Facile Synthesis of 3d Transition-Metal-Doped α-Co(OH)2 Nanomaterials in Water–Methanol Mediated with Ammonia for Oxygen Evolution Reaction

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ABSTRACT: Layered cobalt hydroxides are cost-efficient electrocatalysts for oxygen evolution reaction (OER) in the field of energy conversion. Herein, we developed a facile synthesis method of 3d transition-metal-doped α-Co(OH)2 nanomaterials mediated with ammonia in water–methanol at room temperature. The doping of Cu2+ and Ni2+ leads to flower-like nanostructures similar to pure α-Co(OH)2, whereas the doping of Fe2+ produces nanoparticles with more than 2 times larger surface area in comparison with the Cu2+- and Ni2+-doped nanoflowers. The obtained dispersion with the addition of Naﬁon can be used directly as an electrocatalyst for OER with excellent catalytic activity, especially the overpotential of Fe2+ doped is as low as 290 mV at 10 mA cm−2 and the turnover frequency is improved by 3 times as compared with that of α-Co(OH)2. Furthermore, the catalyst can be loaded onto foam nickel, which presents excellent durability with the current density unchanged under continuous chronoamperometry reaction for as long as 12 h and almost quantitative faradaic efficiency. The superior electrocatalytic properties combined with the simple synthesis without the tedious purification procedure is very promising for OER.

INTRODUCTION

Water splitting into oxygen and hydrogen is a promising strategy toward sustainable renewable energy resources.1–3 There are various methods for water splitting including electrochemical, photocatalytic, photobiological, and thermal decomposition.4–7 Among them, electrochemical approach is simple, cost-effective, and clean and provides great potential for water splitting.8 Electrochemical water splitting involves water oxidation to oxygen at the anode and proton reduction to hydrogen at the cathode. Owing to the sluggish kinetics of oxygen evolution reaction (OER), the conversion efficiency of water to fuel is low.9,10 Thus, development of efficient catalysts to reduce the kinetic barrier for OER is urgent in the field of water splitting.11–14

Layered cobalt hydroxides (LCHs) have gained increasing attention because of their promising electrochemical applications, especially for supercapacitors and electrochemical water splitting.15–17 LCH can be crystallized in two polymorphs as the hydrotalcite-like α-Co(OH)2 and the brucite-like β-Co(OH)2. The β-Co(OH)2 is a thermodynamically stable phase as compared to the metastable α-Co(OH)2 whereas α-Co(OH)2 is theoretically expected to exhibit higher electrochemical activity than β-Co(OH)2.18–20 Some research studies illustrated that amorphous Co(OH)2 presents high electrochemical activity as well.21–24

The application of Co(OH)2 in electrochemical water splitting requires the large surface area or more active sites on the surface of the catalysis.25,26 Several methods for the synthesis of ultrathin nanostructural Co(OH)2 have been developed recently and used as electrocatalysis for OER. Three-dimensional flower-like α-Co(OH)2 hierarchical microspheres were fabricated via a solvothermal method with dodecyl benzene sulfate as a surfactant.27 α-Co(OH)2 and β-Co(OH)2 nanosheets were selectively synthesized through an epoxide precipitation reaction under mediation of fluoride ions.28 Unilamellar cobalt hydroxide nanosheets can be obtained by direct exfoliation of nanococones in formamide.29,30 Ultrathin α-Co(OH)2 nanostructures were prepared through 2-methylimidazolazole-mediated methods with good to excellent electrocatalytic activity.31–33 Transition-metal doping has also been proved as an efficient method to improve the electrocatalytic activity of Co(OH)2.34–37 Copper- or iron-doped Co(OH)2 has been respectively reported to effectively catalyze water oxidation at the overpotential around 300 mV at 10 mA cm−2 current density with the former synthesized via NaBH4 reducing method and the latter precipitated with NaOH in the

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presence of NaNO₃, NH₄F, and sodium citrate under N₂ atmosphere. It is different from NaOH or KOH to only afford [OH⁻] and ammonia can also act as a ligand to resolve Co(OH)₂ through forming Co(NH₃)₆Cl²⁺. Xu and Zeng systematically examined the interconversion of α-Co(OH)₂ and β-Co(OH)₂ mediated with liquid ammonia. They concluded that the addition time of Co²⁺, aging time, and preparative atmosphere play key roles in controlling the phase of Co(OH)₂. Rajamathi et al. successfully synthesized α-Co(OH)₂ mediated with ammonia solution containing an excess of sodium salt. Although α-Co(OH)₂ can be synthesized easily via ammonia-mediated method, to the best of our knowledge, there is still no report about their electrocatalytic application.

