Structural, Photocatalytic and Antibacterial Activity of ZnO and ZrO2 Doped ZnO Nanoparticles

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Abstract: A series of ZnO and ZrO2 doped ZnO catalysts were prepared by sol-gel method. X-ray diffraction analysis of these catalysts showed the formation of phase pure nanoparticles with wurtzite ZnO structure. Scanning electron microscope (SEM) images emphasized the formation of spherical nanoparticles with wurtzite ZnO structure. Transmission electron microscope (TEM) images emphasized that all prepared catalysts are in nanoscale and are spherically shaped. The Methylene Blue (MB) decomposition rate of the synthesized pure ZnO and ZrO2 doped ZnO nanoparticles were studied under the UV–Vis region. In the UV–Vis region, synthesized pure ZnO and ZrO2 doped ZnO decomposed Methylene Blue (MB). However, the MB decomposition rate obtained using pure ZnO was much higher than that by doped ZnO. The antibacterial property test was carried out via disk diffusion method, and the result indicated antibacterial activity of the prepared catalysts.

Keywords: ZnO, Sol-gel, photocatalysis, antimicrobial, ZnO /ZrO2

1. Introduction

Dyes and organic compounds are widely used in industry and daily life. Large amounts of these compounds were released in waste water resulting in considerable problems to microorganisms, aquatic environments and human beings [1-3]. Unfortunately, most of these dyes are chemically stable and cannot be removed by chemical oxidation via traditional biochemical and physicochemical methods used widely [4-6]. Additionally, traditional methods used widely like chlorination, generates carcinogenic and mutagenic by products [7].

Recently, heterogeneous photocatalysis is investigated widely to replace traditional methods because of its ability to completely decompose targeted pollutants including dyes and organic compounds besides inactivating microorganisms such as bacteria and viruses [1, 6-9].

ZnO is a semiconductor material with a wide band gap (3.2eV) [10], low cost, abundant in nature and environmental friendly so it worth to be studied as one of the most promising materials capable of achieving green chemistry [11-13].

As a heterogeneous photocatalyst, ZnO has comparable band gap with TiO2 (3.2eV) [14-15], lower productivity cost [16-18], larger quantum efficiency than TiO2 [19,20] so it absorbs over larger fraction of the solar spectrum than TiO2 [21-28]. Although ZnO and TiO2 have similar band gaps, ZnO has higher photoactivity (by a factor of 2 – 3) in both UV and sunlight irradiation for the decontamination of water [29-35]. This is due to the higher efficiency of ZnO in the production of OH radical and reduced recombination of photo induced electron–hole pairs [16-18, 36-41].

Point defects mainly from oxygen vacancies are the main reason for the higher efficiency of ZnO in the production of OH and reduced recombination of photo induced electron–hole pairs [42-46].

The heterogeneous photocatalytic process is initiated when a semiconductor material such as ZnO or TiO2 is illuminated with photons possess energy equal or greater than the bending energy of electrons in the valence band, resulting in the generation of mobile electrons in the higher energy conduction band (Ecb) and positive holes in the lower energy valence band (Evb) of the catalyst [47].

The photocatalytic reaction depends on holes formed in the valence band which catalyze formation of hydroxyl radicals at the semiconductor surface and mobile electrons in the conduction band which reduce molecular O2. These reactions represent steps to both mineralization of organic species and removal of inorganic cations [48-51].

In this work, we aimed to synthesize nontoxic, environmental friendly and affordable photocatalyst to investigate in the removal of MB as a well-known water pollutant. MB is a heterocyclic organic dye, frequently used in textile, cosmetic and pharmaceutical industries. MB can cause permanent injury to humans and animals on inhalation and ingestion and the risk of the presence of this dye in water may be arisen from the burning effect of eye, nausea, vomiting and diarrhea [52]. Moreover, we studied the antimicrobial activity of ZnO and ZrO2 doped ZnO against gram positive and gram negative bacteria.

