Synthesis, Electrochemical Characterization and Photocatalytic Application of Ceion Doped ZnO nanoparticles using Leaf Extract of *Sesbania Grandiflora* by Green Method

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**Abstract:** Nanosized ZnO particles of specific morphology were synthesized using the plant leaf extracts of *Sesbania Grandiflora* (*Agathikeerai*). The structures and morphology of these fabricated ZnO nanoparticles and Ce ion doped ZnO nanoparticles were characterized by FTIR, SEM-EDAX, AFM and PL. Photodegradation and electrochemical behavior of the nanoparticles were studied. The aqueous *Sesbania Grandiflora* leaf extract acts as a solvent with multiple roles as promoter and capping agent for the synthesis of ZnO and Ce ion doped ZnO nanoparticles. Photocatalytic degradation was also investigated with Bismarck brown dye under UV-irradiation source. The ZnO and Ce ion doped ZnO nanoparticles exhibited potential photocatalytic activity towards the degradation of Bismarck brown dye. Green synthesis using *Sesbania Grandiflora* is found to be the best capping agent for synthesizing nanoparticles.

**Keywords:** Zinc oxide nanoparticles, Green synthesis, *Sesbania Grandiflora*, FT-IR, SEM-EDAX, AFM, PL, Photodegradation, Electrochemical studies

1. Introduction

Green synthesis techniques make use of moderately pollutant free chemicals to synthesis nanomaterials and embrace the use of benign solvents such as water, natural extracts. Green chemistry seeks to reduce pollution at source [1,2]. The advantage of using plants for the synthesis of nanoparticles is that they are easily available, safe to handle and possess a broad variability of metabolites that may aid in reduction. A number of plants are being currently investigated for their role in the synthesis of nanoparticles. ZnO belongs to the class of metal oxides, which is characterized by photo catalytic and photo-oxidising capacity against chemical and biological species [3]. Green synthesis of zinc oxide nanoparticles using Aloe vera [4], gold nanoparticles by alfalfa [5], *Cinnamomum camphora* [6], neem [7], *Embleica officinalis* [8], lemongrass [9] and tamarind [10] has been reported. Therefore the present investigation has been made to synthesize ZnO nanoparticles by *Sesbania Grandiflora*.

*Sesbania Grandiflora* is a plant from family fabaceae cultivated in all over India for its edible flowers. It has synonym *Agatigrandiflora* (Fig.1) and commonly known as Hummingbird Tree, Butterfly Tree. It’s one of the well-known medicinal plants of India. *Sesbania Grandiflora* has been known to have antimicrobial activities [11, 12].

2. Experimental Methods

2.1 Collection of Plant

The plant *Sesbania Grandiflora* was collected in the surroundings of Tirunelveli district, Tamilnadu.

2.2 Preparation of the leaf extract

The collected *Sesbania Grandiflora* leaves were washed several times with water to remove the impurities. Leaves had been dried in the sun shade for 7 days. After the leaves were dried, it is powdered using mortar. The *Sesbania Grandiflora* leaf powder of 10g was used for...
incidence. EDAX measurements were carried out by Carl Zeiss EVO 18 SEM operating at 15 KV using normal analyzer, CH Instruments Electrochemical Workstation studies performed in this study.

2.5. Instrumentation

Nicolet iS5 instrument was used to identify the functional groups of the synthesized zinc oxide nanoparticles. The surface morphology of the nanoparticles was done using Carl Zeiss EVO 18 SEM operating at 15 KV using normal incidence. EDAX measurements were carried out by Quantax 200 with X-Flash-Bruker. The electrochemical analyzer, CH Instruments Electrochemical Workstation model 650C was employed for various electrochemical studies performed in this study.

3. Results and Discussion

3.1. FT-IR Studies:

The FTIR spectrum of ZnO nanoparticles synthesized using aqueous leaf extract of Sesbania Grandiflora was shown in the Fig.2. The broad peak located at 3444.88 cm\(^{-1}\) can be assigned to the O-H stretching vibrations, indicating the presence of hydroxyl groups [17]. Few less intense peaks centered at 2923.69 cm\(^{-1}\), 2853.34 cm\(^{-1}\) and 2426.27 cm\(^{-1}\) are probably due to presence of aliphatic asymmetric C-H stretching vibration, C-H stretching and O-H stretching in carboxylic acid respectively [18]. The peak at 1795.46 cm\(^{-1}\) can be assigned to the -C=O- group and the peak at 1763.17 cm\(^{-1}\) can be assigned to the C-O-C stretching of polysaccharides present in the Sesbania Grandiflora leaf extract [19]. Moreover, the peaks at 1384.24 cm\(^{-1}\) and 1627.76 cm\(^{-1}\) were mainly attributed to the -C=O- group and the peak at 1763.17 cm\(^{-1}\) can be attributed to the O-H stretching and O-H deformation assigned to the water molecule respectively.

