Communication

Co-Based Nanosheets with Transitional Metal Doping for Oxygen Evolution Reaction

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Abstract: Activated two-dimension (2D) materials are used in various applications as high-performance catalysts. Breaking the long-range order of the basal plane of 2D materials can highly promote catalytic activity by supplying more active sites. Here we developed a method to synthesize ultrathin MCoOx (M = V, Mn, Fe, Ni, Cu, Zn) amorphous nanosheets (ANSs). These Co-based ANSs show high oxygen evolution reaction (OER) activity in alkaline solution due to the broken long-range order and the presence of abundant low bonded O on the basal plane. The stable Fe1Co1Ox ANSs also show an overpotential of ca. 240 mV of achieving 10 mA/cm² in OER, better than most reported transition metal-based electrocatalysts.

Keywords: transition metal-based materials; two-dimension nanosheets; amorphous materials; electrocatalysts; low bonded oxygen

1. Introduction

As a fundamental electrochemical half-reaction, oxygen evolution reaction (OER) is involved in various important energy-related technological applications, such as water splitting [1] and Zn-air batteries [2]. However, the sluggish dynamic of the four electron process in OER has highly hindered the development of the oxygen-involved reaction. The relevant reaction process is shown below [3].

\[
\begin{align*}
    \text{OH}^- + * & \leftrightarrow \text{OH}^+ + e^- \\
    \text{OH}^- + \text{OH}^+ & \leftrightarrow \text{O}_2 + \text{H}_2\text{O} + e^- \\
    \text{O}^+ + \text{OH}^- & \leftrightarrow \text{OOH}^+ + e^- \\
    \text{OOH}^- + \text{OH}^- & \leftrightarrow * + \text{O}_2 + \text{H}_2\text{O} + e^-
\end{align*}
\]

Currently demonstrated electrocatalysts for OER are Ru/Ir-based materials [4], which are costly to realize the practical applications. Developing low-cost, efficient electrocatalysts is a potential approach to meet the demand of various applications [5,6]. Transition metal-based catalysts are widely investigated for OER, including oxides [5], phosphides [7], selenides [8], etc. Co-based nanostructures show high catalytic activity and stability in OER, demonstrated by numerous investigations [9–11]. Unfortunately, these emerging catalysts still suffer insufficient development, especially in those novel and facile approaches for preparing desired electrocatalysts of such materials with well-defined nanostructures. Therefore, exploring new methods for synthesizing uniform nanomaterials is significant for a wide range of applications and for developing modern synthetic methodology.

Two-dimension (2D) materials are widely used as electrocatalysts because of their high surface area for contacting electrolytes [12], the low energy barrier for mediums absorption [13], and the Fermi-level nearby density of states that resemble noble metals [14].
However, the active sites for catalytic applications are usually located at the edge and defective sites, such as MoS2 [15], WS2 [16], WSe2 [17], etc. Therefore, the basal plane activation is a primary issue in generating efficient catalysts based on 2D materials. The current methods to activate the basal plane are localized area modification, such as manufacturing defects [15], introducing alien species [18], and partially oxidizing atoms on the basal plane [19]. However, realizing large area activation on 2D materials still is a challenge to obtain desired catalysts. Breaking the long-range order can be an efficient way to generate more active sites or realize the large area activation on 2D materials [20]. For instance, the amorphous FeCo-hydroxide nanosheets (NSs) can obtain more active sites by modifying the OH\(^{-}\) on the basal plane [21]. Meanwhile, breaking the long-range order of FePO\(_4\) also can achieve better OER activity than the crystallized one [22]. Moreover, this activation method can also be used to manipulate the crystal/amorphous feature of FeCoPO\(_4\) to obtain a higher activity of hydrogen evolution reaction [23]. Therefore, exploring the general approach to synthesizing amorphous 2D materials could be an emerging point for developing efficient catalysts.

