Exploration of Methylene Blue Degradation Over ZnO Nanorods Mechanism Using Scavenging Reagents

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http://dx.doi.org/10.13005/ojc/370313

(Received: April 02, 2021; Accepted: June 03, 2021)

ABSTRACT

Hierarchical porous flower-like ZnO structures containing ZnO nanorods were successfully synthesized by precipitation process. The structure containing high aspect ratio nanorods was revealed by scanning electron microscopy (SEM). The EDS analysis revealed the ZnO nanostructures formation as confirmed by the Zn and O peaks. The Fourier-transform infrared spectroscopy (FTIR) spectrum indicated the Zn–O bond vibrational frequency. The typical hexagonal wurtzite ZnO nanostructure with 15 nm crystallite size and the characteristic parameters was perceived from the X-ray diffraction (XRD) data. A 10.13 m².g⁻¹ surface area, 10.05 cm³/g pore volume and 18.25 nm pore diameter were estimated using nitrogen adsorption analysis. Bandgap energy of 3.229 eV was calculated from the optical analysis data. Under ultraviolet light irradiation, the prepared nanoparticles has effectively decolorized the methylene blue dye. The reaction obeyed the pseudo-first-order kinetics, and the degradation mechanism was proposed using radicals scavengers to determine the species involved in the photodegradation process such as isopropanol, p-benzoquinone, and dimethyl sulfoxide. The reactive oxygen atom in the mechanism of photodegradation, and the recyclability of ZnO photocatalysts were studied.

Keywords: ZnO NPs, XRD, SEM, MB photodegradation, Recyclability, Scavenging reagents.

INTRODUCTION

Recently, semiconductor nanomaterials have been the focal point of various research aspects due to their attractive and fascinating optical and electrical properties. Such interesting qualities may mainly be attributed to their size reduction¹. In particular, ZnO nanostructures with a large bandgap (>3.35 eV), great excitonic energy (60 meV) and are mechanically and thermally stable at ambient conditions. These excellent properties have drawn substantial interest for applications such as electronic and optoelectronic devices and lasers²,³ chemical sensing⁴, bio-sensing⁵, biological markers⁶, dye-sensitized solar cells⁷ and electrochemical cells⁸. Different routes are adopted for ZnO nanostructures
preparation, including chemical vapor deposition, pyrolysis, high-temperature decomposition, hydrothermal, sol-gel and precipitation. Precipitation at low temperature is an inexpensive, scalable facile method for large types of ZnO nanostructures fabrication. Precipitation procedures have been successfully employed in prior works to synthesize various ZnO assemblies.

Whether anionic and cationic, industrial dyes are extensively employed in textile; leather processing. Being toxic, carcinogenic and mutagenic to aquatic biological systems, these dyes should be treated before discarding in the runoffs. Still, many types of azo dyes including MB are quite persistent and challenging to degradation methods. Consequently, their interesting photocatalytic and catalytic detoxification have drawn substantial concern in eco-friendly remediation. The photocatalytic demineralization of these hazardous organic dyes is an ecologically preferred approach, as no additional chemicals are needed, and thus, no pollution by-products are produced. During the photodegradation process, where incident radiation with enough energy shines on a semiconductor, it excites electrons from the valence to the conduction band, generating an electron deficiency or hole (h+). Oxygen molecules in the aqueous medium react with the electrons to breed strong reducing O2- ions while the adsorbed water molecules and hydroxide ions react with the (h+) to generate the strong oxidizing •OH radicals, that are considered the primary radicals for the photocatalytic degradation.

In the present work, ZnO nanorods were synthesized through a precipitation process. The nanostructure produced was having 15 nm size, 3.229 eV bandgap energy, and 10.13 m².g⁻¹ surface area. The photocatalyst's ability to decolorize organic dyes was tested using the MB, where the process fitted well with the first order kinetics with a rate constant of 5.9 x 10⁻³ min⁻¹.

