Origin of the Blue Shift in Ultraviolet Absorption Spectra of Nanocrystalline CeO$_{2-x}$ Particles

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Blue shifts of the ultraviolet absorption edge due to the direct-type charge-transfer transition between O 2$p$ and Ce 4$f$ bands are observed in monodisperse CeO$_{2-x}$ nanoparticles, which are produced as toluene sols by a successive micro-emulsification method. The blue shift is closely proportional to the difference in the electrostatic potentials felt by the respective constituent ions on the basis of a classical point charge model, in which both the effective charge and the number of oxygens per unit surface of the nanoparticles are reduced by half. This is the first demonstration of a blue shift in a charge-transfer transition of oxide (ionic) nanoparticles due to a non-quantum size effect.

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1. Introduction

It is well known that optical properties in nanosized materials strongly depend on the particle size. Blue shifts (i.e., shifts to higher frequency) of absorption spectra in nanosized materials are usually regarded as a quantum size effect.$^{1-5}$ However, such is not always the case in oxide nanocrystalline particles, because the quantum size effect is generally unexpected in ionic crystals and the blue shift sometimes occurs for sizes of more than several nanometers in diameter. The blue shifts have been reported in CeO$_{2-x}$ thin films$^{6-9}$ and nanoparticles.$^{10,11}$ However, they are not systematic and appear to be less reliable. Recently we have prepared monodisperse CeO$_{2-x}$, toluene sols in the size range 2–10 nm in diameter from strong acid water suspensions by a successive micro-emulsification, a new fractionation technique to produce monodisperse nanoparticles from widely dispersed suspensions.$^{12,13}$ For such particles, we previously reported blue shifts of the ultraviolet absorption edge (near 1 eV shift for mono-disperse particles of 2 nm diameter),$^{14}$ and anomalous lattice expansions (more than 3% in 1.5 nm diameter particles).$^{15,16}$ It has been suggested by X-ray photoelectron spectroscopy (XPS) that the expansions are due to valence changes of Ce ions induced by oxygen vacancies and the hydration of oxygens on the outermost surface.$^{17}$ The present report demonstrates that the blue shift is well described by an electrostatic potential effect due to the valence change.

2. Experiments and Results

CeO$_{2-x}$ nanoparticle samples S1, S2, and S3, used for XPS measurements, were obtained from the sols as a series of diameters 2.2 ± 0.3, 3.0 ± 0.4, and 3.8 ± 0.6 nm, respectively, by the successive microemulsification, where the particle size was determined as the diameter of the circle having the same area as the electron microscopic images and the range indicates the standard deviation of the particle diameter.$^{17}$ The measurements were carried out using a commercial apparatus (SSX-100, Surface Science Instruments) in the binding energy range from 0 to 1100 eV with monochromated Al Kα line as X-ray source under a pressure of 1–3 × 10$^{-7}$ Pa.

O 2$p$ spectra obtained from the XPS measurements were composed of two peaks assigned to hydroxide (MOH) and metal oxide (M'OM') groups as shown in Fig. 1(A), where M indicates not only Ce but also C as a common contaminant and S as a constituent element of the anion in the SOS (sodium octyl sulfonate) surfactant, and M' denotes Ce and Si (little amount of impurity) shown in the whole XPS spectra.$^{18}$ The peak positions of MOH and M'OM' groups range from 532.0 to 532.5 eV and from 529.5 to 530.5 eV, respectively. The integrated intensity ratio of the hydroxide peak to the metal oxide peak remarkably increased with decreasing the particle size, by more than ten times in the range of 2.2–3.8 nm diameter.

Ce 3d XPS spectra are shown in Fig. 1(B). The peak fitting was performed with background subtraction according to Shirley's procedure$^{19}$ and 100% Gaussian-type peaks, and the assignment was after Vercaemst et al.$^{20}$ SU1 and SU2, and SD represent the shake-up- and shake-down-satellites, respectively. The former have been discussed thoroughly by Fujimori$^{21}$ and the latter has not been elucidated yet.$^{22,23}$ The positions of the main peaks Ce$^{3+}$ 3d$_{3/2}$, Ce$^{4+}$ 3d$_{5/2}$, Ce$^{3+}$ 3d$_{5/2}$, and Ce$^{3+}$ 3d$_{3/2}$ are 917.0, 901.0, 898.5 and 882.5 eV, respectively. This figure reveals that Ce$^{3+}$ ions coexist with Ce$^{4+}$ ions, and the ratio of Ce$^{3+}$ ions increases remarkably with decreasing particle size. This fact suggests that the increase of Ce$^{3+}$ ions is strongly correlated with the hydration of the outermost oxygens shown in Fig. 1(A). Mean valences of Ce ions are obtained from the average between the ratios of integrated intensities of Ce$^{3+}$ 3d$_{3/2}$ and Ce$^{4+}$ 3d$_{3/2}$, and Ce$^{3+}$ 3d$_{5/2}$ and Ce$^{4+}$ 3d$_{5/2}$. The first values are
Fig. 1 (A) XPS O 2p core-level spectra composed of hydroxide (MOH) and metal oxide (M'O'M') groups at higher and lower binding energies, where M = Ce, C, or S and M' = Ce or Si. (B) XPS Ce 3d core-level spectra showing the coexistence of Ce\(^{3+}\) and Ce\(^{4+}\) ions. (a) 2.2 ± 0.3, (b) 3.0 ± 0.4, and (c) 3.8 ± 0.6 nm diameter particles. The peak positions of the satellites around Ce\(^{3+}\) 3d\(_{5/2}\) range from 999.0 to 999.5 eV for SD, from 904 to 905 eV for SU1, and from 907 to 908 eV for SU2, and those around Ce\(^{4+}\) 3d\(_{5/2}\) range from 878.5 to 879.5 eV for SD, from 885.5 to 886.5 eV for SU1, and from 887 to 890 eV for SU2.

