Synthesis of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ porous willow-leaf like structure for enhanced electrocatalytic oxygen evolution reaction

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Abstract

A porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaf like structure was obtained with an annealing treatment with the acetate hydrate precursor. The morphology and structure of precursor and porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ material was well characterized. The as-prepared $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ exhibited good electrocatalytic oxygen evolution reaction (OER) performance with an overpotential of 389 mV at the benchmark of a current density of 10 mA/cm^2 , a low Tafel slope of 61.57 mV/dec and a negligible increase of the overpotential during the stability test of 7200s.

Keywords: porous materials; $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$; willow-leaf like structure; oxygen evolution reaction; electrocatalysts; energy storage and conversion

1. Introduction

In recent years, spinel $\text{A}^{\text{II}}\text{B}^{\text{III}}_{3-x}\text{O}_4$ materials have attracted special attention because of their potential application in various fields, such as lithium-ion batteries [1], photocatalytic and electrocatalytic reaction [2], gas sensing [3], and supercapacitors [4]. So far, many spinel $\text{A}_x\text{B}_{3-x}\text{O}_4$ with different nano-structured morphologies and sizes have been reported [5, 6], to the best of our knowledge, nevertheless, there have been no reports of porous willow-leaf like architecture up

now. Spinel binary metal oxides Co_3O_4 ($\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{O}_4$) have attracted a lot of attention as promising electrode material for electrochemical energy storage and conversion devices. Unfortunately, the largely practical applications of Co_3O_4 -based electrodes are hampered by the poor electrical conductivity, however, ternary ZnCo_2O_4 can exhibit higher electrical conductivity and improved electrochemical activity. In addition, the spinel zinc cobalt oxide ZnCo_2O_4 can be considered as Co_3O_4 ($\text{Co}^{\text{II}}\text{Co}^{\text{III}}_2\text{O}_4$) with Co^{III} substituted by Zn^{II} ions. Therefore, the partially substituted $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ with other different compositions are also high anticipated substitutions with great potential for electrochemical energy storage, but such reports are still limited [7, 8].

The water oxidation, also known as oxygen evolution reaction (OER), electro-catalyst is very important in water splitting technique [9–11]. However, the OER is the critical problem in developing efficient electrolysis of water owing to the inherent sluggish OER kinetics, and thus impedes overall water splitting process with high overpotential. Therefore, the study to develop cheap, plentiful and steady OER catalysts is still highly imperative. To date, some Co-based nano-structured materials have been reported and usually exhibited good OER properties [12, 13], however, seeking for new Co-based nanocatalysts with ample active sites and robust stability is still a meaningful research direction in electrocatalytic technology. Herein, we present the rational design of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ porous willow-leaf like structure for OER electrocatalyst in alkaline media.

2. Experimental section

2.1 Material synthesis

Typically, the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ precursor was synthesized by solvothermal procedure using the mixed solvents of N, N-dimethylacetamide (4.0 mL), ethylenglycol (1.0 mL), H_2O (0.5 mL) and hexylamine (0.1 mL), which were well blended with cobalt (II) acetate tetrahydrate (49.8 mg),

1 zinc acetate dihydrate (22 mg) and polyvinylpyrrolidone (PVP, K30, 200 mg) under vigorous
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3 stirring. The mixture was heated to 180 °C for 12 h, washed by ethanol and water repeatedly and
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6 then collected by centrifugation, and finally dried at 80 °C. The pure $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample was
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8 prepared by sintering the precursor at 400 °C for 2 h in air with a heating rate of 5 °C/min.
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10 11 **2.2 Electrode preparation and measurement**

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14 5 mg of the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ powder was dispersed in a mixture of water (750 μL), ethanol (200 μL)
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16 and Nafion solution (50 μL) under continuous ultrasonication. Subsequently, 10 μL of the catalyst
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18 ink was transferred to a polished glass carbon electrode (0.196 cm^2) and allowed to dry naturally.
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21 All the electrochemical tests were performed by CHI 760E electrochemical workstation.
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25 **3. Results and discussion**

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28 The field-emission SEM images of the as-prepared $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ precursor and porous
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30 $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ structure were presented in Fig.1. The as-prepared $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ precursor exhibits
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32 willow-leaf morphology and compact surface structure with an average size of 2.0 μm in length
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34 and 0.5 μm in width (Fig.1a, b). The PXRD pattern of the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ precursor can be indexed
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36 to the crystalline cobalt acetate hydrate and zinc acetate hydrate (PDF no. 22-1080 and 33-1464,
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38 Fig. 2a). Fig. S1 shows the isotherm plot of the precursor, which indicated the low surface area of
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40 the zinc doped cobalt acetate hydrate (8.66 m^2g^{-1}). The porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ micro-crystals
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42 obtained after annealing process still maintain the willow-leaf like morphology of precursor
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44 (Fig.1c-d) but enriched with open porous architecture (Fig.1d), which can be proved by the
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46 enlarged BET surface area to nearly four times.
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56 The XRD of as-prepared porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample was collected and shown in Fig.2b. All the
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58 diffraction peaks present in the XRD pattern can be indexed to the standard crystallographic
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spectrum of ZnCo_2O_4 (JCPDS 23-1390). The element composition of the porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample matches well with the XRD result with a Zn/Co molar ratio of 1:9 (Fig.2c). Furthermore, the BET analysis of porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample was conducted based N_2 sorption isotherm, and the result indicates porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaf-like structure with a high surface area of $31.98 \text{ m}^2 \text{ g}^{-1}$ and an average pore diameters of $\sim 14.15 \text{ nm}$ (inset in Fig. 2d). The high BET surface area and mesoporous structure of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ could facilitate the transport of electrons and ions during the electrochemical reaction. The scanning transmission electron microscopy (STEM) image in Fig. 3a further demonstrated the porous feature of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaves, the EDX element mapping of an individual willow-leaf in Fig.3b reveals the homogenous distribution of zinc, cobalt and oxygen elements in the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample. The TEM image in Fig.3c shows that the calcining process without disrupting the shape enriches the sample with porous and co-adjacent sheet construction. Fig. 3d shows the HRTEM image of a further magnified top of the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample, the clear fingers indicate the highly crystallinity of the porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ structure, and the interplanar spacing of 0.286 nm can correspond to the (220) plane of cubic spinel ZnCo_2O_4 phase.

