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Article

Visible-light-induced photocatalytic performances of ZnO–CuO nanocomposites for degradation of 2,4-dichlorophenol

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ABSTRACT

Nanostructured ZnO and CuO, and coupled oxides, i.e., ZnCu, Zn₂Cu, and ZnCu₂, with ZnO:CuO molar ratios of 1:1, 2:1, and 1:2, respectively, were successfully prepared through a simple, one-step, microwave-assisted urea–nitrate combustion synthesis, without the use of organic solvents or surfactants. The prepared samples were characterized using X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, energy-dispersive X-ray analysis, transmission electron microscopy, Fourier-transform infrared spectroscopy, diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The optical absorption of ZnO extended into the visible region after CuO loading. The photocatalytic activities of ZnO, CuO, and the coupled oxides were evaluated based on photodegradation of 2,4-dichlorophenol under visible-light irradiation. The coupled metal oxide Zn₂Cu showed the best photocatalytic activity; this was mainly attributed to the extended photore sponsive range and the increased charge separation rate in the nanocomposite. The photocatalytic degradation process obeyed pseudo-first-order kinetics. The results suggest that the coupled metal oxide Zn₂Cu has potential applications as an efficient catalytic material with high efficiency and recyclability for the photocatalytic degradation of organic pollutants in aqueous solution under visible-light irradiation.

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1. Introduction

Heterogeneous photocatalysis has become an important advanced oxidation process for environmental clean-up. TiO₂ and ZnO are well-known photocatalysts, but their wide band gaps, around 3.2 eV, require an excitation wavelength in the ultraviolet (UV) region, and the high recombination rate of the photogenerated electron–hole pairs reduces the photocatalytic efficiency. Much effort has been made to improve the photocatalytic efficiencies of ZnO nanostructures, e.g., by changing their morphologies [1,2], loading with noble metal [3,4], non-metal doping [5], addition of transition metals [6], and coupling with other metal oxides [7–9].

CuO is an important *p*-type material; it has a narrow band gap, is a non-toxic and readily available semiconductor, and has been used to improve the photocatalytic efficiencies of wide band gap semiconductors such as TiO₂, ZnO, and SnO₂ [10–12]. CuO–ZnO mixed metal oxide nanoparticles are more efficient photocatalysts than ZnO, because there is reduced recombination of generated electron–hole pairs in the coupled system [13,14]. Coupling between two semiconductors with appropriate band positions, such as ZnO and CuO, can extend the ZnO photore sponsive range to visible light and shift the photocatalytic process to the ordinary solar-light range; a major portion of solar light is in the visible range [15–17].

ZnO–CuO coupled nanometal oxides have been prepared

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using various methods such as coprecipitation [16], thermal decomposition [15], sol-gel [18], hydrothermal [19], and photodeposition methods [20]. We used microwave-assisted solution combustion synthesis to prepare individual and coupled ZnO–CuO nanometal oxides. Combustion synthesis, which is based on the principles of propellant chemistry, has been extensively used to prepare metal oxide powders, because the process is simple and fast, and gives highly homogeneous fine powders [21,22]. In the synthesis, a thermally induced redox reaction takes place between an oxidant and a fuel. There are many types of combustion synthesis; they mainly differ in terms of the physical states of the reactants or the combustion mode [23].

We adapted the urea–nitrate combustion synthesis for the preparation of individual and coupled ZnO–CuO nanometal oxides; the fuel was urea, a metal nitrate was the oxidant, and the reaction was performed in a microwave oven. ZnO–CuO nanocomposites were successfully synthesized for the first time using this method. Microwave irradiation induces the rotation of molecular dipoles, leading to a higher rate of molecular collisions, generating a large amount of heat within the sample. Microwave-induced interactions occur at the molecular level, therefore the temperature distribution in the solution is homogeneous, causing an explosive reaction followed by vigorous evolution of gases, and nanostructure formation. The reaction can be performed in a domestic microwave oven and the operation is clean, fast, and cheap, consumes less energy than other methods, and no harmful organic solvents are used. The prepared ZnO–CuO nanoparticles were used for the photocatalytic degradation (PCD) of 2,4-dichlorophenol (2,4-DCP) under visible-light irradiation. 2,4-DCP is a precursor in the manufacture of the widely used herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) and is also the major product of 2,4-D transformations caused by solar photolysis and microbial activities in soil and natural water. It is one of the 129 priority pollutants listed by the United States Environmental Protection Agency, because of its carcinogenicity, toxicity, and persistence [24–26].

