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ZnO Nanostructure Shape Effects in Photocatalysis of Methylene Blue

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Abstract

Nowadays, dyes are used in the food industry, textile industry, paper industry, hair coloring, light-harvesting arrays, photoelectrochemical cells, etc. Most of the dyes are nonbiodegradable, toxic, carcinogenic, and consist of organic compounds. These dye wastages are discharged into water bodies and the environment causing serious hazards to the marine ecosystem as well as the humans extensively. To treat toxic dyes traditional methods such as adsorption, activated carbon, ultrafiltration, and reverse osmosis are used for dye removal. But, in these processes pollution from one form transfers to another form causing secondary pollution. In the present study, efficient ZnO nanostructure nanodot, nanorod, nanoplate, and nanoflower) photocatalysts were prepared by ultrasonication-assisted solution method using ethylene glycol, 1-butanol, acetic acid, and water as solvent. ZnO has a wide band gap and it can be excited using UV light. For excellent photocatalysis, electron-hole recombination is suppressed by trapping charge carriers at defect states. Thus, the photocatalytic activity of ZnO is modified by changing its shape, size, and doping with transition metal ions. Here, we discussed the degradation of methylene blue (MB) using different dimensional ZnO nanostructures as a potential photocatalyst. The morphology and surface area of the synthesized samples were analyzed using TEM and BET analysis. Solvent physicochemical properties affect the growth kinetics and morphological evolution. ZnO nanoflower exhibits excellent photocatalytic performance than the other structures towards methylene blue degradation due to their larger surface area. Higher surface area enhances the dye adsorption and photodegradation efficiency to 85% under exposure to visible light after 20 minutes.

Keywords: ZnO Nanostructure, Methylene Blue, Photocatalysis, Degradation, Surface area

INTRODUCTION

Heterogenous photocatalysis is a modern method for degrading both aquatic and atmospheric organic contaminants. In this process, dye molecules degrade into smaller molecules such as carbon dioxide, water, and minerals. The mechanism of photocatalysis mainly involves, the generation of excitons by photon absorption and these excitons react with water or oxygen to produce hydroxide radicals and superoxide anions. These species have excellent oxidation power to degrade dye molecules. The decontamination process of dye using these highly reactive species is called the advanced oxidation process [1,2].

Among various types of photocatalysts, Zinc oxide (ZnO) assisted photocatalysis has received much attention due to its nontoxicity, long-term photostability, and strong oxidizing power [2–4]. ZnO is an direct bandgap metal oxide having a wide band gap of 3.37eV and it can be excited using UV

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light [5,6]. ZnO nano/micro structures with high surface area show excellent photocatalytic activities. For excellent photocatalysis, electron-hole recombination is suppressed by trapping charge carriers at defect states. Thus, the photocatalytic activity of ZnO is modified by changing its shape, size, and doping with transition metal ions [2,7,8]. ZnO nanostructures can be seen in different forms such as nanoparticles, nanorods, nanoplates, nanoflowers, nanoclusters, and nanobelts. In this paper, we discussed the degradation of methylene blue (MB) using different dimensional ZnO nanostructures as a potential photocatalyst.

Experimental

0.1M Zincacetate dihydrate and 0.5M NaOH were dispersed in $C_2H_6O_2$, $C_4H_{10}O$, CH_3COOH and H_2O mixed under ultrasonication. After sonication precipitation was heated at 80°C for 2 hours and kept at rest for a day [9]. The morphology of the synthesized samples was analyzed using a TEM (JEM 2100). The surface area of the resultant products was characterized using BET (Tristar-3020) analysis.

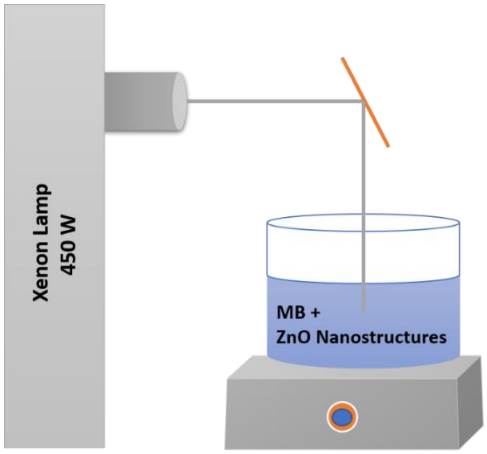

Figure 1. Schematics of photocatalysis experimental setup.