As shown in Figure 1a, the characteristic X-ray diffraction (XRD) peaks of α-Co(OH)₂ at 9.6°, 19.3°, 33.4°, and 59.6° correspond to the lattice distances of (003), (006), (012), and (110) planes of α-Co(OH)₂ (JCPDS no. 46-0605) (Figure 1a). The obtained α-Co(OH)₂ nanoflowers can be directly used as a catalyst, which shows moderate electrocatalytic activity for OER. Interestingly, the electrocatalytic activity can be improved via incorporating the 3d transition metal into α-Co(OH)₂ especially that the Fe doped α-Co(OH)₂ has an overpotential as low as 290 mV at 10 mA cm⁻² current density. The resulted doped α-Co(OH)₂ can be loaded onto nickel foam as an electrode, which demonstrated long durability.

**RESULTS AND DISCUSSION**

Aggregated α-Co(OH)₂ was produced via precipitating Co(NO₃)₂ with ammonia using water as a solvent (Figure S1). However, by replacing water with water–methanol solution, homogeneous green dispersion can be obtained within 30 min, which presented the typical UV–vis absorption peaks of α-Co(OH)₂ at 586 and 642 nm (the inset of Figure 1a). The characteristic X-ray diffraction (XRD) peaks of α-Co(OH)₂ at 9.6°, 19.3°, 33.4°, and 59.6° correspond to the lattice distances of (003), (006), (012), and (110) planes of α-Co(OH)₂ (JCPDS no. 46-0605) (Figure 1a). As shown in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Figure 1b,c, the products have the flower-like nanostructure with two-dimensional petals. The high-resolution TEM (HRTEM) images show the clear lattice fringes of 0.26 nm, which belong to the (012) planes of α-Co(OH)₂ (Figure 1d). The Brunauer–Emmett–Teller (BET) surface area of the product is 42 m²/g, which exhibits the type IV adsorption (Figure S2a). The solvent-induced effects have been demonstrated to play an important role in nanostructure growth processes. Especially, the dual-solvent system of alcohol and water can lead to the formation of ultrathin α-Co(OH)₂ using 2-methylimidazole as the alkali source and the surface modifier. The advantage of the present synthesis method is that it does not need expensive organic ligands and complicated purification process.

In the next step, 3d transition metals were incorporated into α-Co(OH)₂ via adding various amounts of FeCl₃, CuCl₂, or NiCl₂ to the precursor solution. As shown in the XRD patterns in Figure 2, the diffraction peaks of α-Co(OH)₂ were kept unchanged with three extra peaks at 16°, 31°, and 39° for Cu²⁺- and Ni²⁺-doped samples, which can be assigned to Cu₂O(OH)₂ and Ni(OH)₂, respectively. In contrast, the XRD pattern of Fe-doped sample exhibits an obvious broadening of the diffraction peaks and shifts to higher angles (~0.4°) relative to α-Co(OH)₂, which probably indicates the partial substitution of Co²⁺ by Fe³⁺ to form Co₉Fe₈(OH)₁₆. The morphologies of the synthesized 3d transition-metal-doped α-Co(OH)₂ were investigated with SEM and TEM (Figure 3). Copper and nickel doping results in the flower-like nanostructures similar to pure α-Co(OH)₂ (Figure 3a–f). Unexpectedly, iron doping leads to particle-like morphology. Elemental mappings of the doped α-Co(OH)₂ indicate the uniform distribution of 3d transition metal in the products. The BET surface area of the products was 35, 40, and 110 m²/g for Cu-Co(OH)₂, Ni-Co(OH)₂, and Fe-Co(OH)₂, respectively (Figure S2b–d). Especially, Fe-Co(OH)₂ has an obvious mesoporous hole with a width of 3–4 nm. This illustrates that the doping of Cu²⁺ and Ni²⁺ does not change the morphology of Co(OH)₂ significantly. In contrast, the Fe doping leads to nanoparticles with more than 2 times larger surface area in comparison with the nanoflowers.

The produced Co(OH)₂ dispersion with the addition of Nafton was loaded directly onto the glassy carbon working electrode for the electrochemical measurement at 1 M KOH.