2. Experimental

2.1. Synthesis

All reagents were analytical grade and obtained from Merck, India. They were used as received, without further purification.

ZnO nanoparticles were prepared as follows. Zinc nitrate and urea, in a 1:4 molar ratio, were dissolved separately in deionized water (10 mL). The solutions were mixed and stirred for 1 h, giving a clear solution. This solution was exposed in a domestic microwave oven (2.45 GHz and 850 W) for 7 min. The solution boiled and underwent dehydration, followed by decomposition, with the evolution of gases. When the solution reached the point of spontaneous combustion, it vaporized and immediately became solid. The obtained solid was washed well with distilled water and ethanol and dried in a hot-air oven at 80 °C for 2 h. Gaseous products, i.e., N₂, NO₂, CO₂, and H₂O (as water vapor), were released during combustion. CuO nanopar-

ticles were produced using the same procedure, using copper nitrate instead of zinc nitrate; the copper nitrate–urea molar ratio was 1:3. Zinc nitrate and copper nitrate in 1:1, 2:1, and 1:2 molar ratios were dissolved in deionized water, mixed with the required amounts of urea, and treated in a microwave oven to synthesize coupled ZnO–CuO with 1:1, 2:1, and 1:2 molar ratios, denoted by ZnCu, Zn₂Cu, and ZnCu₂, respectively.

2.2. Characterization

The crystallinities of pure ZnO, CuO, and the coupled oxides ZnCu, Zn₂Cu, and ZnCu₂, were determined using X-ray diffraction (XRD; X'pert X-ray diffractometer, Philips; Cu K α radiation, λ = 0.154 nm). X-ray photoelectron spectroscopy (XPS) was performed using a Kratos-Axis 165 instrument equipped with dual Al–Mg anodes, using Mg K radiation ($h\nu$ = 1253.6 eV) and operated at 5 kV and 15 mA with a pass energy of 80 eV and increments of 0.1 eV. Morphological studies and energy-dispersive X-ray (EDX) analysis of ZnO, CuO, and ZnO–CuO were performed using field-emission scanning electron microscopy (FE-SEM; Hitachi S-4800). Transmission electron microscopy (TEM) images were obtained using a Tecnai FE12 instrument operated at 120 kV. Fourier-transform infrared (FT-IR) spectra were obtained using a Bruker Tensor 27 FT-IR spectrophotometer. Diffuse reflectance (DR) UV-visible (UV-vis) spectroscopy was performed (Cary 100 UV-vis spectrophotometer) to estimate the band gap energies. Photoluminescence (PL) spectra were obtained using a Varian Cary Eclipse fluorescence spectrophotometer.

2.3. Photocatalytic reactor set-up and degradation procedure

PCD experiments were performed using a Heber annular visible photoreactor (shown in the Supporting Information). A 300-W tungsten–halogen lamp was used as the visible-light source. The lamp was placed in a borosilicate immersion well at the center of the reactor; the well was surrounded by a circulating water jacket to cool the lamp. The cylindrical borosilicate reactor tubes were of height 36 cm and diameter 1.6 cm. The top portion of the reactor had ports for sample tubes, gas purging, and a gas outlet. PCD was performed by mixing aqueous 2,4-DCP solution (100 mL) and a fixed weight of pure ZnO, CuO, or coupled ZnO–CuO photocatalyst. Prior to irradiation, the slurry was stirred for 30 min to reach adsorption-desorption equilibrium, followed by visible-light irradiation. Air was continuously bubbled into the sample tubes, using an air pump, to provide a constant source of dissolved O₂. Aliquots were withdrawn from the suspension at specific time intervals and immediately centrifuged at 1500 r/min.

