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Green Synthesis of Undoped and Ti DOPED CeO_2 Nanoparticles by the Fruit Extract of *Emblica officinalis* and its Photocatalytic activity

***Muthuchudarkodi R.R. and Ashli A.**

Department of Chemistry, V.O Chidambaram College, Tuticorin –628008, Tamilnadu, India

Abstract : The objective of this paperis to report a non toxic, potential green synthetic method for preparing cerium oxide nanoparticles from ammonium ceric sulphate using *Emblica officinalis* fruit extract as a stabilizing agent. Synthesised nano CeO_2 were characterized using UV-Vis and PL spectroscopic techniques, XRD and SEM. Both the undoped and Ti doped CeO_2 nanoparticles absorb at 253 nm and emit at a wavelength of 352 and 350 nm respectively .The spherical shaped undoped and doped nanoparticles were found to be 23.82 and 24.82 nm in size respectively using Debye-Scherrer's Formula.Photocatalytic degradation of Safranin dye under UV-irradiation was also investigated. 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 : CeO_2 nanoparticles, Green synthesis,*Emblica officinalis*, Photodegradation.

Introduction

Ceriumoxide nanoparticles have been produced using different preparation methods such as sol-gel, thermal decomposition, microemulsion methods, flame spray pyrolysis and microwave assisted solvothermal process lot of toxic by products [Ju-Nam and Lead,2008]. Green synthesized nanoparticles eliminates the formation of these toxic byproducts. CeO_2 nanoparticles have wide applications as gas sensors, fuel cells, solar cellsand reactivity as a catalyst [Mori et al, 2004]. Cerium oxide-based catalysts are widely used as effective oxidation systems due to their unique properies such as redox, oxygen release and storage abilities[Girija *et al*,2011]

Emblica officinalis(gooseberry) is a deciduous tree of family Phyllanthaceae. It is used in medication streating liver injury, atherosclerosis and diabetes[Sabu and kuttan, 2002]. Earlier studies have demonstrated that it shows potentantimicrobial, antioxidant, anti-inflammatory, analgesic and antipyretic, hepatoprotective, antitumor, antiulcerogenic and antidiarrheal activity[Periyanayaham *et al*, 2005].

A lot of work has been done on various photocatalytic materials such as TiO_2, ZnS etc, 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 [Fang *et al*, 2013].

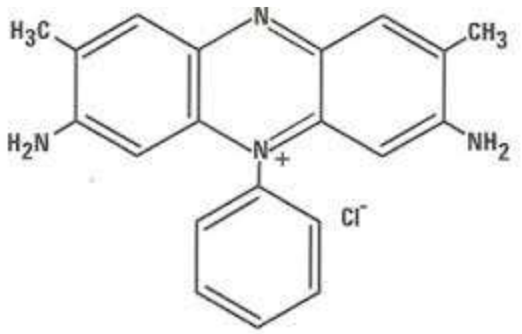
In the present study, bioinspired syntheses and characterisation of undoped and Ti doped ceria nanoparticles is carried out and the removal of safranin dye was investigated.

Materials and Methods

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 *Emblica 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.

*Dye*Safranin (also SafraninO or basicred2)isa biologicalstain usedin histology and cytology.Itsmolecula rweightis350.85 gmol^{-1}and has maximum absorption wavelength around 530nm. The chemical structure of dye is shown in fig below-



Structure of safranin dye

Methods

Preparation of extract

About 10g of the powder of the dried fruits of *Emblica officinalis* was added to 100mLof double distilled water, heated for 20 min and filtered through Whattman No.41 filter paper. The extract was stored in a refrigerator for further syntheses.

Synthesis of undoped and Ti doped Cerium oxide nanoparticles

10 mL of 0.1M ammonium ceric sulphate solution was made upto 100 mL (a). For the synthesis of Ti ion doped CeO_2nanoparticles, 10 mL each of 0.1M ammonium ceric sulphate solution and 1% Ti ion solution(1g of potassium titanium oxalate in 100mL of double distilled water) was taken and made upto 100 mL and stirred in a magnetic stirrer to obtain a homogenous solution (b). To these solutions (a) and (b), 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 characterization and photocatalytic studies.

