



Noble metal-free zeolitic imidazolate framework-based composite for photocatalytic production of green hydrogen

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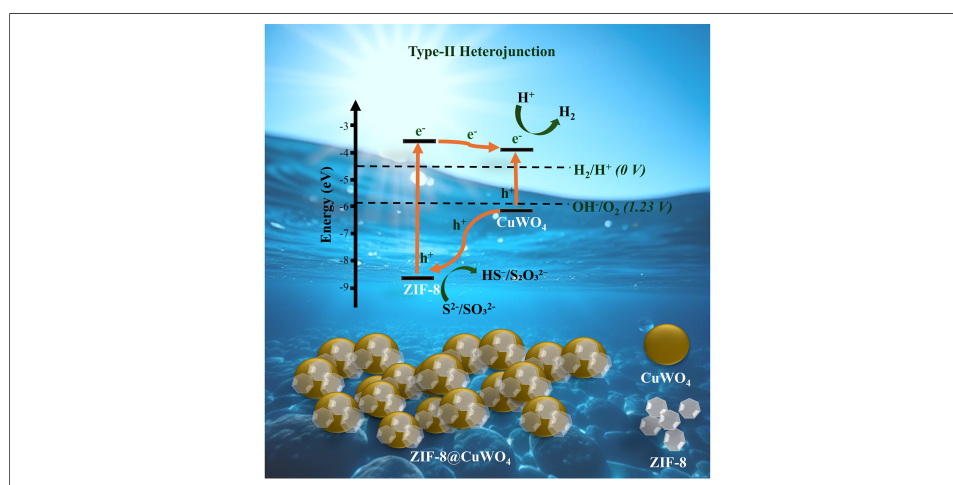
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Abstract

Photocatalytic water splitting could become a major pillar in addressing future demands for carbon-free energy supply. To develop noble-metal-free photocatalyst microstructures, a heterostructure photocatalytic system containing hexagonal Zeolitic Imidazolate Framework-8 (ZIF-8) and oxygen-deficient spherical CuWO₄ nanoparticles was designed. In addition to preventing CuWO₄ aggregation, ZIF-8 promotes the accessibility of active sites, interfacial charge transfer, and separation in the ZIF-8@CuWO₄ composite. In this composite, UV-visible diffuse reflectance spectroscopy reveals substantial light absorption in the UV range, while photoluminescence spectroscopy indicates suppressed electron-hole recombination relative to pristine materials. The as-synthesised ZIF-8@CuWO₄ exhibits a photocatalytic H₂ evolution rate of 2,531 μmol g⁻¹ h⁻¹ under UV irradiation, higher than that of pristine ZIF-8 and CuWO₄. The composite achieves a maximum H₂ production rate of 79 μmol g⁻¹ h⁻¹ under visible light irradiation using Na₂S/Na₂SO₃ (0.35/0.25 M) as the sacrificial hole scavenger. These results highlight that integrating ZIF-8 with CuWO₄

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could offer an effective option for improving photocatalytic green hydrogen production in CuWO_4 -based heterojunction systems.

INTRODUCTION

Hydrogen (H_2) presents a promising clean and renewable energy carrier as it produces only water upon combustion, thereby contributing to CO_2 emission reduction. However, hydrogen is predominantly produced via steam-methane reforming, which is an environmentally unsustainable method^[1,2]. In contrast, “green” hydrogen can be generated through eco-friendly techniques, such as photocatalytic and photoelectrochemical reactions^[3,4].

Solar-driven photocatalytic water splitting using semiconducting materials such as titanium dioxide (TiO_2) and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) is well-established, while metal-organic frameworks (MOFs) have recently emerged as promising photocatalysts due to their high surface area and tunable structure^[5–7]. Over recent decades, various materials have been developed to enhance the efficiency of the hydrogen evolution reaction (HER). However, commercialisation remains challenging due to issues such as low efficiency, shorter lifetimes, and the high cost of stable plasmonic metal co-catalyst nanoparticles, including platinum (Pt) and gold (Au)^[8]. Photocatalysts such as $\text{g-C}_3\text{N}_4$ ^[9], ZnCdS ^[10,11], and TiO_2 ^[12,13] have demonstrated potential for efficient photocatalytic H_2 generation. However, they suffer from various limitations, including a low surface area, rapid charge recombination, and reduced efficiency. Strategies to address these challenges include surface sensitisation^[14], bandgap engineering^[15], metal/non-metal doping^[16], heterojunction development^[17], spectral conversion^[18], co-catalyst coupling^[19], and modification with carbon-based materials^[20], leading to the development of novel semiconductor-based materials^[21].

Among various photocatalysts such as WO_3 , $\text{g-C}_3\text{N}_4$, and TiO_2 , the unique features of copper tungstate (CuWO_4) are favourable to the application in photocatalytic hydrogen production^[22]. CuWO_4 is a semiconductor photocatalyst that exhibits favourable bandgap properties due to the hybridised O-2p and Cu-3d orbitals^[23], which contribute to its valence band position on the normal hydrogen electrode (NHE) scale^[24]. Although TiO_2 is stable under photocatalytic reaction conditions, its activity is mainly limited to the UV region due to its wide band gap (~ 3.2 eV)^[25]. Meanwhile, $\text{g-C}_3\text{N}_4$, a visible light photocatalyst, has been extensively explored^[26]; however, it possesses limited photocatalytic performance due to rapid charge recombination. Similarly, WO_3 also possesses visible light absorption (with a band gap of ~ 2.4 eV)^[27], but the conduction band potential is insufficient for the HER. CuWO_4 , on the other hand, has a narrow band gap (~ 2.2 eV) with improved solar light utilisation, a favourable band-edge position for reduction^[28], and has the potential for constructing a heterojunction with enhanced charge separation. However, pristine CuWO_4 suffers from high carrier recombination rates, limiting its HER performance. To enhance its efficiency, CuWO_4 has been combined with other materials to suppress electron-hole recombination^[29]. For example, Dinh *et al.* found that coating CuWO_4 nanoparticles with the conductive polypyrrole polymer enhanced the H_2 evolution rate to $365 \mu\text{mol g}^{-1} \text{h}^{-1}$ ^[30]. Additionally, vanadium doping was found to reduce electron-hole recombination and improve the reduction potential, as reported by Le Minh Tri *et al.*^[31] Basyach *et al.*^[32] demonstrated that doping CuWO_4 with nickel and subsequently combining it with $\text{g-C}_3\text{N}_4$ ($0.2\text{Ni-CuWO}_4/\text{g-C}_3\text{N}_4$) significantly enhanced H_2 production through improved light absorption^[32], a reduced bandgap, and an increased surface area.

Various MOFs, including ZIF-67^[33], MIL-101^[34], and MIL-125^[35], have demonstrated potential as auxiliary component materials or as photocatalysts by themselves in solar-driven water-splitting, benefiting from their highly porous metal-coordinated architectures with organic linkers. The photocatalytic H₂ production efficiency of MOFs can be systematically tuned by modifying properties such as optical absorption, bandgap energy, and charge transfer dynamics^[36,37]. Functionalisation of UiO-66 and MIL-101 with amino groups (-NH₂), achieved by substituting terephthalic acid with amino terephthalic acid, significantly improves water splitting efficiency compared to their pristine forms^[38]. An effective approach to further enhance the H₂ production performance is to incorporate guest species into MOFs, to form core-shell structures or composite materials^[39]. Heterojunctions between metal oxide semiconductors and MOFs, such as TiO₂/MIL-101^[40] and ZnO/MIL-53^[41], exhibit superior photocatalytic activity due to improved charge separation and light absorption.

Similarly, the Zeolitic Imidazolate Framework-8 (ZIF-8) has been combined with other materials to improve the efficiency of photocatalytic water splitting, benefiting from its high surface area and the three-dimensional porous framework comprising zinc ions and organic imidazoles^[42]. In addition to structural benefits, ZIF-8 can influence photocatalytic efficiency by various physicochemical mechanisms^[43]. Abundant adsorption sites are provided by the porous structure and large surface area of ZIF-8, which facilitate the diffusion of reactants and products during the photocatalytic reaction^[44]. Moreover, coupling ZIF-8 with a semiconductor photocatalyst can increase the heterojunction interface contact area and promote interfacial charge transfer, thus enhancing charge separation^[45]. Therefore, ZIF-8 represents a promising platform for designing a composite with increased surface reactivity and photocatalytic efficiency. For instance, Qureshi *et al.* reported that the Ru nanoparticles achieved an exceptional H₂ evolution rate of 5,245 $\mu\text{mol g}^{-1} \text{h}^{-1}$ in a Z-scheme heterojunction of g-C₃N₄ and ZIF-8^[46]. Cd- and Mn-doped ZIF-8 photocatalysts have demonstrated enhanced charge transfer and H₂ production^[47]; however, their poor stability restricts their practical application. Furthermore, reliance on costly noble metals (e.g., ruthenium) and hazardous elements (e.g., cadmium) undermines the sustainability and economic viability of green hydrogen production.

To address these challenges, researchers have modified ZIF-8 with wide bandgap semiconductors, such as Co-ZIF-8/TiO₂^[48], and ZIF-8/ZnO^[49], which exhibit improved photocatalytic performance compared to pristine ZIF-8, doped-ZIF-8, TiO₂, and ZnO. Despite some advancements, such heterojunctions continue to face issues of low photoconversion efficiency. Therefore, identifying new, more active semiconductors, such as CuWO₄, is crucial for enhancing the efficiency of photocatalysts in practical applications^[50].

However, the incorporation of ZIF-8 into CuWO₄ has been largely unexplored, despite significant progress in MOF-based composites for photocatalytic hydrogen production^[51]. Although the photocatalytic activity of ZIF-8-based heterostructures has shown significant improvement, the relationship among the porous structure, interfacial charge transfer, and photocatalytic activity remains mostly unknown. Furthermore, the effect of ZIF-8 on the accessibility of active sites and the charge-carrier dynamics in CuWO₄-based heterostructures has not been investigated systematically. To address this gap, a ZIF-8@CuWO₄ heterostructure was prepared via an *in situ* growth strategy and evaluated for photocatalytic hydrogen evolution under UV and visible light irradiation. We investigated the synergistic interaction between ZIF-8 and CuWO₄ using detailed structural, textural, optical, and electrochemical characterisation. Our work provides new insight into the role of the MOF-semiconductor interface in enhancing photocatalytic hydrogen production and provides a promising strategy for designing efficient photocatalytic systems.

MATERIALS AND METHODS

Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$, Sigma Aldrich), copper nitrate hemi pentahydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\geq 98\%$, Thermo Scientific), sodium tungstate dihydrate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$, Sigma Aldrich), polyvinylpyrrolidone (PVP) ($(\text{C}_6\text{H}_9\text{NO})_x$, $M_w \sim 10,000$, Thermo Scientific), 2-methyl imidazole (2-MIM, $\text{C}_4\text{H}_6\text{N}_2$, 99% , Sigma Aldrich), methanol (CH_3OH , 99.8% , Central chem), ethanol ($\text{C}_2\text{H}_5\text{OH}$, 96% , Central chem) were used as delivered by the suppliers, without further purification.

Synthesis of CuWO_4 nanoparticles

CuWO_4 nanoparticles were synthesised using the co-precipitation method^[52]. First, two aqueous solutions using 20 mL of deionised water were prepared, one containing 1.163 g (5 mmol) of copper nitrate and the other containing 1.649 g (5 mmol) of sodium tungstate. Then, 0.5 g of PVP was added to the copper nitrate solution and sonicated for 30 min. Both solutions were then mixed, and the final solution was sonicated for one h. The resulting green precipitates were collected, washed with deionised water and ethanol, and dried at 65°C for 24 h. The resulting powder was then calcined at 500°C for 2 h and denoted as CuWO_4 .

Synthesis of ZIF-8@ CuWO_4 heterostructure

The synthesis scheme for the ZIF-8@ CuWO_4 heterostructure is summarised in Scheme 1. The as-prepared CuWO_4 nanoparticles (1 g) were dispersed in methanol (200 mL) for 30 min before 8 g of 2-methylimidazole (2-MIM) was added to form suspension A, which was sonicated for a further 30 min to ensure a homogeneous dispersion of the CuWO_4 nanoparticles. Zinc nitrate hexahydrate (3 g) was dissolved in 200 mL of methanol and stirred for 30 min to form solution B.

Dispersion A was then added dropwise to solution B and stirred at 300 rpm for 3 h at 70°C to prepare the ZIF-8@ CuWO_4 composite powder. The resulting composite was collected by centrifugation at 6,000 rpm, washed five to six times with methanol, and dried for 24 h at 65°C . This composite was denoted as ZIF-8@ CuWO_4 .

