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ORIGINAL ARTICLE

ANTIBACTERIAL BEHAVIOR ON SURFACTANT ASSISTED CERIUM OXIDE NANOPARTICLES

***E.Chandrasekaran and E.Gopinathan**

Department of Physics, Periyar Govt. Arts College, Cuddalore, Tamil Nadu, India

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ABSTRACT

In this paper we have reported, the synthesis and characterization of surfactant assisted CeO_2 nanoparticles by a simple chemical precipitation. The synthesized products were analyzed for XRD, FTIR UV-DRS, PL, AFM, and antibacterial activity. The antibacterial activity of the synthesized samples analyzed against some human pathogens reveal that the capped cerium nanoparticles showed the maximum zone of inhibition against gram positive than gram negative bacteria.

Keywords: Ceria, Nanoparticles, antibacterial activity, Reflection spectra, Optical properties.

1.INTRODUCTION

Polymers are a category of macromolecules. When polymers are used as a capping agent, the diameter of metal oxide nanoparticles can be logically controlled (Majid et al., 2013). Many researchers have studied the effect of CTAB as a capping agent in the preparation of nanostructures. High surface area nano-CeO_2 using surfactant CTAB, $Ce(NO_3)_3$ and NaOH as precipitation agent (Yuejuan et al., 2007) Synthesis of cerium oxide nanoparticles with low degree agglomeration using cationic surfactant Tetra-decyltrimethyl ammonium bromide C_{14}TAB(Krishna Chandarand Jayavel, 2014). The gear-like CeO_2 has been successfully synthesized by a CTAB-assisted hydrothermal method, CeO_2 shows excellent room temperature optical properties, which is likely associated with Ce^{3+} ions and oxygen vacancies in the gear-like CeO_2 samples (Cheng et al., 2014). A new and simple method to directly synthesize stable and crystalline pure phase CeO_2 nanoparticles has been developed using cationic surfactant cetyltrimethylammonium bromide (CTAB) and cerium chloride ($CeCl_3$) at room temperature. Surfactant plays an important role in the preparation of CeO_2 nanoparticles. CeO_2 nanoparticles with a mean particle diameter of 4–6 nm have been successfully prepared (Guofeng, et al., 2010) employed surfactant free non-aqueous synthesis route using $Ce(NO_3)_3$ and octanol as the reactants at a reaction temperature of 150 °C to prepare uniform quasi-octahedral CeO_2 mesocrystals. CeO_2 mesocrystals were synthesized using C_{14}TAB as a surfactant by wet chemical synthesis route. A possible formation mechanism of CeO_2 mesocrystals is proposed on account of aggregation of nanoparticles along with the epitaxial orientation. Mesoporous CuO/CeO_2 bimetal oxides have been synthesized by a simple one-pot method using a cationic surfactant CTAB as structure directing agent and $Cu(NO_3)_2.3H_2O$, $Ce(NO_3).6H_2O$ and NaOH as the inorganic precursor at ambient temperature (Xiaodong et al., 2010).

The present studying is devoted the effect of capping agent and their concentrations on the size and morphology of ceria nanostructures. Moreover, the structural, morphological and optical properties of the synthesized material were investigated.

Synthesis of pure and CTAB capped CeO_2 nanoparticles

In a typical experiment, 0.2M of ammonium ceric sulphate was dissolved in 25 ml of deionized water and 0.2M of copper acetate were mixed up drop by drop. Further, CTAB (cetyl trimethyl ammonium bromide) from different concentrations (0.1-0.3g) were added to the above solution. Finally, 0.3M of oxalic acid was dissolved in 25 ml of deionized water, and added drop wise to the above mixed solution with vigorous stirring. The solution was heated at 60 °C and continuously stirred for 5 hr using magnetic stirrer. The gradual mixing of these solutions formed a pale blue precipitate. Then, the precipitate was washed for several times with water to remove the impurities. The obtained product was dried in a hot air oven at 100 °C for 2 hr, and then the product was annealed at 400 °C in muffle furnace for 6 hr to get pure and capped CeO_2.