Co-based materials are widely used for OER due to their high intrinsic activity, processability at the atomic scale, and low-cost [24,25]. Albeit many strategies have been developed to generate Co-based materials, the common methods cannot generate amorphous nanosheets, such as the hydrothermal method, [26] sol–gel method [27], chemical vapor method [28], etc. In this work, we synthesized various Co-based amorphous nanosheets (ANSs) using the coprecipitation method in a cetyltrimethylammonium bromide (CTAB) solution. We demonstrate the sheet-like morphology of Co-based materials is remained after introducing alien species, including V, Mn, Fe, Ni, Cu, and Zn oxides (Scheme 1). The thickness of CoO\(_x\) and Fe\(_2\)Co\(_1\)O\(_x\) ANSs is only ca. 1 nm. This method can also be used to synthesize ultrathin NiO\(_x\) ANSs. The Fe doping in CoO\(_x\) NSs leads to the oxidation process of Co\(^{3+}\) to Co\(^{4+}\) in OER. CoO\(_x\) ANSs show higher OER activity than the crystallized Co\(_3\)O\(_4\) NSs, demonstrating that low bonded oxygen can also promote the OER. Co-based materials show high activity in OER, with the overpotential of ca. 240 mV for achieving 10 mA/cm\(^2\) (Fe\(_1\)Co\(_1\)O\(_x\) ANSs).

Scheme 1. The growth process of CoO-based ANSs. This method also can be used to synthesize NiO ANSs with Ni substituted Co in the first step.
2. Materials and Methods

We concluded the growth process of CoO-based ANSs, as shown in Scheme 1. Details of synthesis procedure can be found in supporting materials. The Powder X-ray diffraction (XRD) pattern shows the amorphous feature of CoOx ANSs (Figure S1). MCoOx (M = V, Mn, Fe, Ni, Cu, and Zn) ANSs are synthesized by using M/Co molar ratios of 1:1. The amorphous feature remains after doping Fe, being verified by XRD (Figure S1). The Fe, Co, and O show homogeneous distribution being demonstrated by the energy dispersive spectroscopy (EDS) method (Figure S2). The 2D morphologies of MCoOx ANSs are checked by scanning electron microscopy (SEM) (Figure S3). For comparison, crystallized Co3O4 NSs are prepared by annealing CoOx ANSs. Peaks in XRD pattern of Co3O4 NSs are consistent with JCPDS No. 43-1003 (Figure S4).

3. Results

3.1. Electrochemical Performance

The catalytic activity of various Co-based ANSs is tested in a polytetrafluoroethylene (PTFE) bottle. We used Co-based ANSs as electrocatalysts for OER in 1 M KOH at room temperature (current density in this work is normalized by the geometric area of the used electrode). To begin with, we demonstrated that CoOx ANSs show better OER performance than Co3O4 NSs (Figure S5). This result indicates that breaking the long-range order on 2D materials can activate the basal plane for catalytic activity [20]. The electrochemical surface area (ECSA) value is positively related to the number of active sites. The CoOx ANSs possess an ECSA of 4-fold of Co3O4 NSs (Figure S6), demonstrating the highly increased active site numbers in CoOx ANSs. Figure 1a plots the polarization curves of Co-based ANSs. These MCoOx ANSs show better OER activity than commercial IrO2, comparing the overpotential of achieving a current density of 10 mA/cm2 (Table S1). Small Tafel slope benefits the practical applications, where the highly increased current density needs only a low potential increase. The Fe1Co1Ox ANSs show the lowest Tafel slope (ca. 50 mV/dec) value among those prepared MCoOx ANSs (Figure 1b) (Table S1). Figure 1c summarizes the overpotential of achieving 10 mA/cm2 of MCoOx ANSs and commercial IrO2. Fe1Co1Ox ANSs possess an overpotential of ca. 240 mV, which is better than other MCoOx ANSs (Table S1) and the state-of-art Co-based OER catalysts (Table S2) [29–40]. The higher mass activity shows the lower cost of OER catalysts in practical applications. As shown in Figure 1d, The Fe1Co1Ox ANSs show the highest mass activity of ca. 353 A/g, which is ca. 19-fold of commercial IrO2 (ca. 18.53 A/g). Fe1Co1Ox ANSs also show good activity and structural stability in OER at 1.5 V vs. RHE (Figure S7). Compared to the stability test of Co-based NSs (Figure S5), we concluded that Co could be responsible for the high stability of OER activity. Indeed, these results demonstrate the highly promising Fe1Co1Ox ANSs as practical catalysts for OER.

