

# ULTRATHIN IrCo NANODENDRITIC ELECTROCATALYSTS FOR THE OXYGEN EVOLUTION REACTION

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## Abstract

Among the shape-controlled nanostructures of nanocatalysts, nanodendrites (ND) have attracted great interest, because the rich edges and corners atoms resulting from dendrites structure which are conducive for high catalytic activity. In this study, Ir electrocatalysts doped with different amounts of Co were synthesized by an ethylene glycol (EG) reduction method. Ir and IrCo nanocrystals with Ir/Co ratio of 3:1 (IrCo-3:1) showed nanodendrites structure. Among the samples, IrCo-3:1 sample has excellent electrocatalytic activity toward oxygen evolution reaction (OER) in both acid and alkaline conditions with a minimal onset potential (Vs RHE) and a very low Tafelslope than that of IrCo-1:1 and Ir samples. IrCo-3:1 nanodendrites sample also exhibit good stability under both acid and alkaline solution with negligible degradation after 12 h of chronoamperometry test, revealing their excellent stability under OER conditions.

**Keywords:** IrCo nanodendrites, oxygen evolution reaction, electrocatalysis

## Introduction

Renewable sporadic sources, such as solar and winds have a great potential to decrease our dependence on fossil fuel. However, solar and wind energies are alternating and require efficient storage methods for their wide application. A promising large-scale storage way is the conversion of solar and wind into the chemical energy stored in H<sub>2</sub> via the electrochemical water splitting reaction. The water splitting reaction consists of two half reactions, namely, the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) (Stern and Hu, 2014). Oxygen evolution reaction (OER) is the process of generating molecular oxygen through electrochemical oxidation of water, and it holds the key to a number of important energy conversion and storage processes, such as water-splitting and rechargeable metal–air batteries (Xu *et al.*, 2015; Gong *et al.*, 2013; Walter *et al.*, 2010). Earth-abundant materials, such as nickel-based and cobalt-based compounds, are widely discovered as boosted catalysts for oxygen evolution reaction (OER) (Chen *et al.*, 2016; Lu and Zhao, 2015). Despite significant progress having been achieved, the major challenge problem of non-noble metal-based nanostructured materials established so far is that they still underachieve the Ir and Ru benchmarks for OER (Katsounaros *et al.*, 2014; McCrory *et al.*, 2013). Another issue related to non-noble metal catalysts for OER that should be specifically mentioned is that they are generally not stable in strongly acidic condition, which largely obstructs their application in proton exchange membrane water electrolyzer (PEMWEs) in which the corrosive acidic environment has to be used (Park *et al.*, 2012). Only a few noble metals with good OER activity, such as Ir and Ru, can withstand such a harsh condition (Katsounaros *et al.*, 2014; McCrory *et al.*, 2013). Compared to Ru, Ir is supposed to be a more ideal catalyst candidate for OER due to its higher stability (Reier *et al.*, 2015). However, the high cost and limited catalytic performance hamper its practical application. Nanocatalysts have obvious advantage in boosting electrochemical catalysis, because of the reduced usage of noble metals but increased catalytically active sites achieved by their high

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surface area to volume ratio (Nesselberger *et al.*, 2011). Doping non-noble metals can reduce the Ir content of electrocatalysts and meanwhile increase their intrinsic activity owing to the synergistic effects between different metals (Chen *et al.*, 2014). Kim and co-workers described the synthesis of Ir-ND by the direct surfactant-mediated method, which showed an extremely high OER activity that was about 5.5 times more active than commercial Ir black. These results suggest that engineering noble metals into dendritic structure is an attractive approach for achieving high catalytic performance. However, there has been a little study reported on Ir-ND structure for oxygen evolution reaction (OER) (Lee and Kim, 2011). For example, uniform Ir-Cu nanoframes with highly open structures possessed robust electrocatalytic properties toward OER (Pei *et al.*, 2016).

