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Nanocrystalline Ceria through Homogeneous Precipitation in Alcohol-Water Mixed Solvent

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Uniform nanosized 3-6 nm cerium oxide single crystals have been synthesized by ammonia precipitation in alcohol-water mixed solvent. The size was estimated by photon correlation spectroscopy (PCS), X-ray diffraction (XRD) and high resolution transmission electron microscopy (HR-TEM). The surface area of CeO$_2$ nanocrystals were measured by Brunauer-Emmett-Teller (BET) technique. The nanoparticles synthesized were mono-dispersed with a narrow size distribution with low polydispersity index (PDI). The size of the ceria nanocrystals synthesized was found to decrease with decrease in the $\varepsilon$ of the solvent. The crystals precipitated from isopropyl alcohol were highly crystalline. The smallest CeO$_2$ crystals were obtained using ethylene glycol/water medium whereas lowest PDI was obtained from IPA/water system.

[Keywords : CeO$_2$, Nanocrystals, Precipitation, Mixed solvent, HR-TEM]

Introduction

Materials of nanodimension have been attracting increasing interest worldwide for their unique chemical and physical properties compared to bulk due to the enhanced surface area to volume ratio, quantum confinement and consequent changes in the lattice parameter. Ceria (CeO$_2$) is a refractory material possessing face-centred cubic fluorite-type crystal structure, which is stable from room temperature to its melting point. Cerium oxide based materials have been extensively studied and employed in various applications including fast ion conductors, oxygen storage capacitors, catalysts, gas sensors, solid oxide fuel cells and in chemical mechanical polishing. The particle size and size distribution of ceria are important in determining their properties. Cerium oxide materials displaying a bandgap of 3.19 eV exhibit size dependent optical properties and is commonly used as an ultraviolet blocking material.

Thus the development of size and morphology controlled synthetic methods of CeO$_2$ is needed for tapping the full potential of CeO$_2$. Though nanocrystals of ceria can easily be synthesized by aqueous precipitation method, one major disadvantage of this method is the agglomeration of fine particles, which imposes a major challenge to realization of the full potential of nanocrystalline powders, especially CeO$_2$ particles. Chen and Chang observed a linear relationship between the reciprocal of particle size synthesized and the dielectric constant of the reaction medium.

In this report we have synthesized mono-dispersed small nanoparticles of cerium oxide by precipitation of ceria from an alcohol-water mixed solvent using ammonia precipitation and characterized the same by X-ray diffraction, Brunauer-Emmett-Teller (BET) surface area measurement, HR-TEM and light scattering.

Experimental

The CeO$_2$ nanoparticles were synthesized at 50$^\circ$C by ammonia precipitation from an alcohol-water mixed (1:1) solvent using 0.05 M Ce(NO$_3$)$_3$.6H$_2$O as the cerium source. Excess ammonia solution was added to 0.05 M cerium nitrate solution dropwise with vigorous mechanical stirring. In this study, several alcohols including ethanol, n-propanol (PrOH), isopropanol (IPA), ethylene glycol (EG) and polyethylene glycol-300 (PEG) were used. The suspension was stirred for about 1.5 h after ammonia addition. Stable suspensions were obtained with 1:1 mixture of n-propanol and polyethylene glycol-300 solvents. A small portion of this slurry was further used for surfactant coating. The remaining slurry was centrifuged, washed with distilled water and ethanol alternatively for three times, and the precipitate was dried at 60$^\circ$C. The nanoparticles slurry kept separated for coating was surfacted with oleic acid under reflux for ~30 min. After the reflux, the slurry was cooled naturally; the ceria nanoparticles were precipitated and washed using acetone. The precipitate was dispersed and homogenized in non aqueous solvent by ultrasonication.

