

Article

Interface Engineering of ZnO-Decorated ZnFe₂O₄ for Enhanced CO₂ Reduction Performance

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Abstract

Photocatalytic conversion of CO₂ to hydrocarbon fuels offers a promising pathway for sustainable renewable energy production. In this study, a ZnO/ZnFe₂O₄ composite featuring a Type-II heterojunction was synthesized through a facile one-step hydrothermal approach, significantly enhancing visible-light-driven CO₂ reduction activity. The optimized catalyst exhibits CH₄ and CO production rates that are 3.3 and 4.9 times higher, respectively, than those of pristine ZnFe₂O₄ over 6 h. This significant enhancement in photocatalytic performance is attributed to the Type-II band alignment, which not only broadens light absorption but also greatly promotes efficient charge separation. It is corroborated by a series of experimental evidence: a two-fold enhancement in photocurrent response, a 15.1% reduction in PL intensity, decreased electrochemical impedance, and an extended charge carrier lifetime. Furthermore, in situ FTIR spectroscopy confirms that the heterojunction facilitates the formation of key intermediates (specifically *COOH and HCOO[−]). This study highlights the importance of precise interface design based on a Type-II heterojunction in heterostructured composite catalysts and provides mechanistic insights for developing highly efficient CO₂ photoreduction systems.

Keywords: ZnO/ZnFe₂O₄ nanoparticle; oxygen vacancies; photocatalytic CO₂ reduction; interface engineering



Academic Editor: Jonathan Albo

Received: 26 August 2025

Revised: 29 September 2025

Accepted: 2 October 2025

Published: 4 October 2025

Citation: Cai, C.; Sun, Y.; Xiao, Y.; Zheng, W.; Pan, M.; Wang, W. Interface Engineering of ZnO-Decorated ZnFe₂O₄ for Enhanced CO₂ Reduction Performance. *Molecules* **2025**, *30*, 3980. <https://doi.org/10.3390/molecules30193980>

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1. Introduction

The rapid development of global industrialization and urbanization has led to a severe environmental crisis caused by CO₂, posing significant environmental challenges for researchers. Currently, mitigating greenhouse gases primarily through photocatalysis, electrocatalysis, and carbon capture is anticipated to be a key strategy for addressing this crisis [1–4]. Numerous semiconductor and photocatalytic materials, such as TiO₂, ZnO, ZnIn₂S₄, CeO₂, and ZnFe₂O₄, have been developed [5–10]. Among these, photocatalysis represents a widely used green synthesis method in environmental science. It offers advantages including environmental friendliness, lower production costs, and safety. The synthesized nanoparticles exhibit enhanced biocompatibility and good performance, making them suitable for various applications like wastewater treatment, environmental protection, and other bio-related fields [11,12].

However, utilizing light energy to drive the conversion of CO₂ into carbon-based fuels is challenging due to the high stability and low reactivity of the CO₂ molecule, attributed to the high dissociation energy of its C=O bond. The conversion of solar energy

through mild light-driven chemical reactions is of profound importance for developing green and sustainable energy [13]. Related studies have demonstrated that ZnFe_2O_4 nanoparticles possess strong antioxidant activity and high safety. As a novel narrow-bandgap semiconductor material, nano-sized zinc ferrite has been extensively researched and applied in areas such as magnetism, photocatalysis, and energy storage [14–16]. Deng et al. [17] prepared monodisperse ferrite microspheres using a simple one-step solvothermal method. Modulating the hydrophilicity and biocompatibility of these micro/nanomaterials is expected to broaden their applications in advanced magnetic materials, ferromagnetic fluid technology, and biomedicine. Zinc ferrite nanomaterials are synthesized via a variety of methods, including mechanical ball milling, sol-gel, solvothermal synthesis, chemical vapor deposition, and microwave-assisted combustion. The advantages of each method are accompanied by certain trade-offs, such as encompassing elevated impurity levels in the final product, procedures that are both cumbersome and time-consuming, or a dependence on stringent conditions like high temperature and pressure [18]. Therefore, more effective synthesis methods are needed to address these material shortcomings.

Meanwhile, ZnO has a narrow light absorption range, primarily limited to ultraviolet (UV) light, which constitutes only about 4% of solar radiation, thus restricting the full utilization of sunlight. Furthermore, the rapid recombination of photogenerated carriers prevents effective separation of electron–hole pairs and their transfer to the catalyst surface for participation in photocatalytic reactions, leading to reduced photocatalytic activity. Strategies reported to enhance the catalytic activity of ZnO include morphology control, ion doping, semiconductor coupling, and surface noble metal deposition. However, these approaches often suffer from drawbacks such as complex preparation processes and the requirement for specialized equipment like xenon lamps or microwaves during catalysis [19–22].

ZnO is an excellent photocatalyst due to its high electron mobility and fast photo-generated electron transfer rate. However, its wide bandgap restricts light absorption to the UV region. Conversely, ZnFe_2O_4 has a narrower bandgap and strong visible light absorption capability, but suffers from rapid electron–hole recombination and low photocatalytic activity. In this study, a $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite was synthesized via a simple and feasible hydrothermal method. Interface engineering was employed to enhance the visible-light photocatalytic activity, and the corresponding CO_2 reduction performance was systematically evaluated [23–26].

