XAFS study on structure-activity correlations of $\alpha$-Co(OH)$_2$ nanosheets water oxidation catalysts

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Abstract. Understanding the structure-activity of the metal hydroxide materials is critical to the design of an efficient oxygen evolution reaction (OER) catalyst for water oxidation. A challenge is to identify and collect surface active site relative to bulk. Here, we have prepared an ultrathin $\alpha$-Co(OH)$_2$ nanosheet with large exposed surface Co sites as a high-efficiency $\text{O}_2$ evolution catalyst. Using XAFS technique, we have investigated the oxidation state and local structural evolutions of the $\alpha$-Co(OH)$_2$ nanosheets catalyst. A coordination-miss Co sites (CoO$_6$-x) with oxidation state of +3.3 on the nanosheet surface is revealed after the OER procedure, indicating the in situ formation of $\gamma$-CoOOH nanosheet is a key factor leading to an enhanced water oxidation performance.

1. Introduction

The worldwide environment and energy problems have made it urgently important to change the traditional energy production style and exploit renewable energy, such as solar-driven water splitting to $\text{H}_2$ and $\text{O}_2$ [1]. The oxygen evolution reaction (OER) is kinetically sluggish, which decrease the efficiency of the overall photovoltaic water splitting [2]. Accordingly, a number of OER catalyst have been developed to accelerate the charge carrier transfers and utility and to lower the required overpotential.

Transition metal oxides or oxyhydroxides are attractive OER catalysts candidates due to their low cost, excellent OER activity and stability, such like Co and Ni based oxides [3-5]. Therefore, it is a very meaningful work to study the structure-function relationship for this highly active Co-, Ni-catalyst. On the other hand, X-ray absorption fine structure (XAFS) spectroscopy as a local atomic structure sensitive measurement is widely applied in catalysis research. However, relating to the bulk catalyst, it is difficult to identify the detection signal of the surface active site since the proportion of the rest metal atomic is large.

Here, we report that 2-dimensional $\alpha$-Co(OH)$_2$ nanosheets are successfully synthesized, which behave only two CoO$_6$ octahedron slabs thickness and show superior OER activity than the state-of-the-art IrO$_2$ catalyst. Due to the exposed high density active Co site in this nanosheet catalyst, we can reasonably utilize XANES and EXAFS to track the changes of the valency and the local atomic structure during water oxidation reaction.

2. Experimental

Sample synthesis: $\alpha$-Co(OH)$_2$ nanosheet was prepared by a hydrothermal method [5,6]. 0.0952 g CoCl$_2$·6H$_2$O was dispersed in 40 ml DI-water /ethylene glycol (1:3) solution and adjusted the PH value to about 9 by addition of Ammonia solution (28 wt%). Then these solution were transfer to a Teflon-lined stainless steel autoclave and heated at 130 $^\circ$C for 24 h. The $\alpha$-Co(OH)$_2$ and $\gamma$-CoOOH model compound were synthesized by solution means according to the previous report [7,8].
Electrochemical measurements were performed in an electrochemical workstation with a three-electrode system. Electrocatalyst powder and 30 µl Nafion solution were dissolved in 1 ml of a 3:1 mixture of DI-water and ethanol to give the final concentration of 2 mg/ml. Then this dispersion was loaded onto Au/ITO substrate to form a thin film as OER working electrode, platinum mesh as the counter electrode, and saturated Ag/AgCl as reference electrode.

Figure 1. (a) XRD pattern of synthesized α-Co(OH)₂ nanosheet and α-Co(OH)₂ model compound. (b) TEM image for α-Co(OH)₂ nanosheet, (inset) shows the crystal structure of α-Co(OH)₂ nanosheet with two CoO₆ slabs thickness, displaying cobalt (blue), oxygen (red), and chlorine (green) ions.

