Synthesis, Characterization and Application of Zinc Oxide with Micro Polyhedral and Nano Plate Morphologies for Simultaneous Decolorization of Two-dye Mixture in Wastewater

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Abstract

In this work, growth and assembly of the micro polyhedral zinc oxide was performed using air bubble assisted Triton X100, as a templating agent. In absence of air bubbling in the reaction system the nano plate zinc oxide was synthesized. The prepared samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and UV-Vis spectrophotometer. The optical properties of the samples were evaluated by UV-Vis spectrum. Photocatalytic application of the samples for simultaneous decolorization of methylene blue (MB) and methyl orange (MO) dyes mixture in aqueous solution was examined. The Langmuir-Hinshelwood model for decolorization kinetic data was investigated. The reusability of the samples after five consecutive uses was examined. The photocatalytic results indicated that the micro polyhedral zinc oxide is a promising candidate for simultaneous decolorization of the MO and MB dyes (>90%).

Keywords: Micro polyhedral, Nano plate, Photocatalyst, Triton X100, Zinc oxide.

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Introduction
Most dyes found in textile wastewater and other industrial are toxic and carcinogenic to humans and animals; therefore, it is important to treat contaminated wastewater. Several techniques such as adsorption, coagulation/flocculation, electrocoagulation, photocatalytic oxidation and biosorption have been reported to removing of single and multi dye mixture from wastewater [1-7]. Different materials such as magnetic adsorbent, chitosan, TiO₂ suspension, CuO/Cu₂O/Cu composite, MgFe₂O₄/ZnFe₂O₄/PANI composite and modified dolomite for removal of binary mixture of dyes in aqueous solution were applied [8-14]. To date, different morphologies of zinc oxide have been widely used for photocatalytic, catalytic and gas sensor applications [15-18]. Synthesis of zinc oxide with various procedures such as precipitation, sol-gel, microwave irradiation, spray pyrolysis, hydrothermal and solvothermal methods were reported [19-24]. Surfactant assisted synthesis of zinc oxide were reported by many researchers. During synthesis process, surfactant can moderate the crystal growth, thereby helps in size and shape control. Until now, all studies showed that size, morphology and structure of materials had key roles in optical properties [25-28]. In this research, the micro polyhedral and nano plate zinc oxide samples were synthesized and characterized. Air bubble assisted Triton X100 as soft template was applied. Furthermore, photocatalytic application of the samples for simultaneous removal of dyes mixture in aqueous solution was tested.

Experimental
Materials
Methylene blue, methyl orange, sodium hydroxide, zinc acetate dihydrate and Triton X100 were purchased from Merck Company.

Instrumentation
The prepared samples were characterized by using XRD (Holland Philips Xpert, X-ray diffractometer with Cu-Kα radiation), field emission scanning electron microscopy (FE-SEM) and UV-Vis spectrophotometer (Shimadzu, UV-2550).

Zinc oxide preparation
5 drops of Triton X100 were dissolved in 50 mL double distilled water under vigorous stirring and air was blown into the reaction vessel by an aquarium pump. Then, 0.878 g of zinc acetate dihydrate and 0.48 g of sodium hydroxide were added into the above solution. After stirring the mixture for 8 h at room temperature, the product was separated and washed with distilled water several times and
dried at 60 °C. Finally, heat treatment of the product was carried out at 500 °C for 1 h. Moreover; the preparation of zinc oxide was carried out in absence of air blowing in reaction medium.

Photo catalytic experiment

For photo catalytic experiment, 0.10 g of the prepared sample was added in 200 mL of the MO and MB dyes mixture solution (5 mgL⁻¹ with respects to each component), Air was blown into the reaction vessel by an aquarium pump to maintain the solution saturated with oxygen. A high pressure mercury lamp, 400 W, manufactured by Holland Philips, was used as the light source. The progress of photo catalytic decolorization was measured by a UV-Vis spectrophotometer. Then, the degree of photo decolorization (X), as a function of time, was determined as follows:

\[ X = \left( \frac{C_0 - C_t}{C_0} \right) \times 100 \quad \text{Eq. (1)} \]

where, \( C_0 \) is the initial dye concentration, and \( C_t \) is the dye concentration at time t. Furthermore, the adsorption behavior of the dye pollutants over the obtained samples was studied in dark condition.

Results and Discussion

The crystal structure and phase purity of the zinc oxide samples were characterized by XRD pattern (Figure 1 (a and b)). The indexed peaks as (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) are related to the hexagonal wurtzite structure of zinc oxide (JCPDS No. 36-1451).