Herein, we report an efficient wet chemical route to prepare ultrathin IrCo nanodendrites. Such interesting structure with accessible sites, maximized surface area and active sites is highly beneficial for enhancing the electrochemical energy conversion. The IrCo nanodendrites also exhibit outstanding stability with limited overpotential change, as revealed by long term chronopotentiometry measurement. To the best of our knowledge, our IrCo nanodendrite is one of the best OER electrocatalysts in both alkaline and acidic conditions reported to date.

## Materials and Methods

### Preparation and Characterization of 3D IrCo Nanodendrites

All the reagents were of analytical grade, purchased from Beijing Chemical Reagent Factory, and used as received without further purification. In a typical preparation of different ratios of 3D IrCo nanodendrites, 0.2mmol of iridium(III) chloride ( $\text{IrCl}_3$ ) and 0.2 mmol of cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) (prepared by adding different amounts of  $\text{IrCl}_3$  and cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ )) were dissolved in 6mL of surfactant oleylamine and 2 mL of reducing agent ethanediol under magnetic stirring for 4 h. The resulting homogeneous mixture was transferred to a Teflon-lined stainless-steel autoclave and then heated at  $180^\circ\text{C}$  for 12 h before it was cooled to room temperature. The resulting colloidal nanocrystals were collected by centrifugation with 12000 rpm for 20 min and washed by ethanol and cyclohexane for three times before dispersed in cyclohexane. The 3D Ir-Ni and Ir-Cu nanodendrites were also synthesized with the same procedure using  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ .

The morphology of the as-prepared electrocatalysts was observed on an FEI TecnaiG220 transmission electron microscope (TEM).

### Preparation of Catalysts for Electrochemical Characterizations

The prepared 3D IrCo nanodendrite (1 mg) and 5 mg of carbon black were dispersed in 1.5 mL of ethanol, magnetically stirred for 1 h and heated at  $200^\circ\text{C}$  for 5 h. Then it was suspended in 40  $\mu\text{L}$  of 5 wt% Nafion by sonication for 30 min to form a homogeneous ink. 5  $\mu\text{L}$  of the catalyst ink (loading amount of  $\sim 13.5 \mu\text{g Ir cm}^{-2}$ ) was then loaded onto a glassy-carbon electrode (GCE) (diameter: 5.61 mm, area:  $0.247 \text{ cm}^2$ ) from Pine Instruments.

### Electrochemical characterization

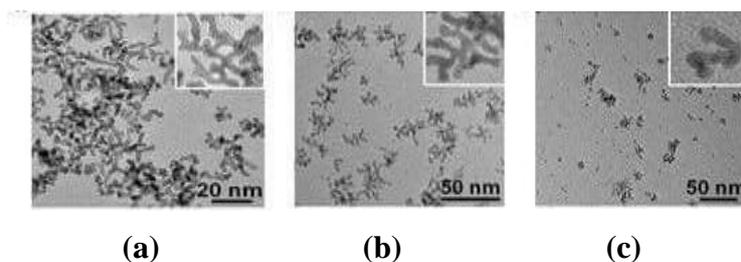
Electrochemical characterization of IrCo nanodendrite was performed using a rotating disk electrode (RDE, Pine Research instrument). A three-electrode system controlled by a CHI 660E electrochemistry workstation was employed to carry out the electrochemical measurements

of as prepared samples with different electrolytes such as 0.5M H<sub>2</sub>SO<sub>4</sub>, 0.05M H<sub>2</sub>SO<sub>4</sub>, 1M KOH, 0.1M KOH. A glassy carbon electrode (0.196 cm<sup>2</sup>) with a thin film of the prepared sample was used as the working electrode. A platinum wire and the saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The reference was calibrated against and converted to reversible hydrogen electrode (RHE). The cell was purged with O<sub>2</sub> for 30 min prior to each set of experiments, and then blanketed with O<sub>2</sub> during the experiment. Linear sweep voltammetry was carried out at 5 mV s<sup>-1</sup>. iR drop was compensated at 95% through the positive feedback using the CHI 660E electrochemistry workstation. The impedance (R) was consistent at multiple potential points (covering both non-OER condition and OER-condition). The Tafel slopes were derived from OER polarization curves obtained at 5mVs<sup>-1</sup> and 95% iR compensation in all the solutions. Chronopotentiometry was carried out under the same experimental setup without compensating iR drop. All potentials measured were calibrated to RHE using the following equation:

