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Particle Size Effect on the Properties of Cerium Oxide (CeO₂) Nanoparticles Synthesized by Hydrothermal Method

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ABSTRACT. The Cerium oxide (CeO₂) nanoparticles with different particle sizes were successfully synthesized by hydrothermal method with different reaction time. The synthesized CeO₂ nanoparticles were characterized by Powder X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM), High Resolution Scanning Electron Microscopy (HRSEM), UV-Vis spectroscopy and FTIR spectroscopy. The effects of the particle size on the structural properties of the prepared samples were investigated using XRD, SEM and HRSEM. The better optical properties exhibited by CeO₂ having smaller particle size has been revealed by UV-Visible study. The Photo-catalytic study showed that the lower particle size CeO₂ nanoparticles have higher Photo-catalytic activity for degradation of Methylene Blue. The optical properties of CeO₂ nanoparticles improve with reduction in the particle size.

Introduction. Rare earth, which has been called an industrial vitamin and a treasury of new materials, has an increasingly important role in technical progress and the development of traditional industries and it is also widely applied in high-technology industries such as information and biotechnology. The particle size of materials affects their basic properties such as lattice symmetry, cell parameters, optical and structural characteristics. Generally, phases in bulk form are unstable in bulk material due to high surface energy, however the surface energy decreases rapidly when size reduces to nanoscale level leading to high stability of materials at nanostructure levels [1]. The surface area and particle size of the CeO₂ nanoparticles have exceptional impact on oversensitivity, conductivity and catalytic activity. Cerium oxide nanoparticles have been widely utilized in various advanced technologies such as solid oxide fuel cells, polishing powders, catalytic materials, sunscreen cosmetic materials, gas sensors and solar cells [2]. Cerium oxide nanoparticles were synthesized using various methods such as chemical precipitation, micro-emulsion, reverse micelles, hydrothermal, ball milling, solution combustion, spray pyrolysis and solvothermal method. Among these methods, hydrothermal method has attracted the most extensive attention, because it is comparatively simple and easy to prepare narrow sized CeO₂ nanoparticles [3-5]. The main objective of this research paper is investigation on the particle size effect on the properties and photo-catalytic degradation of methylene blue of the cerium oxide nanoparticles prepared by hydrothermal method.

Experimental Method

Materials. Cerium nitrate (Ce (NO₃)₂.6H₂O; 432.2 g/mole; 99.9% purity) and Sodium hydroxide (NaOH; 40 g/mole; 99.9% purity) were purchased from Sigma Aldrich Chemicals. These chemicals were used without further purification.

Synthesis. In the synthesis process, 0.217g of Cerium nitrate hexahydrate [Ce (NO₃)₂.6H₂O] and 0.280g of Sodium hydroxide [NaOH] were taken in 5ml and 35ml of distilled water respectively.

Then, these two solutions were mixed and this mixture was stirred at room temperature for 30 min. The solution obtained was transferred to a Teflon lined autoclave which was maintained at a constant temperature of 180° C for 12 hours and 24 hours. The autoclave was allowed to cool down naturally and to reach the room temperature. The final product was collected from the autoclave and washed several times with distilled water and ethanol. The product was dried at 80° C for 6 hours. The dried sample was calcinated at 500°C for 2 hrs. In order to obtain the smaller size CeO₂ nanoparticles to repeat the same procedure, but keep the reaction time 24 hours instead of 12 hours.

Characterizations. The X-ray diffraction (XRD) patterns of the samples were obtained from a Rigaku X-ray diffractometer with Cu-Kα (λ = 1.54187Å) radiation in the range of 10 – 90° at room temperature. The morphology of the particles was studied by QUANTA 200 scanning electron microscope (SEM) and FEI QUANTA FEG 200 High resolution scanning electron microscope (HRSEM). The optical transmittances of the samples were studied by Varian Cary 50 UV-Visible spectrophotometer in the range at 180-850 nm. The FTIR spectra were recorded in the range of 400-4000 cm⁻¹ by PERKIN ELMER SPECTRUM IIFTIR spectrometer.

