7.1. Introduction

Different morphology and dimensionality of ceria nano particle has succeeding role on creating ceria with higher performance. CeO\(_2\) with controlled morphology exposes different crystal planes on the solid crystallites which exhibits interesting chemical and physical properties. Different morphologies of ceria are synthesized and studied, which involves nano rods, nano cube, octahedron or polyhedron, etc.\(^1\) Morphology effect of CeO\(_2\) depends on the executed synthetic methods. Surfaces of ceria can be activated by different factors such as surface area, elemental composition, defects and reactive facets\(^2-^5\). Depending upon the morphology of ceria nanostructures, its catalyzing effect also varied. For example, ceria nano system such as nanowire, nano rod and nanoparticle has different redox behavior towards CO oxidation. One of the major reasons for this was due to the exposed crystal plane on the surface of ceria nanostructures\(^6\). Exposed crystal planes of some ceria nano structures: like nano rod and nanowire \{(100) and (110)\}, nano cube \{(100)\}, ceria nano particle and polyhedron \{(111)\}\(^1\). Nano rod like CeO\(_2\) possessed higher activity for CO oxidation and NO reduction\(^7,^8\). But nanocubes show superior properties in soot combustion\(^9\), hydrogen oxidation\(^10\) and preferential oxidation of CO\(^11\). But due to the existence of large proportion of reactive planes on the surface of ceria nanowire, made it as potential redox catalyst for CO oxidation. Presence of oxygen vacancies and mobility of oxygen in the lattices are significantly altered with morphological parameters\(^6\).
The design and synthesis of rare earth oxide ceria with chelating ligand oxalate have found rare works in the literature. Ceria nano particle from cerium oxalate can be prepared by microwave heating assisted thermal decomposition method\textsuperscript{12}. Upon thermal decomposition of oxalate, it followed stepwise thermal decomposition strategy\textsuperscript{13–15}. It is more important to have a fair knowledge on thermal decomposition behavior of surface modified cerium oxalate up to the formation of CeO\textsubscript{2}/Ce\textsubscript{2}O\textsubscript{3}. Morphological dependency on activation energy can be derived in terms of conversion fraction $\alpha$. Up to now, no exploratory work has done to deal the effect of morphological aspects of cerium oxalate on the creation of ceria with unique surface textures. Hence it has substantial interest to synthesis ceria in different design with appropriately choosing input reactant and surfactant. Besides it is equally important to understand the influence of structural features as the thermal stability or rate of decomposition of oxalate samples. It was investigated that surface modification of a polymeric material is an important tool to tune its degradation rate\textsuperscript{16}. This happens because thermal conductivity of the surface functionalizing agents has pivotal role on reducing thermal stability of polymeric material, thereby increasing rate of its degradation process\textsuperscript{17}. It was noted that the size of oxalate nanoparticle of calcium has noticeable effect on the kinetics of thermal decomposition process. On reducing the size of oxalates, the amount of activation energy needed for the decomposition process was decreased\textsuperscript{18}. Bogatyreva \textit{et al}\textsuperscript{19} studied the effect of surface modification of the nano diamond on its thermal stability. High temperature activation followed by chemical treatment with mineral acids reduced the impurities on the top of the surface of diamond,
thereby reducing the chance of oxidation. Hence it was suggested that up to 773K, nano diamond with stands oxidation process at its surfaces.

Since the radical scavenging and antioxidant properties of ceria, it is worth to note the importance of ceria in anticancerous field. It was investigated that CeO$_2$ nano particles (Nps) are toxic to cancer cells and non-toxic to living cells$^{20}$.