![Figure 1](image-url). XRD pattern of the zinc oxide samples with (a) micro polyhedral and (b) nano plate morphologies.
The morphology of the zinc oxide samples was evaluated by FE-SEM images. The micro polyhedral and nano plate morphologies were formed in presence and absence air bubbling assisted Triton X100 in reaction medium, respectively. The micro polyhedral with diameter of about ~1-3 µm and nano plate consists of nano particles of about ~15-60 nm were obtained (Figure 2(a-d)). In the reaction system, NaOH was served as a source of OH⁻, hydroxyl anion subsequently reacted with Zn²⁺ to form [Zn(OH)₄]²⁻, which was the growth unit for zinc oxide. Air bubbling assisted surfactant as soft template changes the morphology of product, mainly, by controlling the crystal nucleation and growth during preparation. Triton X100 was used in this study due to its surface active properties that facilitate the formation of foam. Therefore, the primary zinc oxide nuclei can be easily incorporated in bubbles fabricated in the triton X100 surfactant.

![Figure 2. FE-SEM images of the samples with micro polyhedral (a, b) and nano plate (c, d) morphologies.](image)

The band gap of the samples can be calculated by the adsorption edge position according to formula: \( E_g = \frac{1240}{\lambda} \), in which, \( \lambda \) can be obtained by making a tangent along the absorption edge [29]. The UV-Vis spectra of the samples was illustrated in Figure 3(a and b). The value of the optical band gap for the micro polyhedral and nano plate zinc oxide were estimated of bout 3.28 and
3.31 eV, respectively. Also, for micro polyhedral zinc oxide a wide visible light absorption range of (~400-700) nm was observed.

Figure 3. UV-Vis spectra of the zinc oxide samples with micro polyhedral (a) and nano plate (b) morphologies.

Before photo catalytic experiments, the adsorption extent of dyes on surface of the samples was measured in dark condition. The adsorption experiments for the micro polyhedral and nano plate zinc oxide indicated that MO and MB dyes of about (44, 15) and (9, 10) (%) adsorbed on surface of the samples after 180 min, respectively. These results showed that, the nano plate zinc oxide has a poor adsorption for dyes removal in aqueous solution. The plots of adsorption percentage versus time were presented in Figure 4(a and b).

Figure 4. The plots of adsorption percentage versus time for MO and MB dyes removal using zinc oxide with micro polyhedral (a) and nano plate (b) morphologies.

The photo catalytic decolorization of MO and MB dyes was respectively determined to be about (91, 94) and (89, 61) (%) for micro polyhedral and nano plate zinc oxide samples, Figure 5(a and b).
According to results, the zinc oxide sample with micro polyhedral morphology has a high photo catalytic activity. The photo catalytic mechanism can be explained by the photo generation of electron-hole pairs (e⁻ and h⁺) in zinc oxide under UV-Vis light illumination. The photo generated electron (e⁻) could be trapped by adsorbed oxygen on zinc oxide surface to form superoxide radical anions (O₂⁻•). The superoxide radicals is further protonated to produce hydroperoxy radical (HOO•) and subsequently H₂O₂. The holes (h⁺) react with surface bounded water or hydroxyl anion to produce hydroxyl radical. The hydroxyl radical is an extremely strong, non-selective oxidant which leads to degradation of dye pollutants. Moreover, adsorbed dyes may be decolorized by the photo-excited holes through means of direct oxidation. Generally, hydroxyl radicals, holes and superoxide radicals act as active reagents for the mineralization of dyes in aqueous solution [30-32].

![Figure 5. The plots of photo catalytic decolorization percentage versus time for dyes decolorization using micro polyhedral (a) and nano plate (b) zinc oxide samples.](image)

The photo catalytic kinetic of dye removal was determined from Langmuir-Hinshelwood model [33, 34] Eq. (2).

$$\ln \frac{C_0}{C_t} = k_{app} t$$  \hspace{3cm} \text{Eq. (2)}$$

where C₀ is the initial dye concentration, Cₜ is the dye concentration at time t and kₚₚ is the apparent rate constant. The linear correlation of ln(C₀/Cₜ) versus time plot suggests a pseudo first- order reaction. The experimental results provide a linear dependence of ln(C₀/Cₜ) versus time, Fig. 6(a and b). The rate constant for photo catalytic decolorization of MO and MB dyes was respectively determined to be about (0.0130, 0.0151) and (0.0124, 0.0051) min⁻¹ for micro polyhedral and nano plate zinc oxide samples.
Figure 6. The plot of \( \ln(C_0/C_t) \) v.s time for dyes decolorization using (a) micro polyhedral and (b) nano plate zinc oxide samples.

Furthermore, for micro polyhedral and nano plate zinc oxide samples the reusability after five consecutive uses were obtained to be (96, 93, 89, 85) and (94, 90, 87, 80)\%, respectively (Figure 7).

Figure 7. Reusability of the (a) micro polyhedral and (b) nano plate zinc oxide samples after five consecutive uses.

Conclusion

In summary, the micro polyhedral and nano plate zinc oxide samples were synthesized using soft template method. This research clearly illustrated that size and morphology has significant effect on optical properties. The results indicated that micro polyhedral zinc oxide exhibit an increasing photo catalytic activity compared to nano plate zinc oxide. The better photo catalytic performance for micro polyhedral zinc oxide could be attributed to lower band gap than the other sample. This sample can be applied for simultaneous removal of MO and MB dyes mixture in wastewater.

Acknowledgements

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References