Research Article

Kinetic Study of Organic Dye Degradation Using ZnO Particles with Different Morphologies as a Photocatalyst

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Zinc oxide (ZnO) particles were successfully synthesized via sol-gel approach using zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and ammonia (NH_4OH) solution as precursors. By adjusting the reaction parameters such as amount of ammonia and reaction time as well as complexing agent aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$, ZnO particles with different morphologies, that is, rodlike, ricelike and disklike could be synthesized. The effectiveness of ZnO particles with different morphologies (rodlike, ricelike and disklike) on the photocatalytic activity has been studied. The results showed that rodlike ZnO particles were the most effective in degrading the Rhodamine B (RhB) solution under the illumination of ultraviolet (UV) light. The rate constant was found to be first order, with rodlike particles the highest (0.06329 min^{-1}), followed by rice-like ZnO particles (0.0431 min^{-1}) and disk-like ZnO particles (0.02448 min^{-1}).

1. Introduction

Photocatalysis of organic compounds such as methyl green and Rhodamine B (RhB) in water is receiving attention due to the severe ecological impact of various industrial and agricultural pollutants [1, 2]. Photocatalytic activities can be classified into homogeneous or heterogeneous reactions depending on the nature of their reactants and materials (semiconductors). Particularly, heterogeneous photocatalytic study using semiconductor materials such as TiO_2 and ZnO, through particulate systems, has become an exciting and rapidly growing area of research in the last few years mainly due to the relatively simple photodecomposition of organic pollutant molecules into less harmful compounds [3–7].

ZnO has been chosen as photocatalyst because of its high catalytic efficiency, low cost, large bandgap (3.37 eV), and nontoxic nature. In fact, it has been shown to be more effective than TiO_2 as photocatalysts in recent studies [8, 9]. The effect of various parameters such as UV light intensity [3], initial dye concentration [3, 10, 11], pH of the medium [10], amount of photocatalyst [3, 11], doping [4, 12], and temperature [13] were reported. However, the

effect of morphology of ZnO particles remains as a field to be explored.

The morphology of ZnO particles can be easily manipulated by tailoring the reaction parameters. By adjusting the temperature, concentration of solution, pH, heating duration, and complexing agent, different morphology of ZnO particles such as nanoprisms [14], nanorods [15], nanoflowers [16], nanosheets [17], and nanodisks [18] could be synthesized, respectively. Different morphology of ZnO particles have different exposed crystal planes. For example, the main exposed crystal plane of ZnO nanodisks is (002) with atomic planar density of $1.1 \times 10^{19} \text{ atoms/m}^2$. The plane is either negatively charge ($-\text{O}$) terminated or positively charge ($-\text{Zn}$) terminated. On the contrary, the main exposed crystal plane of ZnO nanorods is {100} with atomic planar density of $5.9 \times 10^{18} \text{ atoms/m}^2$. These crystal planes are composed of alternating layer of Zn and O atoms. Since the photocatalytic activity has occurred on the active surface of particles, controllable design of ZnO particles with various morphologies is the focus of current research.

In this study, ZnO particles were synthesized by sol-gel method using zinc acetate dihydrate and ammonia solution as precursors. Systematic study on the effect of reaction

FIGURE 1: SEM image of (a) rodlike and (b) flower-like ZnO particles.

parameters such as amount of ammonia, reaction time, and addition of complexing agent on the growth of ZnO particles was carried out. By controlling the process window, several desired morphologies such as ricelike, rodlike, and disklike particles were synthesized. A better insight on the possible growth mechanism of these morphologies was gained. The photocatalytic activity of ZnO particles was evaluated by illuminating the mixture of ZnO particles and RhB with ultraviolet (UV). RhB was chosen as model pollutant because it is one of the most widely used xanthene dyes in the textile industry and has become a common organic pollutant. The efficiency of ZnO particles with different morphologies on the degradation of RhB will be discussed. The study of RhB degradation and understanding its reaction kinetics helped to consider actual effluent for the photocatalytic activities, in view of its complexity in containing diverse types of dyes and other chemicals.

