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Simplistic Synthesis and Enhanced Photocatalytic Performance of Spherical ZnO Nanoparticles Prepared from Arabinose Solution

https://doi.org/10.1515/zna-2019-0059
Received February 25, 2019; accepted June 22, 2019; previously published online July 29, 2019

Abstract: Strenuous efforts have been employed to prepare zinc oxide (ZnO) with eco-friendly methods; however, few studies have reported the fabrication of ZnO using a sustainable procedure. In this study, spherical ZnO nanoparticles were successfully fabricated for photocatalysis applications using a simple and eco-friendly method using an arabinose sugar solution. The ZnO nanoparticles with a wurtzite structure were obtained by combining zinc nitrate and arabinose in water, followed by heating, evaporation, and calcinations at different annealing temperatures. The annealed ZnO photocatalysts were characterised via X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The findings revealed a hexagonal wurtzite structure and good crystallinity with crystallite size increasing from 18 to 31 nm by means of an increase in the annealing temperature. The photocatalytic performance was examined to determine the degradation of mix dye waste. The spherical ZnO nanoparticles showed mix pollutant degradation of 84 % in 25 min at 400 °C.

Keywords: Arabinose; Eco-friendly method; Mixed dye waste degradation; Photocatalysis; ZnO.

1 Introduction

With the improvement of nanomaterials for different applications, many works have studied the synthesis of nanomaterials using synthetic methodologies. The approaches that have been used for fabricating zinc oxide (ZnO) nanomaterials include sol-gel [1], co-precipitation [2], hydrothermal [3], physical vapour deposition [4], chemical vapour deposition [5], and the thermal evaporation method [6]. However, these methodologies are costly and use dangerous chemical compounds and organic solvents that discharge into the environment and cause human health risks [7]. Therefore, ZnO nanoparticles synthesised through a sustainable, eco-friendly method are receiving rising attention because of their low cost and environmental friendliness [8]. Natural polysaccharides, such as pectin [9, 10], hyaluronic acid, and chondroitin-6-sulfate [11] or gum arabic (a complex mixture of glycoprotein and polysaccharides), have been successfully used to fabricate ZnO nanomaterials [11]. However, there are some disadvantages of these methods. For instance, the natural polysaccharide in natural polymers (such as gum arabic and pectin) contains metallic and nonmetallic impurities that can change the preferred properties of the zinc oxide nanoparticles by polluting them with the metallic and nonmetallic elements. Hence, for the fabrication of high-quality ZnO nanoparticles using a green synthesis method, a highly uncontaminated and economical fuel is required. In this regard, because of its low cost and ease of use, arabinose could potentially be used as a mediating material to form ZnO with high purity. However, few studies have been conducted to synthesise ZnO nanoparticles mediated by a monosaccharide (sugar), which can be green methods.

On the basis of previous studies, this research determined that arabinose monosaccharide could possibly promote ZnO production. Therefore, arabinose sugar and zinc nitrate were used to fabricate ZnO nanoparticles. This method was efficient and safe for preparing ZnO nanoparticles, as opposed to traditional approaches that
use hazardous materials. The characteristics of the ZnO nanoparticles such as the structural, morphological, and optical properties, as well as thermal stability, were investigated using X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), ultraviolet-visible (UV-Vis) spectroscopy, and Fourier transform infrared spectroscopy (FTIR) [12, 13]. The influence of annealing on the phase structure, morphologies, elemental composition, optical properties, and photocatalytic properties were investigated and are reported in this paper.

2 Methods

2.1 Green Synthesis of ZnO Spherical Nanoparticles

During the facile fabrication process, 100 mL of 0.3 M zinc nitrate dihydrate solution was stirred well for 30 min. Arabinose solution (100 mL; 33.3 mmol) was then added dropwise to the zinc nitrate solution under vigorous stirring at 90 °C for 6 h. A brown-white powder was formed. After a few minutes, the obtained powder was cooled at room temperature and then ground and annealed at different temperatures such as 400, 500, 600, and 700 °C for 3 h to obtain spherical ZnO nanoparticles, as illustrated in Figure 1. The ZnO powders were characterised in detail in terms of their structural, morphological, compositional, and optical properties, as well as photocatalytic activity, by employing different analytical techniques.

