Hydrothermal Synthesis of the CuWO₄/ZnO Composites with Enhanced Photocatalytic Performance

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ABSTRACT: Photocatalytic technology aiming to eliminate organic pollutants in water has been rapidly developed. In this work, we successfully synthesized CuWO₄/ZnO photocatalysts with different weight ratios of CuWO₄ through facile hydrothermal treatment. Crystal structures, forms, and optical properties of these as-prepared materials were investigated and analyzed. 3% CuWO₄/ZnO showed the optimum photodegradation efficiency toward methylene blue under the irradiation of simulated sunlight for 120 min, the degradation rate of which was 98.9%. The pseudo-first-order rate constant of 3% CuWO₄/ZnO was ~11.3 and ~3.5 times bigger than that of pristine CuWO₄ and ZnO, respectively. Furthermore, the material exhibited high stability and reusability after five consecutive photocatalytic tests. In addition, free radical capture experiments were conducted and the possible mechanism proposed explained that the synergistic effect between CuWO₄ and ZnO accelerates the photodegradation reaction. This work provides a feasible technical background for the efficient and sustainable utilization of photocatalysts in wastewater control.

1. INTRODUCTION

Nowadays, industrial technology promotes economic growth and social convenience, which consumes enormous resource and brings global energy crisis and environmental problems in turn.¹ Especially, water pollution consisting of dyes has brought severe threats to humans. These dyes root from leather, plastic, textile, and other industries, most of which are difficult to biodegrade and even toxic and harmful to aquatic life and human body.^{2,3} To remove the abovementioned pollutants, a variety of techniques have been applied, such as ion-exchange, adsorption, filtration, and catalytic oxidation. However, the effects are not satisfying. Photocatalytic degradation is considered a green method to treat the contaminants because of its nontoxicity, environmental friendliness, and good photostability. This technique makes the best of solar energy to decompose organics into inorganics such as CO₂ and H₂O, thus has drawn increasing attention in environmental remediation.^{4–6} Semiconductor materials, particularly metal semiconductors, have been widely used to disintegrate organic pollutants in wastewater. ZnO, an n-type semiconductor, has potential applications in photocatalysts, solar cells, and gas sensors, ascribing to the characteristics of nontoxicity, high redox potential, mild synthetic conditions, and so forth. So far, various approaches have been employed to fabricate ZnO material, for instance, hydrothermal, sol–gel, and coprecipitation. Multifarious morphologies aiming to increase the specific surface area, active sites, and photocatalytic performance are achieved, including hollow ball,

nanofiber, nanorod, nanofilm, and flower-like particles.^{7–9} However, the band gap of ZnO is about 3.37 eV, that is to say, it can only respond to ultraviolet light, which makes up nearly 4% of sunshine. In addition, ZnO has the drawbacks of photocorrosion and high recombination rate of photoinduced electrons and pairs, limiting the practical use in the photocatalytic reaction significantly.^{10–12} Thus, it is imperative to explore practical processes to broaden the range of photoresponse and improve photodegradation activity of ZnO.

Over the years, continuous efforts have been taken to solve these issues, for instance, doping metal or nonmetal atoms, coupling or capping with another semiconductor to construct heterojunctions, and surface chelation. In general, metal atoms (Fe, Cu, Ag, Mn, etc.), carbon materials (graphene and carbon nanotube), N, and S have been used to dope ZnO.^{13,14} Additionally, when the heterojunction is formed between/among binary or ternary hybrids, photoinduced electrons migrate from the conduction band of one semiconductor to another under light irradiation. Consequently, photocurrent comes into being in the process, prolonging the lifetime of

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Figure 1. XRD (a) and the magnified XRD (b,c) patterns of the samples.

photoexcited electron–hole pairs and blocking their recombination.¹⁵ Hence, doping with narrow band gap semiconductors to construct a heterojunction has been identified as a highly effective way to modify ZnO. Currently, versatile ZnO-based heterojunctions have been proposed in the literature, such as CuO/ZnO,⁸ ZnAl₂O₄/ZnO,¹⁶ and g-C₃N₄/ZnO.¹⁷ Especially, the novel binary or ternary ZnO-based photocatalyst could widen the response range of ZnO from UV to visible light, showing improved photodegradation efficiencies toward organic contaminants, for instance, BiOBr/Ag/ZnO,¹⁸ ZnO/BiOBr/C-Dots,¹⁹ ZnO/CoMoO₄,²⁰ ZnO/Ag/Ag₂WO₄,²¹ and ZnO/NiWO₄/Ag₂CrO₄.²² After the photodegradation reaction, the property of easy separation from the system is vital for recycling the photocatalyst. Thus, magnetic materials have been explored, for example, magnetic ZnO-based nanocomposites, magnetically separable graphitic carbon nitride, and their composites.^{23–25}

