Supporting Information

Coordinative integration of a metal-porphyrinic framework and TiO_2 nanoparticles for the formation of composite photocatalysts with enhanced visible-light-driven photocatalytic activities

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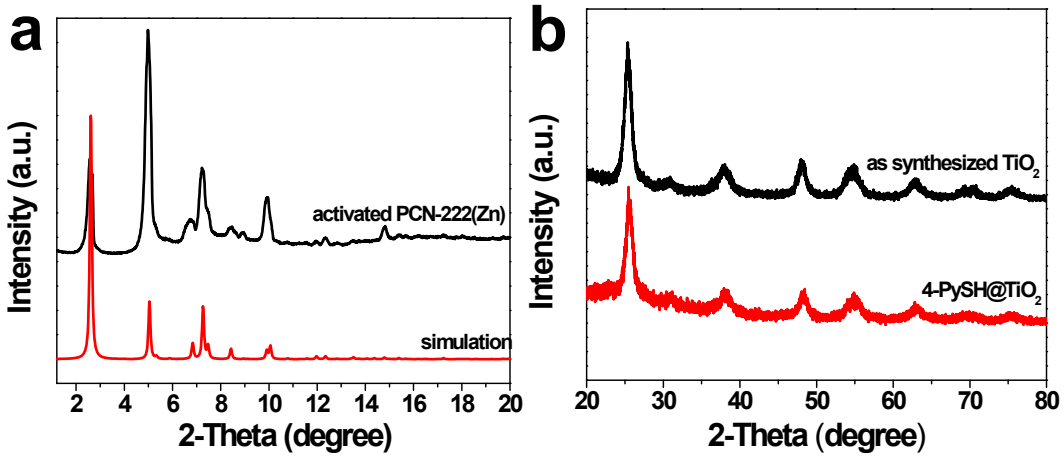

Fig. S1 (a) XRD pattern of the as-synthesized PCN-222(Zn) and the simulated XRD pattern for the PCN-222(Zn) structure created from CIF in reference document. (b) XRD patterns of as-synthesized TiO_2 and 4-PySH@TiO_2.

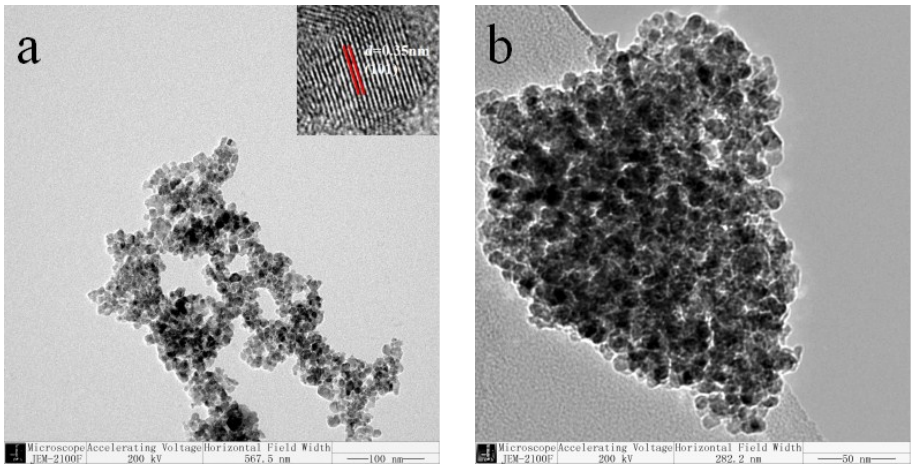

Fig. S2 TEM images of (a) the pristine TiO_2 and (b) the 4-PySH@TiO_2 composite.

