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Synthesis of pearl necklace-like ZnO–ZnWO₄ heterojunctions with enhanced photocatalytic degradation of Rhodamine B

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Pearl necklace-like ZnO–ZnWO₄ heterojunctions composites have been designed and synthesized. The photocatalytic activity of the ZnO–ZnWO₄ heterojunctions depended on the calcination temperature and ZnO–ZnWO₄ molar ratio. The ZnO–ZnWO₄ composites showed higher degradation efficiency than that of ZnO or ZnWO₄ individually. The photocatalytic reaction was enhanced due to the heterojunctions construction, which improved charge separation of the photogenerated electron–hole pairs.

1 Introduction

Using semiconductor photocatalysts to solve environmental remediation, especially waste water decontamination, has attracted extensive attention.¹ Zinc oxide (ZnO) plays an important role in degrading various organic pollutants due to its high activity, low cost, and environmental friendliness.² In the past decade, various morphological ZnO, such as rods, sheets, flowers, hollow nanostructures, porous structures, and core–shell structures, have been synthesized by hydrothermal, electrospinning, and sol–gel methods.^{2,3} Despite achieving great success in the controlled synthesis of single-component ZnO, the photocatalytic efficiency still needs to be improved because of the rapid recombination reaction of photogenerated charge carriers for single semiconductor. Recently, heterostructure composite materials have attracted much attention, because it can improve the primary properties of the constituent materials and create novel functions. Some heterostructure composites have been developed by coupling ZnO with other semiconductors, such as ZnO–WO₃,^{1b,4} ZnO–CdS,⁵ ZnO–TiO₂,⁶ ZnO–BiVO₄,⁷ and ZnO–SnO₂.⁸ Only few works, however, focused on the synthesis of ZnO–ZnWO₄ heterojunctions as well as their employment for the photodegradation of organic compounds.⁹

Zinc tungstate (ZnWO₄) has received considerable attention as an ultraviolet (UV) light driven photocatalyst due to its relatively high activity for degradation of organic compounds.¹⁰ Amouzegar *et al.* reported cubic-shaped nanocrystalline ZnWO₄

prepared by microwave-assisted precipitation technique showed high photocatalytic activity for the degradation of aqueous solution of Rhodamine B (RhB).¹¹ ZnWO₄ was also efficient for the decomposition of malachite green,¹² 4-chlorophenol,¹³ and methyl orange.¹⁴ Herein, ZnO–ZnWO₄ heterostructure with pearl necklace-like morphology was prepared by precipitation method followed by calcination process. Compared with single ZnO and ZnWO₄ phase, the as-obtained ZnO–ZnWO₄ heterostructure shows an enhanced photocatalytic activity in the photodegradation of RhB.

2 Experimental

2.1 Sample synthesis

For preparing the Zn(OH)₂ precursor, NH₄OH solution (25%) was slowly dropped into the vigorously stirred Zn(CH₃COO)₂·2H₂O solution with 0.06 mol L⁻¹ concentration until the pH value reached 10.6. The mixed solution was then heated at 80 °C for 2 h to produce Zn(OH)₂ precipitate. The precipitate was collected by pump filter and rinsed three times with deionized water and ethanol, respectively. Subsequently, the washed precipitate was dried at 80 °C overnight. For preparing tungstic acid (H₂WO₄) precursor, 15 g ammonium tungstate was dissolved in 150 mL deionized water under vigorous stirring for 30 min. Following, 30 mL nitric acid (3 mol L⁻¹) solution was slowly added into the above solution and the mixed solution was further stirred for 1 h at 80 °C. The precipitate produced was collected and washed three times with deionized water and ethanol, respectively. The washed sediment was dried at 80 °C overnight to form the H₂WO₄ precursor.

In order to obtain powders with ZnO/ZnWO₄ molar ratios equalling to 1/0.04, 1/0.08, 1/0.12, the amounts of the precursors were opportunely determined. The corresponding samples were denoted as Z-ZW_{0.04}, Z-ZW_{0.08} and Z-ZW_{0.12}, respectively. A certain amount of Zn(OH)₂ and H₂WO₄ with an equal number

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of Zn and W atoms were used to prepare pure ZnWO_4 . Pure ZnO was synthesized only using $\text{Zn}(\text{OH})_2$ as precursor. Finally, the photocatalysts were obtained by calcining the precursors for 2 h at different temperatures.