Nanometer-scale tungstates containing ZnWO₄, Bi₂WO₆, CuWO₄, and so forth are extensively studied in heterogeneous catalysis.²⁶ Recently, CuWO₄ has been proved as a new promising material in photodegradation organic contaminants and water splitting. CuWO₄ is an n-type semiconductor with the characteristics of excellent chemical stability and specific redox activity. Its band gap is about 2.2 eV, making it photosensitive to visible light.^{27,28} Besides, the matched positions of the conduction band (CB) and valence band (VB) of CuWO₄ and ZnO are favorable to electron transfer. Therefore, CuWO₄ is an ideal semiconductor to construct an n–n heterojunction with ZnO. At present, Mavrič *et al.* synthesized ZnO/CuWO₄ nanocomposite by the wet chemistry method to decompose methyl orange and terephthalic acid.²⁹ Only physical contact between ZnO and CuWO₄ was discussed in the abovementioned report, while the present study focuses on the hydrothermal synthesis of the n–n

heterojunction with strong interaction and proposed mechanism based on free radical trapping experiments. Shekofteh-Gohari reported visible-light-responsive ternary Fe₃O₄/ZnO/CuWO₄ nanocomposites designed by the reflux method. Among the products, 40 wt % Fe₃O₄/ZnO/CuWO₄ exhibited the best degradation performance for methylene blue (MB), the reaction rate constant of which was 0.0136 min^{−1}.³⁰

To the best of our knowledge, the fabrication of CuWO₄/ZnO composites by hydrothermal synthesis was rarely reported. In order to broaden the light response range, prolong the life of photogenerated electrons and holes and enhance photocatalytic activity of ZnO as well as provide the possible technical background support for actual water treatment, herein, we constructed a binary CuWO₄/ZnO n–n heterojunction. The composite photocatalysts with different weight percentages of CuWO₄ were synthesized by the hydrothermal method and characterized. Besides, the possible mechanism of photodegradation of MB under simulated sunlight irradiation was proposed based on the trapping experiments of free radicals.

2. RESULTS AND DISCUSSION

2.1. Structure and Morphology. Figure 1a demonstrates the X-ray diffraction (XRD) patterns of the samples. The main diffraction peaks at $2\theta = 31.7, 34.4, 36.2, 47.5, 56.6,$ and 62.9° are consistent with (100), (002), (101), (102), (110), and (103) planes of the hexagonal ZnO crystal (PDF#36-1451), respectively. For the as-synthesized CuWO₄ sample, the characteristic peaks can be indexed as the triclinic CuWO₄ phase (PDF#21-0307). Obviously, no impurity peaks resulting from reactants or intermediate phases are detected, demonstrating the pure and high crystallinity of CuWO₄/ZnO. Even the CuWO₄ content is as high as 4.5%, no metallic copper or copper tungsten oxide was found, mainly owing to the

Figure 2. Raman spectra of CuWO₄ (a) and 3% CuWO₄/ZnO and ZnO (b).

Figure 3. SEM images of pure CuWO₄ (a), ZnO (b), and 3% CuWO₄/ZnO (c). EDS spectrum of 3% CuWO₄/ZnO (d).

presence of W content as the amorphous phase, the low diffraction intensity, high dispersion, and the substitutional doping of W in the ZnO lattice.^{31–33} Furthermore, with the weight ratios of doped CuWO₄ varying from 2 to 4.5%, the intensities of diffraction peaks show no significant changes. Figure 1b,c reveals the XRD curves of the hybrid catalysts between $2\theta = 30\text{--}40$ and $45\text{--}65^\circ$, respectively. Interestingly, we observe the positions of peaks slightly shift toward the smaller angle in composites than single ZnO, ascribing to the interstition of limited W in the ZnO structure.⁵

