Supporting information

Ligand functionalization on Zr-MOFs enables efficient visible-light-driven H_2O_2 evolution in pure water

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Detection of H_2O_2

The generation of H_2O_2 was detected through iodometry. Briefly, 1 mL of the reaction liquid was added to 1 mL of 0.4 mol·L^{-1} potassium iodide aqueous solution and 1 mL of 0.1 mol·L^{-1} $C_8H_5KO_4$ aqueous solution. Then the solution was mixed and kept for 0.5 h in the dark. After that, the generation of H_2O_2 was estimated according to the strong absorbance of I_3^- at 350 nm recorded by UV-2600. The reaction equation is as follows:

$$H_2O_2 + 3I^- + 2H^+ \rightarrow I_3^- + 2H_2O$$

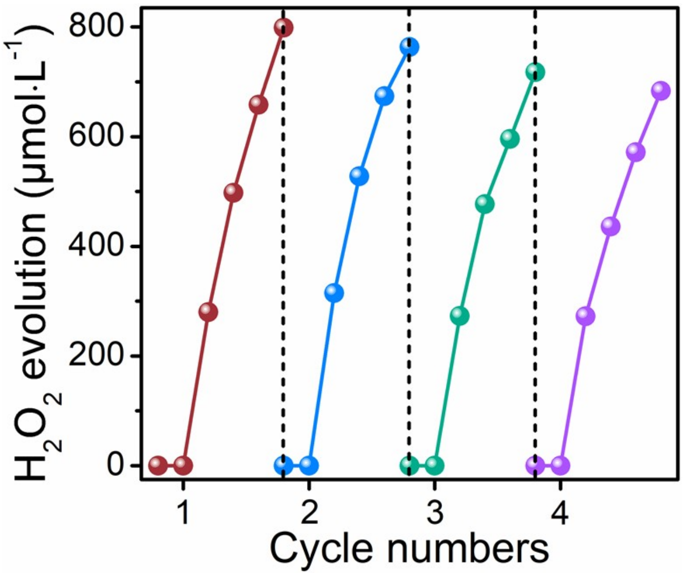

Fig. S1 Cycling experiments of Z-UN for photocatalytic H_2O_2 evolution.

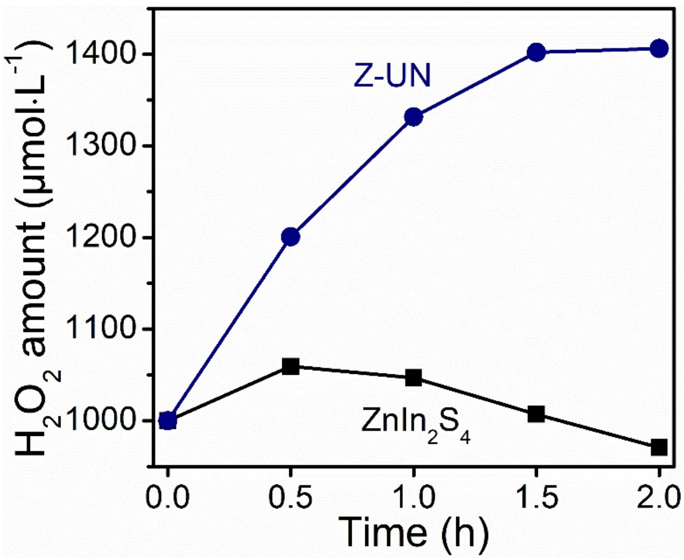

Fig. S2 H_2O_2 decomposition experiments over $ZnIn_2S_4$ and Z-UN. Reaction conditions: 20 mg photocatalysts, 40 mL H_2O_2 aqueous solution with a concentration of 1000 μmol·L^{-1}, 400-780 nm illumination, ambient air and temperature.