2. Results and Discussion

2.1. Interface Structure Construction and Physicochemical Properties

Figure 1a presents the XRD patterns of the synthesized materials. For pure ZnFe_2O_4 , the characteristic diffraction peaks observed at $2\theta = 29.9^\circ, 35.3^\circ, 42.8^\circ, 53.1^\circ, 56.6^\circ$, and 62.2° can be assigned to the (220), (311), (400), (422), (511), and (440) crystal planes, respectively. These peaks match well with the standard pattern for cubic spinel ZnFe_2O_4 (JCPDS No. 79-1105), confirming its phase purity and structure. In the XRD patterns of the $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composites, additional distinct diffraction peaks appear at $2\theta = 31.8^\circ, 34.4^\circ, 36.2^\circ$, and 67.9° . These peaks are indexed to the (100), (002), (101), and (112) planes of hexagonal wurtzite ZnO (JCPDS No. 36-1451), confirming the successful formation of the composite [14,15]. Alongside these ZnO peaks, the characteristic peaks of the cubic spinel ZnFe_2O_4 phase (e.g., (311), (400), (422), (511), (440)) remain present. More importantly, the composite exhibits notable structural improvements in the ZnFe_2O_4 phase compared to pure ZnFe_2O_4 . Among these, the crystallinity of $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ is significantly enhanced, as evidenced by the markedly reduced full width at half maximum (FWHM) of the (311) peak from 0.84 to 0.27, accompanied by a substantial increase in peak intensity. These changes

suggest improved crystallite growth and structural ordering within the composite, as summarized in Table S1. Applying Scherrer's formula to this peak reveals a substantial increase in the average crystallite size of ZnFe_2O_4 , from approximately 10.7 nm in the pure phase to 32.6 nm in the composite (Table 1). The diffraction peaks associated with ZnFe_2O_4 in the composite become noticeably sharper. These observed changes—reduced FWHM (increased crystallite size), lattice contraction, and peak sharpening—collectively indicate enhanced crystallinity and reduced lattice strain within the ZnFe_2O_4 phase in the composite. These results suggest that the presence of ZnO induces interfacial tensile strain and simultaneously promotes the growth of ZnFe_2O_4 crystallites [10,17,19]. The presence of ZnO promotes stress release at the interface, facilitates the formation of a well-defined heterojunction, lowers the surface energy, and drives the orderly growth of ZnFe_2O_4 crystallites. The successful integration of ZnO with ZnFe_2O_4 , leading to these distinct structural modifications, is thus clearly evidenced by the XRD analysis.

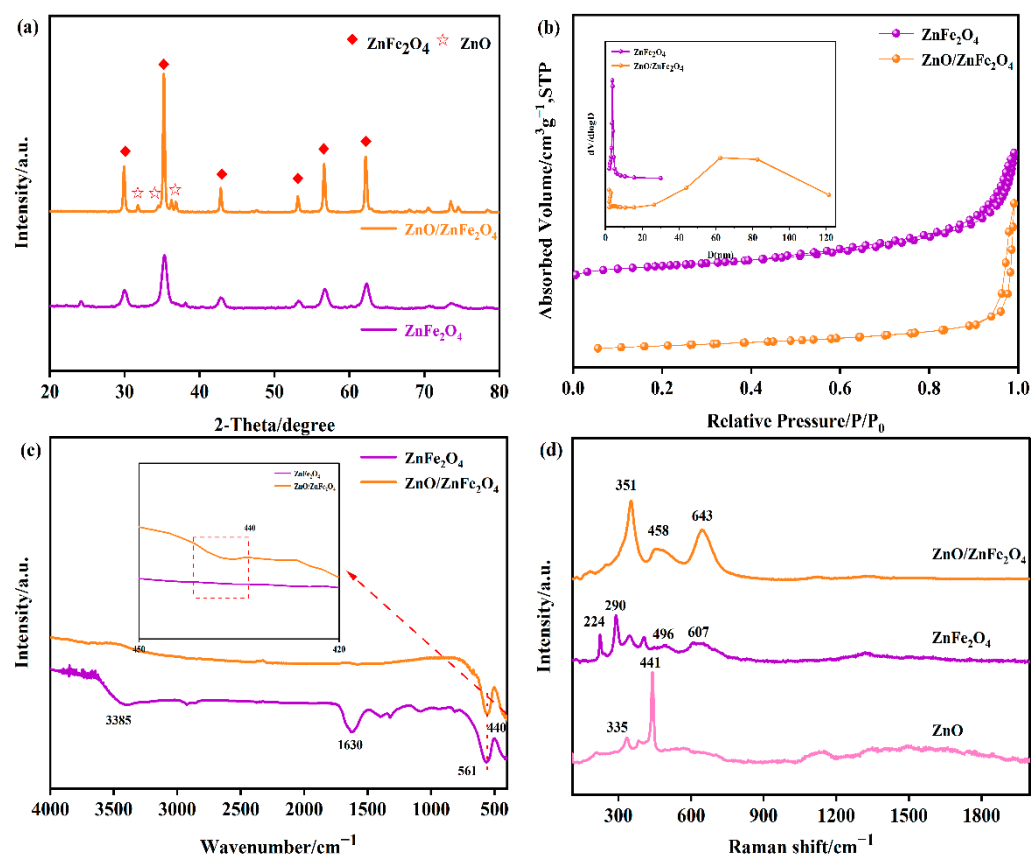


Figure 1. (a) XRD patterns of the synthesized ZnFe_2O_4 , $\text{ZnO/ZnFe}_2\text{O}_4$, (b) N_2 adsorption-desorption isotherms and PSD curves (inset), (c) FT-IR spectra of samples ZnFe_2O_4 and $\text{ZnO/ZnFe}_2\text{O}_4$ catalysts, (d) Raman spectra of samples ZnFe_2O_4 and $\text{ZnO/ZnFe}_2\text{O}_4$ catalysts with different nanomorphologies.

Table 1. XRD structural parameter of samples ZnO and ZnFe_2O_4 .