Characterisation

A range of techniques was employed to characterise the prepared ZIF-8, CuWO_4 , and ZIF-8@ CuWO_4 composite. X-ray powder diffraction (XRD, Panalytical Empyrean DY1098, UK) was used with a Cu K α source to verify their phase purity within a 2θ range of 5° – 70° . Scanning electron microscopy (SEM, JEOL JSM-7600F, Japan) was used in secondary electron mode to examine the morphology and shape of synthesised nanoparticles. By using X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Nexsa G2, USA), constituent elements' surface oxidation and chemical bonding states were determined by selecting a monochromated Al K α source. XPS analysis was conducted with charge correction, which was validated using the standard C-C bond at 284.8 eV. Voigt peak fitting was employed for all peaks using the instrument's software package. The surface area and pore size distribution in the ZIF-8@ CuWO_4 heterostructures were evaluated and compared with pristine materials over an AUTOSORB IQ instrument by using the Brunauer, Emmett, and Teller (BET) and Barrett-Joyner-Halenda (BJH) gas adsorption methods under N_2 gas at 77 K, respectively. The optical properties were investigated over the 200–700 nm wavelength range by a UV-visible double-beam spectrophotometer (UV, Agilent Cary 5000, USA) equipped with a Xenon lamp as the radiation source. Carrier recombination was studied using photoluminescence (PL, Horiba Fluorolog 3: FL 3-21, Japan) and time-resolved photoluminescence (TRPL, Horiba Fluorocube-NL-01, Japan). To determine the flat-band potential and conduction band location, Mott-Schottky measurements were performed for ZIF-8 and CuWO_4 at three different frequencies (1–2 kHz) using electrochemical impedance spectroscopy (EIS, Autolab-PGSTAT204-FRA32M). To conduct these experiments, a three-electrode half-cell containing 0.1 M Na_2SO_3 was used, with a reversible hydrogen electrode (RHE) as the reference and a glassy carbon (GC) rod as the counter electrode. Catalyst inks (4 mg

of photocatalyst, 15 μL of Nafion® (5%, Sigma-Aldrich), 5 mL of ultrapure water) were sonicated, and 10 μL was drop-cast onto a GC disk under argon. To obtain further insight into the electronic structure of the investigated samples, valence band spectra were acquired using XPS. The measurements were performed using a PHI Genesis XPS system (ULVAC-PHI, Inc.) equipped with a monochromated Al K α X-ray source for photoelectron excitation. Valence band spectra were collected with a pass energy of 27 eV and an energy step size of 0.1 eV. The X-ray analysis spot size was 100 μm in diameter, and the power was 25.4 W. Before the measurements, the spectrometer was calibrated using the Fermi edge of a Ni reference foil. The Ni surface was cleaned by Ar⁺ ion sputtering before calibration measurements. The resulting Fermi edge was well defined, and the uncertainty of the energy calibration was estimated to be ± 0.06 eV. Analysis of Valence band spectra was performed using MultiPak software (version 9.9.2).

Photocatalytic H₂ evolution

The photocatalytic hydrogen experiments were carried out in a double-walled borosilicate photocatalytic reactor, as represented in Figure 1^[53]. A linear halogen lamp (500 W) and an HPA Synergy lamp (300 W) were used as the reaction light sources. The photocatalytic experiments were performed in two aqueous suspensions containing 200 mg of the catalyst dispersed in 200 mL of a solution of 0.1 or 0.35 M Na₂S and 0.25 M Na₂SO₃, which were used as sacrificial reagents. A water-cooled flux was used to maintain the reaction temperature at 20 °C in the jacketed reactor throughout the experiment. Before irradiation, the reactor was purged with a high flow of 15.73 mL·min⁻¹ N₂ gas for 30 min to remove the dissolved air that can remain in the reactor. The suspension was then irradiated for 150 min with visible light, followed by a further 150 min with UV light. During the photocatalytic activity measurement, the reactor was continuously stirred to keep the nanoparticles in a suspended state. Instead of the conventional batch method, the produced gases (H₂ and O₂) were continuously monitored with sequential radiation (visible and UV radiation, respectively) and quantified by an online mass spectrometer (MS, Omnistar Pfeiffer Vacuum Co., Germany), which was connected directly to the reactor gas outlet. A more detailed overview of the photocatalytic system can be found elsewhere^[53,54]. At the end of each cycle, the photocatalyst was washed several times with distilled water and absolute ethanol, followed by centrifugation and oven-drying at 60 °C. The recovered solid photocatalyst was weighed again and reinserted into a freshwater solution, which was then irradiated with both Vis and UV light for the first cycle. The solid catalyst was collected again and employed for the second cycle of the photocatalytic water splitting reaction. SEM and XRD measurements were used to characterise the recycled catalyst at each stage.

RESULTS & DISCUSSION

Figure 2 illustrates the XRD analysis, which was performed to elucidate the crystalline phases present in CuWO₄, ZIF-8, and their heterostructure (ZIF-8@CuWO₄). The XRD pattern of pure ZIF-8 exhibits multiple diffraction maxima within the 10–70° 2 θ range, with prominent reflections at $2\theta \approx 7.49^\circ$, 10.48° , and 12.81° , corresponding to the [110], [200], and [211] crystallographic planes, respectively. By contrast, the diffraction pattern of pure CuWO₄ exhibits distinct maxima at $2\theta \approx 18.98^\circ$, 26.06° , 28.74° , 31.71° , and 36.94° , assigned to the [100], $[\bar{1}01]$, [111], $[\bar{1}\bar{1}1]$, and [020] planes of the CuWO₄ crystal structure. These diffraction signatures are consistent with the reference patterns from the ICDD PDF 01-070-1732 and COD PDF 7111973 databases for CuWO₄ and ZIF-8^[55,56], respectively. Pawley fittings were performed over the experimental data using the corresponding CIF files, further confirming the phase purity of the prepared CuWO₄ and ZIF-8 (see Supplementary Figure 1 for PXRD plots with Pawley refinements) and the coexistence of these phases within the ZIF-8@CuWO₄ heterostructure.

The size of CuWO₄ crystals in ZIF-8@CuWO₄ was estimated using the Scherrer equation [Supplementary Table 1], which indicates comparable sizes for CuWO₄, in both its pristine and composite forms, likely attributable to the post-synthetic ultrasonication and the *in-situ* growth process of ZIF-8.

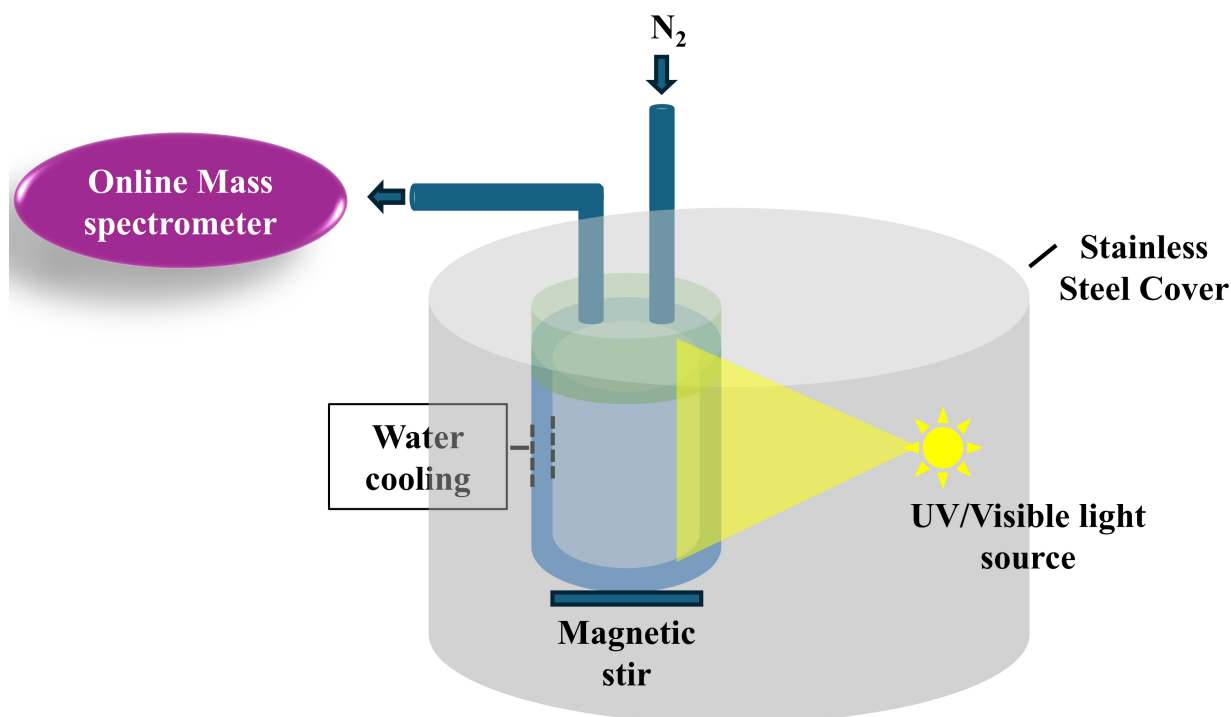


Figure 1. Custom-made photocatalytic reactor setup used in this work for quantifying hydrogen production.

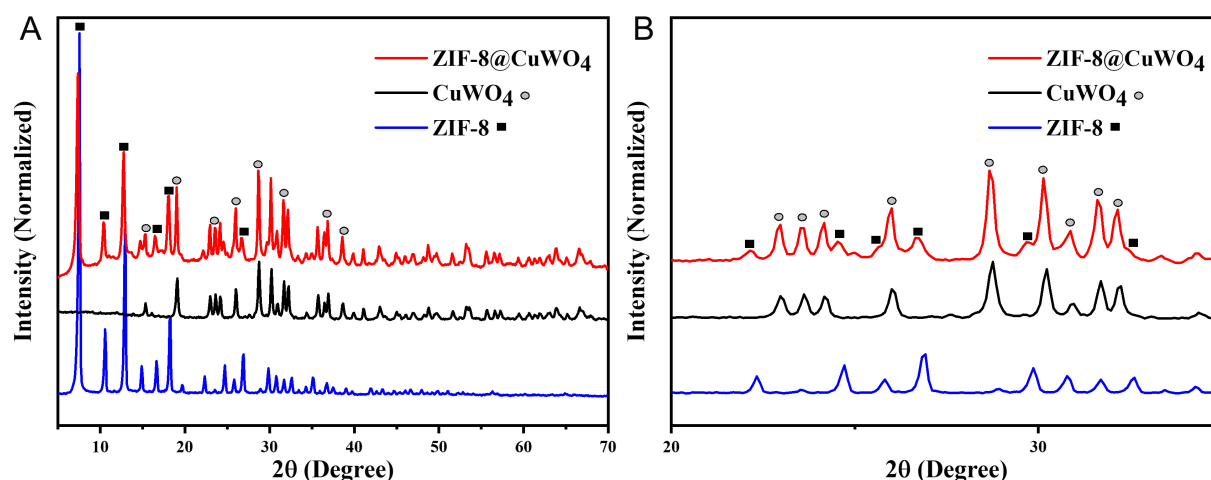


Figure 2. XRD patterns of CuWO_4 , ZIF-8, and ZIF-8@ CuWO_4 composite (A) overall diffraction patterns and (B) enlarged view of 20° – 35° (2θ) region.

The morphology and microstructures of ZIF-8, CuWO_4 , and the ZIF-8@ CuWO_4 composite are shown in Figure 3. ZIF-8 particles exhibit a nanoscale, pseudohexagonal morphology [Figure 3A], which is consistent with that of previously reported structures^[57]. The particle size of ZIF-8 could be considerably reduced by replacing the water solvent with methanol (see Supplementary Figure 2). Figure 3C confirms the successful synthesis of spherical CuWO_4 nanoparticles with an average diameter of $\sim 64 \pm 15$ nm, with some degree of agglomeration. The incorporation of PVP and the application of ultrasonication during synthesis proved effective in achieving homogeneous particle size. The ZIF-8@ CuWO_4 composite has a similar morphology and particle size distribution to pure CuWO_4 [Figure 3E and F]. In the heterostructure, the naturally pseudohexagonal ZIF-8 particulates are more rounded, which may be attributed to a greater density of

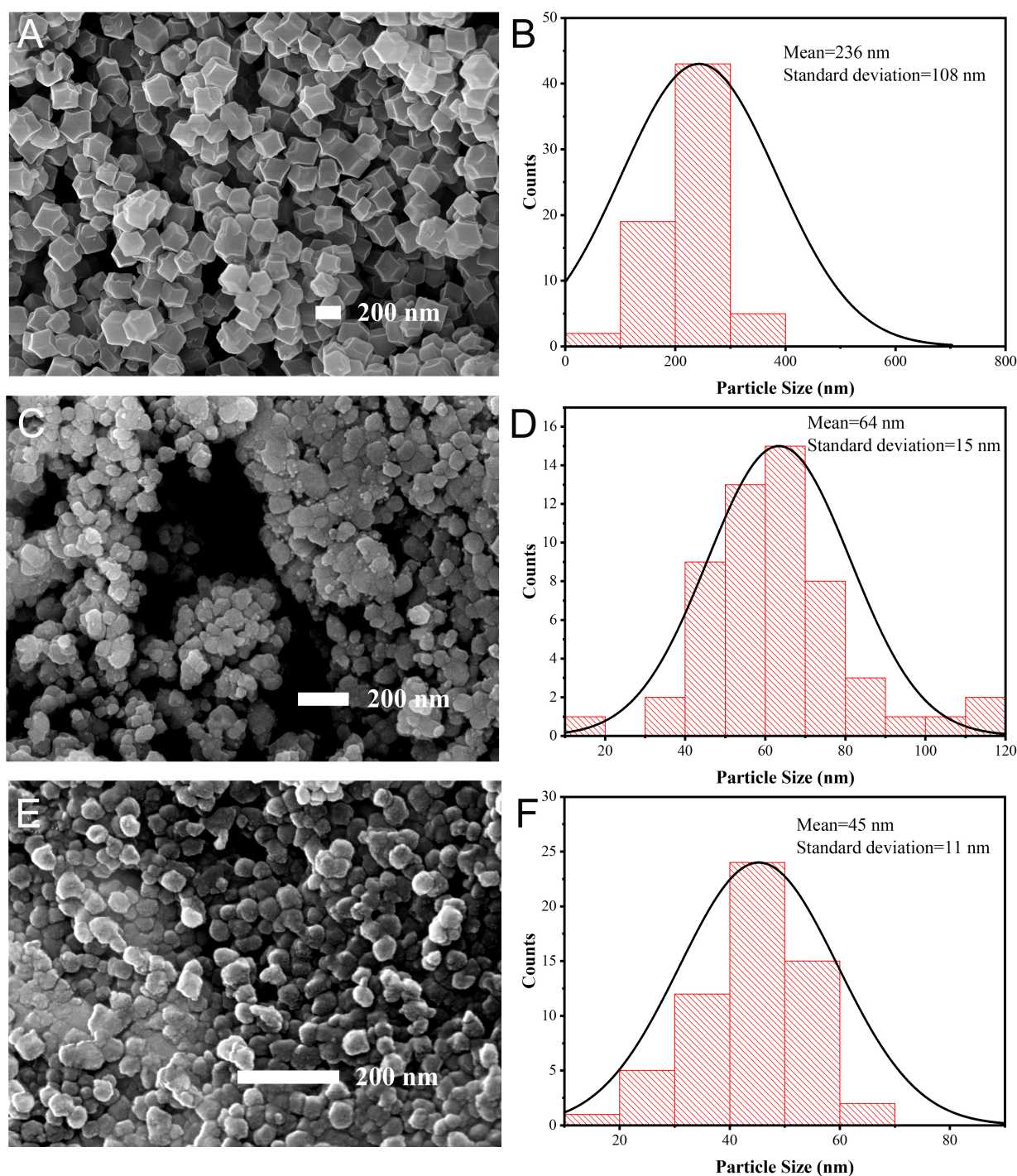


Figure 3. SEM micrographs and the particle size distributions of (A and B) ZIF-8, (C and D) CuWO₄, and (E and F) ZIF-8@CuWO₄.

nucleation sites, promoting preferential ZIF-8 growth with minimised surface energy in the presence of spherical CuWO₄ nanoparticles in the colloidal solution^[58]. Consequently, the coexistence of CuWO₄ and ZIF-8 phases at the nanoscale in the composite is expected to enhance photocatalytic efficiency due to the abundance of surface-active sites.