Corresponding author: **E.Chandrasekaran, Assistant Professor Department of Physics, Periyar Govt. Arts College, Cuddalore, Tamil Nadu, India*

3. RESULTS AND DISCUSSION

Powder X-ray Diffraction Study (XRD)

Fig.1 Shows the XRD patterns of pure and surfactant (CTAB) assisted cerium oxide nanoparticles. All peaks have been indexed to a pure cubic fluorite structure of CeO_2 (space group: Fm3m) [JCPDS card No: 81-0792]. No impurity peaks were observed; hence it is related high purity of the samples. The intensities and positions of the diffraction peaks are in good agreement with the JCPDS file 81-0792. The broad diffractions of the synthesized samples indicating that the crystallite sizes are very small. The crystallite size of the ceria nanoparticles was determined using Scherrer's equation

$$D = \frac{K\lambda}{\beta \cos\theta} \text{ Å} \qquad \text{---------- (1)}$$

Where, D is the particle diameter in Å, k is a constant (shape factor) with a value of 0.89, β is the full width half maximum and λ is the wavelength of the X-rays (1.5406 Å). The determined sizes of the ceria nanoparticles were 10.5 nm for 0.1g, 7.5 nm for 0.2g and 5.1 nm for 0.3g of CTAB capping. Among the three concentrations, on the basis of improved crystallinity, 0.3g of CTAB was chosen as best concentration of capping. The crystallite size of the sample prepared by CTAB (0.3g) is smaller than that of other samples (0.1g & 0.2g of CTAB). It seems that 0.3g CTAB is a more effective than the others for inhibiting crystal growth. The values of lattice parameter (a) were calculated from the XRD spectra.

The Variation of lattice constant and particle size with increasing CTAB concentration are shown in Fig. 2. An increase in the lattice parameter was observed with decreasing in the crystallite size. As a general rule, nanoparticles of oxides exhibit a lattice expansion with reduction in particle size while metal nanoparticles exhibit a lattice contraction. The reciprocal of the diameter (D^{-1}) is proportional to the surface to volume ratio (S/V) and consequently, the increase of the lattice parameter can be related to the higher S/V ratio in the smaller particles, resulting in a higher contribution from the surface layer. In oxide particles, the bonds have a directional character and at the outer surface of each particle there would be unpaired electronic orbital's which would repel each other (Goharshadi et al., 2011). These contributions from the surface layer increases with decreasing particle size and leads to larger values of the lattice parameter than the bulk.

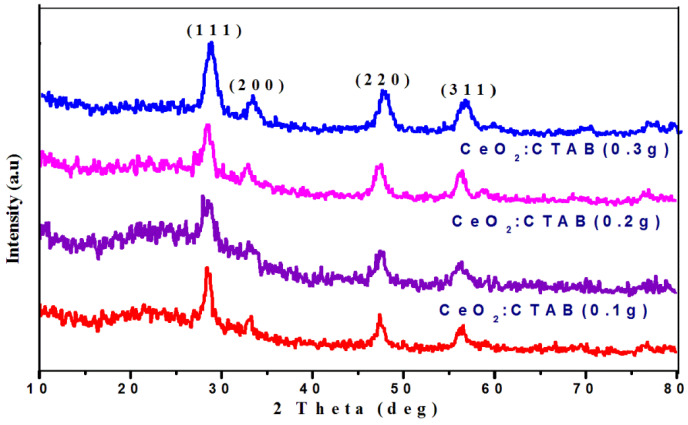

Fig..1 XRD patterns of uncapped and different concentrations of CTAB capped CeO_2 nanoparticles