Results and Discussions

XRD analysis. The XRD patterns of CeO₂ nanoparticles prepared at (a) 12 hours and (b) 24 hours are shown in Fig.1. The peaks are indexed using JCPDS card no: 34-0394. Both samples of CeO₂ nanoparticles have Face Centered Cubic structure with the lattice parameters a = b = c = 5.411 Å and α = β = γ = 90°. The diffraction peaks found at 28.56°, 33.08°, 47.47°, 56.36°, 59.08°, 69.40°, 76.70°, 79.07° and 88.41° and it suggests the formation of nano sized CeO₂. Absence of impurity indicates that pure CeO₂ is synthesized by the hydrothermal method. The average crystallite size (D) of CeO₂ nanoparticles are calculated by the Debye-Scherer equation

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where λ is the wavelength of the Cu-Kα radiation, D is the crystallite size, K is a constant and its value is taken as 0.9, θ is the diffraction angle and β is the full-width at half maximum (FWHM).

The average crystallite size is 12.8 nm for CeO₂ nanoparticles prepared at 12 hours. The average crystallite size is 9.4 nm for the CeO₂ nanoparticles prepared at 24 hours.

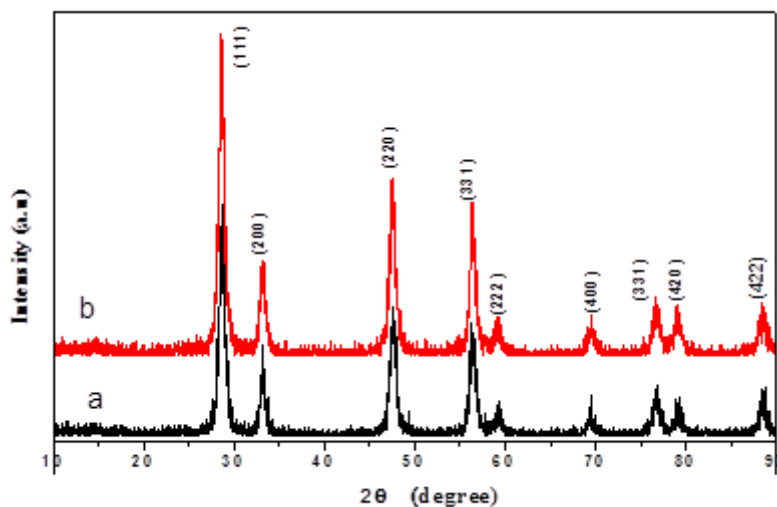


Fig. 1. XRD patterns of CeO₂ nanoparticles prepared at (a) 12 hours and (b) 24 hours.

UV-Visible analysis. The optical property of synthesized CeO_2 was studied by UV-Visible spectrophotometer and results are shown in Fig.2. The UV cutoff wavelength of CeO_2 nanoparticles prepared at 12 hours is 335 nm while the UV cutoff wavelength of CeO_2 nanoparticles prepared at 24 hours is observed at 352 nm. Additionally, UV-Visible spectra showed no other peak related with impurities and defects which confirms that the synthesized nanoparticles are pure CeO_2 . The band gap energy is 3.70eV for CeO_2 nanoparticles prepared at 12 hours whereas the band gap energy is found to be 3.52eV for CeO_2 nanoparticles prepared at 24 hours. The UV- Visible spectra reveal that the smaller size CeO_2 nanoparticles have the better optical properties.

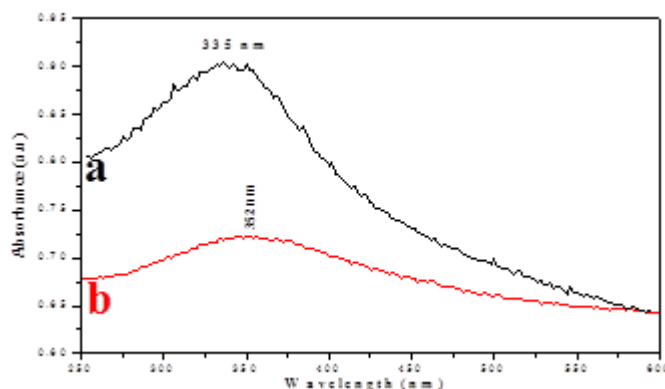


Fig. 2. UV-Vis spectra of CeO_2 nanoparticles prepared at (a) 12 hours and (b) 24 hours.

