Photocatalytic activity of ZnO nanodisks in degradation of Rhodamine B and Bromocresol Green under UV light exposure

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Abstract. Semiconductor-based photocatalyst is an alternative approach for wastewater treatment. The effectiveness of semiconductor nanoparticles to eliminate textile dye substances in the contaminant water has been widely studied in the last decade. This work discusses the photocatalytic activities of ZnO nanodisks by using different dye substance (rhodamine B, RhB and bromocresol green, BCG) under UV exposure. ZnO nanodisks were successfully synthesized through solution precipitation method. The formation of ZnO in hexagonal nanodisks structure was confirmed by XRD, FESEM and EDX analysis. The result showed that the photodegradation efficiency of BCG dye is higher than RhB dye under 75 min of UV irradiation. This could be explained by the dye molecular structure as BCG dyes containing more hydroxyl groups (-OH) than RhB dyes.

1. Introduction

The waste water containing organic compounds has raised serious issue on human health and affected the ecological system [1]. Particularly, organic dyes in water effluent of textile industry are harmful to environment even though present in low concentration [2]. If this water effluent from textile industry is discharged into river without treatment, it will cause water pollutant. The emerging waste water treatment technique that based on semiconductor photocatalysts provides alternative route to photodegrade the organic pollutants [3]. In fact, the effectiveness of using these semiconductor nanoparticles has been widely studied due to its simplicity; low operation cost and decomposes the organic dye into less harmful by-product such as water and carbon dioxide [4].

Metal oxide, such as zinc oxide (ZnO), is well known as multifunctional II-IV compound semiconductor with high photocatalytic activity [5]. The unique properties of ZnO such as large binding energy (60 meV) wide band gap (3.37 eV) at room temperature [6-7], making it a potential
material for various applications e.g. LEDs [8], light emitters [9] and lasers [10]. In addition, the good antibacterial activity [11] and photocatalytic performance in organic compounds removal [12] are useful in waste water treatment plants, textile and paint industry [13]. It is also noted that the physical properties of ZnO nanostructures could be varied by tailoring their morphology into nanoflowers [14], nanoneedles [15], nanowires [16], nanorods [17] and nanodisks [18].

In this study, ZnO nanodisks (NDs) were synthesized by using zinc acetate dehydrate (Zn(CH$_3$COO)$_2$•2H$_2$O) and ammonium hydroxide (NH$_4$OH) as precursors. Whereas, aluminium sulfate (Al$_2$(SO$_4$)$_3$) was used as complexing agent to customize as nanodisks shape. The particles were synthesized via solution precipitation method as it is one of the most commonly used techniques [19]. The advantages of solution precipitation methods are low raw materials cost, low synthesis temperature [20] and the composition of precursors could be adjusted easily [21].

2. Material and Methods

The synthesis of ZnO NDs is described in details in reference [22]. In a typical synthesis, an equal molar of precursors were prepared in two separate beakers, i.e. 6.07 mM of zinc acetate dehydrate (Zn(CH$_3$COO)$_2$•2H$_2$O) was dissolved in 300 ml distilled water and 6.07 mM of aluminium sulphate (Al$_2$(SO$_4$)$_3$) was dissolved in 30 ml distilled water. The solutions were stirred separately while heating at 60 °C for 2 h in water bath. Subsequently, 2 ml of ammonium hydroxide (NH$_4$OH) was added drop by drop into the zinc acetate dehydrate solution. Then, aluminium sulphate solution was added and continuously stirrer for 1 h by maintaining the temperature at 60 °C. The solution was left overnight to wait for the nanoparticles to be formed and settled down. The precipitate was washed several times by deionized water and ethanol. Finally, the precipitate was dried at 100 °C for 8 h.

The sample was characterized by X-Ray diffraction technique (XRD, Bruker Advanced X-ray Solution D8 Diffractometer (Cu K$_\alpha$, $\lambda = 0.154$ nm)) to determine the type of crystal structure and phases; field-emission scanning electron microscope (FESEM, Zeiss Supra 35VP) to reveal its morphology and energy dispersive X-Ray spectroscope (EDX) to identify the elements of the sample.

In photocatalytic study, 1x10$^{-5}$ M of dye aqueous solutions of rhodamine B (RhB) and bromocresol green (BCG), were prepared. A fixed amount of nanoparticles, i.e. 0.10 g, was added into 250 ml of dye aqueous solution and continues to stir in dark condition for 30 min. The mixed solution was irradiated under UV light ($\lambda = 254$ nm). Subsequently, a 2.5 ml of photodegraded dye solution was sampled at every 15 min interval (0, 15, 30, 45, 60 and 75 min). The absorbance of photodegraded dye solutions in the range of 400-700 nm was recorded using UV-Vis spectrophotometer (Cray 50). By measuring the characteristic absorbance peak of organic dyes, i.e. 553 nm for RhB and 620 nm for BCG, the photodegradation efficiency (%) of ZnO NDs was calculated by $\left(1 - \frac{A_t}{A_0}\right) \times 100 \%$, where $A_t$ = initial absorbance and $A_0$ = absorbance at time ‘t’.