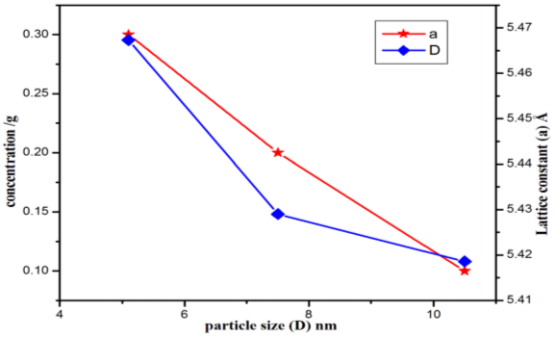

Fig. 2 Variation of lattice constants and particle sizes for capped CeO_2 nanoparticles

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy was used to examine the functional groups present on the surface of the CeO_2 nanoparticles. FTIR spectra of surfactant assisted CeO_2 nanoparticles are presented in Fig. 3 Some weak bands are observed in the region 2800–3020cm^{-1} which are attributed to CTAB surfactant. For CTAB capped particles, it is also known that the band in the range from 451-439 cm^{-1} is a signature of the (Ce–O) stretching vibration indicating the formation of CeO_2 (Majid et al., 2014). The presence of Ce ions produces a small displacement in wave numbers of these bands due to interactions between the metal ions and cationic surfactant. Additional bands around 1115–1000 cm^{-1} are most probably associated to the presence of residual organic or the formation of "carbonate-like" species on the ceria surface (Suresh et al., 2013).

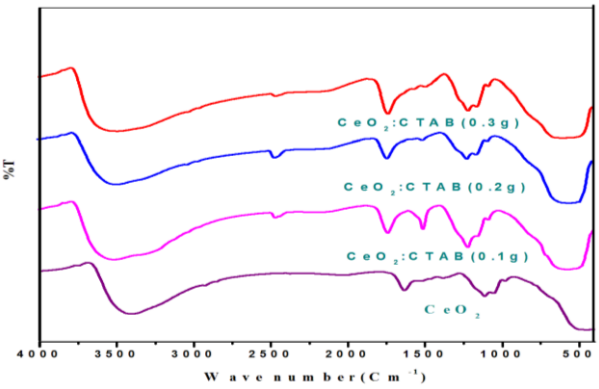

Fig. 3 FTIR spectra of different concentrations of uncapped and CTAB capped ceria nanoparticles

Ultra Violet- Visible Diffuse Reflectance Spectra (UV-Vis DRS)

Fig.4 shows the UV-Vis DRS spectra of surfactant assisted CeO_2 nanoparticles. The spectra showed the samples have intense absorption in the UV region, which trails into the visible region of the spectra. The absorption edges shifted towards the lower wavelength region when increasing concentration of surfactant. From Figure, the absorption edges are positioned at 325-288 nm which, corresponding the band gap values of 3.74, 4.14 and 4.30 eV for capped CeO_2 nanoparticles respectively.

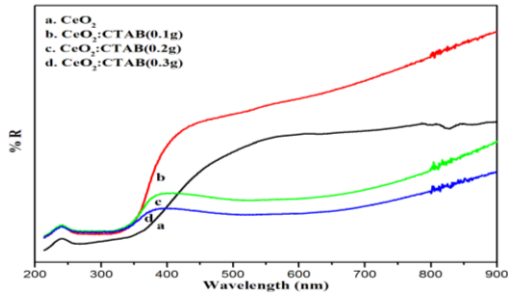

Fig.4. UV-Vis DRS spectra of different concentrations of uncapped and CTAB capped ceria nanoparticles

Photoluminescence (PL)

The PL spectra of CTAB capped CeO_2 nanoparticles with the excitation wavelength of 320 nm are shown in Fig.5. When the capping concentration was increased from 0.1to 0.3 g the intensity of the emission peaks increased gradually. On capped CuO-CeO_2 the intensity of the peaks (344 & 527 nm) increases slightly. The weak emission UV peak at 344 nm is corresponding to the near band-edge emission resulting from the recombination of free excitons. The violet/blue light emission peak at 401 nm observed with decreased particle size could be explained by charge transitions from the 4f band to the valence band of CeO_2. It is easy to observe the hopping from Ce 4f to O 2p. In addition, the defect levels localized between the Ce 4f band and the O 2p band can result in wider emission bands. The low intense blue emission of the cerium oxide samples at 468 nm is related to the abundant defects such as dislocations which is helpful for fast oxygen transportation.