FTIR analysis.

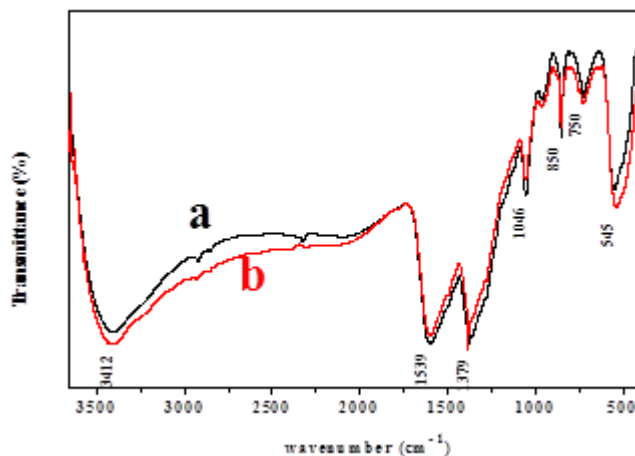


Fig. 3. FTIR spectra of CeO_2 nanoparticles prepared at (a) 12 hours and (b) 24 hours.

The FTIR spectra of CeO_2 nanoparticles prepared by the hydrothermal method with different reaction time are shown in Fig.3. The bands at 545cm^{-1} and 750cm^{-1} are due to the Ce–O stretching vibrations. The bands at 1379cm^{-1} and 1539cm^{-1} are due to the C–O stretching vibration and the band at 3412cm^{-1} is due to O–H vibration of water absorbed from the moisture.

Scanning Electron Microscopy. SEM image of CeO_2 nanoparticles prepared with different reaction time are shown in Fig. 4. The SEM image revealed that the CeO_2 nanoparticles prepared with large size have sphere like structure with average particle size of 110 nm. The HRSEM image revealed that the CeO_2 nanoparticles prepared with small size also have sphere like structure with the average particle size of 23 nm.

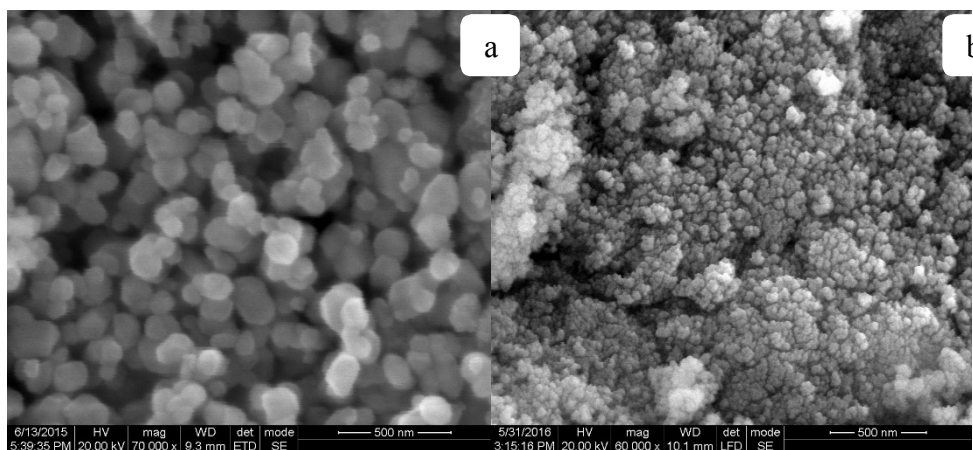


Fig. 4. SEM image of CeO_2 nanoparticles prepared at (a) 12 hours and (b) 24 hours.