2.2 Characterization techniques

The phase composition and crystallinity of the prepared samples were analysed by X-ray diffraction (XRD) using a Rigaku-D diffractometer with Cu K_α radiation. The morphology was investigated by a scanning electron microscope (SEM), equipped with an energy dispersive X-ray spectrometer (EDS) suitable for element identification. Transmission electron microscopy (TEM) observation and scanning TEM (STEM)-EDS elemental mapping were performed by a FEI Tecnai G² F20. UV-diffuse reflection spectra were recorded by a Perkin Elmer Lambda 900 spectrophotometer. The photoluminescence (PL) spectra of the photocatalysts were obtained by a Hitachi F-4500 spectrofluorometer with an excitation wavelength of 325 nm.

2.3 Photocatalytic testing

RhB was used as model dye to evaluate the photocatalytic activity of ZnO, ZnWO_4 and ZnO-ZnWO_4 samples. Photodegradation of RhB was carried out in a 250 mL Pyrex reactor filled with deionized water (60 mL) containing RhB (10 mg L^{-1}) and the photocatalysts (50 mg). The suspension was stirred for 30 min in the dark to obtain adsorption-desorption equilibrium of the dye before illumination. After irradiation with a 250 W Hg lamp ($\lambda = 365 \text{ nm}$), a 5 mL aliquot was taken out at different time intervals and immediately centrifuged. The RhB concentration in the clear solution was analysed by optical characteristic absorption at a wavelength of 553 nm for an RhB solution.

3 Results and discussion

Fig. 1 shows the XRD patterns of ZnO, ZnWO_4 , and ZnO-ZnWO_4 composites calcined at 850°C for 2 h. The standard XRD patterns of ZnO (Fig. 1a) and ZnWO_4 (Fig. 1b) are corresponding to the hexagonal wurtzite and monoclinic phases, respectively. The diffraction peaks of ZnO and ZnWO_4 samples match well with the standard XRD patterns. A peak related to ZnO was detected at $2\theta = 34.42^\circ$ in Fig. 1b. No other impurity peaks were found in the XRD patterns. Fig. 1c displays the XRD patterns of the serials ZnO-ZnWO_4 composites. The intensity of the distinct peak indicates the different percentage content of individual ZnO and ZnWO_4 , respectively. With increasing ZnWO_4 content, the crystallite sizes of ZnO calculated by the Scherrer's equation were 43.97 nm, 39.55 nm, 37.74 nm and 37.40 nm, respectively. It indicates that the crystal growth of ZnO is inhibited by ZnWO_4 .

Fig. 2 shows the representative XRD patterns of Z-ZW_{0.08} samples calcined for 2 h at 750°C , 850°C and 950°C , respectively. With increasing temperature, the Full Width at Half Maximum (FWHM) of diffraction peaks (101) for ZnO and (111) for ZnWO_4 are 0.249° , 0.219° and 0.189° , and 0.250° , 0.204° and