3.2. Structural Characterization

The structural characterizations focus on the Fe1Co1Ox ANSs because Fe1Co1Ox ANSs show the best OER activity (Figure 1). As shown in Figure 2, we use SEM and transmission electron microscopy (TEM) method to character ANSs. SEM and TEM images show that CoOx ANSs have well-defined 2D structures (Figure 2a,b). The selected area electron diffraction (SAED) pattern, inset in Figure 2b, certifies the amorphous feature of CoOx ANSs again. Figure 2b shows that CoOx ANSs possess a thickness of ca. 1 nm. The SEM and low magnification high angle annular dark field (HAADF) images (Figure 2c,d) show the hierarchical nanostructure of Fe1Co1Ox ANSs, with a width of ca. 400 nm. A high-resolution HAADF image verifies the Fe1Co1Ox ANSs thickness of ca. 1 nm, as shown in Figure 2e. EDS mapping shows the homogeneous distribution of Fe, Co, and O (Figure 2f). The ultrathin Co-based ANSs formation can be attributed to the surfactant of CTAB (with a high concentration of 0.05 M) and NaOH (with fast precipitation rate in solution, formation of amorphous MCoOx ANSs) [41]. The concentration of CTAB is above 2-fold its second micelle concentration (0.021 M) [42], leading to the CTAB micelles in reaction solution tending to form two layer structures (Scheme 1). The ultrathin layer
structure and elemental homogeneous distribution of Fe₁Co₁Oₓ ANSs may be caused by the fast nuclei of Fe and Co in alkaline solution during the coprecipitation process. This growth mechanism also works in synthesizing NiOₓ ANSs (Figures S8 and S9).

Figure 1. Electrochemical characterization of MCoOₓ ANSs. Polarization curves (a), specific Tafel slopes (b), specific overpotential of achieving 10 mA/cm² (c), and specific mass activity at 1.5 V vs. RHE (d) of Co-based ANSs. Fe₁Co₁Oₓ ANSs show highest OER activity among these Co-based ANSs.

Figure 2. Structural characterization of CoOₓ ANSs and Fe₁Co₁Oₓ ANSs. SEM image (a) and TEM image of CoOₓ ANSs (b). Inset in (b) is SAED pattern of CoOₓ ANSs. SEM image (c), low magnification HAADF image (d), high magnification image (e), EDS mapping (f) of Fe₁Co₁Oₓ ANSs. Inset in (d) is SAED pattern of Fe₁Co₁Oₓ ANSs. The CoO ANSs and Fe₁Co₁Oₓ ANSs possess similar thickness of ca. 1 nm.
4. Discussion

4.1. Surface Chemistry

The strong synergistic effect between cation and anion in FeCo-based nanocrystals is usually used to generate highly active OER electrocatalysts [43,44]. Herein, X-ray photoelectron spectrum (XPS) is used to check the electronic configuration and O state of CoOx ANSs and Fe1Co1Ox ANSs. Figure 3a shows the survey spectrum of CoOx ANSs and Fe1Co1Ox ANSs. Figure 3b plots the fitted O 1s spectrum. The three characteristic peaks of O 1s are consistent with oxygen atoms bound to metal atoms (530.9 eV), low bonded oxygen (531.8 eV), OH− or surface-adsorbed oxygen (532.7 eV), and water molecules on the surface (533.74 eV) [45]. The CoOx ANSs have a low bonded oxygen ratio of 49.4%, higher than 18.0% of Co3O4 NSs (Figure S10), demonstrating that the broken long-range order of ANSs leads to a high ratio of O in NSs. Moreover, extra Fe doping leads to the larger low bonded O ratio of 45.5% in Fe1Co1Ox ANSs, because Fe can modify the adsorption state of surrounded Co. To clarify this, we analyze the state variations of Co after Fe doping. Figure 3c summarizes the fitted Co 2p spectrum of CoOx ANSs and Fe1Co1Ox ANSs. The peaks located at ca. 796.7 eV and ca. 780.9 eV correspond to Co 2p1/2 and Co 2p3/2 of Co3+, respectively [29]. The peaks of Co2+ appear at ca. 781.1 eV (CoOx ANSs) to ca. 781.8 eV (Fe1Co1Ox ANSs). The Co2+/Co3+ ratio in Fe1Co1Ox ANSs (0.61) is higher than 0.55 in CoOx ANSs. The high Co2+ ratio in Fe1Co1Ox ANSs can be due to the extra Fe bonds on some O near the Co center. Figure 3d shows the fitted Fe 2p spectrum. The peaks located at ca. 720.5 eV and ca. 707.7 eV are consistent with 2p1/2 and 2p3/2 of Fe3+, respectively [46]. Therefore, the Co modulation is determined by the Fe3+, leading to the OER activity increase.