$$E (\text{RHE}) = E (\text{SCE}) + 0.241\text{V} + 0.0591\text{pH}$$

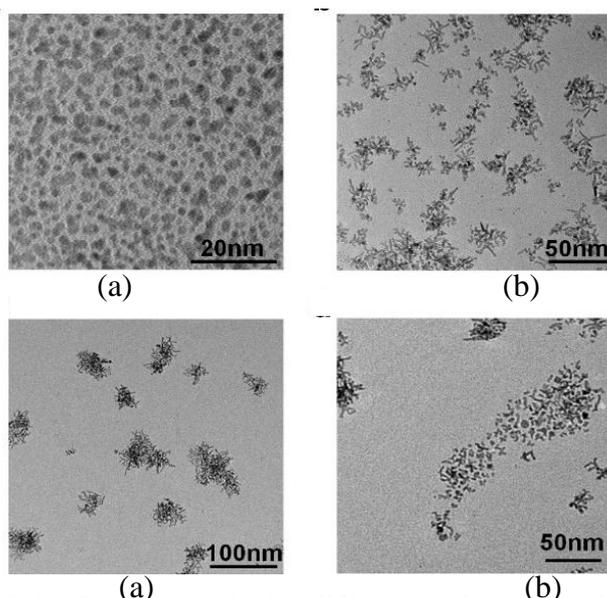
## Results and Discussion

Detailed characterization of the prepared IrCo nanodendrites samples with different adding ratios are shown in Figure 1. Typical transmission electron microscopic (TEM) images (Figures 1(a) and 1(b)) show that only Ir and IrCo-3:1 samples possess nanodendrites structure with branch morphology. When the ratio of Ir is decreased to 1:1, the morphology of nanodendrites converted to be nanoparticles (Figure 1(c)). This indicated that Ir plays an important role in the formation of nanodendrites structure. These nanodendrites are monodispersed with an ultrathin average diameter of 2 nm.



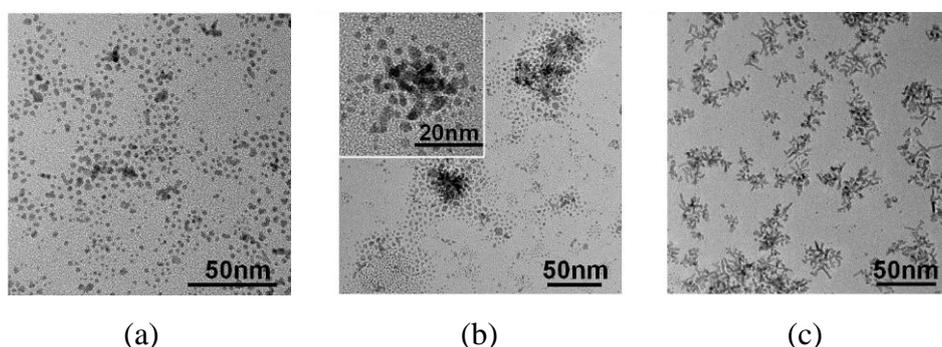
**Figure 1** TEM images of (a) Ir; (b) IrCo-3:1; (c) IrCo-1:1

Dendritic structure will possess many open sites which allow high catalytic activities. To understand the control mechanism behind the successful synthesis, IrCo-3:1 sample was synthesized by varying the ratio of surfactant oleylamine and reductant ethylene glycol (Figure 2). The results revealed that the combined use of oleylamine and glycol was essential for the successful creation of IrCo nanodendrites. Detailed control experiments show that high-quality nanodendrites could only be obtained in the presence of the specific amount of oleylamine and ethylene glycol (Figure 2(b)). It can be also noted that, nanoparticles were obtained when the ratio of oleylamine to glycol was 1 (Figure 2(a)), and the nanodendrites with poor dispersion and homogeneity were obtained when the ratio increased to 4.3 and 7 (Figures 2(c) and 2(d)).