2. Experimental Details

Zinc acetate dihydrate was used as the source of zinc ion whereas ammonia was used as the source of hydroxide ion. Different morphologies of ZnO particles were obtained by varying the amount of ammonia, reaction time, and addition of aluminium sulphate as complexing agent. Then, the synthesized ZnO particles were sent for characterization such as scanning electron microscopy (SEM, FESEM, Zeiss Supra 35VP), X-ray diffraction (XRD, Bruker Advanced X-ray Solution D8 Diffractometer ($\text{Cu K}\alpha$, $\lambda = 0.154 \text{ nm}$)), and photoluminescence measurement (PL, N_2 laser excitation source, 337 nm, pulse rate 20 Hz). Lastly, the photocatalytic study using ZnO particles with different morphologies was conducted. The compound selected to be degraded in this project was Rhodamine (RhB). The photocatalytic activity of ZnO particles was achieved by illuminating mixture of 10 mg ZnO particles and 20 mL RhB ($1 \times 10^{-5} \text{ M}$) with ultraviolet (360 watts UV lamps, Phillips, 254 nm). Then, the degraded RhB solution was sent for UV-Vis analysis (UV-Vis spectrophotometer, Cary 5, 553 nm) to measure the photodegradation efficiency of ZnO particles at room temperature.

3. Results and Discussion

3.1. Effect of Reaction Parameters on the Growth of ZnO Particles.

FIGURE 2: XRD diffractogram of (a) rodlike and (b) flower-like particles.

3.1.1. Effect of Reaction Time. To study the evolution of rodlike morphology, experiments were carried out using 2.0 mL of NH_4OH and reacted for 1 h and 4 h. When reacted for 1 h, as shown in Figure 1(a), rodlike particles were formed. The rodlike structures had a diameter of $155.0 \pm 25.29 \text{ nm}$ and a length of $1134.7 \pm 120.78 \text{ nm}$. The aspect ratio of rodlike particles was 7.5. When it was prolonged to 4 h, an individual flower-like structure composed of nanorods was obtained as shown in Figure 1(b). The diameter of the petals varied from the base to the tips, showing that the petals had sharpened tips with the wider bases that were connected to each other through their wider bases. The diameters of these petals at their tips and bases were between $101.8 \pm 18.84 \text{ nm}$ and $196.7 \pm 67.36 \text{ nm}$, respectively, and the lengths of these petals were $1172.6 \pm 370.38 \text{ nm}$. The EDX analysis on both rodlike and flower-like particles indicates that the atomic percentages of Zn and O have a ratio approximately 1 : 1. No evidence of impurities was found.

Figures 2(a) and 2(b) show the X-ray diffraction (XRD) patterns for rodlike and flower-like particles. Both XRD patterns show peaks at 31.7° , 34.4° , 36.2° , 47.5° , 56.5° , 62.7° , 66.3° , 67.8° , 69.1° , 72.5° , and 79.9° , which correspond to (100), (002), (101), (102), (110), (103), (200), (112), (210), (004), and (202) crystal planes of hexagonal ZnO (JCPDS card no. 36-1451). Extra peaks marked with black dots at 32.9° , 39.5° , 40.8° , 42.2° , 52.5° , 59.6° , and 60.7° are observed

for rodlike particles as shown in Figure 2(a). These peaks are indexed to $\text{Zn}(\text{OH})_2$ (JCPDS card no. 38-0385). The result indicates that $\text{Zn}(\text{OH})_2$ was present in rodlike particles. This could be due to a short reaction time. In fact, a longer reaction time was needed for $\text{Zn}(\text{OH})_2$ to be hydrolyzed to $\text{Zn}(\text{OH})_4^{2-}$ complex ions before ZnO nuclei formed. No other diffraction peaks were found for flower-like particles as shown in Figure 2(b).