Besides, it can inhibit invasion and sensitize cancer cells to radiation therapy and chemotherapy. This Nps are able to protect from cell damage indirectly by priming cells to respond to ROS (Reactive oxygen species) attack or directly by scavenging cellular ROS. It can save healthy cells from radiation induced damage during radiation therapy and provides neuro protection to spinal cord neurons. PEGlycated ceria nanoparticle showed enhanced radioprotection on human liver cell under $\gamma$-irradiation$^{21}$. Shape effect of ceria on the cytotoxic properties is not well studied yet. Therefore, in the present work, different surface modified cerium oxalate (Ce-Ox) was prepared by co-precipitation and hydrothermal methods. Shape effect of cerium oxalate on thermal decomposition behavior for the formation of ceria nano structures is studied. Besides, how the anticancerous and optical properties of ceria are altered with the different surfaces of the ceria nano materials. Fig. 1 represents the comparison of synthesis of Nps with and without using stabilizers.
7.2. Experimental

7.2.1. Method of preparation

In the present work, cerium oxalate is prepared through simple precipitation and hydrothermal route. 3.07mmol cerium nitrate is dissolved in 60mL of distilled water. Add 1.02mmol CTAB and stirred the solution for 2h. The resulting supernatant solution is transferred into a sealed autoclave and kept at 120ºC for 24h. Similar procedure is also conducted with PEG as surfactant. Cerium oxalate is also synthesized through simple precipitation route using sodium oxalate as the precipitating agent and the above mentioned surfactants. The precipitate is filtered and washed with ethanol and water. The precipitate is kept at 80ºC. Fig. 2 shows the PEG assisted synthesis of ceria Nps.
Designation of oxalate samples

H₁ (Ce-Ox- simple precipitation- PEG -800 as surfactant), H₂ (Ce-Ox-hydrothermal-PEG-800 as surfactant), H₃ (Ce-Ox- simple precipitation- CTAB as surfactant), H₄ (Ce-Ox- hydrothermal-CTAB as surfactant).

Designation of prepared oxide samples

P₁ (synthesized branched hexagonal nanorod ceria from H₁), P₂ (synthesized multi branched nano ceria from H₂), P₃ (synthesized nano disc/flower of ceria from H₃), P₄ (synthesized 2D nano sheets of ceria from H₄).

The chemical composition and crystal structures of cerium oxide (prepared \textit{via} thermal decomposition) were studied by XRD. (FT-IR) spectra of the samples was recorded by transmittance method. The prepared cerium oxalate precursor was calcined at 450°C in muffle furnace for 5h. The morphology and topographical studies of the oxide samples were brought with TEM and Field emission scanning electron microscope. UV-Visible spectra of the oxide samples were taken spectrophotometer. Photo luminescent properties are well
characterized by using fluorescence spectrometer at room temperature. Electronic and crystalline properties are well characterized by using HRTEM and SAED pattern. Thermal decomposition properties of oxalates were analyzed by DSC and TG analysis in N\textsubscript{2} (50mL) atmosphere. Raman spectra of the samples were collected using confocal Raman microscope with the excitation of 532nm laser.

7.3. Results and discussion

7.3.1. Material characterization

Fig. 3A represents FT-IR spectra of surface modified Ce-Ox. Figs. 3Aa, b, c &d respectively show H\textsubscript{1}, H\textsubscript{2}, H\textsubscript{3} & H\textsubscript{4}. The broad band observed at 3080–3433cm\textsuperscript{-1} (Fig. 3A) associated with water molecules which are removed only at higher temperature\textsuperscript{22}.

![FT-IR spectra](image)

**Fig. 3** FT-IR spectra (A), TG (B) and DTG curves (C) (at 5Kmin\textsuperscript{-1}) in N\textsubscript{2} atmosphere of surface modified Ce-Ox: H\textsubscript{1} (a), H\textsubscript{2} (b), H\textsubscript{3} (c) & H\textsubscript{4} (d).
Table 1 Mass loss (%) for each Ce-Ox upon thermal decomposition obtained from TG curves

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>53.06</td>
</tr>
<tr>
<td>H₂</td>
<td>49.68</td>
</tr>
<tr>
<td>H₃</td>
<td>54.76</td>
</tr>
<tr>
<td>H₄</td>
<td>42.05</td>
</tr>
</tbody>
</table>

