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Green biosynthesis and characterization of zinc oxide nanoparticles using Corymbia citriodora leaf extract and their photocatalytic activity

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ABSTRACT
We reported a green and simple method for biosynthesizing zinc oxide nanoparticles (ZnO NPs) using Corymbia citriodora leaf extract as reducing and stabilizing agent. SEM, EDX, XRD, UV–VIS spectroscopy, Raman spectroscopy and TGA have been used for characterizing the biosynthesized ZnO NPs. The results indicating the ZnO NPs synthesized by C. citriodora leaf extract have high purity and the average size is 64 nm. The photocatalytic activity of the ZnO NPs has been investigated by degradation methylene blue under visible light irradiation. Due to the smaller size, the biosynthesized ZnO NPs showed an excellent photocatalytic performance.

1. Introduction

Zinc oxide (ZnO) is a well-known \(n\)-type semiconductor with a band gap of 3.37 eV and excitation binding energy of 60 meV, hence is considered as one of the best photocatalysts to degradation of pollutant in water (1–11). In order to enhance the photocatalytic property of ZnO, nano-sized ZnO have been synthesized to increase the surface area and enhance the photocatalytic activity. ZnO nanoparticles (ZnO NPs) are commonly synthesized by wet chemical route (12–14), vapor phase process (15), hydrothermal method (16), precipitation (17) and sonochemical method (18). However, those methods always involve utilization of toxic reagents and expensive instruments along with the tedious process control. Therefore, there is great demand for developing a simple and green method for synthesizing ZnO NPs (19, 20). Recently, biosynthesis of NPs was attracted considerable attention due to its simplicity, low cost and nontoxicity. It was shown that the metal NPs produced by plants are more stable in comparison with those produced by other methods. In order to use an easy and safe green method in scale-up and industrial production of well-dispersed metal NPs, plant extracts are excellent materials. Biosynthesis of ZnO NPs using plants including Poncirus trifoliata (21), Ocimum basilicum L. var. purpurascens (22), Aloe vera (23), Parthenium hysterophorus (24), Astragalus gummifer (25) and Sedum alfredii (26) have been reported in the literature. Corymbia citriodora is a tall tree have been found growing widely in temperate and tropical north eastern Australia. Citronellelal is the major chemical component existed in the C. citriodora, which may produce a reducing effect to certain chemical. In this study, we report for the first time synthesis ZnO NPs using C. citriodora leaf extract as reducing agent. The photocatalytic activity of biosynthesized ZnO NPs also been investigated.

2. Experiments

2.1. Materials

C. citriodora plants were collected from a local nursery in Nanjing and the leaf extract was prepared based on the biosynthesis method (23). Typically, 5 g of C. citriodora leaves were washed with water and cut into small pieces. The leaves then boiled in 30 mL of water for 15 min. After cooling, the leaf extract was filtered, centrifuged and stored in refrigerator. Zinc nitrate hexahydrate (Zn (NO\(_3\))\(_2\)·6H\(_2\)O) and methylene blue (MB) were purchased from Sigma-Aldrich. All other chemicals used were analytical grade reagents without further purification.

2.2. Biosynthesis of ZnO NPs

The C. citriodora leaf extract was added into 0.5 M zinc nitrate solution (2:5 wt%) and kept under continuous
stirring at 80°C for 48 h. The pale white precipitate was obtained through centrifugation and washed with methanol and water. The ZnO NPs were then collected after dried at an oven over night.

2.3. Characterization

The crystal phase information of sample was characterized from 5° to 80° in 20 by a XRD with Cu Ka radiation (D8-Advanced, Bruker, Germany). Surface morphology of ZnO NPs were characterized by scanning electron microscope (SEM, ZEISS SUPRA 40VP combined with EDX, Germany). The optical analysis was obtained by UV–VIS spectrophotometer (HALO RB-10, Dynamica). Thermal gravity analyzer (TGA, TA instruments Q500) was carried out at temperature range of 20–1000°C using a scan rate of 20°C/min.