3. Results and Discussions

Figure 1 (a) shows the XRD patterns of as-synthesized particles. The characteristic diffraction peaks at 20 = 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, 69.0°, 72.5° and 76.9° are corresponding to the crystal planes of (100), (002), (101), (102), (110), (103), (200), (112), (210), (004) and (202) respectively. All diffraction peaks can be assigned to the wurtzite structure of hexagonal ZnO by comparing with ICDD reference code database (98-008-1294), with lattice constants of a = b = 3.25 Å, c = 5.207 Å, $\alpha = \beta = 90°$, $\gamma = 120°$. Additional peaks at 38.8°, 46.4°, 52.6°, 59.8°, 61.2° and 73.85° are assigned to Al$_2$O$_3$, which could be contributed from the surface directing agent, aluminium sulphate (98-006-2983 and 98-006-6546) as labelled in Figure 1(a). The strong and sharp diffraction peaks indicate that the particles were highly crystallized.

Figure 1(b) reveals that the particles consist of large ZnO NDs and some small flower-like ZnO particles. The ZnO hexagonal disk is highlighted in yellow dotted line. The ZnO NDs have average
diameter of 12.301 ± 1.050 µm and thickness of 0.067 ± 0.020 µm. The elemental analysis of ZnO NDs was performed using EDX. As shown in Figure 1(c), the particles composed of Zn, O and Al elements. The atomic percentages of Zn, O and Al are 46.69%, 47.6% and 5.71%, respectively. The small atomic percentage of Al was come from the surface directing agent, Al₂(SO₄)₃. The stoichiometric ratio of Zn:O of the particles is closed to the theoretical value, i.e. ~1:1.

The photocatalytic activity of ZnO NDs under UV light irradiation was evaluated by using two kinds of dye solution, i.e. RhB and BCG dyes. Figure 2(a) and (b) display the absorption spectra in degradation of RhB and BCG dye respectively. The intensity of characteristic adsorption peak of RhB (553 nm) and BCG (620 nm) reduced slowly and the colour of dye solution was faded over time. The photodegradation efficiency (PE) of ZnO NDs for RhB and BCG dye solution is illustrated in Figure 2(c). The BCG dye solution (PE = 44.39%) degraded faster than RhB dye (PE = 21.14%) after 75 min of UV irradiation.

The difference in PE of dyes by ZnO NDs could be explained from their molecular structures. As shown in Figure 3, the partial conjugated π-π* system (benzenic ring) and n–π* bonding (hydroxyl group (–OH) in BCG dye is more easy to destruct [24]. Another fact is the BCG dye containing hydroxyl group (–OH), in which hydrogen/electrostatic bonding with the surface hydroxyl group of ZnO NRs may easy to construct [25]. The •OH radicals generated from ZnO could attack the π–π* system, causing destruction of the conjugated π systems in benzenic rings of BCG dyes. In addition, the BCG dye with more –OH group will have a higher amount of dye absorbance rate with maximum adsorption capacity (q_max). Therefore, ZnO NDs could adsorb and decolourize the BCG dyes better than RhB dyes.

| Element | At % |
|---------|------|
| Zn K    | 46.69|
| O K     | 47.60|
| Al K    | 05.71|

Figure 1. (a) XRD pattern, (b) FESEM image and (c) EDX analysis of ZnO NDs.
Figure 2. UV-Visible absorption spectra of (a) RhB solution and (b) BCG solution photodegraded and (c) their photodegradation efficiency by ZnO NDs under UV irradiation.

Figure 3. Molecular structures of (a) RhB and (b) BCG (green: $\pi-\pi^*$ system and blue: $n-\pi^*$ bonding).
4. Conclusions

ZnO NDs were synthesized successfully through solution precipitation methods at room temperature. It is clearly shows that ZnO NDs are in hexagonal wurtzite crystal structure. The ZnO NDs have an average diameter of 12.301 ± 1.050 µm and thickness of 0.067 ± 0.020 µm. The EDX analysis shows particles composed of Zn and O elements with ratio of ~1:1. A small amount of Al, i.e. 5.71 % which originated from the Al₂(SO₄)₃ was detected. The BCG dye solution degraded faster than RhB dye by using ZnO NDs after 75 min of UV irradiation. This could explained by the presence of more hydroxyl group (~-OH) in BCG dye than RhB dye.

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