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## Aqueous Medium Induced Optical Transitions in Cerium Oxide Nanoparticles

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Experimental and theoretical investigations were performed to investigate the effect of water on optical properties of nanoceria as a function of Ce<sup>3+</sup> concentration. Theoretical studies based on density functional plane-wave calculations reveal that the indirect optical transitions in bare ceria nanoparticles are red-shifted with increase in concentration of Ce<sup>3+</sup>. However, ceria nanoparticles model with adsorbed water molecules show a blue shift in the indirect optical spectra under identical conditions. Direct optical transitions are almost independent of Ce<sup>3+</sup> concentration but show pronounced blue shift in the aqueous environment relative to the bare nanoparticles. The theoretical study is consistent with our experimental observation in difference of shift behaviour in bare and aqueous suspended ceria nanoparticle. This change from red- to blue-shift in indirect optical transitions is associated with polarization effect of water molecules on f-electron states.

Ceria (cerium oxide) is one of the most abundant rare-earth metal oxides. It attracts the interest of researchers due to its particularly high performance in a variety of applications such as catalysis, fuel cells and biomedical applications, especially in nanocrystalline form.<sup>1-7</sup> Bulk cerium oxide has at least two stable stoichiometries: the cubic fluorite-type dioxide (CeO<sub>2</sub>) Fm3m and the hexagonal cerium sesquioxide (Ce<sub>2</sub>O<sub>3</sub>) P-3m.<sup>8,9</sup> Close thermodynamic stability of these stoichiometries leads to continuous range of partially reduced (also called “mixed valence”) CeO<sub>2-x</sub> phases, where oxygen vacancy can be rapidly formed or eliminated.<sup>2</sup> As a result of this “oxygen storage capacity”, ceria is used in number of catalytic processes, most notably for purification of exhaust gases in three-way automotive catalytic converters.<sup>1, 3</sup> It was shown that concentration of Ce<sup>3+</sup> ([Ce<sup>3+</sup>]) in nanoceria also critically influences its optical properties.<sup>10-18</sup> Several studies have been reported on optical properties of nanocrystalline thin films<sup>10-14</sup> and solvent suspended ceria nanocrystallites<sup>15-18</sup>. For both systems direct and indirect optical electronic transitions are associated with O2p→Ce5d and O2p→Ce4f electronic excitations. In the case of nanostructured ceria thin films red shift for both direct and indirect bands was observed experimentally with decrease in the size of nanoparticles.<sup>11-13</sup> In contrast, shift to higher energy in absorption spectra with decrease in size, was observed in toluene and aqueous sols of ceria nanoparticles.<sup>15-20</sup> It should be mentioned that the [Ce<sup>3+</sup>] was varied as a function of particle size and thus is a subject of controversy whether the effect originates due to quantum confinement or due to increasing Ce<sup>3+</sup> concentration<sup>21</sup>. Different theories attributed this blue shift to the changes in valence state of Ce ions<sup>11, 12, 15-18</sup> or the quantum confinement effect<sup>22, 23</sup> and the role of suspending media and its dependence on [Ce<sup>3+</sup>] has been neglected to a large extent.

In present communication we report the possible origin of blue shift in water suspended nanoceria particles and its dependence on [Ce<sup>3+</sup>] using both experimental and computational results at constant particle size. We have synthesized ceria nanoparticles

