XAFS study on the impact of local structure on electrochemical performance for Co$_3$O$_4$ nanowire arrays

Shan Jiang, Weiren Cheng, Jingfu He, Junheng Huang, Qinghua Liu*, Yong Jiang, Shiqiang Wei*

National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

*Email: qhliu@ustc.edu.cn, sqwei@ustc.edu.cn

Abstract. Determining the local structure of catalyst materials is critical for understanding the mechanism of enhanced electrochemical activity in semiconductor electrode. Here, using X-ray absorption fine structure (XAFS) spectra, we reveal that the local disorder structure is formed for the mixed-phase Co$_3$O$_4$ nanowire arrays due to the interaction between the phases of Co$_3$O$_4$ and Co$_2$(OH)$_2$CO$_3$. Comparing to pure Co$_3$O$_4$ nanowire arrays, the mixed phase sample is richer in Co$^{2+}$ and the electronic structure is changed by the local structure, which are demonstrated by the X-ray absorption near-edge structure (XANES) spectra. It is deduced that the mixed-phase Co$_3$O$_4$ nanowire arrays with abundant Co$^{2+}$ sites provide more redox centres in electrochemical reaction than the pure Co$_3$O$_4$ nanowire arrays.

1. Introduction

In order to solve the energy crisis and environment problems, exploring high capacity energy storage device is one of the primary areas of research [1]. Spinel oxide Co$_3$O$_4$ as an important p-type versatile semiconductor has been widely utilized in energy storage devices. Among various Co$_3$O$_4$ electrodes, nanowire arrays electrode [2, 3] is an eminent candidate because of its large surface area per unit volume, high utilization of the active sites, and excellent mass transport property.

In recent years, there have been numerous investigations on the influence of material substrate [4] and annealing temperature [5] on the performance of Co$_3$O$_4$ nanowire arrays electrode. These results have suggested that the various preparation conditions of electrode may change the formed electrode structure and corresponding properties. However, the deep-understanding of the structure-function relationship of Co$_3$O$_4$ nanowire arrays electrode remains unknown. To this end, using a local structure sensitive measurement to correlate the structure and electrochemical properties of Co$_3$O$_4$ nanowire arrays electrodes is essential.
Herein, utilizing extended X-ray absorption fine structure (EXAFS) spectra, we reveal that the local disorder structure of Co$_3$O$_4$ nanowire arrays is formed due to the interaction between the phases of Co$_3$O$_4$ and Co$_2$(OH)$_2$CO$_3$. Moreover, X-ray absorption near-edge structure (XANES) spectra show that the mixed phase sample contains richer Co$^{2+}$ than that of Co$_3$O$_4$ nanowire arrays. These Co$^{2+}$ ions provide redox centers in electrochemical reaction and enhance the electrochemical performance.

2. Experimental
The precursor Co$_2$(OH)$_2$CO$_3$ nanowire arrays were prepared according to the reported hydrothermal method [6]. Then, the precursor was annealed at 350 °C in air for 2 h, leading to the formation of Co$_3$O$_4$. And the precursor was annealed at 350 °C in nitrogen mixed with 5% air for 2 h leading to the formation of mixed phase of Co$_3$O$_4$ and Co$_2$(OH)$_2$CO$_3$. The Co K-edges X-ray absorption fine structure (XAFS) spectra were recorded in the fluorescence mode at BL14W1 station in SSRF.

3. Results and discussion
We performed the electrochemical test and compared the electrochemical performance of the electrode materials annealed under different conditions. As seen from Figure 1(a), two pairs of redox peaks were observed, corresponding to the conversion between different cobalt oxidation states according to literature [7]. From these results we can see that Co$_3$O$_4$ electrode has a better performance than the precursor Co$_2$(OH)$_2$CO$_3$ electrode. While the sample annealed in nitrogen has an even better performance than the Co$_3$O$_4$ electrode. As shown in Figure 1(b), the discharge curve (the
sample annealed in nitrogen) did not change after 20 cycles, indicating that our electrode had relatively good electrochemical stability.

