Supplementary Materials

Noble Metal-Free Zeolitic Imidazolate Framework-Based Composite for Photocatalytic Production of Green Hydrogen

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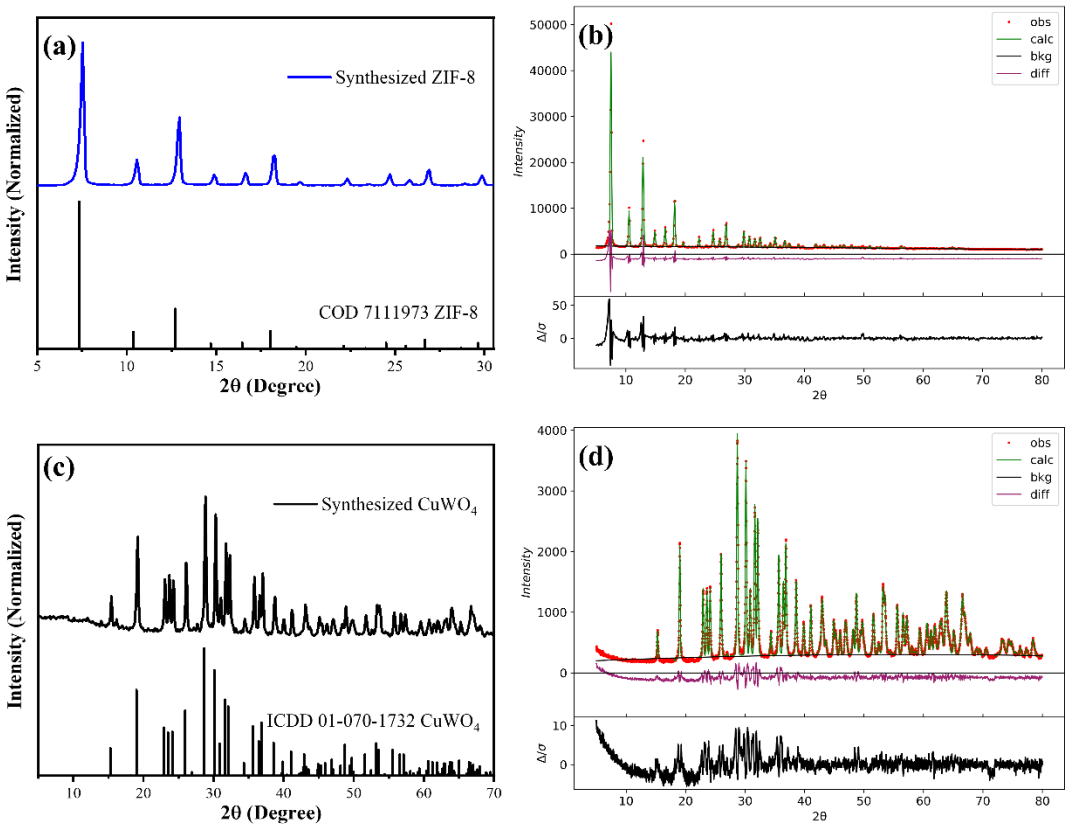

Fig. S1 *PXRD patterns for pristine ZIF-8 ((a) reference comparison, (b) Pawley refinement) and pure $CuWO_4$ ((c) reference comparison, (d) Pawley refinement) using the corresponding CIF files.*

Table S1. Size of $CuWO_4$ phase crystals in pure $CuWO_4$ and ZIF-8@$CuWO_4$ composite (size obtained from XRD data using Scherrer equation).

Sample	***XRD Phase***	***Crystal Size X (nm)***
$CuWO_4$	$CuWO_4$	35
ZIF-8@$CuWO_4$	$CuWO_4$	30

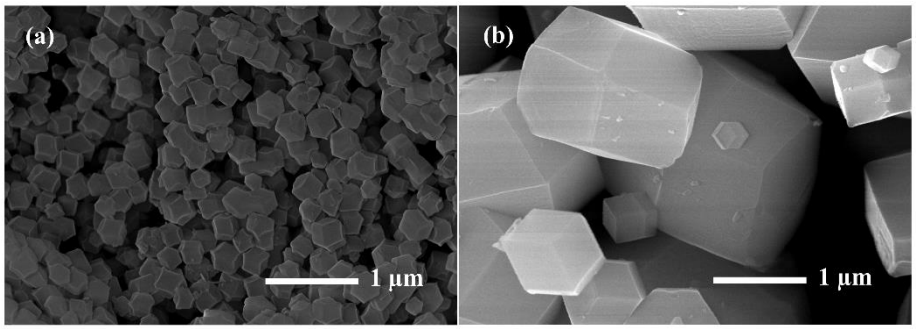

Fig. S2 *SEM images showing the effect of solvent on the ZIF-8 particle size synthesized in (a) methanol, and (b) water*

