

## XANES study the valence state transformation in the ceria nanoparticles with surface modification

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### Introduction

Ceria nanoparticles have been used in various applications such as oxygen sensors, ultraviolets, photovoltaic cell and so on. In order to fine-tune its properties, researches in the past few years were focus on the development of methods for controlling nanoparticle size, and size-dependent phenomena.

However, little is known about the surface-induced structure transformation in the ceria nanoparticles. Here, we determine the structure of ceria nanoparticles by x-ray absorption spectroscopy, and report that the valence of ceria nanoparticles are also affected by the surface binding environment, which is very important for their application in biotechnology, IT, catalysis etc.

### Experimental

Ceria nanoparticles were synthesized in high-pressure SUS 316 cell (inner volume 5.0ml), using ceria hydroxide as precursor. To modify the surface of nanoparticles, an appropriate amount of oleic acid was loaded to the mixture of cerium hydroxide and water. The hydrothermal reaction is performed at 400°C for 10min and terminated by quenching the reactor in the water bath at room temperature. The final product was washed with ethanol and collected by centrifugation.

XAFS spectra at Ce  $L_{3-}$  edge were measured in a transmission mode at room temperature at the BL-7C and 9C stations. To suppress the unwanted harmonics, the angle between the monochromator crystal faces was adjusted to mistune the incident beam by 40%. The incident and output beam intensities were monitored and recorded using helium 70%-nitrogen 30% and nitrogen flowing ionization chamber.

### Results and Discussion

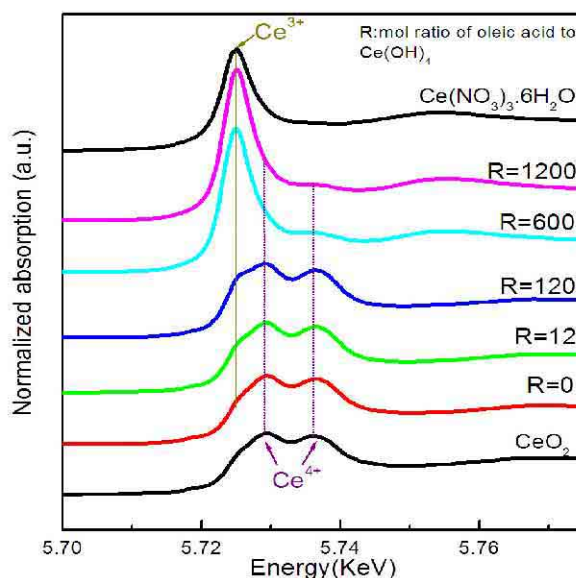


Figure 1. The normalized XANES of ceria nanoparticles, along with two reference compounds  $\text{CeO}_2$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in the range of 5700-5775eV.

The standard  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in triclinic phase has single peak about 5725.5eV, due to the dipole-allowed transition of Ce 2p to Ce 4f<sup>5</sup>d final states, characterizes the Ce in the trivalent state. However, the standard  $\text{CeO}_2$  in cubic phase has a distinct double peaked structure, corresponding to the  $\text{Ce}^{4+}$  valence state. It is immediately apparent that the valence of ceria nanoparticles changes from  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  by increasing of oleic acid in the hydrothermal process.

The results suggest that surface binding environment can effect the nanoparticles structure. Especially, at high concentration, surface modifiers strongly interact with nanoparticles which may led to the transformation of phase and valence in the nanoparticles.

### References

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