Electronic supplementary information (ESI)

Constructing TiO_2@MOF S-scheme heterojunctions for enhanced photocatalytic degradation of antibiotic and Cr(VI) photoreduction

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Contents:

Text S1: Photocatalytic experiments for Cr(VI) reduction

The photocatalytic experiments for aqueous Cr(VI) to Cr(III) were carried out under 300 W Xe irradiation at ambient conditions in a 150 mL quartz reactor containing 20.0 mg photocatalysts which were dispersed into 100 mL of a Cr(VI) aqueous solution (10.0 ppm). Prior to irradiation, the suspension was magnetically stirred for 60 min in the dark to ensure an adsorption–desorption equilibrium and then different volumes of 0.2 M H_2SO_4 were added to adjust the acidity in the reaction, with the pH values determined using a pH detector. During the reduction of aqueous Cr(VI), stirring was maintained to keep the mixture in suspension, 2.0 mL of suspension was withdrawn at regular intervals and the photocatalyst was separated by centrifugation. Then, the Cr(VI) content in the solution was determined colorimetrically by the diphenylcarbazide method (DPC) with a detection limit of 0.005 mg L^{-1}. The Cr(VI) content in the solution at different illumination times was monitored by measuring its maximum absorbance (centered at 540 nm) using a UV visible spectrophotometer.

Table S1 Crystallographic data for Zn-MOF.

Empirical formula	$C_{10}H_{14}O_6P_2Zn$	Formula weight	357.52
Crystal system	monoclinic	Space group	P 1 21/c 1 (14)
a (Å)	4.5297(5)	b (Å)	19.0682(19)
c (Å)	14.6610(15)	α (deg)	90
β(deg)	96.314(4)	γ (deg)	90
Volume ($Å^3$)	1258.64(20)	Z	4
D $(_{calc})$ (g cm^{-3})	1.88661	Mu(Mo-Ka)[mm^{-1}]	
F(000)	728	H,k,l max	4, 22, 16
Temp , k	173(2)	Nref,Npar	2043, 174
R, wR_2	0.1152, 0.1287	S	1.044

Table S2 Selected bond distances (Å) and angles (°) for Zn-MOF.

	bond lengths(Å)		bond lengths(Å)
Zn1- O1	2.147(5)	O1- Zn1	2.015(5)
O3- Zn1	2.128(5)	O5- Zn1	1.984(5)
O6- Zn1	1.928(6)	O6- Zn1- O1	128.6(2)
O6- Zn1- O5	102.1(2)	O6- Zn1- O3	91.7(2)
O5- Zn1- O1	129.2(2)	O1- Zn1- O3	90.6(2)
O5- Zn1- O3	90.2(2)	O5- Zn1- O1	100.1(2)
O6- Zn1- O1	91.6(2)	O3- Zn1- O1	168.3(2)
O1- Zn1- O1	78.6(2)		

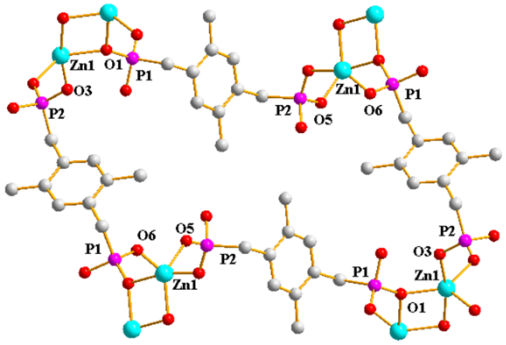

Fig.S1 The structural unit of 44-membered ring.