The XPS spectra for CuWO₄ and the ZIF-8@CuWO₄ composite are presented in Figure 4. In the XPS spectrum of pure CuWO₄ nanoparticles (see Figure 4A), characteristic peaks corresponding to Cu 2p, W 4f, and O 1s were identified. Consistent with energy-dispersive X-ray spectroscopy (EDS) results (see

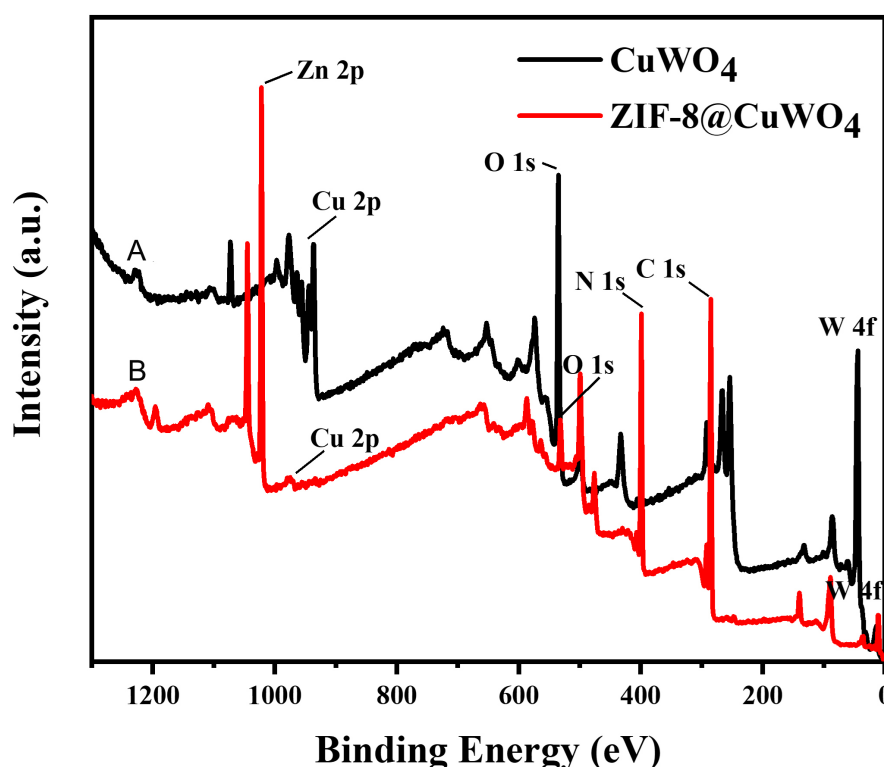


Figure 4. XPS full scan of (A) pure CuWO_4 and (B) ZIF-8@CuWO_4 composite.

Supplementary Figure 3), the XPS spectrum of the ZIF-8@CuWO_4 composite (see Figure 4B) reveals the presence of Cu, W, O, Zn, N, and C.

XPS peak deconvolution was performed to elucidate the oxidation states and chemical environments of the elements present in pure CuWO_4 and the ZIF-8@CuWO_4 composite. Figure 5A shows that the C 1s spectrum of ZIF-8@CuWO_4 is resolved into four components: a dominant C-C/C=C peak at 284.53 eV (42.13%)^[59], two more peaks at 285.36 and 286.29 eV corresponding to C-N (34.23%) and N-C=N (13.17%) bonds of the imidazole ring^[60], and a peak at 291.78 eV attributed to chemisorbed C=O species. The N 1s spectrum [Figure 5B] exhibits peaks at 398.48, 399.15, and 400.24 eV, which respectively correspond to pyridinic, pyrrolic, and graphitic nitrogen in the composite^[61]. These are associated with enhanced photocatalytically active sites in ZIF-8@CuWO_4 ^[61–63].

The Zn 2p spectrum [Figure 5C] displays spin-orbital splitting with Zn $2p_{1/2}$ and Zn $2p_{3/2}$ peaks at 1,044.8 and 1,021.75 eV, respectively. This fact is indicative of Zn^{2+} in the ZIF-8 lattice^[64]. The O 1s spectrum of the ZIF-8@CuWO_4 composite [Figure 5D] shows a peak at 530.2 eV, which is assigned to lattice oxygen, as well as a peak at 531.42 eV, corresponding to adsorbed (or chemisorbed) oxygen^[64]. Additionally, Cu 2p spectra [Supplementary Figure 4A] reveal satellite features that are indicative of Cu^{2+} in the CuWO_4 lattice^[65]. In the ZIF-8@CuWO_4 composite, the binding energies of Cu 2p [Supplementary Figure 4B] and W 4f (Figure 4B, bottom) shift to lower values compared to pure CuWO_4 , suggesting an increased surface electron density^[66]. This shift aligns with observations by Liao *et al.*, who reported similar binding energy reductions for Cu 2p in nickel oxide-modified CuWO_4 , indicating enhanced electron density and effective carrier transfer between NiO and CuWO_4 ^[66]. Comparable trends were observed by Vasilopoulou for WO_3 films synthesised under a hydrogen atmosphere, where reduced carrier recombination was noted relative to air-synthesised WO_3 ^[67]. Previous studies have also shown that $\text{WO}_3 \cdot \text{H}_2\text{O}$ incorporation with ZIF-8 reduces charge carrier

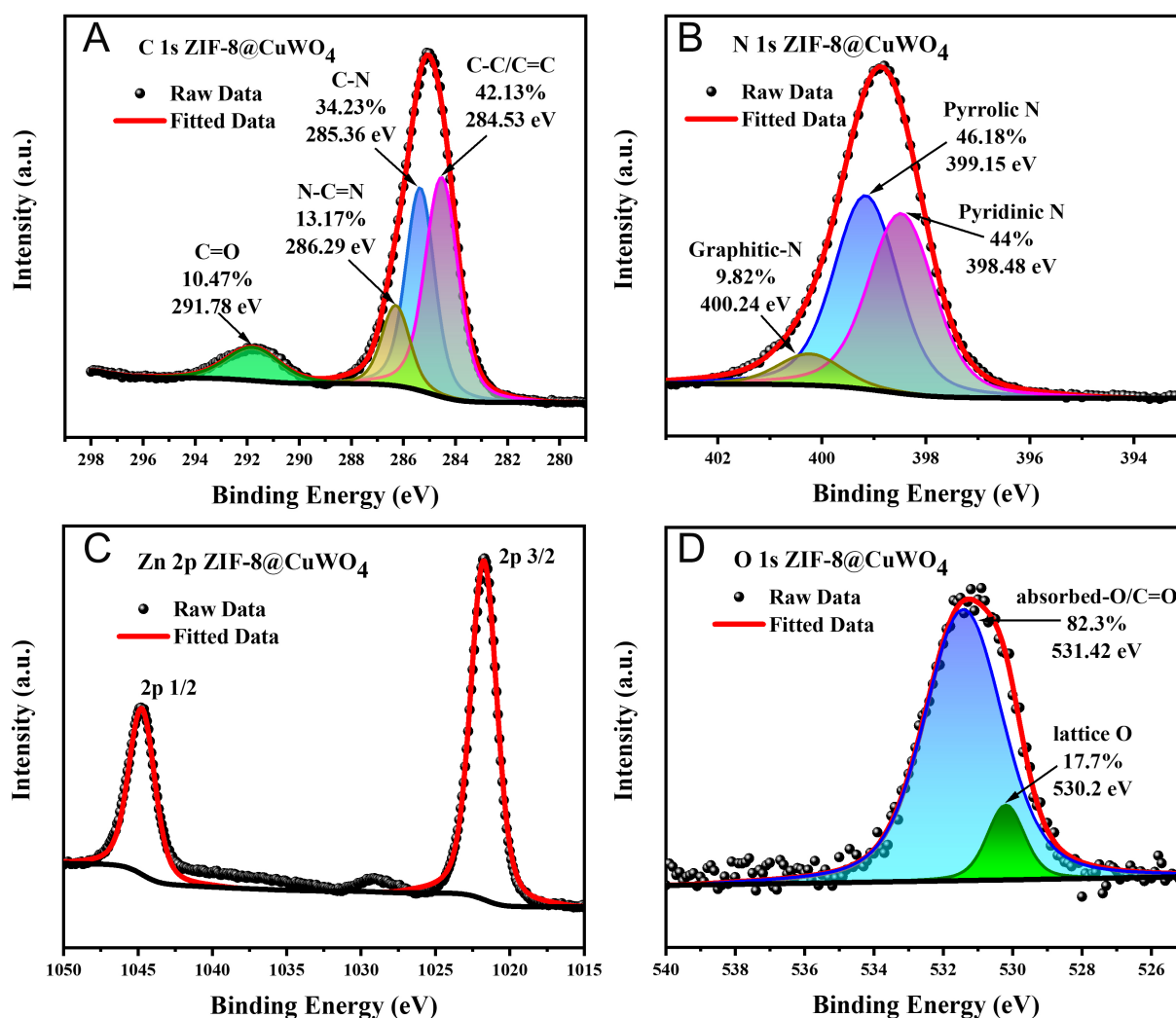


Figure 5. XPS spectra of (A) C 1s, (B) N 1s, (C) Zn 2p, and (D) O 1s of the ZIF-8@CuWO₄ composite.

recombination and promotes photocatalytic activity^[68]. More importantly, referring to a similar reported ZIF-8@Cu-W₁₈O₄₉ system, where ZIF-8 was grown in the presence of Cu doped W₁₈O₄₉ nanowires, a similar negative shift in binding energy for W 4f XPS spectra indicated the robust electronic interaction between the heterointerface of ZIF-8 and Cu-W₁₈O₄₉^[69]. The observed binding energy shifts in ZIF-8@CuWO₄ imply the presence of facilitated electron transport pathways, suggesting the formation of a heterojunction within the composite.

The textural properties of the synthesised ZIF-8, CuWO₄, and ZIF-8@CuWO₄ composite were examined using the BET isotherms and BJH pore size distribution, which are shown in [Supplementary Figures 5 and 6](#), respectively. The specific surface area and porous structure influence the kinetics of reactions by controlling the accessible surface-active sites, reactant adsorption, and mass transport in photocatalysis^[70,71]. As shown in [Table 1](#), the compact structure of pure CuWO₄ with limited porosity was indicated by its low specific surface area of 3.55 m² g⁻¹. Compared with CuWO₄, ZIF-8 displayed a remarkably high BET surface area of 1,150.20 m² g⁻¹ due to its highly porous MOF^[72]. In ZIF-8@CuWO₄, the obtained surface area was 858.86 m² g⁻¹ after integrating CuWO₄ with ZIF-8, which is lower than that of ZIF-8 due to the partial occupancy or blocking of a fraction of micropores by CuWO₄ nanoparticles. However, this surface area remains considerably higher than that of CuWO₄. These results demonstrate that the ZIF-8 framework in

Table 1. BET surface area and pore volume of CuWO₄, ZIF-8, and ZIF-8@CuWO₄ composites

	BET surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)
CuWO ₄	3.55	0.026
ZIF-8	1150.20	0.238
ZIF-8@CuWO ₄	858.86	0.645

ZIF-8@CuWO₄ is largely preserved while maintaining a high density of accessible active sites.

The BJH pore size distribution for ZIF-8@CuWO₄ is shown and compared with that of pristine CuWO₄ and ZIF-8 in [Supplementary Figure 6](#). An almost featureless pore-size distribution was obtained for CuWO₄ with a weak pore volume centred around 180 nm, suggesting the presence of a limited number of interparticle voids. However, ZIF-8 showed a pore size distribution in the 1–4 nm pore size range along with a strong pore volume near 180 nm relative to CuWO₄, supporting its porous network and higher number of interparticle voids^[73]. In ZIF-8@CuWO₄, the pore size distribution from 1–4 nm with a much more pronounced peak around 180 nm was observed, which suggests the retention of intrinsic porosity of ZIF-8 and formation of additional voids and more accessible diffusion pathways in the heterostructure of ZIF-8@CuWO₄.