Raman spectra were also applied to further determine the structures of the as-synthesized catalysts. The spectrum of CuWO₄ shown in Figure 2a agrees with triclinic CuWO₄ reported in the previous literature, the vibrational modes of which contain external and internal modes.²⁷ The external

mode comes from the motion of [WO₆] octahedra against Cu atoms while the internal mode relates to the vibration of O atoms against W inside the distorted octahedral [WO₆] clusters.³⁴ In Figure 2b, four major bands corresponding to ZnO are observed in both ZnO and 3% CuWO₄/ZnO. The characteristic peak at 438 cm⁻¹ results from the nonpolar optical phonon E2 (high) mode of wurtzite ZnO. Signals at 388 and 580 cm⁻¹ result from the A1 (TO) and E1 (LO) mode, respectively. The peak at 331 cm⁻¹ belongs to the second-order Raman spectrum generated by the zone.^{35,36} Notably, two new peaks assigned to the CuWO₄ crystal at 288 and 910 cm⁻¹ appear in CuWO₄/ZnO composites, whose wavenumbers both move toward a higher value in comparison with pure CuWO₄. Such a motion is caused by the geometrical elongation of CuWO₄ nanoparticles.³⁷ Overall, Raman spectra

Figure 4. TEM images of pure ZnO (a), CuWO₄ (b), and 3% CuWO₄/ZnO (c); HRTEM image of 3% CuWO₄/ZnO (d).

Figure 5. XPS spectra of 3% CuWO₄/ZnO: full spectra (a), Zn 2p (b), O 1s (c), and W 4f (d).

Figure 6. Nitrogen adsorption–desorption isotherms (a) and the pore size distribution curves (b) of the samples.

and XRD patterns together certify the successful fabrication of CuWO_4/ZnO photocatalysts.

Morphologies, chemical compositions, and distributions of the materials were analyzed. As shown in Figure 3a, the CuWO_4 sample is composed of a variety of aggregated particles, similar to triclinic structure crystals to some extent, whose diameter ranges from 50 to 100 nm. Pure ZnO displays irregular block-based flakiness, rod, and particle morphologies, as shown in Figure 3b. Furthermore, the overall morphology of the 3% CuWO_4/ZnO composite looks similar to that of pure ZnO, except that the higher density of granular crystals gathers on the lamellar surface on account of the introduction of CuWO_4 nanomaterial. As for the energy-dispersive spectrometry (EDS) spectrum shown in Figure 3d, Cu, Zn, O, and W elements are evidently observed in CuWO_4/ZnO photocatalysts. Additionally, Figure S1 exhibits the EDS elemental mapping images of the samples. As expected, all of the four elements are clearly detected, verifying the successful synthesis of CuWO_4/ZnO photocatalysts. Besides, mass and atomic percentages for elements in the 3% CuWO_4/ZnO composite are demonstrated in Table S1.

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the samples at different magnifications are displayed in Figure 4. ZnO shows flaky-like morphology while CuWO_4 is made up of the triclinic structure with the crystal diameter of 50–100 nm, agreeing with the SEM analysis. For 3% CuWO_4/ZnO shown in Figure 4c, a stable and uniform heterojunction structure is constructed between CuWO_4 and ZnO, indicating the strong interaction between the binary composite. In Figure 4d, two types of lattice fringes are observed in 3% CuWO_4/ZnO . The interplanar spacing at 0.26 nm is the result of the (002) plane for hexagonal ZnO while the fringe spaces at 0.39 nm are assigned to the (110) plane of CuWO_4 .^{18,38} HRTEM further confirms the formation of the CuWO_4/ZnO heterojunction.

The surface elemental composition and the corresponding valence states of 3% CuWO_4/ZnO were further monitored by X-ray photoelectron spectroscopy (XPS) analysis. In Figure 5a, the peaks located at 1019.55, 932.3, 529.5, 282.8, and 35.7 eV belong to Zn, Cu, O, C, and W elements, respectively. In addition, the weight and atom ratios of the abovementioned elements were summarized in the table. The C 1s peak is due to the residual carbon from the XPS instrument. In Figure 5b, the Zn 2p spectrum with decomposed peaks at 1018.15 and 1041.55 eV are attributed to the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ states of Zn(II).²¹ The binding energies at 35.3 and 37.4 eV, as

shown in Figure 5d, result from W $4f_{7/2}$ and W $4f_{5/2}$, verifying the existence of W(VI).³⁸ Additionally, the O 1s peak shown in Figure 5c could be deconvoluted into four peaks: 529.1 eV for Cu–O groups, 530.4 eV for W–O species, 529.5 eV for Zn–O groups, and 531.4 eV for O–H from absorbed water.^{38,39} XPS and the abovementioned analyses verify the successful preparation of CuWO_4/ZnO composites.