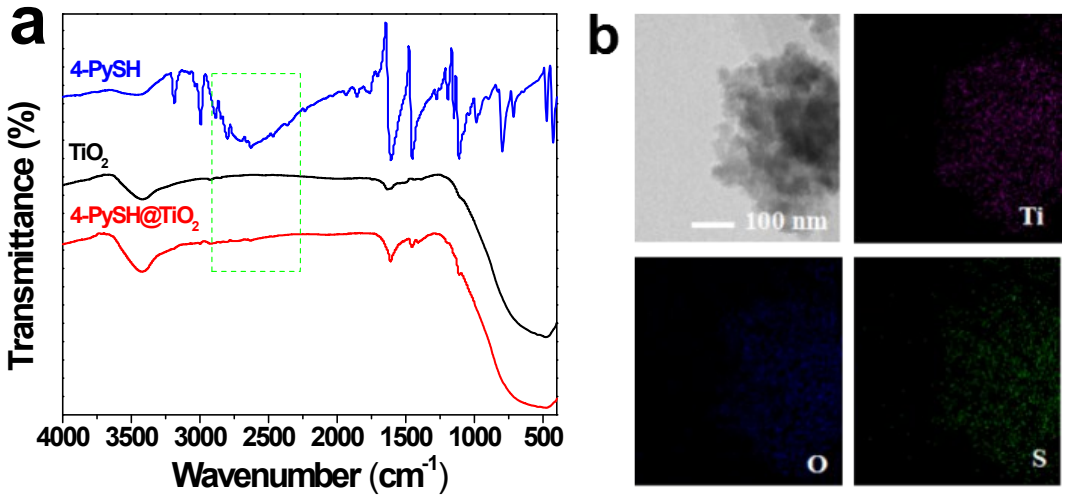

Fig. S3 (a) FTIR spectra of 4-PySH, TiO_2 and 4-PySH@TiO_2. (b) EDX elemental mappings of 4-PySH@TiO_2.

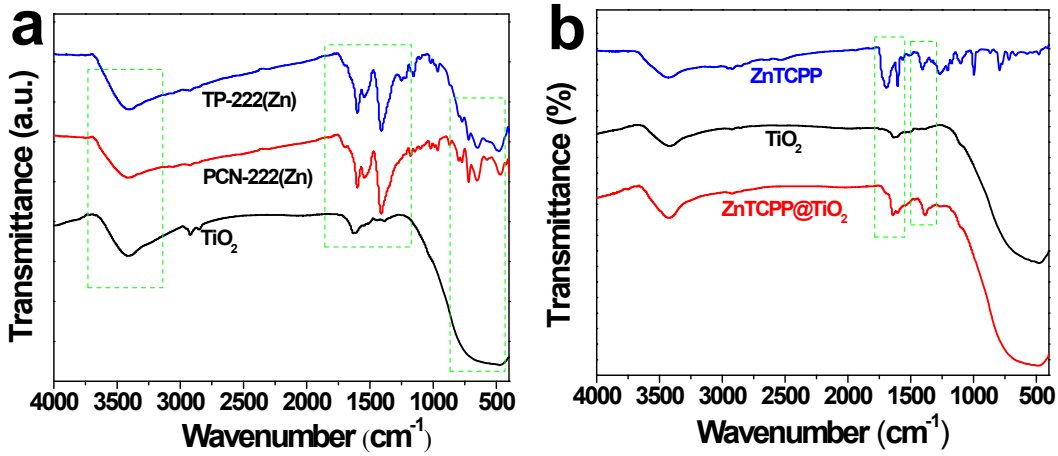

Fig. S4 FTIR spectra of (a) TiO_2, PCN-222(Zn) and TP-222(Zn) and (b) ZnTCPP, TiO_2 and ZnTCPP@TiO_2.

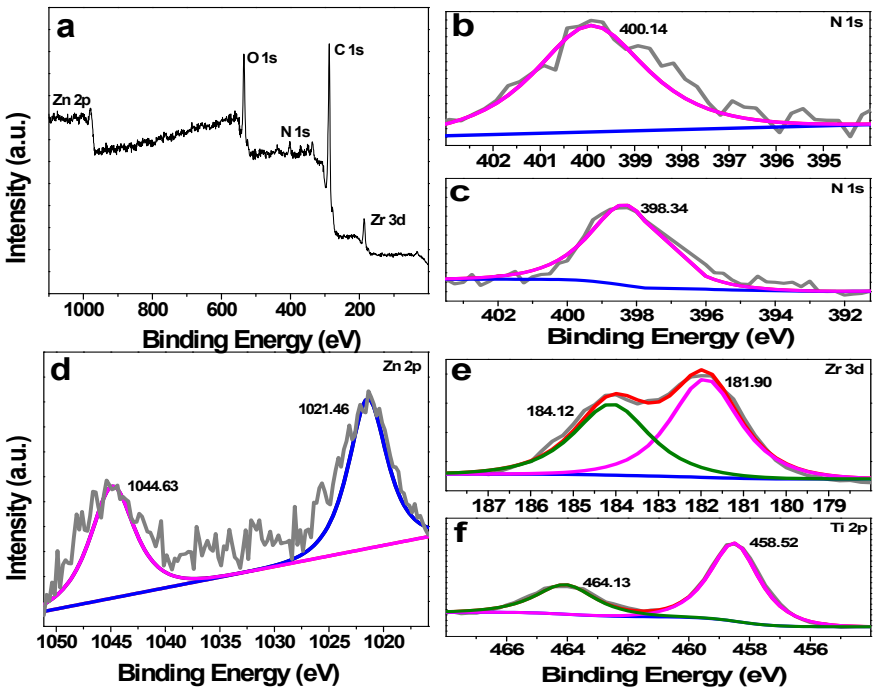

Fig. S5 (a) XPS survey spectrum of PCN-222(Zn). (b) and (c) N 1s XPS spectrum of 4-PySH @TiO_2 and PCN-222(Zn), respectively. (d) Zn 2p XPS spectrum of PCN-222(Zn). (e) and (f) Zr 3d and Ti 2p XPS spectrum of TP-222(Zn), respectively.