In line with these observations, the total pore volume for CuWO₄ and ZIF-8 increased from 0.026 and 0.238 cm³ g⁻¹ to 0.645 cm³ g⁻¹ for ZIF-8@CuWO₄, respectively. This increased pore volume can be attributed to the retained porosity and the formation of interparticle voids due to the incorporation of ZIF-8 with CuWO₄. The high surface area with this hierarchical porosity is expected to enhance reactant adsorption, mass transport, and the accessible active sites, thereby contributing to the enhanced photocatalytic hydrogen evolution of the ZIF-8@CuWO₄ heterostructure^[74]. In addition to these textural advantages, the improved photocatalytic activity is also a result of interfacial charge separation and electronic interactions, as analysed by the PL/TRPL, XPS, and Mott-Schottky measurements.

The UV-vis diffuse reflectance spectra (DRS) of pure ZIF-8, CuWO₄, and the ZIF-8@CuWO₄ composite were recorded and transformed using the Kubelka-Munk function to approximate the absorbance behaviour of these materials and are shown in [Figure 6A](#). Pure CuWO₄ exhibited a broad absorbance band in both the UV and visible regions, with an absorption edge at 400–500 nm. In contrast, ZIF-8 displayed a sharp absorbance band peak at 220 nm, indicative of a wide band gap corresponding to the π - π^* transitions in imidazole rings of the ZIF-8^[75]. For the ZIF-8@CuWO₄ composite, the absorption edge exhibited a redshift towards longer wavelengths, suggesting modified electronic interactions between the two components. Band gap energies were then estimated from Tauc plots assuming indirect allowed electronic transitions ($n = 2$), as commonly reported for CuWO₄-based systems [[Figure 6B](#)], yielding values of 2.22 eV for pure CuWO₄ (2.1–2.5 eV)^[76,77], and 5.13 eV for ZIF-8 (4.8–5.2 eV)^[77,78], consistent with previously reported data. The ZIF-8@CuWO₄ composite exhibited two apparent optical transitions at 2.13 and 4.99 eV, which are slightly shifted compared with individual components. Similar optical transitions have been observed by Anu *et al.* in CuO@ZnO nanocomposites with enhanced carrier density^[79]. Furthermore, Makula *et al.*^[80] demonstrated that a multiphase composite may possess multiple optical transitions, with each component contributing to the overall optical absorption while largely preserving its intrinsic electronic structure. Consequently, these transitions were associated with CuWO₄ (2.13 eV) and ZIF-8 (4.99 eV), whereas their slight shifts are attributed to interfacial electronic interactions within ZIF-8@CuWO₄ heterostructure, which was further supported by shifts in the PL quenching [[Figure 6C](#)], Mott-Schottky analysis [[Figure 7A–C](#)], estimated band positions [[Figure 7D](#)] and XPS valence band maxima [[Figure 7E](#)], potentially improving interfacial charge transfer and photocatalytic performance.

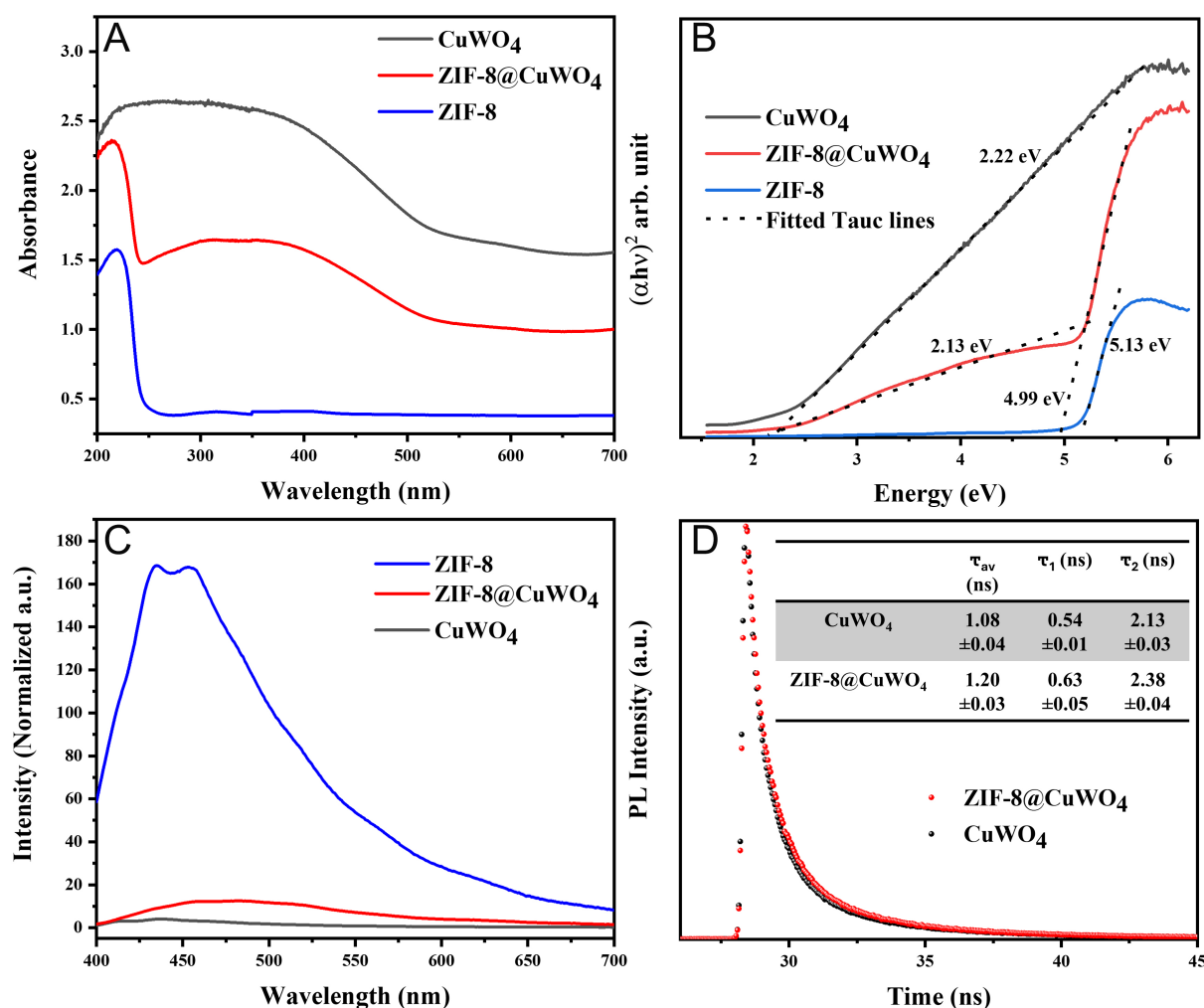


Figure 6. (A) UV-Vis DRS spectra; (B) Tauc plot; (C) Steady-state emission spectra; and (D) Life-time decay for ZIF-8, CuWO₄, and ZIF-8@CuWO₄ composite (excited and detected at 360 and 440 nm, respectively).

The recombination behaviour of photogenerated charge carriers in the synthesised photocatalysts was evaluated using photoluminescence (PL) spectroscopy, whereby changes in the PL intensity provide qualitative insight into electron-hole recombination^[81]. The steady-state PL emission spectra (400–700 nm) of pure ZIF-8, pure CuWO₄, and the ZIF-8@CuWO₄ composite, excited at 364 nm, are presented in Figure 6C. A pronounced PL quenching effect was observed in CuWO₄ and the ZIF-8@CuWO₄, in unambiguous contrast to the intense emission peaks of pure ZIF-8 at 435 and 454 nm. Among these, CuWO₄ exhibited the lowest PL intensity, establishing the relative recombination trend as ZIF-8 >> ZIF-8@CuWO₄ > CuWO₄. The suppressed PL intensity in the ZIF-8@CuWO₄ composite compared to pristine ZIF-8 signifies a substantial reduction in the electron-hole recombination process, which is attributed to enhanced charge transfer at the heterojunction interface. This is consistent with prior studies on hybrid WO₃/ZIF-8 composites^[82]. Despite lower radiative recombination of CuWO₄, the ZIF-8@CuWO₄ composite displays the highest photocatalytic hydrogen evolution (discussed in the latter section), suggesting that PL intensity is not an exclusive determining factor of photocatalytic performance. The activity of the ZIF-8@CuWO₄ composite is attributed to the enhanced interfacial charge transfer and favourable band alignment (discussed in Mott-Schottky analysis and Valence band XPS results), resulting from heterojunction formation.

Further investigation of charge-carrier dynamics was conducted by performing time-resolved luminescence (lifetime) measurements on pure CuWO₄ nanoparticles and the ZIF-8@CuWO₄ composite. The samples

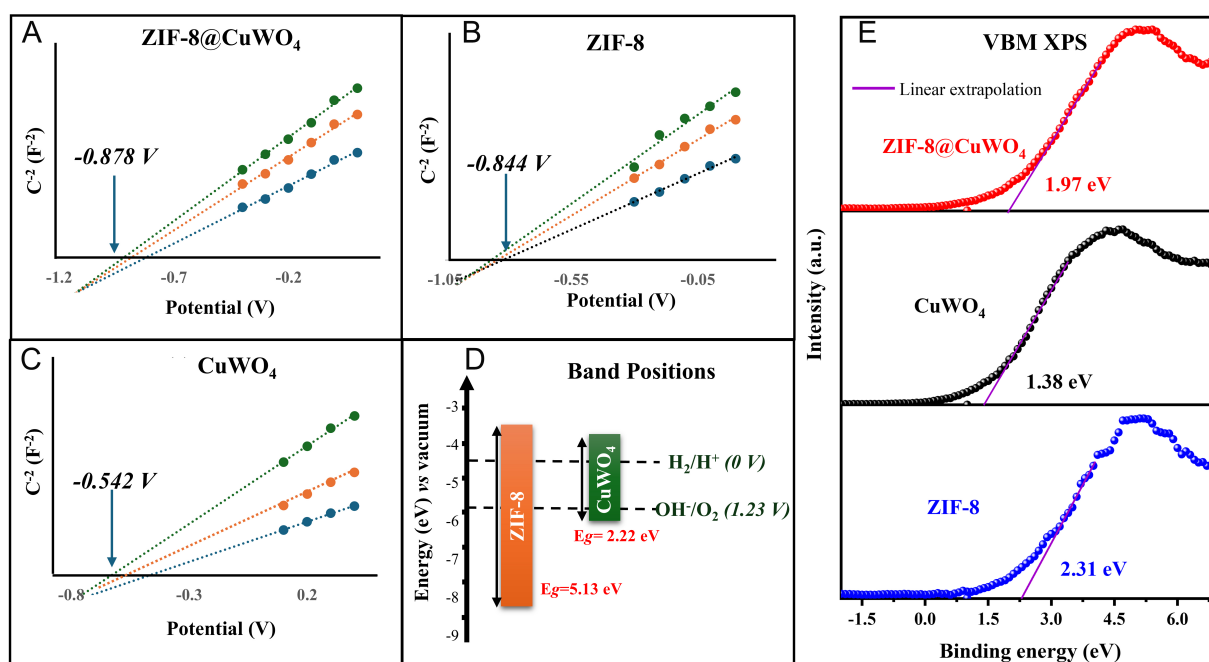


Figure 7. Mott Schottky characteristics at 1,000 Hz (blue fitted lines & dots), 1,500 Hz (orange fitted lines & dots), and 2,000 Hz (green fitted lines & dots), for ZIF-8@CuWO₄ (A), ZIF-8 (B), and CuWO₄ (C), plotted in Na₂SO₃ along with respective estimated band positions (D). The valence-band XPS spectra for ZIF-8@CuWO₄, compared with the pristine CuWO₄, and ZIF-8 (E).

were excited at 360 nm, and emission was detected at 440 nm [Figure 6D]. The decay profiles were fitted using two exponential functions, which indicates the presence of distinct migration pathways and enables the determination of the average carrier lifetime (τ_{avg}). The extracted lifetimes for CuWO₄ and the ZIF-8@CuWO₄ were approximately 1.1 and 1.2 ns, respectively. These values are consistent with the previously reported lifetimes (0.4–2.5 ns) for the CuWO₄-based system^[83,84]. Although this difference is small (0.1 ns), it may indicate a slight improvement in the charge-carrier dynamics, on one hand, improved charge-carrier separation, and on the other hand, enhanced electron-hole transport, resulting in a migration of photogenerated charge carriers to the surface. These findings emphasise the importance of interfacial interactions within the composite and demonstrate the presence of a greater number of photogenerated carriers, further optimising the photocatalytic efficiency of CuWO₄ through ZIF-8 encapsulation^[85].

Mott-Schottky measurements were performed on ZIF-8, CuWO₄, and ZIF-8@CuWO₄ to confirm their redox potential by determining their conduction and valence band positions. This confirmed the characteristics of electron/hole transfer in the ZIF-8@CuWO₄ heterojunction. The flat-band potential of a semiconductor can be obtained through Mott-Schottky analysis. The positive slopes for ZIF-8 [Figure 7B] and CuWO₄ [Figure 7C] at three different frequencies indicated that both are n-type semiconductors, and their flat-band potentials are estimated to be in proximity to their conduction bands, respectively^[86,87].