The Brunauer–Emmett–Teller (BET) measure was adopted to analyze the textural properties of the photocatalysts. In Figure 6a, based on the IUPAC classification, all samples exhibit type IV isotherms with the H3-type hysteresis loop, which suggests the mesoporous structure of the materials.^{31,32} In Figure 6b, the pore diameter distribution was calculated using the Barrett–Joyner–Halenda (BJH) approach using the adsorption branch.¹⁷ The pore size is observed to range from 2 to 15 nm, further verifying the mesoporous structure of the samples. The BET specific surface area, pore volume, and average pore diameter are listed in Table 1.

Table 1. BET Specific Surface Area, Pore Volume, and Average Pore Diameter of the Samples

sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	pore volume ($\text{cm}^3 \text{g}^{-1}$)	average pore diameter (nm)
ZnO	12.07	0.0270	8.007
2% CuWO_4/ZnO	9.35	0.0198	11.357
2.5% CuWO_4/ZnO	10.29	0.0235	10.246
3% CuWO_4/ZnO	10.88	0.0247	7.902
3.5% CuWO_4/ZnO	9.55	0.0209	11.341
4.5% CuWO_4/ZnO	12.38	0.0269	7.524

2.2. Optical Properties. Figure 7a illustrates the absorbance of photocatalysts under irradiation of 250–800 nm light. As can be seen, CuWO_4 exhibits fairly high light absorption capacity in both ultraviolet and visible light regions. ZnO hardly absorbs visible light, corresponding to the absorption edge around 400 nm. Meanwhile, the absorption alters slightly in the UV region after coating CuWO_4 nanoparticles on ZnO. Evidently, in the visible region, the intensity of the composite is much stronger than that of pristine ZnO, and the absorbance increases along with the rise in the CuWO_4 content because of the interfacial interaction between CuWO_4 and ZnO.^{40,41} In addition, Tauc plots $(\alpha h\nu)^{1/n}$ versus photoenergy ($h\nu$) were adopted to determine the variation in the band gap after coupling ZnO with CuWO_4 . In the abovementioned measure, α , h , and ν are named the

Figure 7. DRS (a) and Tauc plots $(\alpha h\nu)^2$ vs $(h\nu)$ (b) for ZnO and CuWO₄/ZnO composites.

absorption coefficient, Planck's constant, and photon frequency, respectively. For direct transitions, n is $1/2$, otherwise, n equals to 2. The intercept of the line is E_g .⁴² In Figure 7b and Table S2, the band gap of hybrids is slightly lower compared with that of ZnO (3.23 eV). The narrower band gap could facilitate the catalysts to utilize low frequency light of sunlight such as visible light and induce more electrons and holes to react in subsequent photodegradation.⁴³

Semiconductors are able to generate electron and hole pairs when irradiated by light of certain wavelength, and under this circumstance, part of them return to the ground state by recombination, thus coming into being photoluminescent.⁴⁴ According to the photoluminescence (PL) spectrum, the migration and recombination state of photoinduced electrons and holes in photocatalysts are surveyed.^{45,46} In Figure 8,

Figure 8. PL spectra of ZnO and CuWO₄/ZnO composites.

obviously, there are two sharp emission peaks in the curves: the one at around 410 nm is due to the recombination of electron–hole pairs and the other appearing at 471 nm cannot be defined because its emission mechanism is controversial.^{47,48} Pure ZnO exhibits the strongest intensity, indicating that the electrons and holes are very likely to recombine on the surface. After introducing CuWO₄ to ZnO, the intensity dramatically weakens, which manifests that CuWO₄ is able to separate photogenerated electrons–holes, and enhanced photocatalytic performance is expected accordingly.