Samples	Crystal Size (nm)	Crystal Parameter (Å)			Standard Card
		a	b	c	
ZnO	1.2	3.250	3.250	5.207	JCPDS No. 36-1451
ZnFe_2O_4	10.7	8.466	8.466	8.466	JCPDS No. 79-1105
$\text{ZnO/ZnFe}_2\text{O}_4$	32.6	3.250	3.250	5.207	JCPDS No. 89-7102

Figure 1b displays the N_2 adsorption-desorption isotherms along with the corresponding pore size distribution curves for both ZnFe_2O_4 and $\text{ZnO/ZnFe}_2\text{O}_4$ samples. The

isotherm for pure ZnFe_2O_4 is classified as type IV, showing an H_1 -type hysteresis loop occurring at relative pressures (P/P_0) between 0.9 and 1.0. This characteristic loop signifies the occurrence of capillary condensation, and its steep profile suggests the presence of relatively uniform cylindrical mesopores. The specific surface area (SSA) and total pore volume of ZnFe_2O_4 were determined to be $115.97 \text{ m}^2/\text{g}$ and $0.137 \text{ cm}^3/\text{g}$, respectively. The pore size distribution (PSD) analysis (Table S2) indicates that the pores are predominantly concentrated within the 1–10 nm range, with an average pore size of 4.73 nm. The $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite also displays a type IV isotherm with an H_1 -type hysteresis loop ($P/P_0 = 0.9\text{--}1.0$). Notably, the hysteresis loop appears steeper and narrower compared to that of pure ZnFe_2O_4 , suggesting improved pore uniformity due to the homogeneous distribution of ZnFe_2O_4 nanoparticles on ZnO . However, a significant alteration is evident in the PSD curve of $\text{ZnO}/\text{ZnFe}_2\text{O}_4$. While mesopores (1–10 nm) remain present, a distinct new peak emerges in the 50–80 nm range, indicative of macropore formation. This shift is presumably attributable to the formation of interstitial voids resulting from the stacking of ZnFe_2O_4 nanoparticles on the lamellar ZnO structures with varied thicknesses during the multi-phase modification process. Consequently, the composite exhibits a significantly reduced SSA and an increased average pore size of 33.44 nm. The coexistence of mesopores and macropores, along with the larger average pore size in $\text{ZnO}/\text{ZnFe}_2\text{O}_4$, may facilitate the diffusion of reactant molecules within the catalyst structure [22].

As evidenced by the FT-IR spectrum (Figure 1c), the broad absorption band centered at 3385 cm^{-1} in ZnFe_2O_4 is associated with the O-H stretching vibration of adsorbed surface water. The distinct medium-intensity peak at 561 cm^{-1} is assigned to the Fe-O stretching vibration, confirming the successful synthesis of ZnFe_2O_4 . In the spectra of the $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composites, the Fe-O stretching vibration remains clearly visible at 561 cm^{-1} . Additionally, a distinct peak appears at 440 cm^{-1} , assigned to the Zn-O stretching vibration within the tetrahedral sites of ZnO . The presence of both characteristic Zn-O and Fe-O vibration bands, coupled with the absence of other significant impurity peaks, confirms the successful synthesis of high-purity $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composites.

Raman spectra (Figure 1d) further reveal the coexistence of spinel-type ZnFe_2O_4 (A_{1g} mode at 607 cm^{-1}) and wurtzite ZnO ($\text{E}_2(\text{high})$ mode at 441 cm^{-1}) in the composite. Notably, both peaks exhibit significant sharpening and blue shifts ($\Delta\nu = +36 \text{ cm}^{-1}$ for A_{1g} , $\Delta\nu = +17 \text{ cm}^{-1}$ for $\text{E}_2(\text{high})$), primarily resulting from interfacial lattice strain and strengthened Zn-O-Fe bonding at the heterojunction interface.

These observations are strongly supported by XRD analysis (Figure 1a), which shows lattice contraction, peak sharpening, and enhanced intensity, collectively indicating that interfacial engineering optimizes crystallinity while introducing controlled microstrain [23].

As shown in the TEM image of the pristine ZnFe_2O_4 (Figure 2a), the material consists of an aggregation of quasi-spherical particles. These particles possess a small grain size, predominantly within the 6–12 nm range. High-resolution imaging identifies distinct lattice fringes with a d-spacing of 0.254 nm, corresponding to the (311) plane of ZnFe_2O_4 . Figure 2b displays the TEM image of the $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite. In contrast to the pure phase, the composite exhibits a ZnO substrate decorated with well-dispersed ZnFe_2O_4 nanoparticles, with particle sizes ranging from approximately 30 to 150 nm. Well-defined lattice fringes are observed, with spacings of 0.260 nm and 0.254 nm, assignable to the (002) plane of ZnO and the (311) plane of ZnFe_2O_4 , respectively. These clear lattice resolutions indicate high crystallinity within the composite, consistent with the sharpening of ZnFe_2O_4 diffraction peaks observed by XRD. The TEM results confirm the successful construction of a $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite with intimate interfacial contact. The distinct lattice mismatch ($d = 0.260 \text{ nm}$ vs. $d = 0.254 \text{ nm}$) and the observed interfacial coupling provide clear evidence for the formation of a well-coupled interface between the ZnO and ZnFe_2O_4 phases [27].