The extent of phenol degradation was monitored using UV-vis spectroscopy (Perkin–Elmer, Lambda 25). The effect of the solution pH was studied by adjusting the pH of the phenol solution containing the catalyst, using dilute HCl and NaOH. The solution pH was measured using a digital pH meter (Hanna pHep HI 98107, 0.2–0.5 pH unit accuracy). The PCD efficiency (η) was calculated as $\eta = C_0 - C_t / C_0 \times 100$, where C_0 is the initial concentration of 2,4-DCP, and C_t is the concentration of 2,4-DCP

at time t . To check the stability and reusability of the catalyst, the resulting suspension was centrifuged at the end of the experiment, and the separated catalyst was reused in subsequent tests. All measurements were repeated twice and the results were reproducible within the experimental error ($\pm 3\%$).

3. Results and discussion

3.1. XRD analysis

The XRD patterns of ZnO, CuO, and ZnO-CuO are shown in Fig. 1. The diffraction peaks for pure ZnO and CuO are in good agreement with those of hexagonal wurtzite ZnO (JCPDS36-1451) and monoclinic CuO (JCPDS05-0661), respectively. The diffraction peaks of both the samples are well defined, showing that the samples are crystalline. The ZnO diffraction peaks are located at $2\theta = 31.84^\circ, 34.52^\circ, 36.33^\circ, 47.63^\circ, 56.71^\circ, 62.96^\circ, 68.13^\circ, \text{ and } 69.18^\circ$, corresponding to the (100), (002), (101), (102), (110), (103), (112), and (201) planes, respectively. This pattern has been indexed as the hexagonal wurtzite phase of ZnO, with lattice constants $a = b = 0.324$ nm and $c = 0.521$ nm.

The diffraction peaks of CuO at $2\theta = 32.49^\circ, 35.63^\circ, 38.81^\circ, 48.91^\circ, 53.56^\circ, 58.31^\circ, 61.63^\circ, 66.39^\circ, 68.08^\circ, 72.41^\circ, \text{ and } 75.23^\circ$ correspond to the (110), ($\bar{1}11$), (111), ($\bar{2}02$), (020), (202), ($\bar{1}13$), ($\bar{3}11$), (220), (311), and ($\bar{2}22$) planes, respectively. This pattern has been indexed as the monoclinic phase of CuO, with lattice constants $a = 0.468$ nm, $b = 0.343$ nm, and $c = 0.513$ nm. For the coupled metal oxides ZnCu, Zn₂Cu, and ZnCu₂, two sets of diffraction peaks are observed; these are ascribed to hexagonal ZnO and monoclinic CuO. No peaks from other phases or impurities were detected. The absence of peak shifts in the XRD patterns of ZnO–CuO indicates that CuO is present on the surface of ZnO and is not substituted into the ZnO lattice [27].

The crystallite sizes d of ZnO, CuO, and coupled metal oxides were calculated using the Debye–Scherrer formula, $d = 0.89\lambda/\beta\cos\theta$ [28], where 0.89 is Scherrer's constant, λ is the X-ray wavelength, θ is the Bragg diffraction angle, and β is the full width at half maximum (FWHM) of the diffraction peak.

Fig. 1. XRD patterns of samples.

The crystallite sizes, which were derived from the FWHMs of the most intense peaks, are listed in Table 1. The ZnO crystallite sizes decreased as the CuO loading increased [29]. The crystallinity degree of the coupled metal oxide Zn₂Cu was higher than those of ZnCu and ZnCu₂, as indicated by the sharp peaks [30].

3.2. XPS analysis

XPS is an important analytical tool for understanding the oxidation states of transition-metal ions and the surface properties of materials. The binding energies in the XPS spectra were calibrated using C 1s (284.8 eV); the results are shown in Fig. 2. The survey spectrum in Fig. 2(a) shows the presence of Zn, Cu, O, and C elements, without any contaminant species. The Zn 2p core level XPS spectrum in Fig. 2(c) is symmetric and centered at 1022.47 eV; this peak is attributed to Zn 2p_{3/2} of Zn(II) and the peak at 1045.53 eV is attributed to Zn 2p_{1/2} of Zn(II) [31]. Fig. 2(d) shows the Cu 2p core level XPS spectrum. Peaks corresponding to the core level 2p_{3/2} and 2p_{1/2} transitions of Cu(II) appear at 934.20 and 953.93 eV, respectively, along with satellites at 942 and 962 eV; these results agree well with the literature values [32,33]. The broad O 1s peak (Fig. 2(b)) consists of two small peaks, one located at 531.08 eV and the other at 532.49 eV. The former arises from inherent O atoms bound to metals, such as Cu and Zn, and the latter comes from surface hydroxyl species [34]. Surface hydroxyl groups play an important role in the photocatalytic process, because they can be trapped by holes generated under irradiation to form hydroxyl radicals, which can suppress electron–hole recombination, thereby increasing the photocatalytic efficiency [35].