Table 1  Estimation of the valence of Ce ions in CeO\(_{2-x}\) nanoparticles, where the particle size, \(D'\), is approximated as the diameter of the sphere of the same volume as \(\pi\) unit cells of the bulk crystal, \((0.5411\text{e})^3\) nm\(^3\), and the average Ce ion valence, \(v\), is evaluated from the electrostatic neutrality condition. The shaded values are excluded, if \(3 \leq v \leq 4\).

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<th>Number of O(^{2-})</th>
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<th>Average valence of Ce, (v)</th>
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4.00, 1.78, and 0.72, and the second values are 5.25, 1.08, and 0.85 for samples S1, S2, and S3, respectively. Therefore, the mean Ce valences \(v\) are estimated to be 3.18, 3.41, and 3.56 for S1, S2, and S3, respectively, by the use of equation \(v = 4 - \left(\sqrt{x/1+x}\right)\), where \(x\) is the ratio of Ce\(^{3+}\) to Ce\(^{4+}\) ions obtained from their XPS peak intensities.

3. Discussion

It is proposed that the blue shift of CeO\(_{2-x}\) nanoparticles is described not by the quantum size effect firstly found in metallic fine particles by Kubo\(^{4,5}\) but by an electrostatic potential effect due to the above valence change.
Figure 1(A) suggests that oxygens on the outermost surface form hydroxides in the strong acid suspension, in advance of the successive micro-emulsification with toluene and surfactant.\textsuperscript{13} Accordingly the effective charge of the surface oxygens becomes $-1$. Average valences of Ce ions, $v$, are calculated under the conditions that the effective charge of the outermost surface oxygens is $-1$, and the number of defects per unit surface in the fluorite structure varies from 0 to 3; i.e., the first, second, third, and fourth models represent the ceria nanoparticles with number of oxygens per unit surface taken as 4, 3, 2, and 1, respectively in Table 1. A log $D'$ vs. $v$ plot obtained from the table is shown in Fig. 2, where $D'$ is the diameter of the sphere equivalent to the volume of $n$ unit cells of the bulk crystal, 0.6713$n$ nm. It is found in the figure that the values obtained from the above analysis of Ce 3$d$ XPS spectra, denoted by the closed circles, agree well with the plot obtained from the third model, in which both the valence and number of oxygens on the outermost surface are reduced by half.

Respective electrostatic potentials felt by O and Ce ions in the nano-particles are obtained from a classical point charge model of the fluorite-type structure for the third model mentioned above, as shown in Fig. 3. The weighted average potentials between sites in the core and at the surface of the particle are shown by closed and open circles, respectively, for O and Ce ions. This figure suggests that the gap between the bands of O 2$p$ and Ce 4$f$ electron states increases with decreasing particle size, because the O 2$p$ and Ce 4$f$ bands, which are at lower and higher energies, respectively,\textsuperscript{24} are further separated by the electrostatic potential charges. Actually, the blue shift of ultraviolet absorption due to the direct-type charge-transfer transition, according to the equation $\Delta E_g = 5.3D^{-2.17}$ (eV)$^{15}$ ($\Delta E_g$ is the difference between band gaps of the nanoparticles and the bulk crystal, and $D$ is the particle size), is closely proportional to the difference between the two electrostatic potentials for particles more than 2.5 nm in diameter as shown in Fig. 4.

4. Conclusions

Average valences of Ce ions estimated by the third model described here are in good agreement with those evaluated by the analysis of XPS spectra. The size dependence of the blue shift in ultraviolet absorption spectra of CeO$_{2-x}$ nanoparticles is well explained down to 2.5 nm diameter particles by the difference between the two electrostatic potentials of O and Ce ions calculated by the third model. This demonstrates for the first time a blue shift in a charge-transfer transition of oxide (ionic) nanoparticles due to a non-quantum size effect. The shift in the spectra of CeO$_{2-x}$ nanoparticles of less than 2 nm diameter will be discussed on the basis of \textit{ab initio} simulation.
of clusters, taking account of the relativistic effect on Ce ions, in the near future.

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REFERENCES