2.2 Characterisation Techniques

The phase structure and average crystallite size of the ZnO nanoparticles were investigated by examining the powder’s XRD patterns. The samples were recorded with a diffractometer (D8 Advance Bruker, Mannheim, Germany) using Cu–Kα radiation (λ = 0.15406 nm). The morphology of the obtained nanopowder was tested through SEM. The specimens were previously oven-dried at 105 °C and coated with a thin film of gold to create electrical conduction on the surface of the ZnO powder. The mode of chemical bonding in the prepared samples was studied by FTIR (Nicolet 6700, Thermo Fisher, Waltham, MA, USA) in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹.

2.3 Photodegradation of Mix Dye Waste

A mixture of methyl orange (MO), indigo carmine (IC), and malachite green (MG) at λmax = 616 nm was selected to assess the photocatalytic performance of the spherical ZnO nanoparticles. A 254 nm UV lamp was employed as the light source and was located 20 cm away from the mixtures. During the test, 50 mg of the catalyst was dispersed in 100 mL of 11 mg/L of the combined dye solution in a 250 mL beaker. The reaction suspension was magnetically stirred for 30 min to achieve adsorption-desorption equilibrium. Afterwards, the suspension solution was illuminated with the UV light. At each time interval, 5 mL of the solution was withdrawn, centrifuged, and filtered through a membrane filter (0.2 µm), after which the residual concentration was measured. The degradation percentage of the dye waste was then calculated as follows [14]:

\[
\text{dye waste removal} \% = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)
\]

where \( C_0 \) and \( C_t \) represent the initial dye waste concentrations (11 mg/L) and time \( t \), respectively.

3 Results and Discussion

3.1 Characterisations of Fabricated ZnO Nanoparticles

3.1.1 Thermal Stability

Figure 2 displays the TGA thermograph of the Zn-arabinose, which indicated two weight-loss stages of the
Figure 2: Thermal stability analysis of Zn-arabinose.

Zn-arabinose during the heating process. In the first stage, between 160 and 295 °C weight loss was caused by the decomposition of the arabinose sugar to small organic compounds such as 2-furancarboxaldehyde, furan methanol, α-angelicalactone, and methyl ester of furoic acid [15]. The second stage took place between 300 and 400 °C, where the weight loss was due to the complete degradation of Zn/organic fragments to produce stable spherical ZnO nanoparticles. Therefore, 400 °C was the optimum heat-treatment condition at which all of the Zn-arabinose was transformed to ZnO nanoparticles.

3.1.2 XRD Analysis

The XRD patterns of the prepared spherical ZnO nanoparticles at different annealing temperatures are displayed in Figure 3. The results of the XRD patterns revealed that the peaks at 31.71°, 34.38°, 36.30°, 47.52°, 56.56°, 62.91°, and 67.93° were well indexed to (100), (002), (101), (102), (110), (103), and (112) planes. These results were equivalent to wurtzite ZnO (JCPDS 36-1451) [16] with well-crystallised ZnO nanoparticles. The XRD patterns also confirm significant changes in the crystallite size with the increase in the annealing temperature from 400 to 700 °C (Fig. 4). This has a hexagonal wurtzite ZnO structure (JCPDS 36-1451) with high purity and crystallinity that increased with annealing temperature. The average crystallite size was calculated using Debye-Scherrer’s formula [17, 18].