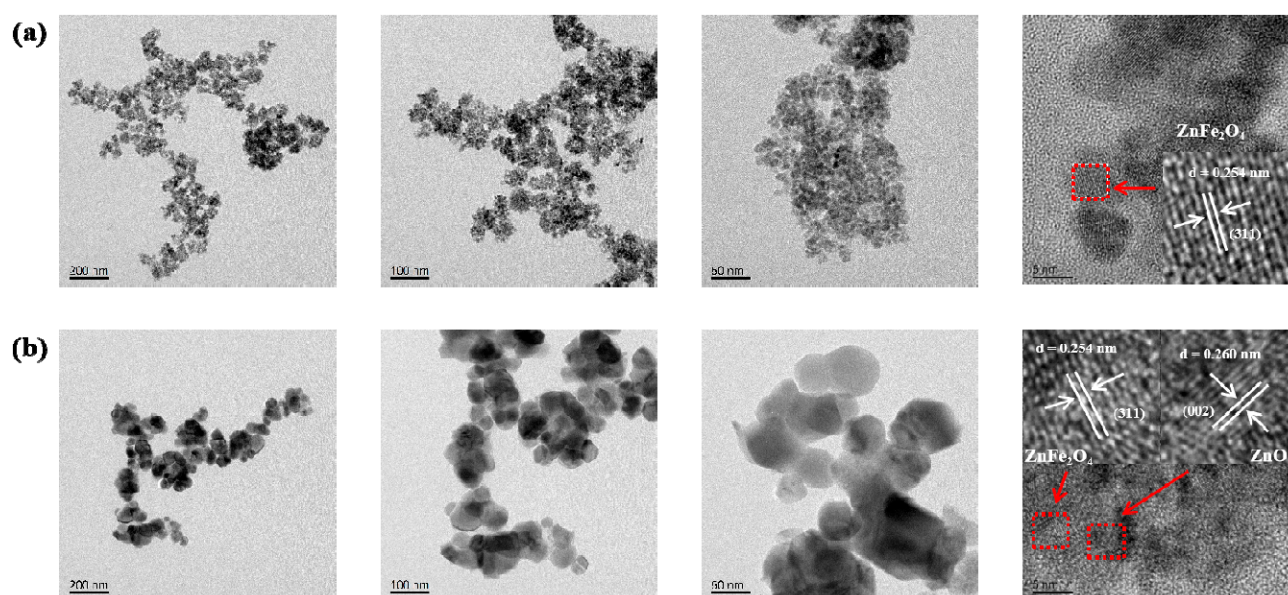


Figure 2. TEM and HRTEM images of (a) ZnFe_2O_4 , (b) $\text{ZnO}/\text{ZnFe}_2\text{O}_4$.

XPS measurements were conducted to examine the chemical states and interfacial characteristics of the samples. The survey scan (Figure 3a) verifies the existence of Zn, Fe, O, and C. In the Fe 2p region (Figure 3c), the peaks observed at 722.7 eV (Fe 2p_{1/2}) and 711.0 eV (Fe 2p_{3/2}) are indicative of Fe²⁺ and Fe³⁺ species, respectively, consistent with the Fe-O and Fe-O-Zn bonding environments in ZnFe_2O_4 . Notably, in the $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite, the Fe 2p peaks exhibit a positive shift of approximately 0.8 eV, while the Zn 2p peaks show a negative shift of about 1.4 eV. The Zn 2p spectrum of pristine ZnFe_2O_4 (Figure 3b) shows binding energies of 1021.32 eV (Zn 2p_{3/2}) and 1044.38 eV (Zn 2p_{1/2}), characteristic of Zn²⁺. In the $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composite, these peaks shift negatively to 1019.88 eV and 1042.94 eV, respectively. The large negative shift in Zn 2p (1.4 eV) exceeds typical heterojunction values (0.1–0.5 eV), suggesting contributions from interfacial dipole formation and local coordination environment changes in addition to charge transfer. These opposing shifts suggest a redistribution of electron density at the interface, consistent with electron transfer from ZnFe_2O_4 to ZnO. Quantitative analysis of XPS-derived elemental molar ratios reveals Zn and Fe ratios of $\approx 0.7:1$ and $3.0:1$, respectively (Table S3). The Fe ratio (3.0:1) closely corresponds to the CO/CH_4 production rate ratio, providing a quantitative correlation between electronic structure modification and catalytic performance [19,22]. The observed increase in electron density around Zn atoms further supports this charge transfer mechanism. The O 1s spectrum (Figure 3d) exhibits three contributions: lattice oxygen in Zn-O (528.28 eV), Fe-O (530.18 eV), and surface-adsorbed water (532.08 eV). After the formation of the composite, the relative concentration of oxygen vacancies (associated with the 530.18 eV peak) increases from 21.3% to 25.3% (Table 2), providing more active sites for CO_2 reduction. These results collectively demonstrate strong interfacial electronic interaction between ZnO and ZnFe_2O_4 , which enhances the material's catalytic properties [28].

Table 2. The chemical state of Zn, Fe and O in the catalysts.

Samples	O Atomic/%			Atomic/%		
	O _{latt}	O _{ads}	O _w	Zn	Fe	O
ZnFe_2O_4	66.2	21.3	12.5	23.8	40.2	36.0
$\text{ZnO}/\text{ZnFe}_2\text{O}_4$	68.6	25.3	6.1	36.4	16.4	47.2

