Green Synthesis of Undoped and Titanium Ion Doped Cerium Oxide Nanoparticles Assisted By Emblica Officinalis and Their Photocatalytic Activity

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Abstract: - The objective of this paper is to report a non toxic, potential green synthetic method for synthesizing cerium oxide nanoparticles from ammonium ceric sulphate using Emblica officinalis fruit extract as a stabilizing agent. Synthesised nano CeO2 were characterized using UV-Vis and PL spectroscopic techniques, XRD and SEM. Both undoped and Ti ion doped CeO2 nanoparticles absorb at 253 nm and emit at a wavelength of 352 nm and 350 nm respectively. Using Debye scherrer formula the size of the spherical shaped undoped and Ti ion doped nanoparticles was found to be 23.82 nm and 24.82 nm respectively. Photocatalytic degradation of Safranin dye under UV-irradiation was also investigated. Both undoped and Ti ion doped cerium oxide nanoparticles possess photocatalytic activity, while the latter shows enhanced degradation efficiency percentage and can be used as effective photocatalyst.

Keywords: Green synthesis, Ceria Nanoparticles, Emblica officinalis, Photocatalytic activity.

INTRODUCTION

Cerium oxide nanoparticles have been produced using different methods such as sol-gel, thermal decomposition, micro emulsion methods, flame spray pyrolysis and microwave assisted solvothermal process [1] producing lot of toxic byproducts. Green synthesized nanoparticles eliminate the formation of these toxic byproducts. CeO2 nanoparticles have wide applications as gas sensors [2, 3], fuel cells [4], solar cells [5] and reactivity as a catalyst [3, 6]. Cerium oxide-based catalysts are widely used as effective oxidation systems due to their unique properies such as redox, oxygen release and storage abilities [7].

Embilica officinalis (gooseberry) is a deciduous tree of family Phyllanthaceae. It is used in medications treating liver injury [8], atherosclerosis [9] and diabetes [10]. Earlier studies have demonstrated that it shows potent antimicrobial, antioxidant [11, 12, 13], anti-inflammatory [14], analgesic and antipyretic [15], hepatoprotective [16], antitumor [17], antiulcerogenic [18, 19] and antidiarrheal [20] activity. A lot of work has been done on various photocatalytic materials such as TiO2, ZnS etc., [28-33], but very less attention is being given to the mixed oxide nanoparticles. The mixed oxide particles have the ability to obtain structures in combination with the properties that neither individual oxide possesses [34].

In this study, bioinspired syntheses and chracterisations of undoped and Ti ion doped ceria nanoparticles were carried out and the removal of safranin dye was investigated.

2.1. Materials

AR grade Ammonium Ceric sulphate $(NH_4)_4Ce(SO_4)_4$ was purchased from Himedia Chemicals and used without further purification. Double distilled water was used throughout the experiment. The fruits of Embilica officinalis were procured from the market of Thoothukudi district, Tamilnadu. It was washed well with water, shade dried, powdered and sieved. The fine powder thus obtained was used for extract preparation.

2.1.1. Dye

Safranin (also safranin O or basic red 2) is a biological stain used in histology and cytology. Its molecular weight is 350.85 g•mol^{-1} and has maximum absorption wavelength around 530 nm. The chemical structure of dye is shown in fig.1.

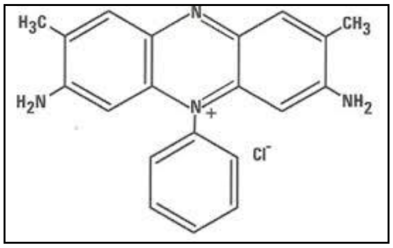

Fig.1. Structure of safranin dye

2.2. Methods

2.2.1. Preparation of extract

About 10g of the powder of dried fruits of Embica officinalis was added to 100ml of double distilled water, heated for 30 min and filtered through Whattman No.41 filter paper. The extract was stored in a refrigerator for the syntheses of ceria nanoparticles.