The frequency observed at 917.52 cm\(^{-1}\) corresponds to O-H bending of carboxylic acid present. The peak at 875.25 cm\(^{-1}\) was due to the formation of tetrahedral coordination of Zn ion [21]. The peaks observed at 825.26 cm\(^{-1}\) and 839.32 cm\(^{-1}\) are due to the weak band (result of C-H out of plane bending) and aromatic -C-H- out of plane bending respectively. The peak at 712.87 cm\(^{-1}\) is due to the presence of R–CH group. The peak at 679.40 cm\(^{-1}\) indicates the stretching vibrations of ZnO nanoparticles which is consistent with the reported data [22]. The characteristic peak appeared at 439.38 cm\(^{-1}\) could be attributed to the metal oxygen (Zn-O) bond.

Fig.3. shows the FTIR spectrum of Ce ion doped ZnO nanoparticles synthesized using aqueous leaf extract of Sesbania Grandiflora. The broad peak located at 3444.51 cm\(^{-1}\) can be assigned to the O-H stretching vibrations, indicating the presence of hydroxyl groups. The peak centered at 2925.62 cm\(^{-1}\) corresponds to aliphatic asymmetric -C-H- stretching vibration. The peaks at 1500.26 cm\(^{-1}\) and 1629.41 cm\(^{-1}\) are due to -C=O- stretching and -C=O- stretching in polyphenols respectively. The bands at 1384.20 cm\(^{-1}\) and 1141.35 cm\(^{-1}\) can be attributed to the aromatic -C=O- bond, -C=O- stretching respectively. The peak located at around 1063.58 cm\(^{-1}\) can be assigned as the absorption peak of –C–O–C– or –C–O–C– stretching. The peak around at 596.39 cm\(^{-1}\) indicating the formation of stretching mode of Ce ion doped ZnO [23]. The peaks corresponding to Zn-O bonds are shifted towards lower wavenumber for Ce doped ZnO nanoparticles, indicating the incorporation of Ce ions in the ZnO lattice [24]. The bands obtained at 659.53, 612.25, 496.91 and 443.59 cm\(^{-1}\) are due to the characteristic stretching vibrations of ZnO nanoparticles [25].
3.3. SEM Analysis

Fig.4 represents the SEM image of ZnO nanoparticles synthesized using SesbaniaGrandiflora leaf extract. This picture substantiates the approximate spherical shape to the ZnO nanoparticles with a granular nature, and most of the particles exhibit some agglomeration [26]. The aggregation of particles should have been originated from the large specific surface area and high surface energy of ZnO nanoparticles [27]. The aggregation occurred may be probably due to the drying process [28, 29]. Fig.5 shows the SEM image of Ce ion doped zinc oxide nanoparticles synthesized using SesbaniaGrandiflora leaf extract and it exhibited distinct spherically balllike structure.

3.4. SEM Image

3.5. Energy Dispersive X-Ray Analysis

In order to confirm the presence of Ce ion doped ZnO nanoparticles synthesized using SesbaniaGrandiflora we perform the EDAX spectroscopy. Fig.6. shows the EDAX spectrum of Ce ion doped zinc oxide nanoparticles synthesized using Sesbaniagrandidflora leaf extract. Ce ion doped zinc oxide nanoparticles were found to have atomic percentage 37.61 of Zn, 19.86 of O, 6.31 of Ce as shown in Table 1. This confirmed the doping of Ce ion in ZnO lattice.
3.6. EDAX Image

![EDAX Image](image)

**Figure 6:** EDAX spectrum of Ce ion doped ZnO nanoparticles synthesized using Sesbania grandiflora leaf extract

**Table 1:** Atomic composition of Ce ion doped ZnO nanoparticles synthesized using Sesbania grandiflora leaf extract

<table>
<thead>
<tr>
<th>Element</th>
<th>Series</th>
<th>Unn.C [wt.%]</th>
<th>Norm.C [wt.%]</th>
<th>Atom.C [at.%]</th>
<th>Error (3 sigma) [wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>K-series</td>
<td>37.61</td>
<td>58.97</td>
<td>30.90</td>
<td>3.22</td>
</tr>
<tr>
<td>Oxygen</td>
<td>K-series</td>
<td>19.86</td>
<td>31.13</td>
<td>66.68</td>
<td>7.68</td>
</tr>
<tr>
<td>Cerium</td>
<td>L-series</td>
<td>6.31</td>
<td>9.90</td>
<td>2.42</td>
<td>0.64</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>63.78</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
</tr>
</tbody>
</table>

