Hydrothermal Synthesis of Gadolinium (Gd) Doped Cerium Oxide (CeO$_2$) Nanoparticles: Characterization and Antibacterial Activity

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ABSTRACT

This present study has been described the synthesis, characterization and antibacterial activity of gadolinium doped cerium oxide nanoparticles. The nanoparticles were prepared by hydrothermal method with various concentrations of gadolinium ranges from 2 mol% to 8 mol%. The X-ray diffraction (XRD) pattern revealed the face-centered cubic structure with crystalline size of 58.3 nm to 57.4 nm with increasing the concentration of gadolinium (2 mol% to 8 mol%). The Ce-O chemical bonding nature was confirmed using Fourier transform infrared spectrometer (FTIR). The field emission scanning electron microscope (FESEM) exhibited fascinating shapes like cube and square of nanoparticles. UV spectrophotometer used to measure the optical behaviors of CeO$_2$ nanoparticles. Band-edge absorption of CeO$_2$ nanoparticles blue shifted upon increasing the gadolinium concentration as compared to undoped CeO$_2$ nanoparticles. The emission behavior of nanoparticles was examined by photoluminescence (PL) spectroscopy. PL spectra reveals a peak shift of CeO$_2$ emission upon gadolinium doped due to oxygen defect. The gadolinium doped CeO$_2$ nanoparticles showed better antibacterial activity against the pathogenic bacteria such as Escherichia coli, Staphylococcus aureus, Bacillus cereus and Salmonella typhi.

Keyword: CeO$_2$ Nanoparticles; Hydrothermal method; Morphology; Antibacterial activity.

INTRODUCTION

Cerium oxide (CeO$_2$) nanostructures are getting more familiarity due to its enhanced properties than that of bulk material. The cerium oxide nanoparticles (CeO$_2$NP$_x$) have unique structure because of their broad applicability to various areas such as microelectronics, optoelectronics, fuel cell technologies, gas sensors, solid state electrolytes and antimicrobial activities. There are
several methods have been proposed for the synthesis of CeO$_2$ nanoparticles$^{5-8}$. The hydrothermal method has advantages over other methods such as efficient synthesis process and morphology controlled growth. The CeO$_2$ NPs played an important role in the remediation of toxicity of microorganism such as bacteria, yeast and fungi$^9$. At lower temperatures it was found that this material has antimicrobial activity against several bacteria and reported the microorganisms were destroyed by the possibility of generation of reactive oxygen species$^{10}$. The CeO$_2$ nanoparticles and cell membrane of bacteria are attracted with each other due to the electrostatic interaction nature. Hence, this interaction indicates the important role of medium charge and microorganism surface nature in the antibacterial activity$^{11}$. Further, the doping effect enhances the physical properties of CeO$_2$ nanostructures for environment remediation. However, there is lack of information on the effect of Gadolinium (Gd) dopants on the structure and morphology in comparison with the undoped ceria. Considering the physical and chemical properties of CeO$_2$ NPs, we made an attempt to synthesis the Gd doped CeO$_2$ NPs by hydrothermal method. The undoped and Gd doped CeO$_2$ nanoparticles were characterized using various structural and spectral techniques. Antibacterial properties of these samples were determined against four pathogenic bacteria to know its bacterial killing efficiencies.

**EXPERIMENTAL**

**Synthesis of Gd doped CeO$_2$ nanoparticles**

Trisodium phosphate solution (0.02 M), 20 ml was slowly drop wise added to 60 ml of 0.1 M solution of cerium nitrate under magnetic stirring. During meanwhile 2, 4, 6, and 8% of gadolinium nitrate solution were added to the above reaction mixture and continuously stirred for 30 min. The reaction mixture under constant stirring was resulted as white colloid. Then, the colloids were transferred to the Teflon coated autoclave vessel (100 ml capacity) for hydrothermal treatment maintained at 180°C for 15 hr. The autoclave vessel was cooled to room temperature. The colloid was removed by centrifugation and thoroughly washed with double distilled water followed by ethanol and dried at 60°C for 5 hr. A blank sample (CeO$_2$) synthesized without gadolinium using the same procedure at same experiment conditions for the purpose of comparison.