2.2.2. Synthesis of undoped and Ti ion doped Cerium oxide nanoparticles

10 mL of 0.1M ammonium ceric sulphate solution was made upto 100 mL. To the above solution, 10mL of the fruit extract was added and stirred for about 30 min. The stirred solution was heated at 80ºC for 2 h till the supernatant liquid got evaporated. The reddish brown residue thus obtained was collected in a previously cleaned, washed and dried silica crucible. It was heated to 600ºC for 2 h in a muffle furnace. The light yellow colored cerium oxide nanoparticles thus obtained was preserved and used for further studies. For the synthesis of Ti ion doped CeO_2 nanoparticles, 10 mL each of 0.1M ammonium ceric sulphate solution and 1% Ti ion solution was taken and made upto 100 mL and stirred to obtain a homogenous solution. To this solution, 10mL of the fruit extract was added and the above procedure is repeated. The light yellow colored titanium ion doped cerium oxide nanoparticles thus obtained was preserved and used for further characterization and photocatalytic studies.

2.3. Photocatalytic activity

The nano ceriumoxide thus synthesized acts as a photocatalyst, degrading organic contaminants, such as safranin dye. In this experiment 0.05g of the synthesized nanoparticles were added to 100ml of 10mg of safranin dye solution. The suspensions were placed in a closed chamber and irradiated with UV light. The photocatalytic reactions and the colour change were monitored for an hour. The rate of decomposition of the dye is calculated by recording the UV-Vis spectra after centrifugation and filtration of the aliquots collected at ten minute intervals [21]. The efficiency of the undoped and Ti ion doped cerium oxide nanoparticles as photocatalyst for photocatalytic degradation was calculated using

$$\eta = [1 - \frac{A_t}{A_o}] \quad x\ 100\%$$

where η is the rate of decomposition of dye in terms of percentage, A_t is the absorbance of dye at time intervals t and A_o is the initial absorbance of the dye.

3. RESULT AND DISCUSSIONS

3.1. UV Visible studies

The UV-Vis spectrum of undoped and Ti ion doped ceriumoxide nanoparticles synthesized using *Emblica officinalis* is shown in Fig.2. The absorption band for undoped CeO_2 nanoparticles was observed at 253nm [22]. It is effectively blue shifted when compared to the absorption wavelength of bulk CeO_2 at 337nm [23]. This blue shift is attributed to the smaller size of nanoparticles [23]. The absorption band below 400 nm is due to charge transfer transitions from 2p orbitals of O^{2-} to 4f orbitals of Ce^{4+} [24].The absorption band obtained for Ti ion doped Ceria nanoparticles is found to have more absorption intensity (hyperchromic) than the undoped CeO_2 nanoparticles. This might be due to the interaction between Co ion and CeO_2 lattice

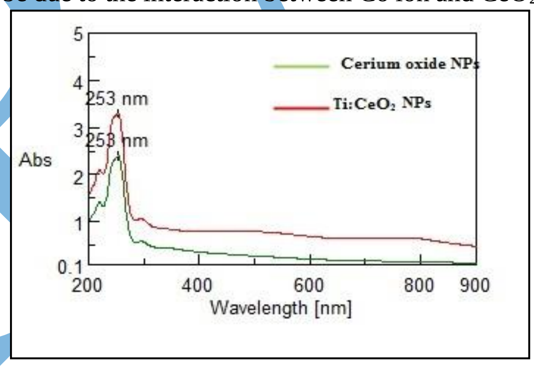

Fig.2. UV-Vis spectra of undoped and Ti ion doped Cerium oxide nanoparticles.

3.2. Photolumiescence studies

The PL spectra of undoped and doped Ceria nanoparticles respectively is shown in Fig.3. The excitation peak is found at 270 nm while the emission peak of undoped and Ti ion doped ceriumoxide nanoparticles are found at 352 nm and 350 nm respectively. The excitation of CeO_2 is supposed to originate from the intial Ce^{4+} - O^{2-} charge transfer transition in the host lattice absorbing the excitation light. The broad band around 350 nm is ascribed to the charge transition from the 4f band to the valence band of CeO_2 [24, 25]. There is decrease in intensity of the emission peak. This might be due to the interaction between Ti ion and CeO_2 lattice. This provides an obvious evidence for the entry of Ti ion in the CeO_2 lattice.