of 3-5 nm in diameter synthesized by wet chemical procedure described elsewhere.<sup>24</sup> The values of direct and indirect optical band gaps were measured using the conventional method.<sup>25</sup> The experimental and theoretical details are provided in the supporting information. The experimental results shown in Figure 1a depict a blue shift of cerium oxide nanoparticles as a function of increase in [Ce<sup>3+</sup>]. For comparison the results on cerium oxide thin films grown under ultra-high vacuum from literature<sup>12</sup> is also plotted on the same graph (Figure 1a). The change in the oxidation state of cerium was confirmed by x-ray photoelectron spectroscopy which demonstrated that cerium was predominantly present in Ce<sup>4+</sup> oxidation state upon oxidation by H<sub>2</sub>O<sub>2</sub>, while aging in acidic solution reduced cerium to the trivalent oxidation state (Ce<sup>3+</sup>) as shown in Figure 1b. The individual particle size of the 3-5 nm was confirmed for both oxidized and reduced surface by transmission electron microscopy as observed in Figure 1c and 1d. Thus the experimental observations reveal the blue-shift in optical transitions with increase in [Ce<sup>3+</sup>] in the nanoparticles and not due to the quantum confinement of nanoparticles as the particle size remained unchanged. An opposite trend as compared to the previously reported experimental data<sup>12</sup> (a red shift in the indirect optical transitions with increase in [Ce<sup>3+</sup>]) could be explained if the solvent effect is taken into account. Strong polarizing effect of aqueous environment results in a blue shift in optical transitions of cerium oxide nanoparticles with increase in [Ce<sup>3+</sup>]. We then challenged the experimental observation using theoretical simulation to illustrate the effect of adsorbed water molecules on the optical properties of nanoceria.

The selection of representative nanoparticle structure is critical for the reliability of the prediction. The smallest possible nanoparticle with octahedral shape was constructed by cutting off (111) planes from the bulk fluorite CeO<sub>2</sub> lattice. These nanoparticles with chemical formula Ce<sub>19</sub>O<sub>32</sub> and Ce<sub>44</sub>O<sub>80</sub> are presented in Figure 2a and are in accordance with the experiment.<sup>26-29</sup> Ceria nanoparticles at the size range considered

are inherently non-stoichiometric and thus we used octahedral non-stoichiometric nanoparticles instead of introducing oxygen vacancies in the most stable stoichiometric ceria nanoparticles.<sup>30, 31</sup> It must be noted however that the size of these nanoparticles is smaller than the nanoparticles used in the experimental study (3-5nm) and thus the  $[\text{Ce}^{3+}]$  in the theoretical study is much higher than the  $[\text{Ce}^{3+}]$  in experimental results. Working with larger sized nanoparticles is currently beyond our computational resources. However, both experimental and theoretical results show the similar trend of increase in band gap with increase in  $\text{Ce}^{3+}$  concentration in water (Figure 2b) and hence we believe that the different range of concentration of  $\text{Ce}^{3+}$  does not change the overall effect of water on the optical properties of nanoceria.

To investigate the effect of water on nanoceria we considered ceria nanoparticles with 12 and 24 water molecules adsorbed on the surface (for  $\text{Ce}_{19}\text{O}_{32}$  and  $\text{Ce}_{44}\text{O}_{80}$  models, respectively) to provide 1 mL of the surface coverage. Effect of the other molecules or ions in bulk liquid water was neglected. Adsorbed water forms two hydrogen bonds with the oxygen atoms on the surface of the nanoparticle in a configuration similar to the one reported by Fronzi et al.<sup>32</sup> Binding energy between ceria nanoparticles and  $\text{H}_2\text{O}$  was calculated to be 0.54 eV per adsorbed water molecule, in close agreement with the previous DFT studies.<sup>13, 14, 32</sup>