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

Also, the lattice parameters \( a \) and \( b \) were obtained via the following equations:

\[ a = \frac{\lambda}{\sqrt{3 \sin \theta}} \quad \text{and} \quad c = \frac{\lambda}{\sin \theta} \]

and the volume of unit cell was estimated through the following equation:

\[ v = 0.866 \times a^2 \times c \]

\( d \)-spacing values were obtained from Braggs’s equation as follows:

\[ d = \frac{\lambda}{2 \sin \theta} \]

The variation of crystallite size, lattice parameters, and \( d \)-spacing results are presented in Table 1. It is worth noting that the average crystallite sizes of ZnO samples annealed at 400, 500, 600, and 700 °C was 18.23, 24.06, 27.64, and 31.19 nm, respectively. The average \( c/a \) ratio is in agreement with that of the hexagonal wurtzite structure of ZnO, indicating that the influences of heat treatment still preserve the ZnO structure.

Figure 3: XRD diffraction patterns of spherical ZnO nanoparticles at different annealing temperatures.

Figure 4: Relationship between full width at half maximum and crystalline size with annealing temperature.
Table 1: d-spacing, crystalline size (D; nm), lattice parameters, and unit cell (v) of ZnO nanoparticles with different annealing temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>2Θ(101)</th>
<th>d-spacing</th>
<th>FWHM</th>
<th>Crystalline size (nm)</th>
<th>Lattice parameters</th>
<th>c/a</th>
<th>Unit cell (v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>36.13</td>
<td>2.484</td>
<td>0.479</td>
<td>18.23</td>
<td>3.257</td>
<td>5.222</td>
<td>1.6033</td>
</tr>
<tr>
<td>500</td>
<td>36.16</td>
<td>2.482</td>
<td>0.363</td>
<td>24.06</td>
<td>3.263</td>
<td>5.221</td>
<td>1.6030</td>
</tr>
<tr>
<td>600</td>
<td>36.20</td>
<td>2.479</td>
<td>0.316</td>
<td>27.64</td>
<td>3.254</td>
<td>5.214</td>
<td>1.6023</td>
</tr>
<tr>
<td>700</td>
<td>36.22</td>
<td>2.478</td>
<td>0.280</td>
<td>31.19</td>
<td>3.253</td>
<td>5.212</td>
<td>1.6022</td>
</tr>
</tbody>
</table>

FWHM, full width at half maximum.

The average crystallite size, lattice parameters, and unit cell volume estimated from all aforementioned equations are present in Table 1.

### 3.1.3 SEM Image Analysis and Energy-Dispersive X-Ray (EDX) Investigation

The morphology of the specimens was investigated using field emission scanning electron microscopy (FESEM) and is shown in Figure 5a–d. It can be noted that the samples showed spherical nanoparticles at room temperature with particle sizes increasing with incremental increases in the annealing temperature. To check the formation and purity of ZnO prepared, the EDX analysis was employed. The spectra of ZnO at 700 °C (Fig. 5f) clearly showed a strong response at 1 and 0.5 keV attributed to Zn and O, respectively. Moreover, a weak peak at 8.6 and 9.5 were also due to Zn. Besides, the weight percentages of the elements Zn and O achieved from EDX results were 78.30 % and 21.7 %, respectively.

### 3.1.4 UV-Vis Analysis and Band Gap Determination

The optical properties (UV-Vis) of ZnO spherical nanoparticles at 400, 500, 600, and 700 °C annealing temperatures are portrayed in Figure 6a. It is demonstrated that the absorption edges of the ZnO nanoparticles have the values around 371, 373, 378, and 381 nm at annealing temperatures of 400, 500, 600, and 700 °C, respectively. These findings could be attributed to the creation of crystal defects in the form of oxygen vacancies with higher calcination temperature [19]. Indeed, these vacancies of oxygen may be neutral $V_0$, singly charged $V_0^+$, and doubly charged $V_0^{++}$ [20]. This shift in the absorption peak to a higher wavelength with annealing temperature also results in lessening the band gap of ZnO nanoparticles as estimated in the literature [21, 22]. The UV light absorbance at 371 nm may be ascribed to the movement of electrons between the conduction band (CB) and the valence band (VB). Diffuse reflectance spectroscopy analysis has been conducted to evaluate the effect of annealing on the band gap energy of the spherical ZnO nanopowder. The band gap energy of the samples has been calculated thanks to the Tauc equation [23]:

