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X-ray absorption study of ceria nanorods promoting the disproportionation of hydrogen peroxide†

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A quasi in situ X-ray absorption study demonstrated that the disproportionation of hydrogen peroxide (H₂O₂) promoted by ceria nanorods was associated with a reversible Ce³⁺/Ce⁴⁺ reaction and structural transformations in ceria. The direction of this reversible reaction was postulated to depend on the H₂O₂ concentration and the fraction of Ce³⁺ species in ceria nanorods.

Fluorite-structured cerium oxide (or ceria) nanomaterials have attracted great interest from chemistry, materials and engineering communities because of their broad applications in catalysis, sensors, biomedicine, and fuel cells. Ceria has long been known to generate reactive oxygen species by catalyzing the disproportionation of hydrogen peroxide (H₂O₂). This system has displayed enhanced catalytic activities towards the degradation of pollutants. Ceria nanomaterials have also been reported to scavenge free oxygen radicals and reduce toxic H₂O₂ molecules in biological systems. These chemical properties of ceria nanomaterials have been ascribed to the interconversion of the cerium ions between their +3 and +4 states coupled with the formation of oxygen vacancy defects in ceria. However, due to the altered experimental environments such as the vacuum requirement in XPS and limited quantitative capability of UV/Vis spectroscopy, artefacts and misinterpretations in studies using these techniques are often hard to identify.

In situ X-ray absorption spectroscopy (XAS) has been regarded as a versatile tool to elucidate changes in atomic structures and oxidation states of catalysts during reactions. For example, Wang et al. utilized this technique to illustrate metallic copper in the Cu/ceria catalyst as the active species in catalyzing the water gas shift reaction. Quasi in situ XAS techniques have also been applied in catalysis studies to overcome challenges such as chemical compatibility of reactors and strong photon absorption by reactors in the implementations of in situ XAS techniques. For instance, Bergmann et al. applied the quasi in situ XAS technique to reveal reversible structural changes of a crystalline Co₃O₄ catalyst in an oxygen evolution reaction.

Herein we report our quasi in situ XAS study of the oxidation states of cerium and the local structures in ceria nanorods upon catalyzing the disproportionation of H₂O₂. Ceria nanorods were selected over ceria nanoparticles in this study because they are often reported to have higher catalytic activities. In our XAS experiments, a wet chemical environment enabled by a tris(hydroxymethyl)aminomethane (Tris) buffer solution was employed to prevent the reaction system from drying out and to maintain the pH of the system. Since the reaction mechanism strongly depends upon the pH of the reaction, this method allows reliable quantitative evaluation of reaction species in ceria samples. Our study revealed reversible changes in the oxidation states of cerium and local atomic structures of ceria in the H₂O₂ disproportionation reaction. In our experiments, ceria nanorods were first added to a solution containing 10 mM H₂O₂ and 0.1 M Tris buffer (pH = 7.54) to yield a reaction mixture with a nanorod concentration of 500 mg L⁻¹. Samples of this suspended mixture were pipetted out at various reaction times (T = 10 min to 10 h) to wet filtered papers which were then analyzed by XAS. A control experiment without H₂O₂ was used.

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† Electronic supplementary information (ESI) available: Experimental details, microstructure and electronic property analysis by TEM, XRD, XPS and XAS. See DOI: 10.1039/c5cc10643e
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for comparisons. These control data were regarded as our data at $T = 0$ h (see experimental details in the ESI†).

The initial morphology, microstructure and chemical state of as-synthesized ceria nanorods1,3 were characterized by transmission electron microscopy, X-ray diffraction (XRD) and XPS (see Fig. S1, ESI†). The ceria nanorods were 50–200 nm in length and 5–12 nm in diameter. The XRD pattern of the nanorods was indexed according to the ICDD card 04-013-4361 and was found to display a cubic Fm3m structure of CeO2. The oxidation states of surface cerium atoms were qualitatively analyzed by XPS. The fraction of Ce$^{3+}$ on the surface was determined to be ca. 20%, indicating a defective surface structure of this as-synthesized ceria sample (Fig. S3, ESI†).