We compared the calculated projected density of states (PDOS) of ceria nanoparticles with PDOS for bulk  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ .<sup>33</sup> The calculated values of  $E_{\text{in}}$  for indirect  $\text{O}2\text{p} \rightarrow \text{Ce}4\text{f}$  and  $E_{\text{d}}$  for direct  $\text{Ce}4\text{d} \rightarrow \text{Ce}4\text{f}$  electronic transitions are c.a. 2.38 eV each for bulk  $\text{CeO}_2$ . The corresponding experimental values for electronic transitions to the localized 4f states within the band gap are equal to 3.3 and 3.6 eV respectively.<sup>10</sup> The theoretical values of optical band gap for bulk ceria are underestimated even at DFT+U theory level, and can be overcome only by using hybrid DFT approach.<sup>33, 34</sup> The direct band gap of bulk ceria on the other hand corresponding to the  $\text{O}2\text{p}-\text{Ce}5\text{d}$  transition has an experimental value of 6 eV<sup>35</sup> which is in close agreement with our calculated value of  $E_{\text{d}} = 5.33$  eV. In the case of  $\text{Ce}_2\text{O}_3$ , the band gap of 2.4 eV was reported, which is associated with intra-atomic  $\text{Ce}4\text{f} \rightarrow \text{Ce}5\text{d}$  transition.<sup>36</sup> Comparing PDOS of bulk ceria with corresponding values for the model ceria nanoparticles (Figure 3), one can observe that electronic properties of nanoceria are qualitatively closer to  $\text{Ce}_2\text{O}_3$  rather than to  $\text{CeO}_2$ . For the model ceria nanoparticles the calculated values for indirect ( $\text{O}2\text{p}-\text{Ce}4\text{f}$ ) and direct ( $\text{O}2\text{p}-\text{Ce}5\text{d}$ ) transitions are equal to 2.31 eV and 3.37 eV for  $\text{Ce}_{19}\text{O}_{32}$ , 2.52 eV and 3.3 eV for  $\text{Ce}_{44}\text{O}_{80}$  respectively. Calculated location of indirect band is found to be approximately 0.8 – 1 eV below the direct band. This is in a good agreement with the experimental observations, which report the indirect band located c.a. 0.5 eV below the direct one.<sup>12, 13</sup> Calculated trends in the optical band gaps for  $\text{Ce}_{19}\text{O}_{32}$  and  $\text{Ce}_{44}\text{O}_{80}$  agree with dependence of the band gap on  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio observed in nanostructured ceria films.<sup>12</sup> The small discrepancy arises from the size of theoretical model of nanoceria which is significantly smaller than the experimentally obtained nanoparticles.

We further investigated the optical band gap dependence on the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio, considering nanoceria of fixed size with varying number of oxygen vacancies. Results of theoretical study (shown for  $\text{Ce}_{44}\text{O}_{80}$ ) are summarized in Figure 2b. Calculated values of optical indirect band gap for both the nanoceria particles ( $\text{Ce}_{19}\text{O}_{32}$  and  $\text{Ce}_{44}\text{O}_{80}$ ) are smooth functions of  $[\text{Ce}^{3+}]$  while the values of direct band gap for both bare and water covered nanoceria are nearly independent of  $[\text{Ce}^{3+}]$ .

While  $E_{\text{d}}$  values are close for  $\text{Ce}_{19}\text{O}_{32}$  and  $\text{Ce}_{44}\text{O}_{80}$  nanoparticles (they differ by about 0.07 eV), adsorption of the water molecules leads to significant (0.3eV) blue shift in  $E_{\text{d}}$ . More quantitative comparison with experimental values is complicated by the fact that only the size dependence of  $E_{\text{d}}$  had been reported, without direct measurements of change in  $[\text{Ce}^{3+}]$  at constant particle size. Current and future experiments from our group are aimed at filling this gap in later communications. Both the models of nanoceria demonstrate red-shift in indirect optical band gap with increase in  $[\text{Ce}^{3+}]$  in the absence of water. The value of  $E_{\text{in}}$  steadily decreases from 2.52 eV for  $[\text{Ce}^{3+}]=0.36$  to 1.89 eV for  $[\text{Ce}^{3+}]=0.84$ . The slope of  $E_{\text{in}}$  increases with increase in  $[\text{Ce}^{3+}]$ . The theoretical results for latter case are in good qualitative agreement with experimental measurements performed on nanostructured ceria thin films.<sup>12, 13</sup> In contrast, the presence of water increases the value of  $E_{\text{in}}$  observed by both computational modeling and experimental measurements as a function of  $[\text{Ce}^{3+}]$ . Theoretically obtained increase in  $E_{\text{in}}$  in the considered range of  $[\text{Ce}^{3+}]$  is c.a. 0.2 eV, nearly twice less than experimentally observed variation in  $E_{\text{in}}$ . This difference in values could arise from the different range of  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio under investigation.