![Figure 2](image-url)
alkaline solution. To obtain reliable data, multiple cyclic voltammetry (CV) tests were performed before the linear sweep voltammetry (LSV) experiment was carried out. Figure 4a shows the LSV curves of all the electrodes with the scan rate of 10 mV s$^{-1}$. $\alpha$-Co(OH)$_2$ obtained in water$-methanol$ solution exhibits moderate OER performance with the onset potential of 1.40 V and the overpotential of 340 mV at 10 mA cm$^{-2}$. In comparison, $\alpha$-Co(OH)$_2$ obtained in pure water displays much poorer OER performance. The doping of Ni$^{2+}$ does not improve the performance. In contrast, the incorporation of Cu$^{2+}$ or Fe$^{2+}$ reduces the overpotential significantly (Figure 4a). After carefully optimizing the ratio of 3d transition metal to Co$^{2+}$, the samples containing 30% Cu$^{2+}$ or 20% Fe$^{2+}$ in mole gave rise to the lowest overpotential of 295 and 290 mV at 10 mA cm$^{-2}$, respectively (Figure S3). For comparison, LSV experiments of the 3d metal doping Co(OH)$_2$ synthesized at pure water were undertook to give rise to the negative results similar to Co(OH)$_2$@H$_2$O (Figure S3). This indicates that the using solvent has an important effect on the reactivity for the same element content catalysis, which the pure water leads to the aggregated morphology (Figure S1).

Encouraged by these results, we then investigated the stability of $\alpha$-Co(OH)$_2$, Cu-Co(OH)$_2$, and Fe-Co(OH)$_2$ via performing the continuous CV between 0.0 and 0.6 V (vs Ag/AgCl) at a scan rate of 100 mV s$^{-1}$. The LSV curve of Fe-Cu(OH)$_2$ has no obvious change even after 1000 continuous cycles, whereas the curves of $\alpha$-Co(OH)$_2$ and Cu-Co(OH)$_2$ change slightly (Figure 4b). These indicate that Fe-Co(OH)$_2$...
not only has the lowest overpotential but also is of excellently stability. Additionally, the turnover frequencies (TOFs) were measured. The TOF values of $\alpha$-Co(OH)$_2$, Cu-Co(OH)$_2$, and Fe-Co(OH)$_2$ are $1.24 \times 10^{-3}$, $3.24 \times 10^{-3}$, and $4.00 \times 10^{-3}$ s$^{-1}$, respectively. The value of Fe-Co(OH)$_2$ is the highest and 3 times higher than that of $\alpha$-Co(OH)$_2$.

To better understand the OER process, the electrocatalytic kinetics of the OER process were evaluated using Tafel plots (Figure 4c). Fe-Co(OH)$_2$ has the lowest Tafel slope of 69 mV dec$^{-1}$ compared to 81 and 95 mV dec$^{-1}$ for $\alpha$-Co(OH)$_2$ and Cu-Co(OH)$_2$, indicating its quicker electrocatalytic kinetics and higher OER electrochemical catalytic activity. The large Tafel slope of Cu-Co(OH)$_2$ is probably due to the raised LSV curve before 1.5 V caused by the copper oxidation peak. Furthermore, electrochemical impedance spectroscopy (EIS) was conducted to evaluate the electron transport ability and further study the OER kinetics. Equivalent circuit model is shown in the inset in Figure 4d. The solution resistance ($R_s$) values of the samples are the same as 12 $\Omega$. The electron-transfer resistance ($R_{ct}$) values of $\alpha$-Co(OH)$_2$, Cu-Co(OH)$_2$, and Fe-Co(OH)$_2$ is 29, 17, and 15 $\Omega$, respectively (Figure 4d). The smaller $R_{ct}$ values of Fe-Co(OH)$_2$ and Cu-Co(OH)$_2$ indicate their more efficient charge transport during the electrochemical OER process than $\alpha$-Co(OH)$_2$. Furthermore, the electrochemically active surface areas (ECSAs) were estimated from the electrochemical double-layer capacitance ($C_{dl}$) in the non-faradaic region in the scan rate range of 1–20 mV s$^{-1}$ (Figure S4). The $C_{dl}$ are 41.17, 60.75, and 109.11 mF cm$^{-2}$ for $\alpha$-Co(OH)$_2$, Cu-Co(OH)$_2$, and Fe-Co(OH)$_2$, respectively (Figure 4e). The improved catalytic activity of Cu-Co(OH)$_2$ and Fe-Co(OH)$_2$ can be attributed to the lower charge-transfer resistance and the larger electrochemical surface area than Co(OH)$_2$ because of Cu or Fe doping.