2.3. Photocatalytic Activity and Stability. The photocatalytic degradation rate = $(1 - c_t/c_0) \times 100\%$, where c_0 and c_t mean the concentration of MB aqueous solution for the initial and at reaction time t , respectively.¹⁶ Before the photocatalytic activity test, we investigated the adsorption of the dye and samples by adding 3% CuWO₄/ZnO into MB aqueous solution, followed by stirring for 150 min in the dark. In Figure 9a, the degradation rate of MB without light is nearly 0, meaning that the concentration of MB is almost constant. Therefore, the effect of adsorption of the dye on the surface of the samples could be neglected. What is more, in the photodegradation test, the sample and dye were stirred for 30 min in the dark to establish an absorption and desorption balance. At the first glance, the degradation rates of CuWO₄/ZnO hybrid photocatalysts are remarkably higher than those of bare ZnO and CuWO₄ after irradiation for 120 min. This is ascribed to the enhanced visible light response and lowered photoexcited electrons–holes recombination efficiency after coupling CuWO₄ nanoparticles with ZnO.⁴⁹ Impressively, when the mass percentage of CuWO₄ alters from 2 to 3%, the rate increases from 83.3 to 98.9%. Nevertheless, noteworthy decay is discovered with a further increased dopant, indicating the presence of an optimum amount of CuWO₄ in CuWO₄/ZnO composites. Similar results have been obtained in the previous literature related to heterojunctions, such as, CuO/ZnIn₂S₄,² Ag/ZnO,⁵ ZnIn₂S₄/Bi₂WO₆,⁴¹ and CuO–CuWO₄/TiO₂.⁵⁰ This phenomenon can be due to the synergistic effects between CuWO₄ and ZnO. In this work, the optimum value for the amount of CuWO₄ intercalated into the ZnO lattice is 3 wt %, varying from the result in another report, which can be due to the different synthesis methods.^{29,51} When excessive CuWO₄ aggregates on the surface of ZnO, CuWO₄ absorbs the incident light and consequently impedes the access of photons to ZnO or CuWO₄ acts as recombination centers of photogenerated electrons and holes, resulting in reduced photodegradation efficacy.^{2,41}

Moreover, the kinetics for photodegradation of MB agree with the pseudo-first-order equation: $\ln(c_0/c_t) = kt$, where k is the rate constant.⁴⁶ Figure 9b reveals the linear simulation profiles of the samples. Clearly, in comparison with pristine ZnO and CuWO₄, the CuWO₄/ZnO composites display a higher k value, confirming the excellent photocatalytic performance of the CuWO₄/ZnO heterojunction. Among them, 3% CuWO₄/ZnO has the highest k of 0.03656 min^{−1}, which is ~ 11.3 and ~ 3.5 times as high as that of bare CuWO₄ and ZnO, respectively. Compared to the previous literature,³⁰

Figure 9. Photocatalytic degradation rate of MB (a) and kinetic linear simulation curves (b) of different samples. Recyclability of 3% CuWO₄/ZnO (c) and XRD patterns of fresh and after five cycles of reactions of the 3% CuWO₄/ZnO photocatalyst (d).

the CuWO₄/ZnO composites have better photocatalytic performance.

To the best of our knowledge, the optical absorption ability, photoinduced electrons–holes recombination rate, and surface properties are vital factors to impact the performances of catalysts during the practical photocatalytic process. Given this, in Table 1, nearly all the hybrids have smaller BET surfaces than pristine ZnO (12.07 m² g^{−1}). The reduced area of ZnO after introducing CuWO₄ is related to the excessive accumulation of CuWO₄ on the surface of ZnO during precipitation and centrifugation procedures. It should be noted that the hybrids exhibit much better photocatalytic performance than ZnO, suggesting that the high light absorption capacity and low electrons–holes recombination rate are more decisive than the specific surface area in this research.

Because of energy shortage and high cost in practical water treatment, the stability and reusability of photocatalysts are crucial factors that should be taken into consideration.⁵² Herein, the photocatalysts were centrifuged, washed, and dried after the reaction for repetitive photodegradation of MB under the same conditions. Surprisingly, 3% CuWO₄/ZnO can still remove 98.1% MB after five cycles of photodegradation, as shown in Figure 9c. In addition, Figure 9d displays the diffraction curves of the 3% CuWO₄/ZnO catalyst before and after the cycling reactions. As expected, the two curves display similar peak intensities and positions, manifesting the stable crystal structure of 3% CuWO₄/ZnO. Accordingly, we deduce that the as-synthesized catalysts possess sufficient stability and recyclability for water treatment, which are environmental

friendly and beneficial for lowering the cost in actual management.