Thus, both values of optical band gaps for direct and indirect transitions depend on the aqueous environment. Polarization by the water molecules leads to significant blue shift in  $E_{\text{d}}$  that is independent of  $[\text{Ce}^{3+}]$  or number of f-electrons. This independence is expected from  $\text{O}2\text{p} \rightarrow \text{Ce}5\text{d}$  electronic transition. Energy of d-levels is independent of f-electrons, and in turn  $E_{\text{d}}$  is independent of  $[\text{Ce}^{3+}]$ . In contrast, value of  $E_{\text{in}}$  depends on structure of f-band and is sensitive to the amount of f-electrons in the system. For bare nanoceria particles increase in concentration of f-electrons (due to increase in  $[\text{Ce}^{3+}]$ ) leads to energy downshift of the f-band. This energy level shift with increase in its occupation number is typical for vacant orbitals. On the other hand, polarization effect of adsorbed water molecules leads to the shift of f-band to the blue region due to increase in the number of electrons occupying this band. This can be attributed to the ligand field effect, where nonbonding electrons on the metal atom are destabilized by the exchange repulsion with the donor electron pair of the oxygen atom. It can also be noticed from Figure 3 that the adsorption of water leads to splitting of empty f-level. The appearance of multiple peaks in indirect optical transitions also explains the difficulty in determining the dependence of band gap for indirect optical transitions of nanoceria in some of the earlier work.<sup>16</sup> These difficulties are addressed in this work by considering the effect of solvent induced splitting of f orbital.

Monotonic dependence of  $E_{\text{in}}$  on  $[\text{Ce}^{3+}]$  opens the possibility to determine the concentration of oxygen vacancies in ceria nanoparticles with high precision using optical methods. This technique is expected to be much more sensitive and accurate than the methods based on nanoparticle size measurements.<sup>22</sup> Our calculations demonstrate that even though small number of oxygen vacancies does not affect the nanoparticle size, they strongly influence the optical properties. Introduction of vacancies leads to the increase of nanoparticle's "lattice constant", derived from the average Ce-Ce distance ( $a_0 = \sqrt{2} d_{\text{Ce-Ce}}$ ). For bare  $\text{Ce}_{44}\text{O}_{80-n}$  ceria nanoparticles, equilibrium values of the lattice parameter are equal to 5.296, 5.298, 5.303, and 5.316 Å for  $n=0, 1, 2$  and 3 respectively. While  $a_0$  remains within  $\pm 0.003$  Å range for  $n=0, 1, 2$ , the  $E_{\text{in}}$  value undergoes pronounced changes from 2.52 to 2.38 eV. Both these values are in a very good agreement with experimentally reported values.<sup>12, 22</sup> For a small variation in  $[\text{Ce}^{3+}]$  changes in  $a_0$  are

almost negligible, whereas changes in  $E_{in}$  are substantial. Our experimental and theoretical results show that the local environment (such as water) can influence the optical characteristics of the cerium oxide nanoparticles. At this point, authors are convinced that the origin of blue shift in ceria nanoparticles is due to the destabilization effect of water molecules on the f-electron states in cerium oxide.

### Acknowledgements

We thank the National Science Foundation (NIRT CBET 0708172) and National Institute of Health (R01: AG031529-01) for funding this work. Computational work was performed using Stokes HPCC facility at UCF Institute for Simulation and Training (IST) and resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. A portion of the research was performed using EMSL, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL).

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Electronic Supplementary Information (ESI) available: [Please check the supplementary information for additional details]. See DOI: 10.1039/b000000x/

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