$$ (a \nu)^{1/n} = A(\nu - E_g) $$

where $\nu$ is the Planck’s constant, $v$ is the frequency, $a$ is the absorption coefficient, $E_g$ is the band gap energy, $A$ is a proportionality constant, and $n$ refers to the type of electron transition (for directly allowed transitions, $n = 1/2$). As depicted in Figure 6b, the value of the energy band gap was found to be 3.2, 3.18, 3.17, and 3.16 eV for ZnO at 400, 500, 600, and 700 °C, respectively. It can be noticed that the value of ZnO at 400 °C was shifted to a lower value of ZnO at higher annealing temperature (from 3.2 to 3.16 eV). This band gap narrowing is could be due to improved crystallinity with the increase in annealing temperature.

### 3.1.5 FTIR Study and Purity

The formation of spherical ZnO nanoparticles and their purity were investigated employing FTIR spectroscopy at room temperature in the range of 400–4000 cm$^{-1}$ (Fig. 7). The vibration absorption was clear at peaks 460, 1575, and 3432 cm$^{-1}$. The strongest peak at 460 cm$^{-1}$ belongs to the stretching vibration Zn–O mode, confirming the formation of spherical ZnO nanoparticles [19]. The spectrum of ZnO at different annealing temperatures showed the absorption band at 3432 cm$^{-1}$, which is characteristic of the O–H stretching of water molecules on the surface of the ZnO nanoparticles. Another small peak located at 2343 cm$^{-1}$ corresponds to CO$_2$ molecules that are present in air [24].

### 3.2 Photocatalytic Activity of Spherical ZnO Nanoparticles

To scrutinise the photocatalytic activity of the spherical ZnO catalysts, they were probed through photodegradation of a mixture of three dyes (MO, IC, and MG) as typical environmental toxins. A spectrum of the mixtures of dye waste at 616 nm (maximum adsorption wavelength)
Figure 5: (a–d) FESEM images of ZnO nanoparticles at different annealing temperatures from 400 to 700 °C and (f) EDX spectra of ZnO nanoparticles at 700 °C.

is illustrated in Figure 8a. The degradation and kinetics of the photodegradation of dye mixtures were evaluated using ZnO nanoparticles annealed at different temperatures under UV light irradiation with standard experimental conditions as displayed in Figure 8b, c. It is a well-known truth that an incident photon with $\lambda < 390$ nm can make an exciton, i.e. a bound electron-hole pair in spherical ZnO photocatalyst. These electron-hole pairs on the surface of the ZnO nanoparticles via a series of oxidation-reduction reactions produce intermediates such as $O_2^*$, $HO_2^*$, and $H_2O_2$, which lastly breed OH$^*$ radicals in the existence of dissolved $O_2$. These OH$^*$ radicals are extremely strong oxidizing agents that can cause the disruption of the aromatic rings of the mixed dye molecules, resulting in their decomposition [25].

The effect of annealing of ZnO nanoparticles on the photocatalytic degradation of pollutants was demonstrated thanks to the Langmuir-Hinshelwood
where $t$ represents the illumination time (min) and $k$ is the rate of degradation constant.

It can be observed that the photocatalytic degradation rate of the model pollutants decreased with the increase in the annealing temperature from 400 to 700 °C (Fig. 8a, b; Tab. 2). This observation may be due to the diminution of surface area and increases in the agglomerations of the ZnO nanoparticles, which is proved by SEM results (Fig. 5). Furthermore, this finding could be also because a ZnO nanoparticle at 400 °C has fine and small particle size. A similar result was observed in [19, 27]. Indeed, the spherical ZnO nanoparticles annealed at 400 °C eliminated 84 % of the simulated dye wastes after 25 min of illumination with a rate constant equal to 0.0867 nm$^{-1}$ as shown in Figure 8d and Table 2.