2.4. Photocatalytic Mechanism. To determine the major species acted in the abovementioned photocatalytic reactions, free radical capture experiments were performed using BQ, IPA, TEOA, and AgNO₃ as the scavengers for •O₂[−], •OH, h⁺, and e[−], respectively. In Figure 10, the degradation rates decline dramatically after adding TEOA and IPA, implying h⁺ and •OH might play primary roles in the catalytic reaction. By

Figure 10. Photodegradation activities of MB by 3% CuWO₄/ZnO in the presence of different scavengers.

contrast, BQ and AgNO₃ suppress the photocatalytic process to some extent, which proves that $\cdot\text{O}_2^-$ and e^- make the moderate and minor contributions to the photodegradation of MB, respectively.

Based on the abovementioned trapping experiment results, a possible mechanism for the CuWO₄/ZnO catalyst with enhanced photocatalytic performance is proposed, as illustrated in Figure 11. The VB and CB potentials of CuWO₄ and

Figure 11. Proposed photocatalytic mechanism of CuWO₄/ZnO composites for degradation of MB under simulated sunlight irradiation.

ZnO were determined by empirical formulas: $E_{\text{VB}} = X - E^e + 0.5 E_g$, $E_{\text{CB}} = E_{\text{VB}} - E_g$. X represents the absolute electronegativity of the semiconductor (5.75 eV for ZnO and 6.23 eV for CuWO₄) and E^e is the energy of free electrons *versus* hydrogen (4.5 eV).^{53,54} The energies of VB and CB for ZnO calculated from the abovementioned equations are 2.865 eV and −0.365 eV, while the corresponding values for CuWO₄ are 2.83 eV and 0.63 eV. ZnO and CuWO₄ are both n-type semiconductors and their Fermi energy levels are close to the energies of their CB, respectively. The CuWO₄/ZnO n–n heterojunction has proved to be successfully constructed in the contact interface of the semiconductors. Under simulated solar light irradiation, the electrons of ZnO will be induced and transferred to the CB, leaving holes on the VB, and such a phenomenon occurs on CuWO₄ as well. Because the potential of the electrons in the CB of ZnO is lower than that of CuWO₄, the CB electrons of ZnO are able to migrate to the CB of CuWO₄ until the equilibrium of their Fermi levels. Even after the equilibrium has been achieved, the internal electric field formed on the interface of the CuWO₄/ZnO n–n heterojunction could still promote the photoinduced electron transfer.^{54–56} Such an electron transfer path restrains photoexcited electrons–holes from recombining and further enhances the photocatalytic activity. Simultaneously, the CB electrons of ZnO capture O₂ molecules and reduce them to $\cdot\text{O}_2^-$ owing to their lower potential [−0.365 V *vs* normal hydrogen electrode (NHE) in aqueous solution at pH 0] than that of O₂/ $\cdot\text{O}_2^-$ (−0.33 V *vs* NHE), while VB holes of ZnO and CuWO₄ oxidize H₂O or OH[−] to form $\cdot\text{OH}$. Afterward, $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ directly decompose MB to CO₂, H₂O, and other small molecules.

The whole reaction process is summed up as follows

3. CONCLUSIONS

To sum up, we hydrothermally fabricated CuWO₄/ZnO composite photocatalysts and characterized. The catalysts exhibited significantly improved photocatalytic performances. 3% CuWO₄/ZnO showed the highest degradation rate of 98.9% toward MB. This can be due to the fact that the composites possess higher visible light adsorption capacity and lower photogenerated electrons–holes recombination rate. The reusability test indicated that the as-prepared composites were stable and recyclable. Moreover, the photodegradation mechanism was proposed based on free radical trapping experiments. The synergistic effects and well-matched band gap energy of CuWO₄/ZnO heterojunctions facilitated the migration of photoinduced electrons from ZnO to CuWO₄, consequently restraining electrons–holes from recombining. In brief, CuWO₄/ZnO photocatalysts synthesized by the hydrothermal method show promising potential in industrial wastewater treatment.