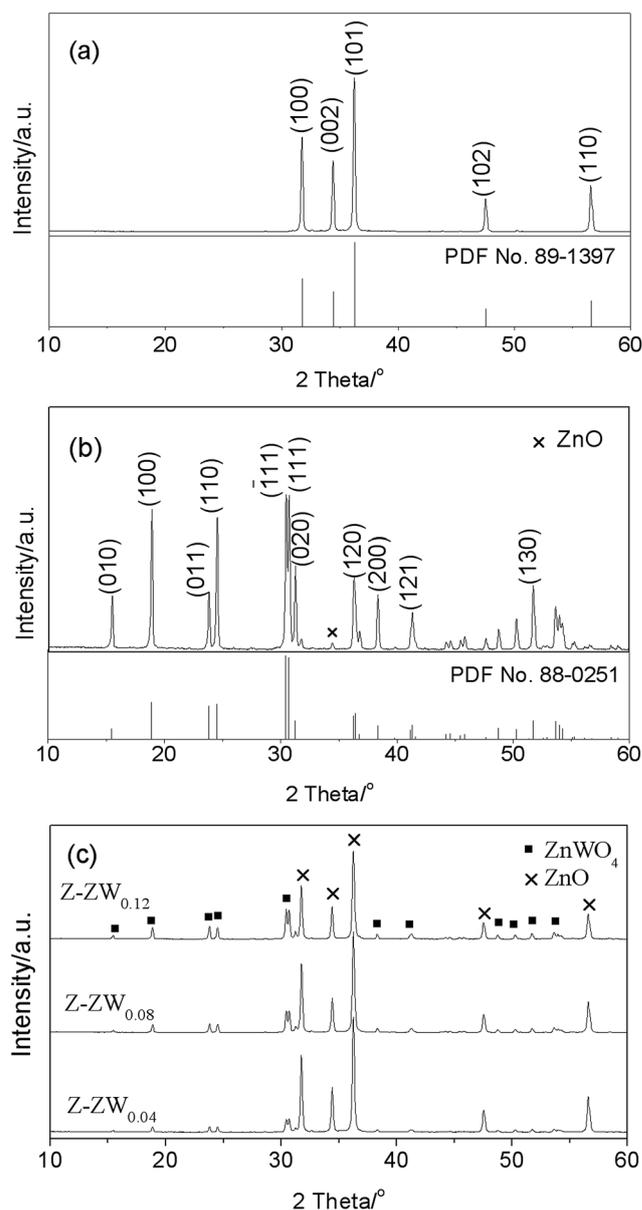


Fig. 1 XRD patterns of ZnO (a), ZnWO_4 (b), and ZnO-ZnWO_4 (c) composites calcined at 850°C for 2 h.

0.198° , respectively, showing the peaks of both phases become sharper. It indicates that the crystallinity can be improved by raising calcining temperature, which is consistent with the published works.^{3a}

The morphologies of the samples were observed by SEM. Fig. 3 shows the SEM images of ZnO, ZnWO_4 , and ZnO-ZnWO_4 heterojunctions calcined at 850°C for 2 h. It displays the rod-like ZnO with average length $3 \mu\text{m}$ and the needle-like ZnO with average length $4.5 \mu\text{m}$. After loading ZnWO_4 , the pearl necklace-like particles were found. Furthermore, hollow structures were observed at one side of the rod-like/needle-like particles as highlight by circles (Fig. 3b and c). With the increase of the ZnWO_4 content, the pearl necklace-like morphology become predominant and the hollow structure



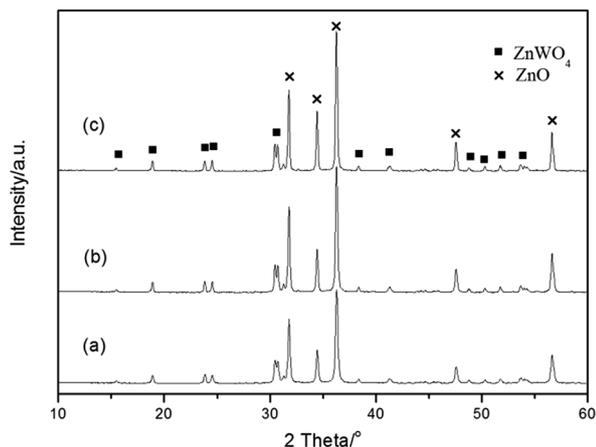


Fig. 2 XRD patterns of Z-ZW_{0.08} calcined for 2 h at different temperatures, 750 °C (a), 850 °C (b), and 950 °C (c).

diminished gradually, as shown in Fig. 3d. The particle size of ZnO decreased with increasing ZnWO₄ content. ZnO with smaller particle size and crystallite size contributes to their influence on charge carrier recombination rate and specific surface area, which may enhance the photocatalytic performance.¹⁵ For the ZnWO₄ (Fig. 3e), some particles adhere to slantprism-like ZnWO₄ surface, while others agglomerated. Clearly, the morphologies of ZnO–ZnWO₄ samples depend on the molar ratio of ZnO to ZnWO₄.

The element composition of the ZnWO₄ sample was analyzed by EDS. Zn and W elements were detected in