The flat-band potentials vs. RHE, for ZIF-8 and CuWO₄, were -0.844 and -0.542 V, respectively. In the previous report on CuWO₄/Cu_{1-x}Zn_xWO₄/ZnWO₄ hybrid sandwiched heterojunction, Mott-Schottky analysis was consistent with their n-type behaviour, having flat-band potentials (varied from -0.2 to -0.3 V) for various Zn-doped CuWO₄^[88]. Similarly, Huang *et al.* obtained consistent n-type Mott-Schottky curves with a flat-band potential of -0.862 V for ZIF-8 in ZIF-8@ZIF-67 core-shell structures^[89]. Using the flat band potential data and the band gap estimated through the Tauc plot (see [Supplementary Material Equations 1–3](#), where flat band potential values are converted to Energy vs. vacuum and approximated as conduction band

Table 2. Estimated band positions of ZIF-8 and CuWO₄ using Mott Schottky analysis and UV-visible spectroscopy

	Flat band (V vs. RHE)	CB (V vs. RHE)	VB (V vs. RHE)	Band gap (eV)	CB (eV vs. vac.)	VB (eV vs. vac.)
ZIF-8	-0.844	-0.844	4.286	5.13	-3.656	-8.786
CuWO ₄	-0.542	-0.542	1.678	2.22	-3.958	-6.178

CB: Conduction band, VB: valence band, Vac.: vacuum, RHE: reversible hydrogen electrode, where CB and VB were calculated using a vacuum reference level of 4.50 eV (0 V vs. RHE = -4.50 eV).

potential), the conduction (CB) and valence bands (VB) positions for ZIF-8 and CuWO₄ were also calculated, and the results are shown in Table 2.

A comparison of both ZIF-8 and CuWO₄ revealed that ZIF-8 had a more negative reduction potential for H⁺/H₂. Contrarily, CuWO₄ requires less energy to excite the electrons for the photocatalytic reaction. In the ZIF-8@CuWO₄ heterostructure, a slight negative shift in the flat band potential to -0.878 V was observed [Figure 7A], which indicates the interfacial electronic interaction and equilibration of the Fermi level between ZIF-8 and CuWO₄^[90]. Together, the ZIF-8@CuWO₄ heterojunction offers better redox ability and can result in higher photocatalytic hydrogen production as compared with the pristine materials.

The interfacial interaction between CuWO₄ and ZIF-8 in the ZIF-8@CuWO₄ composite was further investigated and supported by analysing their valence band XPS spectra. Figure 7E represents the comparison of valence band XPS spectra, where the valence band maximum (VBM) was estimated by linear extrapolation of the leading edge of the valence band spectrum to the background level. The intercept was assigned as the VBM binding energy relative to the Fermi level ($E_f = 0$ eV). As shown in Figure 7E, the estimated VBM values for ZIF-8 and CuWO₄ were 2.31 and 1.38 eV, respectively. However, the VBM value for ZIF-8@CuWO₄ was 1.97 eV, which lies between those of pristine materials. Compared with pure ZIF-8, the VBM of the composite was shifted ~0.34 eV closer to the Fermi level, which suggests the redistribution of electrons within the ZIF-8@CuWO₄ heterojunction and the equilibration of the Fermi level between the contacting components^[91]. This change provides direct evidence of interfacial electronic coupling within ZIF-8@CuWO₄, which is favourable for the separation and migration of charge carriers. These VBM results are consistent with the Mott-Schottky measurements, where a similar shift for ZIF-8@CuWO₄ in flat band potential (-0.844 to -0.878 V) was observed after heterojunction formation, confirming that the interaction between ZIF-8 and CuWO₄ in the composite modified the electronic structure and promoted the interfacial charge transfer.

The photocatalytic performance of the synthesised materials was evaluated through HER under UV and visible light irradiation, using aqueous Na₂S and Na₂SO₃ as sacrificial agents [Supplementary Figure 7A]. Figure 8 shows the photoinduced real-time hydrogen evolution for pure ZIF-8, CuWO₄, and the ZIF-8@CuWO₄ composite monitored continuously by an online mass spectrometer under sequential radiation (visible and UV radiation, respectively). In the control experiment, negligible H₂ or O₂ production was detected in the absence of light irradiation or a photocatalyst. Under irradiation, both ZIF-8 and CuWO₄ exhibited measurable H₂ evolution, with respective rates of 1.5 and 2.9 μmol·g⁻¹·h⁻¹ for ZIF-8 and 2.5 and 26 μmol·g⁻¹·h⁻¹ for CuWO₄ under visible [Figure 8A] and UV light [Figure 8B], respectively. In the case of decorating CuWO₄ with ZIF-8 (ZIF-8@CuWO₄), the H₂ evolution rates of 44 and 1,112 μmol·g⁻¹·h⁻¹ were observed under visible and UV excitation, respectively, using 0.1 M Na₂S and 0.25 M Na₂SO₃ as sacrificial agents. This marked improvement in the photocatalytic activity for ZIF-8@CuWO₄ relative to individual components suggests enhanced interfacial charge transfer and suppressed electron-hole recombination within the heterojunction^[91]. Under visible light irradiation, the ZIF-8@CuWO₄ heterostructure achieved a

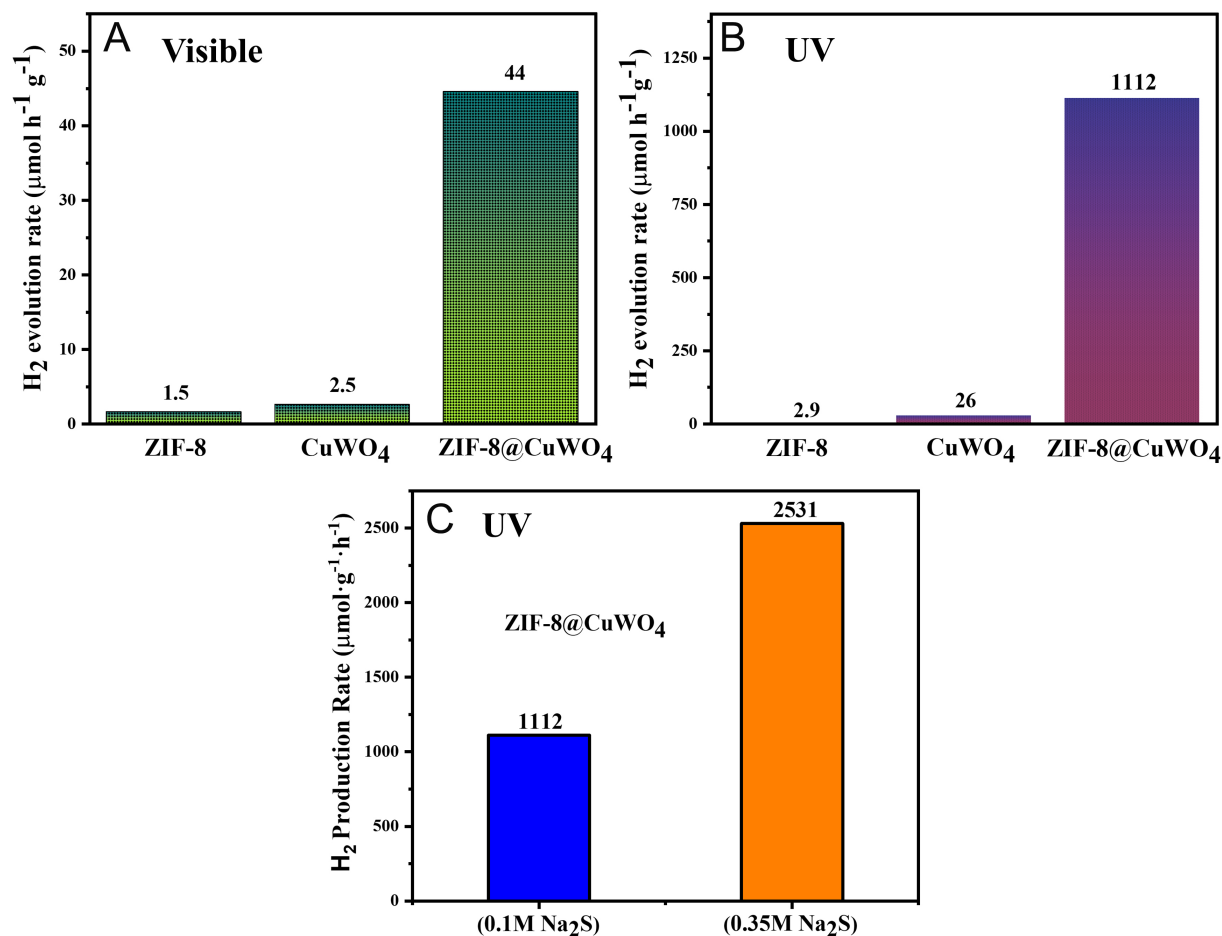


Figure 8. Photocatalytic H₂ evolution for ZIF-8, CuWO₄, and ZIF-8@CuWO₄ composite with maximum H₂ evolution rates using 0.1 M Na₂S and 0.25 M Na₂SO₃ as sacrificial agents under (A) visible and (B) UV irradiations, respectively; (C) Impact of molarity of Na₂S (0.1–0.35 M) along with constant Na₂SO₃ (0.25 M) as sacrificial agents over the photocatalytic H₂ evolution rates for ZIF-8@CuWO₄ composite under UV irradiation.

slightly enhanced photocatalytic hydrogen evolution rate compared with CuWO₄, which is still very low in comparison with the hydrogen produced under UV-light irradiation by the composite. This limited performance can be attributed to the limited utilisation of the visible region by the composite and the low efficiency of photogenerated electron/hole pairs. However, the heterostructure formation promotes the interfacial charge separation within the ZIF-8@CuWO₄ composite, while cocatalyst loading could be used to further improve its visible-light photocatalytic activity.

The H₂ evolution of ZIF-8@CuWO₄ is lower than that of some of the state-of-the-art photocatalysts summarised in Table 3, yet remains within the performance range reported for several previously studied heterostructure photocatalyst systems. For instance, the heterostructure of TiO₂ with NH₂-MIL-125 MOF (TiO₂/NH₂-MIL-125) exhibited a comparable H₂ evolution rate of 44 μmol·g⁻¹·h⁻¹ under visible irradiation^[92]. Additionally, the evolution rates of H₂ obtained by noble-metal Pt islands in CuBi₂O₄^[93], CDs@BiVO₄ quantum dots^[94], and ZnO@rGO derived from ZIF-8@rGO over carbon sponge^[95] fall within a similar or lower activity range under similar experimental conditions. These comparisons indicate that the ZIF-8@CuWO₄ heterojunction demonstrates competitive photocatalytic performance among composite photocatalysts.

Table 3. H₂ evolution performance of ZIF-8@CuWO₄ composite compared with other reported photocatalysts

Sample	H ₂ evolution rate (UV) ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	H ₂ evolution rate (visible) ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Sacrificial agent	Ref.
TiO ₂ @NH ₂ -MIL-125	-	44	Triethanolamine	[92]
Pt/CuBi ₂ O ₄	-	8.1	KOH	[93]
5% CDs/BiVO ₄ QDs	-	11.5	-	[94]
ZnO _{ZIF-8} /RGO/C	-	14.6	Methanol	[95]
WS ₂ /CdS	-	19,200	Lactic acid	[96]
3%Pt/ α -Fe ₂ O ₃ /g-C ₃ N ₄	-	31,400	Triethanolamine	[97]
Hollow Zn _{0.6} Cd _{0.4} S cages	-	56,800	0.75/1.05 M Na ₂ S/Na ₂ SO ₃	[98]
Bulk, exfoliated g-C ₃ N ₄	58.5, 343.8	18.2, 35.9	Triethanolamine	[99]
TiO ₂ , MoS ₂ @TiO ₂ /TiN	30.8, 128.8	-	0.5/0.67 M Na ₂ S/Na ₂ SO ₃	[100]
TiO ₂ @MoS ₂	171.2	-	Methanol	[101]
5 wt% WB _{5-x} -WB ₂ /TiO ₂	-	81	Ethanol	[102]
P25	68	-	Methanol (50 vol.%)	[103]
P25	500	-	Methanol (20 vol.%)	[104]
ZIF-8@CuWO ₄	1,112	44	0.1/0.25 M Na ₂ S/Na ₂ SO ₃	This Work
ZIF-8@CuWO ₄	2,531	79	0.35/0.25 M Na ₂ S/Na ₂ SO ₃	This Work

This enhancement in the photocatalytic activity of ZIF-8@CuWO₄ heterostructure, compared with pristine ZIF-8 and CuWO₄, is attributed to the increased porosity, more accessible active sites, and optimised optical and interfacial electronic properties as suggested by BET/BJH textural results, PL/TRPL studies, Mott-Schottky analysis, and valence band XPS estimations. Notably, the interaction between the pyrrolic and pyridinic nitrogen functional groups in ZIF-8 and the CuWO₄ phase enhances charge separation and electron-hole transfer rates^[78]. The high surface area and porosity of ZIF-8 provide a greater number of accessible catalytically active sites compared to pristine CuWO₄^[105]. In pure ZIF-8, the presence of Zn²⁺ ions and the 2-methylimidazole ligands in the framework results in intense PL emissions [Figure 6C] due to π - π^* transitions^[106]. However, within the ZIF-8@CuWO₄ composite, the reduced band gap favours n- π^* transitions, thereby promoting charge transfer^[106,107]. This synergistic effect, coupled with the electronic interactions at the interface, results in an efficient photocatalytic system as compared with as-synthesised pristine materials, where CuWO₄ enhances electron density while ZIF-8 provides extensive active surface sites^[42,82,85].