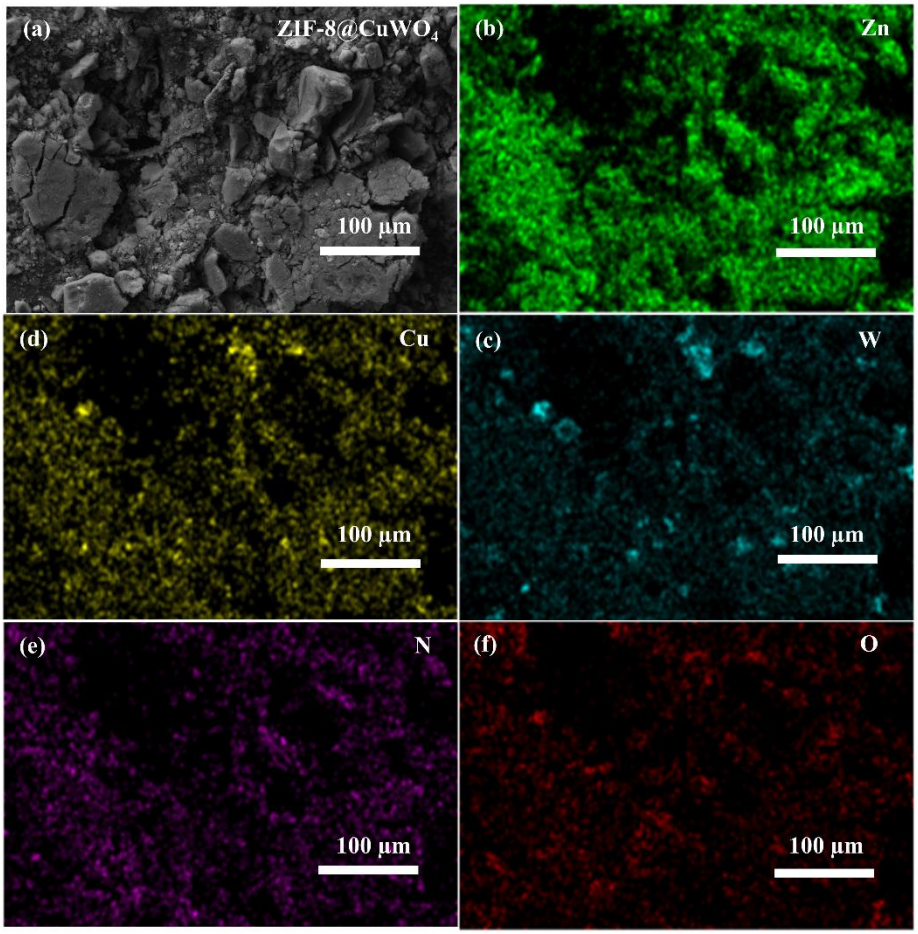

Fig. S3 *SEM image of (a) ZIF-8@$CuWO_4$ with EDS elemental mapping (b-f)*

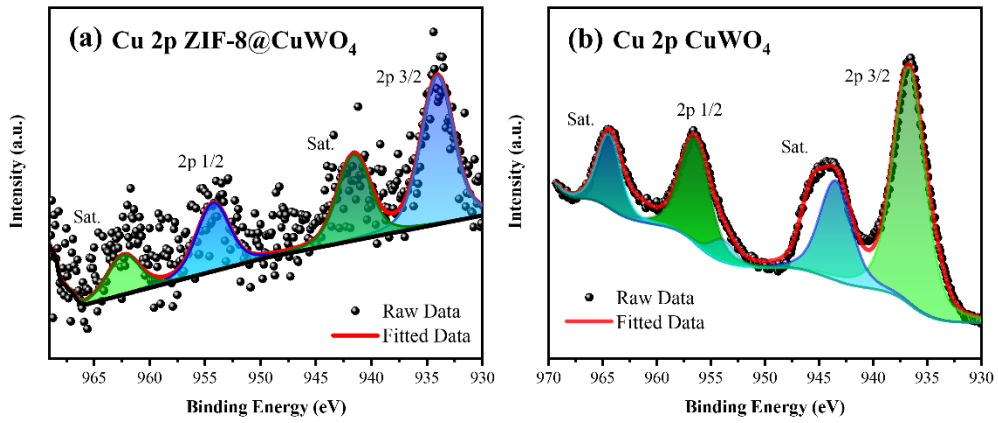

Fig. S4 *XPS peak deconvolution of Cu 2p in (a) ZIF-8@$CuWO_4$, and (b)$CuWO_4$, respectively*