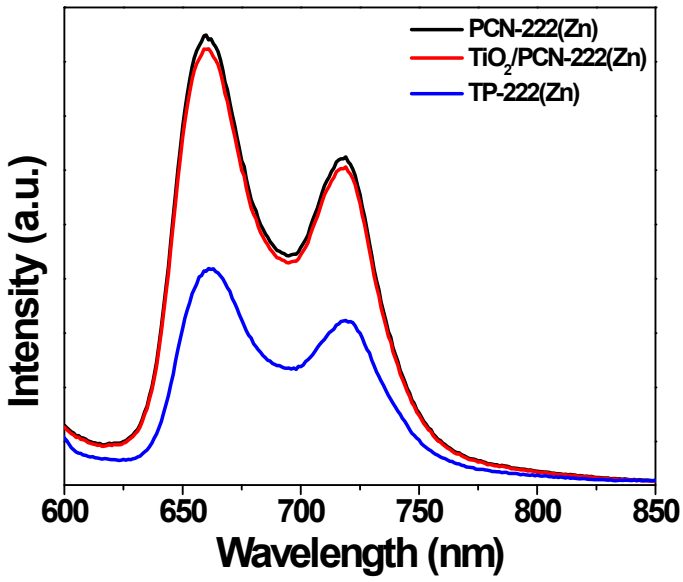

Fig. S6 PL emission spectra (excited at 457 nm) of PCN-222(Zn), TiO_2/PCN-222(Zn) and TP-222(Zn).

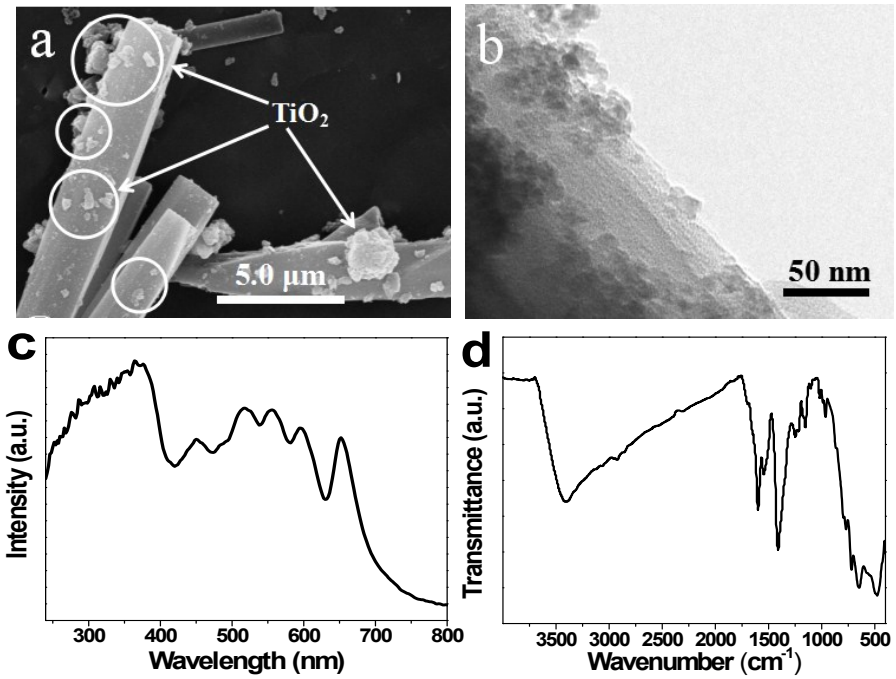

Fig. S7 (a) SEM image, (b) TEM image, (c) UV-visible diffusive reflectance spectra and (d) FTIR spectra of the mixture of TiO_2 and PCN-222(Zn) (TiO_2/PCN-222).