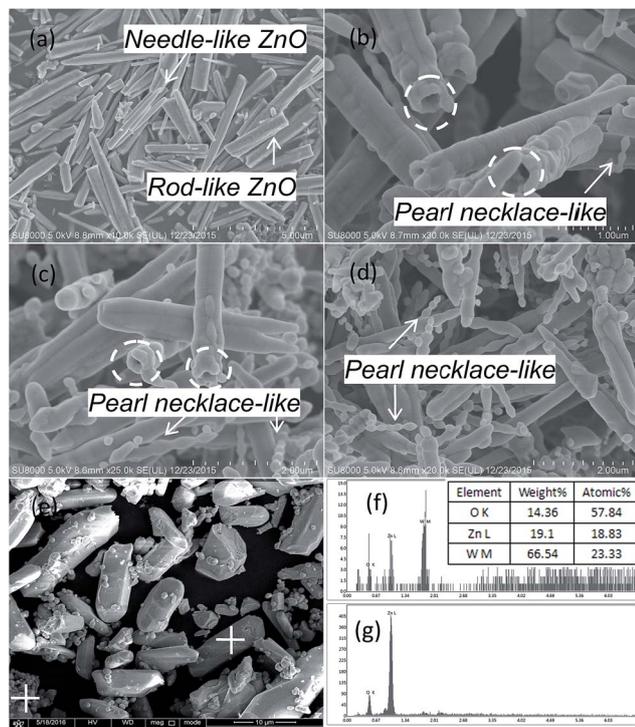


Fig. 3 SEM micrographs of ZnO (a), Z-ZW_{0.04} (b), Z-ZW_{0.08} (c), Z-ZW_{0.12} (d), ZnWO₄ (e), and EDS spectra of ZnWO₄ (f and g).

slantprism-like shape ZnWO₄ sample and the element ratio of W to Zn was *ca.* 1 : 1 (Fig. 3f, carbon derived from the conductive adhesive). However, only Zn and O elements were detected in agglomerated ZnWO₄ particles (Fig. 3g). EDS confirmed that there is a small amount of ZnO in the ZnWO₄ sample, which is consistent with the XRD result.

As one kind of ZnO–ZnWO₄ heterojunctions, Z-ZW_{0.08} was further characterized by TEM and STEM-EDS elemental mapping. The low-magnification TEM image demonstrates that the Z-ZW_{0.08} shows pearl necklace-like morphology, as presented in Fig. 4a. The high-resolution TEM (HR-TEM) image (Fig. 4b) clearly displays that the ZnWO₄ nanoparticles with a particle size of about 3 nm distribute on the surface of ZnO. The elemental mapping (Fig. 4c) shows that W element is uniform distributed in the sample, which demonstrates ZnWO₄ nanoparticles distribute well on the surface of ZnO.

The ultraviolet-visible (UV-vis) absorption spectra of ZnO, ZnWO₄ and ZnO–ZnWO₄ composites are shown in Fig. 5. The band gap values (E_g) of the photocatalysts were determined by extrapolating the linear part of the plots of $(\alpha h\nu)^2$ versus the energy of exciting light.^{9b} The calculated band gap energies of ZnO, Z-ZW_{0.08}, Z-ZW_{0.12}, and ZnWO₄ are 3.20 eV, 3.19 eV, 3.18 eV and 3.17 eV, respectively. It can be seen that the presence of ZnWO₄ caused the absorption shift towards long wavelength region, which may result from the formation of the energy level of vacancy oxygen since W⁶⁺ was doped into the crystal lattice of ZnO.¹⁶

The photocatalytic activities of the powders were tested by degradation of RhB solution under UV light irradiation. Fig. 6 shows the effect of calcination temperature on the photocatalytic activity of Z-ZW_{0.08} sample. The highest efficiency was obtained when the sample was calcined at 850 °C, whereas the powders calcined at 750 °C and 950 °C are less active. The

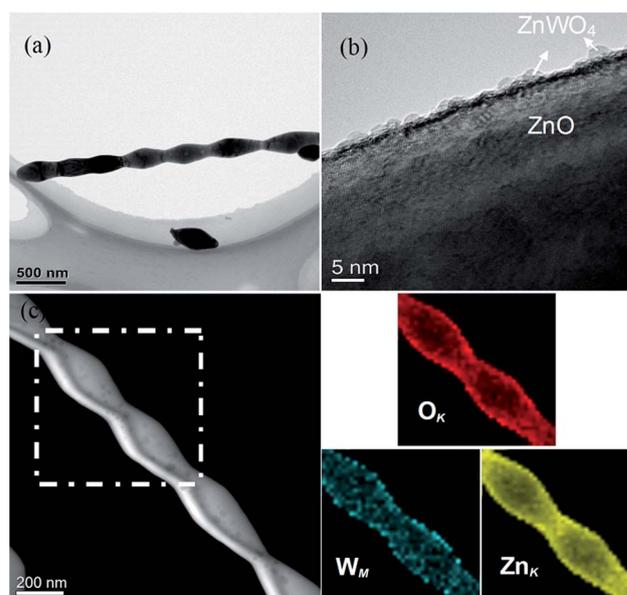


Fig. 4 Low-magnification TEM (a), HR-TEM (b) images and STEM-EDS elemental mapping (c) of Z-ZW_{0.08}.