**Figure 2** TEM images of IrCo-3:1 prepared with different ratios of oleylamine to glycol  
(a) 1:1 (b) 3:1 (c) 4.3:1 (d) 7:1

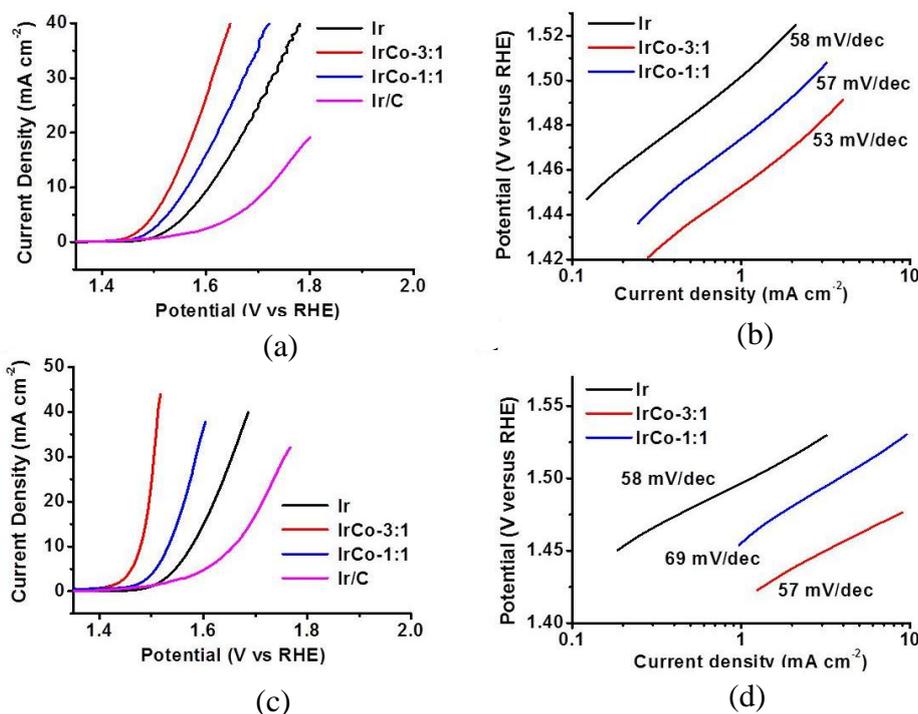
To gain in-depth understanding of the formation mechanism, the growth process of Ir superstructure was carefully investigated at different reaction times. Figures 3(a) - 3(c) show the TEM images of the growth intermediates collected at different reaction durations. As shown in Figure 3(a), untidy nanoparticles were formed by the end of the 4h reaction time. As the reaction proceeded for 8h, many branched structures were formed (Figure 3(b)) by combining nanoparticle seeds. Together with the assembling and growth of the branched nanocrystals, nanodendrites were observed after 12 h (Figure 3(c)). Therefore, the growth of the IrCo nanodendrites includes two steps: (i) the initial formation of primary seed crystal at the early stage and (ii) the subsequent self-assembling and growth into nanodendrites to minimize their surface energy at high temperature.