The phase identification of the solid products were done by powder X-ray diffraction patterns using a Philips X’Pert PRO diffractometer using CuK$_\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$) on oven dried powders in the 2$\theta$ range of 20-65 degree at a scanning rate of 2$\theta$.min$^{-1}$ and a step size of 0.02$^\circ$. High resolution transmission electron microscopy (HR-TEM) technique was used to characterize the morphologies of the materials and phase to confirm particle size and crystal structure. HR-TEM data were taken on powder deposited on a 400 mesh copper grid.
coated with transparent carbon using a FEI Tecnai 30 G² S-Twin high resolution transmission electron microscope equipped with a Gatan CCD camera and operated at 300 kV. Size measurements on the stable suspensions of cerium oxide nanocrystals were performed at 25°C by static light scattering (also referred to as photon correlation spectroscopy, PCS) on a Zetasizer 3000 HSA (Malvern, Worcestershire, UK). Nitrogen adsorption isotherms on nanocrystalline selected CeO₂ samples were determined at liquid nitrogen temperature (77 K) using a Micromeritics Gemini 2360 surface area analyser. The specific surface area of the CeO₂ powders were calculated from the N₂ adsorption data using the Brunauer-Emmett-Teller (BET) technique.

Results and Discussion

X-ray diffraction patterns for all the nano-ceria samples were identical and all peaks were identified as CeO₂ with cubic fluorite structure (JCPDS 34-0394) having space group Fm3m (225). However, the peaks were significantly broader due to small crystallite size and associated strain. One of the selected XRD patterns of CeO₂ synthesized from ethanol-water mixture is given in Fig. 1.

The crystallite size ($D_{\text{XRD}}$) of CeO₂ powders was calculated from the X-ray line broadening by applying full-width-half-maximum ($\beta$) of the characteristic peak (111) to the Scherrer formula,¹⁰ given in Eqn 1.

$$D_{\text{XRD}} = \frac{0.9\lambda}{\beta \cos \theta} \quad ..(1)$$

where $\lambda$ is the wavelength of incident X-ray and $\theta$ is the diffraction angle for the (111) plane. The sample codes, some experimental conditions and selected results are given in Table I. The dielectric constants given in Table I have been calculated from the individual dielectric constants of pure solvents based on the assumption of valid “rule of mixture”.

It has been found that the ceria crystallites synthesized from pure water ($\varepsilon = 80$) are larger than that obtained from mixed solvents with lower dielectric constants (Table I). There is small extent of agglomeration in CeO₂ particles precipitated in mixed ethanol, PrOH and IPA as evidenced from the PCS data (Table I). As shown in Table I, the $\varepsilon$ value (dielectric constant) decreases in the following order: H$_2$O > PEG > EIOH > PrOH > IPA and the particle sizes of the ceria powders synthesized using these alcohols decreased almost in the same order except in the case of PEG. Average particle size ($D_{\text{BET}}$) from BET surface area has been calculated using the standard equation (Eqn 2) assuming that the CeO₂ particles are spherical and non porous.¹⁵

$$D_{\text{BET}} = \frac{6}{\rho \varepsilon} \quad ..(2)$$

Table I: Sample names, dielectric constant of the mixed solvent used and particle size obtained from different methods of analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dielectric constant ($\varepsilon$) of mixed solvent</th>
<th>BET constant area (m².g⁻¹)</th>
<th>$D_{\text{XRD}}$ (nm)</th>
<th>$D_{\text{BET}}$ (nm)</th>
<th>$D_{\text{PCS}}$ (nm) (PDI)</th>
<th>$D_{\text{TEM}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-H₂O</td>
<td>80</td>
<td>134.9</td>
<td>6.0</td>
<td>6.1</td>
<td>nd²</td>
<td>7.2</td>
</tr>
<tr>
<td>Ce-EIOH</td>
<td>52.2</td>
<td>142.9</td>
<td>5.3</td>
<td>5.8</td>
<td>12.4 (0.215)</td>
<td>6.2</td>
</tr>
<tr>
<td>Ce-PrOH</td>
<td>50.1</td>
<td>143.3</td>
<td>5.1</td>
<td>5.7</td>
<td>15.4 (0.446)</td>
<td>nd</td>
</tr>
<tr>
<td>Ce-IPA</td>
<td>47.8</td>
<td>145.2</td>
<td>4.8</td>
<td>5.6</td>
<td>11.2 (0.211)</td>
<td>5.2</td>
</tr>
<tr>
<td>Ce-EG</td>
<td>49.6</td>
<td>166.9</td>
<td>4.3</td>
<td>4.8</td>
<td>6.4 (0.203)</td>
<td>3.7</td>
</tr>
<tr>
<td>Ce-PEG</td>
<td>54.1</td>
<td>170.3</td>
<td>3.5</td>
<td>4.9</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

# not done
where \( \rho \) is the true density of CeO\(_2\), i.e. 7.28 g cm\(^{-3}\) and \( A \) is the BET surface area. \( D_{\text{BET}} \) is in good agreement with \( D_{\text{XRD}} \) as well as with \( D_{\text{TEM}} \) except in the cases of EG and PEG (Table I).