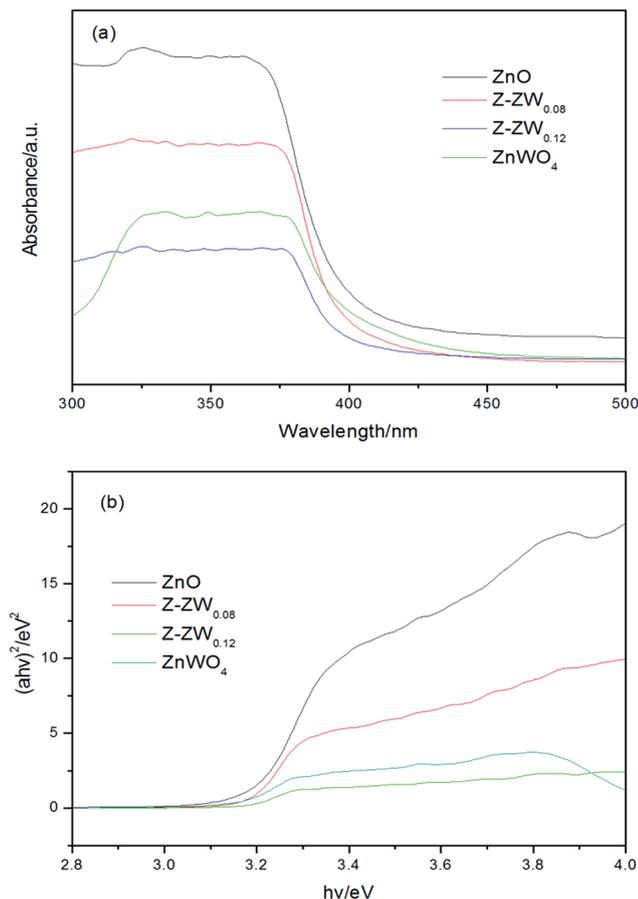


Fig. 5 (a) UV-vis diffuse reflectance spectra, (b) $(\alpha h\nu)^2$ versus energy plots.

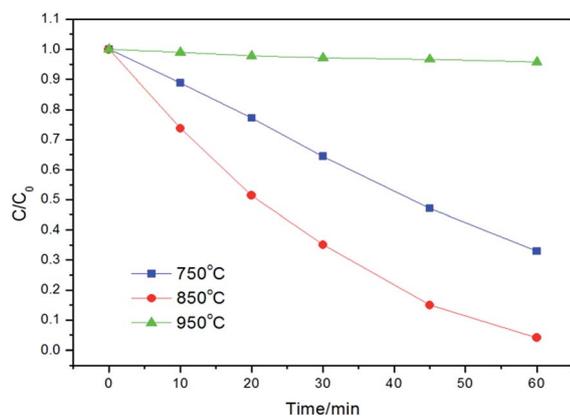


Fig. 6 Photodegradation kinetics of RhB over Z-ZW_{0.08} calcined for 2 h at different temperatures.

crystallinity of the sample increased with raising the calcination temperature, which reduced the recombination of photo-generated carriers.^{9b,17} However, the higher calcination temperature resulted in the decrease of surface area, larger particle size, and decrease of dispersion in solution, which caused an adverse effect on the harvest of light and the adsorption of dye, producing a negative effect on activity.