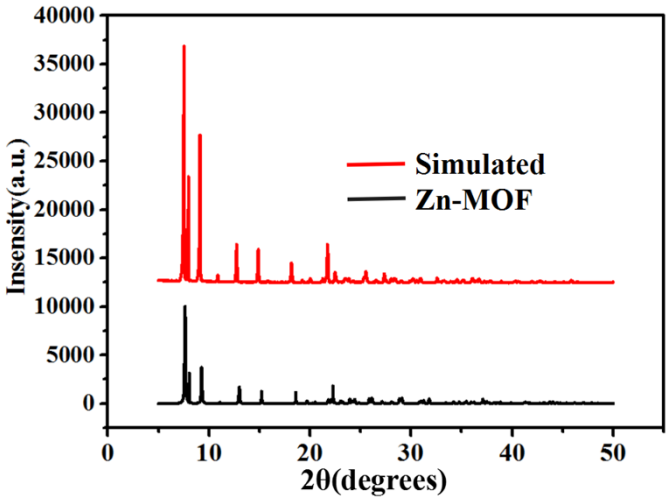

Fig.S2 PXRD pattern and simulated pattern of Zn-MOF.

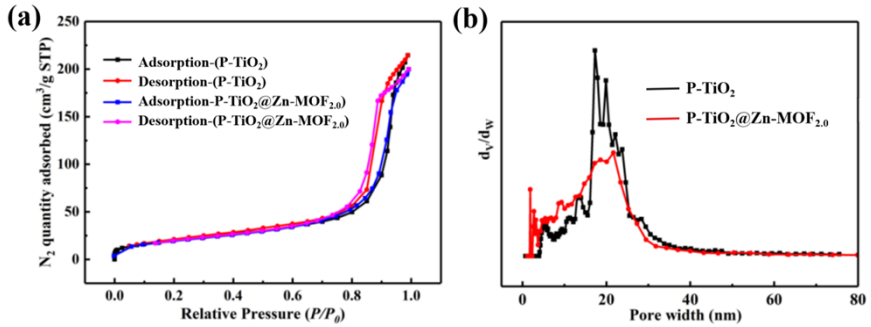

Fig.S3 (a)N_2 absorption isotherms of P-TiO_2 and P-TiO_2@Zn-$MOF_{2.0}$; (b) the particle size distribution obtained by NLDFT kernel.

Table S3 Specific surface areas, pore volume and mean pore diameters for P-TiO_2 and P-TiO_2@Zn-$MOF_{2.0}$.

Materials	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average diameter of mesoporous (nm)
P-TiO_2	74.16	0.3326	17.94
P-TiO_2@Zn-$MOF_{2.0}$	71.06	0.3089	14.53

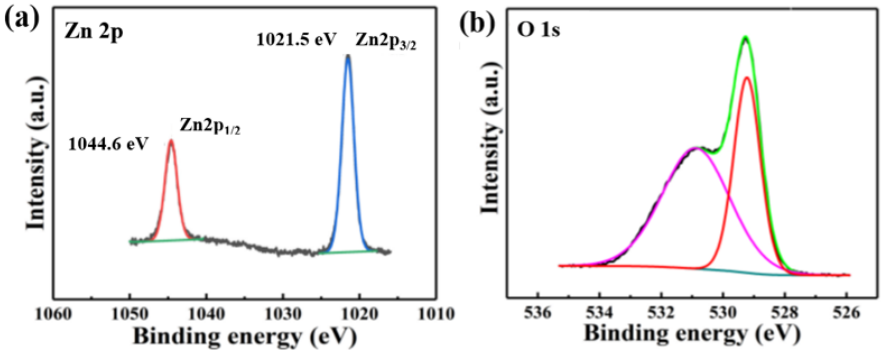

Fig.S4 Zn (a) and O1s (b)XPS spectrum of P-TiO_2@Zn-$MOF_{2.0}$.