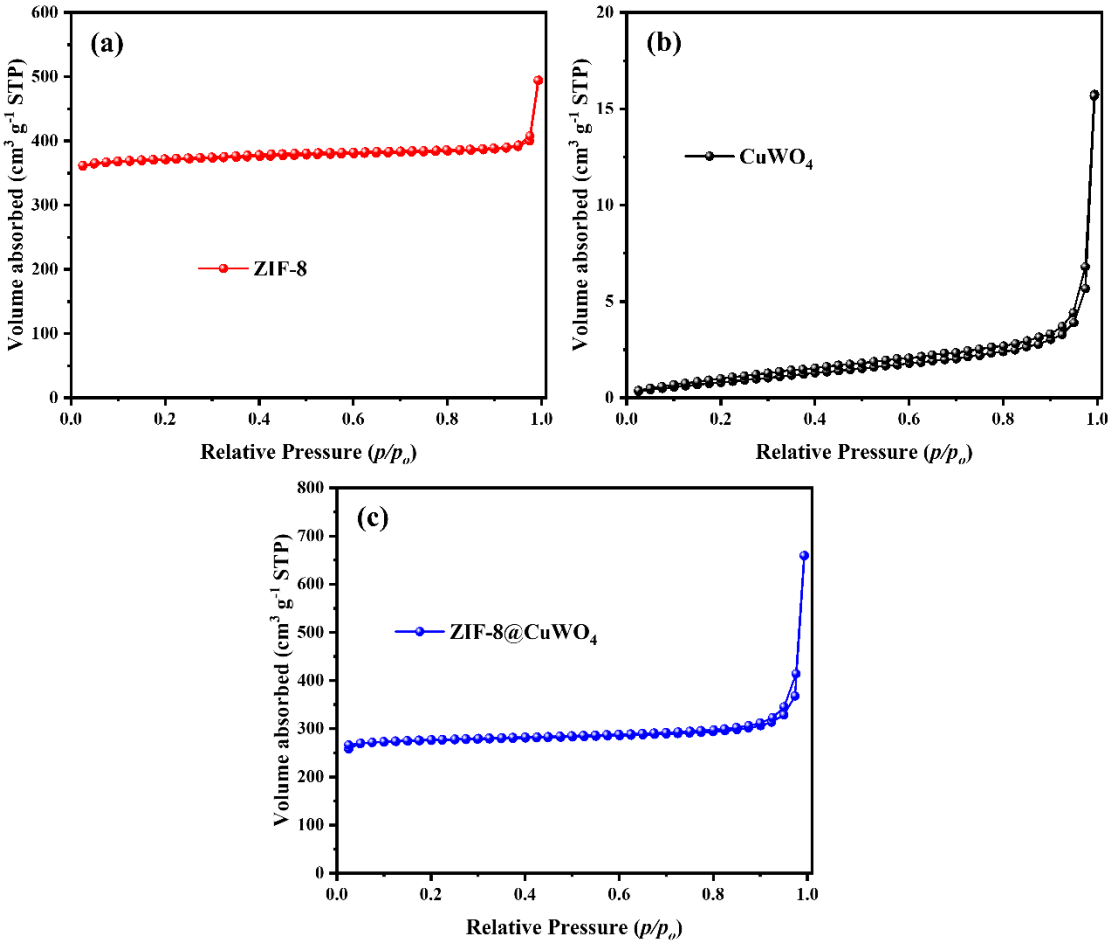

Fig. S5 *BET N_2 physisorption Isotherms of (a) ZIF-8, (b) $CuWO_4$, and (c) ZIF-8@$CuWO_4$*