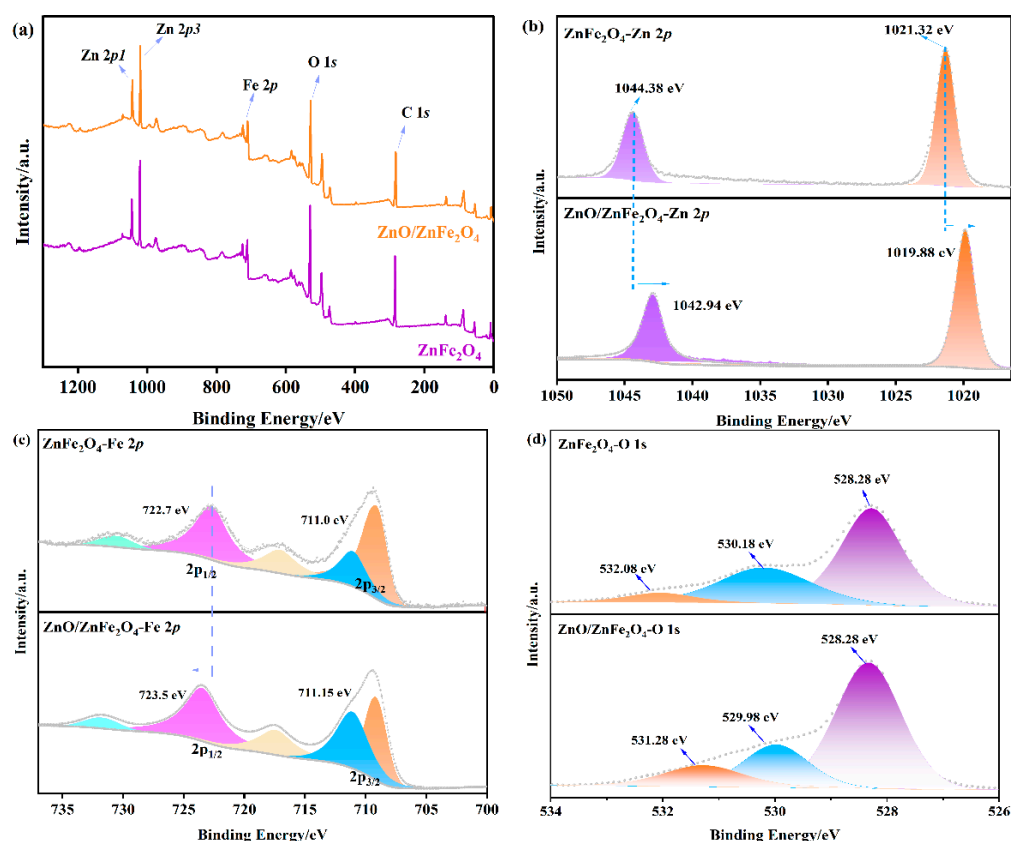


Figure 3. XPS of (a) survey spectra, (b) Fe 2p, (c) Zn 2p, and (d) O 1s of ZnFe_2O_4 and $\text{ZnO}/\text{ZnFe}_2\text{O}_4$.

2.2. Photoelectric Characteristics and Charge Separation Effect

Figure 4a–c presents the UV-visible diffuse reflectance spectra (DRS) of ZnFe_2O_4 and $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ composites. The $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ sample exhibits significantly enhanced light absorption across both UV and visible regions (500–700 nm) compared to pristine ZnFe_2O_4 , along with a broader visible-light response range. This pronounced absorption enhancement indicates improved photocatalytic potential. The optical bandgaps (E_g) determined from the absorption onset (λ_g) via the tangent method (Figure 4b) are 1.96 eV for ZnFe_2O_4 and 2.12 eV for $\text{ZnO}/\text{ZnFe}_2\text{O}_4$, calculated using $E_g = 1240/\lambda_g$ (eV). The observed E_g widening in the composite is attributed to interfacial lattice strain (consistent with the Raman blue-shift). While bandgap widening typically reduces photoabsorption, the introduction of ZnO ($E_g \approx 3.2$ eV) extends the UV response. Importantly, the net enhancement in visible-light absorption originates from two synergistic effects: an increase in oxygen vacancies introducing defect states within the bandgap, as corroborated by XPS O 1s analysis, and interfacial engineering-induced band tailing that broadens the optical response range [25,27,28].

The Mott-Schottky curves (Figure 4c) exhibit positive slopes for both materials, confirming n-type semiconductor behavior [29]. The flat-band potential (E_{FB}) approximates the conduction band potential (E_{CB}) within ± 0.1 eV for n-type semiconductors. The tangent extrapolation method yields E_{CB} values of -0.96 V (vs. NHE) for ZnFe_2O_4 and -0.75 V (vs. NHE) for ZnO (Figure S1). Using the relation $E_{CB} = E_{VB} - E_g$ [30], the valence band potentials (E_{VB}) are calculated as $+1.0$ V and $+2.44$ V (vs. NHE) for ZnFe_2O_4 and ZnO, respectively.

Based on the band alignments, a type-II heterojunction is formed between ZnO and ZnFe_2O_4 . This configuration promotes the transfer of photogenerated electrons from the conduction band of ZnFe_2O_4 (-0.96 eV) to that of ZnO (-0.75 eV), thereby facilitating CO_2 reduction on the ZnO surface. Simultaneously, photogenerated holes migrate from the

valence band of ZnO (+2.44 eV) to that of ZnFe₂O₄ (+1.0 eV), where oxidation reactions occur (Figure 4d). This charge separation mechanism is further supported by the enhanced photocurrent response (Figure 4e–g) and reduced charge transfer resistance observed in EIS measurements [31].