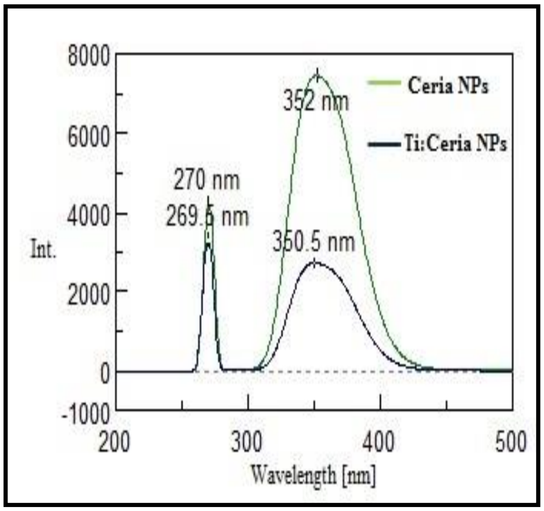

Fig.3. Emission spectra of undoped and Ti ion doped ceriumoxide nanoparticles.

3.3. XRD Analysis

Structural parameters of undoped and Ti ion doped cerium oxide nanoparticles were calculated from the XRD pattern. The average crystallite size (D) was calculated using the well known Scherrer's formula.

$$D = k\lambda / \beta\cos\theta$$

where D is the average crystalline diameter in nanometer (nm), k is the Scherer constant equal to 0.94, λ is the wavelength of the X-ray radiation used and is equal to 1.5406Å, β is the full width at half maxima (FWHM) intensity of the diffraction peak (in radian) and θ is the Bragg diffraction angle of the concerned diffraction peak. The X-ray diffraction pattern of undoped and Ti ion doped ceriumoxide nanoparticles is shown in Fig.4a and Fig.4b. According to the standard JCPDS Card No.89-8436, the peaks at 2θ having values around 28º,32º,47º,56º,58º,69º,76º,78º,88º,95º correspond to the planes 111, 200, 220, 311, 222, 400, 331, 420, 422, 333 [26]. The size (D) of synthesized undoped and Ti ion doped nanoparticles were found to be 23.82 nm and 24.82 nm respectively. The above planes indicate that the cerium oxide nanoparticles have FCC cubic fluorite structure [27].

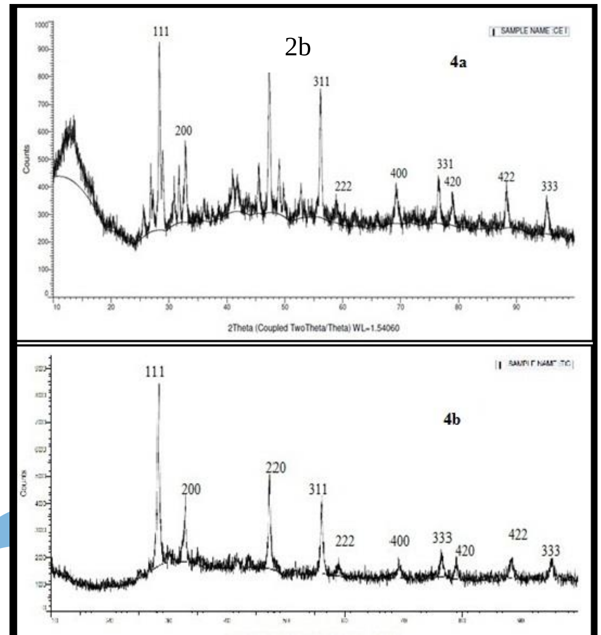

Fig.4a. XRD pattern of undoped Ceria nanoparticles
Fig.4b. XRD pattern of Ti:Ceria nanoparticles.

3.4. Scanning Electron Microscopy

The SEM micrographs (fig.5a and fig.5b) clearly show that the nanoparticles of undoped and Ti ion doped CeO_2 were found to have crack free, continuous surface with agglomerated spherical shaped nanoparticles.