At first, $10 \text{ }\mu\text{L}$ of the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ ink was dropped casting onto the 5 mm glass carbon electrode to form a modified electrode, the detail electrode preparation was shown in the experiment section. The electrochemical active surface area (ECSA) of the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample was evaluated in advance by scan the cyclic voltammetry (CV) curves at the speed of $5\sim 25 \text{ mV/s}$ in the voltage window of $1.3\sim 1.4 \text{ V}$ (vs. RHE) (inset in Fig. 4a) from the CV curve (Fig.S2) and fit the liner slope of the current density at 1.35 versus different scan rate (Fig. 4c). The high ECSA of 11.6 mF cm^{-2} afford the porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaf with high electrocatalytic activity in

OER process. Then, the electrocatalytic properties of the porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaves were investigated in detail. All the electrochemical tests conducted in an O_2 -saturated alkaline solution. The linear sweep voltammetry (LSV) test was used to assess the electrochemical performance and conducted in a three electrode system obtained at a scan rate of 5 mV/s (Fig.4b). In order to analysis the OER performance the potential of working electrode verse Ag/AgCl was firstly converted to a reversible hydrogen potential (RHE) and the overpotential were calculated from:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + 0.197\text{V} \quad (1)$$

$$\eta = E_{\text{RHE}} + 1.23\text{V} \quad (2)$$

The overpotential for achieving the current density of 10 mA cm^{-2} is very important for OER process, which is about 10% efficiency of solar-to chemical conversion and is one benchmark of a current density. The willow-leaf-like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ exhibits an overpotential of 389 mV without iR compensation at this current density can comparable to the previously reported Co-based nanomaterial electrodes[14], especially to the ZnCo_2O_4 ($\eta = 0.39 \text{ V}$) obtained by electrochemical deposition, calcination and followed corrosion steps[15], hierarchical $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ nanoarrays (1:2, $\eta \sim 0.37 \text{ V}$) [16], the ZnCo_2O_4 micro-spindle ($\eta = 0.389 \text{ V}$) and better than the ZnCo_2O_4 truncated drums ($\eta = 0.419 \text{ V}$) [17] at the same concentration of alkaline electrolyte of 1M. The OER kinetics of willow-leaf-like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ particle is estimated by the Tafel slope, which is the liner slope b of LSV curve fitted by the Tafel equation: $\eta = b \log j + a$ (3)

The Tafel slope for $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ is 61.57 mV/dec (Fig.4c), which is much smaller than the reported values of the Co_3O_4 porous nanowires (72 mV dec^{-1}) [18], Zn-Doped CoSe_2 (88 mV dec^{-1}) [19], and nanoporous hollow Co_3S_4 nanosheets (90 mV dec^{-1}) [20], suggesting the high reaction kinetics during OER process of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ due to its high conductivity. Furthermore, the chronoamperometry test at constant current density of 10 mA/cm^2 was carried to evaluate the

1 stability of the $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ sample. To deliver a current density of 10 mA/cm^2 during 7200 s, the
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3 OER overpotential of willow-leaf-like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ exhibits negligible deterioration (Fig.4d), and
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6 the result indicates the good durability of porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ in alkaline condition. The porous
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9 $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaves with moderate BET surface area can afford higher ESCA than the
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12 ZnCo_2O_4 truncated drums sample, which is related to the good OER catalytic property with high
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14 density of electrocatalytic active sites and better permeability of electrolyte.
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16 17 **4. Conclusion**

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20 The as-prepared porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ structure exhibited a relatively high electrocatalytic
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22 activity and catalytic stability for OER process. The overpotential of willow-leaf-like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$
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24 at the current density of 10 mA cm^{-2} can compare to the reported Co-based electrocatalysts. The
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27 Tafel slope for willow-leaf-like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ particle is close or smaller than some typical
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29 catalysts. The features of the porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaf like structure promise an application
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31 of a cheap and efficient electrocatalyst.
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44 45 **References**

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Fig. 1 (a,b) SEM images of willow-leaf like precursors and (c, d) the as-synthesized porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ structures with different magnification.

Fig. 2 Powder X-ray diffraction pattern of the precursor (a) and as-synthesized $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ (b). (c) EDX spectrum of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$. (d) Nitrogen adsorption-desorption isotherm and BJH pore size distribution plot (inset) of $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$ willow-leaf.

Fig. 3 (a) STEM images of willow-leaf like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$. (b) EDX mapping of the porous $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$. (c-d) TEM and HRTEM images of willow-leaf like $\text{Zn}_{0.3}\text{Co}_{2.7}\text{O}_4$.

Fig. 4 (a) A profile of current density against the scan rate, inset is the CV curves obtained at the scan rate of 5~25 mV/s. (b) LSV curve recorded at a sweep speed of 5 mV/s. (c) Tafel plots of OER currents in (b). (d) The chronoamperometry curves at the current density of 10 mA/cm².