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Green Synthesis, Characterization of ZnO nanoparticles and Ceion doped ZnO nanoparticles assisted *Sesbania Grandiflora* for photocatalytic application

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Abstract

The synthesis of semiconductor nanoparticles is an expanding research area due to the potential applications in the development of nanotechnologies. The ZnO nanoparticles have been synthesized by adding a leaf extract of Sesbania Grandiflora into the aqueous solution of zinc nitrate. The aqueous Sesbania Grandifloraleaf extract acts as a solvent with multiple roles as promoter, capping agent and reductantfor the synthesis of undoped ZnO and Ce ion doped ZnO nanoparticles. Zinc oxide nanoparticles were characterized by using UV-Visiblespectrophotometer, XRD and TEM. The size of the ZnO nanoparticles and Ce ion doped ZnO nanoparticles were estimated to be 43.09 nm and 46.72 nm using Debye-Scherrer equation. Photocatalytic degradation was also investigated with Indigo carmine dye under UV-irradiation source. The ZnO and Ce ion doepd ZnO nanoparticles exhibited potential photocatalytic activity towards the degradation of Indigo carmine dye. Green synthesis using Sesbania Grandiflorais found to be the best capping agent for synthesizing nanoparticles.

Keywords: Zinc oxide nanoparticles, Green synthesis, *Sesbania Grandiflora*, UV-Vis, XRD, TEM, Photodegradation.

Introduction

The field of nanotechnology is one of the most active researches in modern material science. In recent years, green synthesis of metal oxide nanoparticles is an interesting issue of the nanoscience and nanobiotechnology. Zinc oxide nanoparticles exhibit high catalytic efficiency, strong adsorption ability, high isoelectric point, biocompatibility, and fast electron transfer kinetics for biosensing purposes. Green chemistry seeks to reduce pollution at source[1]. Green synthesis of zinc oxide nanoparticles using Aloe vera[2], gold nanoparticles by alfalfa[3], Cinnamomu mcamphora[4], neem[5], Emblica officianalis[6], lemongrass[7] and tamarind[8] have been reported. Therefore the present investigation has been made to synthesize ZnO nanoparticles by Sesbania Grandiflora.

Sesbania grandiflora**:** *Sesbania grandiflora* L. is a plant from family fabaceae cultivated in all over India for its edible flowers. It has synonym *Agatigrandiflora* (Figure-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[9,10].

Figure-1
Sesbania grandiflora

It is a 3–8 m long and the colour of the flowers is red and white in colour. It contains alkaloids, phenols, flavonoids, carbohydrates, saponins, phytosterols, Triterpenes[11], amino acids and alcohol[12]. Leaves are used to disinfect throat and cure kidney diseases. Saponins have been extensively used as detergents, pesticides and molluscicides and also have beneficial health effects.

Methodology

Collection of Plant: The plant *Sesbania grandiflora* was collected in the surroundings of Tirunelveli district, Tamilnadu.

Preparation of the leaf extract: The collected Sesbania Grandifloraleaves 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 Grandifloraleaf powder of 10g was used for synthesis purpose. The weighed 10g leaf powder was mixed gently with 100ml of distilled water, boiled in 80^{o}C for 60min; until the colour of the solution changes from watery to yellow. Then the extract was filtered through What man No.1 filter paper, stored at room temperature in order to use for further studies.

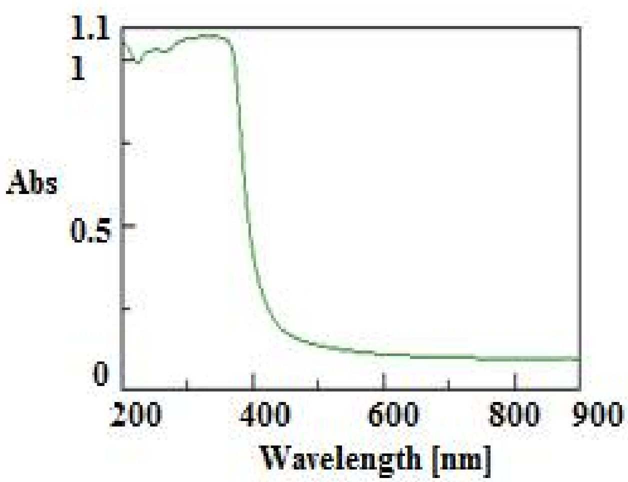
Synthesis of ZnO nanoparticles and Ce ion doped ZnO nanoparticles using *Sesbania grandiflora* leaf extract: 5g Zinc Nitrate was added to the leaf extract under vigorous stirring. After 15 min stirring the solution was heated at a temperature of about 60^{0}C. The yellow coloured paste was finally calcined at 400^{0}C for 2h. The ZnO nanoparticles so obtained were preserved in the air-tight vials for further studies[13]. Similar procedure was adopted for the synthesis of Ce ion doped ZnO nanoparticles using 1% cerium nitrate as the precursor material.