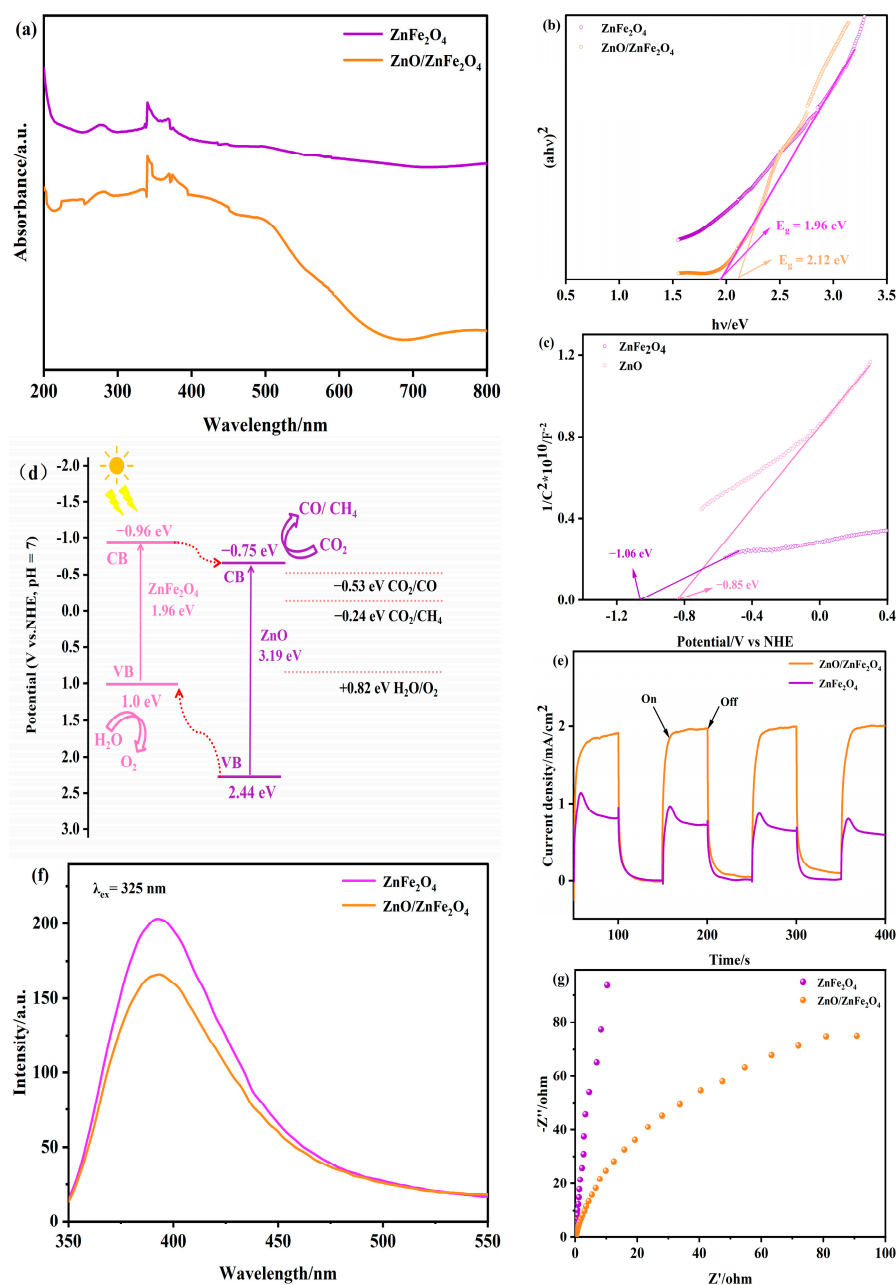


Figure 4. (a–c) UV-vis DRS, (d) proposed photocatalytic mechanism, (e) transient photocurrent response plots, (f) PL, and (g) EIS of ZnO and ZnO/ZnFe₂O₄.

The efficient spatial separation of electrons and holes suppresses recombination, as confirmed by the 15.1% decrease in PL intensity (Figure 4f, Table S4). The synergistic effect of improved charge separation and widened visible-light absorption collectively enhances the photocatalytic CO₂ reduction performance of the ZnO/ZnFe₂O₄ composite.

2.3. Photocatalytic Performance

The photocatalytic CO₂ reduction performance was evaluated in a solid-gas phase reaction system containing CO₂ and water vapor under irradiation from a 300 W xenon lamp (λ ≥ 420 nm). For each test, 20 mg of catalyst was evenly spread on a sample holder.

The reaction atmosphere, consisting of high-purity CO₂ and water vapor, was introduced by injecting 0.3 mL of deionized water into the reactor as the proton source. The products were analyzed using an online gas chromatograph (GC9790II) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD), using high-purity argon as the carrier gas.

As shown in Figure 5, the ZnFe₂O₄ sample produced no detectable CH₄ or CO during the initial 4 h. Trace amounts of CH₄ (0.016–0.024 $\mu\text{mol}\cdot\text{g}^{-1}$) and CO (0.018–0.035 $\mu\text{mol}\cdot\text{g}^{-1}$) were observed between 5 and 6 h.

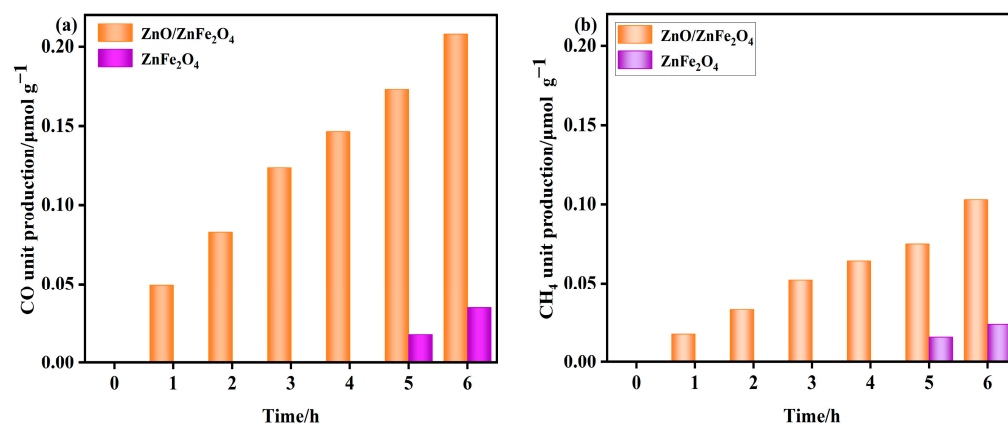


Figure 5. (a,b) Product unit yields of ZnO and ZnO/ZnFe₂O₄ catalysts (unit yield of CO and CH₄).

In contrast, the ZnO-decorated ZnFe₂O₄ composite exhibited significantly enhanced photocatalytic activity. CH₄ and CO were detected from the first hour onward, with cumulative yields reaching 0.103 $\mu\text{mol}\cdot\text{g}^{-1}$ and 0.208 $\mu\text{mol}\cdot\text{g}^{-1}$ after 6 h, respectively. These values correspond to 3.3-fold and 4.9-fold enhancements in CH₄ and CO production compared to pure ZnFe₂O₄. Moreover, the composite demonstrated excellent stability over the reaction period.

The markedly improved activity and earlier onset of CO₂ reduction indicate that interface engineering through ZnO decoration plays a critical role in facilitating catalytic performance. The modified interface provides abundant active sites, enhances CO₂ adsorption and activation, and promotes efficient charge separation by suppressing the recombination of photoinduced charge carriers throughout the ZnFe₂O₄ matrix. These synergistic effects collectively contribute to the superior CO₂ reduction performance of the ZnO/ZnFe₂O₄ composite [32].

2.4. Mechanism of Photocatalytic CO₂ Reduction

As shown in Figure 6a, ZnFe₂O₄ exhibits characteristic -OH stretching vibrations in the range of 3750–3550 cm^{-1} , along with signals at 2356 cm^{-1} and 2342 cm^{-1} corresponding to physically adsorbed CO₂. The intensity of these adsorption peaks increases over time; however, no clear evidence of CO₂ reduction intermediates or products is observed within 30 min of light irradiation, indicating limited photocatalytic activity. This result is consistent with the delayed production of CO and CH₄ until the 5th hour during activity tests.