Figure 2. (a) Polarization curves and (b) Tafel polts of α-Co(OH)₂ nanosheet and IrO₂ catalyst coating on Au/ITO electrode in 1 M KOH medium. The inset in (a) shows Chronopotentiometric measurements at J = 10 mA/cm² for α-Co(OH)₂ nanosheet.

Figure 3. (a) XANES spectra, (c) EXAFS spectra and (inset) oscillation function k²χ(k) of α-Co(OH)₂ nanosheet before OER (black), α-Co(OH)₂ nanosheet after OER (red), α-Co(OH)₂ model compound (green) and γ-CoOOH model compound (blue) respectively. (b) XRD pattern for α-Co(OH)₂ nanosheet before and after OER procedure at 10 mA cm⁻².

XAFS measurements at Co K-edge were carried out in fluorescence mode at beamline U7C of the National Synchrotron Radiation Laboratory (NSRL), beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The storage rings of NSRL, SSRF were operated at 0.8 GeV with the...
current of 250 mA, at 3.5 GeV with the current of 300 mA, respectively. The X-ray energy was calibrated by using a Co foil. All the acquired XAFS data were processed by the IFEFFIT software packages.

3. Result and discussion
X-ray diffraction pattern (XRD) in figure 1a suggest that comparing with the α-Co(OH)$_2$ model compound, α-Co(OH)$_2$ nanosheet possesses a highly (001) preferred orientation. Figure 1b displays the transmission electron microscopy (TEM) image of α-Co(OH)$_2$ nanosheet, which are several hundred nanometers in size with the average thickness of only about 1.6 nm. These results demonstrate that the ultrathin α-Co(OH)$_2$ nanosheet with largely exposed (001) face were successfully fabricated (see inset of figure 1b).

To determine the water oxidation activities of α-Co(OH)$_2$ nanosheet, the linear sweep voltammetry was carried out at a scanning rate of 2 mV s$^{-1}$ in 1 M KOH electrolytes. The iR-corrected polarization curves (figure 2a) recorded with the α-Co(OH)$_2$ nanosheet reveal a markedly small OER overpotential of 320 mV at current density of 10 mA cm$^{-2}$, which is obviously lower than the state-of-the-art IrO$_2$ electrocatast (overpotential = 340 mV at 10 mA cm$^{-2}$). Tafel curves shown in figure 2b were derived from the OER polarization curves at the current density from 1-10 mA cm$^{-2}$. The characteristic of catalytic activity for the α-Co(OH)$_2$ nanosheet is also reflected by its Tafel slope of 48 mV dec$^{-1}$, even lower than that of IrO$_2$ about 59 mV dec$^{-1}$. The durability measurement was carried out for more than 60 min in alkaline environment. Inset image of Figure 2a shows the α-Co(OH)$_2$ nanosheet have good electrochemical stability as the overpotential remained nearly constant at OER current of 10 mA cm$^{-2}$. These results demonstrate that the α-Co(OH)$_2$ nanosheet exhibit an excellent oxygen evolution activity, even higher than the precious metal IrO$_2$ electrocatalyst.

In order to give an in-depth understanding of the structure-activity correlation of the α-Co(OH)$_2$ nanosheet, oxidation state and structure before and after the OER procedure were characterized by X-ray absorption fine structure (XAFS) measurement (including XANES). Figure 3a presents the XANES spectra of α-Co(OH)$_2$ nanosheet before and after the OER procedure. The α-Co(OH)$_2$ model compound and γ-CoOOH model compound synthesized by solution means have oxidation state of +2[7] and +3.3[8] respectively. With increasing formal oxidation state, the edge position of the compound will shift to higher energy. The edge shape and position of α-Co(OH)$_2$ nanosheet (7720.2 eV) is similar to that of α-Co(OH)$_2$ model compound (7720.1 eV), however, after bearing an OER current for more than 60 min, the edge shape and position of α-Co(OH)$_2$ nanosheet (7724.0 eV) are obviously changed and match well with that of γ-CoOOH model compound (7724.8 eV), indicating an increase average oxidation state of Co centers about +3.3 and proportion of Co site contain a formal oxidation state of Co (IV). Similar phenomenon that anodization leads to the higher oxidation state active metal centers has been also observed for NiOOH compound [3,9].