X-ray absorption near edge structure (XANES) experiments were performed to investigate the redox behavior of ceria nanorods catalyzing the H$_2$O$_2$ disproportionation reaction. The Ce L$_3$-edge XANES spectra of ceria nanorods were collected at different reaction times during a 10 h reaction. Four of the XANES data scanned at the reaction times of 0 h, 0.5 h, 2 h and 10 h are illustrated in Fig. 1. The differences in the intensities of these spectra were demonstrated by the zoomed-in areas of the peaks. The intensity of the XANES spectrum of ceria nanorods significantly decreased in the first 0.5 h. After another 1.5 h of reaction, the intensity returned to its original magnitude. This was indicated by the XANES data collected at $T = 2$ h, which had a similar intensity to the one at $T = 0$ h. As the reaction further proceeded, the XANES spectrum at $T = 10$ h demonstrated negligible changes in both the spectral intensity and shape when compared with those at $T = 0$ h and $T = 2$ h.

To reveal the changes in the Ce oxidation state, a quantitative analysis was performed by curve-fitting the XANES spectra with an arctangent function to simulate the edge jump and Gaussian functions for peak features21–23 (Fig. 2a). The center of the arctangent function was set at the inflection point of the main edge. Peaks A and B at 5737.7 eV and 5730.8 eV were associated with the Ce$^{4+}$ ions in ceria, corresponding to the 2p4f$^0$5d$^*$ and 2p$^{3/2}$, 5d$^*$ refers to the presence of an excited electron in the 5d band, and L represents a ligand hole in the anion orbital. Peak C, at 5726.3 eV, was associated with the Ce$^{3+}$ valence state. Peak D, located at 5720.5 eV in the pre-edge region, was assigned to the final states of 2p4f*, which was forbidden by the selection rule due to a 5d ad-mixture with the 4f state.19,24,25 With a delocalized d character at the bottom of the conduction band due to the cubic crystal-field splitting of Ce 4f states, the transition was partially allowed to appear as a small peak. 4f$^*$ referred to the presence of an excited electron in the 4f band.

The Ce L$_3$-edge XANES spectra of all samples showed the coexistence of Ce$^{3+}$ and Ce$^{4+}$ states, with the Ce$^{4+}$ state being dominant in all samples. The fractions of Ce$^{3+}$ and Ce$^{4+}$ in the samples were calculated using the following equations:

\[
[\text{Ce}^{3+}] = \frac{A(\text{Ce}^{3+})}{A(\text{Ce}^{3+}) + A(\text{Ce}^{4+})}
\]

\[
[\text{Ce}^{4+}] = \frac{A(\text{Ce}^{4+})}{A(\text{Ce}^{3+}) + A(\text{Ce}^{4+})}
\]

where $A(\text{Ce}^{3+})$ and $A(\text{Ce}^{4+})$ were the total integrated peak areas corresponding to the Ce$^{3+}$ and Ce$^{4+}$ XANES signals, respectively. According to Fig. 2b, the Ce$^{3+}$ fraction (expressed in percentage) in ceria nanorods increased from 20.6% at $T = 0$ h to 21.4% at $T = 0.5$ h. It then slowly decreased to 20.8% at $T = 2$ h. After a 3 h-reaction, the Ce$^{3+}$ fraction approached 20.6%, which was very similar to its original value. During the reaction period between 3 h and 10 h, the overall percentage of Ce$^{3+}$ kept...
decreasing but varied insignificantly. It stayed at around the level of 20.2% at the end of reaction. Note that the changes in the Ce$^{3+}$ fraction detected by XANES were not likely due to the adsorption of Ce ions from the dissolution of ceria onto ceria nanorods. Our inductively coupled plasma-mass spectrometry studies concluded that the concentration of Ce ions in the reaction mixtures was less than 1 ppb (see details in the ESI†).

