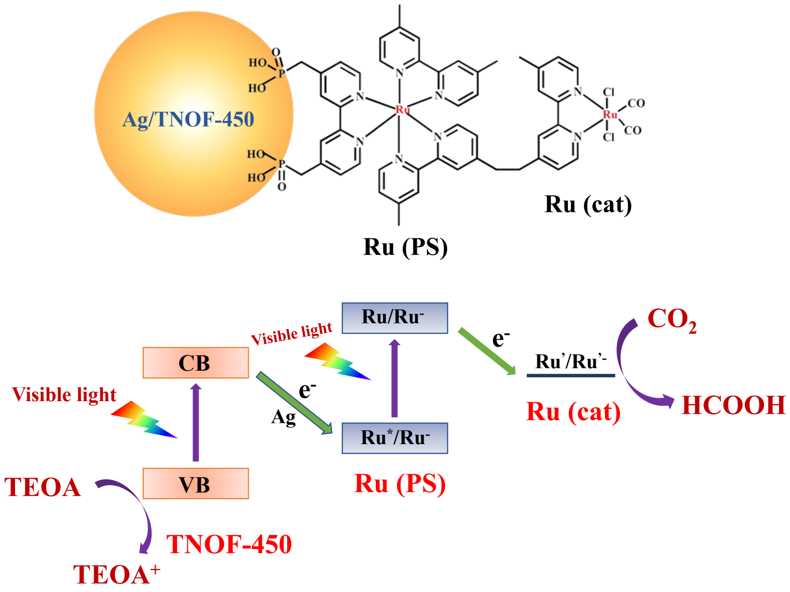


Fig. S6 The Z-scheme CO_2 reduction system consisting of Ag/TNOF-450 and **RuRu′** under visible-light ($\lambda > 400$ nm).

Under visible-light irradiation, both the TNOF-450 and the photosensitizer in **RuRu′** were excited simultaneously. The excited electrons in the conduction band of TNOF-450 can transfer to the excited photosensitizer unit, producing one-electron-reduced species of photosensitizer, from which the intramolecular electron transfer to the catalytic unit in **RuRu′**, and followed by reduction of CO_2 into HCOOH. In this work, the photocatalytic CO_2 reduction was performed using the as-prepared **RuRu′**/Ag/TNOF-450 catalyst under visible-light, where Ag can transfer the electrons from TNOF-450 to the photosensitizer in **RuRu′**.

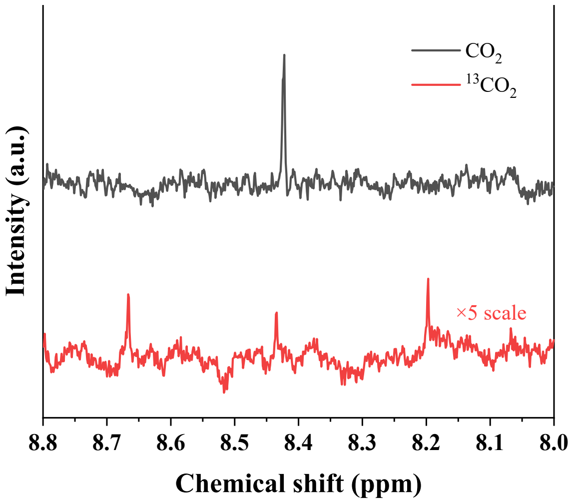


Fig. S7 ^{1}H NMR spectra of a reactant solution (2 mL of MeCN/TEOA mixed solution) containing 10 mg of **RuRu'**/Ag/TNOF-450, measured after filtration. The photocatalyst suspension was irradiated at 370–500 nm (λ_{max} = 410 and 460 nm) using a merry-go-round-type apparatus with an LED light for 15 h under $^{13}CO_2$ (650 Torr) or saturated unlabeled CO_2.

Table S3 Comparison of the activities of TNOF-450 photocatalyst with other photocatalysts for CO_2 reduction.

Sample	Reaction condition and time	Light source	Product	HCOOH production (μmol)	$TON_{(HCOOH)}$	$Selectivity_{(HCOOH)}$	ref
RuRu'/Ag/TNOF-450	saturated CO_2, MeCN/TEOA (4:1, 4 mL), 15 h	400 W high pressure Hg lamp (λ > 400 nm)	HCOOH, H_2	2.6 ± 0.2	2.2×10^2	97.2%	**This work**
N-TiO_2	CO_2 (g), H_2O (g)	300 W Xe lamp (λ > 400 nm)	CH_3OH	——	——	——	*Chinese J. Catal.*, **2015**, 36, 2127-2134
Nb-TiO_2	CO_2 (g) flow	30 W white bulbs	CH_4, CO	0.0	0.0	——	*J. Colloid Interf. Sci.*, **2019**, 540, 1-8
N-TiO_2	CO_2 (g) + H_2O (g) (30 : 1)	Xe lamp (315 < λ < 600 nm)	H_2, CH_4, CO, C_2H_6, C_3H_8	——	——	——	*Catal. Sci. Technol.*, **2020**, 10, 1688-1698
N-TiO_2	CO_2 (g) + H_2O	13 W fluorescent	H_2, CH_4, C_2H_4,	——	——	——	*Appl. Catal. B-*

	(g)	integrated bulbs, 6h	C_2H_6				*Environ.*, **2015**, 168-169, 114-124
N-TiO_2/CuO	saturated CO_2, H_2O	20 W Xe lamp (350 < λ < 800 nm)	H_2, HCOOH	1.65	——	~ 94.5%	*J. Photochem. Photobiol.*, **2022**, 11, 100125
Ru’/mpg-C_3N_4	saturated CO_2, MeCN/TEOA (4:1, 4 mL), 5 h	450 W Xe lamp (λ > 400 nm)	H_2, CO, HCOOH	19.345	> 200	>80%	*Chem. Commun.*, **2013**, 49, 10127-10129
RuRu’/Ag/g-C_3N_4	saturated CO_2 (g), DMA/TEOA (4:1, 4 mL), 40 h	400 W high pressure Hg lamp (λ > 400 nm)	HCOOH, CO, H_2	~ 67	> 3.3 × 10^4	87-99%	*J. Am. Chem. Soc.*, **2016**, 138, 5159-5170
RuRu’/$Pb_2Ti_2O_{5.4}F_{1.2}$	saturated CO_2, MeCN/TEOA (4:1, 4 mL), 15 h	400 W high pressure Hg lamp (λ > 400 nm)	HCOOH, H_2	0.6	26	> 99%	*J. Am. Chem. Soc.*, **2018**, 140, 6648-6655

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