The very strong peak observed at 1633.9 cm⁻¹ corresponds to the combined effect of asymmetric bending and stretching of water molecule. The strong peak observed at 1318.4 cm⁻¹ represents the asymmetric stretching of CO₂ molecule associated with oxalate ligand group. The band observed at 523.8 cm⁻¹ stands for M-O stretching frequency. Thermal decomposition behavior of cerium oxalate depends on the nature of surface modifier, its chemical bond with surface of the oxalate sample, mechanism and kinetics of thermal reaction. From the TG curves (Fig. 3B), it is understood that the method of preparation of the sample (history) also depends on the rate of mass loss process during thermal decomposition. It can be realized from the kinetics of decomposition that, significant variation with distinct surface textures of cerium oxalate upon the rate of formation of ceria. The mass loss (%) corresponding to each surface modified Ce-Ox by the thermal decomposition process are displayed in Table 1. It was found that mass loss (%) for the sample H₄ (42.05%) is lower than others indicating lower thermal stability of array of nano hexagonal Ce-Ox. Highest mass loss was found for nano disc Ce-Ox (H₃), 54.76% and nano flower petals Ce-Ox (H₁), 53.06% prepared by co-
precipitation method. Ce-Ox synthesized through hydrothermal methods (H_2 & H_4) has lower percentage of mass loss. Theoretical mass loss for the formation of ceria from cerium oxalate was found to be 52.48%. The higher experimental mass loss was occurred with the degradation of surfactant along with Ce-Ox. Fig. 3C shows the DTG curves of all surface modified Ce-Ox, H_1 (Fig. 3C: a), H_2 (Fig. 3C: b), H_3 (Fig. 3C: c) and H_4 (Fig. 3C: d). DTG curves passes through with non-homogeneous behavior at several regions of the temperature, implying partially overlapped multistep process. Sample H_4 and H_1 occur at much lower temperature for the formation ceria nano particle than other samples, whereas sample H_2 take place at higher temperature for the production of nano particle.

Fig. 4A represents FE-SEM images of Ce-Ox nano materials (sample H_1, H_2, H_3 & H_4). Fig. 4Aa shows the Ce-Ox nano flower petals (H_1). Fig. 4Ab exposes like nano plates of Ce-Ox (H_2). Fig. 4Ac displays like nano discs/flower of Ce-Ox (H_3). Array of nano hexagons of Ce-Ox (H_4) is represented in Fig. 4Ad. Fig. 4B displays the DSC curves of nano materials of Ce-Ox at 2Kmin\textsuperscript{-1}. DSC curve shows two main stages up to the temperature 800K, the first stage corresponding to the loss of crystallized water of Ce-Ox and second for the decomposition of oxalates forming ceria nano structures.
Fig. 4 FE-SEM images (A) and DSC curves (B) of oxalate samples at 2Kmin⁻¹; H₁ (a), H₂ (b), H₃ (c) & H₄ (d)

It is displayed that changing the surface morphology of Ce-Ox, changes in the decomposition as well as dehydration temperature was occurred (Fig. 4B). This happens due to the difference in the diffusion controlled reaction mechanisms of solid state decomposition of each nanomaterial of Ce-Ox. Ce-Ox nano flower petals (H₁) (Fig. 4A:a) undergo dehydration at lower temperature (380.13K) than others (Fig. 4B:a). The samples H₂, H₃ & H₄ losses water at 394.22K, 395.94K and 387.4K (Figs. 4B:b, c & d). On moving to the decomposition part at 2Kmin⁻¹, H₄ has lower decomposition temperature 669.46K (Fig. 4B:d) than H₁, H₂ & H₃. Hence it is informed that the significant influence of morphology of Ce-Ox on the thermal decomposition behavior of Ce-Ox up to the formation of ceria nano particle.
Fig. 5 The DSC curves of Ce-Ox at 2, 4, 6 and 8Kmin\(^{-1}\) in N\(_2\) atmosphere.