In summary, during the 10 h long H$_2$O$_2$ disproportionation reaction, the surface Ce$^{4+}$ of ceria nanorods was reduced to Ce$^{3+}$ by the H$_2$O$_2$ molecules in the beginning of the first 0.5 h, and then was slowly oxidized back to Ce$^{4+}$ in the next 9 h. The surface reaction in aqueous solutions was governed by the surface potential and the overall reductive potential of ceria and H$_2$O$_2$. High concentration of H$_2$O$_2$ exhibited high reduction potential and thus was expected to reduce surface Ce$^{4+}$ to Ce$^{3+}$ at the beginning. The slow oxidative process of ceria was likely due to the oxidizing power of H$_2$O$_2$, which became dominant after a dramatic decrease of H$_2$O$_2$ concentration in the solution. In addition, the defective ceria surface with high concentration of Ce$^{3+}$ decreased the reduction potential of the ceria surface, and was postulated to enable ceria to be oxidized by H$_2$O$_2$.

Local structures surrounding Ce atoms were probed using the extended X-ray absorption fine structure (EXAFS) technique. The experimental data were analyzed using the IFEFFIT software package. The Fourier transformers of Ce L$_3$-edge $k^3$-weighted $\chi(k)$ of EXAFS spectra depicted the changes in the local structure of Ce atoms with respect to the reaction time (Fig. 3 and Fig. S4, ESI†). The fitting parameters of EXAFS spectra are shown in Table 1 and Table S1 (ESI†). The as-synthesized ceria nanorods exhibited a coordination number of 5.8 in the first Ce–O shell. An extra peak appeared at around 1.65 Å after the addition of hydrogen peroxide. Owing to the “shortness” of this $R$ value, this peak could be attributed to the presence of superficial chemical structures with a Ce–O bond, possibly similar to the one reported in a cerium[III] oxo complex, [Ce–O(L$_{ORE}$)]$_2$(H$_2$O)]-MeC(O)NH$_2$. This peak attained its highest intensity at $T$ = 0.5 h. The intensity then slowly decreased after 2 h reaction time until $T$ = 10 h. This trend was consistent with the changes in Ce$^{3+}$ fraction from XANES data analysis, indicating the modification of local structures caused by reactions with H$_2$O$_2$. The coordination number of the Ce–O bond at 2.34 Å reached its minimum value of 4.7 at $T$ = 0.5 and 2 h, and slowly increased to 5.8 at $T$ = 10 h, which was closer to that of ceria samples before reaction (i.e. at $T$ = 0 h).

The redox cycle of the ceria sample revealed by the EXAFS data agreed well with the intensity changes in the XANES data, implying a reduction-and-oxidation cycle of ceria with H$_2$O$_2$ during the 10 h reaction. Based on our XANES and EXAFS results, we proposed that ceria underwent a redox cycle process in the Fenton-like reaction with H$_2$O$_2$ as follows:

Ceria reduction process:

$$\text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow \text{Ce}^{3+} + \text{HO}_2^* + \text{H}^+ \quad (1)$$

Ceria oxidation processes:

$$2\text{Ce}^{4+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ce}^{4+} + 2\text{H}_2\text{O} \quad (2)$$

$$4\text{Ce}^{3+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Ce}^{4+} + 2\text{H}_2\text{O} \quad (3)$$

In a concentrated H$_2$O$_2$ solution, H$_2$O$_2$ molecules were proposed to serve as reducing agents and convert the surface Ce$^{4+}$ to Ce$^{3+}$, resulting in the increase of Ce$^{3+}$ fraction and the decrease of an average coordination number of oxygen atoms around Ce atoms at 2.34 Å.

The hydroperoxyl radical (HO$_2^*$) byproduct in eqn (1) was known to involve in the conversion of the Ce oxidation state in ceria. Besides the reaction species described in eqn (1), other reactive oxygen species such as O$_2^*$, $^3$O$_2$, O$_2$ and OH$^*$ had been proposed to form in the reduction reaction. These unstable oxygen species could undergo interconversions with each other through electron transfers. Overall, these species altered the surface coordination and chemical potential of ceria, and therefore regulated the chemical states of cerium in ceria nanorods.