Ethylene glycol and PEG (\( \epsilon \) being 49.6 and 54.1 respectively) have resulted in much smaller ceria crystal than expected. This is probably due to the presence of diol functional groups in these two alcohols. TEM photographs of surfactant coated sample Ce-IPA, Ce-EG, Ce-EtOH and one of their fast fourier transform of the electron diffraction are given in Fig. 2. It is evident from the TEM image of CeO\(_2\) precipitated in isopropyl alcohol medium (IPA) (Fig. 2A) and HR-images of other samples (not shown here) that they are single crystals. The crystal facets in HR-TEM of fcc ceria are indexed to different planes. The average particle size (\( D_{\text{TEM}} \)) was obtained by analysing the size data obtained for more than 100 particles for all samples, from multiple TEM images. \( D_{\text{TEM}} \) for Ce-IPA (Fig. 2A), Ce-EtOH (Fig. 2B) and Ce-EG (Fig. 2C) were 5.2, 6.2 and 3.7 nm respectively. Water produced CeO\(_2\) crystals of average size of ~6 nm under the similar conditions. Small extent of agglomeration was observed in the product from EG based mixed solvent.

No obvious defects or dislocations can be found in the particles. Lesser extent of clustering of primary particles in alcohol media is due to the comparatively lesser extent of hydrogen bonding in the solvent as the dielectric constants for mixed solvents are lower (less polar) than that of water. A typical desorption-adsorption isotherm of CeO\(_2\) precipitated in PEG is shown in Fig. 3.

The N\(_2\) adsorption isotherms taken on CeO\(_2\) samples were of classical type II nature. Therefore, the resulting particles are inferred to be non porous with well defined crystalline structures. The size measurement data done on stable suspensions of surfactant coated nanoparticles in non polar solvent (kerosene) using photon scattering technique are given in Table I and a selected profile on CeO\(_2\) synthesized from ethylene glycol-water solvent is shown in Fig. 4.

The average size and distribution obtained from TEM analysis is also shown in the same figure for comparison. The photon scattering profile against population for sample Ce-EG (Fig. 4) shows an average size of 6.4 nm with polydispersity index of 0.203. The width of the profile is ~3 nm at half maximum for both the measurements. The small width and polydispersity index of PCS data indicate that the size distribution of ceria nanocrystals is very narrow or monomodal. The difference of ~2 nm in the size data from two measurements is due to the length of oleic acid chain (~0.9 nm)\(^{17}\) attached to the ceria NP core increasing the diameter of the particles tumbling under thermal motion in suspension.

\[ \text{Fig. 2 – HR-TEM images of oleic acid surfacted CeO}_2\, \text{samples: A) Ce-IPA, Fast Fourier transform is shown on the right-top and a magnified crystal image below showing different crystal facets (111), (200) and (220) of cubic CeO}_2\; \text{B) Ce-EtOH with } D_{\text{TEM}} \, 6.2 \, \text{nm; and C) Ce-EG with } D_{\text{TEM}} \, 3.7 \, \text{nm} \]

\[ \text{Fig. 3 – The adsorption-desorption isotherms of Ce-PEG with average crystallite size (} D_{\text{XRD}} \text{) of 3.5 nm indicating a type II behaviour} \]

\[ \text{Fig. 4 – The hydrodynamic size distributions of surfacted CeO}_2\, \text{(Ce-EG) in kerosene obtained from light scattering (PCS) and TEM analysis. The schematic presentation of the difference in size for the CeO}_2\, \text{core from TEM and hydrodynamic diameter from PCS is shown in the inset} \]
Conclusions

CeO$_2$ nanoparticles in the size range 3-6 nm have been prepared via homogeneous precipitation from alcohol-water mixed solvent. Ethylene glycol medium produced smallest nanocrystals. Mixed solvent with lower dielectric constant produced smaller CeO$_2$ crystals. The particles were highly crystalline making it possible to get very high resolution TEM images of the nanoparticles. All the small CeO$_2$ nanocrystals are single crystals. PCS size data proves that agglomeration is comparatively less in alcohol-water mixture for all the powders.

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