2.4. Photocatalytic degradation of MB

The photocatalytic activity of the biologically synthesized ZnO NPs and the ZnO NPs prepared with hydrothermal method (27) was compared by monitoring the decolouration of heterocyclic dye MB under visible light irradiation. In a typical process, 20 mg ZnO NPs were added into a quartz tube containing a MB solution (50 mL, 20 mg/L), which was placed with a 15 cm distance from the lamp. Prior to the illumination, the suspension was magnetically stirred in the dark for 30 min to reach the adsorption–desorption equilibrum. At given time intervals, 2 mL of suspension was sampled and centrifuged, the supernatant was collected for absorption analysis on a UV–VIS spectrophotometer. The absorbance of MB at 664 nm was used for measure the residual dye concentration.

3. Results and discussion

The formation of ZnO NPs during the biosynthesis could be observed visually. The color of reaction solution slowly changed from yellowish-green to pale white after mixing the leaf extract with zinc nitrate for several hours. Figure 1(a) shows the SEM image of biosynthesized ZnO NPs. It can be seen that the ZnO NPs reduced by C. citriodora leaf extract have excellent dispersibility. This excellent dispersibility could ascribe to the organic compounds adsorb on the surface of ZnO NPs from C. citriodora, which provides sufficient surface charges between individual ZnO NPs. Figure 1(b) shows the TEM image, it can be seen that the biosynthesized ZnO NPs exhibit polyhedron shape with a size range between 20 and 120 nm (Figure 1(c)). The elemental information of synthesized

Figure 1. (a) SEM and (b) TEM images of biosynthesized ZnO NPs, (c) particle size distribution graph and (d) EDX spectrum of ZnO NPs.
sample was analyzed by EDX. As shown in Figure 1(d), the spectrum of sample presents the only existence of O and Zn, indicating the high purity of formed ZnO NPs. Figure 2 shows the FTIR spectrum of C. citriodora leaf extract. It can be seen that the strong absorption peaks observed at 3300 and 1620 cm$^{-1}$ can assigned to O–H stretch and N–H bend functional groups. Weaker bands observed at 2955, 777 and 633 cm$^{-1}$ can be assigned to –C–H stretch (alkanes), C–H (aromatics) and –C=C–H (alkynes).

The absorption peaks at 1520 and 1431 cm$^{-1}$ can be attributed the C=C bending and C–C stretching of aromatic rings, respectively (28, 29). The peak at 1053 cm$^{-1}$ assigned to the C–N stretching mode in aliphatic amines (30, 31). The formation of ZnO NPs may attribute to the chemicals presence in the C. citriodora such as citronnellal, linalool, catechin, gallic acid, courmaric acid and protocatechuric acid, which can act as reducing agents as well as stabilizing agents (32). Table 1 summarizes the comparison of our biosynthesized ZnO with other literatures.

Figure 3(a) represents the XRD pattern of biosynthesized ZnO NPs, the peaks at 32.1°, 34.6°, 36.1°, 47.7°, 56.4°, 63.1° and 68.1° can be indexed to hexagonal wurtzite ZnO (JCPDS 36–1451). Furthermore, no other peaks have been detected in the sample, further confirmed the biosynthesized ZnO NPs owning a high purity. The mean crystalline size was calculated from the XRD peaks using Scherrer’s equation and found to be 21 nm (33).

Figure 3(b) shows the UV–VIS absorption spectrum of the biosynthesized ZnO NPs. It can be observed the spectrum exhibits a characteristic absorption peak at 386 nm due to the electron transitions from the valence band to the conduction band. Figure 2(c) displays the plot of the Kubelka-Munk remission function for biosynthesized ZnO NPs. The band gap of ZnO NPs can be defined as 3.07 eV.