![Figure 3](image-url)

**Figure 3.** XPS spectrum of CoOx ANSs and Fe1Co1Ox ANSs. Survey spectrum (a), O 1s spectrum (b), Co 2p spectrum of CoOx ANSs and FeCoOx ANSs (c), and Fe 2p spectrum of FeCoOx ANSs (d). The Fe loading on CoOx ANSs makes the change of Co 2p peaks, verifying the strong synergistic effect between Fe and Co oxides in 2D structures.

4.2. Reaction Process

The high valance Co ions are considered the active sites for OER at a high potential of 1.24 to 1.54 V vs. RHE (Co3+ and Co4+) [47]. The intrinsic activity of Co-based materials is usually determined by the Co3+ and Co4+ formation during OER. The abundant low

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bonded oxygen can promote the high Co cations formation; Refs. [48,49] meanwhile lead to the formation of delocalized electrons in Co, and thus promote the adsorption efficiency of water molecules on Co cations and enhance conductively and catalytic activity [50–52]. Furthermore, the low bonded O in CoOx ANSs can be regarded as pre-activated O2− or O3, which can be preferentially oxidized or released during OER and thus promote the OER [53]. These appearances are demonstrated by the fact that low bonded O-rich CoOx ANSs have higher OER activity than Co3O4 NSs (Figures S5 and S6). Moreover, the Fe can promote the OER activity of Co by decreasing the intermediate formation energy [54], the adsorption energy of OH−, and the desorption efficiency of O during OER [55]. This feature can lead to an ECSA value increase [46]. Figure 4a shows that Fe1Co1Ox ANSs possess the ECSA value of ca. 75.1 mF/cm², which is 2-fold of CoOx ANSs (ca. 31.8 mF/cm²). Moreover, the changed electronic state on Co also can promote the conductivity, which shows an impact on efficacious charge transfer between support and catalysts [1,48]. The charge transfer resistance (Rct) is analyzed by electrochemical impedance spectrum (EIS) (measured at 1.53 V vs. RHE), as shown in Figure 4b. The Rct of Fe1Co1Ox ANSs is ca. 9.6 Ω, which is smaller than 39.7 Ω of CoOx ANSs, suggesting an accelerated charge transfer coefficient between FeCoOx ANSs and support. Indeed, the outstanding OER activity of FeCoOx ANSs may originate from the abundant low bonded O, intrinsic activity of Co, which is highly activated by Fe3+.

![Figure 4](image_url)

Figure 4. Analysis of catalysts and electrode. ECSA (a) and Nyquist plots (b) of ANS. The Fe doping can effectively promote the reactive sites with ca. 2-fold (a). The charge transfer efficiency between glassy carbon support and FeCoOx ANSs is very low (b). ECSA is calculated from double layered capacitance (Cdl) at 1.15 V vs. RHE.