3.3. FT-IR analysis

The FT-IR spectra of ZnO, CuO, and Zn₂Cu are shown in Fig. 3. ZnO shows a wide band at about 430 cm^{−1}, which is attributed to the Zn–O bond. CuO has a broad peak in the range 490–600 cm^{−1}, corresponding to the Cu–O bond [36]. The peak in the range 484–593 cm^{−1} for the coupled metal oxide Zn₂Cu corresponds to the combined absorptions of Zn(II)–O and Cu(II)–O bonds [15,16]. The broad absorption at 3430 cm^{−1} present in all samples is assigned to the stretching vibration of adsorbed water, because nanocrystalline materials have high surface to volume ratios, and therefore adsorb moisture. The weak absorption at 1650 cm^{−1} is attributed to the bending vibration of the adsorbed water molecules [37,38]. The less intense peaks, at 1030 and 1360 cm^{−1}, are assigned to the C–O and O–C–O stretching modes, respectively, of carbonate species formed on the catalyst surfaces from adsorbed CO₂ [39].

Table 1
Band gaps, rate constants, and R^2 values.

Catalyst	Crystallite size	Band gap (eV)	k (min ^{−1})	R^2
ZnO	44.5	3.17	0.0027	0.9956
CuO	22.2	2.15	0.0050	0.9891
ZnCu	36.3	2.98	0.0048	0.9904
Zn ₂ Cu	37.5	2.91	0.0070	0.9929
ZnCu ₂	34.4	2.89	0.0054	0.9912

Fig. 2. XPS spectra of Zn_2Cu . (a) Survey spectrum; (b) O 1s; (c) Zn 2p; (d) Cu 2p.

3.4. Morphological and size analyses

The morphologies and particle sizes of the individual and coupled metal oxides were investigated in detail using FE-SEM and TEM analyses. The FE-SEM images of ZnO, CuO, and the

Fig. 3. FT-IR spectra of ZnO (1), CuO (2), and Zn_2Cu (3).

coupled metal oxide Zn_2Cu , at different magnifications are shown in Fig. 4. ZnO nanoparticles show that they are irregular spheres. The CuO nanoparticles are spherical with sizes in the range of 15–20 nm, and the Zn_2Cu consists of small spherical particles of CuO dispersed on the surface of ZnO. The FE-SEM results show that the particles are aggregated; this is caused by the large amount of heat generated during the combustion reaction.

EDX was used to determine the compositions of the nanoparticles. The spectra of ZnO, CuO, and Zn_2Cu are shown in Fig. 5. ZnO has peaks corresponding to Zn and O, CuO has Cu and O peaks, and Zn_2Cu has Zn, Cu, and O peaks; the respective compositions are shown in the figure. The compositions of ZnO and Zn_2Cu show the presence of oxygen vacancies.

The morphologies and particle sizes of ZnO and Zn_2Cu were further investigated using TEM; the results are shown in Fig. 6.

Both samples had a largely aggregated spherical morphology. The ZnO particle size is in the range of 40–50 nm, and that of the coupled metal oxide is in the range of 10–40 nm. This is in good agreement with the XRD results. The selected-area electron diffraction (SAED) patterns (insets) show the fine polycrystalline natures of ZnO and Zn_2Cu .

Fig. 4. FE-SEM images of ZnO (a, b), CuO (c, d), and Zn₂Cu (e, f).

3.5. DR spectroscopy

Optical DR spectra of ZnO, CuO, ZnCu, Zn₂Cu, and ZnCu₂ were recorded at room temperature. The band gap energy was estimated using the Tauc equation, $(h\nu\alpha)^{1/n} = A(h\nu - E_g)$, where h is Planck's constant, ν = the vibration frequency, α is the absorption coefficient, E_g is the band gap energy, and A is a proportionality constant. The value of the exponent n indicates the nature of the sample transition [40,41]. The acquired DR spectrum was converted to a Kubelka–Munk function; the vertical axis is converted to the quantity $f(r)$, which is proportional to the absorption coefficient, α , therefore α in the Tauc equation is

substituted by $f(r)$. For experiments, the relationship therefore becomes $[f(r)h\nu]^2 = A(h\nu - E_g)$. The Kubelka–Munk plots are shown in Fig. 7.