Photocatalyticactivity

The nanoceriumoxide thus synthesized can act as a photocatalyst, degrading organic contaminants, such as safranin dye. In this experiment 0.05g of the synthesized undoped and Ti doped cerium oxide nanoparticles were added to 100mL of 10mg of safranindye solutions separately. These suspensions werec ontinuously stirred for 60 min in the dark before irradiation to reach equilibrium in absorption and desorption of the ceriumoxide nanoparticles in the organic dye solution. Then the suspensions were placed in a closed chamber and irradiated with sunlight. The photocatalytic reactions and the colour change were monitoredby taking 3 ml aliquots, every 10 min, from the reaction mixture for an hour. The rate of decomposition of the dye is calculated by recording the UV-Vis spectra after centrifugation and filtration [Jinglinha *et al*, 2013].

The efficiency of the doped and undoped cerium oxide nanoparticles as a photocatalyst for photocatalytic degradation was calculated using

$$\eta = [1 - \frac{A_0}{A_t}] \quad x\ 100\%$$

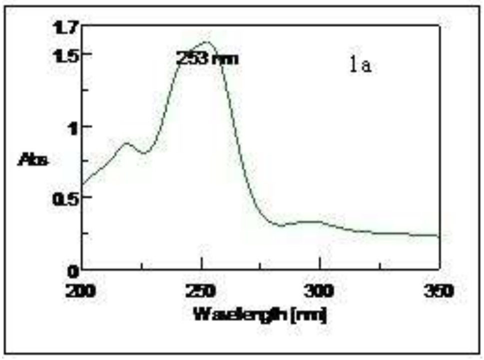
where η is the rate of decomposition of dye in terms of percentage, A_t is the absorbance of dye at time intervals t and A_o is the initial absorbance of the dye.

Results and Discussions

Optical studies

Uv-visible spectroscopy

The UV-Vis spectrum of undopedand Ti doped ceriumoxide nanoparticles synthesized using *Emblica officinalis* is shown in Fig.3a and 3b. The absorption band for undoped CeO_2nanoparticles was observed at 253nm[Manoharan and Vishista,2013]. It is effectively blue shifted when compared to the wavelength of bulk CeO_2at 337nm. This blue shift is attributed to the smaller size of nanoparticles and the quantum size effect[Ansari, 2010]. The absorption band below 400 nm is due to charge transfer transitions from O 2p to Ce 4f [Wang *et al*,2007]



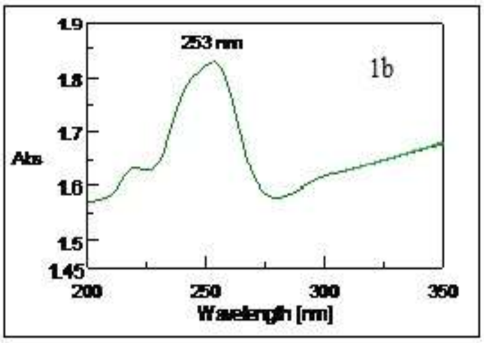


Fig.1a.Uv-vis spectra of undoped nano CeriumoxideFig.1b.Uv-vis spectra of Ti doped nano Ceriumoxide

Photoluminescence studies

The luminescence properties of the prepared nanoparticles were studied using the photoluminescence spectrum of the samples. Fig 2a and 2b shows the PLspectra of undoped and doped Ceria nanoparticles respectively. The excitation peak is found at 270 nm while the emission peak of undoped and doped ceriumoxide nanoparticles are found at 352 and 350 nm respectively. The excitation of CeO_2 is supposed to originate from the initial Ce^{4+} - O^{2-} CT 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[Masui *et al*, 1997]. There is decrease in intensity of the emission peak. This might be due to the interaction between Ti ion andCeO_2lattice. This provides an obvious evidence for the entry of Tiion in the CeO_2lattice.

