Efficient Electrolytic Water Splitting with FeCoPt Trimallelic Cubic Nanocatalysts

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Abstract. Electrocatalytic water splitting to hydrogen energy provides an environmental, cost-effective, and sustainable approach to address worldwide energy and carbon emission challenges. Here we report a facile method for preparing trimetallic cubic nanoparticles for electrolytic overall water splitting by galvanic replacement of FeCo alloys with Pt salt solution. The as-synthesized FeCoPt trimetallic nanocatalysts demonstrated excellent activity and stability for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) catalytic performance in 1.0 mol L⁻¹ KOH. The FeCoPt-2 sample afforded a current density of 10 mA cm⁻² at a low overpotential of 178 mV for HER and 305 mV for OER. The present study provides a facile and cost-effective synthetic process to prepare trimetallic FeCoPt nanocatalysts as high-performance electrocatalysts for overall water splitting.

1. Introduction
The ever-incrementing industrial activities generate increasing demands of energy, causing serious carbon emissions and greenhouse effect related to the consumption of traditional fossil fuels. A promising and sustainable approach to address worldwide energy and climate change challenges has been electrochemical water splitting to hydrogen energy [1]. The overall water splitting involves a hydrogen evolution reaction (HER) on the cathode and an oxygen separation reaction (OER) on the anode. Both of the two reactions require highly active catalysts to reduce the energy of overpotential for water splitting. Precious metals (Pt/C, Ir/C) and metal oxides (RuO₂, IrO₂) are currently commercially mature catalysts for HER and OER [2, 3]. However, the scarcity and high cost of these precious metals have hindered their widely practical application. Therefore, it is still great demand of developing highly active and cost-effective catalysts for HER and OER.

Great effort has been worked on searching for transition metal-based catalysts instead of precious catalysts for HER or OER [4]. Among these non-precious catalysts, transition metals such as Fe, Co and Ni and their alloys are considered as potential substitutes. Co and Ni-based composites have OER catalytic activity comparable to RuO₂ and IrO₂ in alkaline media [5]. Fe based composites have excellent oxygen reduction reaction (ORR) catalytic activity, such as Fe-N, Fe-C catalysts [6]. In addition, alloying is also an effective approach to improve the electrochemical performance [7]. Studies have shown that the synergistic effect among metal elements in alloys would optimize their local coordination environment and electronic structure [7, 8]. Compared with pure metals, the degree of freedom of alloys increases, which is beneficial to the modulation of their electrochemical catalytic
activity. Despite studies have successfully synthesized various metals and alloys as effective HER or OER catalysts, most of them can only catalyze one kind of electrochemical reaction in a certain solution, hindering their practical application in overall water electrolysis. Therefore, the preparation of high activity and low-cost catalysts which are effective in both HER and OER with excellent activity and stability, is still continuously pursued.

In this paper, we prepared cubic FeCo alloys by hydrazine reducing method, which showed good OER activity in alkaline media, but the HER activity was relatively poor. Considering the excellent HER activity and stability of metallic Pt in various pH environments, we incorporated Pt into the FeCo alloys through galvanic replacement reaction, to boost the catalyst's activity and stability for the overall water splitting. As a result, FeCoPt trimetallic nanostructures were successfully constructed, and displayed excellent electrocatalytic activity for overall water splitting. The FeCoPt catalyst afforded a current density of 10 mA cm⁻² at a low overpotential only 0.178 V for HER and 0.305 V for OER under the same electrolyte of 1.0 mol L⁻¹ KOH.