The photocatalytic activity of the prepared ZnO nanostructures was carried out in MB using an experimental setup as shown in Figure 1. In a typical experiment, 1mg of ZnO nanostructures were dispersed in 10µM dye solution under continuous magnetic stirring for 30 minutes in dark to obtain a colloidal solution. The suspension was continuously irradiated with a Xenon lamp (450W) and take UV absorption (JASCO V-570) spectra of the sample were recorded after 20 minutes.

The percentage of photodegradation efficiency was calculated using the equation,

$$D = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

Where A_0 is the initial absorbance of MB and A_t is the absorbance of MB at time interval t [2].

RESULTS AND DISCUSSION

Figure 2 shows the synthesis procedure and crystal growth mechanism of ZnO nanostructures in various solvents such as $C_2H_6O_2$, $C_4H_{10}O$, CH_3COOH and H_2O. A notable difference in morphology was observed in four different solvents are reaction medium. These results confirm that solvent properties seriously affect the growth mechanism. The growth mechanism consists of two stages. In primary stage is nucleation and the secondary stage is the growth process. In nucleation, zinc hydroxide units are formed and decomposed into a few nanometer-sized ZnO growth units. The secondary stage is more complex than the primary stage. The formed ZnO growth units are assembled and form various morphologies. In this stage solvent properties greatly affect the growth mechanism. Instead of these properties, electrostatic force and van der Waals force also plays a critical role in ZnO nanostructure formation.

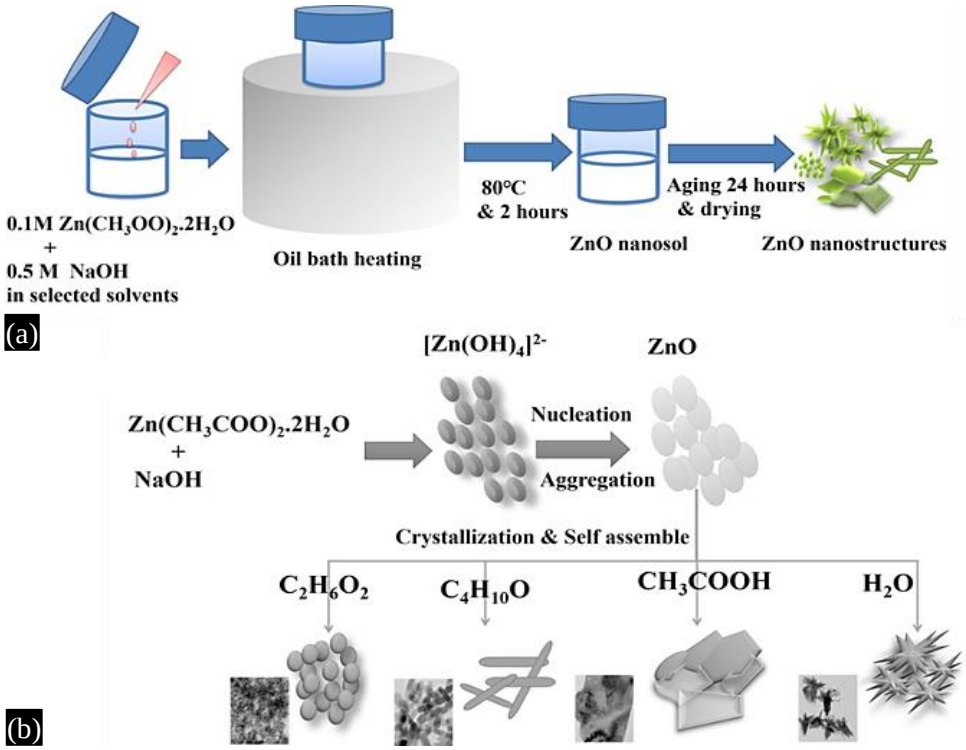

Figure 2. Schematic representation of (a) synthesis method and (b) growth mechanism of ZnO nanostructure synthesis using various solvents [9].