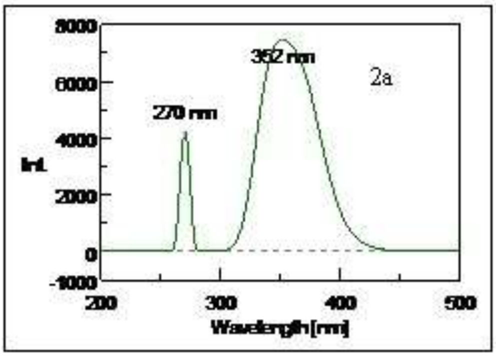


Fig.2a. Emission spectra of undoped ceriumoxide nanoparticle

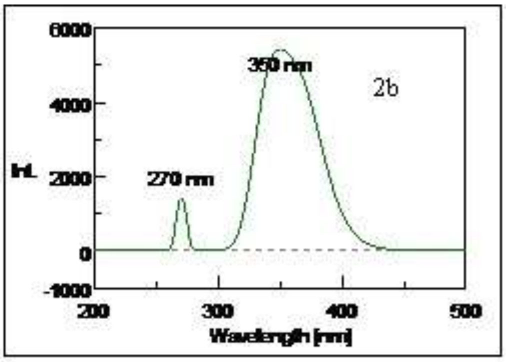


Fig.2b.Emission spectra of Ti doped ceriumoxide nanoparticles.