2. Experimental Section

2.1. Materials
Ferrous sulfate (FeSO₄·7H₂O, 99.5%), cobalt chloride (CoCl₂·6H₂O, 99%), poly(ethylene glycol) (PEG, mw=400), cyclohexane (99.5%), hydrazine (85 wt%), sodium hydroxide (NaOH, 96%), potassium hydroxide (KOH, 98%), and ethanol (99.5%) were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, China). Potassium tetrachloroplatinate (K₂PtCl₄, 99.9%) was purchased from Aldrich. Nafion perfluorinated resin solution (5 wt%) was purchased from Alfa Aesar. All reagents were used as received without further purification. Ultrapure water used for all experiments was distilled through a Millipore Synergy water purification system with a resistivity of 18.2 MΩ.

2.2. Synthesis of FeCo and FeCoPt nanocatalysts.
FeCo alloys were synthesized by hydrazine reducing method [9]. 6.88 g of PEG, 0.8 mL of cyclohexane, 0.64 g of CoCl₂·6H₂O, and 0.72g of FeSO₄·7H₂O were dissolved in 50 mL of water under argon protection atmosphere. After ultrasonic irradiation for 90 min at room temperature, the above mixture was heated to 78 °C. A solution composed of 20 mL of NH₂-NH₂·H₂O (85 wt%) and 2.5 g of NaOH was added to the heated mixture. After reaction for 30 min, FeCo alloys were obtained by centrifuged and washed with water through three centrifugation/redispersion cycles, then washed twice with ethanol, and finally redispersed in 50 mL of ethanol.

Galvanic replacement of FeCo alloys by Pt salt solution for FeCoPt nanocatalysts was conducted as follows: The galvanic replacement of FeCo alloys was initiated by adding certain volumes of K₂PtCl₄ (20 mM) alcoholic solution to the above FeCo alloys's dispersion (0.25 mL). The reaction mixture was gently mixed for 2 min immediately after the addition of Pt solution, and then left undisturbed at 50°C oil bath for 6 h. The as-obtained FeCoPt nanocatalysts were washed with ethanol three times through centrifugation/redispersion cycles, and finally dried at 50 °C under vacuum. The degrees of the Pt replacement were controlled by adjusting the volumes (0.156, 0.313, 0.625, 1.25 mL) of K₂PtCl₄ solution added. The obtained FeCoPt samples were labeled as FeCoPt-1, FeCoPt-2, FeCoPt-3, and FeCoPt-4, respectively.

2.3. Material Characterizations
X-ray diffraction (XRD) patterns of the as-obtained products were recorded on a Bruker D8 Advanced X-ray diffractometer using Cu Kα radiation (λ = 0.1542 nm). The diffraction data was recorded for 20 angles between 15° and 80°. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV. Scanning electron microscope (SEM) images and energy dispersive X-ray spectrometer (EDS) analyses were performed on a FEI Novo Nano-450 field emission scanning electron microscope.
2.4. Electrochemical Measurement

Electrochemical measurements were carried out on a CHI 660E electrochemical workstation (CH Instruments, China) at room temperature. We used a standard three-electrode system composed of a saturated calomel electrode (SCE) serving as the reference electrode, a Pt wire serving as the counter electrode, and a glassy carbon electrode (GCE) loaded with the FeCoPt sample serving as the working electrode. The GCE was first polished with 0.3 mm alumina slurry and thoroughly washed with water and ethanol before use. 4 mg of FeCoPt sample was mixed with 250 µL of ethanol, 720 µL of water and 30 µL of Nafion (5 wt%) solution, followed by sonication for 0.5 h to form a uniform colloidal ink. 5 µL of the catalyst ink was loaded on the pre-polished GCE (d = 3.0 mm, S = 0.07069 cm²). The mass of the catalysts loaded on each GCE was kept at 20 μg. Linear sweep voltammetry (LSV) was performed in 1 mol L⁻¹ KOH solution with a scan rate of 5 mV s⁻¹. All the potentials measured vs. SCE were converted to reversible hydrogen electrode (RHE) according to the Nernst equation:

\[ E_{\text{RHE}} = E_{\text{SCE}} + 0.2415 + 0.059 \cdot pH \]  

