

ARTICLE

Aqueous Medium Induced Optical Transitions in Cerium Oxide Nanoparticles

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Supporting Information

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Materials and Methods:

Theoretical Simulation: In order to understand the optical properties of ceria nanoparticles, we performed density functional theory (DFT) calculations using plane-wave based Vienna ab initio simulation package (VASP 4.8).^{1, 2} The electronic ground state was determined using local density (LDA) approximation. We used LDA+U version with local part described by Ceperley-Adler function. On site Coulomb and exchange interaction were treated by a single effective parameter $U_{\text{eff}}=U-J$. Plane waves were included up to an energetic cutoff of 415 eV, electronic wave functions were described using the projected augmented wave (PAW) method and $U_{\text{eff}}=5$ eV.³ The same protocol was recently employed for investigation of ceria and it was shown that LDA+U approximation demonstrates better agreement with experiment for structure properties than generalized gradient approximation (GGA+U) approach.⁴ The interaction energy between nanoceria and water molecules were estimated using GGA+U since this value is overestimated when LDA is used. PW91 exchange-correlation function was employed with $U_{\text{eff}}=3$ eV.^{5, 6} Supercells were chosen with at least 10 Å between replicas to remove periodicity artifacts.

Reversible Change in Color of CNPs: In order to simulate the reversible color changes in nanoceria treated with hydrogen peroxide, we investigated the electronic structure of $\text{Ce}_{19}\text{O}_{32}$ with adsorbed O_2 molecule. The most energetically favorable configuration was found to include O_2 molecule attached to nanoceria vertex as shown in inset of Fig.3a.

Transmission Electron Microscopy: High-resolution transmission electron microscopy (HRTEM) images were obtained using Fei-Tecna F-30 electron microscope operated at 300 KV with a point-to-point resolution of ~0.2 nm. The TEM samples were prepared by coating the holey carbon-coated copper grids with few drops of solution. Images were collected from the grids dried overnight in vacuum and non-dried grids to remove any artifacts that may arise from drying process. 15-20 nm agglomerates with individual particle size of 3-5nm were consistently observed in the sample. The individual particle size did not change with aging or drying of nanoparticles.

X-ray Photoelectron Spectroscopy (XPS): Qualitative analysis of the oxidation state of cerium in CNPs was gauged from XPS analysis of the samples using PHI ESCA 5400 spectrophotometer operated at 300W at a base pressure of 2×10^{-8} torr or less and Al K α as source of X-rays. The samples for the XPS analysis were prepared in glove box with continuous flow of argon by drop coating a 5mM suspension of CNPs on a silicon wafer. To ensure the uniformity of sample preparation equal amount of sample was dropped on the silicon wafer for coating. The samples were then transferred to a sealed sample transfer chamber inside the glove box for transferring to the XPS chamber without any exposure to ambient atmosphere to avoid any interference of atmosphere with the valence chemistry of cerium. The spectrophotometer was calibrated using a gold standard prior to XPS run and any charge shift in the samples was corrected using adventitious carbon as a reference at binding energy of 284.8 eV.⁷

UV-Visible Spectrophotometry and Measurement of Concentration of Ce^{3+} oxidation state: The optical properties of samples were ascertained using UV-Visible spectrophotometer. The composition of Ce^{3+} was determined indirectly by measuring the absorption of Ce^{4+} using UV-Visible spectrophotometer (Lambda 750S). The original concentration of 5mM nanoceria sample was diluted to 0.5mM to record the changes in absorbance with aging time. The absorption maximum at 298 nm following 1 day of the addition of hydrogen peroxide was assumed to originate from 100% concentration of Ce^{4+} ions. A calibration plot was obtained by measuring the absorbance at 298 nm with serial dilutions. This calibration plot was used to estimate the concentration of Ce^{4+} oxidation state in nanoceria by measuring the absorbance at 298 nm, after the addition of hydrogen peroxide and aging time.

Synthesis of Nanoparticles: Cerium oxide nanoparticles were synthesized using previously published protocols. Cerium nitrate hexahydrate was dissolved in DI water and stirred. The solution was filtered using 200nm filter (ANODISC) to remove any unwanted and undissolved impurities. The solution was then oxidized using excess of oxidizers and the pH of the solution was maintained at 2.5 – 4.0. The solution was then aged at room temperature to catalyze the formation of nanoceria with predominant trivalent oxidation state of cerium.

Oxidation of Cerium: For experimental work the concentration of cerium in its reduced state [Ce^{3+}] in nanoceria particles suspended in water was controlled chemically by oxidizing Ce^{3+} to Ce^{4+} using hydrogen peroxide.⁸ The oxidation is accompanied by change in color of the solution from colorless to yellow/orange depending on hydrogen peroxide concentration. It was recently established that chemical reaction between ceria nanocrystals and hydrogen peroxide results in the formation of the yellow and orange complexes with O_2^{2-} ions.⁹ Our computational results show that such coloring of nanoceria- O_2^{2-} complex is caused by electron transfer from O_2^{2-} ions on nanoceria surface to cerium ions. These transitions are distinctly different from the optical properties of nanoceria itself and were not discussed further. Aging of this ceria solution in acidic medium regenerates the Ce^{3+} .

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