2. Experimental

2.1. Preparation of Catalysts:

2.1.1. Zinc Oxide nanoparticles synthesis:

Zinc Oxide nanoparticles were prepared by sol-gel method from zinc acetate dihydrate and oxalic acid using ethanol as solvent [53-54]. ZnO gel was obtained by dissolving 10.99g zinc acetate dihydrate in 300ml ethanol (C2H5OH) and refluxing for 30 minutes. 17.71g oxalic acid (H2C2O4) was mixed with 200ml of ethanol; stirred for 1 hr at 50 °C and added to the previous solution slowly. The final mixture was refluxed at 50 °C for 60 minutes before left cool down to room temperature. Finally, the prepared ZnO gel was dried at 80 °C for 2 hrs (xerogel), and the powder calcined under flowing air (0.1mmolS⁻¹) for 3 hrs at (400,500 and 600 °C).

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2.1.2. ZrO₂ doped zinc oxide Synthesis:

Zirconium nitrate was dissolved in ethanol and added to ZnO gel, stirred for 1 hr, dried at 80 °C for 20 hrs to form xerogel and finally calcined at 500 °C to synthesize 0.005, 0.01, 0.015 and 0.02 ZrO₂/ZnO molar ratios.

1.2. Characterization of catalysts:

XRD was used to determine the nature and the size of crystalline phases of ZnO and ZrO₂ doped ZnO. Patterns were obtained with hand pressed samples mounted on a Philips PW 1830 goniometer using the Cu Kα line (λ =0.15458 nm) radiation under 40 kV and 100 mA and scanning with the 20 ranging from 10˚ to 70˚ [54].

ZnO and ZrO₂ doped ZnO particles sizes were examined by a Jeol JSM-840 scanning electron microscope (SEM) under high vacuum and acceleration voltage of 200 KeV. The samples were deposited onto carbon tape and coated with gold in a Blazers plasma sputterer (30s at 30mA).

Particle size and shape of nano ZnO and ZrO₂ doped ZnO particles were examined by a JEM-2100F transmission electron microscope (TEM) at a voltage of 300 KeV. Transmission electron micrograph gives directly the size and shape distributions. The powders are dispersed in Ethanol by stirring in an ultrasonic tank for 15 min. A drop of this suspension was then mounted on a carbon-coated copper grid for analysis [41].

The total acidity of all catalysts was determined by means of the potentiometric titration method using an Orion 420 digital model using a double junction electrode. In this method, 0.1gm catalyst was heated under vacuum, and then 10 ml of acetonitrile was added. After agitation for 2hrs, the suspension was titrated by 0.01N N-butyl amine digital model using a double junction electrode. In this method, 0.1gm catalyst was heated under vacuum, and then 10 ml of acetonitrile was added. After agitation for 2hrs, the suspension was titrated by 0.01N N-butyl amine and scanning with the 20 ranging from 10˚ to 70˚ [54].

Photocatalytic activity measurements of ZnO and 0.005M ZrO₂/ZnO powders were evaluated by measuring the degradation of MB in water under the UV/Vis light. The MB degradation was carried out at 20 °C with external lamp(400w UV/Vis lamps, Halogen Mercury lamp).

The amount of catalyst powder [ZnO] was kept at 1g.L⁻¹, the initial concentration of MB, C₀, was 10mgL⁻¹, and the pH of the solution was fixed to 7.

Photoactivity experiments were realized with varying operating variables: three different pH values (2.5, 7 and 10) adjusted with aqueous solution of HCl and NaOH and four initial concentrations of MB, C₀(10, 20, 50 and 100 mgL⁻¹).

Before each photocatalytic test, the mixture was kept in the dark for 30 minutes to ensure that the adsorption-desorption equilibrium was reached before illumination. The sample was then taken out at the end of the dark adsorption period, just before the light was turned on, in order to determine MB concentration in solution, C₀.

The experiment starts by turning on the lamp. After a given irradiation time sample was taken, centrifuged and the MB photodegradation monitoring was performed on a Shimadzu, MPC-2200 UV-Vis spectrophotometer [53].

Antimicrobial activity of heterogeneous catalysts was tested against a panel of gram positive staphylococcus Aureus and gram negative candida Albicans. Each of the catalysts was dissolved in DMSO and solution of the concentration 1mg/ml was prepared separately. Paper discs of watt man filter paper were prepared with standard size (5cm), were cut and sterilized in an autoclave.