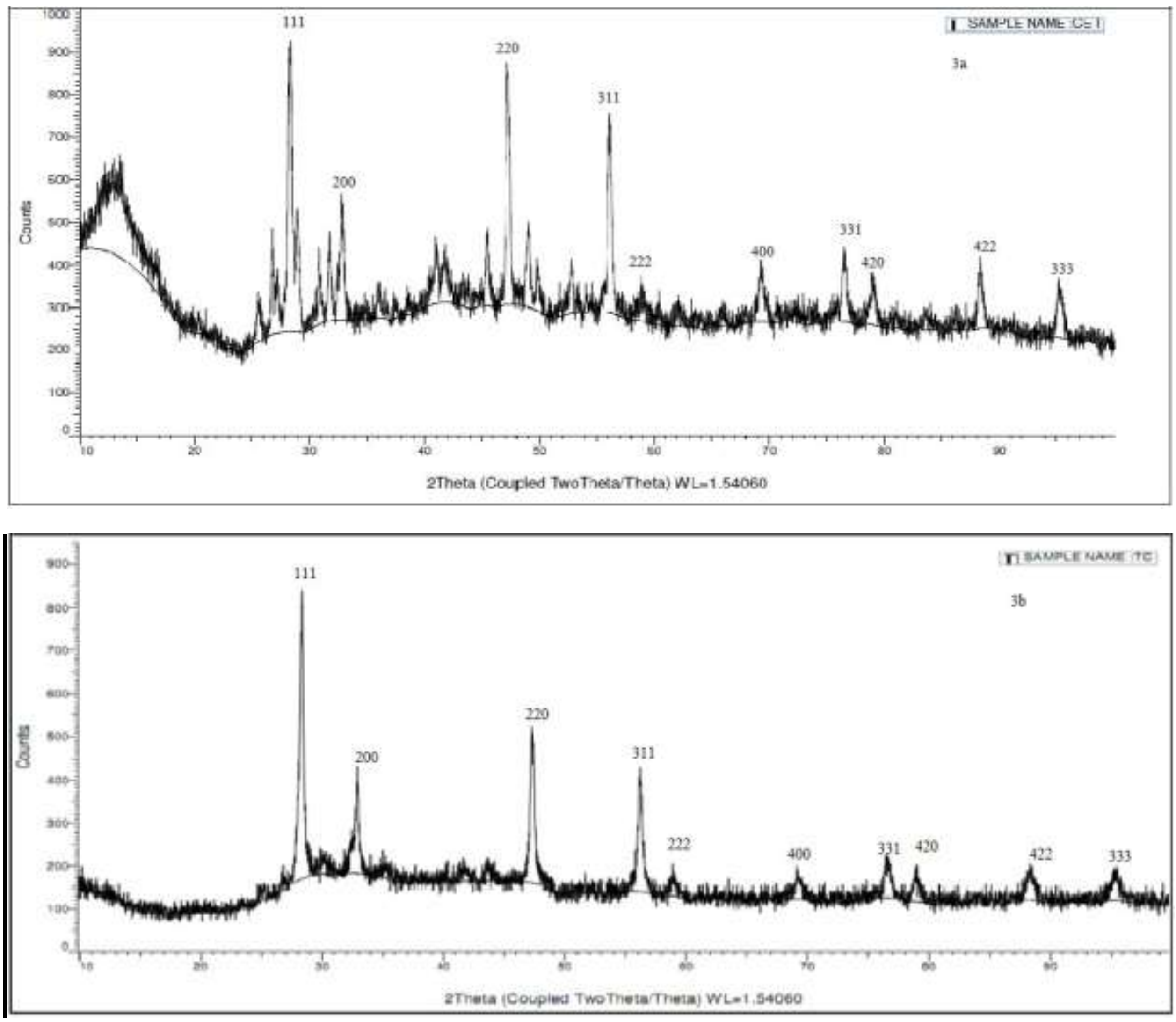
XRD Analysis

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

D = kλ / βcosθ

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.

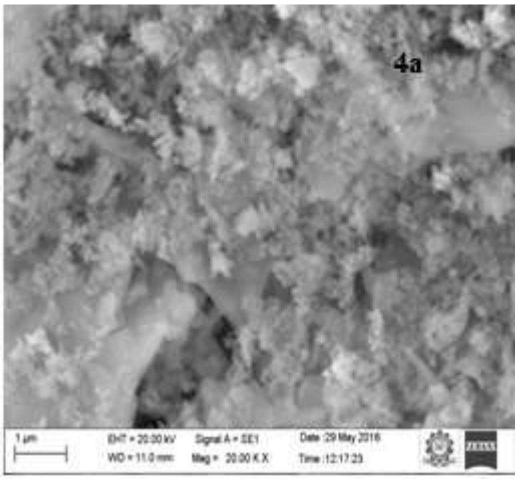
The X-ray diffraction pattern of undoped and doped ceriumoxide nanoparticles is shown in Fig.3a and 3b. The peaks present at2θ having values around 28º,32º,47º,56º,58º,69º,76º,78º,88º,95º correspond to the planes 111, 200, 220, 311, 222, 400, 331, 420, 422, 333 is in accordance with standard JCPDS Card No.89-8436.The size (D) of synthesized doped and undoped nanoparticles was found to be 24.82 nm and 23.82nm respectively by using the scherrer's formula. The above planes indicate that the cerium oxide nanoparticles haveFCC cubic fluorite structure[Saipriya *et al*,2014].



XRD pattern of Fig(3a) undoped nanoCeO_2(3b) Ti:CeO_2 nanoparticles.

Scanning Electron Microscopy

Scanning Electron Microscope was employed to analyze the morphology and the growth features of the as prepared nanoparticles. From the SEM micrographs shown in the figure 4a and 4b. The nanoparticles of undoped and doped CeO_2were found to have crack free, continuous surface with agglomerated spherical nanoparticles.



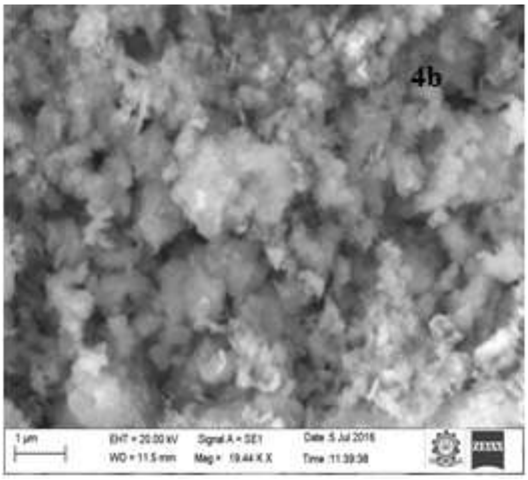


Fig 4a.SEM image of undoped CeO_2 nanoparticles Fig 4b. SEM image of Ti:CeO_2 nanoparticles

Photocatalytic studies

Photocatalytic degradation of safranin

The photocatalytic activity of transition metal doped CeO_2nanoparticles was examined through the degradation of safranin dye in aqueous solution by UV-Visible spectrophotometer. When a photon of UV-Vis light strikes the Ti metal doped CeO_2 nanoparticles surface an electron (e^-) from its valence band jumps to the conduction band leaving behind a positively charged hole (h^+) in valence band. These holes (h^+) react with the chemisorbed H_2O molecules to form reactive species such as OH radicals, which subsequently react with dye molecules to cause complete degradation of dye.