TGA of the biosynthesized ZnO NPs was carried out and the result is shown in Figure 4(a). There are two different mass loss behaviors have been observed in the curve. The first weight loss (approximately 9.2%) before 200°C is due to the loss of chemisorbed water. The second weight loss (approximately 5.2%) at temperature range between 340°C and 420°C could ascribe to desorption and subsequent evaporation of some organic molecules belong to C. citriodora.

Figure 4(b) shows the Raman spectrum of biosynthesized ZnO NPs. A dominant peak is absorbed at 440 cm$^{-1}$, corresponding to the band characteristic for the Wurtzite hexagonal phase of ZnO Raman active branches (E$_2$) (34). Two peaks at 331 and 380 cm$^{-1}$ are shown to be as E$_{2h}$-E$_2$ (multiphonon) and A$_{1T}$ modes, respectively (35). Moreover, another peak located at 582 cm$^{-1}$ is related to the E$_1$ mode due to the oxygen deficiency, suggesting the existence of oxygen vacancies in the ZnO NPs (36).

The photocatalytic activity of biosynthesized ZnO NPs was investigated by degradation of MB under visible light illumination. Another ZnO NPs were prepared

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Plant</th>
<th>ZnO size (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(NO$_3$)$_2$</td>
<td>P. trifoliata fruit</td>
<td>21.12</td>
<td>Nagajyothi et al. (21)</td>
</tr>
<tr>
<td>Zn(NO$_3$)$_2$</td>
<td>O. basilicum leaf</td>
<td>50</td>
<td>Abdul Salam et al. (22)</td>
</tr>
<tr>
<td>Zn(NO$_3$)$_2$</td>
<td>Aloe barbadensis leaf</td>
<td>20–40</td>
<td>Sangeetha et al. (23)</td>
</tr>
<tr>
<td>Zn(NO$_3$)$_2$</td>
<td>C. citriodora leaf</td>
<td>20–120</td>
<td>This work</td>
</tr>
</tbody>
</table>

Table 1. Comparison of C. citriodora leaf extract synthesized ZnO NPs with literatures.
using hydrothermal method according to Pant’s report and employed as control group (33). Typically, 20 mg ZnO sample was added into 15 mL MB solution. Prior to the illumination, the suspension was magnetically stirred in the dark for 30 min to reach the adsorption-desorption equilibrium. At given time intervals, 1 mL of suspension was sampled and centrifuged, the supernatant was collected for absorption analysis on a UV–VIS spectrophotometer. The absorbance of MB at 664 nm was used for measure the residual dye concentration. The photodegradation time profiles of C/C₀ are shown in Figure 5, where C₀ and C are the initial concentration of MB and concentration after irradiation. It can be seen that the MB only shows a tiny self-degradation under the visible light irradiation for 90 min. However, the both ZnO NPs exhibit clearly photocatalytic performance. After 90 min irradiation, 83.45% and 59.47% of MB have been degraded by biosynthesized ZnO and hydrothermal synthesized ZnO, respectively. The superior photocatalytic activity of biosynthesized ZnO may be attributed to the smaller size compared with the ZnO NPs prepared through hydrothermal reaction, which could provide larger surface area for absorbing and degrading dye molecules.

4. Conclusion

In this study, we reported a simple and eco-friendly method for synthesizing ZnO NPs using C. citriodora leaf extract as novel reducing and stabilizing agent. The bio-synthesized ZnO NPs showed excellent dispersibility with average size of 64 nm. XRD indicates the formed ZnO is hexagonal wurtzite phase. This approach could be potentially used to industrial large scale synthesis of ZnO NPs. The photocatalytic activity of biosynthesized ZnO NPs have been evaluated by the photodegradation of MB. The results showed that the biosynthesized ZnO NPs have higher photocatalytic performance than normal hydrothermal prepared ZnO due to the smaller size.

Disclosure statement

No potential conflict of interest was reported by the authors.

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