The paper discs soaked in the desired concentration of the complex solution were placed aseptically in the petridishes containing nutrient agar media (agar 20g + beef extract 3g + peptone 5g) and seeded with staphylococcus aureus or candida Albicans. Each of the catalysts were tested against a panel of gram positive staphylococcus aureus or candida Albicans. The petridishes were incubated at 36 °C and the inhibition zone were recorded after 24hrs of incubation. Each treatment was replicated three times. The antibacterial activity of a common standard antibiotic ampicillin and antifungal colitrimazole was also recorded using the same procedure as above at the same concentration and solvents [56]. The % activity index for the complex was calculated by the following formula:

\[
\text{% activity index} = \frac{\text{Zone of inhibition by test compound(diameter)}}{\text{Zone of inhibition by standard(diameter)}} \times 100
\]

3. Results and Discussion

3.1. XRD Analysis:

The XRD patterns of prepared samples are shown in Fig.1. The sharp and intense peaks indicate that ZnO and ZrO₂ doped ZnO samples are highly crystalline. All of the indexed peaks indicate that all the samples are the typical wurtzite hexagonal structure (JCPDS card No.36-1451) [57]. No phases for ZrO₂ were observed. The intensity of (101) and (002) peaks increases with increasing ZrO₂ content because the ionic radius of Zr⁴⁺ (0.84 Å) is larger than that of Zn²⁺ (0.74 Å). Consequently, the more Zn²⁺ ions are substituted by Zr⁴⁺, the more lattice expansion occurs and ZnO particles become larger [58-59]. These results indicate that the Zr atoms have entered into the ZnO lattices instead of forming other lattices.
3.2. SEM Analysis:
The surface morphology of the prepared catalysts was examined by SEM analysis. The SEM images show that the particles to some extent are aggregated. Fig.2(I) shows that ZnO has irregular spherical shape. However, in Fig.2(II, III) The SEM micrographs of the 0.01M ZrO$_2$/ZnO and 0.02M ZrO$_2$/ZnO appear in spherical shape perfectly. Fig.2 shows also that ZnO and ZrO$_2$/ZnO nanoparticles have particle size ranging between 90 to 150nm.

The difference in the particle sizes shown by XRD and SEM analysis for ZnO and ZrO$_2$ doped ZnO could be due to particles aggregation [57]. In addition, the SEM measurements are based on the difference between the visible grain boundaries, while XRD calculations measure the extended crystalline region that diffracts X-ray coherently. Hence, XRD method has more straight criterion and leads to smaller sizes [60].

![Figure 1: XRD pattern of (a) ZnO, (b) 0.01M ZrO$_2$/ZnO, (c) 0.02M ZrO$_2$/ZnO](image)

3.3. TEM analysis:
Figure 3 TEM images illustrate ZnO and ZrO$_2$/ZnO nano particles are almost hexagonal (spherical) in shape and are agglomerated up to some extent. The average

![Figure 2: SEM images of (I) ZnO, (II) 0.01M ZrO$_2$/ZnO and (III) 0.02M ZrO$_2$/ZnO](image)
nanoparticles diameter measured of ZnO is < 25nm as shown in Fig. 3 (I). The particles size increases with increasing ZrO₂ content. Fig.3 (II) shows that when ZrO₂ content increased to 0.01M ZrO₂/ZnO a slight increase in grain size is observed, however, when it increases to 0.02M ZrO₂, the grain size increases sharply to about 0.2 µm as shown in Fig.3 (III). Consequently, TEM results illustrated in Fig.3 roughly agrees with XRD shown in Fig.1 in that ZnO crystal size increases by increasing ZrO₂ content.