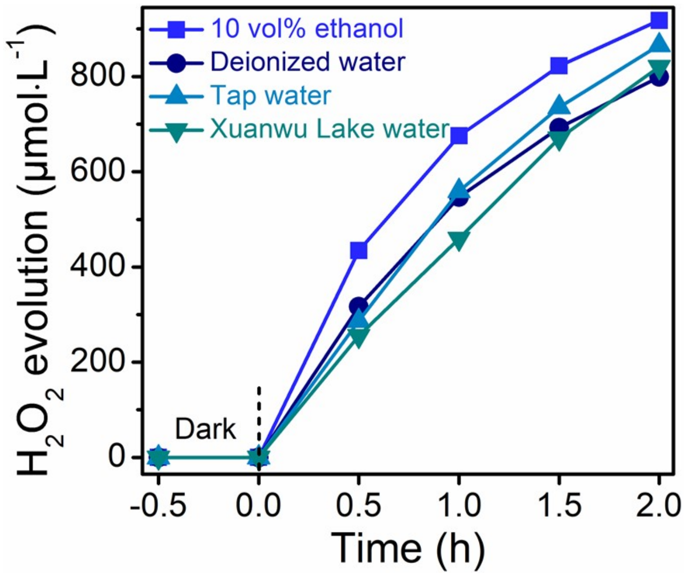

Fig. S3 Photocatalytic evolution of H_2O_2 over Z-UN using the diverse solution: 10 vol% ethanol, deionized water, tap water and Xuanwu Lake water.

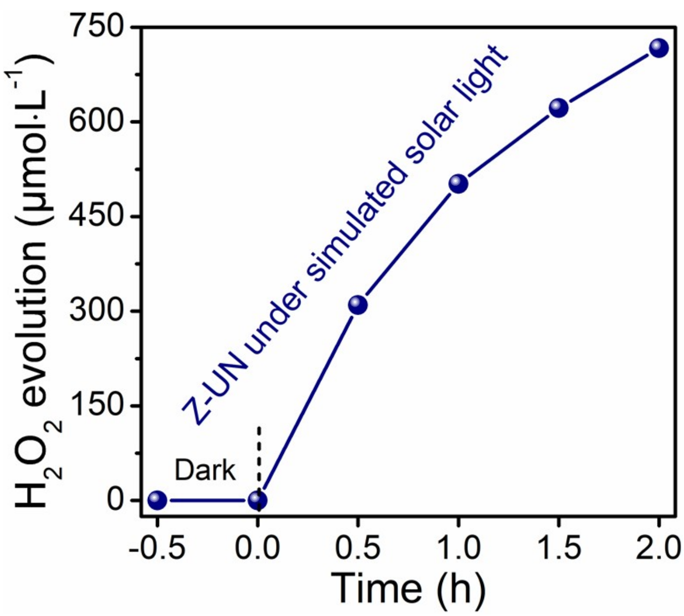

Fig. S4 Photocatalytic evolution of H_2O_2 over Z-UN under simulated solar light (light filter: AM1.5, light intensity: 100 mW·cm^{-1}).

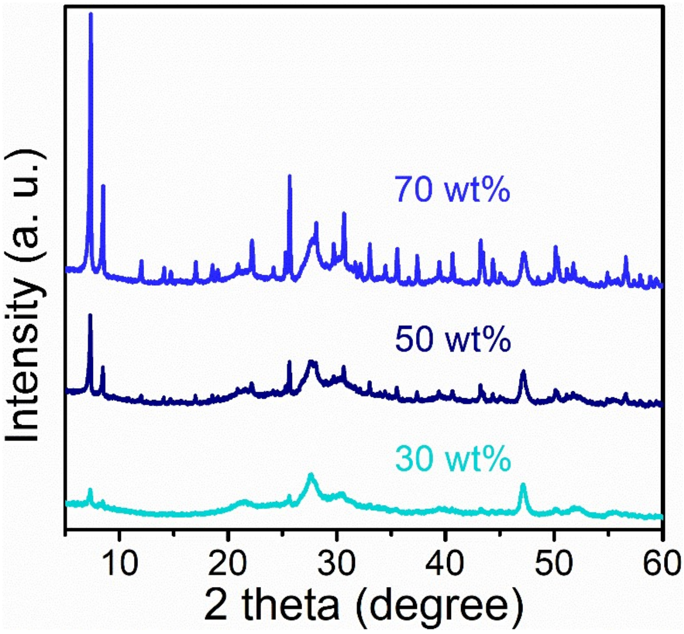

Fig. S5 XRD patterns of $ZnIn_2S_4$/UiO-66-NH_2 hybrids with 30, 50 and 70 wt% of UiO-66-NH_2.