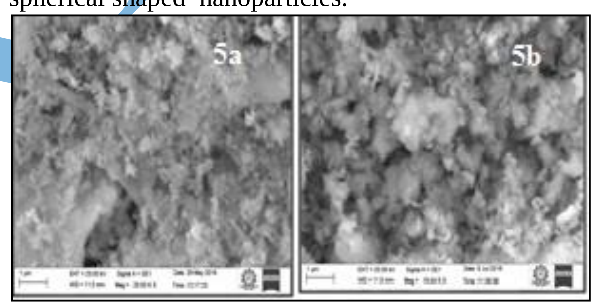

Fig.5a. SEM image of undoped Ceria nanoparticles **Fig.5b. SEM image of Ti ion doped Ceria nanoparticles**

The UV visible absorbance values of safranin dye solution shows absorption wavelength at 520 nm. The decrease in intensity of the characteristic absorption band suggests that the chromophoric structure responsible for the characteristic absorption band is breaking down. Fig.6. and Fig.7. show the decrease in the intensity of absorbance spectra of safranin dye in the presence of the undoped and doped CeO_2 nanoparticles as photocatalyst. It was observed that the maximum degradation efficiency of safranin dye within 60 min irradiation time was about 58% in the presence of undoped CeO_2 nanoparticles and 92% in the presence of Ti ion doped nanoparticles. The reason for high catalytic activity of the synthesized nanoparticles is ascribed to the high surface area which determines the active sites of the catalyst and accelerates the photocatalytic degradation. Therefore, it is observed that the Ti ion doped CeO_2 nanoparticles possess much higher photocatalytic activity than the undoped CeO_2 nanoparticles.

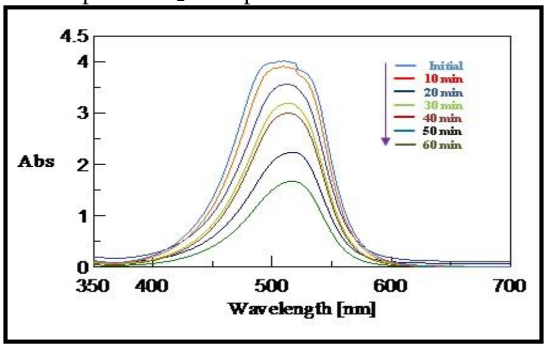

Fig.6. UV-Visible absorption spectra of safranin in the presence of undoped CeO_2 nanoparticles

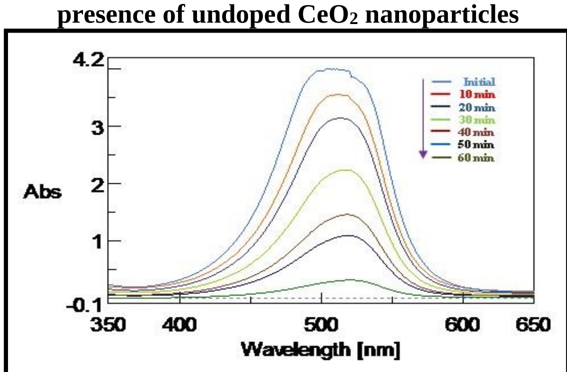

Fig.7. UV-Visible absorption spectra of safranin in the presence of Ti ion doped CeO_2 nanoparticles

5. CONCLUSION

Undoped CeO_2 and Ti ion doped CeO_2 nanoparticles were synthesized using aqueous fruit extract of *Emblica officinalis*. The blue shifted UV-Vis absorption peak at 253nm confirmed the nano-size of the synthesized CeO_2 nanoparticles. The intensity of the absorption peak increased for Ti ion doped CeO_2 nanoaparticles. In the PL spectra, the broad band around 350 nm is ascribed to the charge transfer transition from the 4f band to the valence band of CeO_2. The size of undoped and Ti ion doped CeO_2 nanoparticles were calculated from the x-ray diffractogram and were found to be 23.82 nm and 24.82 nm respectively. SEM micrographs showed the surface morphology and confirmed nanostructure of the synthesized particles. Ti ion doped ceria nanoparticles exhibited enhanced photocatalytic activity and can be used efficiently as photocatalyst.

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