The crystalline structure of the powders was investigated by X-ray powder diffraction (XRD) using Bruker high-resolution diffractometer equipped with Cu-Ka radiation (1.5418 Å), operating at 40 kV and 40 mA. Morphological images were recorded by field emission scanning electron microscopy (FE-SEM) using high-resolution Jeol JSM 7600F and transmission electron microscopy (TEM) using JEOL, JEM-2100. The Brunauer–Emmett–Teller (BET) specific surface area was assessed via N2 adsorption–desorption isotherms by employed ASAP 2020 Micromeritics device. The optical properties were determined by means of diffuse reflectance spectroscopy (DRS) using JASCO V-770 spectrophotometer in the wavelength range 300-800 nm. Vibration and bending modes of the all samples were documented by means of Fourier Transform Infrared (FTIR) spectra (JASCO FI-IR 460 spectrometer) in the range 400-4000 cm⁻¹.

Photodegradation using Methylene Blue

For the degradation MB as a typical contaminant dye, 10 mg/L was used to inspect the ZnO photocatalytic activity. Prior to commencing the experiment, 0.050 g of ZnO were dispersed in 150 mL of MB solution and stirred in the dark for 60 min to reach equilibrium. Afterwards, the photocatalytic evolution was monitored under 265 nm ultraviolet illumination. Throughout the photocatalytic course, (6 mL) of the solution was withdrawn at various times interludes, then centrifuged to clear the solution and then its absorbance was examined between 200 and 700 nm using UV–Vis spectrophotometer. The photocatalytic degradation percentage was computed the equation:

\[ MB\% = \frac{C_0 - C_t}{C_0} \times 100 \]  

Knowing that \( C_t \) and \( C_0 \) are the initial concentration (10 mg/L) and time t MB concentration, respectively.

Trapping of Reactive Oxygen Species (ROS)

To study the photocatalytic degradation mechanism of MB over the surface of ZnO nanoparticles, scavenging reagents were used to...
determine the responsible reactive oxygen species by using isopropyl alcohol (IPA) for scavenging hydroxyl radicals (HO\(^{-}\))\(^{27,28}\), p-benzoquinone (PBQ) for scavenging superoxide radicals (O\(_{2}^{-}\))\(^{27,28}\), disodium ethylenediaminetetra acetic acid (Na\(_2\)EDTA) for scavenging photogenerated holes (h\(^{+}\))\(^{29}\), and dimethyl sulfoxide for scavenging photogenerated electrons (e\(^{-}\))\(^{29}\). The decrease in photocatalytic activity, produced by scavenging reagent, would signify the reactive oxygen species responsible for the photodegradation. (50.0 mmol/L) concentrations were used except for PBQ, which its optimum concentration was 1.0 mmol/L for 10.0 mg/L of MB\(^{29}\).

**RESULTS AND DISCUSSION**

**XRD analysis**

The XRD pattern of the fabricated NPs (Fig. 1) displays an archetypal XRD configuration of ZnO crystal pattern as inveterated by \(2\Theta \approx 31.58, 34.24, 36.10, 47.32, 56.38, 62.64, 67.82\) and 68.98\(^{\circ}\) that serially correspond to the (100), (002), (101), (102), (110), (103), (200), (112 and (201) Miller indices indexed to the hexagonal wurtzite ZnO\(^{30}\) and in agreement with the pdf #36-1451 card for ZnO\(^{31}\).

The purity of the prepared sample is confirmed by the absence of any peak due to impurity. The sharp peaks displayed in the pattern designates the synthesis of a highly crystalline material in the nanometer range.

![XRD patterns of ZnONPs](image)

The crystallite sizes (D) of the ZnO NPs was computed according to Scherrer’s formula\(^{32}\)

\[
D = \frac{0.90\lambda}{\beta\cos\theta}
\]

The terms, \(\Theta\) and \(\beta\) are respectively assigned to the CuK\(\alpha\) line (1.5406 A\(^{\circ}\)), the XRD diffraction angle and th (FWHM). The crystallite size of ZnO was determined using the most intense peak and was found to be 15.32 nm. The lattice parameters and the spacing between planes as designed as a, c and d respectively were calculated using equations 3-5.\(^{33-35}\)

\[
a = \frac{\lambda}{\sqrt{3}\sin\theta_{100}} \\
c = \frac{\lambda}{\sin\theta_{002}} \\
d = \frac{\lambda}{2\sin\theta}
\]