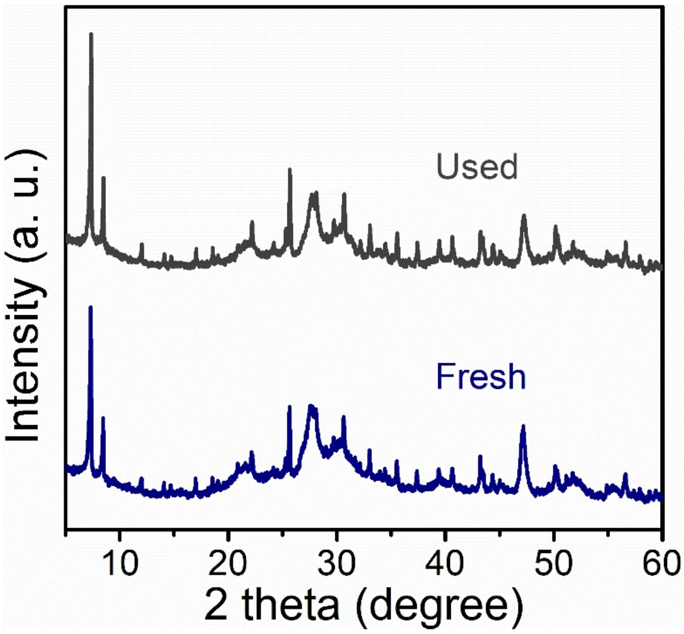

Fig. S6 XRD patterns of Z-UN before and after cycling experiments.

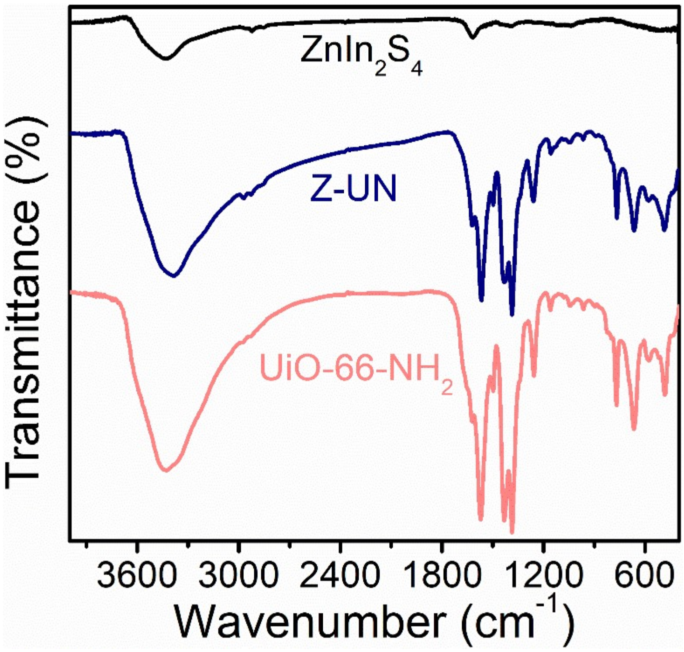

Fig. S7 FTIR spectra of UiO-66-NH_2, Z-UN and $ZnIn_2S_4$.

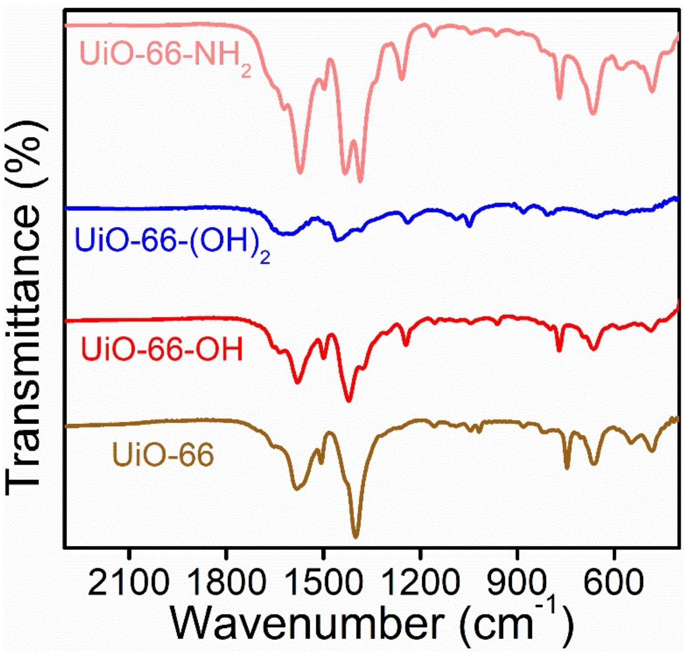

Fig. S8 FTIR spectra of UiO-66-NH_2, UiO-66-$(OH)_2$, UiO-66-OH and UiO-66.