The impact of the sacrificial agent concentration on the photocatalytic reaction was also examined [Supplementary Figure 7B and Figure 8C]. During this reaction, the molarity of Na₂S increased from 0.1 to 0.35 M while the molarity of Na₂SO₃ remained constant at 0.25 M. This resulted in a significant improvement in the hydrogen evolution rate under UV irradiation, increasing from 1,112 to 2,531 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. However, under visible light, the efficiency was negligible (44 to 79 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) due to limited electron/hole pair production, which becomes the limiting factor as the concentration of Na₂S increases. Conversely, UV irradiation increases electron/hole pair generation, enabling Na₂S to effectively scavenge holes, and accelerates the hydrogen evolution performance^[108].

The proposed electron-hole transfer mechanism is illustrated in [Scheme 2](#). Upon irradiation of light on ZIF-8@CuWO₄, both ZIF-8 and CuWO₄ generated electrons and holes in their CB and VB, respectively. Subsequently, the photogenerated electrons migrate from the CB of ZIF-8 to the CB of CuWO₄, facilitating the reduction of protons to generate H₂ at the CB of CuWO₄. Simultaneously, the photoinduced holes transfer from the VB of CuWO₄ to the VB of ZIF-8, thereby facilitating charge separation. The presence of Na₂S/Na₂SO₃ as sacrificial agents further enhances photocatalytic activity by scavenging the holes on the ZIF-8 surface and generating HS[−] and S₂O₃^{2−} species. These species suppress charge carrier recombination and improve efficiency^[109]. This effective electron/hole transfer resulted in the formation of a Type-II heterojunction between ZIF-8 and CuWO₄ in the ZIF-8@CuWO₄ composite, as suggested by Mott-Schottky, Valence band XPS, and PL/TRPL results.

An important feature of the photocatalyst and its performance is the recyclability and reusability. Recyclability of ZIF-8@CuWO₄ composite as a photocatalyst is shown in [Supplementary Figure 8](#). The photocatalytic H₂ evolution rate decreases from 2,531 to 1,336 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ after reusing the photocatalyst for a second time in the third cycle [[Figure 9](#)], during which the photocatalyst water-splitting experiment was run over ~15 h in the presence of Vis and UV light. The decrease in photocatalytic activities in each cycle may be due to the intrinsic instability of ZIF-8, which undergoes gradual hydrolysis under water and UV irradiation, due to intensified ligand optical absorption and defect formation^[110,111]. The morphological changes of the as-synthesised ZIF-8@CuWO₄ and recycled ZIF-8@CuWO₄ (after 3rd cycle) were compared in the respective SEM images (acquired at the same magnification) and are shown in [Supplementary Figure 9A](#) and [B](#). The recycled composite displayed a transformation from dispersed nanoparticles to hollow microspherical aggregates, which further suggested the structural evolution of the ZIF-8@CuWO₄ heterostructure. These morphological changes could be associated with the accumulation of organic residue originating from the partial degradation of the ZIF-8 or oxidation products of the sacrificial agent on the catalyst surface. For further understanding, the XRD analysis of recycled ZIF-8@CuWO₄ composite was compared with the XRD patterns of standard reference and as-synthesised samples, as shown in [Supplementary Figure 9C](#). The characteristic diffraction maxima for ZIF-8 at $2\theta \approx 7.5^\circ$ and 12.8° became very weak, further suggesting the partial degradation of the ZIF-8 phase in ZIF-8@CuWO₄ during photocatalytic reaction. While the CuWO₄ phase was still dominantly observed, with several diffraction peaks shifted to higher 2θ values, suggesting structural modification of recycled ZIF-8@CuWO₄. Based on the proposed type-II heterojunction charge transfer mechanism, the partial degradation of ZIF-8 may be correlated with the hole-induced oxidation of the MOF framework during prolonged photoreaction. Although most holes are scavenged by the Na₂S/Na₂SO₃ sacrificial agents, a small fraction of holes may oxidise the ZIF-8 framework under prolonged irradiation, consistent with the observed structural changes. These findings demonstrate the necessity of carefully designing the MOF-based photocatalysts for practical use under visible irradiation. The ZIF-8@CuWO₄ composite remains stable under visible light and still achieves H₂ evolution rates of 44/79 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (visible) and 1,112/2,531 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ (UV) from water without the need for a noble-metal co-catalyst.

CONCLUSION

A novel ZIF-8@CuWO₄ heterojunction composite was successfully synthesised by growing ZIF-8 around spherical CuWO₄ nanoparticles using an easy *in situ* sonication-assisted approach. This hybrid photocatalyst exhibits significantly improved charge separation and efficient interfacial charge transfer between its constituent phases, directly evidenced by the shifts observed in the Mott-Schottky and valence band XPS analysis. While retaining a high degree of light absorption from CuWO₄, the composite also benefits from increased structural porosity and density of surface-active sites primarily contributed by ZIF-8. Consequently, the ZIF-8@CuWO₄ composite achieved hydrogen production rates of 44 and 1,112 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$

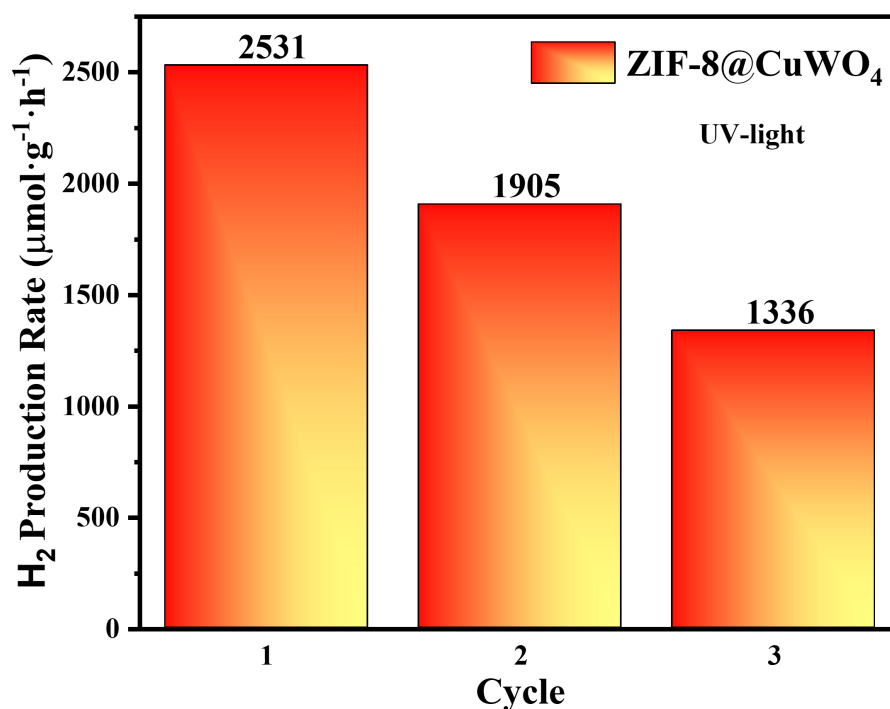


Figure 9. Photocatalytic H₂ evolution rates for recycled ZIF-8@CuWO₄ in comparison with fresh ZIF-8@CuWO₄ under UV-light irradiations.

under visible and UV irradiation, respectively, exceeding the performance of the pristine ZIF-8 and CuWO₄. Reducing the overall electron/hole recombination through increasing the molarity of the sacrificial agent further improved this photocatalytic activity to 79 and 2,531 μmol·g⁻¹·h⁻¹ under visible and UV light, respectively. Despite ZIF-8@CuWO₄ photocatalytic activity decreasing over time under UV irradiation due to photo-accelerated hydrolysis, the composite remains stable under visible light. It achieves this comparable photocatalytic activity without the need for toxic or expensive noble-metal co-catalysts, highlighting its potential as a cost-effective, scalable platform for sustainable green hydrogen production.

DECLARATIONS

Authors' contributions

Writing - original draft, writing - review & editing, methodology, formal analysis, data curation, software, conceptualisation: Iqbal, M. U.

Writing - review & editing, writing - original draft, validation, methodology, formal analysis: Rana, S.

Methodology, data curation, software, conceptualisation: Zitnan, M.

Writing - review & editing, methodology, investigation, formal analysis: Ashling, C. W.

Methodology, data curation, formal analysis: Pérez-Ramos, M.; Nadeem, I.

Methodology, investigation, formal analysis: González-Rodríguez, M.

Validation, funding acquisition, resources, project administration: Galusek, D.

Writing - review & editing, validation, investigation, conceptualisation: Núñez, P.

Writing - review & editing, validation, investigation, supervision, conceptualisation: Wondraczek, L.

Writing - review & editing, funding acquisition, validation, investigation, supervision, project administration, methodology, conceptualisation: Velázquez, J. J.

Availability of data and materials

The data supporting the findings of this study are available within this Article and its [Supplementary Materials](#). Further data are available from the corresponding authors upon request.

AI and AI-assisted tools statement

During the preparation of this manuscript, the AI tool DeepAI was used solely for the graphical abstract background. The tool did not influence the study design, data collection, analysis, interpretation, or the scientific content of the work. All authors take full responsibility for the accuracy, integrity, and final content of the manuscript.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

REFERENCES

1. Cho, H. H.; Strezov, V.; Evans, T. J. Environmental impact assessment of hydrogen production via steam methane reforming based on emissions data. *Energy Rep.* **2022**, *8*, 13585-95. [DOI](#)
2. Kadam, R. S.; Sutar, P. R.; Yadav, G. D. Energy and environmental assessment of industrial-scale hydrogen production: comparison of steam methane reforming, electrolysis, and Cu-Cl cycles. *Int. J. Hydrogen. Energy.* **2025**, *106*, 994-1005. [DOI](#)
3. Lagioia, G.; Spinelli, M. P.; Amicarelli, V. Blue and green hydrogen energy to meet European Union decarbonisation objectives. an overview of perspectives and the current state of affairs. *Int. J. Hydrogen. Energy.* **2023**, *48*, 1304-22. [DOI](#)
4. Ding, Y.; Wang, C.; Zhao, H. Large-scale, long-term hydrogen generation at a liter level via plastic photoreforming. *Matter* **2025**, *8*, 102408. [DOI](#)
5. Nishioka, S.; Osterloh, F. E.; Wang, X.; Mallouk, T. E.; Maeda, K. Photocatalytic water splitting. *Nat. Rev. Methods. Primers.* **2023**, *3*, 42. [DOI](#)
6. Khan, M. A.; Mutahir, S.; Shaheen, I.; Qunhui, Y.; Bououdina, M.; Humayun, M. Recent advances over the doped g-C₃N₄ in photocatalysis: a review. *Coord. Chem. Rev.* **2025**, *522*, 216227. [DOI](#)
7. Liu, J.; Gong, Z.; Wu, D.; et al. MOFs as platforms for multiscale structural regulation: new frontiers in photocatalyst design. *Microstructures* **2025**, *5*, 2025056. [DOI](#)
8. Gong, L.; Chu, Q.; Liu, X.; Tan, Y. Plasmonic platinum nanoparticles-tungsten oxide nanoarchitectures as visible light photocatalysts for highly efficient overall water splitting. *J. Mater. Chem. A.* **2022**, *10*, 21161-76. [DOI](#)
9. Zhu, B.; Cheng, B.; Fan, J.; Ho, W.; Yu, J. g-C₃N₄-based 2D/2D composite heterojunction photocatalyst. *Small. Struct.* **2021**, *2*, 2100086. [DOI](#)
10. Gao, X.; Zeng, D.; Yang, J.; et al. Ultrathin Ni(OH)₂ nanosheets decorated with Zn_{0.5}Cd_{0.5}S nanoparticles as 2D/0D heterojunctions for highly enhanced visible light-driven photocatalytic hydrogen evolution. *Chin. J. Catal.* **2021**, *42*, 1137-46. [DOI](#)