The morphology of ZnO nanostructures was analyzed using TEM analysis shown in Figure 3. More details about morphological evolution crystal growth mechanism, optical, structural, and defect state analysis were discussed in our previous publication [9].

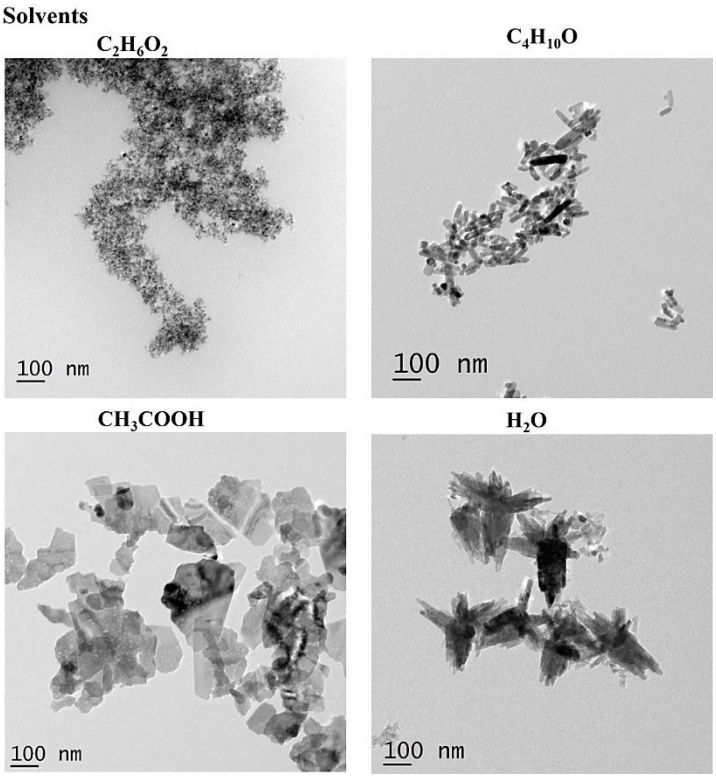

Figure 3. TEM image of synthesized ZnO nanostructures in various solvents [9].

Here we focused on the shape effects in photocatalytic properties of this synthesized ZnO nanostructure in MB degradation. A schematic representation of MB photodegradation using ZnO nanostructures as photocatalyst is shown in Figure 4. The photodegradation process consists of several steps [10].

Under visible light illumination ($hv > E_g$) , ZnO absorbs photons to produce electron-hole pairs. The generated electrons moved into the conduction band (CB) leaving a hole in the valence band (VB)
$ZnO + hv \rightarrow ZnO\ (e_{CB}^- + h_{VB}^+)$

The electron in CB (e_{CB}^-) react with oxygen from superoxide radicals.

$O_2 + 2e^- \rightarrow O_2^-$

The highly active superoxide radicals produce hydrogen peroxide.

$O_2^{-\cdot} + 2H^+ \rightarrow 2HO_2^{\cdot}$

$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2$

Hydrogen peroxide reacts with electrons to form active hydroxyl radicals.

$H_2O_2 + e^- \rightarrow OH^{\cdot} + OH^-$

The holes in VB (h_{VB}^+) oxidize the H_2O or directly interact with MB to produce hydroxyl radicals.