Photocatalytic Measurement: Nanosized ZnO particle is a good photocatalyst to degrade organic contaminants, such as Indigo Carmine (IC) dye. The dye solution was prepared by dissolving 10mg powder of Indigo Carmine dye in 100ml distilled water. 0.1g Ce ion doped ZnO nanoparticles was added to 100ml of prepared Indigo Carmine dye solution and the mixer was stirred magnetically for 60min in shadow before exposing to sunlight. Then the colloidal suspension was placed in a closed chamber and irradiated with sunlight. The reactions were observed one by one in every time interval of 10 min for 1hr. Finally, the rate of dye decomposition was monitored by taking 4ml samples from each set and recording the UV-Vis spectra in the wavelength after centrifugation and filtration[14].

Instrumentation: UV-Vis spectrophotometer (JASCO V-650) was used to obtain the absorption spectrum of the synthesized zinc oxide nanoparticles. The synthesized nanoparticles were investigated with a Philips CM 200 model using 200kV electron acceleration voltage and with a resolution of $2.4A^{0}$. XRD measurements were made by Panalytical X'Pert Powder X'Celerator Diffractometer measurement range: 10 to 80 degree in 2θ.

Results and Discussion

Ultraviolet-Visible Spectra Analysis: The UV-Vis spectra of ZnO nanoparticles and Ce ion doped ZnO nanoparticles synthesized using *Sesbania Grandiflora* leaf extract were shown in Figure-2 and Figure-3.The absorption band at 363 nm and 357 nm was observed for ZnO and Ce ion doped ZnO nanoparticles respectively. It was effectively blue shifted when compared to the wavelength of bulk ZnO appeared at 385 nm[15]. The absorption wavelengths are seen to be slightly shifted towards lower wavelength. This blue shift might be attributed to the smaller size of nanoparticles. The blue shifted absorption peak was due to the quantum confinement effect[16].



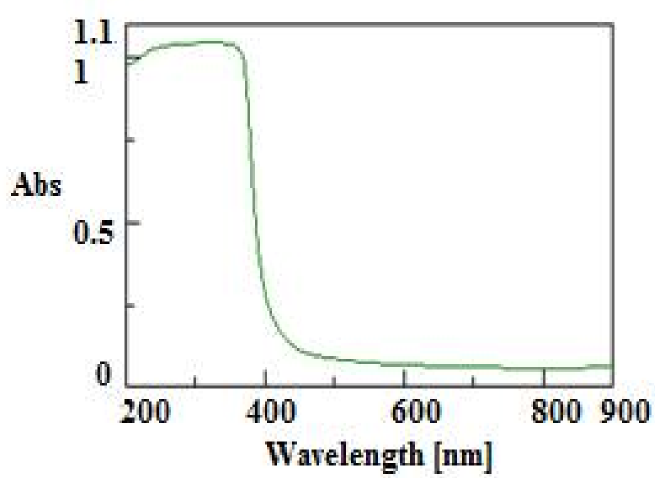


Figure-2
UV-Vis spectrum of ZnO nanoparticles Figure-3 UV-Vis spectrum of Ce ion doped ZnO nanoparticles

XRD: Structural parameters of ZnO nanoparticles and Ce ion doped ZnO nanoparticles synthesized using *Sesbania Grandiflora* leaf extracts were calculated from the XRD pattern. Calcination at 400^0C is essential for complete removal of water and to obtain higher crystallinity. The average grain size (D) was attained by using Debye-Scherrer Equation (1).

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta} \quad (1)$$

Where D is average crystalline diameter in nanometer (nm), k is Scherrer constant equal to 0.94, λis wavelength of the X-ray radiation used and its equal to 1.5406Å, βis the corrected line broadening of the nanoparticles, and θis the Bragg angle.

X-ray diffraction pattern of ZnO nanoparticles was shown in Figure-4.The sharp peaks appearing at about 2θ of 36.25^0, 31.7^0, 34.4^0, 47.62^0, 56.60^0, 62.85^0, 67.94^0, 92.86^0 and 95.38^0 were assigned to {111}, {100}, {002}, {102}, {110}, {103}, {112} and {102} plane values of ZnO nanoparticles. This XRD pattern was well matched with the standard JCPDS Card No. 36-1451. The size of ZnO nanoparticles obtained were estimated to be 43.09 nmusing Debye-Scherrer equation.