Fig. 6 FT-IR spectra (A) and XRD patterns (B) of ceria: P\(_1\) (a), P\(_2\) (b), P\(_3\) (c) & P\(_4\) (d)
Fig. 5 represents the DSC curves at 2, 4, 6 and 8Kmin\(^{-1}\) for the samples \(H_1\) (Fig. 5a), \(H_2\) (Fig. 5b) \(H_3\) (Fig. 5c) and \(H_4\) (Fig. 5d). It was observed that increasing temperature, the absorbed heat energy was decreased than lowest temperature reaction. Besides, increasing heating rate, marked increasing in the absorbed heat energy with respect to \(\beta\), but this shift was found to be only at lower reaction and rather disappeared at higher temperature reaction. It was noticed that the peak width of sample \(H_4\) is higher at all heating rates than other samples.

Figs. 6A &B show the FT-IR spectra and XRD patterns of different surface modified ceria; where a, b, c and d represent respectively branched hexagonal nano rod (\(P_1\)), multi branched (\(P_2\)), nano disc/flower (\(P_3\)) and array of nano hexagons (\(P_4\)). The IR band at 3000-4000cm\(^{-1}\) corresponds to water molecule associated with oxides. The band at 520-550cm\(^{-1}\) corresponds to M-O bond. Fig. 6B represents the diffraction peaks corresponding to cubic fluorite type structure of ceria (JCPDS Card No. 34-0394). Among the different morphologies of ceria, intensities of diffraction peaks are comparable.

Fig. 7 shows the FE-SEM images of formed ceria nano materials. Nano ceria \(P_1\) (Fig. 7a) have surface morphology of hexagonal rod with branching in one direction. But \(P_2\) shows nano rod morphology with branches in many directions. These branches to the surfaces were occurred due to the influence of surfactant PEG. Ceria nano material, \(P_3\) (Fig. 7c) and \(P_4\) (Fig. 7d) display like nano discs/flower and array of 2D nano sheets respectively. From the surface morphological analysis of ceria, it can be seen that thermal
decomposition of Ce-Ox nano materials significantly altered its shape. Both the synthetic route and surfactants used affect the morphology of Ce-Ox, which has influence on the creation varieties of ceria nanostructures.

Fig. 7 FE-SEM images of ceria nano structures prepared from Ce-Ox; P₁ (a), P₂ (b), P₃ (c) and P₄ (d).
Fig. 8 TEM images of ceria nano structures; P₁ (a), P₂ (b), P₃ (c) and P₄ (d).

Fig. 8 shows the TEM images of ceria nano materials. Thermal decomposition of Ce-Ox nano flower petals P₁ yields nano hexagonal particles having size 2.11-3.98 nm (Fig. 8a). The inter planar distance was found to be 0.3 nm (Fig. 9a). This indicates the presence of branched nano hexagons with lattice fringes similar to inter planar distance of cubic fluorite type structure of ceria. Thermal reactions of branched Ce-Ox (H₂) resulted in the formation of aggregates of nanoparticle with size in the range of 3.8-8.39 nm (Fig. 8b). The distance between two successive planes of this branched ceria was found to be 0.32 nm (Fig. 9b).
Fig. 9 HRTEM images of P₁ (a), P₂ (b), P₃ (c) and P₄ (d).

Fig. 10 SAED patterns of ceria: P₁ (a), P₂ (b), P₃ (c) and P₄ (d).
The nano disc/flower like Ce-Ox (H₃) upon thermal decomposition yields nano discs/flower of ceria (P₃). These nano discs/flower are composed of ceria nanoparticles of size 4.6-8.8nm (Fig. 8c). The inter planar distance was observed to be 0.33nm (Fig. 9c). Array of nano hexagonal Ce-Ox (H₄) altered its surface textures upon thermal decomposition to yield 2D nano sheets (P₄) (Fig. 7d), these sheets are composed of ceria nano spheres having size in the range of 2.92-9.32nm (Fig. 8d). The inter planar distance of P₄ was observed to be 0.28nm (Fig. 9d), indicating the cubic fluorite type structure. The calculated values of lattice constant for each ceria nano structures are listed in Table 2.