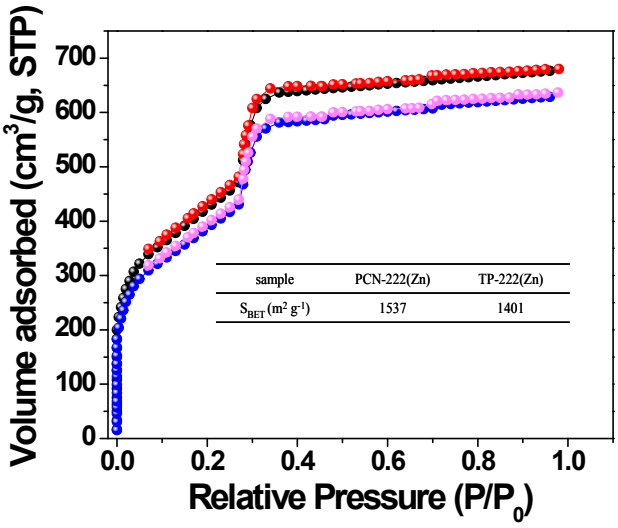

Fig. S8 N_2 adsorption-desorption isotherms measured for PCN-222(Zn) and TP-222(Zn) together with their specific surface area.

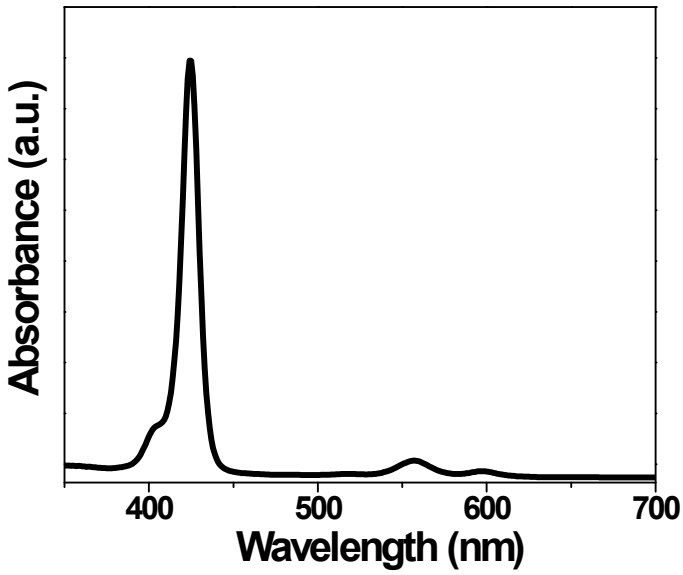

Fig. S9 UV-visible absorption spectra of the porphyrinic ligand (ZnTCPP) of PCN-222(Zn) in DMF solution.