The UV visible absorbance values of pure safranin dye solution shows maximum wavelength at 520 nm. The characteristic absorption value at 520 nmwas used to track the photocatalytic degradation process. Fig 5a and 5b shows the decrease in absorbance values of the safranin dye under uv-vis irradiation in the presence of undoped and doped ceriumoxide nanoparticles. The decrease in intensity of the characteristic absorption band suggests that the chromophore structure responsible for the characteristic absorption band is breaking down leading to the decoloration of the red dye solution. From the absorbance spectra, it was observed that the maximum degradation efficiency of safranindye within 60 min irradiation time was about 58% for undoped CeO_2nanoparticles and 92% for Ti doped nanoparticles.The results showed that Ti deposited on the surface of CeO_2 increases efficiency of degradation. Thus, Ti dopedCeO_2 nanoparticles possess much higher photocatalytic activity than undoped CeO_2 nanoparticles

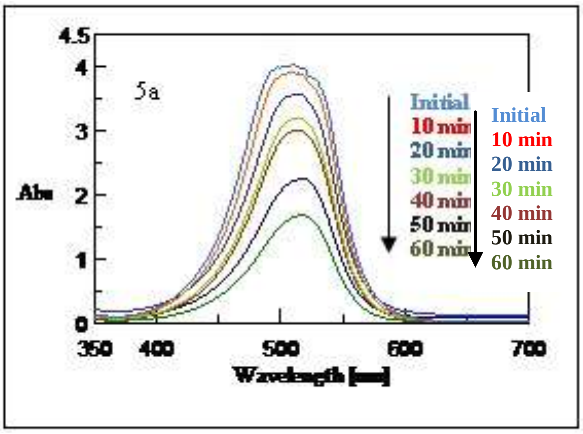


Fig 5a.UV-Vis absorption spectra of safranin dye in the presence of undoped CeO_2 nanoparticles

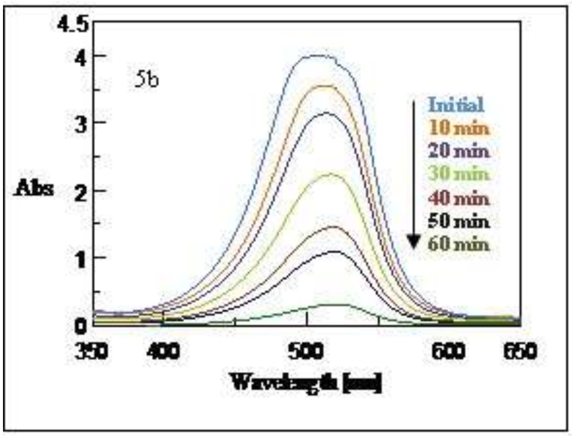


Fig 5b.UV-Vis absorption spectra of safranin dye in the presence of Ti:CeO_2 nanoparticles

Conclusion

Undoped CeO_2 and Ti doped CeO_2nanoparticles are synthesized using aqueous fruit extract of*Emblica officinalis*. The blue shifted UV-Vis absorption peak at 253nm confirmed the nano-size of the synthesizedCeO_2 nanoparticles. The absorbance value increases in Ti doped CeO_2 nanoaparticles. In the PL spectra, the broad band around 350 nm is ascribed to the charge transition from the 4f band to the valence band of CeO_2. The size of undoped and doped CeO_2 nanoparticles was calculated from the x-ray diffractogramand was found to be 23.82 and 24.82 nm respectively. SEM micrographs showed the surface morphology and confirmed nanostructure of the synthesized particles. Ti:CeO_2nanoparticles exhibited enhanced photocatalytic activity and can be efficiently used as photocatalyst.

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