The formation of ZnO particles on the above study is proposed as follows [19, 20]. When zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2$ was dissolved in water, it dissociated into zinc ion, Zn^{2+} , and acetate ion, CH_3COO^- , as shown in (1). Then, CH_3COO^- ions were hydrolyzed and released OH^- ion as shown in (2). When ammonia solution was added, NH_4OH was dissolved in the water and hydrolyzed to ammonium ion, NH_4^+ , and hydroxide ion, OH^- , as shown in (3):

Subsequently, tetraaminezincate ion, $\text{Zn}(\text{NH}_3)_4^{2+}$, zinc hydroxide, $\text{Zn}(\text{OH})_2$, or tetrahydroxozincate ion, $\text{Zn}(\text{OH})_4^{2-}$ may be formed. The OH^- ion may react with Zn^{2+} ion to form $\text{Zn}(\text{OH})_2$ white precipitate as shown in (4) or $\text{Zn}(\text{OH})_4^{2-}$ complex ion as suggested in (5). Zn^{2+} ions may also react with NH_4^+ ion to form $[\text{Zn}(\text{NH}_3)_4]^{2+}$ complex ion as shown in (6). Both $\text{Zn}(\text{OH})_4^{2-}$ complex ion and $[\text{Zn}(\text{NH}_3)_4]^{2+}$ complex ion could be served as growth units for ZnO nuclei,

Finally, ZnO nuclei was crystallized as a result of the reaction of $[\text{Zn}(\text{NH}_3)_4]^{2+}$ complex ion and OH^- ion as shown in (7). $\text{Zn}(\text{OH})_4^{2-}$ complex ion could be transformed into ZnO nuclei as proposed in (8). ZnO nuclei could also be formed from $\text{Zn}(\text{OH})_2$ but only after the formation of $\text{Zn}(\text{OH})_4^{2-}$ growth unit by reacting with OH^- ion as shown in (9):

FIGURE 3: Schematic diagram of formation of rodlike and flower-like ZnO particles.

The negative-charged $\text{Zn}(\text{OH})_4^{2-}$ complex ions were preferentially adsorbed onto the positive-charged (001) Zn plane and subsequently dehydrated and entered into the crystal lattice. The growth rate of the (001) plane was greatly favored. The more rapid the growth rate, the quicker the disappearance of the basal plane. Thus, rodlike ZnO particles with elongated c -axis surrounded by six $\{100\}$ planes was formed. While the growth rates of some $\{101\}$ planes were relatively smaller than those of (001), they remained to form needle-like tips.

Similar observation, that is, formation of flower-like particles from nanorods with prolong reaction time has been reported by Jiang et al. [21]. The proposed growth mechanism is illustrated in Figure 3. Nanorods grow and contact with each other during the synthesis process. Secondary nucleation occurs on the surface of some of the nanorods, resulting in formation of flower-like particles.

3.1.2. Effect of Ammonia Concentration. As shown by (5) and (6), varying the ammonia concentration could affect the concentration $\text{ZnO}(\text{OH})_4^{2-}$. By reducing the volume of NH_4OH , that is, from 2.0 mL to 1.5 mL, conelike and ricelike nanoparticles were synthesized instead of rodlike particles. Figure 4(a) shows conelike particles with a diameter of 146.8 ± 21.20 nm and a length of 216.3 ± 26.30 nm at the earlier stage of particles growth (0.5 h). As the reaction time was prolonged to 2 h, the particles became ricelike as shown in Figure 4 (b). The ricelike particle looked like a twin-cone structure, composed of two cones with round bottom connected to each other. This can be identified with the well-resolved slit observed in the middle of the particles. The EDX analysis indicates that the atomic percentages of Zn and O had a ratio approximately 1 : 1. No evidence of other impurities was found.

Figure 5 shows the X-ray diffraction (XRD) patterns of conelike particles and ricelike particles. The XRD pattern of conelike particles shows peaks correspond to crystal planes of hexagonal ZnO (JCPDS card no. 36-1451). Extra peaks marked with black dots are indexed to $\text{Zn}(\text{OH})_2$ (JCPDS card no. 38-0385). This shows that $\text{Zn}(\text{OH})_2$ was present in conelike particles attributed to short reaction time that is

FIGURE 4: SEM image of (a) conelike particles and (b) ricelike particles.