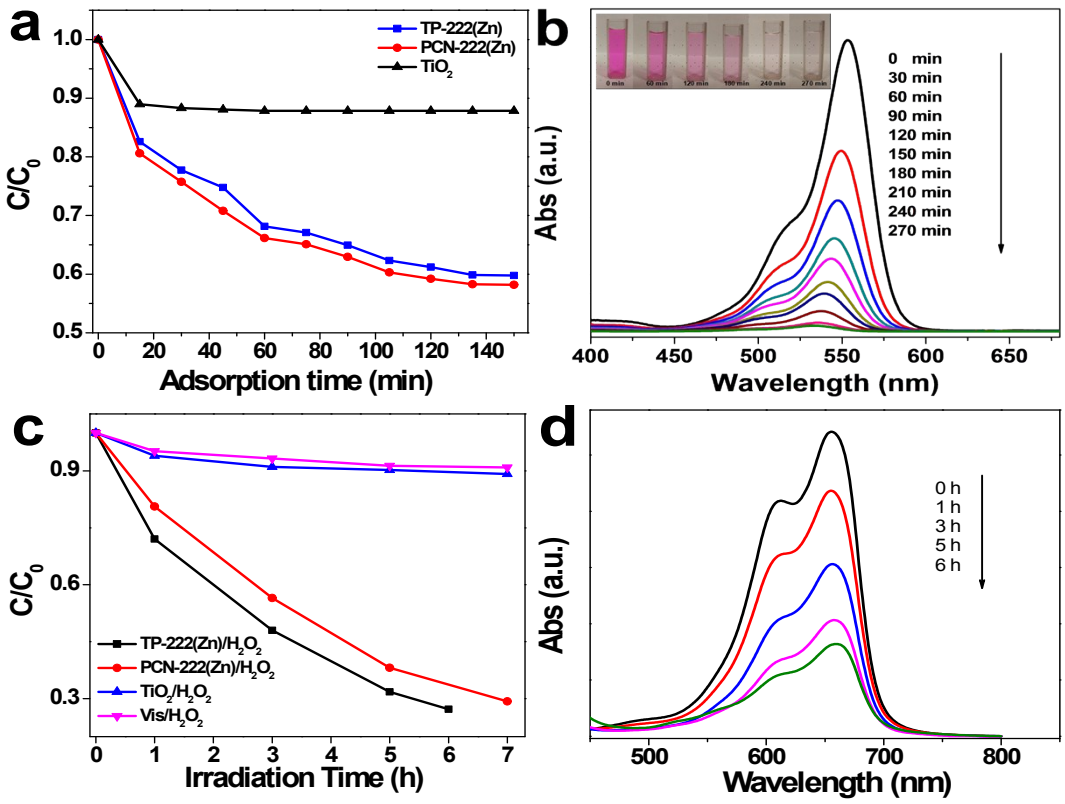

Fig. S10 (a) Adsorption equilibrium plots of RhB solution over TP-222(Zn), PCN-222(Zn) and TiO_2. (c) C/C_0 *versus* irradiation time curves for degrading MB. (b) and (d) Absorption spectra of RhB and MB solutions under different irradiation time by using TP-222(Zn), respectively. The inset shows the color changes of the RhB solutions corresponding to the six degradation times from 0 min to 270 min.

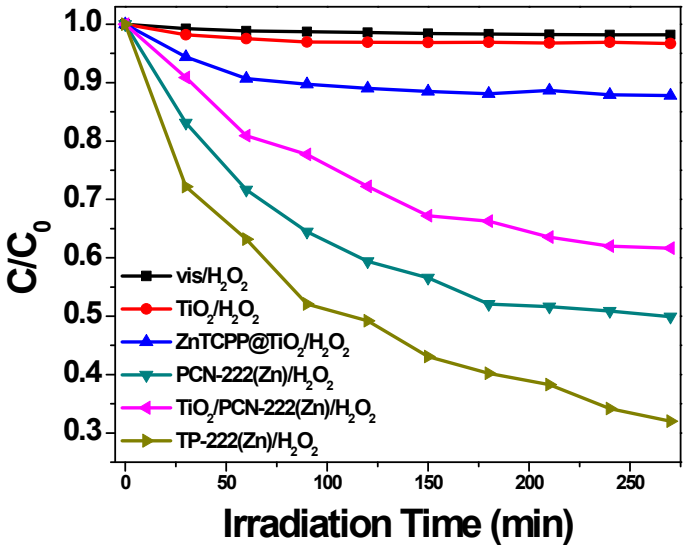

Fig. S11 Degradation of 2,4-DNP in different photocatalytic systems under visible light irradiation. (Experimental conditions: samples, 2, 2.4 or 2.2 mg; 2,4-DNP, 50 ml/20 mg L^{-1}; 30 wt% H_2O_2, 2 ml.)

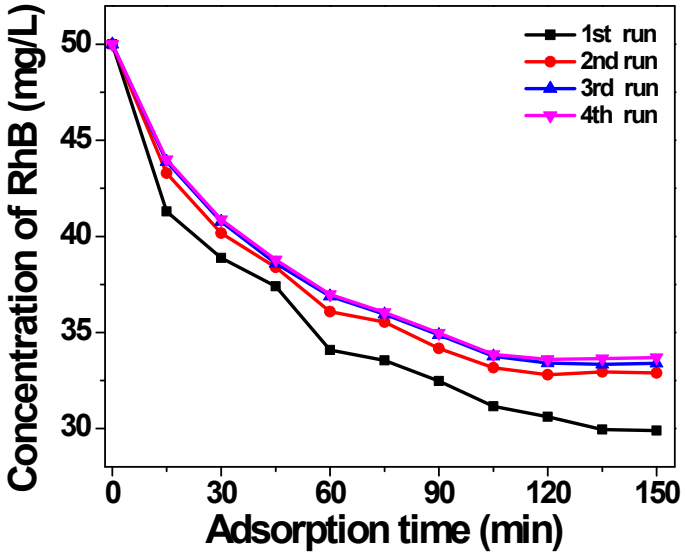

Fig. S12 Adsorption equilibrium plots of RhB solutions over the TP-222(Zn) composite for four cycles.