In contrast, the ZnO/ZnFe₂O₄ catalyst shows enhanced signals associated with -OH (3750–3550 cm^{-1}) and CO₂ (2356 cm^{-1} and 2342 cm^{-1}) along with the rapid appearance of reduction intermediates under illumination, thereby facilitating the subsequent photocatalytic reduction process. As illustrated in Figure 6b, the appearance of a formate (HCOO[−]) peak at 1036 cm^{-1} , as well as signals corresponding to key C₁ pathway intermediates—such as *CHO at 1050, 1065, and 1078 cm^{-1} , *CH₃O at 1310 and 2971 cm^{-1} , and formyl (*CHO) at 1700 cm^{-1} —confirms active carbon hydrogenation. The emergence of a *CH₃ peak at 2881 cm^{-1} and the gradual intensification of the 2971 cm^{-1} peak after 12 min indicate

the formation of C-H-bonded species, suggesting CH_4 generation (the adsorbed methyl vibration peak of CH_4) [33]. Additionally, intermediates critical for CO formation are identified: $^*\text{COOH}$ at 1373 cm^{-1} and $1541\text{--}1714\text{ cm}^{-1}$, HCO_3^- at 1391 and 1430 cm^{-1} (protonated precursor), and weakly adsorbed $^*\text{CO}$ at 2078 cm^{-1} (Figure S2), which readily desorbs to facilitate CO release [34].

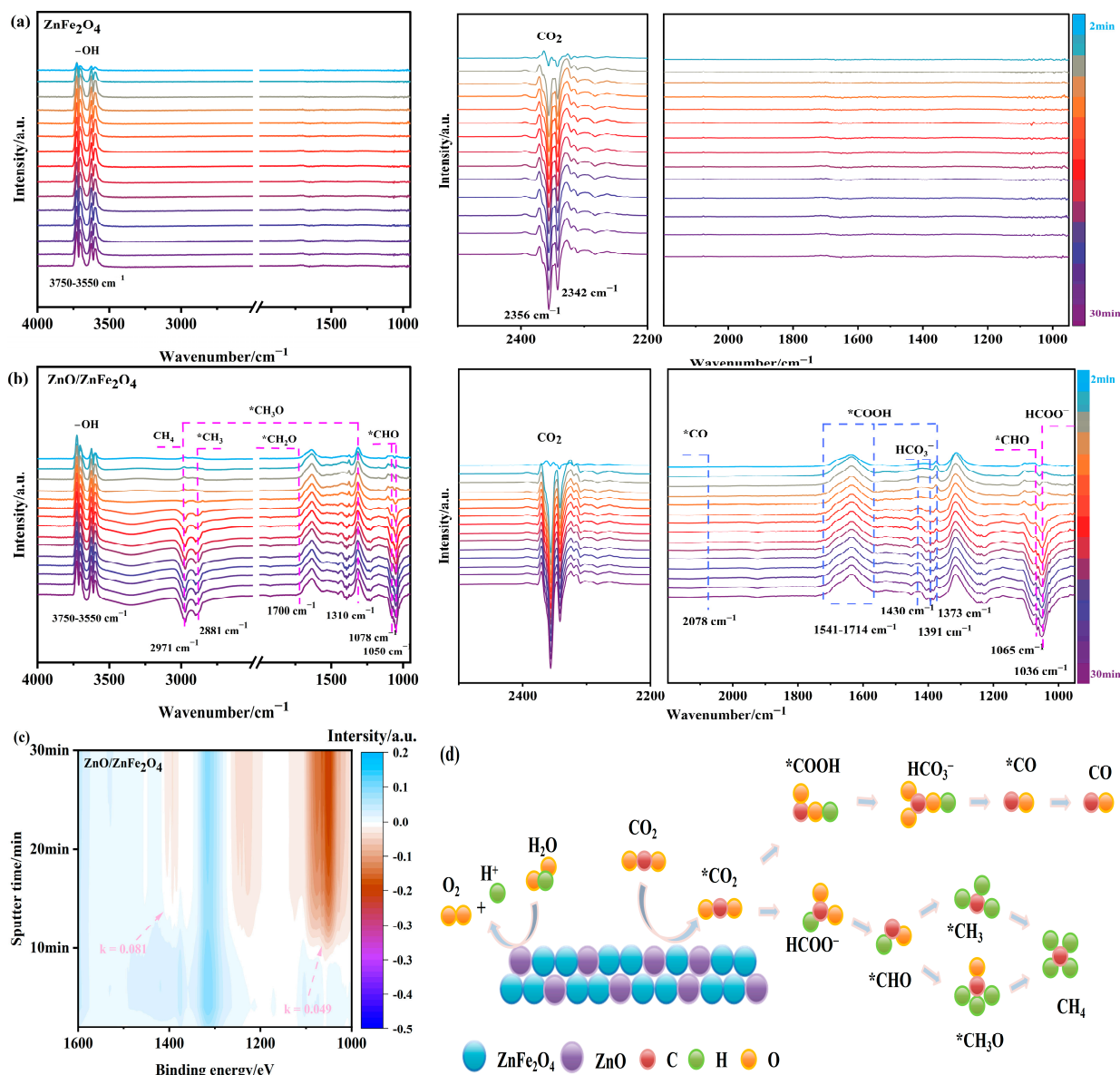


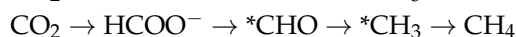
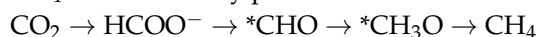
Figure 6. (a–c) In situ FTIR and (d) the possible processes for CO_2 reduction of $\text{ZnO/ZnFe}_2\text{O}_4$.

Time-dependent analysis of these characteristic peaks revealed formation rate constants of $0.081\text{ mV}\cdot\text{s}/\text{min}$ for the CO pathway and $0.049\text{ mV}\cdot\text{s}/\text{min}$ for the CH_4 pathway (Figures 6c and S3), indicating that the CO formation rate is 1.65 times faster than that of CH_4 . This kinetic result aligns well with the product distribution observed in photocatalytic tests (Section 2.3).