Photocatalytic analysis. The Photocatalytic activities of the CeO_2 nanoparticles under visible-light irradiation have been evaluated using methylene blue (MB). In a typical process, 1mmol of Methylene blue aqueous solution and 0.5 g of catalyst were mixed. Prior to a photocatalytic reaction, the photocatalyst suspension was sonicated to reach adsorption equilibrium with the photocatalyst in darkness. The above solution was photoirradiated using Halogen-lamp as light source under continuous stirring. At various time intervals, the concentrations of MB in the photocatalytic reaction were analyzed by using an UV-Vis spectrometer. The degradation of MB by CeO_2 nanoparticles have been investigated comparing the UV-Vis spectra of the original and degraded MB solutions recorded at various time intervals in the wavelength range from 400nm to 800nm respectively as shown in the Fig. 5 (a). The absorption of MB solution at around 661 nm decreases with increased exposure to light irradiation in the presence of CeO_2 nanoparticles. Fig. 5 (b) exhibits the amendment in absorption spectra for the photo-catalytic degradation of MB at dissimilar time periods CeO_2 nanoparticles prepared at (I) 12 hours and (II) 24 hours. The results clearly indicate that degradation of MB is increased for the smaller sized CeO_2 nanoparticles [6] and also the CeO_2 nanoparticles act as effective photocatalyst in degradation of methylene blue from the aqueous medium.

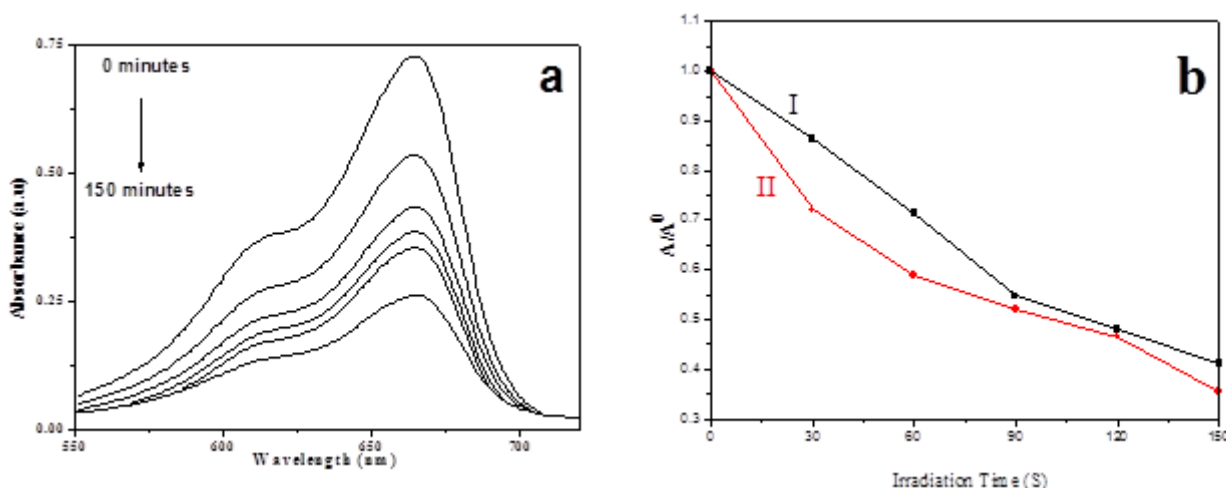


Fig. 5. UV- Vis spectra of the MB degradation under visible light irradiation in the presence of CeO_2 nanoparticles (a) prepared at 24 hours, (b) Comparison of Change in absorbance vs irradiation time of the CeO_2 nanoparticles prepared at (I) 12 hours and (II) 24 hours.

Summary. CeO₂ nanoparticles were successfully synthesized by hydrothermal method with different reaction time. The prepared CeO₂ nanoparticles were analyzed by Powder X-ray diffraction, UV-Visible spectroscopy, Fourier transform infrared spectroscopy, Scanning electron microscopy and High resolution scanning electron microscopy. The XRD studies revealed that the CeO₂ nanoparticles have face centered cubic structure and have the average grain size of 12.8nm for 12 hours and 9.4nm for 24 hours. From the SEM studies, the average particle size of CeO₂ nanoparticles prepared at 24 hours was found to be 23 nm. The UV-visible spectroscopic study indicates that they are legitimately transparent in the entire UV-Vis region and the smaller size CeO₂ nanoparticles have band gap energy of 3.52eV. The UV-Visible spectra revealed that the smaller size CeO₂ nanoparticles have the better optical properties. The Photocatalytic analysis revealed that the smaller size CeO₂ nanoparticles are potential photocatalyst for the degradation of methylene blue.

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