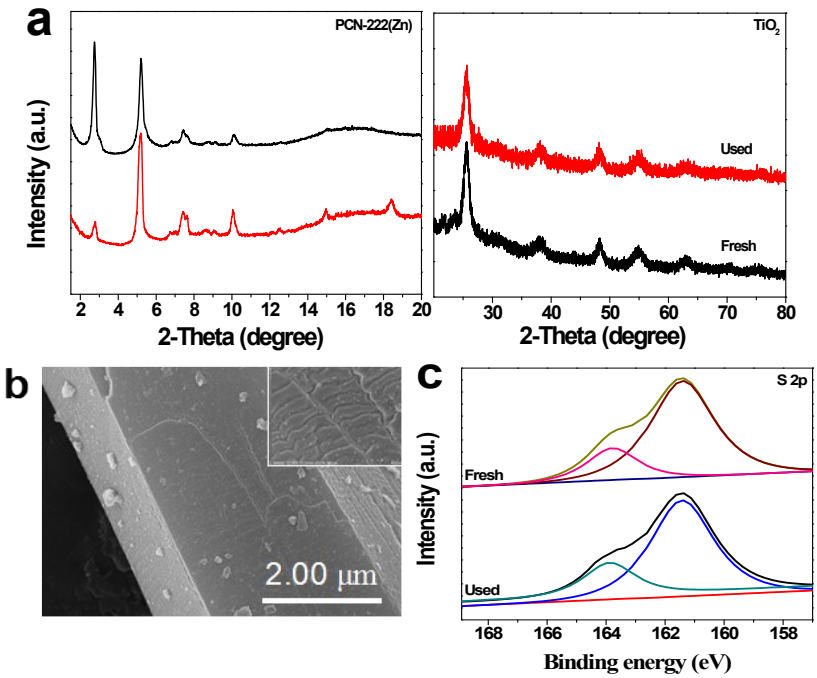

Fig. S13 (a) XRD patterns of the TP-222(Zn) composite before and after four photocatalytic degradation cycles. (b) SEM images of the TP-222(Zn) composite after four photocatalytic degradation cycles under visible light irradiation. (c) Comparison of S 2p XPS spectrum of the TP-222(Zn) composite before and after four photocatalytic degradation cycles.

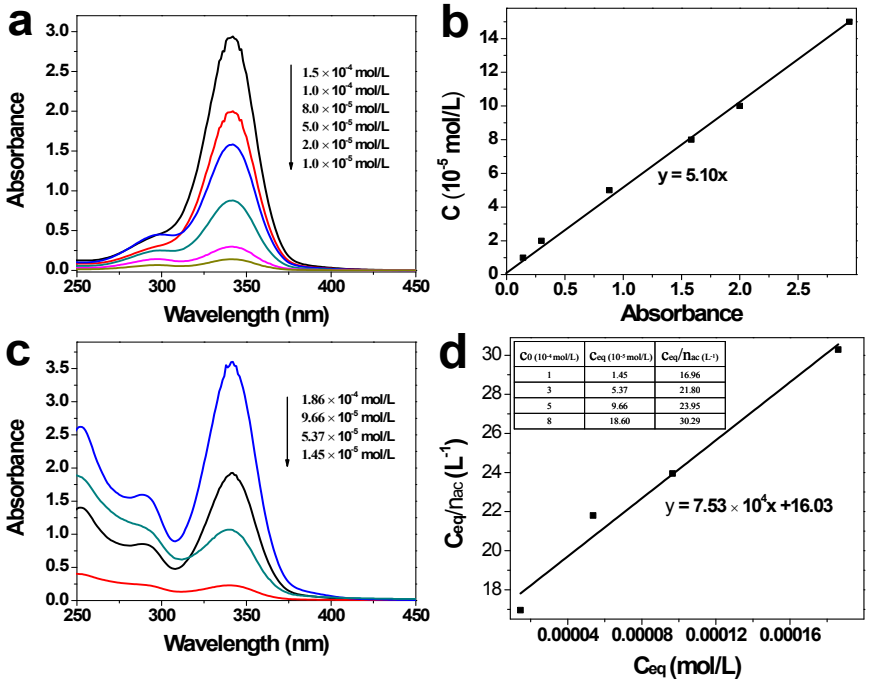

Fig. S14 Binding constant measurements. (a) UV-Vis absorption spectra of 4-PySH with different concentrations. (b) The fitted plot of C (4-PySH in EtOH) *versus* absorbance together with the corresponding fitting function. (c) UV-Vis absorption spectra of 4-PySH after adsorbing on TiO_2 NPs for 72 h. (d) The fitted plot of C_{eq}/n_{ac} *versus* C_{eq} together with the corresponding fitting function. The inset shows the values of C_0, C_{eq} and C_{eq}/n_{ac}.