The major agent responsible for the forming of an electron-hole pair on the surface of the ZnO photocatalyst is the energy gap between the valence and CB, which is referred to as the band gap. The larger particle size of ZnO resulted in a minimal band gap [28, 29]. It can be noticed that with the increase in the annealing temperature, the particle size increases, which results in the diminution of the energy band gap. In addition, with smaller particle size, the surface area of the ZnO photocatalyst is also increased. Both of these agents favour improved photocatalytic activities of a ZnO photocatalyst.

Moreover, the introduction of the native defects in the ZnO particles in the form of neutral ($V_O$), singly charged ($V_O^+$), or doubly charged ($V_O^{2+}$) oxygen vacancies at elevated annealing temperatures up to 700 °C also plays a crucial role in the improvement of photocatalytic efficiencies of the fabricated spherical ZnO nanoparticles. These defects in the ZnO diminish the electron-hole recombination, increase the quantum yield, and result in better photocatalytic activities of ZnO nanoparticles. For our results, the photocatalytic performance for the spherical ZnO photocatalyst with higher annealing temperatures of 500–700 °C decreased, and this could be ascribed to the reduction of surface area due to the agglomerations of the ZnO particles [30].

### 3.3 Photocatalytic Degradation Mechanism

A possible photocatalytic mechanism for the degradation of organic pollutant by spherical ZnO is shown in Figure 9. By means of irradiating the as-fabricated ZnO catalyst with visible light, the electrons in the VB is excited to the CBs. Then, a corresponding number of holes are formed in the VB, as shown in Figure 9. In addition, the CB reacts with the dissolved oxygen to offer a superoxide radical, which resulted in the creation of hydroxide radicals [31].
Figure 8: (a) The UV-Vis spectra of the dye waste, (b, c) pseudo-first-order kinetics graph of ZnO at various annealing temperatures for the dye mixture photodegradation, and (d) the photodegradation percentage of ZnO for the dye waste.

Table 2: Energy band gap, rate constant, and degradation efficiency of ZnO nanoparticles.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>ZnO 400 °C</th>
<th>ZnO 500 °C</th>
<th>ZnO 600 °C</th>
<th>ZnO 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order constant (10^{-3} \text{ min}^{-1})</td>
<td>86.7</td>
<td>51.2</td>
<td>31.3</td>
<td>24.4</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.981</td>
<td>0.983</td>
<td>0.961</td>
<td>0.963</td>
</tr>
<tr>
<td>Degradation efficiency (%)</td>
<td>84</td>
<td>66</td>
<td>47</td>
<td>39</td>
</tr>
</tbody>
</table>

Figure 9: Proposed mechanism of photocatalytic degradation of mix dyes.
Afterwards, the VB reacts with H2O molecules to make hydroxide radicals. As a result, the ·OH radical produced in the solution is a physically influential oxidizing agent for mixed dye degradation. Therefore, the organic pollutant mixture is mineralised owing to the joint action of H+ and the powerful oxidizing species ·OH.

4 Conclusion

In summary, we developed a simplified green method using arabinose solution in fabricating spherical ZnO nanoparticles at different annealing temperatures. A major benefit of this approach is that mass production can be achieved at a low cost without using more chemicals, and this is interesting with respect to the study of many applications. The findings showed high thermal stability of the product with good crystallinity. In addition, the average crystallite size calculated from XRD has increased from 18.23 to 31.19 nm with the annealing temperature. Moreover, EDX analysis indicated that the Zn and O content of the spherical ZnO at 700 °C is 78.3 and 21.7 wt%, respectively. Furthermore, the photocatalytic performance of ZnO nanoparticles shows that the high photocatalytic degradation of the simulated dye wastes was at the minimum annealing temperature.

5 Highlights

Spherical (ZnO) nanoparticles were successfully fabricated using a green method via arabinose sugar solution. The photocatalytic performance was examined through the degradation of mixture dye waste. The spherical ZnO nanoparticles at 400 °C show mix pollutants degradation of 84 % in 25 min.

References