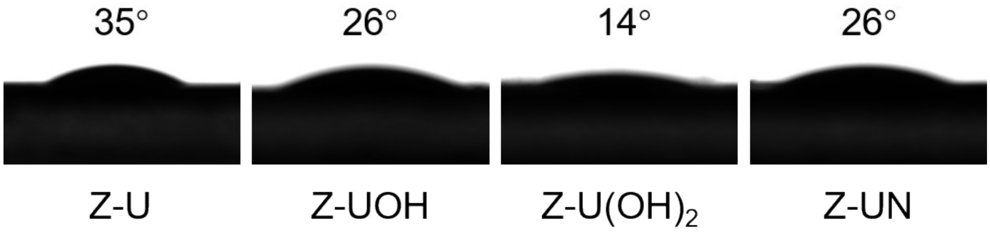

Fig. S9 Water contact angle optical images of Z-U, Z-UOH, Z-U$(OH)_2$ and Z-UN after 0.06 s of water contact.

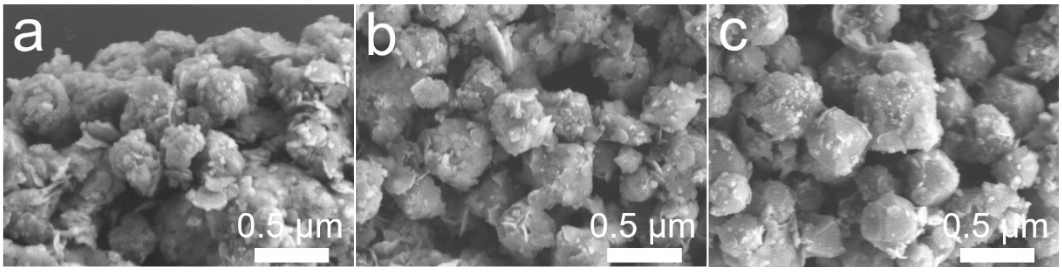

Fig. S10 SEM images of $ZnIn_2S_4$/UiO-66-NH_2 hybrids with 30 (a), 50 (b) and 70 (c) wt% of UiO-66-NH_2.

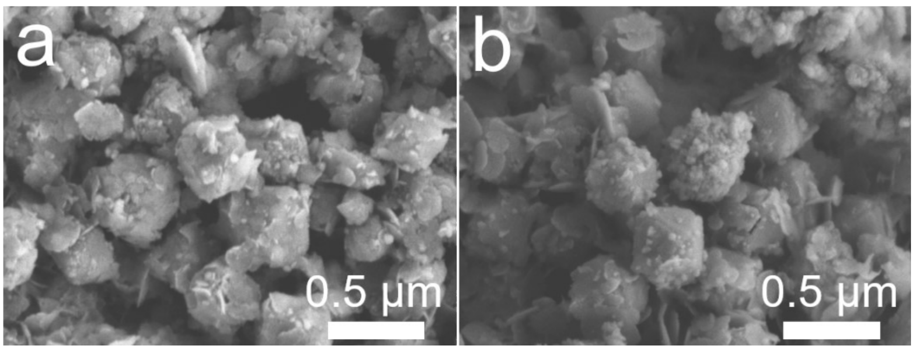

Fig. S11 SEM images of Z-UN before (a) and after (b) photocatalytic reaction.