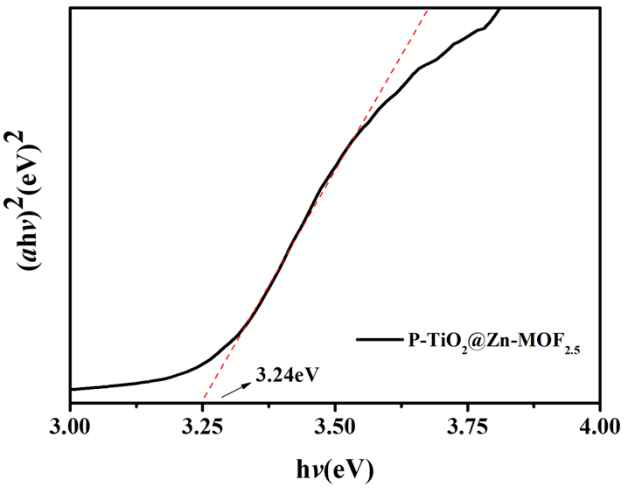

Fig. S5 The band gap energy of P-TiO_2@Zn-$MOF_{2.5}$.

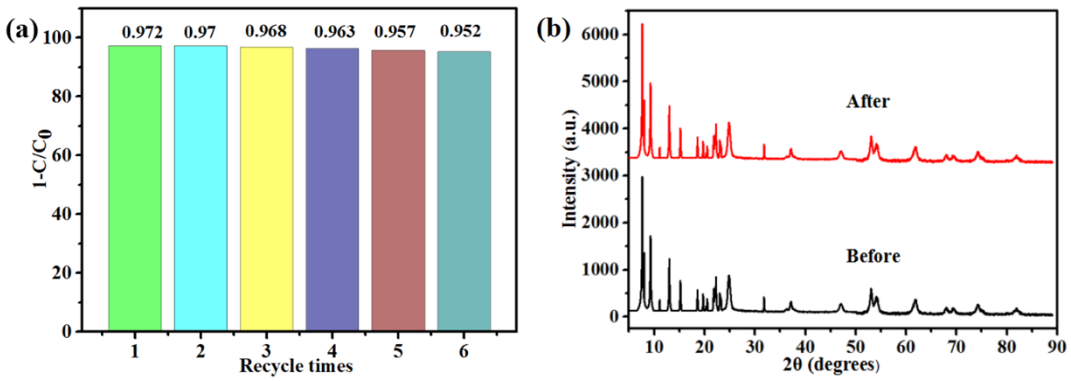

Fig. S6 Photocatalytic CIP degradation during six consecutive runs of P-TiO_2@Zn-$MOF_{2.0}$(a); The PXRD patterns for P-TiO_2@Zn-$MOF_{2.0}$ before and after CIP degradation(b).