FIGURE 5: XRD diffractogram of (a) conelike particles and (b) ricelike particles.

0.5 h. Meanwhile, no peaks of Zn(OH)_2 was observed from the XRD pattern of ricelike particles as shown in Figure 5(b). Ricelike particles were obtained when reacted for 2 h. The presence of Zn(OH)_2 was eliminated by prolonging the reaction time. This result is consistent with the observation in Section 3.1.1, that is, longer reaction time is required to transform Zn(OH)_2 to Zn(OH)_4^{2-} complex ions in order to produce ZnO nuclei.

The conelike ZnO particles were formed due to uneven and multidimensional growth of ZnO particles. The surface of the round bottom of each cone, that is, (002), could comprise the negatively charge O^{2-} -terminated plane or the polar positively charge Zn^{2+} -terminated planes. Thus, a one-dimensional polar field was established from the O^{2-} -terminated to Zn^{2+} terminated. According to the polar-field-induced assembly concept, two single cones with opposite polar field directions assembled spontaneously during the crystal growth process to counterbalance the polar fields. As a result, this led to the formation of the twin-cone structures or known as ricelike structure. The schematic diagram of conelike and ricelike particles formation is suggested in Figure 6.

FIGURE 6: Schematic diagram of formation of conelike and ricelike ZnO particles.

3.1.3. Effect of Complexing Agent. Without complexing agent of $\text{Al}_2(\text{SO}_4)_3$, conelike structures were obtained from the solution as shown in Figure 4(a). However, addition of $\text{Al}_2(\text{SO}_4)_3$ into the precursor solution produced disklike particles instead of conelike particles as shown in Figure 7(a). The nanodisks had a thickness of 13.5 ± 1.03 nm. Besides, some of the disks had a hole in the middle, forming ZnO nanorings. As shown in Figure 7(b), the EDX spectrum of disklike particles indicates that it composed of Zn, O, Al, and S elements. The Al and S elements were from the addition of aluminium sulphate $\text{Al}_2(\text{SO}_4)_3$ as complexing agent. Figure 8 shows the X-ray diffraction (XRD) patterns for disklike particles. The XRD patterns show peaks correspond to crystal planes of hexagonal ZnO (JCPDS card no. 36-1451). Extra peaks marked with asterisks are assigned to Al_2O_3 , which could be attributed to precipitation and oxidation of Al^{3+} ions that originated from aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$.

As proposed by Ye et al., the growth of disklike ZnO particles was mediated by the adsorption of aluminate ion, Al(OH)_4^- [22]. The Al(OH)_4^- ions were obtained as a result of reaction between $\text{Al}_2(\text{SO}_4)_3$ and NH_4OH . The Al(OH)_4^- ions were presumed to be bonded to the positively charged Zn^{2+} -terminated (0001) surface of ZnO and suppressed the growth along the [0001] direction. This allowed the lateral growth to occur. Disklike ZnO particles were thus formed. On the contrary, the formation of ringlike ZnO particles was suggested due to the dissolution of ZnO [18]. As time passed by, there was a depletion of OH^- ion in the solution. Therefore, there would be a decrease in Zn(OH)_4^{2-} growth units. To compensate the decrease in Zn(OH)_4^{2-} complex ions, the equilibrium of (8) was shifted to the left, which resulted in the dissolution of ZnO. The (001) plane was removed instead of nonpolar {100} plane because

FIGURE 7: (a) SEM image and (b) EDX spectrum of disklike particles.

FIGURE 8: XRD diffractogram of disklike particles.

{100} plane had a lower surface energies than (001) plane. Therefore, {100} plane was more stable than (001) plane. The schematic diagram of disklike and ringlike particles formation is proposed in Figure 9.