11. González-Rodríguez, M.; Díaz-Coello, S.; Díaz-González, S.; et al. Highly efficient Zn_xCd_xS catalysts with sphalerite structures synthesized via a novel green method for hydrogen production by water splitting. *RSC. Adv.* **2024**, *14*, 37763-73. DOI PubMed PMC
12. Zhao, C.; Ren, L.; Shi, Y.; Wang, X.; Huang, W.; Xie, H. Advances and recent applications in high-energy {001} facets of anatase TiO₂: a review. *J. Environ. Chem. Eng.* **2025**, *13*, 115764. DOI
13. Yang, N.; He, T.; Chen, X.; et al. TiO₂-based heterojunctions for photocatalytic hydrogen evolution reaction. *Microstructures* **2024**, *4*, 2024042. DOI
14. Manisha; Kumar, V.; Kumar Sharma, D. Fabrication of dimensional hydrophilic TiO₂ nanostructured surfaces by hydrothermal method. *Mater. Today. Proc.* **2021**, *46*, 2171-4. DOI
15. Mo, G.; Jin, Y.; Deng, Y.; et al. Band-gap engineering of isorecticular hydrogen-bonded organic frameworks for boosting photocatalytic hydrogen evolution. *Angew. Chem. Int. Ed.* **2026**, *65*, e25987. DOI
16. Mangiri, R.; Reddy, N. P.; Bae, J. Transition-metal-doped ZnIn₂S₄ photocatalysts for enhanced solar hydrogen production. *ChemCatChem* **2026**, *18*, e01670. DOI
17. Shang, Y.; Wang, C.; Yan, C.; et al. An efficient and multifunctional S-scheme heterojunction photocatalyst constructed by tungsten oxide and graphitic carbon nitride: design and mechanism study. *J. Colloid. Interface. Sci.* **2023**, *634*, 195-208. DOI
18. Wondraczek, L.; Tyystjärvi, E.; Méndez-Ramos, J.; Müller, F. A.; Zhang, Q. Shifting the sun: solar spectral conversion and extrinsic sensitization in natural and artificial photosynthesis. *Adv. Sci.* **2015**, *2*, 1500218. DOI PubMed PMC
19. Montes-Monroy, J. M.; Manzorro, R.; Valenzuela, L.; Ivanez, J.; Pérez-Omil, J. A.; Keller, N. H₂ production by formic acid decomposition on ceria-modified Ru/TiO₂ catalysts under dual photonic/thermal excitation. *Catal. Today.* **2024**, *441*, 114852. DOI
20. Wan, Y.; Liu, Q.; Xu, Z.; et al. Interface engineering enhanced g-C₃N₄/rGO/Pd composites synergetic localized surface plasmon resonance effect for boosting photocatalytic CO₂ reduction. *Carbon. Lett.* **2024**, *34*, 1143-54. DOI
21. Bahadoran, A.; Liu, Q.; Ramakrishna, S.; Sadeghi, B.; De Castro, M. M.; Cavaliere, P. D. Hydrogen production as a clean energy carrier through heterojunction semiconductors for environmental remediation. *Energies* **2022**, *15*, 3222. DOI
22. Sreenivasulu, M.; Rajanna, M. R.; Katakoti, S. R.; et al. Synergistic CuWO₄/NiS₂ binary nanostructures for efficient photocatalytic hydrogen production. *ACS. Appl. Nano. Mater.* **2026**, *9*, 8009-22. DOI
23. Liu, Q.; Cai, P.; Li, H.; Ji, X.; Zhang, D.; Pu, X. Visible-light-driven hydrogen evolution over CdS/CuWO₄ S-scheme heterojunctions: dual synergistic enhancement via interfacial charge transfer and photothermal activation. *Chin. J. Catal.* **2026**, *81*, 299-309. DOI
24. Goswami, J.; Basyach, P.; Purkayastha, S. K.; Guha, A. K.; Hazarika, P.; Saikia, L. Boosting the photodegradation of rhodamine B with the CuWO₄/g-C₃N₄ heterojunction by introducing biomass derived N-CQDs as an electron mediator: mechanism and DFT calculations. *New. J. Chem.* **2023**, *47*, 22304-19. DOI
25. Fazil, M.; Ahmed, J.; Ahmad, T. Enhanced photo/electrocatalytic efficiency of Zn-decorated TiO₂ nanostructures for sustainable hydrogen evolution. *Catal. Today.* **2025**, *445*, 115103. DOI
26. Zhang, X.; Yang, P. Advances in noble metal-modified g-C₃N₄ heterostructures toward enhanced photocatalytic redox ability. *Int. J. Miner. Metall. Mater.* **2024**, *31*, 2368-89. DOI
27. Zhang, J.; Geng, Y.; Sun, C.; et al. Efficient near-infrared photocatalytic hydrogen production based on WO_{3-x} modified Bi₂S₃ nanoflowers. *Appl. Catal. A. Gen.* **2026**, *724*, 121100. DOI
28. Erdem, N. G.; Caglar, B.; İnan, E.; Tuna, Ö.; Ertis, İF.; Bilgin Simsek, E. Incorporation of CuWO₄ with hollow tubular g-C₃N₄: harnessing the potential in photocatalytic degradation, hydrogen production, and supercapacitor applications. *Renew. Energy.* **2026**, *256*, 124235. DOI
29. Ling, S.; Qu, P.; Jiang, S.; Feng, Z.; Kong, B.; Wang, W. Investigations of defect physics and quenching effect for optimizing n-type carrier concentration in CuWO₄ photocatalyst. *Inorg. Chem.* **2026**, *65*, 4592-607. DOI
30. Dinh, P. H.; Pham, T.; Trung, D. Q.; et al. CuWO₄ decorated by polypyrrole (PPy) protector/sensitizer for novel photocatalytic and stable water splitting for hydrogen generation. *Int. J. Hydrogen. Energy.* **2020**, *45*, 21442-9. DOI
31. Le Minh Tri, N.; Trung, D. Q.; Van Thuan, D.; et al. The advanced photocatalytic performance of V doped CuWO₄ for water splitting to produce hydrogen. *Int. J. Hydrogen. Energy.* **2020**, *45*, 18186-94. DOI
32. Basyach, P.; Deb, J.; Sk, S.; et al. Controlled Ni doping on a g-C₃N₄/CuWO₄ photocatalyst for improved hydrogen evolution. *Phys. Chem. Chem. Phys.* **2023**, *25*, 23033-46. DOI
33. Wu, H.; Ullah, M.; Jiang, L.; et al. Controllable synthesis of porous 3D Pd loaded ZIF-67/g-C₃N₄ hierarchical nanostructure for efficient detection of NO₂ gas at room temperature. *Colloids. Surf. A. Physicochem. Eng. Asp.* **2023**, *666*, 131363. DOI
34. Wang, C.; Hou, S.; Ma, M.; et al. Recent development of MIL-101(Cr) for photocatalysis: a mini review. *J. Water. Process. Eng.* **2024**, *66*, 106040. DOI

35. He, Y.; Lv, T.; Xiao, B.; et al. Research progress of MIL-125 and its modifications in photocatalytic hydrogen evolution. *J. Mater. Chem. C* **2023**, *11*, 6800–18. [DOI](#)
36. Ramollo, K. V.; Ramohlola, K. E.; Maponya, T. C.; Hintsho-Mbita, N. C.; Modibane, K. D. Current developments on MIL-based metal-organic frameworks for photocatalytic hydrogen production. *Int. J. Hydrogen. Energy* **2025**, *180*, 151728. [DOI](#)
37. Zou, X.; Shi, Q.; Cheng, M.; et al. Metal-organic framework-based materials for photocatalytic hydrogen peroxide production: insights into mechanism, modification strategies, and environmental applications. *Adv. Energy. Mater.* **2025**, *15*, 2501424. [DOI](#)
38. Hendrickx, K.; Vanpoucke, D. E. P.; Leus, K.; et al. Understanding intrinsic light absorption properties of UiO-66 frameworks: a combined theoretical and experimental study. *Inorg. Chem.* **2015**, *54*, 10701–10. [DOI](#)
39. Zhang, M. Y.; Li, J. K.; Wang, R.; Zhao, S. N.; Zang, S. Q.; Mak, T. C. W. Construction of core-shell MOF@COF hybrids with controllable morphology adjustment of COF shell as a novel platform for photocatalytic cascade reactions. *Adv. Sci.* **2021**, *8*, 2101884. [DOI](#) [PubMed](#) [PMC](#)
40. Zhang, X.; Zhu, Z.; Rao, R.; et al. Highly efficient visible-light-driven photocatalytic degradation of gaseous toluene by rutile-anatase TiO₂@MIL-101 composite with two heterojunctions. *J. Environ. Sci.* **2023**, *134*, 21–33. [DOI](#)
41. Fawzy, A.; Mahanna, H.; Mossad, M. Effective photocatalytic degradation of amoxicillin using MIL-53(Al)/ZnO composite. *Environ. Sci. Pollut. Res.* **2022**, *29*, 68532–46. [DOI](#) [PubMed](#) [PMC](#)
42. Nazir, M. A.; Najam, T.; Shahzad, K.; et al. Heterointerface engineering of water stable ZIF-8@ZIF-67: adsorption of rhodamine B from water. *Surf. Interfaces.* **2022**, *34*, 102324. [DOI](#)
43. Varangane, S.; Vennapoosa, C. S.; Tiwari, A.; Nataraj, S. K.; Yendrapati, T. P.; Pal, U. *In situ* synthesis of Cu-doped ZIF-8 for efficient photocatalytic water splitting. *Appl. Organomet. Chem.* **2022**, *36*, e6815. [DOI](#)
44. Zheng, H.; Wu, D.; Wang, Y.; et al. One-step synthesis of ZIF-8/ZnO composites based on coordination defect strategy and its derivatives for photocatalysis. *J. Alloys. Compd.* **2020**, *838*, 155219. [DOI](#)
45. Angela, S.; Bervia Lunardi, V.; Kusuma, K.; et al. Facile synthesis of hierarchical porous ZIF-8@TiO₂ for simultaneous adsorption and photocatalytic decomposition of crystal violet. *Environ. Nanotechnol. Monit. Manag.* **2021**, *16*, 100598. [DOI](#)
46. Qureshi, W. A.; Haider, S. N.; Ali, R. N.; et al. Room temperature preparation of novel g-C₃N₄/RuNP/ZIF-8 Z-scheme heterojunction for solar-light driven H₂ generation. *Int. J. Hydrogen. Energy* **2024**, *77*, 808–16. [DOI](#)
47. Kshirsagar, S. D.; Shelake, S. P.; Islam, H.; et al. In situ decoration of Cd_{0.05}Mn_{0.05}Zn_{0.90} (ZIF-8) photocatalyst for solar-driven hydrogen production. *Int. J. Hydrogen. Energy* **2025**, *137*, 1260–8. [DOI](#)
48. Saleh, M. R.; El-Bery, H. M.; Abdelhamid, H. N. Co@ZIF-8/TiO₂ heterojunction for green hydrogen generation. *Appl. Organomet. Chem.* **2022**, *37*, e6995. [DOI](#)
49. Chandrasekaran, K.; Verma, D.; Uyama, H.; Okhawilai, M. Core-shell ZnO@ZIF-8-derived nitrogen-doped carbon nanotubes for the effective removal of methyl orange. *Water. Cycle* **2025**, *6*, 412–27. [DOI](#)
50. Cao, F.; Sun, Y.; Duan, X.; et al. Interfacial engineering of CuWO₄/WO₃ thin films precisely fabricated by ultrasonic spray pyrolysis for improved solar water splitting. *Catal. Sci. Technol.* **2023**, *13*, 4550–7. [DOI](#)
51. Swain, P.; Priyadarshini, P.; Behera, D.; Parida, K. Rational design of zeolitic imidazolate framework-metal oxide hybrids toward green and sustainable photocatalysis. *ACS. Omega* **2026**, *11*, 21457–84. [DOI](#) [PubMed](#) [PMC](#)
52. Almaghami, H.; Al-Ghamdi, W.; Basfer, N.; Bayahia, D. S. Effect of copper tungstate nanoparticles on the structural, optical, and dielectric properties of carboxymethyl cellulose/polyvinyl alcohol nanocomposite films. *Phys. B.* **2025**, *701*, 416969. [DOI](#)
53. Velázquez, J.; Fernández-González, R.; Díaz, L.; Pulido, Melián, E.; Rodríguez, V.; Núñez, P. Effect of reaction temperature and sacrificial agent on the photocatalytic H₂-production of Pt-TiO₂. *J. Alloys. Compd.* **2017**, *721*, 405–10. [DOI](#)
54. Díaz, L.; Rodríguez, V. D.; González-Rodríguez, M.; et al. M/TiO₂ (M = Fe, Co, Ni, Cu, Zn) catalysts for photocatalytic hydrogen production under UV and visible light irradiation. *Inorg. Chem. Front.* **2021**, *8*, 3491–500. [DOI](#)
55. Liu, S.; Shi, G.; Cui, N.; Zi, B.; Qi, K. ZnWO₄/CuWO₄ photocatalysts for the degradation of tetracycline hydrochloride and antibacterial application. *J. Water. Process. Eng.* **2026**, *86*, 109812. [DOI](#)
56. Wu, L.; Tai, Z.; Wang, Z.; et al. In-situ Cu-doped ZIF-8 for enhanced photocatalytic H₂ evolution by regulating hydrogen adsorption. *J. Environ. Chem. Eng.* **2025**, *13*, 116526. [DOI](#)
57. García-Palacín, M.; Martínez, J. I.; Pasetta, L.; et al. Sized-controlled ZIF-8 nanoparticle synthesis from recycled mother liquors: environmental impact assessment. *ACS. Sustain. Chem. Eng.* **2020**, *8*, 2973–80. [DOI](#) [PubMed](#) [PMC](#)
58. Gu, J.; Huang, J.; Jin, Z.; Wei, T. Multidimensional engineering of ZIF-8-based electrocatalysts for carbon dioxide reduction: a mini review. *Chem. Commun.* **2025**, *61*, 13015–34. [DOI](#)
59. Abd El Khalk, A. A.; Betiha, M. A.; Mansour, A. S.; Abd El Wahed, M. G.; Al-Sabagh, A. M. High degradation of methylene blue using a new nanocomposite based on zeolitic imidazolate framework-8. *ACS. Omega* **2021**, *6*, 26210–20. [DOI](#) [PubMed](#) [PMC](#)