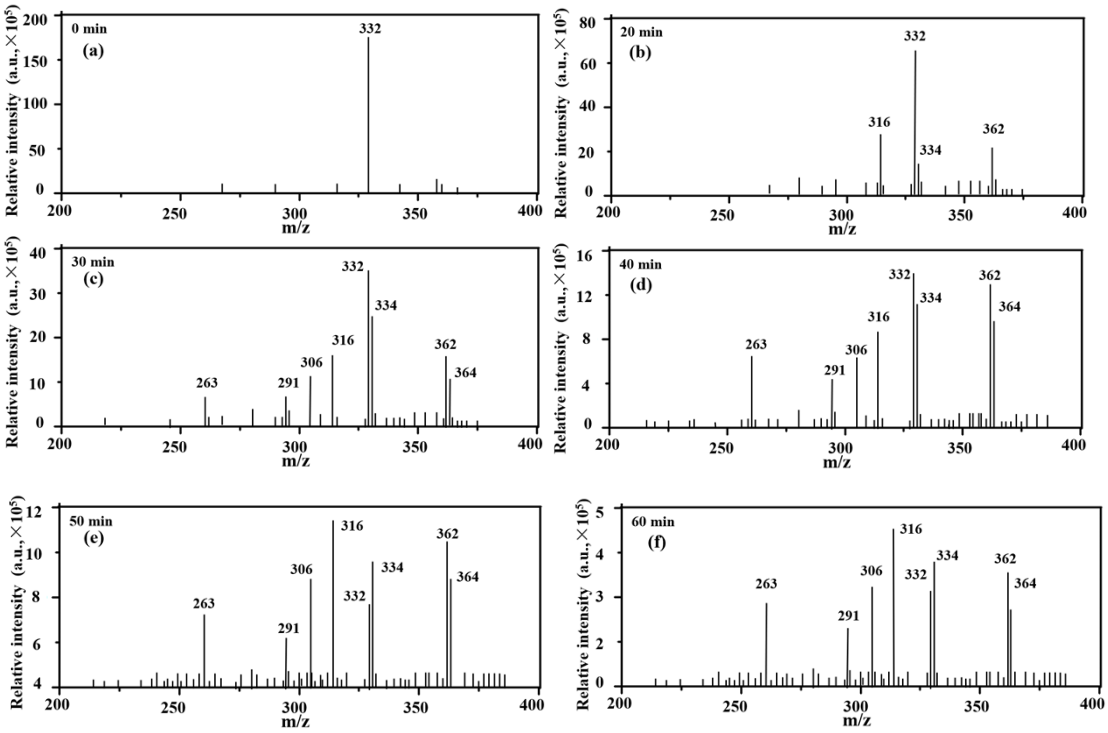

Fig. S7 The mass spectra of intermediates during CIP degradation.

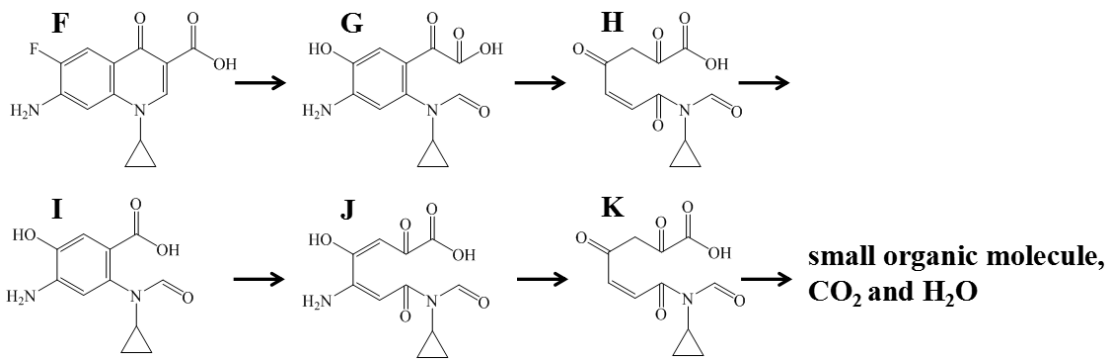

Fig. S8 The transformation pathways of product F from CIP.

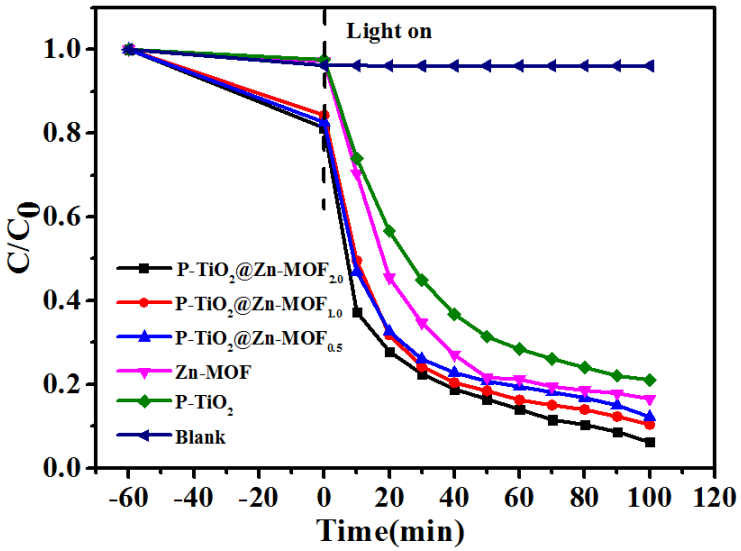

Fig. S9 The photocatalytic degradation of TC by different catalysts.