### 4.3. Fe Doping Amount

As the above results show, Fe plays an important role in determining the OER activity of Fe1Co1−xOx ANSs. The OER activity is amount doping dependent in synergistic hybrids. The Fe1Co1−xOx ANSs with different Fe atom doping show similar onset potential in OER (around 1.42 V vs. RHE) (Figure S11), far lower than the one of 1.49 V vs. RHE in CoOx ANSs (70 mV). Moreover, Figure S5a shows that the onset potential of Co3O4 NSs is 1.52 V vs. RHE, lower than the one in CoOx ANSs (30 mV). These results indicate that the OER rate and characteristic activity are major determined by the Fe but not the low bonded oxygen in Fe1Co1Ox ANSs. After Fe doping, the adsorption energy state of these negatively charged species on the Co3+/Co4+ delocalized center can be different, which is sensitive to the difference in the electron affinity between Fe (15 kJ/mol) and Co (63 kJ/mol) [48]. The high electron affinity of Co ensures the high concentration of negatively charged species around Co cations with low bonded or activated O surrounded, with accelerated Co3+/Co4+ formation during OER [49]. The concentrated negatively charged species around Co in Fe1Co1−xOx ANSs also relates to the Fe doping ratio in the ANS’s system [6,56–59]. Fe1Co1−xOx ANSs with different Fe molar ratio doping show modified charge transport efficiency (Figure S11b). Fe1Co1Ox ANSs show the lowest Tafel slope of 50 mV/dec, verifying the highest adsorption/desorption efficiency on delocalized Co cations center with low bonded or activated O surrounded in OER. By further increasing
the Fe doping to 0.8 mmol, the Tafel slope increases (67 mV/dec) because Fe oxides itself is not good OER catalysts. Therefore, optimization of Fe doping in Fe$_{1}$Co$_{1}$O$_{x}$ ANSs determines the OER activity by changing the absorption/desorption on Co$^{3+}$/Co$^{4+}$ cations surrounded by low bonded O and activated O.

5. Conclusions

In conclusion, we developed a general approach for preparing ultrathin Co-based ANSs with abundant low bonded oxygen. The intrinsic OER activity of Co-based ANSs can be modified by introducing alien species, where the Fe doped Co NSs possess the highest OER activity. Such superior OER activity of Fe$_{1}$Co$_{1}$O$_{x}$ ANSs benefits from the promoted oxidation process of Co$^{3+}$ to Co$^{4+}$, high intrinsic catalytic activity, and large electrochemically active surface area. We believe that this work developed a potential way to generate highly efficient catalysts based on activated 2D materials.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12111788/s1, Figure S1: XRD pattern of as-prepared CoO$_{x}$ and Fe$_{1}$Co$_{1}$O$_{x}$ NSs; Figure S2: EDS mapping of Fe$_{1}$Co$_{1}$O$_{x}$ ANSs in SEM modes; Figure S3: SEM images of MCoO$_{x}$ NSs. These NSs are based on Co, with M: Co molar ratio of 1:1 in solution; Figure S4: XRD pattern and SEM image of Co$_{3}$O$_{4}$ NSs. Because of the thermal relaxation, the annealed Co$_{3}$O$_{4}$ NSs shows good crystalline. SEM image clarifies the 2D feature of Co$_{3}$O$_{4}$ NSs (Figure S4b); Figure S5: Electrochemical characterization of CoO$_{x}$ ANSs and Co$_{3}$O$_{4}$ NSs. Polarization curves (a), Tafel slopes (b), stability test of CoO ANSs (c), and stability test of Co$_{3}$O$_{4}$ NSs (d); Figure S6: ECSA of CoO$_{x}$ ANSs and Co$_{3}$O$_{4}$ NSs. $C_{dl}$ is tested from 1.15 V vs. RHE; Figure S7: Accelerating degradation of Fe$_{1}$Co$_{1}$O$_{x}$ ANSs in OER. Stability test of Fe$_{1}$Co$_{1}$O$_{x}$ ANSs (a) and structure of FeCoO$_{x}$ ANSs after use (b) in alkaline solution. The collective electron transport (a) and sustained 2D feature (b) in OER demonstrate the high stability of FeCoO$_{x}$ ANSs for adapting long-time oxidizing condition; Figure S8: SAED and TEM images of NiO$_{x}$ ANSs. The NiO$_{x}$ ANSs also show ultrathin 2D feature. In contrast, the width of NiO$_{x}$ ANSs (ca. 200 nm) is much smaller than CoO$_{x}$ ANSs (>1 um); Figure S9: EELS of NiO$_{x}$ ANSs. The EELS spectrum demonstrates that the Ni-based NSs prepared in CTAB solution is composited by Ni and O; Figure S10: XPS spectrum of Co 2p and O 1s of Co$_{3}$O$_{4}$ NSs; Figure S11: Electrochemical test of Fe$_{1}$Co$_{1}$O$_{x}$ ANSs with different Fe feeding in preparing step. The Co feed amount in these materials is 0.4 mmol; Table S1: Parameter of electrocatalysts for OER in 1 M KOH; Table S2: Collection of reported Co-based electrocatalysts on glassy carbon electrode for OER in 1 M KOH. References [29–40] are cited in the supplementary materials.

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