Fig. 7a and b show the kinetics of RhB degradation in the presence of ZnO, ZnWO₄ and ZnO–ZnWO₄ composites calcined at 850 °C. The degradation of RhB could be described by the first-order kinetics of $-\ln(C_t/C_0) = kt$, where k is the apparent reaction rate constant, and C_0 and C_t are the initial concentration and the concentration at reaction time of RhB, respectively. After 60 min of UV irradiation, 8%, 71%, 91%, 96% and 86% of RhB were degraded by ZnWO₄, ZnO, Z-ZW_{0.04}, Z-ZW_{0.08} and Z-ZW_{0.12}, respectively. The photoactivity of ZnWO₄ was very low compared to that of ZnO, but all the ZnO–ZnWO₄ samples showed higher photocatalytic activity than single ZnO or ZnWO₄. The photocatalytic activities of the composites were found to be related to the ZnO/ZnWO₄ molar ratio. The Z-ZW_{0.08} shows the highest photocatalytic activity. In the Z-ZW_{0.12} sample, a large amount of free ZnWO₄ particles exists, which are less activity, leading to a lower photoactivity.⁴ Therefore, there is an optimum ZnWO₄ content that leads to maximum photocatalytic efficiency. The k values were calculated by the initial slope of the concentration versus time profiles (Fig. 7b). It can be seen that Z-ZW_{0.08} sample owns the highest rate constant of 0.035 min⁻¹.

The recombination of electron–hole pairs can release energy, which can be detected by PL emission. Lower photoluminescence intensity indicates a lower recombination of electron–hole pairs, resulting in superior photocatalytic activity.^{1e} The PL spectra of the ZnO, ZnWO₄ and Z-ZW_{0.08} samples obtained at the excitation wavelength of 325 nm are shown in Fig. 7c. The PL intensities of ZnO and Z-ZW_{0.08} could be ignored compared with that of ZnWO₄. The enlarged PL spectra of ZnO and Z-ZW_{0.08} at the range of 400–600 nm in the inset panel shows that the composites sample has a lower recombination rate of photogenerated electron–hole pairs. The PL results display the importance of the heterostructure of ZnO/ZnWO₄ in blocking the recombination of electrons and holes. In order to

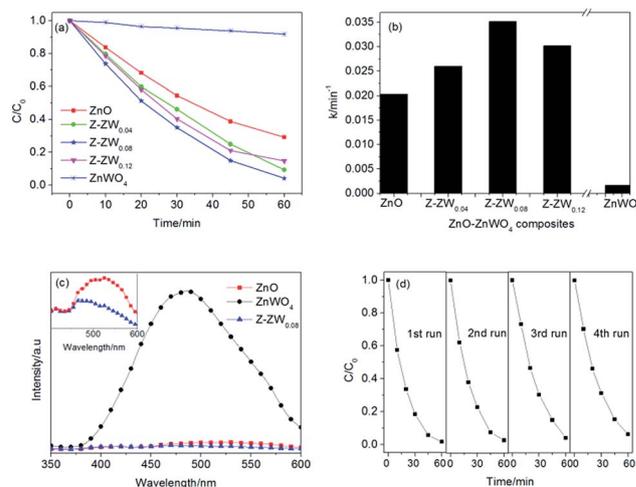


Fig. 7 Photodegradation kinetics of RhB over ZnO, ZnWO₄, and ZnO–ZnWO₄ composites calcined at 850 °C for 2 h (a and b); room temperature PL spectra of as-synthesized samples obtained at the excitation wavelength of 325 nm (c); cycling runs for the photocatalytic degradation of RhB over Z-ZW_{0.08} (d).



evaluate the stability of the Z-ZW_{0.08} photocatalyst, a recycling test was carried out. The result is displayed in Fig. 7d. The degradation rate of RhB still remained over 90% after four cycles.

The enhancement in the photocatalytic activity of Z-ZW_{0.08} sample arose from the heterojunctions between ZnO and ZnWO₄. The formation of the heterojunctions may improve the charge separation efficiency of photoexcited carriers in ZnO–ZnWO₄ composites. The potentials of valence band (VB) and conduction band (CB) of a semiconductor can be calculated according to the following empirical equations:

$$E_{\text{VB}} = X - E^{\text{e}} + 0.5E_{\text{g}} \quad (1)$$

$$E_{\text{CB}} = E_{\text{VB}} - E_{\text{g}} \quad (2)$$

where E_{VB} is the valence band edge potential, E_{CB} is the conduction band edge potential, X is the electronegativity of the semiconductor, which is the geometric mean of the electronegativity of the constituent atoms, E^{e} is the energy of free electrons on the hydrogen scale (about 4.5 eV), E_{g} is the band gap energy of the semiconductor.^{1e,1h} Based on the eqn (1) and (2), the E_{CB} potentials of ZnO and ZnWO₄ were calculated to be –0.31 and 0.145 eV, respectively. The E_{VB} potentials of ZnO and ZnWO₄ are determined to be 2.89 and 3.315 eV, respectively. A mechanism for electron–hole separation and transport of ZnO–ZnWO₄ heterojunctions is proposed (Fig. 8).