Determining the binding constant of 4-PySH to TiO_2 surface.[1]

In these experiments, 50 mg TiO_2 NPs were immersed in four ethanol solutions of 4-PySH for 72 h (the concentrations are respectively 1×10^{-4}, 3×10^{-4}, 5×10^{-4} and 8×10^{-4} mol/L). TiO_2 NPs were subsequently removed by centrifugation and the supernatant was subjected to UV-Vis absorption spectroscopy analysis in order to determine the equilibrium concentration (C_{eq}) of the 4-PySH ethanol solution. The adsorption capacity (n_{ac}) of 4-PySH was calculated from the difference in the concentrations before and after equilibration with TiO_2 NPs, in which the concentrations were determined by the fitting function of C *versus* absorbance (as shown in Fig. S14b). Then, the data were plotted according to the Langmuir isotherm equation:

$$\frac{C_{eq}}{n_{ac}} = aC_{eq} + b$$

The binding constant (K, M^{-1}) is calculated as $K = a/b$ based on the fitted line in Fig. S14d.

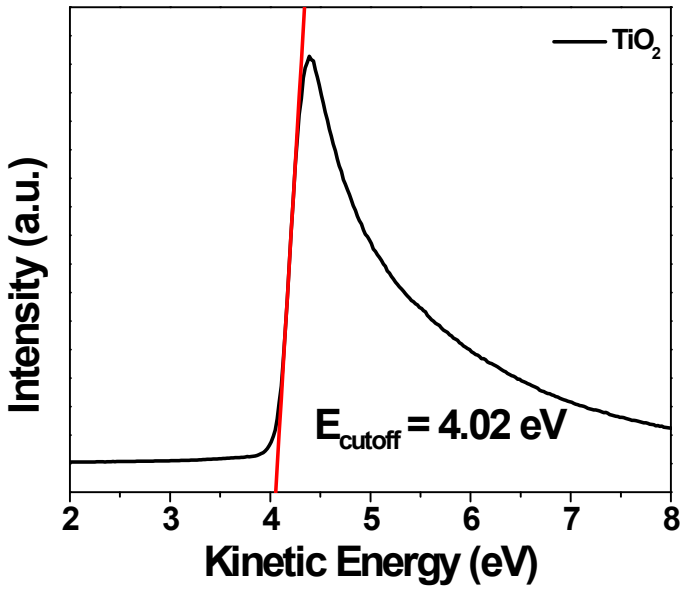

Fig. S15 UPS spectra and E_{cutoff} of the pristine TiO_2.

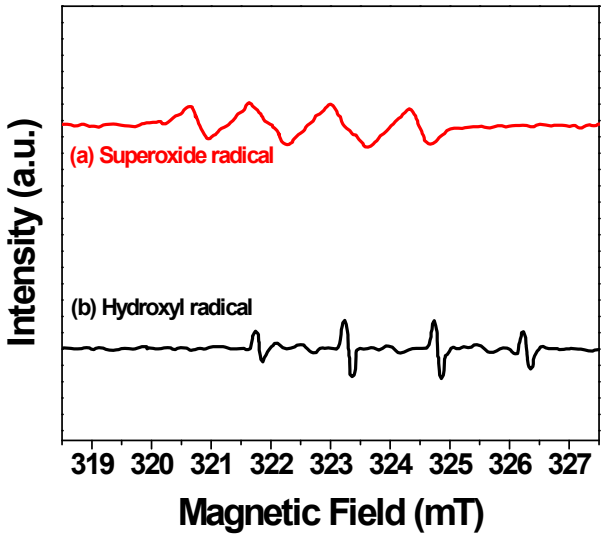

Fig. S16 DMPO spin-trapping EPR spectra of the TP-222(Zn) without H_2O_2 system in methanol dispersion for DMPO-•O_2^- (a) and the TP-222(Zn) with H_2O_2 system in aqueous dispersion for DMPO-•OH (b).

Table S1 The operating conditions used for ICP-MS measurements.

Nebulizer	Babington
Spray chamber	Quartz
Reaction gas flow rate	2 mL min^{-1}
Carrier gas flow rate	1.15 L min^{-1}
RF power	1500 W
Resolution (amu)	2 ~ 260
Integration time	1 s
Replicates	3
Detector mode	Auto
Analytical masses	Ti (47), Zr (92)

Table S2 Loading amounts of TiO_2 NPs in composite TP-222(Zn) determined by ICP-MS.

