



# High valence chromium regulated cobalt-iron-hydroxide for enhanced water oxidation



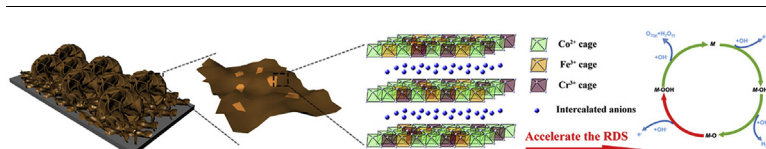
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## HIGHLIGHTS

- CoFeCr hydroxide microspheres are successfully prepared by electro-deposition.
- The composite shows improved performance on water oxidation and durability.
- The synergistic effect modifies Co at lower oxidation valence during reaction.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

In this report, a Cr regulated ternary CoFeCr hydroxide microsphere composite for enhanced water oxidation was fabricated using a facile electro-deposition method. The incorporation of Cr affects the oxidation state of Co and compared to the binary cobalt-iron hydroxide composite, the ternary composite shows excellent electrocatalytic performance for oxygen evolution reaction (OER) in alkaline media, whose onset potential is only around 1.43 V vs reversible hydrogen electrode (RHE) and the overpotential is merely of 270 mV to achieve a current density of  $100 \text{ mA cm}^{-2}$  in 1 M KOH. This enhanced oxygen evolution activity is attributed to the “regulation effect” of chromium. In other words, during water oxidation, chromium in the composite is partially oxidized into high valence 6+ and the electrons generated by this oxidation reaction can be transferred to the cobalt sites to maintain cobalt at a relatively lower oxidation valence state (but OER active), which accelerates the third electron-transfer process ( $\text{M-O} + \text{OH}^- \rightarrow \text{M-OOH} + \text{e}^-$ ).

## 1. Introduction

Water splitting is one of the most promising approaches for energy conversion, which can efficiently fix the electricity into chemical media-hydrogen. In practice, water splitting is typically performed in strong alkaline electrolyte as most of the transitional metal-based electrodes cannot survive in strong acid condition due to the instability issue [1,2]. But the performances of such catalysts are still heavily impeded by the sluggish half reaction of oxygen evolution reaction (OER) which involves a four-electron-transfer process [3,4]. Therefore, besides the theoretically defined electrolysis potential value of 1.23 V, extra energy input is required to enable the decomposition of water

molecules [1,4]. Although noble-metal-based materials such as  $\text{IrO}_2$  and  $\text{RuO}_2$  can efficiently oxidize water into oxygen within an acceptable overpotential range, the industrial application for water splitting is still hindered by the high cost of such noble metals. Hence, the development of the next-generation catalytic materials made of earth abundant element is thus urgently needed [1–4].

A series of transition metal compounds (TMCs) have been developed as noble-metal-free catalysts for water oxidation. Particularly, TMC layered double hydroxide (LDH) is found to be the state-of-the-art catalyst due to its large electrochemical surface area (ECSA) and defect-abundant  $t_{2g}$  orbitals of  $\text{MO}_{6-x}$  centre, which could induce fast electron transfer and accelerate the  $\text{OH}^-$  anions adsorption reactions [4–6]. For

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example, Xie et al. fabricated  $\beta$ -NiOOH nanomesh by Ostward ripening to enlarge the ECSA and the defected-nanomesh showed a higher catalytic activity as calculated by density functional theory (DFT) [7]. It has also been reported that once NiOOH phase is contaminated with iron, its catalytic ability increases dramatically, leading to the benchmark NiFe LDH catalysts [2,8]. Although lots of work has been done on the NiFe LDH system, there is still around 200 mV overpotential to onset the OER.

It has also been reported that the ideal OER electrocatalyst is that the  $e_g$  occupancy of surface transition-metal cations is close to unity and cobalt with a  $t_{2g}^6 e_g^1$  electronic configuration gives the ideal  $e_g$  filling of OER electrocatalyst [5]. A spinel Ag-doped  $\text{Co}_3\text{O}_4$  nanoarrays can even survive and exhibit high OER activity in acid media [9]. Furthermore, cobalt-based compounds, like nickel-based composites, exhibit much enhanced OER performance once iron is introduced [10–14]. To further improve its performance, CoFe nanosheets with vacancy/defect were developed to modify the surface and electronic structure [6,15–18]. Apart from CoFe, a series of high-valence regulated cobalt-based composites including CoCr, CoMn, CoFeSe, CoFeBi and CoFeV were reported as active OER catalysts because of the tuned electronic structure after introducing a second or even a third element [19–23]. However, there is still a performance gap between the benchmark NiFe LDH and the existing cobalt-based composites [4].

Herein, by introducing  $\text{Cr}^{3+}$  into CoFe hydroxide layered structure via a facile electrodeposition process, a ternary CoFeCr TMC hydroxide catalyst is developed and shows excellent OER performance in alkaline media, outperforming the benchmark NiFe hydroxide catalyst. The co-electrodeposition of  $\text{Co}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions onto nickel foam (NF) substrate yields a layer of monodispersed microspheres of CoFeCr composites. As illustrated in Fig. 1, by introducing chromium into cobalt-iron composite, the nanosheet unit gradually aggregates into microspheres following the route 2, which is different from the morphology of the CoFe nanosheet composite formed via route 1. The dynamic growth of the CoFeCr composite microspheres and mechanism for OER enhancement have been investigated in detail through scanning electron microscopy (SEM), transmission electron microscopy (TEM), Inductively Coupled Plasma Optical Emission Spectrometer

(ICP-OES), X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), etc.