Figure-5 shows the XRD pattern of Ce ion doped ZnO nanoparticles synthesized using *Sesbania grandiflora* leaf extract. The spectrum of Ce:ZnO exhibits sharp peaks at 2θ equal to 27.03^0, 29.14^0, 32.85^0, 34.398^0, 36.227^0, 47.533^0, 49.246^0, 56.5432^0, 62.83^0, 66.36^0. These peaks are identified to originate from pattern {111}, {100}, {100}, {101}, {102}, {110}, {103}, {200}, {112}, {201} planes of JCPDS 36-1451[17]. The increase in FWHM suggests that Ce is incorporated into the ZnO matrix. Polycrystalline nanoparticles with a hexagonal wurtzite structure (zincite) and cubic structure CeO_2 from the JCPDS (No.75-0390) card[18]. The size of the Ce ion doped ZnO nanoparticles obtained were estimated to be 46.72 nm using Debye-Scherer equation.

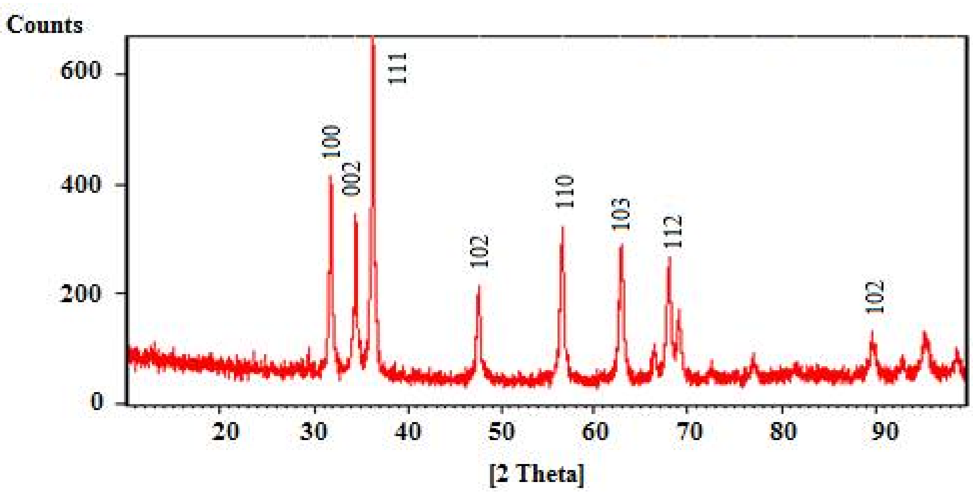


Figure-4
XRD spectrum of ZnO Nanoparticles synthesized using *Sesbania Grandiflora* leaf extract

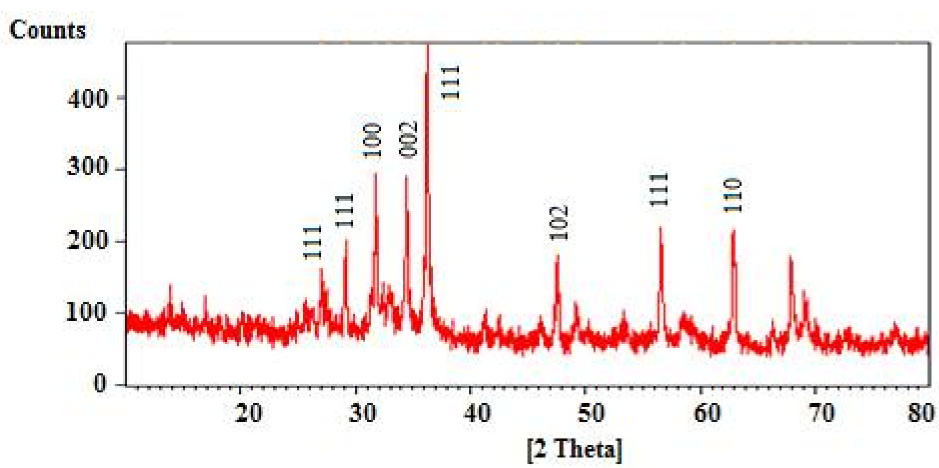


Figure-5
XRD spectrum of Ce ion doped ZnO Nanoparticles synthesized using *Sesbania Grandiflora* leaf extract

Transmission Electron Microscopy (TEM): The TEM monograph (Figure-6) clearly shows the distribution of spherical Ce ion doped ZnO nanoparticles. Selected area electron diffraction pattern shows the crystalline nature of nanoparticles and are identified to originate from the planes {100}, {002}, {111}, {102}, {110}, {103} and {112} as shown in Figure-7. TEM image reveals the size of the Ce ion doped ZnOnanoparticles to be 50nm.