**Investigation of Nanoparticles**

The crystal structure of CeO$_2$ and Gd doped CeO$_2$ nanoparticles were determined by powder X-ray diffraction technique. XRD patterns were recorded using X-ray diffractometer (XRD, Shimadzu-6000) using CuK$_\alpha$ radiation ($\lambda$=1.5408 Å). The surface morphology of CeO$_2$ and Gd doped CeO$_2$ nanoparticles were studied using a scanning electron microscope (SEM, JOEL JSM-6390). The presence of functional groups was confirmed using Fourier transform infrared spectrometer (FTIR, Brucker-Tensor 27). UV-absorption spectra of synthesized nanoparticles were carried using spectrophotometer UV-Vis (UV-Vis, Jasco V530). The photoluminescence (PL) emission spectra were measured at an excitation wavelength of 340 nm using Photoluminescence spectroscopy (Horiba Jobin, Fluoromax-4) at room temperature.

**Antibacterial Activity of Gd doped CeO$_2$**

The antibacterial activity of CeO$_2$ and Gd doped CeO$_2$ nanoparticles were studied against pathogenic bacteria such as *Escherichia coli*, *Staphylococcus aureus*, *Bacillus cereus* and *Salmonella typhi* using agar disc diffusion method. For this study, CeO$_2$ and Gd dope CeO$_2$ nanoparticles were prepared at the concentration of 1 mg/ml using dimethylsulfoxide (DMSO) as solvent$^{12}$. Then, the dispersed nanoparticles were impregnated into each sterile disc using micropipette under aseptic condition. The overnight bacterial culture was prepared using sterile nutrient broth. Then, all the grown bacterial culture was aseptically transferred to the sterile Mueller-Hinton agar medium using sterile cotton swab. After, the impregnated discs were kept on culture swapped Mueller Hinton Agar medium using sterile forceps. Finally, all the inoculated plates were allowed to incubate for 24 h. using bacteriological incubator. After incubation, the zone of inhibition was measured against the bacterial strains.
RESULTS AND DISCUSSION

FTIR Functional group studies
A broad peak observed at 3357 cm⁻¹ is attributed to the OH stretching vibrations of moisture content present in atmosphere¹³. The band obtained at 2424 and 1042 cm⁻¹ are due to the presence of organic impurities in the sample. The peak at 2424 cm⁻¹ is due to the presence of dissolved or atmospheric CO₂ in the samples. A sharp peak obtained at 1629 cm⁻¹ corresponds to the bending vibrations of H-O-H which is partly overlapping the O-C-O bond¹⁴. A band at 1379 cm⁻¹ is due to the N-O stretching vibrations of oxygen atom present in the ceria nanoparticles. A peak noticed at 818 cm⁻¹ is attributed to the O-Ce-O bonding nature of ceria nanoparticles. The small bands obtained at 700, 615 and 545 cm⁻¹ are corresponding to Ce-O stretching mode¹⁵. Thus FTIR spectra of the samples confirm the formation of Gd-CeO₂ nanoparticles.

XRD structural studies
The crystal structure, grain size and the lattice parameters of Gd-CeO₂ NPs were analyzed from the XRD spectra is shown in Fig. 2. The XRD pattern of the Gd-CeO₂ NPs is well indexed with the standard data [JCPDS card no. 75-0162]¹⁶. The XRD pattern reveals the crystalline nature of the synthesized Gd-CeO₂ nanoparticles. The peaks obtained at 2θ values at 28.5, 33.0, 47.4, 56.3, 59.0, 69.4, and 76.7° are corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (3 3 1) planes. Our result is similar with the existing literate data of the CeO₂¹⁷.

In Gd doped CeO₂ NPs, the 2θ value of (111) plane is shifted towards lower side when the concentrations of Gd is increased. It happened due to the replacement of dopant ion in the CeO₂ lattice¹⁸. In addition, the peak broadening taken place in Gd doped CeO₂ nanoparticles as compared with that of pure CeO₂ synthesized without Gd. The broadening of the peak in Gd doped CeO₂ NPs clearly indicates the smaller sized particles as shown in Fig. 2. The average crystallite size calculated using Debye-Scherrer’s formula was found in the range between 57.4-58.3 nm¹⁹. The size of Gd doped CeO₂ nanoparticles decreased with increasing the concentration of Gd²⁰. The average sizes of Gd-CeO₂ NPs are summarized in Table 1.

Table 1: XRD content for undoped and Gd doped CeO₂ nanoparticles.