It was observed that lattice constant of each ceria nano structure is altered. Changes occurred for each ceria lattice constant and inter planar distance is ascribed to the existence of difference in the experiencing lattice strain which arises due to the difference in particle size and oxygen ion vacancies. Decreasing of particle size and inter planar distance for the samples causes the lattices to be relaxed by creating new oxygen ion vacancies. Sample P₁ acquired lower particle size distribution compared to others. Hence, this sample reduces its lattice strain by creating more number of oxygen ion vacancies by converting more Ce⁴⁺ to Ce³⁺.
Table 2 The values of lattice constant, particle size and inter planar distance of ceria nanostructures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice constant (nm)</th>
<th>Particle size (nm)</th>
<th>Inter planar distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₁</td>
<td>0.52</td>
<td>2.11 - 3.98</td>
<td>0.30</td>
</tr>
<tr>
<td>P₂</td>
<td>0.55</td>
<td>3.80 - 8.39</td>
<td>0.32</td>
</tr>
<tr>
<td>P₃</td>
<td>0.57</td>
<td>4.60 - 8.80</td>
<td>0.33</td>
</tr>
<tr>
<td>P₄</td>
<td>0.49</td>
<td>2.92 - 9.32</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Fig. 10 shows SAED patterns of each synthesized ceria nanostructures. P₁, P₂ & P₃ show highly crystalline ceria nano particle. But P₄, array of nano sheets composed of nano sphere like particles exhibited semi crystalline nature as evident from the SAED pattern (Fig. 10d).

7.3.2. Photo physical properties

7.3.2.1. UV-absorbance

![Graph](image)

**Fig. 11** UV-Visible absorbance spectra of ceria nanostructures (A); P₁ (a), P₂ (b), P₃ (c) and P₄ (d) & Tauc plots (B); P₁ (a), P₂ (b), P₃ (c) and P₄ (d).
Fig. 11A represents UV-Visible absorbance spectra of the entire ceria nano structures which show broad strong absorption below 400nm. The absorbance spectrum shows two absorption maxima. The peaks about 256nm correspond to charge transfer from O\(^2\)\((2p)\) to Ce\(^{3+}\) (4f) orbitals in CeO\(_2\), while UV A absorption at 340nm are responsible for CT from O\(^2\)\((2p)\) to Ce\(^{4+}\) (4f) orbitals\(^{25}\). Fig. 11A: a, corresponds to ceria hexagonal nano rods (P\(_1\)) while Figs. 11A: b, c &d respectively represent ceria with multi branches (P\(_2\)), nano discs/flower (P\(_3\)) and nano sheets (P\(_4\)). On comparing the UV-absorbance, nano discs/flower (P\(_3\)) show highest UV- absorbance. Fig. 11B displays Tauc plots for each ceria nanostructure. Figs. 11B: a, b, c &d respectively represent Tauc plots for P\(_1\), P\(_2\), P\(_3\) & P\(_4\). Lower \(E_g\) value was observed for 2D nano sheets (Fig. 11B: d). It is followed that \(E_g\) value in the order of P\(_4\) < P\(_1\) < P\(_2\) < P\(_3\). \(E_g\) values calculated from the Tauc plots is listed in the Table 3. This confirms that UV-absorbance and optical band gap significantly altered with respect to morphology of ceria.

**Table 3** The values of optical band gap \(E_g\) calculated from Tauc plots

<table>
<thead>
<tr>
<th>Sample</th>
<th>(E_g) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(_1)</td>
<td>2.77</td>
</tr>
<tr>
<td>P(_2)</td>
<td>2.87</td>
</tr>
<tr>
<td>P(_3)</td>
<td>2.97</td>
</tr>
<tr>
<td>P(_4)</td>
<td>2.73</td>
</tr>
</tbody>
</table>

**7.3.2.2. Luminescent properties**

Fig. 12 shows the significance of photo luminescent (PL) spectra of ceria nano structures at an excitation wavelength of 340nm.
It was observed that depending upon the surface morphology of ceria, distinct level of intensity of emission band was occurred. Hence surface morphology of nanostructures plays significant influence in the emission band intensity. Fig. 12a represents PL of ceria with branches in one direction (P₁). Figs. 12b, c &d represent PL of ceria P₂, P₃ &P₄. Emission band consists of good violet bands at 419nm (2.96eV), blue emission band at 483nm (2.57eV) and green emission band at 529nm (2.35eV). It was reported that PL emission in the range of 400-550nm (< 3eV) are highly associated with oxygen vacancies with trapped electrons which localized between Ce (4f) and O (2p) band in CeO₂. Highest luminescent intensity was observed for P₃.