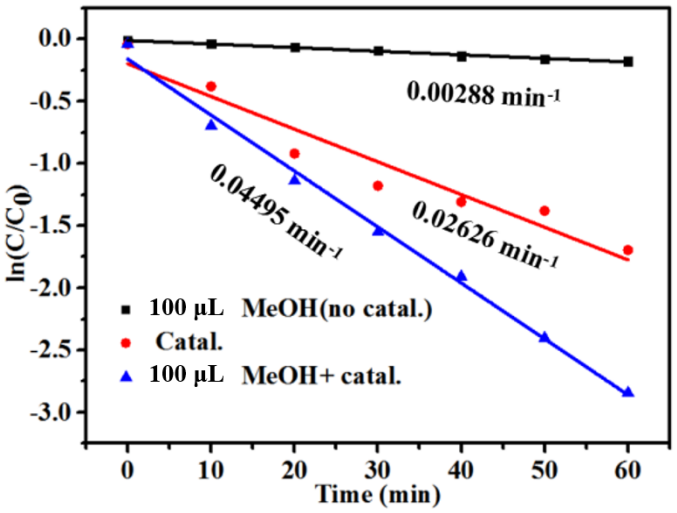

Fig. S10 Kinetics curves of photocatalytic reduction of Cr(VI) for P-TiO_2@Zn-$MOF_{2.0}$ at different conditions.

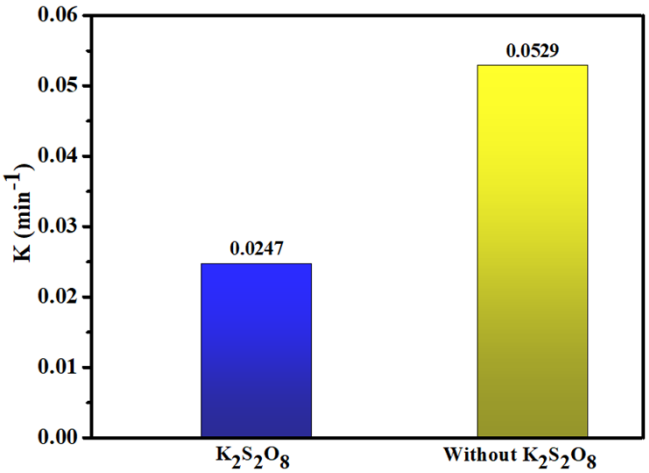

Fig. S11 Photocatalytic reduction of Cr(VI) over P-TiO_2@Zn-$MOF_{2.0}$ with or without electron scavenger of $K_2S_2O_8$ (0.1 mmol).

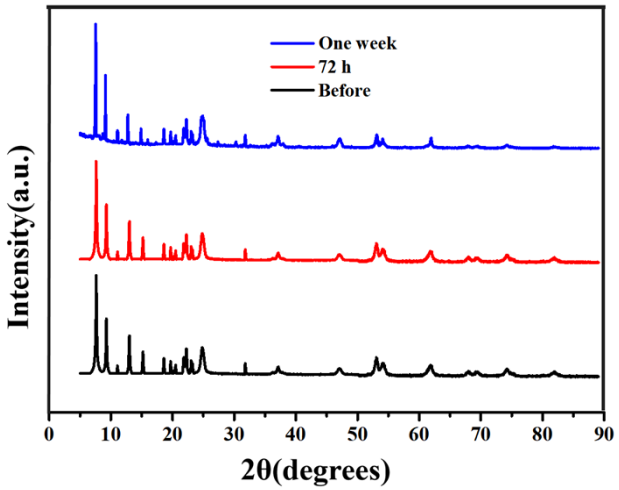

Fig. S12 PXRD patterns of P-TiO_2@Zn-$MOF_{2.0}$ before and after immersing in acid for 72 hours and 7 days, respectively.