<table>
<thead>
<tr>
<th>Samples</th>
<th>2θ (deg)</th>
<th>Crystallite size (nm)</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂</td>
<td>28.53</td>
<td>58.24</td>
<td>3.126</td>
</tr>
<tr>
<td>CeO₂: Gd (2%)</td>
<td>28.47</td>
<td>57.99</td>
<td>3.134</td>
</tr>
<tr>
<td>CeO₂: Gd (4%)</td>
<td>28.48</td>
<td>57.85</td>
<td>3.131</td>
</tr>
<tr>
<td>CeO₂: Gd (6%)</td>
<td>28.45</td>
<td>57.56</td>
<td>3.132</td>
</tr>
<tr>
<td>CeO₂: Gd (8%)</td>
<td>28.51</td>
<td>57.40</td>
<td>3.132</td>
</tr>
</tbody>
</table>

Optical studies
UV-Vis absorption spectra of as-synthesized and Gd doped CeO₂ nanoparticles are shown in Fig 3. The as-synthesized CeO₂ nanoparticles show a strong absorption peak at 345 nm. Its corresponding bandgap energy (E_g) obtained is 3.62 eV was calculated using $E_g = \frac{1242}{\lambda_{absorption}}$ relationship. The bandgap energy found to be slightly increased to 3.67 eV on increasing the concentration of Gd from 2 mol % to 8 mol %. It is believed that the decreased in the size
of particles due to the increase of Gd concentration. The absorption value reveals the charge transfer from $\text{O}^{2-}$ to $\text{Ce}^{4+}$ energy levels in $\text{CeO}_2$ crystal lattice. The absorption wavelength and their corresponding bandgap energy values are presented in Table 2.

Table 2: Bandgap energy for undoped and Gd doped $\text{CeO}_2$ nanoparticles.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Abs. Wavelength (nm)</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CeO}_2$</td>
<td>343</td>
<td>3.62</td>
</tr>
<tr>
<td>$\text{CeO}_2$: Gd (2mol %)</td>
<td>341</td>
<td>3.64</td>
</tr>
<tr>
<td>$\text{CeO}_2$: Gd (4mol %)</td>
<td>340</td>
<td>3.65</td>
</tr>
<tr>
<td>$\text{CeO}_2$: Gd (6mol %)</td>
<td>339</td>
<td>3.66</td>
</tr>
<tr>
<td>$\text{CeO}_2$: Gd (8mol %)</td>
<td>338</td>
<td>3.67</td>
</tr>
</tbody>
</table>

PL emission Studies

Spectra of Gd doped $\text{CeO}_2$ nanoparticles are revealed in Fig. 4. All Gd doped $\text{CeO}_2$ samples showed excitation at 340 nm. As-synthesized sample showed strong emission peak at 377 nm and it resembles to the transition of electron from localized $\text{Ce}^{3+}$ state to valence band of $\text{O}^{2p}$. In addition, an emission peak at 434 nm and 466 nm was originated from defect states widely existing between $\text{Ce}^{3+}$ states to $\text{O}^{2p}$ of valence band. Moreover, an emission nature was gradually decreased beyond the range of 470 nm and also it was extended upto 550 nm. This emission range is related to charge transfer from $\text{Ce}^{3+}$ energy level to $\text{O}^{2p}$ level of valence band. Similarly, from the Gd doped $\text{CeO}_2$ nanoparticles, the localized $\text{Ce}^{3+}$ state to $\text{O}^{2p}$ of valence band transition related emission nature is taken place gradually decreased due to Gd ions in the $\text{CeO}_2$ crystal lattice causes doping effect.

SEM morphology studies

The images of pure $\text{CeO}_2$ exhibit well defined cube and square shape uniform sized particles. The particles are uniformly dispersed. However, some distortion found in the Gd doped $\text{CeO}_2$ nanoparticles. Four samples ($\text{CeO}_2$) were synthesized using 2, 4, 6 and 8 mol% of Gd.
Among four samples, two samples synthesized using 2 mol% (low concentration) and 8 mol% (high concentration) of Gd were characterized as representative samples. As shown in Fig 5 (a) pure CeO$_2$NPs show well defined shaped cubic crystals. The particles in the images are uniformly distributed. The cubic crystalline structure of 2 mol% Gd doped CeO$_2$ show slight distortion in its structure Fig.5 (b). Similarly, the crystalline structures of CeO$_2$ nanocrystals are evenly distributed during the doping of 8 mol% Gd with slight distortion Fig. 5 (c). It is clearly reveals that the addition of Gd to CeO$_2$ slightly changed the morphology of CeO$_2$. The appearance of feather like fibre on the surface of cubic CeO$_2$ nanocrystals indicate the effect of Gd in the formation of CeO$_2$ crystal lattice.

