Exploring the local structure of Fe in Co$_{3-x}$Fe$_x$O$_4$ electrode by XAFS

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Abstract. Determining the local structure of dopant atoms is critical for understanding the mechanism of enhanced photoelectrochemical activity in doping-modified semiconductor photoelectrodes. Here, we have synthesized Fe-doped Co$_3$O$_4$ nanowire arrays photoanodes on Ti foil and detected the local structure and role of Fe atoms via X-ray absorption fine structure (XAFS) spectra and electrochemical impedance measurements. The XAFS analysis shows that Fe dopants are doped into Co$_3$O$_4$ and occupy the octahedral sites. Coupling with Co atoms at octahedral sites, Fe dopants significantly increases the carrier density by an order of magnitude and results in a five-fold increase of the photoconversion efficiency. These results provide some guidance for optimization of Co$_3$O$_4$ as a practical photoanode material.

1. Introduction

Efficient production of hydrogen from water and sunlight is a strategy to meet the energy demand for all over the world [1]. To reach high conversion efficiency in the water splitting process, photoanode materials need to satisfy the essential requirements: ample solar light absorption, facile photo-carrier transport and catalytic oxygen evolution reaction (OER) [2]. Co$_3$O$_4$ is an ideal candidate photoanode material due to a small band-gap of ~1.6 eV [3] and its catalytic effect for water oxidation [4]. However, the photoconversion efficiency of Co$_3$O$_4$ is limited by the poor conductivity.

For a long time, there is hardly any report about photo response property of Co$_3$O$_4$. Recently, Woodhouse et al reported that Fe-doped Co$_3$O$_4$ is deemed to be useful for photoelectrolysis of water due to well photo-response property [5]. To clarify the role of Fe dopants, the structural and electronic properties of the Co-Fe-O ternary spinel oxides system were studied using density-functional theory calculation [6]. However, since there is no report about occupation sites of Fe atoms, the calculated results via assuming Fe atoms occupation of tetrahedral or/and octahedral sites are disorderly and shallow. It is necessary to clarify the sites of Fe dopants in Fe-doped Co$_3$O$_4$ in order to figure out the reason of enhanced photocurrent.

In this work, vertical orient Fe-doped nanowire arrays were synthesized on Ti foil by hydrothermal method. Co$_3$O$_4$ nanowire arrays were used as the matrix due to the large surface area of nanowire which was benefit for Fe deposition and doping [7]. It is found that Fe dopants successfully doped into lattice of Co$_3$O$_4$ by substitution for Co of octahedral sites. After Fe doping, the conductivity of Fe-doped sample significantly increase.
2. Experimental

Co₃O₄ nanowire arrays were prepared according to the recently reported hydrothermal method [8]. For Fe doping, pristine sample was dipped into the same reaction solution as prior work [9], maintaining at 120 °C for 30 min. The precursor was marked as Fe-deposited sample and it was annealed at 600 °C in air for 4 hours before becoming Fe-doped sample. The Co and Fe k-edges X-ray absorption fine structure (XAFS) spectroscopy were recorded in the fluorescence mode at U7 C beamline in the National Synchrotron Radiation Laboratory (NSRL).

3. Results and discussion

To study the performance of Fe-doped sample, IPCE and photocurrent measures were carried out. The light absorption of pristine sample obviously decreases at around 800 nm presented in Fig 1a, corresponding to the band-gap of Co₃O₄ of ~1.6 eV [10]. It is of high interest that uniformly high IPCE values is observed for Fe-doped sample though the slight blue shift of absorption edge, with the value of ~10% until 450 nm and remaining ~1 % at 650 nm at 0.1 V vs Ag/AgCl as shown in Fig 1c. In contrast, the IPCEs of pristine and Fe-deposited samples in the whole region are all under 3% and sharply decreases as the irradiation wavelength increases, tailing off at around 600 nm. The IPCEs of Fe-doped sample is much higher than that of Fe-deposited sample, indicating there is some structural change after second annealing. As a matter of course, the increased IPCEs of Fe-doped sample result in a strong raise of photocurrent to 400 A/cm² at 0.1 V vs Ag/AgCl (see Fig 1b), corresponding to a photocurrent conversion efficiency of 0.37% presented in Fig 1d, which is near five-fold higher than that of pristine and Fe-deposited samples.