SEM and TEM images of the Co$_2$(OH)$_2$CO$_3$ precursor and the electrode annealed under different conditions are presented in Figure 2. The Co$_2$(OH)$_2$CO$_3$ precursor film showed 1D nanowire arrays architecture (Figure 2(a)). The morphology of the sample before and after annealing treatment did not change much, maintaining the nanowire arrays structure (Figure 2(b) and (c)). TEM image (Figure 2(d)) was a bunch of the nanowire arrays scratched from the Ti foam.

Figure 3(a) provided the XRD patterns of the precursor film, the sample annealed in nitrogen and in air. All the reflection peaks of the precursor film could be well indexed to crystalline orthorhombic basic cobalt carbonate hydroxide Co$_2$(OH)$_2$CO$_3$ (JCPDS 38-0547). After heat treatment in air, all the diffraction peaks were attributed to spinel Co$_3$O$_4$ phase (JCPDS 42-1467). This result indicates that the crystalline Co$_3$O$_4$ has been formed after annealing treatment, also supported by the color change of the product from the original pink to black. The precursor annealed in nitrogen mixed with a little amount of air resulted in a different phase with that annealed in air. There are several peaks corresponding to Co$_3$O$_4$ and Co$_2$(OH)$_2$CO$_3$, displaying a mixed phase. This is probably because the nitrogen atmosphere has a reduction effect.

![Figure 3](image3.png)

**Figure 3.** (a) XRD patterns, (b) Co K-edge XANES spectra, (c) oscillation function $k^2\chi(k)$ at the Co K-edge, and (d) FTs curves of Co$_2$(OH)$_2$CO$_3$ precursor film (blue line), mixed phase (red line), and Co$_3$O$_4$ (black line).

![Figure 4](image4.png)

**Figure 4.** XPS patterns of Co 2p (a), O1s (b), (Co$_2$(OH)$_2$CO$_3$ (blue line), mixed phase (red line) and Co$_3$O$_4$ (black line)).

To clarify the atomic structure of the Co atom in mixed phase, X-ray absorption fine structure (XAFS) technique was used as a sensitive local structure probe [8]. The XANES spectra, extended-XAFS (EXAFS) $k^2\chi(k)$ functions and their Fourier transforms (FTs) at Co K-edge of annealed and pristine samples are shown in Figure 3(b)–(d). We further performed XANES linear combination fitting. The results provided the exact content of each phase of 0.175 and 0.825 for Co$_3$O$_4$ and Co$_2$(OH)$_2$CO$_3$, respectively. EXAFS spectra in $k$ space of the mixed phase displayed a similar oscillation with the precursor Co$_2$(OH)$_2$CO$_3$. An increase of the degree of disorder and a
reduction of the coordination number were deduced from the FTs curve (Figure 3(d)) for the sample annealed in nitrogen. They may result from a distortion of the surface structure.

The composition of samples synthesized under different annealing conditions was further identified by XPS characterization. The typical core spectra of Co and O elements were measured and are shown in Figure 4(a) and (b). The peaks near 779.7 and 790.3 eV, and 794.9 and 804.5 eV in the Co core spectra can be assigned to Co 2p3/2 and Co 2p1/2, respectively. Co 2p peak binding energy of Co2(OH)2CO3 is higher than those in Co3O4[9]. O1s spectra of the mixed phase sample displayed two peaks, which appeared in Co3O4 (530 eV) and Co2(OH)2CO3 (531.3 eV). We can see that the Co 2p peaks of the mixed phase located near that of Co3O4, and it may be caused by the increased ratio of Co3O4 on the mixed phase surface. Therefore, combining the XAFS results, it can be deduced that the mixed phase had a richer Co2+ content compared with Co3O4. The mixed-phase Co3O4 nanowire arrays electrode with abundant Co2+ sites provide more redox centers in electrochemical reaction than the pure Co3O4 nanowire arrays electrode [10].

4. Conclusions

In summary, we have synthesized the vertically oriented Co3O4 nanowire arrays by hydrothermal route. SEM results show that the nanowire morphology did not change after annealing treatment, but XRD results show that the composition is a mixed phase of Co3O4 and Co2(OH)2CO3. The XAFS analysis confirmed that the mixed phase has local structure distortion and richer Co2+ which result in an improvement of electrochemical performance. These results may provide some guidance for improving cobalt-based catalysts as electrochemical electrode materials.

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