Evaluation of Antibacterial activity

Antibacterial activity of undoped and Gd doped CeO$_2$ nanoparticles were evaluated against pathogenic bacteria such as Escherichia coli, Staphylococcus aureus, Bacillus cereus and Salmonella typhi. The antibacterial results of nanoparticles are shown in Fig. 6. The average zone of inhibition exhibited by pure CeO$_2$ and various concentration of Gd doped CeO$_2$ nanoparticles are presented in Table 3. The pure CeO$_2$NPs did not show any activity against four bacteria. Whereas, the Gd doped CeO$_2$ nanoparticles showed good antibacterial activity. The result obtained from the antibacterial study reveals that the killing efficiency of Gd doped CeO$_2$NPs increased with increasing the concentration of Gd. The zone of inhibition clearly show that the killing potential of CeO$_2$ significantly increased by the Gd doping with Gd doped CeO$_2$.

The 2 mol% Gd doped CeO$_2$ showed 13, 13, 15 and 15 mm zone of inhibition against E.coli, B.cereus, S. aureus and S. typhi, respectively. After increasing the concentration of Gd to 4 mol%, the antibacterial activity against the same bacteria increased to 19, 19, 18 and 28 mm. In 6 mol%, the measured zone of inhibition was 24, 23, 21 and 24 mm. As shown in Table 3, 8 mol% of Gd doped CeO$_2$NPs showed maximum zone of inhibition against all those bacteria as 28, 26, 23 and 26 mm. Among the four tested samples, 8 mol% Gd doped CeO$_2$ nanoparticles exhibit maximum bacterial activity against E.coli. Finding new biomaterials to kill such bacteria is a needy one. The increased concentration of Gd doping with CeO$_2$ increases the antibacterial activity. It is due to the decreased particle size and increased surface to volume ratio. It is noted that the bandgap energy of the samples increased with increasing the concentration of Gd. Similarly, emission spectra of the Gd doped CeO$_2$NPs shifted towards longer wavelength as compared with pure CeO$_2$NPs. In XRD pattern, the particle size decreases with increasing the concentration of Gd. The antibacterial activity of the Gd doped CeO$_2$NPs found to be increased with increasing the concentration of Gd. The formation of Gd doped CeO$_2$NPs reveals the crystalline and smaller sized nanoparticles. As the band gap energy increases, the particle size decreases.

<table>
<thead>
<tr>
<th>Bacterial strains</th>
<th>Zone of Inhibitions (mm)</th>
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<tbody>
<tr>
<td></td>
<td>Various Concentrations of Gadolinium</td>
</tr>
<tr>
<td></td>
<td>2mol %</td>
</tr>
<tr>
<td>E. coli</td>
<td>13 mm</td>
</tr>
<tr>
<td>B. cereus</td>
<td>13 mm</td>
</tr>
<tr>
<td>S. aureus</td>
<td>15 mm</td>
</tr>
<tr>
<td>S. typhi</td>
<td>15 mm</td>
</tr>
</tbody>
</table>

Fig. 6. Anti-bacterial activity of Gd doped CeO$_2$ nanoparticles with different bacterial strains.
decreases, thus Gd doping produce smaller CeO₂NPₜ nanoparticle. The smaller size particles easily transmit into the cell walls. It also increases the interaction between nanoparticle and the outer surface of the bacteria which induce more toxicity to the bacteria. Hence the Gd doped CeO₂NPₜ showed maximum zone of inhibition against pathogenic bacteria.

CONCLUSIONS

Pure CeO₂ and Gd doped CeO₂NPₜ were successfully synthesized. A face-centre cubic crystal structure was confirmed from XRD patterns and their calculated crystalline sizes were 57.4 - 58.3 nm. A blue-shifted absorption was observed from UV optical spectrum and their calculated bandgap energy values were 3.62 - 3.67 eV. The Ce-O chemical bonding nature and the presence of functional groups were confirmed from FTIR spectrum. A cube shaped surface morphology was observed from FESEM images. Further, the antibacterial activity of nanoparticles were studied against different types of bacteria and observed enhanced killing effects. From the overall observations, we have concluded that the increasing concentration of Gd doping from 2 mol% to 8 mol% has shown an enhanced results such as decreased crystalline size, morphology change and antibacterial activity.

REFERENCES