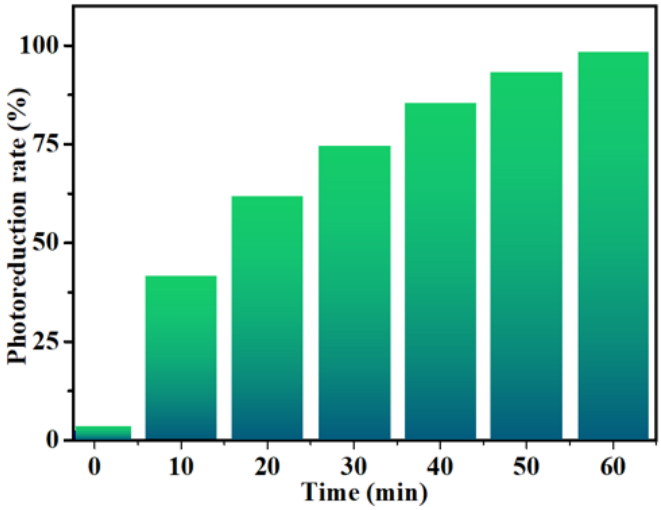

Fig. S13 The time-dependent Cr(VI) photoreduction efficiency of P-TiO_2@Zn-$MOF_{2.0}$ in the electroplating waste water (pH = 1.98)

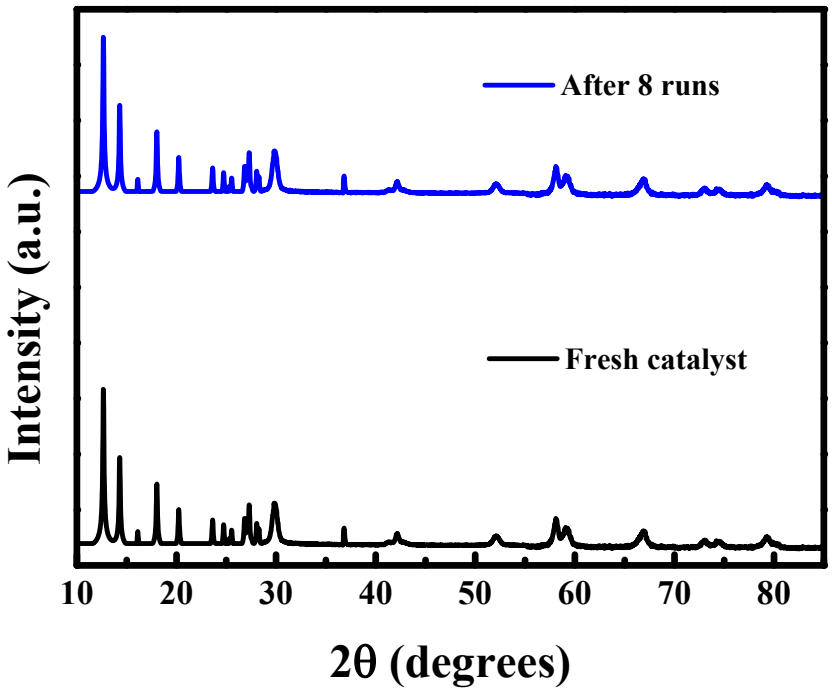

Fig. S14 PXRD of P-TiO_2@Zn-$MOF_{2.0}$ after 8 runs.