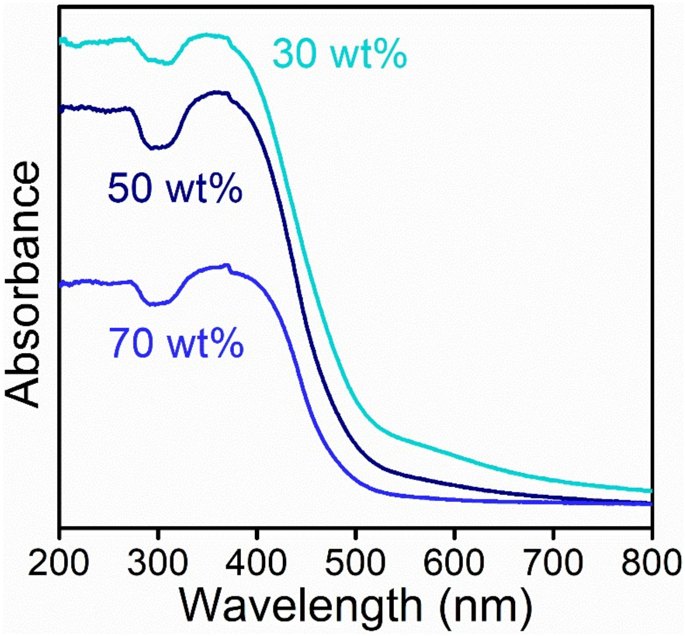

Fig. S12 UV-vis DRS of $ZnIn_2S_4$/UiO-66-NH_2 hybrids with 30, 50 and 70 wt% of UiO-66-NH_2.

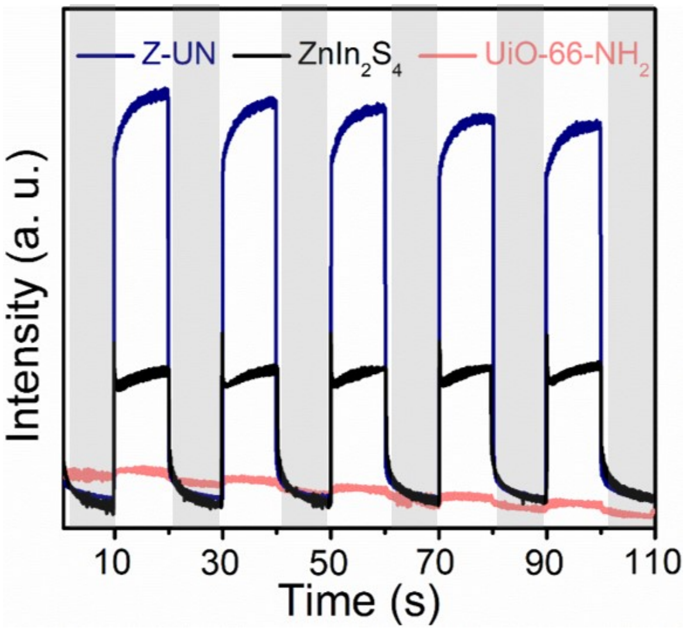

Fig. S13 Photocurrent spectra of Z-UN, $ZnIn_2S_4$ and UiO-66-NH_2.

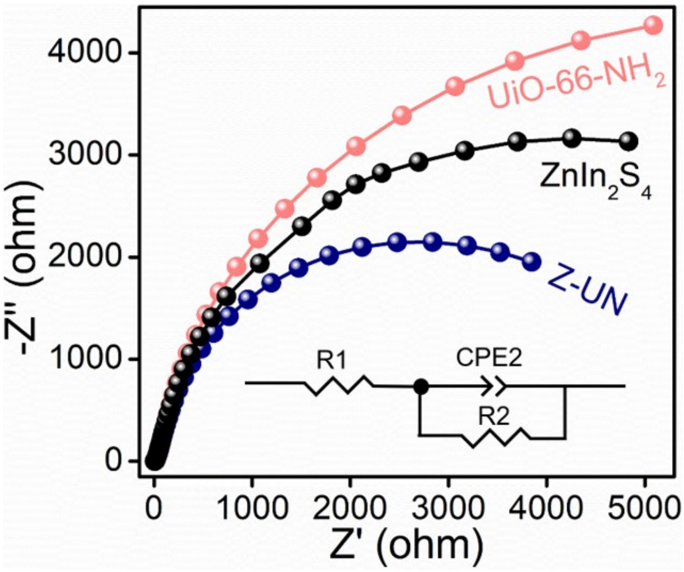

Fig. S14 EIS Nyquist plots of Z-UN, $ZnIn_2S_4$ and UiO-66-NH_2.