Extrapolation of the linear regions in the plots of $[f(r)h\nu]^2$ versus $h\nu$ gives E_g values for ZnO and CuO of 3.17 and 2.15 eV, respectively, and those for ZnCu, Zn₂Cu, and ZnCu₂ are 2.98, 2.91, and 2.89 eV, respectively. The addition of CuO alters the absorption edge of ZnO, and these of the coupled metal oxides are slightly red shifted compared with that of ZnO. This is mainly attributed to the strong interactions between the surface oxides of Zn and Cu [35]. The interfaces between the two semiconductors, i.e., p -type CuO and n -type ZnO, are tight and their band edges are well matched [42].

Fig. 5. EDX results for ZnO (a), CuO (b), and Zn₂Cu (c).

3.6. PL analysis

PL analysis is important in understanding the fates of electron-hole pairs formed during photoexcitation [43]. PL emission spectra of ZnO, CuO, and ZnO–CuO are shown in Fig. 8.

The intense peak at 395 nm for ZnO and the coupled oxides is attributed to band–band emission, and the blue–green emissions at 435 and 497–565 nm are caused by oxygen vacancies.

Fig. 6. TEM images of ZnO (a) and Zn₂Cu (b) (SAED patterns are shown as insets).

Fig. 7. Kubelka-Munk plots for ZnO, CuO, ZnCu, Zn₂Cu, and ZnCu₂.

CuO shows emissions in the range of 485–594 nm. Pure ZnO nanoparticles give high-intensity PL signals. The PL intensities are lower for the coupled oxides, and Zn₂Cu shows the lowest PL intensity. The PL emission mainly results from the recombination of photogenerated electrons and holes, therefore a lower PL intensity indicates a lower recombination rate of electron-hole pairs and better photocatalytic activity [44]. The PL analysis therefore suggests that Zn₂Cu would have the best photocatalytic activity.

Fig. 8. PL spectra of samples.

3.7. Photocatalytic activity

3.7.1. Effect of catalyst composition

PCD of 2,4-DCP was performed using an initial 2,4-DCP concentration of 50 ppm, a catalyst concentration of 50 mg/100 mL, neutral pH, and an irradiation time of 240 min over ZnO, CuO, and the coupled oxides ZnCu, Zn₂Cu, and ZnCu₂. On irradiation with visible light, the maximum degradation was obtained using Zn₂Cu (82%), as shown in Fig. 9(a).

The enhanced PCD achieved using Zn₂Cu is attributed to a lower recombination rate of electron-hole pairs in Zn₂Cu, as a result of efficient interparticle electron transfer, as indicated by the PL results. It can also be attributed to the better crystallinity of Zn₂Cu compared with those of the other coupled oxides. CuO absorbs in the visible region and has a band gap of 2.1 eV, but its degradation efficiency is lower than that of Zn₂Cu, because of the faster recombination of generated electron-hole pairs resulting from the narrow band gap.

The changes in the absorption spectra of 2,4-DCP exposed to visible light for various irradiation times (0, 30, 60, 90, 120, 150, 180, and 240 min) in the presence of Zn₂Cu are shown in Fig. 9(b). The absorption maxima at 284 and 199 nm decreased gradually with irradiation time. Coupling of CuO with ZnO

Fig. 9. (a) PCD catalytic efficiencies of ZnO, CuO, ZnCu, Zn₂Cu, and ZnCu₂; (b) Degradation of 2,4-DCP on Zn₂Cu; (c) Kinetic plots of $\ln(C_0/C_t)$ vs irradiation time.

therefore significantly improves the photocatalytic activity. The photodegradation of 2,4-DCP in the presence of the prepared catalysts follows pseudo-first-order kinetics; this can be expressed as $\ln(C_0/C) = kt$, where C_0 is the initial concentration of 2,4-DCP, C is the concentration of 2,4-DCP at irradiation time t , and k is the rate constant [33]. The plots of $\ln(C_0/C)$ versus t are shown in Fig. 9(c); the relationships are linear. The first-order rate constants were evaluated from the slopes of the plots. The rate constants, with R^2 , values are given in Table 1. The small deviations from first-order kinetics observed for CuO could be the result of slow diffusion of adsorbed 2,4-DCP or of intermediates from the catalyst surface [45].