3.7. AFM Spectral Studies

AFM spectra were recorded for the ZnO and Ce ion doped ZnO nanoparticles deposited on the glass plate. Fig.7. shows the AFM spectral image of ZnO nanoparticles synthesized using *Sesbania grandiflora* leaf extract with a scanning area to 0m X 3.13μm, we found spongy shape distributed over the surface [30]. These particles are between 0m Y 3.13μm in length and the size is in the range of 20-50nm. Fig.8. shows the AFM spectral image of Ce ion doped ZnO nanoparticles synthesized using *Sesbania grandiflora* leaf extract with a scanning area to 952nm X 2.19μm. These particles are between 1.89μm Y 3.13μm in length. The shape of Ce ion doped ZnO nanoparticles is spongy layered form and the size is in the range of 30-50nm.

3.8. AFM Image

![AFM Image](image)

**Figure 7:** AFM image of ZnO Nanoparticles synthesized using *Sesbania Grandiflora* leaf extract

**Figure 8:** AFM image of Ce ion doped ZnO Nanoparticles synthesized using *Sesbania Grandiflora* leaf extract
3.9. Photoluminescence

PL spectra were measured for the ZnO and Ce ion doped ZnO nanoparticles synthesized using aqueous leaf extract of *Sesbania grandiflora* in the range of 200-700 nm are shown in Fig.9 and Fig.10. The wavelength of excitation chosen for the samples is 350 nm. It is interesting to note from that although the excitation spectra of ZnO and Ce ion doped ZnO nanoparticles appear similar, an appreciable change in luminescence intensity is observed in the doped samples compared to the undoped samples. For doped samples there is increase in excitation intensity. This might be due to the interaction between Ce ion and ZnO lattice. This provides an obvious evidence for the entry of Ce ion in the ZnO lattice. Photoluminescence investigation evidenced the high crystalline nature of the undoped and doped ZnO nanoparticles.

3.10. PL Spectrum

Figure 9: PL spectra of ZnO nanoparticles

Figure 10: PL spectra of Ce doped ZnO nanoparticles

3.11 Electrochemical Analysis

3.11.1 Electrochemical Impedance Measurements

EIS measurements were obtained in the frequency range from 100000Hz to 0.01Hz by using amplitude of 0.5V. EIS was applied to study the resistance ability of the ZnO and Ce ion doped ZnO nanoparticles. The Nyquist plot representation of impedance spectra of green synthesized ZnO and Ce ion doped ZnO nanoparticles in pH=1 medium were shown in Fig.11and Fig.12. The different parameters were tabulated (Table.2). The values of charge transfer resistance increases for ZnO and Ce ion doped ZnO nanoparticles when compared to the bare. The values of conductance are high for ZnOand Ce ion doped ZnO nanoparticles when compared to the bare. These facts reveal that both the ZnO and Ce ion doped ZnO nanoparticles have high conductivity.

Figure 11: EIS of undoped ZnO nanoparticles synthesized using *Sesbania Grandiflora* Leaf extract

Figure 12: EIS of Ce ion doped ZnO nanoparticles synthesized using *Sesbania Grandiflora* Leaf extract

<table>
<thead>
<tr>
<th>Name of Plant material</th>
<th>Nanoparticles</th>
<th>$f_{max}$ (Ωcm$^{-2}$)</th>
<th>$C_{dl}$ (µFcm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>2165</td>
<td>4314</td>
<td>1.704</td>
</tr>
<tr>
<td><em>Sesbania Grandiflora</em></td>
<td>ZnO</td>
<td>3559</td>
<td>6922</td>
</tr>
<tr>
<td></td>
<td>Ce:ZnO</td>
<td>3546</td>
<td>6976</td>
</tr>
</tbody>
</table>

3.11.2. Cyclic Voltammetry

Cyclic voltammograms were recorded in the pH 1.0 for 1.0 ml of ZnO and Ce ion doped ZnO nanoparticles synthesized using aqueous leaf extract of *Sesbania Grandiflora*. The Glassy Carbon Electrode was (GCE) as working electrode Vs Ag/AgCl. ZnO nanoparticles and Ce ion doped ZnO nanoparticles showed one oxidation peak and one reduction peak in pH 1 conditions. The background current was recorded for all sweep rates studied in the potential range from -1.0 to 1.0 V and subtracted properly in calculating the peak currents.