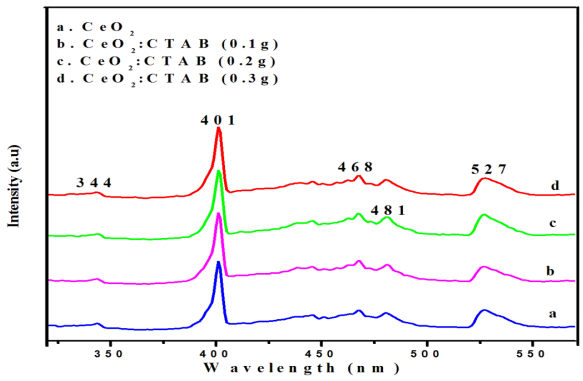

Fig. 5. PL emission spectra of uncapped and different concentrations of CTAB capped CeO_2 nanoparticles

Ce 4f level with a width of 1 eV is localized at the forbidden gap, which lies at 3 eV over the valence band (O 2p). At room temperature, electron transition mainly occurred from defects level to O 2p level. From the Figure, the oxygen defect level located in the forbidden gap is in the range of 1 eV around Ce 4f band The defects energy levels between Ce 4f and O 2p are dependent on the temperature and density of defects in the crystal (Guofeng et al., 2010).The weak blue-green emission peak at 481 are possible due to surface defects in the CeO_2 nanoparticles, the low intensity green emission at 527 nm may be due to the low density of oxygen vacancies during the preparation of the CeO_2 samples. It is noticed that there is a change in the intensity of emission peaks by increasing the capping agent, which indicates that the capping layers did result in size changes or increased surface defect. As a result change in the optical properties of synthesized pure and copper doped CeO_2 nanoparticles is ascribed to the effects of surfactant CTAB on the band structures of ceria nanoparticles and further have impacted the electronic transitions, give rise to uniform particle growth behaviors, the content of oxygen vacancies, and the presence of low valence ions (Phoka et al., 2009.)

Atomic Force Microscopy

AFM was used to investigate the surface morphology of surfactant assisted CeO_2 nanoparticles. Fig.6 reveals the fact that sample showed distinct spherical shape with solid dense structure with uniform distribution of particles. From the Figure shows that the agglomeration of larger particles having size about 50-65 nm for CeO_2.

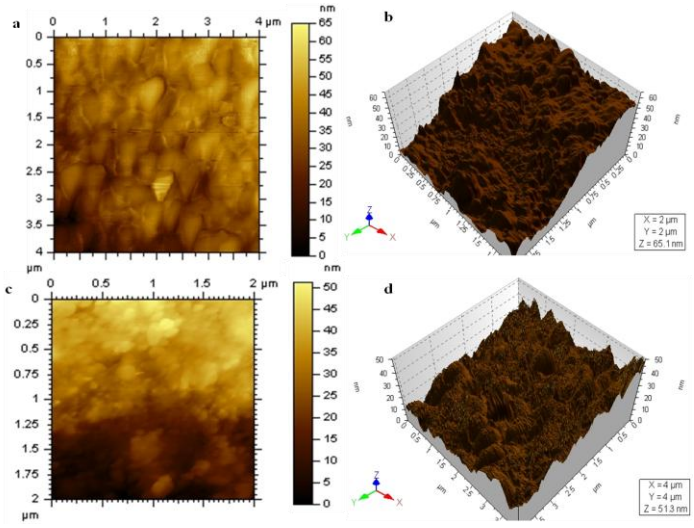

Fig.6 AFM images of (a, c), CTAB capped (0.3g) CeO_2 and (b, d) corresponding 3D view