3.2. Photoluminescence Property of ZnO Particles. Figure 10 shows the photoluminescence (PL) spectra of disclike, rod-like, and ricelike ZnO particles. Both near-band-edge emission (NBE, 389 nm) and a broad green emission (centered at 572 nm) are observed from all the samples. This broad green emission is commonly referred to a deep level or trap-state emission attributed to the singly ionized oxygen vacancy

FIGURE 9: Schematic diagram of formation of disklike and ringlike ZnO particles.

[23]. It has also been reported by Vanheusden et al. that free-carrier depletion at the particle surface, and its effect on the ionization state of the oxygen vacancy, can strongly impact the green emission intensity [24]. Thus, it might be deduced that different morphologies of ZnO particles, which are different in term of atomic packing density and arrangement of Zn and O atoms, may lead to different surface depletion when exposed to air. The surface depletion in the disclike ZnO particles may be less than in the other morphologies, which might be attributed to the decreasing trend at 572 nm in Figure 10. Nevertheless, the strongest UV and green emission emitted from flower-like particles indicates that the amount of photogenerated electrons and holes are the largest. A large amount of photogenerated electrons and holes is needed to improve the efficiency of

FIGURE 10: Room temperature photoluminescence spectra of ZnO particles with different morphology.

FIGURE 11: Degradation of RhB by rodlike ZnO particles when exposed to UV radiation for 0 min, 20 min, 40 min, 60 min, and 80 min.

RhB degradation. In addition, the low ratio of NBE/green emission indicates that the crystal quality of samples is poor as they contain many crystal defects.

3.3. Photocatalytic Study of ZnO Particles. To evaluate the effectiveness of ZnO particles with different morphologies as photocatalyst, RhB solution was used as a model compound. The mixture of RhB solution with ZnO particles with specific morphology was exposed to UV light (254 nm). Figure 11 shows the degradation of RhB solution over a period of time using rodlike ZnO particles as photocatalyst. The color of RhB slowly faded when exposed to UV radiation for 0 min, 20 min, 40 min, 60 min, and 80 min.

The photodegradation efficiency of ZnO particles (ricelike, rodlike, and disklike) were studied by monitoring the UV-Vis absorbance spectra of RhB at maximum peak of 553 nm as shown in Figure 12. Figure 12(a) shows the absorption spectra of photocatalytically degraded RhB aqueous solutions in the presence of ricelike ZnO particles during different UV irradiation times. The absorbance peak of RhB significantly decreased to 0.050 after 60 min of UV irradiation, then continued down to 0.039 of the initial absorbance (1.084) upon prolonging the irradiation time to 80 min.

Figure 12(b) shows the absorption spectra of photocatalytically degraded RhB aqueous solutions in the presence of rodlike ZnO particles during different UV irradiation times. The absorbance peak of RhB significantly decreased to 0.0210 after 60 min of UV irradiation and then down to 0.006 upon prolonging the irradiation time to 80 min. During the degradation of RhB dyes over disklike ZnO particles (Figure 12(c)), the absorbance peak of RhB decreased to 0.231 after 60 min of UV irradiation and then continued down to 0.161 upon prolonging the irradiation time to 80 min.

Figure 13 shows the comparison between the photodegradation of RhB with and without ZnO particles. Under UV-light irradiation, but in the absence of ZnO particles, the absorbance of RhB changed little (2.98%) after irradiation. This indicates that the photo-induced self-sensitized photolysis of RhB can be neglected. However, the photodegradation was enhanced when ricelike, rodlike, and disklike ZnO particles were added as catalysts. The absorbance of RhB aqueous solutions diminished gradually with the increasing exposure time in the presence of ZnO particles. The photodegradation efficiency of ricelike, rodlike, and disklike ZnO particles can be deduced from Figure 13. The residual absorbance of RhB at 80 min UV irradiation in the presence of ricelike, rodlike, and disklike ZnO particles were 0.006, 0.039, and 0.161, respectively. Thus, rodlike ZnO particles were the most effective in degrading RhB, followed by ricelike and disklike ZnO particles.