![Figure 1](image1.png)

Figure 1. (a) UV-vis absorption spectra, (b) Current density, (c) IPCE, and (d) PCE of pristine, Fe-deposited, and Fe-doped samples.

![Figure 2](image2.png)

Figure 2. Top view FESEM imagine of Fe-deposited (a) and Fe-doped (b) sample (inset of Fig b exhibits corresponding cross-section imagine). (c) shows TEM imagine of a bunch of nanowires. (d) displays the XRD pattern of pristine, Fe-deposited and Fe-doped sample.

The structural details of the samples are exhibited to find out the origin of the enhanced photocurrent by Fe doping. FESEM and TEM images demonstrate standing bunches of nanowires with diameter of ~160 nm, length of ~1.4 μm and each bunch consists of about ten nanowires. As shown in Fig 2a, there are lots of flower-like clusters of ferric compound with size of ~200 nm homogeneously paving on the top of Fe-deposited sample and these ferric compounds disappear after second annealing (see Fig 2b). The XRD patterns of samples presented in Fig 2c suggest all diffraction peaks of pristine sample could be well indexed to crystalline Co₃O₄ (JCPDS 73-1701). But for Fe-deposited sample, there are two new peaks at 20 of 26.6° and 35.5°, corresponding to (310) and (211)
faces of FeO(OH) [11]. However, no peak corresponding to Fe₂O₃ or FeO(OH) is observed in XRD pattern of Fe-doped sample, indicating Fe atoms have doped into the lattice of Co₃O₄ as well.

To clarify the atomic structure of Fe dopants, X-ray absorption fine structure (XAFS) technique was used as a sensitive local structure probe [12]. The extended-XAFS (EXAFS) \( k^2 \chi(k) \) functions and their Fourier transforms (FTs) at Co and Fe K-edge of Fe-doped and/or pristine samples are shown in Fig 3a,b along with that of Fe₂O₃ and Fe₃O₄ as references. Obviously, the existence of Fe₂O₃ and Fe₃O₄ can be safely excluded since their EXAFS spectral of Fe K-edge in region of 5-11 Å⁻¹ are significantly different from that of Fe-doped sample as well as the corresponding FT curves. Similarly, Fe atoms are likely to dope into the lattice of Co₃O₄ by substitution of Co sites, since their EXAFS spectral and corresponding FTs curves are similar to each other. In spinel structure of Co₃O₄, there are two different Co sites: tetrahedral (tet) and octahedral (oct) and the ratio of tet:oct is 1:2. For Co of tetrahedral sites, there are 4 nearest Co-O bonds and 12 next-nearest Co-Co bonds at distances around 1.9 Å and 3.3 Å, respectively. On the contrary, for Co of octahedral sites, the coordination numbers for the nearest Co-O bonds, next-nearest and third-nearest Co-Co bonds is all 6 with corresponding distances around 1.9Å, 2.8Å and 3.3Å, respectively. Considering the theory ratio of tet:oct of 1:2, the theory calculated coordination numbers of the nearest Co-O bond, next-nearest and third-nearest Co-Co bonds are 5.3, 6 and 8 respectively. The fitting results summarized in table 1 show that at the central atoms of Co, the bond lengths of nearest Co-O bond, next-nearest and third-nearest Co-Co bonds are 1.93 Å, 2.85 Å and 3.34 Å with corresponding coordination numbers of 5.3, 6.0 and 7.8 respectively. These fitted parameters are close to the theory values mentioned above, suggesting the ratio of tet:oct in Fe-doped sample is near 1:2. For the central atoms of Fe, the bond lengths corresponding to nearest Fe-O bond, next-nearest Fe-Co and third-nearest Fe-Co bonds are fitted to be 1.97 Å, 2.87 Å and 3.41 Å with coordination numbers of 5.5, 6 and 8 respectively, all a little larger than that of the central Co atom [6]. The fitted coordination numbers indicate that Fe atoms favor the substitution of octahedral sites with proportion of at least 90 percent as shown in Fig 3b (empty circle). According to walsh’s theory calculation work, the octahedral Fe sites favor coupling with Co of octahedral sites, resulting in boarder conduction band which increase the conductivity of Fe-doped Co₃O₄ [6]. The enhanced conductivity is useful for carriers and photo-carriers transfer.