4. EXPERIMENTAL SECTION

4.1. Materials. Copper sulfate pentahydrate (CuSO₄·5H₂O), zinc acetate dihydrate ((CH₃COO)₂Zn·2H₂O), and triethanolamine (TEOA) were purchased from Aladdin (Shanghai, China). Sodium tungstate dihydrate (Na₂WO₄·2H₂O), sodium hydroxide (NaOH), MB, and isopropyl alcohol (IPA) were supplied by Damao (Tianjin, China). Silver nitrate (AgNO₃) and *p*-benzoquinone (BQ) were provided by Macklin (Shanghai, China). All chemicals mentioned above were analytical reagents and used without purification.

4.2. Synthesis of CuWO₄. CuWO₄ samples were prepared by means of coprecipitation. In detail, 10 mmol CuSO₄·5H₂O and 10 mmol Na₂WO₄·2H₂O were separately dispersed in 80 mL of deionized water. Afterward, Na₂WO₄ was slowly dropped into CuSO₄ solution under fierce agitation. NaOH (0.1 mol/L) was introduced into the suspension until the pH was 8. Subsequently, the abovementioned suspension was refluxed at 85 °C for 3 h and cooled naturally to 25 °C. Through centrifugation, washing with absolute ethanol and deionized water, drying at 80 °C for 6 h, and calcination at 500 °C for 3 h, the final products were obtained.

4.3. Fabrication of CuWO₄/ZnO Photocatalysts. CuWO₄/ZnO photocatalysts were prepared *via* a hydrothermal process. First, 10 mmol (CH₃COO)₂Zn·2H₂O and excessive NaOH were added to 50 mL of deionized water, respectively. Next, a certain amount of obtained CuWO₄ was sonicated into (CH₃COO)₂Zn solution for 15 min, and then, NaOH was scattered into the abovementioned mixture drop-by-drop and agitated for 30 min. After that, the blend was transferred to a 250 mL Teflon-lined autoclave and reacted at 120 °C for 12 h and cooled to 25 °C naturally. Finally, the precipitates were centrifuged, washed with deionized water and absolute ethanol until the filtrate was neutral, and dried at 80 °C for 8 h. ZnO powders were prepared by a similar method without adding CuWO₄ for comparison. The as-prepared

CuWO₄/ZnO composites with different weight ratios of CuWO₄ were denoted as X CuWO₄/ZnO (X = 2, 2.5, 3, 3.5, and 4.5%).

4.4. Characterization. The crystal structures were analyzed using a Germany Bruker D8 ADVANCE X-ray diffractometer with Cu-K α irradiation. Raman spectra were detected on a LabRAM Aramis (France) with 532 nm laser. Scanning electron microscopy (SEM) was conducted on a JEOL JSM 6700 F instrument. The morphologies were investigated by the JEOL model JEM 2100 EX transmission electron microscope. XPS spectra were analyzed on the Axis Ultra apparatus. The absorbance was tested using a Hitachi U-3010 spectrophotometer using BaSO₄ as the reference. The PL spectrum was identified through an F-4500 fluorescence spectrophotometer excited with the wavelength of 320 nm. The specific surface areas, nitrogen adsorption–desorption isotherms, and pore size distribution were monitored via the Micromeritics ASAP2460 analyzer.

4.5. Photocatalytic Efficiency Test. To explore the photocatalytic activities of CuWO₄/ZnO catalysts, photo-degradation of MB aqueous solution tests was conducted. The light source was a 300 W xenon lamp. An AM 1.5 cutoff filter was adopted to acquire the simulated sunlight. First, 30 mg of the photocatalyst was dispersed in 150 mL, 20 mg/L MB aqueous solution. The mixture was constantly stirred for 30 min in the darkness, and an adsorption/desorption equilibrium was established. Then, the lamp was switched on, 3.5 mL of suspension was pipetted every 30 min, and centrifuged. Finally, the absorbance of the filtrate was detected using a UV-2450 spectrophotometer. The reactor temperature was maintained stable by circulating cold water.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c01220>.

Elemental mapping images of 3% CuWO₄/ZnO; weight and atomic percentages for different elements in the 3% CuWO₄/ZnO composite; and E_g , degradation rate, S_{BET} , and rate constant k of the samples (PDF)

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Notes

The authors declare no competing financial interest.

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