	Concentration (μg L^{-1})		Loading amounts of
	Ti	Zr	TiO_2 NPs (wt.%)
Before photocatalysis	4.2	6.9	18.3
After photocatalysis	2.9	5.4	16.6
TiO_2/PCN-222(Zn)	0.9	4.5	7.6

The loading amounts of TiO_2 NPs in the TP-222(Zn) composite or the mixture of TiO_2 NPs and PCN-222(Zn) is calculated based on the detected concentrations of Ti and Zr and also based on the formual ($C_{48}H_{32}ZnN_4O_{16}Zr_3$) of PCN-222(Zn) with the formual weight of 1259.84.[2]

Table S3 Comparative study of the photocatalytic activity of the TP-222(Zn) composite with other materials including MOF materials and non-MOF materials in the complete photocatalytic degradation of RhB under visible light irradiation.

Catalysts	Volume of RhB solution (ml)	Conc. of RhB solution (mg L^{-1})	Conc. of catalyst (mg L^{-1})	Degradation time (min)	References
MIL-53(Fe)	25	10	400	70	[3]
g-C_3N_4/MIL-125(Ti)	100	50	400	60	[4]
Ag_2CO_3/UiO-66(Zr)	30	14.37	500	120	[5]
Fe_2O_3@SnO_2	25	25	600	40	[6]
BiOCl	15	60	667	60	[7]
TiO_2/CdS	70	15	1000	120	[8]
Ag_3PO_4/WS_2	20	4.79	1000	10	[9]
3DOM g-C_3N_4	70	10	1000	40	[10]
Bi_3NbO_7	50	4.79	1000	50	[11]
Bi_2WO_6	100	10	500	50	[12]
Bi_2S_3/$Bi_2O_2CO_3$	50	4.79	1000	30	[13]
TP-222(Zn)	50	50	48	270	This work

Table S4 Dynamics analysis of emission decay of PCN-222(Zn) and TP-222(Zn).

	τ_1 (ns) (Rel.%)	τ_2 (ns) (Rel.%)	τ_{av} (ns)
PCN-222(Zn)	0.3 (68.6)	2.3 (31.4)	1.8
TP-222(Zn)	0.9 (59.8)	5.4 (40.2)	4.5

Supplementary Reference

1 Y. Pellegrin, L. L. Pleux, E. Blart, A. Renaud, B. Chavillon, N. Szuwarski, M. Boujtita, L. Cario, S. Jobic, D. Jacquemin and F. Odobel, *J. Photoch. Photobio.*, 2011, **219**, 235–242.

2 D.-W. Feng, Z.-Y. Gu, J.-R. Li, H.-L. Jiang, Z.-W. Wei and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 10307–10310.

3 C.-H. Zhang, L.-H. Ai and J. Jiang, *J. Mater. Chem. A*, 2015, **3**, 3074–3081.

4 H. Wang, X.-Z. Yuan, Y. Wu, G.-M. Zeng, X.-H. Chen, L.-J. Leng and H. Li, *Appl. Catal., B*, 2015, **174–175**, 445–454.

5 Z. Sha, H. S. O. Chan and J.-S. Wu, *J. Hazard. Mater.*, 2015, **299**, 132–140.

6 N. Wang, Y.-C. Du, W.-J. Ma, P. Xu and X.-J. Han, *Appl. Catal., B*, 2017, **210**, 23–133.

7 W.-W. Liu, Y.-Y. Shang, A.-Q. Zhu, P.-F. Tan, Y. Liu, L.-L. Qiao, D.-W. Chu, X. Xiong and J. Pan, *J. Mater. Chem. A*, DOI: 10.1039/c7ta02724a

8 C. Xue, T. Wang, G.-D.Yang, B.-L. Yang and S.-J. Ding, *J. Mater. Chem. A*, 2014, **2**, 7674–7679.

9 H.-J. Yu, Y. Yu, J.-H. Liu, P.-Y. Ma, Y.-C. Wang, F. Zhang and Z.-Y. Fu, *J. Mater. Chem. A*, 2015, **3**, 19439–19444.

10 B. Lin, G.-D. Yang, B.-L. Yang and Y.-X. Zhao, *Appl. Catal., B*, 2016, **198**, 276–285.

11 Q.-Q. Wang, L.-P. Yuan, M. Dun, X.-M. Yang, H. Chen, J.-L. Li and J.-C. Hu, *Appl. Catal., B*, 2016, **196**, 127–134.

12 C.-M. Li, G. Chen, J.-X. Sun, H.-J. Dong, Y. Wang, C.-D. Lv, *Appl. Catal., B*, 2014, **160–161**, 383–389.

13 N. Liang, J.-T. Zai, M. Xu, Q. Zhu, X. Wei and X.-F. Qian, *J. Mater. Chem. A*, 2014, **2**, 4208–4216.