$OH^- + h^+ \rightarrow OH^{\cdot}$

$H_2O + h^+ \rightarrow H^+ + OH^{\cdot}$

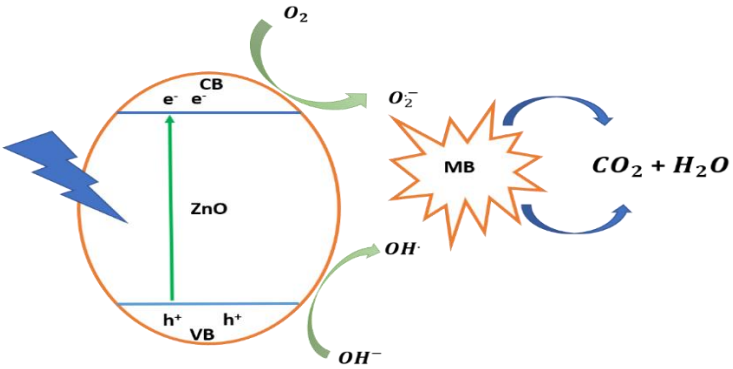

Figure 4. Schematic representation of methylene blue photodegradation.

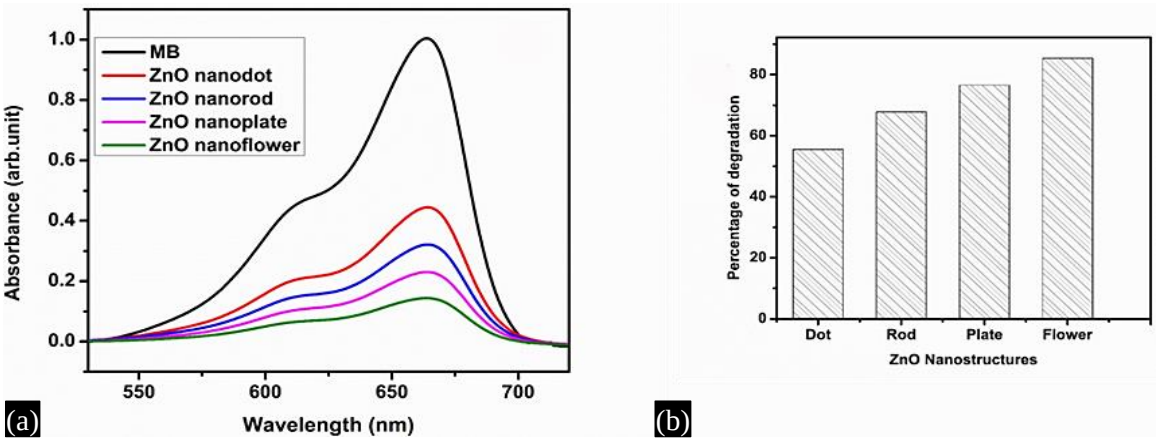

Figure 5. (a) Absorption and (b) Percentage of degradation spectra of methylene blue.

These resulting superoxide radicals and hydroxyl radicals degrade the dye molecules on the surface of the catalyst producing harmless byproducts.

$$OH^{\cdot} \, or O_2^{-\cdot} + MB \rightarrow CO_2 + H_2O + degradation\ products$$

Figure 5 shows the change in absorption spectra and percentage of degradation with different dimensional ZnO nanostructures as a catalyst after 20 minutes of photodegradation time. It can be seen that the degradation ability of catalysts varied according to their morphology. The percentage of photocatalytic degradation with ZnO nanoflower as a catalyst was found to be 85%. ZnO nanoplate used as catalyst degradation percentage is about 77%. The dye degradation using ZnO nanorod and nanodot as a catalyst are 66% and 56% respectively. ZnO nanoflower has the highest degradation rate, which means that the nanoflower structure is the best catalyst for the degradation of MB. These results revealed that photocatalytic performance depends on the morphology of the catalyst. The specific surface area of ZnO nanoflower, nanoplate, nanorod, and nanodot estimated from BET analysis is to be 60.39m^2/g, 40.91m^2/g, 27.67m^2/g and 19.26m^2/g, respectively. The larger surface of nanoflower could creats more surface active sites for the adsorption of dye molecules, which increases the photocatalytic reactions [2].

CONCLUSIONS

The present study explored the shape-dependent photocatalytic activity of ZnO nanostructure in the process of degradation of methylene blue. From this, we understand that photocatalysis highly depended on the morphology of the catalyst. The increased surface area of nanostructures provides more active sites for dye adsorption which enhances the catalytic reaction.

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