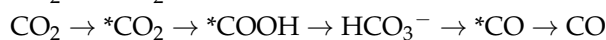
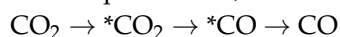
These results demonstrate that the $\text{ZnO/ZnFe}_2\text{O}_4$ interface promotes the formation and stabilization of reduction intermediates, substantially enhancing the CO_2 photocatalytic reduction activity compared to ZnFe_2O_4 alone.

Based on the in situ FTIR evidence, two primary reaction pathways are proposed for product formation (Figure 6d): the CO pathway via $^*\text{COOH}$ intermediate and the CH_4 pathway through progressive hydrogenation of $^*\text{CH}_3\text{O}$ species.

CH₄ formation may proceed via:



For CO production, the routes may proceed via:



In conclusion, the introduction of ZnO facilitates interfacial engineering that enhances CO₂ adsorption, promotes key intermediate formation, and accelerates reaction kinetics, providing valuable insights for the rational design of efficient CO₂ reduction photocatalysts [35].

3. Experimental Section

3.1. Materials

Detailed materials are provided in S3.1 (Supplementary Materials).

3.2. Preparation of ZnFe₂O₄ and ZnO Microspheres via Solvothermal Method

ZnFe₂O₄ was synthesized via a solvothermal method. Briefly, Zn(NO₃)₂·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in ethylene glycol with a molar ratio of Zn:Fe = 1:2. ZnO was prepared using a procedure similar to that of ZnFe₂O₄, but without the addition of Fe(NO₃)₃·9H₂O. To adjust the alkalinity of the solution, 20 mL of NaOH aqueous solution (40 g/L) was added under continuous stirring. Detailed materials are provided in S3.2 (Supplementary Materials).

3.3. Preparation of ZnO/ZnFe₂O₄ Composite via Sodium Hydroxide-Assisted Method

The ZnO/ZnFe₂O₄ composite was synthesized with a nominal Zn:Fe = 1.5:2. Similarly, 20 mL of NaOH solution (40 g/L) was introduced to maintain alkaline conditions during the synthesis. The resulting product was collected, washed, and dried for further characterization. Detailed materials are provided in S3.3 (Supplementary Materials).

3.4. Catalysts Characterization

Detailed materials are provided in S3.4 (Supplementary Materials).

3.5. Photocatalytic CO₂ Reduction Reaction

Detailed materials of the photocatalytic CO₂ reduction reaction were provided in S3.5 (Supplementary Materials).

4. Conclusions

In this study, a one-step modification strategy was developed to decorate ZnFe₂O₄ with ZnO nanoparticles, forming a unique interfacial architecture that significantly enhances visible-light photocatalytic CO₂ reduction. Comprehensive multiscale characterization reveals the following key insights:

- (1) **Interfacial Optimization of Crystalline Structure:** XRD and TEM analyses indicate that the presence of ZnO promotes the growth of ZnFe₂O₄ crystallites, increasing the average grain size from 10.7 nm to 32.6 nm. This is accompanied by a sharpening of the (311) diffraction peak, suggesting improved crystallinity [36]. Lattice parameter analysis reveals interfacial tensile strain (a reduction in the lattice constant *a* from 8.452 Å in pure ZnFe₂O₄), further supported by a Raman blue shift in the A_{1g} mode (+36 cm^{−1}).
- (2) The opposite XPS binding energy shifts of Zn 2p (−1.4 eV) and Fe 2p (+0.8 eV) suggest an interfacial electron transfer from ZnFe₂O₄ to ZnO, leading to an increased electron

density around Zn and a decreased density around Fe. Mott–Schottky analysis confirms that the conduction band potential of ZnO is -0.75 eV while that of ZnFe_2O_4 is -0.96 eV, which is consistent with the formation of a Type-II heterojunction. Additionally, the oxygen vacancy concentration increases to 25.3% (from O 1s spectra), which facilitates extended visible-light absorption.

- (3) **Enhanced Charge Separation and Transport:** The built-in electric field formed at the Type-II heterojunction interface promotes directional migration of photogenerated electrons, resulting in a two-fold increase in photocurrent intensity (Figure 4e) and a 15.1% reduction in PL intensity (Figure 4f). Electrochemical impedance spectroscopy (EIS) shows reduced charge transfer resistance, collectively contributing to suppressed electron–hole recombination and prolonged carrier lifetime.
- (4) **Synergistic Effects of Interface Engineering:** The $\text{ZnO}/\text{ZnFe}_2\text{O}_4$ system overcomes the inherent limitations of the individual components (e.g., rapid charge recombination in ZnFe_2O_4 and narrow light response of ZnO). Through the Type-II band alignment, the composite achieves synergistic broad visible-light absorption ($E_g = 2.12$ eV) and strong reduction capacity ($E_{CB} = -0.96$ eV), leading to a dramatic improvement in CO_2 photoreduction performance. After 6 h of visible-light irradiation, the production rates of CH_4 and CO increased by 3.3 and 4.9 times, respectively, compared to pure ZnFe_2O_4 .

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules30193980/s1>.

Author Contributions: Conceptualization, Writing—original draft, Software, C.C.; Writing—review and editing, C.C., Y.S., M.P. and W.W.; Writing—review, W.W.; performed experiments, Y.X. and W.Z. All authors have read and agreed to the published version of the manuscript.

Funding: Provincial Young and Middle-aged Teachers Education and Research Project of Fujian (Science and Technology) (JAT241231); Provincial First-class Undergraduate Major Construction Project for “Environmental Science” in 2021 (SJZY-2022-02); Provincial First-class Undergraduate Program of Virtual Simulation Experimental Teaching in 2020 (SJJC-2020-04); Provincial Education and Teaching Research of Fujian in 2024 (FBJY20240020).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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