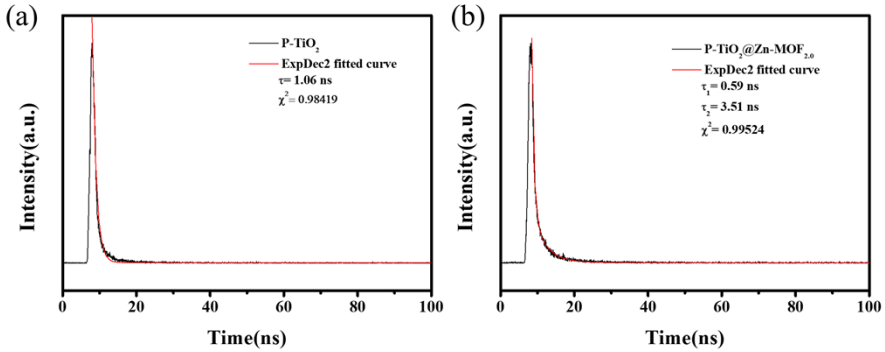

Fig. S15 The fitted decay curves of P-TiO_2 (a) and P-TiO_2@Zn-$MOF_{2.0}$(b)

Table S4 Comparison of the CIP reduction capacity of P-TiO_2@Zn-$MOF_{2.0}$ with other photocatalysts.

Catalyst/mg	V (mL)/ C_0 (mg L^{-1})	Light source	Time (min)	Result (%)	K (min^{-1})	Ref.
P-TiO_2/Zn-$MOF_{2.0}$/20	100/10	300 W Xe lamp	60	97.2	0.023	This work
MOF-derived C-TiO_2/50	100/10	300 W Xe lamp	120	72.4	0.0085	[1]
Bi_2MoO_6/GQDs/TiO_2	5/10	300 W Xe lamp	150	90.21	0.015	[2]
Vo-TiO_2/Ta_3N_5-3 /50	50/10	300 W Xe lamp	90	95.7	0.0249	[3]
CTH-0.5/80	100/15	300 W Xe lamp	60	87	/	[4]

Table S5 Comparison of the Cr(VI) reduction capacity of P-TiO_2/Zn-$MOF_{2.0}$ with other photocatalysts.

Catalyst/mg	V (mL)/ C_0 (mg L^{-1})/pH	Light source	Time (min)	Result (%)	K (min^{-1})	Ref.
P-TiO_2/Zn-$MOF_{2.0}$/20	100/10/1.98	300 W Xe lamp	60	92.8	0.045	This work
$CuAl_2O_4$/TiO_2	60/30/2.0	200 W tungsten	180	95	0.016	[5]
10Ag@C-TCZ/50	100/5/3.0	500 W Xe lamp	120	95.5	/	[6]
0.2CDs-TNs[a] /50	50/10/3.0	500 W Xe lamp	120	99.2[a]	0.027	[7]
GO/TiO_2[b]/500	1000/10/2.0	8 W Hg lamp	420	99.6[b]	0.4228	[8]
MIL-125(Ti)-derived COOH	200/5/2.0	/	90	61.8	/	[9]

[a] CDs-TNs = carbon dots-TiO_2 nanosheets. [b] GO/TiO_2 = a graphene oxide@TiO_2 composite.

Table S6 Ion contents and properties of raw electroplating wastewater.

item	concentration (mg/L)	item	concentration(mg/L)
pH value	1.98	Ca^{2+}	35.83
TOC	98.72	Ba^{2+}	76.01
Cr(VI)	102.48	SO_4^{2-}	653.31
Na^+	61.63	NO_3^-	1501.42
K^+	25.68		

Table S7 The fitted parameters obtained from decay curves of the samples

Sample	E_w	τ_1 (ns)	τ_2 (ns)	χ^2
P-TiO_2	350 nm	1.0585	-	0.98419
P-TiO_2@Zn-$MOF_{2.0}$	350 nm	0.5893	3.5054	0.99524

Table S8 Comparison of calculation results and experimental results of VBM and CBM of materials.

Zn-MOF	VBM vs. NHE (eV)	CBM vs. NHE (eV)
Calculation results	3.84	-0.20
Experimental results	3.97	-0.17
P-TiO_2		
Calculation results	2.80	-0.51
Experimental results	2.76	-0.53

Note: Absolute vacuum (E_{AVS}) is 0 eV, and standard hydrogen electrode (Ee) is 4.6 eV.

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