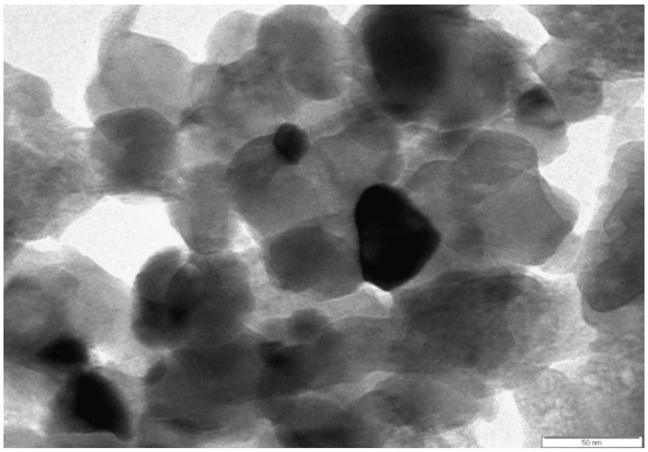


Figure-6
TEM image ofCe ion doped ZnO nanoparticles

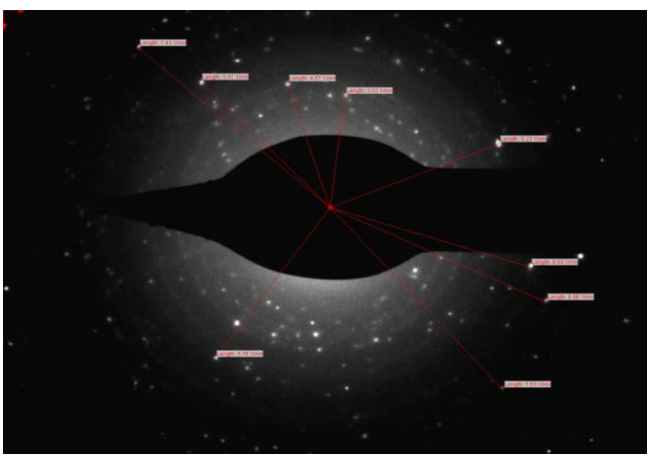


Figure-7
SAED pattern ofCe ion doped ZnO nanoparticles

Photocatalytic activity: The UV visible absorbance values of pure Indigo carmine dye solution shows absorption wavelength at 608nm. The characteristic absorbance value at 608nm was used to track the photocatalytic degradation process. From Figure-8it can be clearly noticed from the recorded values that no significant changes of the concentration of Indigo carmine dye after 3h irradiation, which indicated that pure Indigo carmine dye solution, cannot be easily degraded by UV light. The degradation efficiency of pure Indigo carmine dye within 3h irradiation time was about 45%. The result showed that the photocatalytic activity of pure Indigo carmine 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 Figure-9 and Figure-10. The dye degradation (%) was calculated by using the following equation (2) and its variant with the time of sunlight exposure was shown in Figure-11.

$$\text{Dye degradation (\%)} = \frac{C_0 - C_t}{C_0} \times 100\% \qquad (2)$$

Where C_0 is the initial concentration of Indigo Carmine and C_t is the concentration of the dye solution at the selected irradiation time.

Figure-11 shows the bleaching of Indigo carmine dye on photodegrdation 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.