When the absorbance data are plotted as $\ln(A_0/A)$ of the time-dependent normalized dye concentrations (which is the ratio between the initial concentration and the concentration upon reaction) in Figure 14, linear plots are obtained. This indicates that the decomposition of RhB follows a first order kinetics regardless the morphology of ZnO particles. The rate constant of rodlike ZnO particles is the highest, that is, 0.06329 min^{-1} (std. error: 0.00236, R-square: 0.99311), followed by ricelike particles (0.04317 min^{-1} , std. error: 0.00323, R-square: 0.97266) and disklike particles (0.02448 min^{-1} , std. error: 0.00076, R-square: 0.99514). The highest rate constant of rodlike ZnO particles could be due to the highest surface area to volume ratio. The surface area to volume ratio for rodlike ZnO particles was 0.030 nm^{-1} whereas the ricelike ZnO particles was 0.017 nm^{-1} . A larger surface area can provide more photocatalytic reaction centers for the absorption of reactant molecules. In addition, a larger surface area is also effective for UV light adsorption and thus generates more electrons and holes [25]. This correlates with the observation of PL result in Figure 10 where the rodlike ZnO particles produced strongest UV and green emission, followed by ricelike and disklike particles. The higher the number of carriers, the better the photocatalyst is. Thus, a better photocatalytic activity for ZnO nanorods is achieved as a result of enhanced absorption capacity.

Among the three different types of ZnO particles, disklike ZnO particles appeared to be more inferior compared to rodlike and ricelike ZnO particles. This may be due to the presence of ringlike ZnO particles. The (001) plane of ringlike ZnO particles was removed during the dissolution of ZnO. Therefore, less surface area will be exposed to UV

FIGURE 12: Absorbance spectra of Rhodamine B aqueous solutions with different ZnO particles after UV irradiation with different time, (a) ricelike, (b) rodlike and (c) disklike ZnO particles.

adsorption. Besides, this may be also due to the presence of Al element as reported in the EDX analysis. The Al contamination adhered to the exposed plane of disklike ZnO particles may deter the UV adsorption. Hence, the photocatalytic performance of disklike ZnO particles was affected.

The degradation of RhB solution by ZnO particles could be explained by mechanism below [25, 26]. When ZnO particles were illuminated by UV light with energy greater than the band gap energy, the conduction-band electrons (e_{CB}^-) and valence-band holes (h_{VB}^+) were generated on the surfaces of ZnO particles as shown in (10). Holes could react with water adhering to the surfaces of ZnO particles to form highly reactive hydroxyl radicals ($\cdot OH$) as in (11).

Meanwhile, oxygen acted as an electron acceptor by forming a superoxide radical anion ($O_2^{\cdot -}$) as in (12). Rhodamine B was believed to be destroyed through direct oxidation by the $\cdot OH$ radicals and $O_2^{\cdot -}$ radicals as shown in (13),

FIGURE 13: Comparative studies of the photocatalytic activity of ricelike, rodlike and disklike ZnO particles.

	Rodlike	Ricelike	Dislike
Slope	0.06329	0.04317	0.02448
St. error	0.00236	0.00323	7.65E-04
R-square	0.99311	0.97266	0.99514

FIGURE 14: Degradation of RhB by ZnO particles with different morphologies.

4. Conclusions

ZnO particles have been successfully synthesized using zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and ammonia (NH_4OH) solution as precursors via sol-gel approach. By carefully controlling the process window, various morphologies of ZnO particles such as ricelike, rodlike, cone-like, flower-like, and disklike could be produced. In the photocatalytic study, rodlike ZnO particles showed the best photocatalytic efficiency, followed by ricelike and disklike

ZnO particles. This may be due to a larger surface area to volume ratio of rodlike ZnO particles. On the other hand, disklike ZnO particles performed poorly for the degradation of RhB. This may be attributed to the presence of ringlike ZnO particles and/or contamination of Al^{3+} ions, contributed from the aluminium sulphate solution (complexing agent).

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