3.4. Acidity test:
The surface acidity of the investigated catalysts was determined by non-aqueous titration of n-butyl amine (PK_a=10.73), which is a basic molecule suitable for titrating the medium and strong acid sites on the surface of the investigated catalysts. Fig.4: illustrates the variation of the electrode potential for the investigated catalysts calcined at 500 °C with volume added from n-butyl amine. This figure shows that, as the acid sites of the solid become neutralized, a buffer behavior becomes more apparent. The trend of the titration curve is asymptotic, leading to a characteristic value on the potential (mV) axis [55]. This is related to the volume added from n-butyl amine / g needed for neutralization of the surface acidity. The magnitude of change of the electrode potential in this method is related to the surface acidity of the catalyst. Table 1: shows the volume of n-butyl amine / g needed for the neutralization of the surface acidity of catalysts as a function of ZrO₂ content and the total number of acid sites / g. This technique was carried out by measuring the electrode potential (mV) as a function of the progressive increase of the n-butyl amine concentration expressed as (mmol n-butyl amine / g catalyst) [55]. The total number of acid sites / g of the catalysts were calculated from the following relation:

\[
\text{Total number of acid sites} / g = (\text{ml equivalent} / g) \times N \times 1000
\]

(Where N is Avogadro's number).

\[\text{Figure 3}:\text{ TEM images of (I) ZnO,(II)0.01M ZrO}_2/\text{ZnO and(III) 0.02M ZrO}_2/\text{ZnO}\]

\[\text{Figure 4}:\text{Acidity curves for (a) ZnO, (b) 0.005M ZrO}_2/\text{ZnO, (c) 0.01M ZrO}_2/\text{ZnO, (d) 0.015M ZrO}_2/\text{ZnO, (e) 0.02M ZrO}_2/\text{ZnO}\]

\[\text{Table 1}:\text{Volumes of n-butyl amine/g and total number of acid sites/g}\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>ml added</th>
<th>Total № of acid sites/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.35</td>
<td>2.1×10^19</td>
</tr>
<tr>
<td>0.005M ZrO₂/ZnO</td>
<td>0.30</td>
<td>1.81×10^19</td>
</tr>
<tr>
<td>0.01M ZrO₂/ZnO</td>
<td>0.266</td>
<td>1.6×10^19</td>
</tr>
<tr>
<td>0.015M ZrO₂/ZnO</td>
<td>0.25</td>
<td>1.5×10^19</td>
</tr>
<tr>
<td>0.02M ZrO₂/ZnO</td>
<td>0.23</td>
<td>1.38×10^19</td>
</tr>
</tbody>
</table>
3.5. Photocatalytic Activity:
The photocatalytic activity of ZnO and ZrO2 doped ZnO was investigated using MB Dye. MB was irradiated under UV–Vis light in absence of catalyst (photolysis), in absence of light (adsorption) and under UV–Vis light in presence of catalyst (photocatalysis). The results of the studies are illustrated in Fig.6. It is observed that direct photolysis did not cause any significant degradation in absence of catalyst. In the presence of ZnO without irradiation, MB showed a slight adsorption on ZnO surface but no degradation occurred. Irradiation of MB under UV–Vis light caused 99% degradation in 60 min. The photodegradation leads to the conversion of organic carbon into harmless gaseous CO2 and that of nitrogen and sulfur heteroatoms into inorganic ions, such as nitrate and ammonium, and sulfate ions, respectively [61].

3.5.1 Effect of calcination temperatures on the photocatalytic activity:
The effect of calcination temperature on ZnO photocatalytic efficiency in degradation of MB is depicted in Fig.7. It can be noticed that the degradation efficiency increased with increasing calcination temperature from 400 °C to 500 °C and then decreased greatly with further increase in calcination temperature to 600 °C. This deterioration in ZnO photodegradation efficiency at 600 °C is related to particle segregation. It is reported that photocatalytic activities of ZnO calcined at temperatures beyond 500 °C decreases rapidly due to increasing particle size and sintering of crystallites [20, 62]. This confirms that the particle size and crystallinity also plays an important role in deciding the catalyst performance along with surface area. ZnO catalyst calcined at 500 °C was found to be the most active catalyst for the photodegradation of MB under UV/Vis light. Thus, it is used as catalyst for optimizing key parameters of the photodegradation of MB under UV/Vis light.