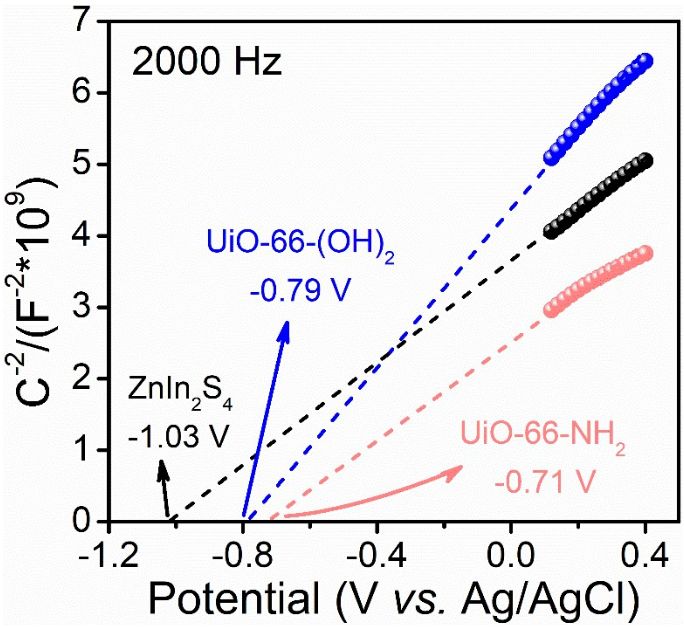

Fig. S15 Mott-Schottky plots of $ZnIn_2S_4$, UiO-66-$(OH)_2$ and UiO-66-NH_2 at 2000 Hz.

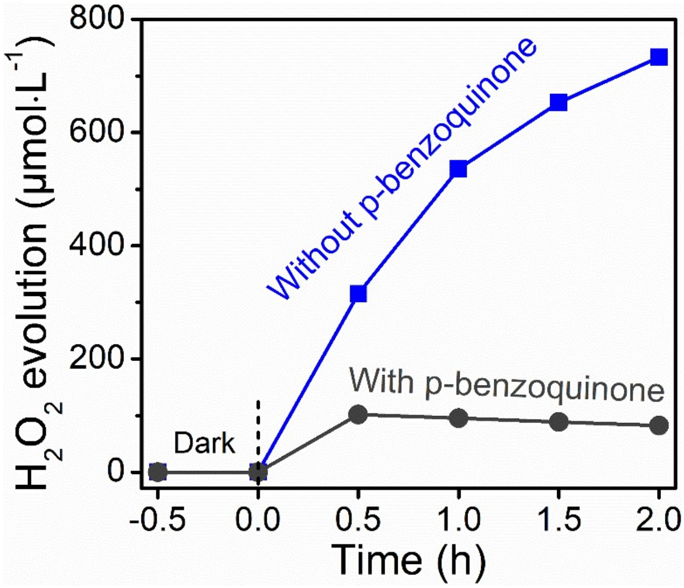

Fig. S16 Photocatalytic H_2O_2 evolution over Z-U(OH)$_2$ with and without p-benzoquinone.

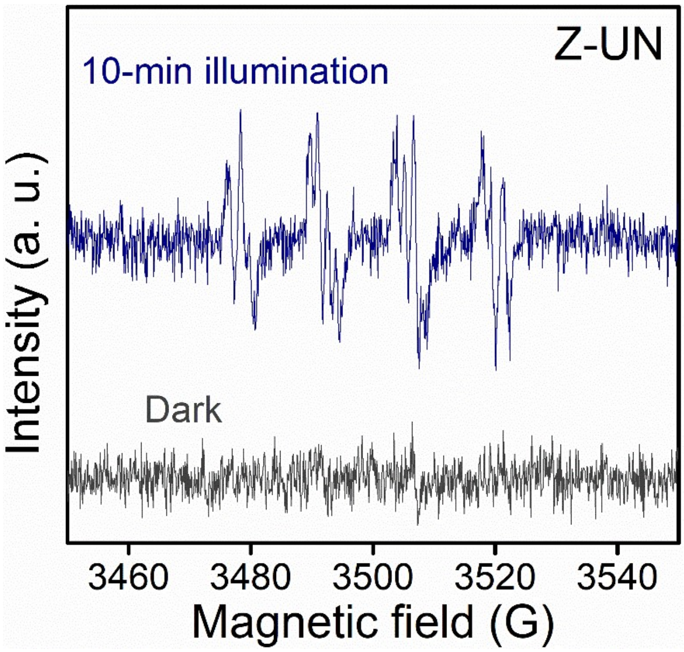

Fig. S17 EPR spectra of DMPO-·OH adducts over Z-UN at dark and 10-min illumination.