3.7.2. Effect of pH

The pH is an important factor in photodegradation. The effect of pH on the photodegradation of 2,4-DCP was studied in the pH range 3–11, with an initial 2,4-DCP concentration of 50 ppm and a Zn₂Cu dosage of 50 mg/100 mL. The results are shown in Fig. 10(a).

The 2,4-DCP degradation rate increased from pH 3 to pH 7 and then decreased with increasing pH. This is caused by changes in the electrostatic attraction or repulsion between phenol molecules and the catalyst. The zero point charge (ZPC) of Zn₂Cu is around 8 and the surface is positively charged in acidic solution (pH < p_{H_{ZPC}}) and negatively charged in alkaline solution (pH > p_{H_{ZPC}}) [42]. The pK_a of 2,4-DCP is 7.89, therefore at pH 7.8 and below, 2,4-DCP is only partly dissociated. At low

pH values (below p_{H_{ZPC}} of ZnO), the semiconductor surface carries a net positive charge, which facilitates adsorption of neutral or negatively charged chlorophenols or their intermediates on the catalyst. This in turn leads to their efficient photocatalytic degradation. The decrease in the overall oxidation rate of 2,4-DCP at high pH can be attributed to decreased 2,4-DCP adsorption on the catalyst surface, because at this pH the catalyst surface is negatively charged and phenol is dissociated to phenoxide ion [46].

3.7.3. Effect of Zn₂Cu dosage

To optimize the photocatalyst dosage for 2,4-DCP degradation, experiments were performed using Zn₂Cu dosages of 25–100 mg/100 mL, at a constant 2,4-DCP concentration of 50 ppm and pH 7; the results are shown in Fig. 10(b).

The photodegradation of 2,4-DCP under irradiation for 240 min without addition of a photocatalyst is negligible. The 2,4-DCP photodegradation rate increases with increasing Zn₂Cu dosage from 25 to 50 mg/100 mL and then decreases. This is because of the increase in the total active surface area and the availability of more active sites on the catalyst surface for photoreactions. However, on increasing the catalyst dosage further, the photodegradation rate decreases. A high catalyst dosage increases the turbidity of the suspension, leading to a shielding effect and reduced light penetration. The absorption of light by the photocatalyst is therefore limited and fewer catalytic sites can be activated. The surface area also decreases as

Fig. 10. PCD efficiencies of Zn₂Cu at various pH values (a), with various Zn₂Cu dosages (b), with various 2,4-DCP concentrations (c), and for different runs (d).

a result of nanoparticle agglomeration at high photocatalyst dosages [25,47–48].

3.7.4. Effect of initial 2,4-DCP concentration

The effect of the initial phenol concentration on its photodegradation was investigated from 25 to 100 ppm, at pH 7 and a Zn₂Cu dosage of 50 mg/100 mL; the results are shown in Fig. 10(c). The photodegradation efficiency increased slightly with increasing initial phenol concentration, i.e., from 25 to 50 ppm; when the phenol concentration was increased further, the degradation efficiency decreased. At low phenol concentrations, the number of catalytic sites is not the limiting factor and the degradation rate is proportional to the substrate concentration. As the concentration of 2,4-DCP increases, increasing numbers of phenol molecules are adsorbed on the photocatalyst surface.

The number of reactive species ($\bullet\text{OH}$ and $\text{O}_2^{\bullet-}$) required for the degradation of the pollutant on the catalyst surface remains constant for a given light intensity, catalyst amount, and irradiation time. The number of OH radicals is therefore insufficient for pollutant degradation at higher concentrations. As a result, the phenol degradation rate decreases as the concentration increases [25,49]. In addition, an increase in the substrate concentration can lead to the generation of intermediates, which can be adsorbed on the catalyst surface. Slow diffusion of generated intermediates from the catalyst surface can result in deactivation of active sites on the photocatalyst, resulting in a reduction in the degradation rate. Zn₂Cu can be reused, with little change in its efficiency, for at least four consecutive cycles, as shown in Fig. 10(d).