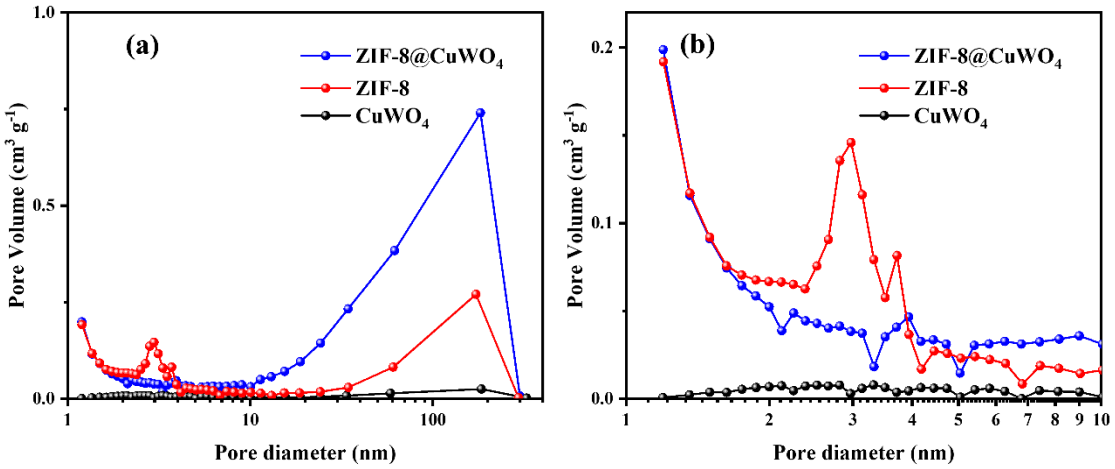

Fig. S6 *(a) BJH Pore size distribution of ZIF-8, $CuWO_4$, and ZIF-8@$CuWO_4$ with (b) enlarged pore diameter up to 10 nm (x-axis).*

Bandgap estimation

Bandgap estimation was done based on Mott-Schottky analysis and UV-visible spectroscopic analysis

$$E_{FB} = -(E_{V\ vs\ RHE} + 4.5)\ (eV) \qquad \text{Equation (1)}$$

$$E_{FB} \approx E_{CB}\ (eV) \qquad \text{Equation (2)}$$

$$E_{CB} = E_{VB} - E_g \qquad \text{Equation (3)}$$

where E_{FB} = flat band potential versus vacuum, $E_{V\ vs\ RHE}$ = Flat band potential versus reversible hydrogen electrode, E_e = Energy of a free electron on hydrogen scale (ca. 4.5 eV), E_g = Band gap through the Tauc plot, E_{CB} = Estimated conduction band potential of the semiconductor, E_{VB} = Estimated valence band potential of the semiconductor.

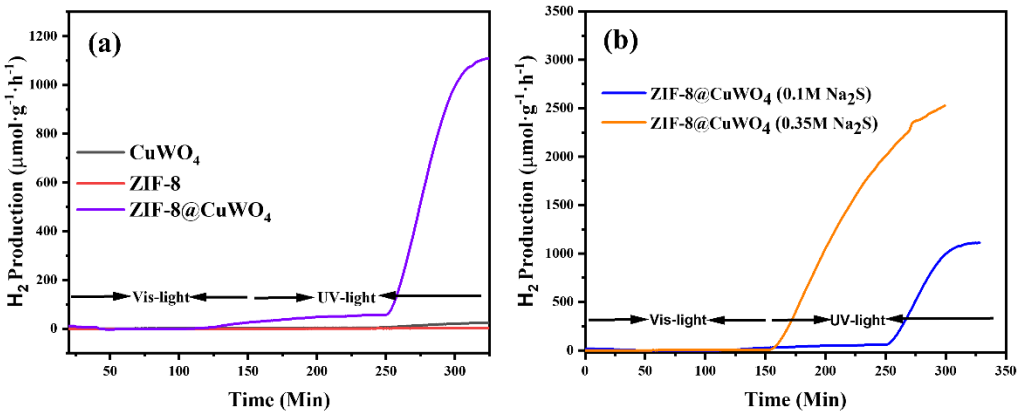

Fig. S7 *(a) Photocatalytic H_2 evolution for ZIF-8, $CuWO_4$, and ZIF-8@$CuWO_4$ composite, (b) Impact of molarity of Na_2S (0.1-0.35M) along with constant Na_2SO_3 (0.25 M) as sacrificial agents over the photocatalytic H_2 evolution for ZIF-8@$CuWO_4$ composite measured continuously under visible and UV irradiations, respectively.*

