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Surface engineering by a novel electrochemical activation method for the synthesis of Co^{3+} enriched $Co(OH)_2$/CoOOH heterostructure for water oxidation

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HIGHLIGHTS

- $Co(OH)_2$/CoOOH heterostructure is obtained by a electrochemical activation method.
- High content Co^{3+} species exist on the surface of the catalyst.
- The growing process of $Co(OH)_2$/CoOOH is illuminated and characterized.
- The $Co(OH)_2$/CoOOH nanoplates show higher OER activity than the β- $Co(OH)_2$.

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ABSTRACT

The large-scale application of oxygen evolution reaction electrocatalysts is limited by many challenges such as sluggish kinetics, low conductivity, and instability. Remarkably, Co^{3+} plays a vital role in oxygen evolution catalytic process because Co^{3+} ions are regarded as active sites. Developing catalysts with high Co^{3+} content is highly promising to improve the efficiency of water oxidation. In this study, we report a novel design method through controlling pH value and potential guided by *Pourbaix* diagram to synthesize surface Co^{3+}-rich catalyst. The as-prepared catalyst possesses enhanced electrode-electrolyte contact area and lower diffusion resistance. In alkaline media, this catalyst exhibits promising oxygen evolution performance, with lower onset overpotential, satisfactory overpotential, and high value of turnover frequency (TOF).

1. Introduction

Water splitting is considered to be one of the most effective strategies to obtain hydrogen gas via direct or photo-driven electrolysis of water ($2H_2O \rightarrow O_2 + 2H_2$) [1–3]. At present, the efficiency of water electrolysis is mainly limited by the oxygen evolution reaction (OER), since the four-electron transfer process [$4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ in alkaline media] usually requires a large overpotential and thus results in inherently sluggish kinetics [4–8]. Therefore, developing earth-abundant catalysts with excellent catalytic activity and stability for OER remains a significant challenge [9].

In recent years, various earth-abundant transition-metal materials including nitrides [10], oxides [11,12], (oxy) hydroxides [13], sulfides [14], and phosphides [14] have been extensively investigated as OER catalysts. Among them, cobalt hydroxides have recently aroused wide concern because of their low cost and application potential for OER. Owing to its unique two-dimensional (2D) structure, cobalt hydroxide permits sufficient contact between electrode and electrolyte, which is beneficial for the rapid charge transfer [15]. Nevertheless, the OER catalytic activity of this material is still hindered by its low electrical conductivity. Efforts like modifying the composition and regulating the surface valence-state of Co species have been made to tackle this problem. Particularly, it is reported that Co^{3+} atoms with intermediate spin in the octahedral and square pyramidal symmetry could prominently lower the electric resistance [16] of cobalt hydroxides. Moreover, when serving as active sites to catalyze OER, the Co^{3+} ions with lower coordination number could maximize the H_2O adsorption energy [17] and promote the deprotonation of OOH species to form O_2 [16,18]. Hence, fabricating Co-based catalysts with high Co^{3+} content might be a promising strategy to improve the efficiency of water oxidation. To this end, methods like coating with oxidant [19] and introducing a highly electronegative support [17] have been developed to

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promote the OER efficiency of Co-based materials despite the fact that these synthetic processes are usually too complex to meet the requirement for large-scale production.

It is known that the redox ability of materials could be reflected by the value of electrode potential, which is used to estimate the possibility of the electrochemical reaction. For the electrode reaction in which H^+ and OH^- participate, the value of electrode potential which could be calculated from the *Nernst* equation dependents on the pH value of the solution. *Pourbaix* diagram, a picture depicting the relationship between the value of solution pH and electrode potential, could serve as a guide for predicting the order of electrode reactions within a certain pH range. The valence state of metal ions is closely related to the potential and pH value. Particularly, introducing Co^{3+} species are crucial for the enhancement of water oxidation efficiency as discussed above. Inspired by the *Pourbaix* diagram of Co [20], we designed a two-step electrodeposition and electrochemical activation method to synthesize surface Co^{3+}-rich catalysts. The first step was to deposit metal cobalt on Ti foil as precursor, while the second step was the activation of the precursor under a constant current. During the activation process, the electrodeposited Co precursor with amphoteric property first dissolved in alkaline solution and then reacted with OH^- to obtain $Co(OH)_2$. Furthermore, the $Co(OH)_2$ could partially evolve into CoOOH under given potential and pH value, forming a $Co(OH)_2$/CoOOH heterostructure. As a result, the prepared surface Co^{3+}-rich catalyst exhibited higher catalytic activity toward OER in comparison with β-$Co(OH)_2$ nanosheets, indicating the pivotal role of superficial Co^{3+} in enhancing the catalytic activity. Moreover, the method used in this work exhibits several advantages including precisely controlled valence state, facile preparation, low-cost, and potential for large-scale production. To the best of our knowledge, there is almost no literature reporting on this design idea. We hope this designed method can play a guidance role for developing other similar target products with specific valence state.