Tafel slope was obtained by the polarization curves for quantification of the HER and OER activities of the catalysts, calculated according to the following equation:

\[ \eta = a + b \cdot \log J \]  

Where \( \eta \) is the overpotential, \( a \) is the Tafel constant, \( b \) is the Tafel slope, and \( J \) is the current density. The overpotential of OER was calculated as follows:

\[ \eta = E_{\text{RHE}} - 1.23 \]

Figure 1. XRD patterns of FeCoPt nanocatalysts and FeCo alloys. The standard patterns of Fe₇Co₃ (JCPDS no. 48-1817) and Pt (JCPDS no. 04-0802) were also shown for comparison.

3. Results and Discussion

3.1. Characterizations of FeCoPt nanocatalysts

XRD patterns of the obtained FeCo and FeCoPt samples are shown in Figure 1. The diffractions in Figure 1(a) at 44.8 and 65.3°, corresponding to the (110) and (200) characteristic reflections of Fe₇Co₃ alloys (JCPDS no. 48-1817), gradually weaken or even disappear as the added amount of Pt increase (Figure 1(b-f)), whereas appearing the characteristic diffraction peaks of metallic Pt (JCPDS no. 04-0802) at 39.8° (111), 46.3° (200) and 67.4° (220) whose intensities increase with the amount of Pt added. When the amount of Pt substitution was increased to a certain amount (FeCoPt-3), the diffraction peaks of FeCo alloys completely disappeared. The above experimental results indicate that the FeCo alloys were gradually galvanic replaced by Pt from the outer surface to the inside. At the same time, some new diffraction peaks appear at 22.8 and 28.1°, which are similar to the characteristic diffraction (100) and (110) planes of CoPt (JCPDS no. 29-0499) or FePt (JCPDS no. 29-0716), indicating that the Pt atoms entered into the FeCo lattices and replaced the Fe or Co atoms.
Figures 2(a) and 2(b) show SEM and TEM images of the FeCo alloy, respectively, showing that the sample consists of FeCo alloy nanocubes with an average size of 131.5 nm. Some FeCo nanoparticles are self-aligned due to their magnetic dipole interaction. As seen from Figure 2(c~f), FeCo alloys begin to be replaced by Pt from the face center of the FeCo nanocubes. With the increase of Pt replacement, the face center of the nanocubes to be concave, however, the cubic skeleton maintains. The cubic frame begins to disrupt started from FeCoPt-3 sample, and deformed severely in FeCoPt-4.

Figure 2. (a) SEM image of the obtained FeCo nanocubes. TEM images of the obtained (b) FeCo, (c) FeCoPt-1, (d) FeCoPt-2, (e) FeCoPt-3, and (f) FeCoPt-4 samples.

The EDS spectrum was used to investigate the degree of Pt replacement for the FeCo alloys. The atomic percentage of the FeCo, FeCoPt-1, FeCoPt-2, FeCoPt-3, and FeCoPt-4 were shown in Figure 3. As quantified by EDS, the Fe:Co atomic ratio of the FeCo alloys is 65.3:34.7, approximately 7:3 of integer ratio, in good agreement with the XRD results. As the amount of Pt salt added increases, the Pt content in the FeCoPt samples increases. As the Pt replacement progresses, the atomic ratio of Fe gradually decreases, however, the atomic ratio of Co remained basically unchanged, indicating that Pt mainly galvanic replaced Fe atoms.

Figure 3. The atomic percentages of Pt, Fe, and Co in the FeCo, FeCoPt-1, FeCoPt-2, FeCoPt-3, and FeCoPt-4 samples, as quantified by EDS.