To detect the phase and local atomic structure transformation of α-Co(OH)$_2$ nanosheet, XRD pattern and EXAFS data were obtained. XRD pattern in figure 3b clearly exhibits a small decrease in interplanar spacing of (003) and (006) face, it can be explained by the phase change from α-Co(OH)$_2$ nanosheet to γ-CoOOH nanosheet [5,7-8]. The XANES and EXAFS results showing in figure 3c display that the position of peaks in the FT EXAFS spectrum of α-Co(OH)$_2$ nanosheet after OER is similar to those of γ-CoOOH model compound, and the shortening of Co-O distances (see Table 1) is most likely due to the formation of Co-O dangling bonds in the surface Co octahedron which in turn favors local structural distortions and a concomitant decrease of the interplanar spacing. In addition, the Co-O coordination number decrease from 5.9 for the α-Co(OH)$_2$ nanosheet before OER to 5.0 for the nanosheet catalyst after OER, revealing the presence of O vacancies in the surface Co octahedron (CoO$_{6-x}$) during the water oxidation reaction. The coordination-miss Co sites (CoO$_{6-x}$) with oxidation state of +4 can facilitate the formation of hydroperoxy (OOH) species [3,9]. Based on the discussion above, it can be suggested that the outstanding catalytic activity of α-Co(OH)$_2$ nanosheet originated in the formation of γ-CoOOH nanosheet with the highly oxidized Co site and CoO$_{6-x}$ structure.
4. Conclusions
In summary, we have prepared an ultrathin α-Co(OH)$_2$ nanosheet as an high-efficiency O$_2$ evolution catalyst. The XANES and XRD results reveal that the γ-CoOOH nanosheet of the valency about +3.3 in Co site was in situ formed when water oxidation process occurs. Further detected by EXAFS indicate that the Co-O neighbor number reduce from 5.9 to 5.0 leading to a coordination-miss CoO$_{6-x}$ octahedron structure, which may facilitate the oxygen evolution and enhance the catalytic activity. Our results will provide helpful design insights for high performance catalysts.

Table 1. EXAFS fitting parameters$^a$

| Sample                        | Path | N$^b$ | R (Å)      | $\sigma^2$(Å$^2$) | $\Delta E^\theta$(eV) |
|-------------------------------|------|-------|------------|-------------------|--------------------|
| α-Co(OH)$_2$ nanosheet before OER | Co-O | 5.9 (0.2) | 2.09 (0.01) | 0.009 (0.001) | -1.8               |
|                               | Co-Co | 5.0 (0.2) | 3.12 (0.01) | 0.007 (0.001) |                   |
| α-Co(OH)$_2$ nanosheet after OER | Co-O | 5.0 (0.2) | 1.89 (0.01) | 0.005 (0.001) | -3.2               |
|                               | Co-Co | 5.1 (0.2) | 2.84 (0.01) | 0.006 (0.001) |                   |
| α-Co(OH)$_2$ standard sample | Co-O | 6.0 | 2.10 (0.01) | 0.009 (0.001) | -1.2               |
|                               | Co-Co | 6.0 | 3.12 (0.01) | 0.007 (0.001) |                   |
| γ-CoOOH standard sample | Co-O | 6.0 | 1.90 (0.01) | 0.004 (0.001) | -2.8               |
|                               | Co-Co | 6.0 | 2.85 (0.01) | 0.005 (0.001) |                   |

$^a$Fitting region 1 \(\leq R \leq 3.2\), 2.5 \(\leq k \leq 12\). Values in parenthesis indicate uncertainties.

$^b$Coordination number of standard sample were fixed to the theoretical values.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (Grants No. 11179004, U1332111, 11305174 and 11135008).

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