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical grade and were used without further purification. Titanium foil (99% pure, 0.5 mm thick) was purchased from Goodfellow Cambridge Ltd. Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), ammonium nitrate (NH_4NO_3), boric acid (H_3BO_3), and sodium citrate ($Na_3C_6H_5O_7{\cdot}2H_2O$) were purchased from Chuan Dong Ltd. Commercial IrO_2 catalyst was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd., Deionized water was used for washing. All aqueous solutions were prepared using Milli-Q water (18.25 MΩ cm). Before using, Ti foils were pretreated in concentrated HCl solution and then rinsed by DI water and absolute ethanol alternatively for several times.

2.2. Preparation of Co^{3+}-rich catalysts

The cobalt precursor was deposited on a piece of Ti foil with a 1.0 cm^2 geometric area under a constant current of −0.6 A and the deposition time was 60 s. A three-electrode system, comprised of a piece of Ti foil as working electrode, a Pt sheet as counter electrode, and a saturated Ag/AgCl reference electrode, was used for the electrodeposition. The electrolyte contained 2.5 mM $CoCl_2{\cdot}6H_2O$, 2.5 mM H_3BO_3 and 6.8 mM $Na_3C_6H_5O_7{\cdot}2H_2O$. The Co^{3+}-rich catalysts were prepared by activating the Co precursor on Ti foil under a constant current of 0.01 A in 0.01 M KOH. According to the time of constant current activation, the prepared samples were denoted as Co^{3+}-24 h, Co^{3+}-33 h and Co^{3+}-42 h. The solution was stationary during deposition process, and the electrolyte temperature was kept at 298 ± 2 K.

2.3. Preparation of β-$Co(OH)_2$

β-$Co(OH)_2$ was deposited on a piece of Ti foil with a 1.0 cm^2 geometric area under a constant current of −5.0 mA and the deposition time was 1800 s. The electrolyte contained 0.02 M $Co(NO_3)_2{\cdot}6H_2O$ and 0.05 M NH_4NO_3. The electrolyte temperature was kept at 343 ± 2 K.

2.4. Preparation of IrO_2 catalyst on Ti foil

5 mg of commercial IrO_2 catalyst was dispersed in 990 μL of water-ethanol solution ($V_{water}/V_{ethanol}$ = 50/49), and then 10 μL Nafion (10 wt. %) was added into the solution. After sonication for 30 min, 100 μL of the mixed solution was slowly loaded onto a piece of pretreated Ti foil with a surface area of 1.0 cm^2 and dried at room temperature. The loading amount of IrO_2 is 0.5 mg cm^{-2}.

2.5. Material characterization

The crystal structure of the samples was characterized by X-ray power diffraction (XRD; Shimadzu ZD-3AX, CuKα radiation) at a scan rate of 1° per min in the angular range from 5° to 90°. The morphology of the materials was investigated using a scanning electron microscopy (SEM, JSM-7800 F) and high resolution transmission electron microscope (HRTEM, FEI, Tecnai G2F20, America). The X-ray photoelectron spectroscopy (XPS) were conducted on ESCALAB 250 Thermo Fisher Scientific using a magnesium anode (Mg 1253.6 eV) as X-ray source, all XPS spectra were corrected by the C 1s line at 284.8 eV. The chemical composition is further comfired by fourier transform infrared spectroscopy (FTIR, Nicolet Magna IR550) under rage of 400–4000 cm^{-1}. All of the samples were scratched from the Ti foil for physical characterization.

2.6. Electrochemical characterization

All the electrochemical measurements were employed on a CHI 660 E electrochemical analyser (CH Instruments, Inc., Shanghai) with a standard three-electrode system including the electrodeposited catalysts on a Ti foil as working electrode, a graphite rod and a saturated Ag/AgCl electrode as counter electrode and reference electrode, respectively. The electrolyte was O_2 saturated 1.0 M KOH solution and all measurements were carried out at ambient temperature (298 ± 2 K). The potential, measured against an Ag/AgCl electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to $E_{vs.\ RHE} = E_{vs.\ Ag/AgCl} + E^{\theta}_{Ag/AgCl} + 0.059\ pH$. Linear sweep voltammetry (LSV) tests were carried out at a scan rate of 5 mV s^{-1}. The electrochemically active surface areas (ECSA) of the catalysts were compared by the value of double-layer capacitance (C_{dl}) obtained from CVs at the potential of 0.56–0.66 V $_{vs.}$ Ag/AgCl with various scan rates of 2, 4, 6, 8, and 10 mV s^{-1}. The C_{dl} values were extracted by plotting the current density variation ($\Delta j = (j_a - j_c)/2$) against the scan rates of Cyclic Voltammetry (CV) tests. The EIS was measured using AC impedance spectroscopy over a frequency range of 100000 Hz − 0.01 Hz at η = 400 mV. Chronoamperometry measurements were carried out at potential of 1.63 V vs. RHE (corresponding to a current density of 10 mA cm^{-2}) to evaluate the long-term stability of the samples.

2.7. Calculations

Details involving the calculation of exchange current density (j_0), mass activity (MA) and turnover frequency (TOF) are shown below:

The value of the exchange current density (j_0) was calculated from the Tafel equation ($\eta = a + b \log j$), as shown in the following equation [21,22]:

$$j0 = 10^{-a/b} \quad (1)$$