Where \(\theta_{100}\) and \(\theta_{002}\) correspond the Miller indices (100) and (002) correspondingly, the a and c values are inconsistent with the ZnO (JCPDS) card\(^{36}\), connoting the synthesis of the nano-size ZnO. Moreover the d-spacing calculated via the theoretical formula (4) and Bragg’s law (5) are almost identical (Table 1). The length of the Zn–O bond was obtained from the formula (6).

\[
L = \sqrt\left(\frac{a^2}{2} + (0.5 - \mu)^2c^2\right)
\]

Here \(\mu\) is a factor that describes the magnitude of the atom displacement from its neighbor alongside the c axis, as articulated by (7):

\[
\mu = \frac{a^2}{3c^2} + 0.25
\]

The obtained Zn–O bond value (Table 1) is around the previously reported 1.9767 A\(^{\circ}\) value\(^{37,38}\). The strain-induced broadening in nanopowder due to crystal imperfection and distortion was calculated using the formula\(^{39}\)

\[
\varepsilon = \frac{\beta}{4\cos\theta}
\]

The micro-strain (\(\varepsilon_{Z}\)) along the c-axis was estimated using the expression\(^{40}\)

\[
\varepsilon_{Z} = \frac{c - c_0}{c_0}
\]

The terms c and c\(_0\) (5.2066 Å) stand for the computed typical lattice parameters in that order. For the ZnO, the micro-strain is equal to 0.51% which is tensile strain type that may stimulate the crystallite’s orientation along the z-axis\(^{41}\).
Table 1: The ZnO NPs data obtained from the XRD analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>β</th>
<th>2θ</th>
<th>D(nm)</th>
<th>a(A₀)</th>
<th>c(A₀)</th>
<th>c/a</th>
<th>d(A₀)</th>
<th>d*(A₀)</th>
<th>u</th>
<th>Zn-O(A₀)</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Values</td>
<td>0.5481</td>
<td>36.1</td>
<td>15.32</td>
<td>3.2687</td>
<td>5.2335</td>
<td>1.6011</td>
<td>2.4861</td>
<td>2.4903</td>
<td>0.38</td>
<td>1.9889</td>
<td>0.0025</td>
</tr>
<tr>
<td>±0.0003</td>
<td>±1.44</td>
<td>±0.75</td>
<td>±0.163</td>
<td>±0.210</td>
<td>±0.124</td>
<td>±0.125</td>
<td>±0.011</td>
<td>±0.080</td>
<td>±0.0001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SEM analysis

The sample’s SEM micrograph displayed in Fig. 2(a) shows a large hierarchical porous flower-like structure consisting of several flake-like structures under low magnification. At medium magnification (Fig. 2b), several scattered rod-like nano-structures were covering the flakes’ surface. The detailed micrograph Fig. 2c exhibits high aspect ratio (8.5) nanorods. The (EDS) spectrum (Fig. 2d), snapped from a dense NPs region divulges strong peaks assigned to Zn, O atoms, whereas weaker signal form S discernible as well. The existence of the S element may have come from the sulfate in the zinc precursor.

FTIR bonding analysis

FTIR spectra of the ZnO have been recorded to inspect the nature of bonds in the prepared materials, in the range 400–4000 cm⁻¹ (Fig. 3). The peaks at 3462 cm⁻¹ and 1647 cm⁻¹ are respectively due to O–H stretching and O–H bending vibrations of water molecule. This is due to water molecules’ existence on the nanostructures’ surface. The band positioned at 2376 cm⁻¹ may indicates CO₂ molecules in the air. The peak at 418 cm⁻¹ corresponds to Zn-O symmetric bending vibration, and the peak at 604 cm⁻¹ is due to the weak vibration of Zn-O⁻. The other peak at 785 cm⁻¹ attributed to Zn-S symmetric bending, confirming the EDS finding.