3.5.2 Effect of ZrO2 doping concentration on photocatalytic properties of ZnO:
Fig.8 shows the photocatalytic degradation of MB on ZnO with different concentrations of ZrO2. Decrease in photocatalytic efficiency by increasing concentration of ZrO2 as a dopant is observed. This deficiency in photocatalytic activity arises from the fact that ZrO2 has band gap around 5 eV and it cannot undergo direct band gap excitation at UV/Vis light [57]. The increase in particle size showed by XRD analysis (Fig.1) and TEM analysis (Fig.3) in ZrO2 doped ZnO catalysts may be another reason for its photocatalytic deficiency.

Figure 5: Effect of ZrO2 content on total number of acid sites and initial potential of acid sites

Figure 6: Photocatalytic degradation efficiency of ZnO and 0.005M ZrO2/ZnO at 10ppm MB and 0.05g of ZnO and ZrO2/ZnO.

Figure 7: Photocatalytic degradation curves of MB on ZnO treated under different temperatures

Figure 8: Photocatalytic degradation efficiency of ZnO and ZrO2/ZnO at 10ppm MB and 0.05g of ZnO and ZrO2/ZnO.
3.5.3 Effect of initial pH:

pH is an important factor that influences the photodegradation process of various pollutants. Effect of different values of pH (2.5, 7, 10) on the photo catalytic degradation of MB at constant concentration (10mg/L) and amount of [ZnO]=1g/L is illustrated in Fig.9. Photodegradation efficiency of MB is increased by increasing pH values from pH 2.5~10. This variation is related to the change in electrostatic attraction or repulsion between dye molecules and catalyst. MB is a cationic dye and therefore the electrostatic attraction between the dye molecules and catalyst surface is greatly improved at pH =10.

The observed enhancement in the degradation of MB at pH=10 can be attributed to the presence of excess hydroxyl groups on the catalyst surface. This results in the formation of more hydroxyl radicals (OH) so electrostatic attraction will increase and then the photodegradation of MB increases [63]. The low photodegradation of MB in acidic medium (pH=2.5) is due to slight dissolution of ZnO and the catalyst surface will be protonated (have +Ve charge) so there will be electrostatic repulsion [64].

![Figure 9: Photo degradation efficiency of MB at different pH values](image)

3.5.4 Effect of initial concentration of MB

Dye concentration was investigated using initial concentrations of MB (10ppm, 20ppm, 50ppm and 100ppm), 0.05gm of catalyst and 50mL of dye solution at pH=10. The results illustrated in Fig.10(a, b), show that undoped ZnO had higher efficiency in photodegradation of MB at all concentrations.

Also it can be observed that the photodegradation efficiency decreased by increasing the dye concentration. It is well known that photodegradation efficiency basically depends on the amount of hydroxyl radicals formed on the surface of the catalyst. As the concentration of dye increases, amount of dye adsorbed on the catalyst surface increases, consequently generation of hydroxyl radicals will be reduced. Furthermore, as the concentration of MB increases, the fewer photons reach the catalyst surface. As a result, the production of hydroxyl radicals that can attack the pollutants will decrease and photocatalytic efficiency decreases [65-66].

![Figure 10: Effect of initial concentration of MB on the photodegradation efficiency of a) ZnO and b) 0.005M ZrO₂/ZnO under UV–Vis light](image)
3.5.5. Kinetic studies of MB degradation using ZnO and 0.005 M ZrO2/ZnO under UV-Vis light:

Kinetic studies of many organic pollutants have been modeled using Langmuir-Hinshelwood equation. This model is given by the equation below:

$$ r = \frac{dc}{dt} = K_{app} C $$

Where $r$ is the degradation rate (mg/L/min), the apparent constant of degradation (1/min), $C$ is the concentration of MB dye (mg/L) at any time $t$.

The integration of this equation with limitation: $C = C_0$ for $t = 0$ leads to the following equation:

$$ \ln \frac{C_0}{C} = K_{app} t $$

A straight line is obtained by plotting $\ln \frac{C_0}{C}$ vs. time, the slope of which upon linear regression equals the apparent first-order rate constant $K_{app}$ [53].

