Green synthesis of CeO$_2$ nanoparticles using *Artocarpus heterophyllus* leaf extract for photocatalytic activity

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Contents

Green Synthesis Process

Experimental Procedure

Results and Discussions

Applications of CeO2 nanoparticles
CeO₂ - a Promising Material

**Properties:**
- High reactivity
- Unique UV absorption ability
- High temperature stability
- High hardness

**Common synthesis methods:**
- Sol–gel, hydrothermal, sonochemical
- Flame spray pyrolysis
- Reverse micelle route
- Combustion
- Complex thermodecomposition method

**Applications:**
- Solid oxide fuel cell
- Gas sensor
- Luminescent materials
- Photocatalyst
- Disease treatment: Oxidative stress, Parkinson’s disease

**Structure:**
Face-centered cubic

Why Green Synthesis

- Environment friendly
- No need of high temperature pressure
- Energy efficient
- Non-toxic method
- Scaled up for large synthesis of nanoparticles
- Natural coating on nanoparticles

Basic mechanism of green synthesis:

1. Plant Extract
2. Metal Ion Solution
3. Extract + Metal Ion Solution
4. Synthesis Process
5. Nanoparticles
Experimental Procedure

Step-1 Preparation of leaf extract

Step-2 Addition of leaf extract in Ce(NO₃)₃·6H₂O solution and heating it at 80 °C with continuous stirring until it becomes dry and then kept at oven at 120 °C for 12 hours

Step-3 Washing and grinding of dried powder

Step-4 Heat treatment for 3 hours at different temperatures

Step-5 Grinding after heat treatment before characterization

Step-6 Repeating step 2 varying precursor and leaf extract concentration
Results and Discussions - DSC Analysis

Fig. 1: DSC and TGA graphs for (a) 0.01M, (b) 0.025M, (c) 0.055M and (d) 0.1M precursor concentration obtained at 10 °C/min heating rate.
Structural Analysis - XRD

![PXRD patterns of all samples in as prepared and at 250 °C annealed condition with precursor to leaf extract ratio of 1:1, 1:2, 1:3 and 1:4 respectively.]

- No peak appeared before heat treatment – amorphus
- Crystallization starts at 250°C
- Better crystallinity for 1:3 ratio

Fig.2: PXRD patterns of all samples in as prepared and at 250 °C annealed condition with precursor to leaf extract ratio of 1:1, 1:2, 1:3 and 1:4 respectively
Fig. 3: PXRD patterns for (a) 0.01M, (b) 0.025M, (c) 0.055M and (d) 0.1M precursor concentration samples after heat treatment at 700, 800 and 800 °C.
Table 1: Lattice Parameter Calculation for Cubic CeO2 (ICDD 01 – 078 – 5328) from Nelson-Riley plot

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Conc. (M)</th>
<th>( a_{\text{NR}} ) Nelson – Riley (Å)</th>
<th>( a_{\text{D}} ) Database (Å)</th>
<th>( \Delta a = a_{\text{NR}} - a_{\text{D}} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>0.01</td>
<td>5.4</td>
<td>5.41</td>
<td>−0.01</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>5.4</td>
<td></td>
<td>−0.01</td>
</tr>
<tr>
<td></td>
<td>0.055</td>
<td>5.4</td>
<td></td>
<td>−0.01</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>5.4</td>
<td></td>
<td>−0.004</td>
</tr>
</tbody>
</table>

Negligible difference between standard & our observed value

Required equations:

\[ f(\theta) = \frac{1}{2} \left[ \frac{\cos^2 \theta}{\sin \theta} + \frac{\cos^2 \theta}{\theta} \right] \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (1) \]

\[ a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2) \]
Crystal size of the nanoparticles is determined by using Scherrer formula:
\[ D = \frac{k\lambda}{\beta \cos \theta} \]

Where,
- \( D \) = Crystallite size (in nm) = FWHM of hkl peak (in radians)
- \( K = 0.9 \) (For spherical shape)
- \( \theta \) = Bragg angles (in degrees)
- \( \lambda = 0.15405980 \) nm

**Williamson-Hall method**
\[ \beta \cos \theta = K\lambda/D + 4\varepsilon \sin \theta \]
Table 3: Crystallite Size of the samples annealed 900 °C calculated from Scherer equation, modified Scherer equation and Williamson-Hall method

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Precursor Concentration (M)</th>
<th>Crystallite Size Scherrer for (111) only (nm)</th>
<th>Crystallite Size Williamson – Hall (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>0.01</td>
<td>27</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.025</td>
<td>25</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>0.055</td>
<td>29</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>29</td>
<td>21</td>
</tr>
</tbody>
</table>
Microstructure Analysis

Magnification X 50000

<table>
<thead>
<tr>
<th>Image</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>a = 0.01 M</td>
</tr>
<tr>
<td>b</td>
<td>b = 0.025 M</td>
</tr>
<tr>
<td>c</td>
<td>c = 0.055 M</td>
</tr>
<tr>
<td>d</td>
<td>d = 0.1 M</td>
</tr>
</tbody>
</table>
Microstructure Analysis

Fig. 5: EDX analysis of 0.1M sample annealed at 900 °C

Presence of Phosphorus (P) is confirmed by EDX results.
Magnetic Property Analysis

Fig. 6: Magnetic property of 0.1M sample annealed at 400 °C and 900 °C

Higher magnetization obtained at higher temperature
Fig. 7: UV-Vis reflectance spectra of all samples annealed at 500 °C and 900 °C

Reflectance/absorption range increases with the increasing annealing temperature
Optical Property Analysis

Kubelka-Munk function:

\[ F(R) = \frac{(1 - R)^2}{2R} \]

Fig.8 : Band gap of all samples at 900 °C
Optical Property Analysis

Table 4: Band gap of all samples annealed at 900 °C determined by Kubelka-Munk Plot

<table>
<thead>
<tr>
<th>Precursor concentration</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01M</td>
<td>2.3</td>
</tr>
<tr>
<td>0.025 M</td>
<td>2.4</td>
</tr>
<tr>
<td>0.055 M</td>
<td>1.9</td>
</tr>
<tr>
<td>0.1 M</td>
<td>2.2</td>
</tr>
</tbody>
</table>

✓ Band gap of bulk CeO2 3.3 eV
✓ Band gap obtained by green synthesis is lower
✓ Enhanced photocatalytic property
Photocatalytic Activity

Max absorbance at 663 nm

UV-vis spectra of 30µM MB solution before and after charging CeO₂ nanoparticles

Pseudo first order kinetic model for the degradation of MB dye using CeO₂ nanoparticles

Slow Degradation Rate due to Absence of O₂ Vacancies in CeO₂ which were grabbed by CePO₄

\[ K_{app} = \frac{y}{x} \]
<table>
<thead>
<tr>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Use of abundant leaf as reducing agent to avoid toxic chemicals</td>
</tr>
<tr>
<td>✓ Structural analysis of the synthesized samples</td>
</tr>
<tr>
<td>✓ Particle size 20 nm after annealing at 900 °C</td>
</tr>
<tr>
<td>✓ Better optical property obtained</td>
</tr>
<tr>
<td>✓ Magnetic property observed</td>
</tr>
<tr>
<td>✓ Better photocatalytic property attained</td>
</tr>
</tbody>
</table>