![PL spectra of ceria nano structures; P₁ (a), P₂ (b), P₃ (c) and P₄ (d).](image)

**Fig. 12** PL spectra of ceria nano structures; P₁ (a), P₂ (b), P₃ (c) and P₄ (d).
7.3.3. Thermal properties

7.3.3.1. Estimation of Ea values for the decomposition process of Ce-Ox up to the formation of nano structures

During thermal decomposition process, self–generated reaction condition has predominant role on controlling the reaction pathways\textsuperscript{26}. Change in the internal gaseous pressure can alter the smoothness of heat transfer process, which affects kinetics of the reaction. Cerium oxalate decomposes to ceria through multistage decomposition stages. Due to the experimental inconvenience of separately tracking the each component process; the deconvolution of overall kinetic information into reaction component is the only possible method for interpreting multistage reaction scheme\textsuperscript{27,28}. Each kinetically resolved stage is studied by formal kinetic analysis. Fig. 13 shows the deconvoluted DSC curve of the sample H\textsubscript{4} at 2Kmin\textsuperscript{-1}.

\textit{Ea} for each independent process was measured by using \textit{Friedman plots}. The determination of \textit{Ea} values for each stage was based on \textit{Eq. 1}. Plots of ln (\textit{da/dt}) vs \textit{T}\textsuperscript{\textdegree} known as \textit{Friedman plots}\textsuperscript{29-31}, for the series of kinetic data at different \(\alpha\) recorded under linear non-isothermal condition were examined for determining the values of \textit{Ea}. From the slope of the plot, the values of \textit{Ea} can be evaluated. \(A\) can be calculated from the intercept, after incorporating the best reaction model \(f(\alpha)\) using modified Sestak-Berggren model(SB \((m, n)\))\textsuperscript{32,33}. 
\[ \frac{d\alpha}{dt} = A \exp\left( -\frac{Ea}{RT} \right) f(\alpha) \]  

\[ f(\alpha) = \alpha^n (1 - \alpha)^m \]  

**Fig. 13** The deconvoluted DSC curve of sample $H_4$ at $2Kmin^{-1}$.

Fig. 14 shows the Friedman plots for first (Fig. 14a), second (Fig. 14b), third (Fig. 14c), fourth (Fig. 14d) and fifth (Fig. 14e) stages of thermal decomposition of array of nano hexagonal Ce-Ox ($H_4$), which were used for finding the initial values of $Ea$ and $A$ of the sample $H_4$. Similarly, initial values of $Ea$ and $A$ values of other oxalate samples were also calculated by the Friedman plot. The contribution of each stage was calculated from the area or quantity of heat absorbed in the DSC curve. The method of kinetic deconvolution procedure (*as described in previous chapters*) was executed for finding the optimized values of $Ea$. 


Fig. 14 Friedman plots at different $\alpha$ value of first (a), second (b), third (c), fourth (d) and fifth stages (e) of thermal decomposition of array of nano hexagonal Ce-Ox ($H_4$).
<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁</td>
<td>47.15</td>
<td>48.13</td>
<td>130.37</td>
<td>146.24</td>
<td>68.40</td>
</tr>
<tr>
<td>H₂</td>
<td>42.98</td>
<td>79.59</td>
<td>123.26</td>
<td>134.07</td>
<td>245.03</td>
</tr>
<tr>
<td>H₃</td>
<td>89.04</td>
<td>62.47</td>
<td>53.96</td>
<td>162.77</td>
<td>266.26</td>
</tr>
<tr>
<td>H₄</td>
<td>36.67</td>
<td>37.67</td>
<td>43.76</td>
<td>69.75</td>
<td>75.53</td>
</tr>
</tbody>
</table>