Nitrogen adsorption isotherms

The isotherm profile delivers evidence
about surface consistency, and it could be generally characterized as displayed in Fig. 4 the nitrogen adsorption-desorption isotherm for the ZnO sample is type II, as categorized by IUPAC and Brunauer-Emmet-Teller (BET). The isotherm shows a type H3 hysteresis loop, distinctive of accumulated particles with mesoporous solids and free monolayer-multilayer adsorption. This hysteresis at P/P0 range 0.5 and 1 is attributed to condensation in the mesopores related to the inter-particle cavities of the ZnO structure. The point, at the start of the linear central part of the chart, shows the step where the monolayer coverage is completed and multilayer adsorption starts. The specific surface of 10.13 m².g⁻¹ estimated applying the BET conventional method is a characteristic of a material with a crystallized material. 10.05 cm³/g and 18.25 nm, are the pore volume and pore diameter, respectively. The particle size distribution Fig. 4 reveals that the average around 30 nm, which is consistent with the isotherm analysis data.

Optical properties and bandgap determination

To examine the optical properties of the ZnO NPs its UV-Visible spectrum was verified and plotted in Fig. 5. The graph exhibits a sharp absorption edge rising at 400 nm, which is shifted to a higher wavelength relative to the standard ZnO peak. The diffuse reflectance spectroscopy (DRS) analysis and (αhv)² versus hv plots were carried out to probe the band energy of ZnO NPs Fig. 5, which was found to be 3.229 eV as estimated applying the Tauc equation.

\[
(\alpha hv)^n = A(hv - E_g)
\]  

(10)

Here h, ν, α, and E_g are Planck’s constant, frequency, absorption coefficient and bandgap energy. A is a constant, and n represents the electron transition type (for directly allowed transitions, n = 1/2). The Eg for the NPs (3.229eV) is less than the standard 3.37 eV value for ZnO.

Methylene Blue (MB) photodegradation

The UV-photodegradation of 10 mg/L Methylene Blue (MB) dye solution was done to monitor the photocatalytic actions of the ZnO NPs. 30 mg of nanomaterials were sonicated in 100 mL of MB solution. Prior to commencing photocatalysis, the solution was stirred for 40 min in the dark to achieve equilibrium. Then, the photocatalytic evolution was probed under ultraviolet irradiation at λ=265 nm. Throughout the photocatalysis course, 5 mL of the solution was pipetted at different times intervals, centrifuged to eliminate suspended nanoparticles, and its absorbance was examined between 500 and 800 nm using UV–Vis spectrophotometer. The proportion of the photocatalytic degradation was assessed using the relation:

\[
MB \% = \frac{A_0 - A_t}{A_0} \times 100
\]  

(11)

Where A₀ and Aₜ are the initial and time t MB absorbance, respectively.

The photocatalytic action of the ZnO nanostructures was scrutinized by photodegrading the MB organic contaminant dye. The process was observed by determining the MB absorbance at λ_max = 662 nm and different UV radiation time intervals Fig. 6. A gradual decrease in absorbance is evidence of enhanced catalytic efficiency of the ZnO Fig. 6. The data reveals a catalytic competence by the ZnO photocatalyst Fig. 7 a, which is higher than that shown by BaTiO₃ nanoparticles that showed comparable results but with a lower MB concentration. The result is in general similar to many previously reported findings for Ag/ZnO, ZnO/NiFe₂O₄ and SrFe₁₂O₁₉ for the degradation of MB. The MB photocatalytic degradation kinetics is...
demonstrated in Fig. 7 b, where the data was plotted according to the pseudo-first kinetics model.

\[ \ln \left( \frac{C}{C_0} \right) = ln \left( \frac{dC}{dt} \right) = kt \]  

(12)

The graph demonstrates pseudo-first-order kinetics as reflected by \( R^2 \) value (0.97). The rate constant calculated from the slope is equal to \( k = 5.9 \times 10^{-3} \text{ min}^{-1} \), \( t_{1/2} = 117 \text{ min} \) and \( E_a = 12.72 \text{ kJ} \). Comparable results showing the consistency of MB photocatalytic degradation with the first order kinetic model were testified using different nanomaterials.