**Figure 3** TEM images of IrCo-3:1 prepared at different reaction times: (a) 4h (b) 8h (c) 12h

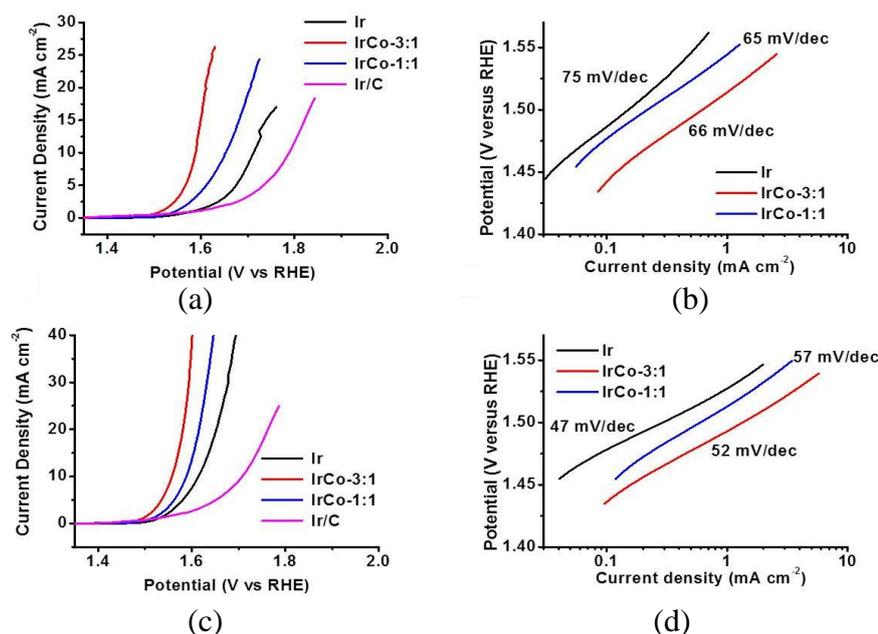
In order to study the performance of 3D IrCo nanodendrite catalysts, the OER activity in acidic solutions were investigated (Figure 4). Before the electrochemical activity test, the catalysts were scanned at a sweep rate of  $50 \text{ mV s}^{-1}$  for 20 cycles in the electrolyte until a stable cyclic voltammogram was obtained. The polarization curves were recorded at a slow scan rate of  $5 \text{ mV s}^{-1}$  and iR compensation. It was found that all the catalysts have higher OER activities in  $0.5 \text{ M H}_2\text{SO}_4$  than those tested in  $0.05 \text{ M H}_2\text{SO}_4$ . The 3D IrCo-3:1 nanodendrites show the minimal onset potential of  $\sim 1.45 \text{ V}$  versus RHE in  $0.05 \text{ M H}_2\text{SO}_4$  and  $\sim 1.41 \text{ V}$  versus RHE in

0.5 M H<sub>2</sub>SO<sub>4</sub> for OER (Figures 4(a) and 4(c)). In 0.5 M H<sub>2</sub>SO<sub>4</sub>, 3D IrCo-3:1 nanodendrites only need 0.21 V overpotential to achieve 10 mA cm<sup>-2</sup>, which is better than those of Ir only and IrCo-1:1 sample. Moreover, IrCo-3:1 nanodendrites also exhibit a very low Tafel slope of 53 mV dec<sup>-1</sup> and 57 mV dec<sup>-1</sup> in 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M H<sub>2</sub>SO<sub>4</sub> solution (Figure 4(b) and 4(d)), which is better than the commercial Ir/C (20%). As a comparison, the Ir only samples show lower activity compared with 3D IrCo-3:1 sample, indicating the enhanced catalytic performance of Ir modifying with Co.



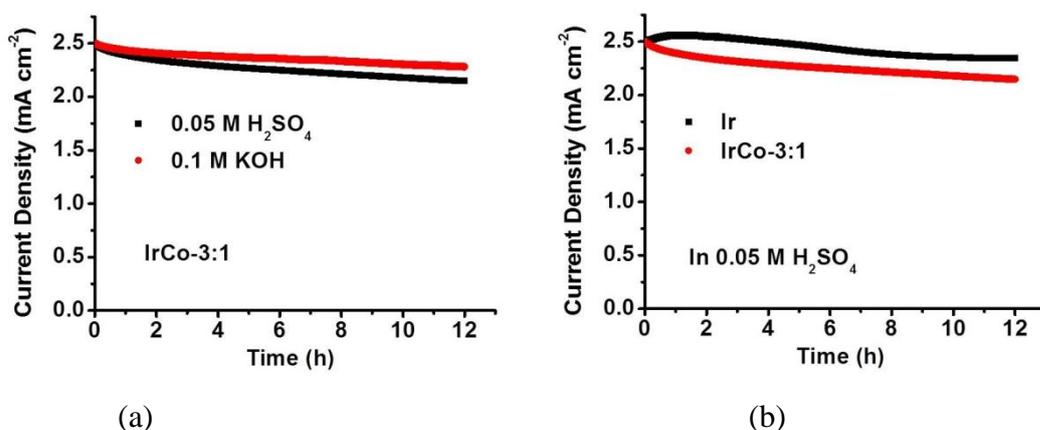
**Figure 4** Electrochemical performance of Ir, IrCo-3:1 and IrCo-1:1 nanodendrites catalysts in acidic condition. (a) The polarization curves of different catalysts in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution at the scan rate of 5 mV s<sup>-1</sup> with iR-compensation and (b) their Tafel plots at the scan rate of 5 mV s<sup>-1</sup>. (c) The polarization curves of different catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at the scan rate of 5 mV s<sup>-1</sup> with iR-compensation and (d) their Tafel plots at the scan rate of 5 mV s<sup>-1</sup>.