Antibacterial activity

Fig.7 shows the antibacterial activity of the surfactant assisted ceria nanoparticles against different human pathogens was investigated by disc diffusion method. Three different concentrations (50, 100, 200 µg/ml) were used to test against gram positive and gram negative bacteria's. The concentration increases inhibition values increased. However, the capped nanoparticles shown zone of inhibition was found against gram positive and gram negative was obtained for the synthesized (0.3g) capped ceria nanoparticles. The zone of inhibition values are listed in Table 1.

Table 1 Zone of inhibition values for CTAB (0.3g) assisted cerium oxide nanoparticles

Name of the organisms	Diameter of zone of inhibition (mm) concentration of the (µg/ml)			Antibiotics
	200	100	50	
	13.2±0.78	12.3±0.57	10.0±0.50	19.3±0.57
S. aureus	12.6±0.76	11.7±0.57	9.0±0.50	18.3±0.57
B. subtilis	12.0±0.50	10.1±0.78	8.6±0.76	23.8±0.76
E. coli	11.5±0.50	10.3±0.57	9.6±0.78	19.5±0.50
P. aeruginosa	13.2±0.78	12.3±0.57	10.0±0.50	19.3±0.57

*** Mean, ± = Standard deviation, Inculdind disc (6mm) diameter, mm = millimeter, µg/ml=microgram per milliliter,*

From Table 1 shows that the gram positive bacteria shows higher zone of inhibition than the gram negative bacteria which indicates that synthesized samples exhibits a stronger bactericidal effect upon gram positive than gram negative bacteria. It may be suggested that the antibacterial effect is also strongly dependent on the type of target micro organism. The potential reason for the antibacterial activity of cerium oxide nanoparticles adhered to the cell wall of bacteria and penetrated through the cell membrane this resulted into inhibition of bacterial cell growth and multiplication. The binding of nanoparticles to the outer membrane of gram positive causes the inhibition of active transport, dehydrogenase and periplasmic enzyme activity and eventually the inhibition of RNA, DNA and protein synthesis, which finally leads to cell lysis for the gram positive bacteria. Generally, the nano materials release ions, which react with the thiol groups (-SH) of the proteins present on the bacterial cell surface which leads to cell lysis (Zhang. and Chen, .2009). From the present study we conclude that, capped cerium nanoparticles could be used as an effective antibacterial agent against the tested human pathagons infections.