## 2. Experimental

### 2.1. Materials synthesis

All the chemicals were purchased from supplier and used without further purification. Nickel foam (NF, 1.5 mm thickness, 110 ppm) or copper foam (CF, 1.5 mm thickness, 110 ppm) as substrate was washed and ultra-sonicated in 4.0 M hydrochloric acid (HCl, 32.0% RCI LABSCAN Ltd) for 10 min to remove oxides on the surface. Then the substrate was rinsed by Mill-Q water ( $18.2 \text{ M}\Omega \text{ cm}^{-1}$ ) three times and dried under  $\text{N}_2$  flow. The substrate material was cut into a certain size and sealed with Teflon tape with the exposed geometric surface area of  $1 \times 1 \text{ cm}^2$ . Thereafter, the substrate was used as the working electrode in a standard three-electrode system, where graphite plate and Ag/AgCl (1.0 M KCl) are counter electrode and reference electrode, respectively. The depositing bath contains 0–48 mM cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Chem-Supply), 0–48 mM iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Chem-Supply) and 0–24 mM chromium nitrate ( $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , Jax Chemicals). The electrodeposition was carried out under an applied potential of  $-1.0 \text{ V}$  vs Ag/AgCl (1.0 M KCl) by using CHI760D potentiostat for 0–7200 s. The as-prepared electrode was slowly taken out from electrolyte and rinsed by Mill-Q water and dried in  $\text{N}_2$  flow. To prepare the commercial catalytic electrode as control sample, 20 mg Ir/C catalyst (20% Ir on Vulcan XC-72, Premetek Co.) was dispersed into the solvent mixed with  $480 \mu\text{l}$   $\text{H}_2\text{O}$ ,  $480 \mu\text{l}$  absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , Chem-Supply) and  $40 \mu\text{l}$  Nafion (5%, Aldrich). The suspension was ultra-sonicated for 20 min to obtain the homogeneous ink and then drop-casted and dried onto the NF or CF substrate, whose mass loading was  $2.0 \text{ mg cm}^{-2}$ .

### 2.2. Materials characterization

The scanning electron microscopy (SEM, JSM7001F) and high-resolution transmission electron microscopy (HRTEM, Philips CM200) were employed to observe the micro morphology of the as-prepared

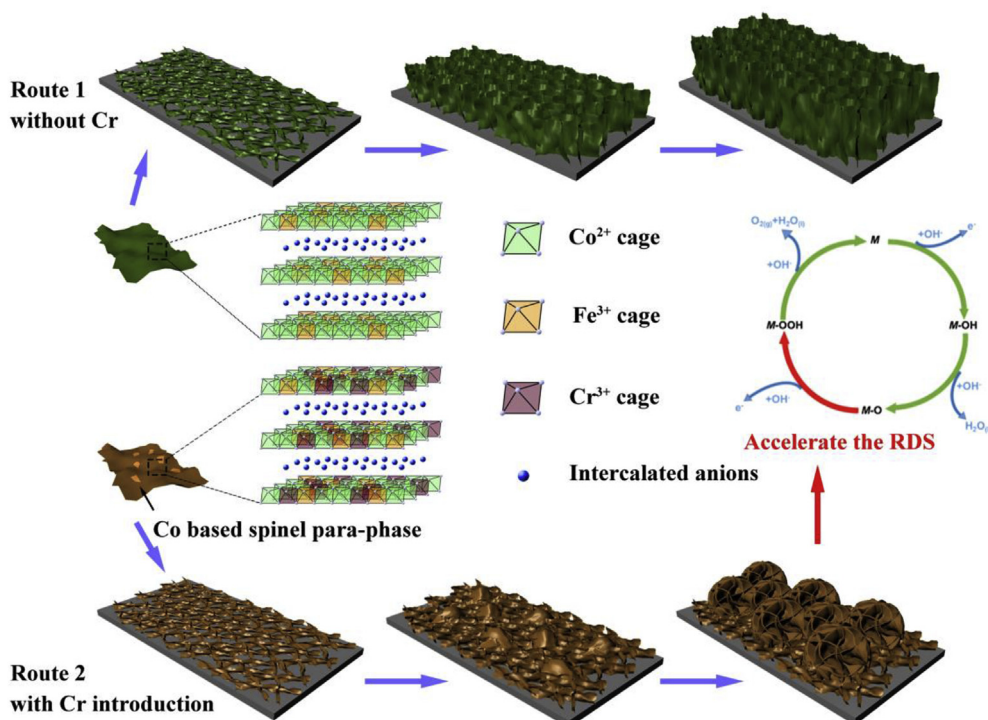


Fig. 1. Schematic of the growth of the CoFe nanosheet and CoFeCr microsphere composites.

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