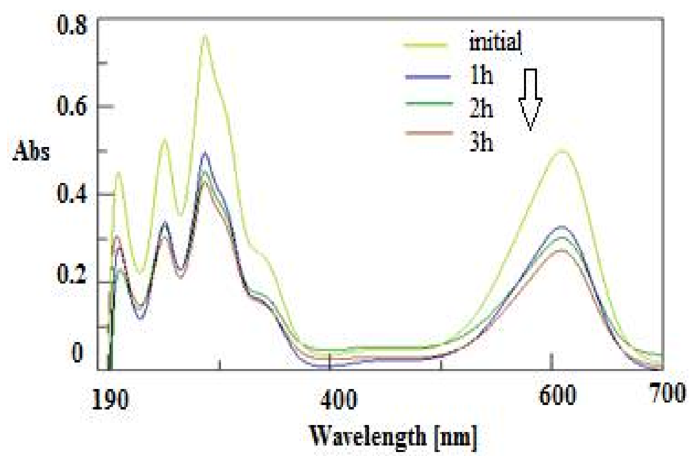


Figure-8
Photocatalytic degradation of pure Indigo Carmine

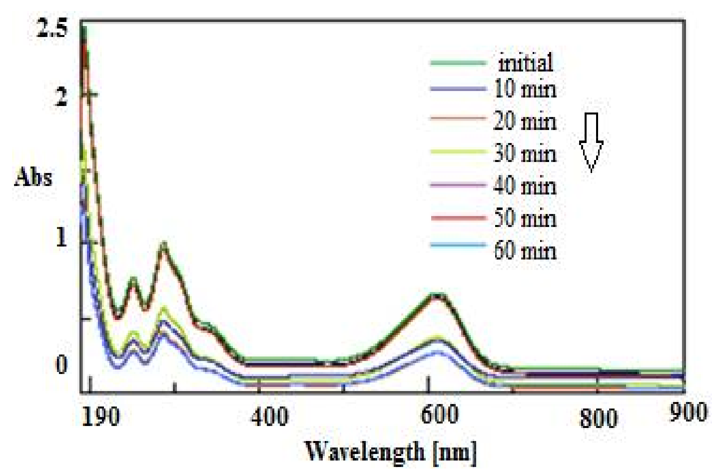


Figure-9
Photocatalytic degradation of Indigocarmine using ZnO nanoparticles synthesized from *Sesbania grandiflora* leaf extract

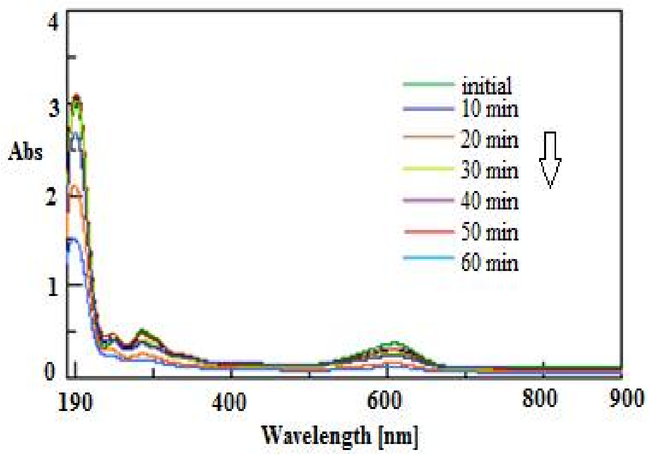


Figure-10
Photocatalytic degradation of Indigo carmine using Ce ion doped ZnO nanoparticles synthesized from *Sesbania grandiflora* leaf extract

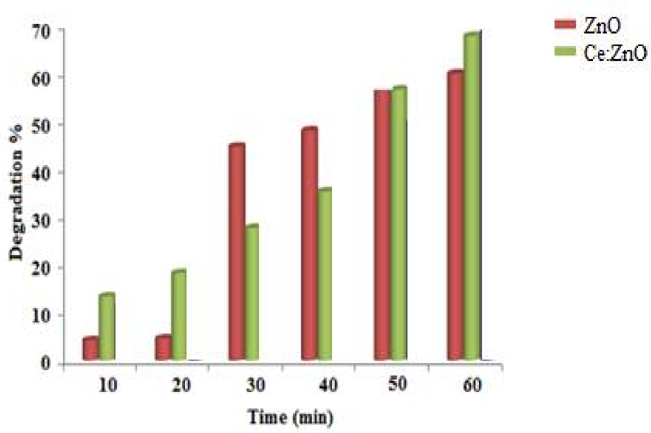


Figure-11
Degradation of Indigo Carmine dye using ZnOand Ce ion doped ZnO nanoparticles synthesized from *Sesbania grandiflora* leaf extract

Conclusion

Zinc oxide and Ce ion doped zinc oxide nanoparticles are synthesized (simple and cost effective) using aqueous leaf extract of *Sesbania grandiflora* (Agathikeerai). The UV spectra of ZnO nanoparticles and Ce ion doped ZnO nanoparticles exhibited absorption peaks at 363nm and 357nm. The XRD patternmatched with the JCPDS File No (36-1451) and the size was estimated to be 43.09nm for ZnO nanoparticles and 46.72nm for Ce ion doped ZnO nanoparticles. TEM analysis confirms that the size of the Ce ion doped ZnO nanoparticles was found to be 50 nm. Thephotocatalytic study concludes that these bio-ZnO nanoparticles have efficiency to degrade IC dye under solar irradiation. Therefore they can find application in water purification and textile industries.

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