The comparison of \( Ea \) value for the formation of each nano structure is listed in Table 4. Significance of surface characteristics of each Ce-Ox upon the thermal reaction condition can be depicted from finding the \( Ea \) value throughout each stage. From the Table 4, it is known that array of nano hexagonal Ce-Ox (H₄) takes easiest reaction path for removing crystallized water and for forming 2D nano sheets as the end product. Comparatively higher amount of activation energy was needed by Ce-Ox nano disc/flower (H₃) to form as nano discs/flower as the reaction product. This means that H₃ proceeds through the diffusion controlled reaction mechanism which tends to higher thermal prevention for the decomposition. Change in \( Ea \) value was observed throughout the reaction at different extent for samples H₁ & H₂. This informs that synthetic route and substrate surface characteristics control the thermal reaction programs for forming ceria nanostructures.

The plots used for finding optimized \( Ea \) values are represented in Figs. 15, 16, 17 and 18 for first, second, third, fourth and fifth stages of decomposition of each Ce-Ox.
Fig. 15 The Friedman plots at different $\alpha$ value of first (a), second (b), third (c), fourth (d) and fifth (e) stages of thermal decomposition of the sample $H_1$. 
The plots at specified α values were drawn only for most linearly fitted data. For some plots, slope at specified α values are coinciding to each other. Fig. 19 depicts how thermal event occurs in the initial stages of the sample H₄ (Figs. 19a & b), reminding that \( E_a \) value decreases with reaction (for first) and \( E_a \) value almost constant towards the end of the stage (for second). Change in \( E_a \) value occurs due to the happening of change in reaction pathway as the reaction progresses. Fig. 19 also shows the dependence of \( E_a \) with respect to α for third (c), fourth (d) and fifth (e) stages respectively.

Fig. 16 The Friedman plots at different α value of first (a), second (b), third (c), fourth (d) and fifth (e) stages of thermal decomposition of the sample H₂.
Fig. 17 The *Friedman plots* at different $\alpha$ value of first (a), second (b), third (c), fourth (d) and fifth (e) stages of thermal decomposition of the sample $H_3$
Fig. 18 The Friedman plots at different $\alpha$ value of first (a), second (b), third (c), fourth (d) and fifth (e) stages of thermal decomposition of the sample H$_4$. 

**Diagram Description:**
- Each plot represents the Friedman plot for a specific stage of thermal decomposition.
- The plots show the relationship between $\ln\left[\frac{d\alpha}{dt}\right] (s^{-1})$ and $10^3 T^{-1} (K^{-1})$.
- Different stages (a)-(e) are distinguished by their respective axes and trend lines.
- The $\alpha$ values vary across the plots, with markers indicating specific stages.

**Mathematical Expression:**
\[
\ln\left[\frac{d\alpha}{dt}\right] (s^{-1}) = k T^{-1} (K^{-1})
\]
Fig. 19 Dependence of $E_a$ vs $\alpha$ for first (a) second (b), third (c), fourth (d) and fifth (e) stages for the sample $H_4$. 
### 7.3.4. Micro Raman spectra

![Micro Raman spectra](image)