The kinetics of decomposition of MB at different concentrations using ZnO and 0.005M ZrO2/ZnO at pH = 10 is illustrated in Fig.11(a, b). The results show that the photocatalytic decomposition of MB by ZnO and 0.005 M ZrO2/ZnO can be described by the first-order kinetic model. The plots of the concentration data gave a straight line. The correlation coefficient ($R$) for the fitted line and the rate constants ($K_{app}$) are calculated and their values are grouped in Table 2. $R^2$ is a measure of the strength and direction of the linear relationship between ln($C_0/C$) and time ($t$). The more $R^2$ values approach 1, the more the relation will be linear indicating that the reaction is first order reaction.

![Figure 11: Kinetic fit for the degradation of MB with a) ZnO and b) 0.005M ZrO2/ZnO](image-url)

**Table 2:** Rate constants and correlation coefficients for catalytic photodecomposition of MB

<table>
<thead>
<tr>
<th>$C_i$(mg/l)</th>
<th>$K_{app}$</th>
<th>$R^2$</th>
<th>$K_{app}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.1426</td>
<td>0.964</td>
<td>0.0531</td>
<td>0.956</td>
</tr>
<tr>
<td>20</td>
<td>0.0378</td>
<td>0.931</td>
<td>0.0136</td>
<td>0.957</td>
</tr>
<tr>
<td>50</td>
<td>0.0105</td>
<td>0.951</td>
<td>0.0058</td>
<td>0.981</td>
</tr>
<tr>
<td>100</td>
<td>0.0088</td>
<td>0.996</td>
<td>0.0041</td>
<td>0.958</td>
</tr>
</tbody>
</table>
4.6. Antibacterial activity:
In this work, bacterial strains of positive staphylococcus Aureus and negative candida Albicans were employed during the antibacterial test. ZnO and ZrO₂ doped ZnO samples exhibited a remarkable antibacterial activity against tested bacterial strains as shown in table 3. The antibacterial activity of a common standard antibiotic ampicillin and antifungal colitrimazole was also recorded using the same procedure at the same concentration and solvents to be considered as reference drug.

4. Conclusions
In recent work, ZnO and ZrO₂ doped ZnO nanoparticles have been prepared by sol-gel method. The X-ray diffraction (XRD) studies confirmed the formation of Wurtzite hexagonal phase of polycrystalline ZnO and ZrO₂ doped ZnO. SEM analysis showed that ZnO and ZrO₂ doped ZnO nano composites had a spherical shape. TEM analysis coincides with XRD analysis in that ZnO and ZrO₂ doped ZnO were in nano scale lower than 25 nm and increased in volume by increasing ZrO₂ content. Photocatalytic experiments showed that undoped ZnO is photocatalytically more active than ZrO₂ doped ZnO catalysts. However, ZrO₂ doped ZnO showed improvement in antimicrobial activity.

References

Table 3: Shows the antibacterial activities of ZnO and ZrO₂ doped ZnO against tested organisms

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>S.Aureus (mg/ml)</th>
<th>C.Albicans (mg/ml)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Diameter inhibition zone of (in mm)</td>
<td>% activity index</td>
<td>Diameter inhibition zone of (in mm)</td>
</tr>
<tr>
<td>1</td>
<td>ZnO</td>
<td>7</td>
<td>30.4</td>
</tr>
<tr>
<td>2</td>
<td>0.005MZO₂/ZnO</td>
<td>8</td>
<td>34.8</td>
</tr>
<tr>
<td>3</td>
<td>0.01MZO₂/ZnO</td>
<td>8</td>
<td>34.8</td>
</tr>
<tr>
<td>4</td>
<td>0.015MZO₂/ZnO</td>
<td>11</td>
<td>47.8</td>
</tr>
<tr>
<td>5</td>
<td>0.02MZO₂/ZnO</td>
<td>8</td>
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</tr>
<tr>
<td>Ampicillin</td>
<td>23</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>Colitrimazole</td>
<td>NA</td>
<td>---</td>
<td>27</td>
</tr>
</tbody>
</table>

- NA: No activity

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