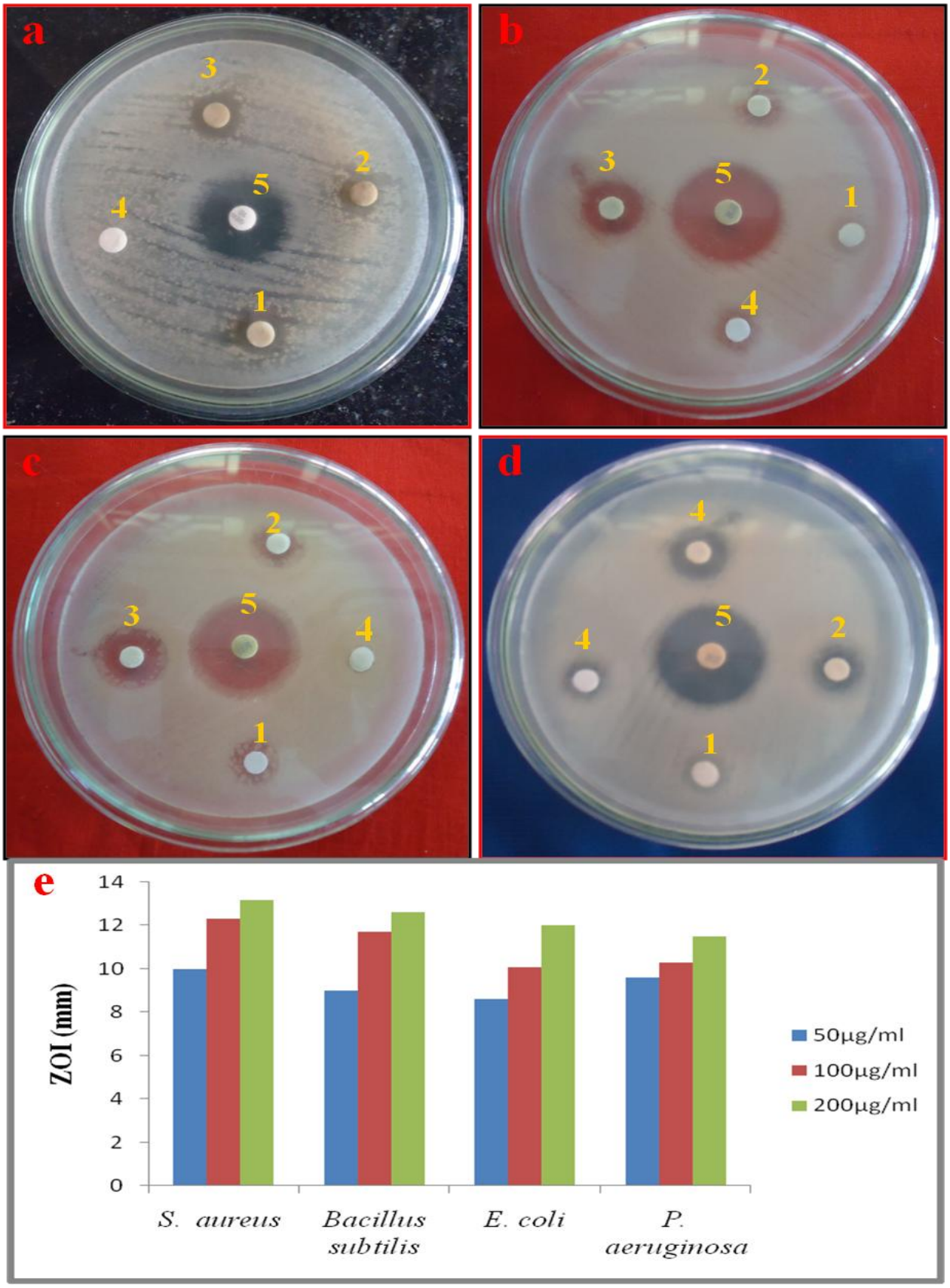

Fig.7 (a, b, c, d) Antibacterial activity of CTAB (0.3g):CeO_2 NPs (e) zone of inhibition values for different concentration

4.CONCLUSION

In conclusion we have reported the synthesis and characterization of surfactant assisted CeO_2 nanoparticles by a simple chemical precipitation. The XRD patterns of CeO_2 surfactant assisted products show pure phase of cubic-fluorite ceria structure. Among the various levels of capping, 0.3g of CTAB capping shows smaller sized particles. The FTIR results clearly indicate that the surface of the nanoparticles was chemically bonded with the surfactant. The DRS analysis confirms that the absorption edges of capped ceria were blue shifted compared to the uncapped CeO_2. PL emission studies show that there is a change observed in the intensity of emission peaks by increasing the concentration of CTAB, which indicates that the capping layers did result in size changes or increased surface defect. The AFM analyses showed dense and uniform distribution of nanoparticles and are spherical in shape with smooth morphology. The antibacterial activity of the synthesized samples analyzed against some human pathogens reveal that the capped cerium nanoparticles showed the maximum zone of inhibition against gram positive than gram negative bacteria. The results of this study clearly indicate that the ceria nanoparticles synthesized by a chemical precipitation method using cationic surfactant is a promising material for effective antibacterial agent after further clinical trials.

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