**Fig. 20** Micro Raman spectra of CeO$_2$ nano structures; P$_1$ (a), P$_2$ (b), P$_3$(c) and P$_4$ (d)

The influence of surface morphology of ceria nanostructures are further confirmed by Raman scattering (Fig. 20). The spectrum shows the main band at 465.34 cm$^{-1}$, which is responsible for the first order triply degenerated F$_{2g}$ mode of vibration characteristic to the cubic structure of CeO$_2$. The weak band near to 600 cm$^{-1}$ is associated with the intrinsic oxygen ion vacancies due to the presence of Ce$^{3+}$ ions. Several factors caused for the change in Raman peak position and line width of main band. These include phonon confinement, strain, broadening associated with size distribution, defects, and variations in phonon relaxation with particle size. It was
observable from the spectrum that comparatively higher intensity for the sample P₁ (Fig. 20a), P₂ (Fig. 20b) and P₃ (Fig. 20c). But lower intensity for the band was appeared for P₄. The increased intensity of the band is associated with increased oxygen ion vacancies. For the sample P₄, widening of the characteristic peak was observed than others. Therefore this sample experiences lattice strain by the creation of more oxygen ion vacancies. Presence of more oxygen ion vacancies in the lattice of ceria, make it as better radical scavenger. Raman intensity ratio was calculated from the relative intensity of weak band near to 600cm⁻¹ and intense peak at 465.34cm⁻¹. Figs. 21a-d displays the micro Raman spectra corresponding to the weak band near to 600 cm⁻¹ for the samples P₁, P₂, P₃ and P₄ samples respectively.

**Table 5** Raman intensity ratio for each ceria nanostructures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Raman intensity ratio (I₆₀₀/I₄₆₅)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₁</td>
<td>0.005</td>
</tr>
<tr>
<td>P₂</td>
<td>0.005</td>
</tr>
<tr>
<td>P₃</td>
<td>0.173</td>
</tr>
<tr>
<td>P₄</td>
<td>0.008</td>
</tr>
</tbody>
</table>
Fig. 21 Micro Raman spectra of P₁ (a), P₂ (b), P₃(c) and P₄ (d) corresponding to the weak band at near to 600 cm⁻¹.

From the Table 5, highest Raman intensity ratio was found for sample P₃. From the earlier reports³⁶, number of oxygen ion vacancies is best described with Raman intensity ratio. Hence, concentrations of oxygen ion vacancies are found to be large for the sample P₃.
7.3.5. Cytotoxicity studies

**Fig. 22** Results of *in vitro* cytotoxic studies for different ceria nanostructures: P₁ (a), P₂ (b), P₃(c) & P₄ (d)

Fig. 22 shows the results of *in vitro* cytotoxicity for different surface modified ceria, using Dalton’s Lymphoma ascite cells. Procedure for assay is described in chapter 2. This assay exposed highest percentage of inhibition for cancerous cell by the sample P₁, branched hexagonal ceria nanorods (Fig. 22a) than other ceria nano materials considered. The value of IC₅₀ was observed at drug concentration of 105.3μgmL⁻¹ for sample P₁. 73% of inhibition of cancer cells by P₁ was occurred at concentration of 200μgmL⁻¹. Multi branched (P₂, Fig. 22b), nano disc/flower (P₃, Fig. 22c) & nano sheet
(P₄, Fig. 22d) like ceria performed comparatively lesser cytotoxicity towards cancer cells than nano hexagonal branched rods of ceria (P₁). Hence the significance of surface morphologies of ceria nanomaterial has great influence in performing it as anticancerous drug. Ceria with surface modified by PEG, P₁ displayed as better anticancer drug.

7.4. Conclusion

Nano flower petals, nano plates, nano disc/flower and array of nano hexagonal Ce-Ox were synthesized via simple precipitation and hydrothermal methods. Executing thermal decomposition strategy for the oxalate precursors; surface modified ceria nanostructures like branched hexagonal nano rod, multi branched, nano discs/flower and nano sheets were synthesized and characterized. Surface modification of Ce-Ox has pivotal role on the thermal decomposition strategy, particle size and shape, formation of oxygen ion vacancies, optical and anticancerous properties. It was explored that for the formation of nano sheet like ceria, Ea values are lowered. But nano discs/flower of Ce-Ox has higher thermal prevention for the decomposition process to produce nano discs/flower of ceria. Enhanced luminescent and UV-absorbing properties were observed for nano disc/flower like ceria. But enhanced inhibition (73%) towards Dalton’s Lymphoma ascite cells was performed by ceria (P₁), surface modified with PEG (branched hexagonal nanorod).
7.5. References