Both ZnO and ZnWO₄ are n-type semiconductors and their band gaps match well with each other to form type II heterojunction.¹⁸ The CB of ZnO is lower than that of ZnWO₄, thus photogenerated electrons transfer easily from CB of ZnO to that of ZnWO₄ through the well-developed interface, and the photo-induced holes shift from VB of ZnWO₄ to that of ZnO. Therefore, the ZnO–ZnWO₄ heterojunctions could act as an active center for hindering the rapid recombination of photo-generated electron–hole pairs. The electrons accumulated in the CB of ZnWO₄ can be captured by O₂ to produce superoxide radical ($\cdot\text{O}_2^-$) and hydrogen peroxide (H₂O₂), which can interact to produce a powerful oxidant (hydroxyl radical, $\cdot\text{OH}$) to decompose RhB. The holes accumulated in the VB of ZnO take

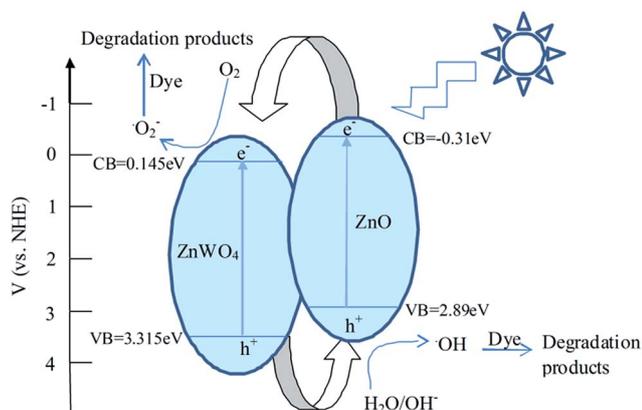


Fig. 8 Degradation schematic mechanism of RhB over ZnO–ZnWO₄ composites.

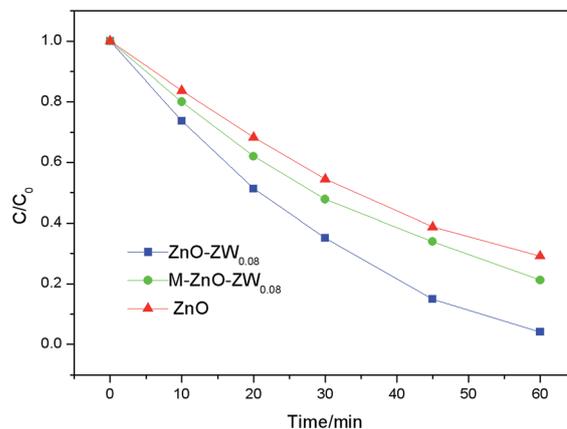


Fig. 9 Photocatalytic degradation of RhB over ZnO, Z-ZW_{0.08}, and M-Z-ZW_{0.08}.

part in the oxidation process to make OH[−] or H₂O species to produce reactive hydroxyl radicals.^{1a,19}

To further confirm the heterojunctions effect, the photocatalytic degradation of RhB was also studied in the presence of a mechanical mixture of ZnO and ZnWO₄, which is labelled as M-Z-ZW_{0.08}. As shown in Fig. 9, the photocatalytic activity of the M-Z-ZW_{0.08} sample is higher compared to that of ZnO but much lower than that of Z-ZW_{0.08}. This result demonstrates that the Z-ZW_{0.08} composite can form intimate interface in the heterojunctions, rather than form loose interfaces existing in the mechanically mixed samples.

4 Conclusions

The pearl necklace-like ZnO–ZnWO₄ heterojunctions were successfully synthesized by precipitation method followed by calcination. The photocatalytic activity of ZnO–ZnWO₄ composites was found to be dependent on the calcination temperature and ZnO/ZnWO₄ mol ratio. The photoefficiency of the ZnO–ZnWO₄ heterojunctions was better than that of ZnO and ZnWO₄. Z-ZW_{0.08} composite powders show the best photocatalytic degradation performance for degradation of RhB with degradation efficiency about 96% under UV irradiation in 60 min. The enhanced photoactivity is due to the reduction in the recombination of photo-generated electrons and holes. This work provides a facile method to design and fabricate ZnO–ZnWO₄ heterojunctions with special morphology.

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