-
60. Men, J.; Luo, C.; Li, L.; et al. Construction of Cu-doped multilayer ZIF-8 for efficient photocatalytic hydrogen production from water splitting. *Int. J. Hydrogen. Energy*. **2026**, *248*, 155797. DOI
61. Sun, S.; Yang, Z.; Cao, J.; Wang, Y.; Xiong, W. Copper-doped ZIF-8 with high adsorption performance for removal of tetracycline from aqueous solution. *J. Solid. State. Chem.* **2020**, *285*, 121219. DOI
62. Azuara-Tuexi, G.; Muñoz-Sandoval, E.; Guirado-López, R. A. N 1s core-level binding energies in nitrogen-doped carbon nanotubes: a combined experimental and theoretical study. *Phys. Chem. Chem. Phys.* **2023**, *25*, 3718-36. DOI PubMed
63. Soliman, A. I. A.; Abdel-Wahab, A. A.; Abdelhamid, H. N. Hierarchical porous zeolitic imidazolate frameworks (ZIF-8) and ZnO@N-doped carbon for selective adsorption and photocatalytic degradation of organic pollutants. *RSC. Adv.* **2022**, *12*, 7075-84. DOI PubMed PMC
64. Feng, S.; Jia, X.; Yang, J.; Li, Y.; Wang, S.; Song, H. One-pot synthesis of core-shell ZIF-8@ZnO porous nanospheres with improved ethanol gas sensing. *J. Mater. Sci. Mater. Electron.* **2020**, *31*, 22534-45. DOI
65. Jovanovski, S.; Popović, M.; Novaković, M.; Jugović, D.; Gloginjić, M.; Ristova, M. Preparation of CuWO₄ films by thermal annealing of simultaneously RF/DC magnetron co-sputtered Cu-W films. *Ceram. Int.* **2025**, *51*, 43604-12. DOI
66. Liao, J.; Wu, Q.; Ye, X.; et al. Visible-light-induced electron density enrichment of the active sites in the core-satellite structured CuWO₄@NiO for fast hydrogen generation from ammonia borane methanolysis. *Chem. Eng. J.* **2023**, *476*, 146599. DOI
67. Vasilopoulou, M.; Soultati, A.; Georgiadou, D. G.; et al. Hydrogenated under-stoichiometric tungsten oxide anode interlayers for efficient and stable organic photovoltaics. *J. Mater. Chem. A*. **2014**, *2*, 1738-49. DOI
68. Changkija, M.; Dhar Purkayastha, D. Engineered WO₃/H₂O/ZIF-8 hybrid membrane for synergistic wastewater treatment. *Chem. Eng. J.* **2026**, *532*, 174244. DOI
69. Yao, X.; Zhu, C.; Zhou, J.; et al. Boosting urea synthesis in simulated flue gas electroreduction by adjusting W-W electronic properties. *Green. Chem.* **2024**, *26*, 8010-9. DOI
70. Zaid, M.; Parveen, A.; Saleem, Z.; Khan, W.; Bahadur, J. Photocatalytic behavior of nickel and silver doped ZnS nanoparticles: reassessing the role of metal dopants. *Inorg. Chem. Commun.* **2025**, *182*, 115449. DOI
71. Lianmawii, L.; Mohondas Singh, N. Photocatalytic degradation of tartrazine dye using CoS, NiS, and ZnS: a comprehensive study on isotherms, kinetics, thermodynamics, and photoluminescence analysis. *Mater. Chem. Phys.* **2025**, *346*, 131354. DOI
72. Missaoui, N.; Kahri, H.; Demirci, U. B. Rapid room-temperature synthesis and characterizations of high-surface-area nanoparticles of zeolitic imidazolate framework-8 (ZIF-8) for CO₂ and CH₄ adsorption. *J. Mater. Sci.* **2022**, *57*, 16245-57. DOI
73. Bukka, V. V. R.; Sarin, P. Effects of particle size reduction on the pore structure and accessibility in natural porous materials. *Energy. Fuels*. **2024**, *38*, 9578-87. DOI
74. Zhao, H.; Liu, J.; Zhong, N.; et al. Biomass photoreforming for hydrogen and value-added chemicals Co-production on hierarchically porous photocatalysts. *Adv. Energy. Mater.* **2023**, *13*, 2300257. DOI
75. Mphuthi, L. E.; Erasmus, E.; Langner, E. H. G. Metal exchange of ZIF-8 and ZIF-67 nanoparticles with Fe(II) for enhanced photocatalytic performance. *ACS. Omega*. **2021**, *6*, 31632-45. DOI PubMed PMC
76. Bharagav, U.; Reddy, N. R.; Rao, V. N.; et al. CuWO₄ as a novel Z-scheme partner to construct TiO₂ based stable and efficient heterojunction for photocatalytic hydrogen generation. *Int. J. Hydrogen. Energy*. **2022**, *47*, 40391-406. DOI
77. Dai, X.; Feng, S.; Zheng, W.; et al. Ag-AgBr/g-C₃N₄/ZIF-8 prepared with ionic liquid as template for highly efficient photocatalytic hydrogen evolution under visible light. *Int. J. Hydrogen. Energy*. **2022**, *47*, 10603-15. DOI
78. Gamal, S.; Kospa, D. A.; Ibrahim, A. A.; Ahmed, A. I.; Ouf, A. M. A. A comparative study of α-Ni(OH)₂ and Ni nanoparticle supported ZIF-8@reduced graphene oxide-derived nitrogen doped carbon for electrocatalytic ethanol oxidation. *RSC. Adv.* **2024**, *14*, 5524-41. DOI PubMed PMC
79. Anu, A.; Abdul, Khadar. M. CuO-ZnO nanocomposite films with efficient interfacial charge transfer characteristics for optoelectronic applications. *SN. Appl. Sci.* **2019**, *1*, 1057. DOI
80. Makula, P.; Pacia, M.; Macyk, W. How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV-vis spectra. *J. Phys. Chem. Lett.* **2018**, *9*, 6814-7. DOI PubMed
81. Sun, D.; Liu, J.; Kang, Y.; et al. Architectural engineering of yolk-shell TiO₂@g-C₃N₄ S-scheme heterojunctions via a peroxidation strategy for enhanced photocatalytic hydrogen evolution. *Appl. Surf. Sci.* **2026**, *735*, 166680. DOI
82. Jin, Z.; Zhang, Y. Efficient photocatalytic hydrogen production achieved by WO₃ coupled with NiP₂ over ZIF-8. *Catal. Surv. Asia*. **2019**, *24*, 59-69. DOI
83. Zhang, D.; Zhang, D.; Zhao, F.; et al. Synergistic enhancement of photocatalytic hydrogen evolution in ZnIn₂S₄/CuWO₄ via an S-scheme heterojunction and the photothermal effect. *J. Mater. Chem. A*. **2024**, *12*, 33546-58. DOI
84. Le, N.; Tran, T. V.; Dang, T. T.; Chung, J. S.; Choi, W. M.; Hur, S. H. Oxygen vacancies promoted W-O-Mo interfacial bonding for stable CuWO₄ photoanodes with accelerated charge transfer. *Int. J. Hydrogen. Energy*. **2026**, *204*, 153307. DOI

85. Zheng, H.; Chen, Z.; Huang, C.; Gao, L.; Dong, T.; Hu, J. Hollow CdS nanotubes with ZIF-8 as co-catalyst for enhanced photocatalytic activity. *J. Colloid. Interface. Sci.* **2022**, *606*, 1882-9. DOI
86. Cheng, C.; Wang, J.; Zhao, Z.; et al. S-scheme SrTiO₃/porous ZnO derived by pyrolysis of ZIF-8 composite with efficient photocatalytic activity for pollutant degradation. *J. Alloys. Compd.* **2022**, *896*, 163064. DOI
87. Chen, W.; Li, L.; Li, L.; et al. MoS₂/ZIF-8 hybrid materials for environmental catalysis: solar-driven antibiotic-degradation engineering. *Engineering* **2019**, *5*, 755-67. DOI
88. Ma, L.; Su, J.; Liu, M.; Zhang, L.; Li, Y.; Guo, L. Enhanced photocatalytic activity over a novel CuWO₄/Cu_{1-x}Zn_xWO₄/ZnWO₄ hybrid material with sandwiched heterojunction. *J. Mater. Res.* **2016**, *31*, 1616-21. DOI
89. Huang, Z.; Zhou, J.; Zhao, Y.; et al. Stable core-shell ZIF-8@ZIF-67 MOFs photocatalyst for highly efficient degradation of organic pollutant and hydrogen evolution. *J. Mater. Res.* **2021**, *36*, 602-14. DOI
90. Lin, Y.; Feng, Z.; Li, P.; et al. Molten salt in situ reconstruction realizes ultrafast charge transfer at cobalt-doped-CeO₂/CeO₂ S-scheme interface for photocatalytic H₂O₂ production. *Chem. Eng. J.* **2025**, *522*, 167927. DOI
91. Yang, Y.; Li, Y.; Tao, S.; et al. Interfacial charge transfer in 2D/2D S-scheme Bi₂MoO₆/MoS₂ heterojunction for enhanced photocatalytic antibiotic degradation. *Chem. Eng. J.* **2025**, *522*, 167608. DOI
92. Sun, L.; Yuan, Y.; Wang, F.; Zhao, Y.; Zhan, W.; Han, X. Selective wet-chemical etching to create TiO₂@MOF frame heterostructure for efficient photocatalytic hydrogen evolution. *Nano. Energy*. **2020**, *74*, 104909. DOI
93. Djaballah, A.; Bagtache, R.; Benlembarek, M.; Trari, M. Synthesis and characterization of Pt/CuBi₂O₄. Application to photocatalytic H₂ evolution under visible light. *J. Photochem. Photobiol. A. Chem.* **2024**, *447*, 115186. DOI
94. Wu, X.; Zhao, J.; Guo, S.; et al. Carbon dot and BiVO₄ quantum dot composites for overall water splitting via a two-electron pathway. *Nanoscale* **2016**, *8*, 17314-21. DOI
95. Su, Y.; Li, S.; He, D.; et al. MOF-derived porous ZnO nanocages/rGO/carbon sponge-based photocatalytic microreactor for efficient degradation of water pollutants and hydrogen evolution. *ACS. Sustain. Chem. Eng.* **2018**, *6*, 11989-98. DOI
96. Archana, B.; Kottam, N.; Nayak, S.; Chandrasekhar, K. B.; Sreedhara, M. B. Superior photocatalytic hydrogen evolution performances of WS₂ over MoS₂ integrated with CdS nanorods. *J. Phys. Chem. C*. **2020**, *124*, 14485-95. DOI
97. She, X.; Wu, J.; Xu, H.; et al. High efficiency photocatalytic water splitting using 2D α-Fe₂O₃/g-C₃N₄ Z-scheme catalysts. *Adv. Energy. Mater.* **2017**, *7*, 1700025. DOI
98. Chen, J.; Chen, J.; Li, Y. Hollow ZnCdS dodecahedral cages for highly efficient visible-light-driven hydrogen generation. *J. Mater. Chem. A*. **2017**, *5*, 24116-25. DOI
99. Todorova, N.; Papailias, I.; Giannakopoulou, T.; et al. Photocatalytic H₂ evolution, CO₂ reduction, and NO_x oxidation by highly exfoliated g-C₃N₄. *Catalysts* **2020**, *10*, 1147. DOI
100. Wu, C.; Liu, K.; Li, Y.; et al. Dual-modified hollow spherical shell MoS₂@TiO₂/TiN composites for photocatalytic hydrogen production. *Energy. Technol.* **2021**, *10*, 2100265. DOI
101. Li, Y.; Zhang, P.; Wan, D.; Xue, C.; Zhao, J.; Shao, G. Direct evidence of 2D/1D heterojunction enhancement on photocatalytic activity through assembling MoS₂ nanosheets onto super-long TiO₂ nanofibers. *Appl. Surf. Sci.* **2020**, *504*, 144361. DOI
102. Yu Kurenkova, A.; Radina, A. D.; Baidyshev, V. S.; et al. Photocatalytic H₂ generation and CO₂ reduction by WB_{5-x} cocatalyst of TiO₂ catalyst. *Appl. Surf. Sci.* **2024**, *661*, 160095. DOI
103. Fan, W.; Lai, Q.; Zhang, Q.; Wang, Y. Nanocomposites of TiO₂ and reduced graphene oxide as efficient photocatalysts for hydrogen evolution. *J. Phys. Chem. C*. **2011**, *115*, 10694-701. DOI
104. Montoya, A. T.; Gillan, E. G. Enhanced photocatalytic hydrogen evolution from transition-metal surface-modified TiO₂. *ACS. Omega*. **2018**, *3*, 2947-55. DOI PubMed PMC
105. Chafiq, M.; Chaouiki, A.; Suhartono, T.; Ko, Y. G. Albumin protein encapsulation into a ZIF-8 framework with Co-LDH-based hierarchical architectures for robust catalytic reduction. *J. Mater. Chem. A*. **2023**, *11*, 23984-98. DOI
106. Song, Y.; Hu, D.; Liu, F.; Chen, S.; Wang, L. Fabrication of fluorescent SiO₂@zeolitic imidazolate framework-8 nanosensor for Cu²⁺ detection. *Analyst* **2015**, *140*, 623-9. DOI
107. Xu, F.; Pan, J.; Li, B.; et al. ZIF-8 decorated WO₃ nanoplates with robust surface activation for the enhanced performances in photocatalytic N₂ fixation. *ChemistrySelect* **2021**, *6*, 5411-8. DOI
108. Maaß, M. C.; Tasch, A.; Jooss, C.; Waitz, T. Photocatalytic hydrogen evolution using ZnS particles and LEDs. *J. Chem. Educ.* **2022**, *99*, 2086-92. DOI
109. Zhang, M.; Shang, Q.; Wan, Y.; Cheng, Q.; Liao, G.; Pan, Z. Self-template synthesis of double-shell TiO₂@ZIF-8 hollow nanospheres via sonocrystallization with enhanced photocatalytic activities in hydrogen generation. *Appl. Catal. B. Environ.* **2019**, *241*, 149-58. DOI

-
110. Taheri, M.; Tsuzuki, T. Photo-accelerated hydrolysis of metal organic framework ZIF-8. *ACS. Mater. Lett.* **2021**, *3*, 255-60. DOI
111. Wang, H.; Jian, M.; Qi, Z.; et al. Specific anion effects on the stability of zeolitic imidazolate framework-8 in aqueous solution. *Microporous. Mesoporous. Mater.* **2018**, *259*, 171-7. DOI

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