Consequently, X-ray photoelectron spectroscopy (XPS) measurements were carried out to examine the electronic structure of $\alpha$-Co(OH)$_2$, Cu-Co(OH)$_2$, and Fe-Co(OH)$_2$. The obtained spectra show distinctive peaks of Co, Cu, Fe, and O (Figure S5), indicating the successful doping of Cu$^{2+}$ and Fe$^{2+}$ in $\alpha$-Co(OH)$_2$. The high-resolution Co 2p spectra of $\alpha$-Co(OH)$_2$, Cu-Co(OH)$_2$, and Fe-Co(OH)$_2$ are shown in Figure 5a. There is a slight shift of 0.24 and 0.41 eV for Co 2p$_{3/2}$ and 0.15 and 0.2 eV for Co 2p$_{1/2}$ in Cu-Co(OH)$_2$ and Fe-Co(OH)$_2$ toward lower binding energy as compared with that of $\alpha$-Co(OH)$_2$. The shift of the binding energy in Cu- and Fe-doped $\alpha$-Co(OH)$_2$ reveals the strong coupling between Cu, Fe, and Co for the doped $\alpha$-Co(OH)$_2$.53,54 In addition, we can...
observe that the content of Co$^{2+}$ increases and the content of Co$^{3+}$ decreases after doping. This means that doping facilitates the formation of hydroperoxo (OOH) species, which was regarded as the active phase for many Co-based OER catalysts.\(^5\) The O 1s XPS spectra for Cu-Co(OH)$_2$ and Fe-Co(OH)$_2$ also present the obvious shift toward lower binding energy side (Figure 5b). These indicate the strong electronic interaction between Cu and Fe with $\alpha$-Co(OH)$_2$.\(^3\) The high-resolution Cu XPS curve of Cu-Co(OH)$_2$ can be ascribed as Cu 2p$_{3/2}$ (935.2 eV) and Cu 2p$_{1/2}$ (955.1 eV) with two shake-up satellite peaks (943.1 and 962.9 eV). For the high-resolution Fe XPS spectra of Fe-Co(OH)$_2$, two main peaks of Fe 2p$_{3/2}$ (712.6 eV) and Fe 2p$_{1/2}$ (725.8 eV) with the satellite peak at 717.6 eV are observed, demonstrating the presence of Fe$^{3+}$.\(^5\) Fe$^{3+}$ is usually considered as a redox-active species that can cooperate with Co to participate in the redox-hopping-type charge transfer, resulting in better OER activity.\(^{26}\)

As can be seen from the above results, Fe-Co(OH)$_2$ has the smallest Tafel slope and electron-transfer resistance with the largest electrochemical double-layer capacitance, which presents the best catalytic activity among the tested catalysts. To extend its application in water splitting, Fe-Co(OH)$_2$ was synthesized by the ammonia-mediated synthesis route. The electrode of Fe-Co(OH)$_2$/nickel foam was tested in a two-electrode system with an Autolab Nova III electrochemical workstation. The glassy carbon electrode (GCE) with a diameter of 3 mm was selected as the working electrode. For the preparation of catalyst ink, 40 $\mu$L of ethanol solution of Nafion (5 wt %) was added to 1 mL of Co(OH)$_2$ reaction mixture and sonicated for 30 min. Subsequently, 6 $\mu$L of catalyst ink was dropped on the GCE and then dried overnight at room temperature. The electrochemical tests were carried out on a standard three-electrode system with an Autolab Nova III electrochemical workstation. An Ag/AgCl electrode with 3 M KCl solution and a platinum foil were used as the reference and counter electrodes, respectively. KOH solution (1.0 M, pH = 13.9) was used as the electrolyte. All potentials measured were calibrated to the reversible hydrogen electrode (RHE) using the following equation:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \ \text{pH} + 0.22 = \eta + 1.23$$

LSV curves were recorded at a scan rate of 10 mV s$^{-1}$. The impedance spectra were recorded under 0.602 V (vs Ag/AgCl) in the frequency range from $10^2$ to 0.1 Hz with a sinusoidal 5 mV amplitude, possibly.

The TOF values were calculated from equation

$$\text{TOF} = \frac{J \times A}{4 \times \pi \times \eta \times M}$$

where $J$ is the current density at a fixed overpotential (e.g. $\eta = 300$ mV), $A$ is the geometrical surface area of the electrode, $F$ is the Faraday constant (a value of 96 485 C mol$^{-1}$), and $M$ is the mole of metal on the electrode. All the metal atoms are assumed to be the catalytically active sites, which indicates that the minimum values of TOF were calculated.
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02504.

SEM image, N₂ sorption isotherms, LSV polarization curves, CV curves, and XPS spectra (PDF)

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