3.2. Electrochemical Performance
We first investigated the HER catalytic activities of the obtained FeCoPt cubic nanocatalysts. The HER measurements were performed under a standard three-electrode system in 1.0 mol L⁻¹ KOH with a scan rate of 5 mV s⁻¹. In the polarization curves (Figure 4a), FeCo alloys show an obvious HER
response. After the introduction of Pt to the FeCo, the FeCo-based samples showed improved catalytic activities and reduced onset potentials. The overpotentials required to achieve a 10 mA cm\(^{-2}\) current density were about 0.409 V for FeCo, 0.269 V for FeCoPt-1, 0.178 V for FeCoPt-2, 0.227 V for FeCoPt-3, and 0.263 V for FeCoPt-4. FeCoPt-2 displayed lowest required overpotential and Tafel slope (97.02 mV dec\(^{-1}\)), revealing faster HER kinetics and suggesting Volmer step-water dissociation (H\(_2\)O + e\(^-\) → H + OH\(^-\)) is rate-determining step in alkaline media [10, 11]. As the amount of Pt replacement increases, the catalytic performance of HER increases first and then decreases. As showed in Figure 2, Pt first replaced the surface atoms of the FeCo nanocubes, whose catalytic surface can be fully utilized before the FeCo surface was saturated replaced, hence, the HER catalytic performance increased gradually in the initial replacement stage. After the FeCo surface be saturated replaced, Pt started to replace the inner atom of the cubes, the effective catalytic area per unit mass is reduced, resulting the decrease of the catalytic performance.

Electrocatalytic stability is important to the catalyst’s performance. We tested the durability of FeCoPt-2 OER catalyst using chronoamperometry method. The long-term OER running curve in Figure 4(c) of FeCoPt-2 shows good stability without obvious current loss after a continuous 200 min test.

![Figure 4](image_url)

Figure 4. (a) The HER polarization curves for different catalysts at a scan rate of 5 mV s\(^{-1}\). (b) Tafel plots for different nanocatalysts. (b) Stability test for FeCoPt-2 nanocatalysts (without iR corrections).

To investigate the OER catalytic performance of the obtained FeCoPt cubic nanocatalysts, we conducted the electrochemical measurements under a standard three-electrode system in 1.0 mol L\(^{-1}\) KOH. Figure 5 shows the linear sweep voltammograms (LSVs) of the FeCoPt and FeCo samples at a scan rate of 5 mV s\(^{-1}\). The OER overpotentials required to achieve a 10 mA cm\(^{-2}\) current density were about 0.297 V for FeCo, 0.292 V for FeCoPt-1, 0.305 V for FeCoPt-2, 0.318 V for FeCoPt-3, and 0.329 V for FeCoPt-4. The calculated Tafel slopes were 101.9 mV dec\(^{-1}\), 108.1 mV dec\(^{-1}\), 100.4 mV dec\(^{-1}\), 85.0 mV dec\(^{-1}\), and 74.4 mV dec\(^{-1}\), respectively. FeCoPt-1 and FeCoPt-2 exhibited competitive overpotentials and Tafel slopes, demonstrating the desired electrocatalyst for OER.

![Figure 5](image_url)

Figure 5. (a) The OER polarization curves for different catalysts at a scan rate of 5 mV s\(^{-1}\). (b) Tafel plots for different nanocatalysts.
4. Conclusions
In summary, we successfully developed a facile method for preparing trimetallic cubic FeCoPt nanoparticles as both excellent HER and OER catalyst in alkaline media. Incorporation of Pt into FeCo alloys can tune the metal proportions of the FeCoPt nanocatalysts, leading to the enhancement of HER and OER activity. As the amount of Pt incorporation increases, the catalytic performance of HER and OER increases first and then decreases, existing an optimal Pt incorporation for HER or OER. The FeCoPt nanocatalysts can efficiently boost the electrolysis of overall water splitting in alkaline solution with fast kinetics. The FeCoPt-2 showed excellent catalytic activities that afforded a current density of 10 mA cm\(^{-2}\) at a low overpotential of 178 mV for HER and 305 mV for OER. These findings provide some insights into the rational design of cost-effective trimetallic catalysts for OER and HER catalysis.

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