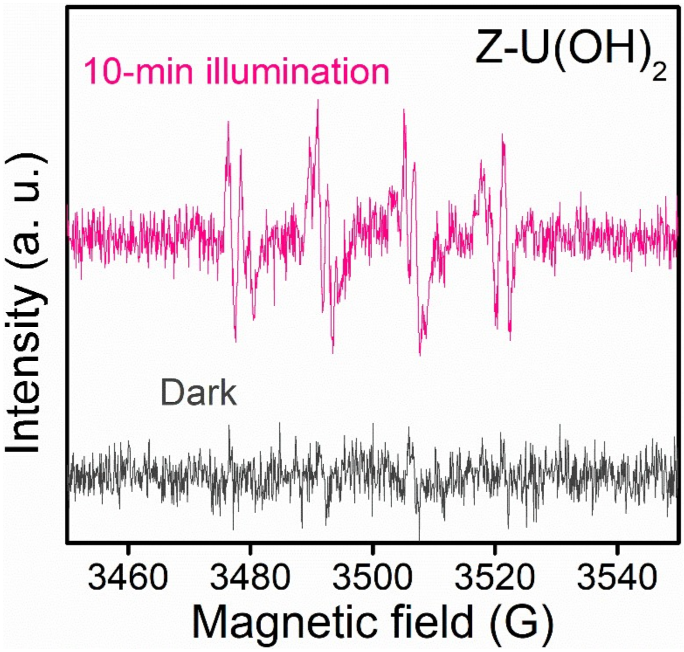

Fig. S18 EPR spectra of DMPO-·OH adducts over Z-U(OH)$_2$ at dark and 10-min illumination.

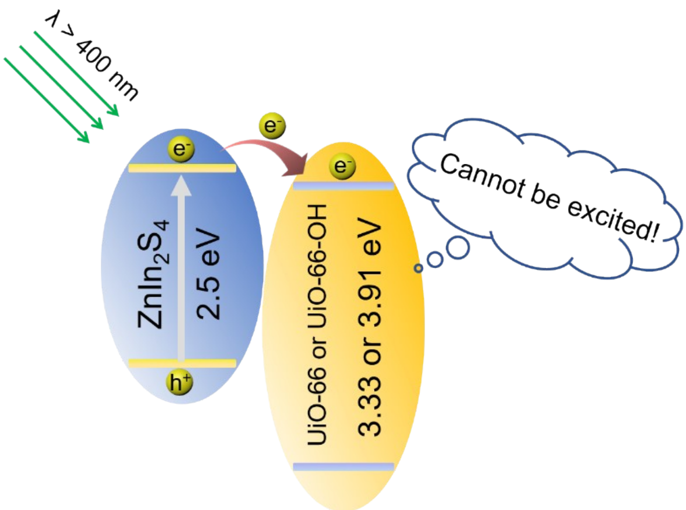

Fig. S19 Charge excitation and transfer over Z-U or Z-UOH under visible-light illumination.

Table S1 Data comparison of photocatalytic H_2O_2 evolution over MOF-based photocatalysts.

Photocatalysts	Light	Sacrificial agents	Gas	Evolution rates ($\mu mol \cdot g^{-1} \cdot h^{-1}$)	Ref.
Alkylated MIL-125	>420 nm	Benzyl alcohol	Air	313	S1
OPA/MIL-125-NH_2	>420 nm	Benzyl alcohol	Air	866	S2
MIL-125-$NH_2(TiO_2)/Ti_3C_2$	>420 nm	Isopropanol	O_2	278	S3
ZIF-8/C_3N_4	>420 nm	No	O_2	2641	S4
MIL-125-PDI	>420 nm	No	O_2	24	S5
UiO-66-B	AM1.5	Isopropanol	O_2	1002	S6
MIL-125-NH_2@ZnS	>420 nm	Benzyl alcohol	O_2	600	S7
MIL-88B-NH_2@$ZnIn_2S_4$	>420 nm	No	Air	209	S8
Z-U(OH)$_2$	**400-780 nm**	**No**	**Air**	**733**	this work
Z-UN	**400-780 nm**	**No**	**Air**	**799**	this work

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