The cyclic voltammetric behaviour of 1.0 ml of ZnO nanoparticles in 0.1M H$_2$SO$_4$ (pH 1.0) was studied at GCE as shown in Fig 13. In this cyclic voltammogram, one sharp anodic peak and one cathodic peak were observed in the potential range from −1.0 V to 1.0V. The cathodic and anodic peaks were seen around the potential at -0.7123 V and 0.3256 V respectively. The values of peak current and peak potential are presented in Table 3.
The cyclic voltammetric behaviour of 1.0 ml of Ce ion doped ZnO nanoparticles in 0.1M H2SO4 (pH 1.0) was studied at GCE as shown in Fig. 14. In this cyclic voltammogram, one sharp anodic peak and one small cathodic peak were observed in the potential range from −1.0V to 1.0V. The cathodic and anodic peaks were seen around the potential at -0.6789V and 0.4291V respectively. The values of peak current and peak potential are presented in Table 3. The peak potentials obtained for doped samples were entirely different from the behaviour obtained for undoped samples confirming the formation of doped samples.

### Table 3: Cyclic voltammetric behaviour data of ZnO and Ce ion doped ZnO nanoparticles in pH 1.0

<table>
<thead>
<tr>
<th>Name of Plant material</th>
<th>Nanoparticles</th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E(V)</td>
<td>I(A)</td>
<td>E(V)</td>
</tr>
<tr>
<td>SesbaniaGrandiflora</td>
<td>ZnO</td>
<td>0.3256</td>
<td>9.664×10^-6</td>
</tr>
<tr>
<td></td>
<td>Ce:ZnO</td>
<td>0.4291</td>
<td>4.899×10^-5</td>
</tr>
</tbody>
</table>

### 3.12. Photocatalytic Activity

The UV visible absorbance values of pure Bismarck brown dye solution shows absorption wavelength at 460nm. The characteristic absorbance value at 460nm was used to track the photocatalytic degradation process. Fig. 15 can be clearly noticed from the recorded values that no significant changes of the concentration of Bismarck brown dye after 3 hrs irradiation, which indicated that pure Bismarck brown dye solution, cannot be easily degraded by UV light. The degradation efficiency of pure Bismarck brown dye within 3 hrs irradiation time was about 28%. The result showed that the photocatalytic activity of pure Bismarck brown dye was very less when compared with the ZnO nanoparticles and Ce ion doped ZnO nanoparticles synthesized using Sesbania Grandiflora leaf extract. The dye degradation in presence of bio synthesized nanoparticles was verified by the decrease of the peak intensity during 60min exposure in solar light shown in Fig.16 and Fig.17. The dye degradation (%) was calculated by using the following equation (2).

\[
\text{Dye degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \% \quad (1)
\]

Where \(C_0\) is the initial concentration of Bismarck brown and \(C_t\) is the concentration of the dye solution at the selected irradiation time. Fig.18. shows the bleaching of Bismarck brown dye on photodegradation in the presence of ZnO and Ce ion doped ZnO nanoparticles as photocatalyst. The degradation efficiency was higher in the presence of Ce ion doped ZnO nanoparticles than that for ZnO nanoparticles.
The conductivity of chemically synthesized nanoparticles is high and is used as an electronic material. The Ce ion doped ZnO nanoparticles have high $R_{ct}$ and low $C_{dl}$ values show effective resistance. From cyclic voltammetric studies, good redox behaviour was observed for ZnO and Ce ion doped ZnO nanoparticles synthesized using Sesbaniagrandiflora. The photocatalytic study concludes that these bio-ZnO nanoparticles have efficiency to degrade Bismarck brown dye under solar irradiation. Therefore they can find application in water purification and textile industries.

4. Acknowledgement

The authors are thankful to Department of Science and Technology (FAST TRACK and FIST) New Delhi for using Jasco UV-Visible Spectrophotometer and CHI-650 Electrochemical Workstation at V. O. Chidambaram College.

References


3.13 Conclusion

ZnO and Ce ion doped ZnOnanoparticles are synthesized (simple and cost effective) using aqueous leaf extract of Sesbaniagrandiflora. The FT-IR studies showed an absorption peak at 437 cm$^{-1}$ (Zn-O linkage) which indicated the formation of zinc oxide nanoparticles. The aqueous Sesbaniagrandiflora leaf extract reveals the presence of phyto constituents like alcohol, aldehyde and amine which were the surface active molecules, stabilize the nanoparticles. The surface morphology of the ZnO and Ce ion doped ZnOnanoparticles was characterized by SEM analysis and suggested different morphological structures. Chemical purity and stoichiometry of the samples were investigated by EDAX Spectroscopy, in order to confirm the presence of Zn, O and Ceions in the material.AFM study reveals the surface morphology of the synthesized ZnO and Ce ion doped ZnO nanoparticles. PL Spectra revealed the change of luminescence intensity in the Ce ion doped sample compared to the ZnO sample with almost a linear increase in excitation intensity. Impedance spectroscopy is employed to study the conductivity of nanoparticles. The conductivity of chemically synthesized nanoparticles is high and is used as an electronic material. The Ce ion doped ZnO nanoparticles have high $R_{ct}$ and low $C_{dl}$ values show effective resistance.