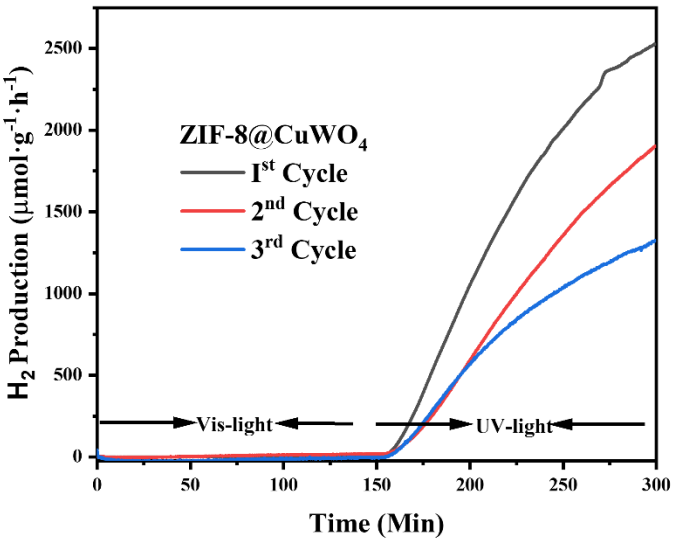

Fig. S8 *Photocatalytic H_2 evolution for recycled ZIF-8@$CuWO_4$ in comparison with fresh ZIF-8@$CuWO_4$ measured continuously under visible and UV irradiations, respectively.*

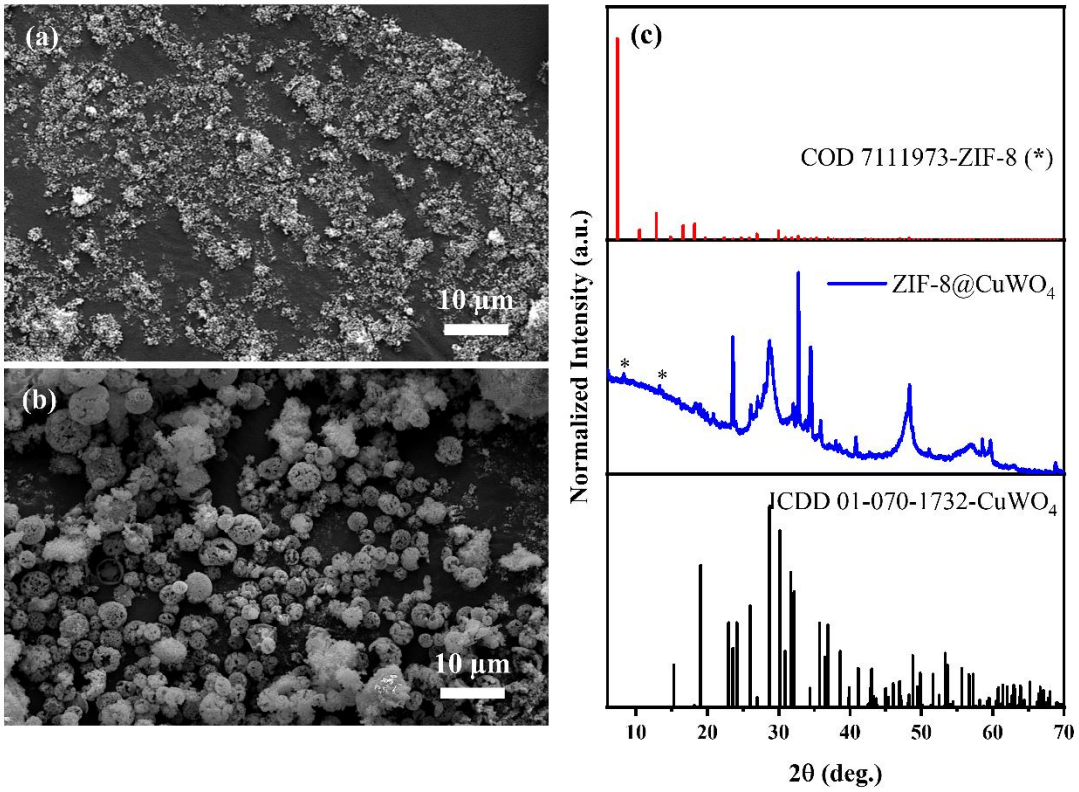

Fig. S9 *SEM images of ZIF-8@$CuWO_4$ (a) pristine (I^{st} cycle), (b) after second recycle (3^{rd} cycle), and (c) XRD graph of recycled ZIF-8@$CuWO_4$ after photocatalytic experiments.*