A possible mechanism is proposed, based on previous reports [50,51], to explain the synergistic effects of CuO coupling on the photocatalytic activity of ZnO; the proposed mechanism is shown in Fig. 11.

At the CuO/ZnO heterojunction, the conduction band (CB) and valence band (VB) of CuO are located between those of ZnO [52]. Photoexcited electrons in the CB of ZnO are therefore transferred to the CB of CuO at the ZnO–CuO interface, and the photoexcited holes in the VB of ZnO are transferred to the VB of CuO. The holes in the VB of CuO can oxidize OH[−] groups, be-

cause its VB is positioned more positively than the standard redox potential, +1.99 V [vs normal hydrogen electrode (NHE); Eq. (1)]

The electron density in the CB of ZnO is depleted, and that in the CB of CuO is enhanced. The CuO CB position is lower than the standard redox potential, therefore direct electron transfer to molecular O₂ and hydroperoxyl ($\text{HO}_2^{\bullet}$) radicals, which require −0.33 V (vs NHE) and −0.046 V (vs NHE), respectively, is difficult, as shown in Eqs. (2) and (3). Electrons in the CB of CuO are therefore transported to O₂ species through the processes shown in Eq. (4). According to this explanation, the photocatalytic activity at the CuO/ZnO heterojunction would be less efficient.

Although ZnO has a band gap of 3.2 eV, and requires UV light for excitation, under visible-light irradiation, a certain percentage of PCD takes place on ZnO. ZnO and the coupled oxides contain defects such as oxygen vacancies, as seen from the PL and EDX analyses of these samples. Stepwise electronic excitation could occur from the VB of ZnO to its CB through the defect levels present in the band gap (Fig. 11a). Excited electrons from the CB of CuO can be transferred to low-lying defect levels in ZnO but not to its CB. This could lead to the desired delay in electron–hole pair recombination and could account for the enhanced PCD at the ZnO–CuO interface.

According to Wang et al. [51], the electrons transferred to the CB of CuO at the TiO₂–CuO interface reduce CuO to Cu₂O. The band positions of ZnO and TiO₂ are similar, therefore if we can extend the same explanation to the ZnO–CuO coupled system, there could be a similar restructuring process taking place at the interface, with CuO being reduced to Cu₂O with the electrons transferred to the CuO CB. The restructured ZnO–CuO photocatalyst would have exposed ZnO–Cu₂O–CuO interfaces (Fig. 11b). On the restructured photocatalyst, the photoexcited electrons in the CB of Cu₂O could transfer to the CB of ZnO, and

Fig. 11. Schematic diagram of energy band structure in ZnO–CuO composite.

the photoexcited holes in the VB of ZnO could transfer to the VB of Cu₂O. This explanation needs further exploration and experimental verification.

4. Conclusions

A visible-light-active Zn₂Cu photocatalyst was synthesized using a microwave-assisted combustion method and was characterized. The photocatalytic activity in the degradation of 2,4-DCP was investigated, and the coupled metal oxide Zn₂Cu showed the maximum activity. The photocatalytic efficiency of ZnO was significantly improved by the synergistic effect of CuO coupling. The photodegradation of 2,4-DCP followed first-order kinetics. The optimized reaction conditions were pH 7, Zn₂Cu dosage 50 mg/100 mL, and initial 2,4-DCP concentration 50 ppm. Under the optimum reaction conditions, 82% photodegradation was achieved within 240 min of irradiation. Zn₂Cu is a reusable photocatalyst and can be used for at least four cycles with little change in its activity. A probable photodegradation mechanism is proposed.

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Graphical Abstract

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Visible-light-induced photocatalytic performances of ZnO–CuO nanocomposites for degradation of 2,4-dichlorophenol

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A coupled metal oxide, Zn₂Cu, with a ZnO:CuO molar ratio of 2:1 efficiently degraded 2,4-dichlorophenol under visible-light irradiation. This was mainly attributed to the extended photoresponsive range and increased charge separation rate in the Zn₂Cu nanocomposite.

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