In 0.1 M KOH and 1 M KOH, IrCo-3:1 nanodendrites also show the lowest onset potential of ~1.49 V and ~1.48 V versus RHE and only requires an overpotential of ~0.31 V and ~0.28 V to achieve the current density of 10 mA cm<sup>-2</sup> (Figures 5(a) and (c)). Moreover, IrCo-3:1 nanodendrites also exhibit a very low Tafel slope of 66 mV dec<sup>-1</sup> and 52 mV dec<sup>-1</sup> in 0.1 M KOH and 1 M KOH solution (Figures 5(b) and 5(d)). The best activity of IrCo-3:1 sample is mainly because of the combining ultrathin 3D nanodendrite design and Co modified. Both of the OER performances in acidic and alkaline conditions are more preferable than those of most recently reported catalysts, making 3D IrCo nanodendrites among the most active electrocatalyst for OER reported to date.



**Figure 5** Electrochemical performance of Ir, IrCo-3:1 and IrCo-1:1 nanodendrites catalysts in alkaline condition. (a) The polarization curves of different catalysts in 0.1 M KOH solution at the scan rate of  $5 \text{ mV s}^{-1}$  with iR-compensation and (b) their Tafel plots at the scan rate of  $5 \text{ mV s}^{-1}$ . (c) The polarization curves of different catalysts in 1 M KOH solution at the scan rate of  $5 \text{ mV s}^{-1}$  with iR-compensation and (d) their Tafel plots at the scan rate of  $5 \text{ mV s}^{-1}$ .

The long-term durability of a catalytic electrode is another crucial issue to consider for practical applications. When operating the OER at constant overpotentials, stable corresponding current densities were observed in both 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M KOH solution ( $\sim 2.5 \text{ mA cm}^{-2}$ ) with negligible degradation (14% and 9%, respectively) after 12 h of testing (Figure 6(a)), revealing their excellent stability under OER conditions. Notably, as shown in (Figure 6(b)), Ir nanodendrites are more stable than IrCo-3:1 sample, which may due to the dissolution of Co in Ir-Co alloy under acidic condition.



**Figure 6** Stability testing of (a) IrCo-3:1 nanodendrites sample in 0.05 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M KOH solution (b) Ir only and IrCo-3:1 nanodendrites samples in 0.05 M H<sub>2</sub>SO<sub>4</sub> solution at constant potentials

## Conclusion

In conclusion, Co doped Ir nanodendrites samples of different molar ratios were synthesized by hydrothermal reduction method at different reaction times and were characterized by TEM. Among these samples, only IrCo-3:1 sample at 12 h reaction time possesses nanodendrites structure with branch morphology like Ir only sample. Catalytic activity towards oxygen evolution reaction (OER) of as synthesized catalysts at various electrolytes at broad pH ranges was also investigated. IrCo-3:1 catalyst exhibits an enhanced OER activity compared to IrCo-1:1 and Ir only catalysts due to nanodendrites structure with many active sites on the surface of each branch and modifying of ultrathin nanodendrite Ir with transition metal Co. Given its excellent performance in both alkaline and acidic media, the 3D Ir nanodendrites structure may find broad applications in various water splitting, chemical conversions, and beyond. It is worthy noted that, although the IrCo catalysts contain negligible Co, the modifying effect can change the morphology as well as enhance the electrocatalytic activity.

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