Blocking of Reactive Oxygen Species (ROS)

The data in Table 2 presents that using isopropanol, as a scavenging reagent for hydroxyl radical did not affect the photodegradation efficiency, regardless of ZnO nanostructure photocatalyst identity. This observation implied that hydroxyl radical has no role in the photodegradation process of MB. However, the use of para-benzoquinone, for superoxide radical, the photodegradation efficiency was falling down, from 75% (in the absence of all scavenging reagent) to 45%. This result showed that superoxide radical's minor role in the photodegradation of MB. However, the use of disodium ethylenediaminetetraacetic acid for the photogenerated holes, caused a remarkable reduction in photodegradation efficiency 75% to 16% over ZnO. This observation demonstrates the importance of holes direct interaction with MB on ZnO nanorods’ surface in photocatalytic degradation. The role of electrons photogenerated was also examined by using dimethylsulfoxide (DMSO).

It was found that they did not dramatically affect photodegradation, which was lowered from 75% to 54% over ZnO. This result indicated that MB photodegradation did not depend on photogenerated electrons over ZnO. Based on scavenging reagents experiments, we conclude that the valence band is where photodegradation of MB on ZnO occurs.

Table 2: Effects of scavenging reagents on MB photocatalytic degradation over ZnO photocatalyst

<table>
<thead>
<tr>
<th>Scavenging reagent</th>
<th>None</th>
<th>IPA</th>
<th>DMSO</th>
<th>PBQ</th>
<th>Na2EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB photocatalytic degradation</td>
<td>75%</td>
<td>75%</td>
<td>54%</td>
<td>45%</td>
<td>16%</td>
</tr>
</tbody>
</table>

Photocatalyst Recycling

We examined the recyclability of ZnO photocatalysts for reuse in the industrial sector. We found that the photodegradation efficiency decreased from 73% (first cycle) to ~68% (second cycle) to 42% (third cycle) over ZnO nanorods (Table 3). This decrease in photodegradation efficiency with the reused photocatalyst could be due to photodegradation products' accumulation on the photocatalyst surface.

Table 3: ZnO photocatalyst recovering for MB photodegradation

<table>
<thead>
<tr>
<th>Cycle number</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB photodegradation</td>
<td>73%</td>
<td>68%</td>
<td>42%</td>
</tr>
</tbody>
</table>

Mechanism of Photocatalysis

Ultraviolet light irradiation cause electrons...
excitation offering them enough energy to transit from the valence band (VB) to the conduction band (CB) of ZnO nanoparticles, opening positive holes (h⁺) in the VB (ZnO \rightarrow e_{CB} + h_{CB}^{+} \text{[63]})\). The strong oxidative species O₂⁻ \cdot generated from the electrons and O₂ reaction (O₂+ e⁻ → O₂⁻ \cdot) associate with H⁺ from solution to generate the peroxide H₂O₂ \text{[64]} (O₂+ 2H⁺ + e_{CB}^- \rightarrow H₂O₂). The produced H₂O₂ then goes through chain reactions with electron to the avail the active •OH radicals \text{(H₂O₂ + e⁻ → OH⁻ + •OH)}. Similarly •OH can be created via the h⁺/ surface adsorbed H₂O reactions\textsuperscript{21}. The degradation process proceeds by the consecutive attacks on the organic dye by •OH radicals (R + •OH → R•+ H₂O) or h⁺ (R + h⁺ → R⁺ → products)\textsuperscript{65}. Fig. 8 is a diagrammatic exemplification for the proposed photodegradation mechanism.

**CONCLUSION**

ZnO NPs of 15 nm size of archetypal wurtzite structure and cell parameters were efficaciously prepared through a precipitation approach. The SEM images exposed flower-like structures NPs, which were further found to compose primarily of Zn and O elements as supported by the EDS analysis. Moreover, the establishment of Zn–O bonding was exhibited by the FTIR vibrational frequency assignments. According to the optical examination, the synthesized nanomaterials showed 3.229 eV bandgap. The reaction was pseudo-first-order kinetics, and the degradation mechanism was proposed using scavenging reagents. They were suggesting that the photodegradation of MB on ZnO occurs on its valence band. Also, the recyclability of the photocatalysts was studied. This photocatalyst application for MB degradation marks it an excellent candidate for pollutant dyes detoxification.

**ACKNOWLEDGEMENT**

The authors wish to express thanks to Imam Mohamed Ibn Saud Islamic University, where this work has been done.

**Conflicts of Interest**

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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