<table>
<thead>
<tr>
<th>T (h)</th>
<th>Atom</th>
<th>$N$ (Ce) ± $\sigma$ (Ce)</th>
<th>$R$ (Å) ± $\sigma$ (Å)</th>
<th>$\sigma^2$ (10$^{-3}$ Å$^2$) ± $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>O</td>
<td>5.8 ± 0.6</td>
<td>2.30 ± 0.01</td>
<td>4.7 ± 1.2</td>
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<tr>
<td></td>
<td>Ce</td>
<td>5.6 ± 0.4</td>
<td>3.83 ± 0.03</td>
<td>1.8 ± 0.6</td>
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<tr>
<td>0.5</td>
<td>O</td>
<td>0.9 ± 0.3</td>
<td>1.65 ± 0.02</td>
<td>3.9 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>Ce</td>
<td>4.7 ± 0.4</td>
<td>2.32 ± 0.01</td>
<td>3.9 ± 0.8</td>
</tr>
<tr>
<td>2</td>
<td>O</td>
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<td>1.66 ± 0.02</td>
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</tr>
<tr>
<td></td>
<td>Ce</td>
<td>4.5 ± 0.3</td>
<td>2.33 ± 0.01</td>
<td>3.6 ± 0.8</td>
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<tr>
<td>10</td>
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<td>1.68 ± 0.03</td>
<td>6.6 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>Ce</td>
<td>5.8 ± 0.4</td>
<td>2.33 ± 0.01</td>
<td>6.6 ± 0.8</td>
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<tr>
<td></td>
<td>Ce</td>
<td>4.9 ± 0.3</td>
<td>3.83 ± 0.03</td>
<td>1.1 ± 0.4</td>
</tr>
</tbody>
</table>

The inset shows the corresponding EXAFS spectra in $k$-space. Data: thick lines; fittings: thin lines.
As the reaction proceeded, the concentration of H$_2$O$_2$ decreased and ceria nanorods possessed significant population of Ce$^{3+}$ on their surfaces. These two factors led to changes in solution potential and ceria surface potential, which consequently promoted the oxidation of Ce$^{3+}$ to Ce$^{4+}$ by H$_2$O$_2$ molecules (eqn (2)). During the H$_2$O$_2$ decomposition process, a lot of bubbles provide reactive sites for the adsorption of peroxide species and participate in the disproportionation of H$_2$O$_2$ molecules.\textsuperscript{11}

Our hypothesized redox cycle could also be conjectured from the reported Pourbaix diagram of the Ce(m/n)–H$_2$O–H$_2$O$_2$ aqueous system.\textsuperscript{29} Depending on the pH of solutions, H$_2$O$_2$ concentration and the surface potential of ceria, H$_2$O$_2$ could exhibit dual behavior, either acting as an oxidizing agent or a reducing agent.\textsuperscript{29} The standard potentials of H$_2$O$_2$/HO$_2^*$ and Ce$^{4+}$/Ce$^{3+}$ are 1.5 V and 1.44 V, respectively.\textsuperscript{28} The similarity of these two electrochemical potentials potentially permitted the reversible reaction (eqn (1)–(3)) to occur because the concentration of H$_2$O$_2$ and the Ce$^{3+}$ fraction of the nanorod surface changed during the catalyzed reaction.

To summarize, we demonstrated the application of a quasi in situ XAS technique to elucidate the changes in chemical states of cerium and local structures in ceria nanorods in their reaction with H$_2$O$_2$. Our measurements under wet conditions allowed reliable analysis of chemical states of cerium and the structures in ceria due to minimal environmental modifications and disturbance to the ceria nanorods. The observed reversible structural changes of ceria nanorods were strongly correlated with the Ce$^{3+}$/Ce$^{4+}$ conversion and changes in the H$_2$O$_2$ concentration.

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