Figure 3. (a) oscillation function \( k^2 \chi(k) \) at the Co K-edge and Fe K-edge of pristine, Fe-doped, Fe₂O₃, Fe₃O₄ and (b) their FTs curves (the empty circles show the fitting results).

Figure 4. (a) Mott-Schottky plots and (b) Nyquist plots of pristine, Fe-deposited, and Fe-doped samples.

The conjecture of increased conductivity of Fe-doped sample can be confirmed by the results of electrochemical impedance measurement (Mott-Schottky) shown in Figure 4a,b, which was used to determine the capacitance and impedance of the samples. Carrier density can be calculated from the slope of Mott–Schottky plots using the equation: \( N_d = \frac{2(e\varepsilon_0)}{d(1/C^2)dV} \) Where \( \varepsilon \) of Co₃O₄ is 12.9 [10]. Three samples all show p-type behavior according to the negative slopes shown in Fig 4a. The calculated carrier density of pristine sample is 8.8×10²⁶ cm⁻³, consistent with other reported results [13], which is closed to that of Fe-deposited sample (5.2×10²⁶ cm⁻³). Whereas, that of Fe-doped sample is calculated as 8.6×10²⁷ cm⁻³, an order of magnitude larger than that of pristine one. The
enhanced carrier density, which is linearly proportional to conductance according to the formula: \[ \sigma = n \mu \], leads to lower impedance for Fe-doped sample as shown in Nyquist plots (see Figure 3b), in which circle radius is positive correlation with impedance. Thus, the coupling between the octahedral sites Co and Fe is benefit for enhanced photocurrent. These results may provide some guidance for the future design and optimization of Co$_3$O$_4$ as photoelectrode.

Table 1. The fitted structure parameters around Co and Fe atoms in Fe-doped sample

| Central atoms | Path      | R (Å)       | N  | \(\sigma^2(\text{Å}^2)\) |
|---------------|-----------|-------------|----|-------------------------|
| Co            | Co-O      | 1.93 ± 0.01 | 5.3 ± 0.5 | 0.005 ± 0.0002          |
|               | Co-Co     | 2.85 ± 0.01 | 6.0 ± 0.6 | 0.007 ± 0.0008          |
|               | Co-Co     | 3.34 ± 0.02 | 7.8 ± 0.8 | 0.008 ± 0.0009          |
| Fe            | Fe-O      | 1.97 ± 0.01 | 5.5 ± 0.3 | 0.006 ± 0.0007          |
|               | Fe-Co     | 2.87 ± 0.02 | 6.0 ± 0.5 | 0.008 ± 0.0007          |
|               | Fe-Co     | 3.41 ± 0.02 | 5.6 ± 0.6 | 0.009 ± 0.0008          |

4. Conclusions
In summary, we have synthesized the vertical orient Fe-doped Co$_3$O$_4$ nanowire arrays on Ti foil by hydrothermal. SEM and XRD results show clusters of FeO(OH) disappear after second annealing, indicating Fe atoms dope into the matrix. The XAFS analysis further confirm the Fe atoms have substituted for Co of octahedral sites in the lattice of Co$_3$O$_4$, resulting in a five-fold increase of photoelectric conversion efficiency of 0.37%. By electrochemical impedance analysis, the enhanced photocurrent is attributed to increased carrier density and decreased transfer barrier by Fe doping. These results may provide some guides for improved Co$_3$O$_4$ as a photoanode.

Acknowledgments
This work was supported by the National Natural Science Foundation of China (Grant Nos. 11135008, 11105151, 10979044, and 10979041) and Knowledge Innovative Program of The Chinese Academy of Sciences (KJCX2-YW-N40).

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