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In situ synthesis of a novel organic-inorganic composite as a non-noble metal electrocatalyst for the oxygen evolution reaction

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ABSTRACT

Offering new techniques for efficient design and fabrication of inexpensive and earth-abundant catalysts for the development of oxygen evolution electrodes is a fundamental approach to promote sustainable energy processes. Herein, we report the in situ synthesis of a novel organic-inorganic composite directly onto carbon paste electrode (CPE) surface, as a robust substrate to incorporate Nickel-Iron (Ni-Fe) metal ions without using any binders or energy consumer techniques. Polyoxometalate (POM) and o-Anisidine (oA) are composite components that can be easily combined on the electrode surface (oA-POM/CPE). Ascribed to the synergy of context and metal ions, the as-prepared electrode affords a high catalytic activity and stability towards oxygen evolution reaction (OER), and gained a current density of 10 mA cm^{-2} at overpotential of 330 mV. Moreover, the distinct electrocatalytic activity is illustrated by varying the amount of Fe in immersion solution, which proves the change made in percentage ratio of Ni-Fe in immersion solution that consequently affects Ni-Fe percentage value on electrode surface. This represents the competition between metal cations in creating complex with composite. Collectively, this simple strategy provides a promising way for the development of effective and non-noble metal-based OER electrocatalysts.

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Introduction

The water splitting is broadly considered as a strategy to store large-scale and sustainable energy from renewable sources (e.g., sunlight) and to overcome the concerns about global warming caused by the excessive consumption of fossil fuels [1–7]. Hydrogen has the potential to realize our demand for a future clean energy source with zero greenhouse gas emissions. Electrochemical water splitting is an uncomplicated

procedure to produce pure hydrogen and oxygen [1]. Nevertheless, the water oxidation reaction is mostly cited as an impasse in fuel forming cycles due to the complexity of this multistep proton-coupled electron transfer [8]. An effective electrocatalyst is required for oxygen evolution reaction (OER) in order to accelerate the reaction, and enhance the energy conversion efficiency. Currently, the best-known and most active OER catalysts are precious metal oxides, such as IrO_2 and RuO_2 [9]. However, these catalysts suffer from their high cost and poor long-term stability in alkaline solution [10].

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Therefore they are not suitable for large-scale applications. Alternatives comprising first-row transition metals that are naturally abundant and catalytically active, like nickel [11], cobalt [12], iron [13], manganese [14] and their mixed [15–17,55], have been subject of numerous researches because of their promising electrocatalytic properties.

Mixed Ni-Fe oxide/(oxy)hydroxide catalysts have shown to be of special interest because they are the most active and stable catalysts measured in basic media [18–23]. Enormous amount of endeavor has been invested to fabricate active and stable mixed Ni-Fe electrocatalysts for OER in alkaline solutions. At the moment, many of high activity catalysts in alkaline electrolyte are nanostructured $Ni_xFe_y(OH)_2$ powders [23,24], which are coated onto various substrate with the aid of polymeric binders such as Nafion. The use of insulating binders can decrease the contact between electrolyte and active sites of catalyst, and deteriorate the electrical conductivity of electrode, leading to diminished activity [25]. To prevent this issue, synthesis catalyst on the electrode surface can be an appropriate solution. Electrodeposition of Ni-Fe composite catalysts onto the surface of two and three-dimensional substrates have been reported [26–29], yet this process has required equipment and precise control of the nucleation and growth operations.

Previously, we applied the metal–polymer modified carbon and multi-walled carbon nanotube paste electrode for electrocatalytic oxidation of some biological compounds [30], several carbohydrates [31,34], ethylene glycol [32] and methanol [33]. In the process of preparing the electrodes, nickel or nickel-cobalt ions were incorporated into the polymeric matrix by immersion of the polymeric modified electrode in a cation solution without applying any potential.

Polyoxometalates (POMs) are a unique class of inorganic, anionic, nanometer sized metal-oxygen cluster compounds that are prominent in their electrochemical redox properties and oxidizing abilities [35,36]. Attachment of a transition metal cation on the surface of a POM anion using coordinate covalent bonds can provide efficient electrocatalyst to water oxidation process. However, high solubility of these compounds in aqueous solutions leads to instability on the surface of the electrode as heterogeneous catalyst. A variety of methods such as hybridization [37], precipitation [38], and immobilization on a suitable solid support [39] have been reported for heterogenization of POMs. Bulky organic amines, which often act as encapsulating cations, are used as “shrink-wrapping” agents in the self-assembly process of POM-base organic-inorganic hybrid [40]. Strong hydrogen bonding interactions between primary amino group of organic unit and the bridging oxygen atoms of Keggin-type POM creates an insoluble composite [41], which can incorporate various transition metal cations.

In the present work, we describe a facile method to fabricate a modified carbon paste electrode (CPE) by using the in situ formation of insoluble organic-inorganic hybrid on the surface of CPE, and then, incorporated nickel-iron ions by immersing the modified electrode in a mix aqueous solution of nickel and iron nitrate (Ni-Fe solution).

At the first step, a mixture of graphite powder plus Keggin-type POMs (Phosphotungstic acid) were blended by hand mixing and by adding paraffin, the obtained paste was

inserted in the bottom of electrode tube (POM/CPE). At the next step, POM/CPE was placed in an aqueous solution of o-Anisidine (oA) in order to create an organic-inorganic hybrid (oA-POM/CPE). At the final step, oA-POM/CPE was immersed at the open circuit in Ni-Fe solution for dispersion of transition metal ions to as-prepared substrate (Ni-Fe/oA-POM/CPE).

We investigated the electrocatalytic OER activity of Ni-Fe/oA-POM/CPE in a standard three-electrode system, while the working electrode was continuously rotating at 1600 rpm to eliminate the generated oxygen bubbles. The fabricated modified electrodes exhibited a low overpotential, good stability and durability in alkaline solutions.

Experimental section

Preparation of the electrodes

A mixture of graphite powder (180 mg) (particle diameter: 0.10 mm, from Merck) plus phosphotungstic acid (20 mg) (from Merck) were patiently blended by hand mixing with a mortar and pestle for 20 min. High viscosity paraffin oil (100 mg) (from Fluka) was then added and mixed well until a homogeneous paste was obtained. The prepared paste was firmly packed in the bottom of a rotating electrode body (ca. 3 mm internal diameter). The electrode surface was polished on a weighing paper until a smooth surface was observed (POM/CPE).

In order to compare electrode stability between Ni-Fe/POM-modified electrode and Ni-Fe/oA-POM-modified electrode, POM/CPE was placed at open circuit in a well stirred aqueous solution of 75 mM $Ni(NO_3)_2$ and 25 mM $Fe(NO_3)_3$ (75:25 mol/mol), (nickel nitrate and iron nitrate used in this work were in analytical grade of Merck) and accumulation of nickel and iron were conducted by complex formation between metal ions with oxygen sites [42] in the phosphotungstic acid (Ni-Fe/POM/CPE).

To create the organic-inorganic hybrid at the electrode surface, the as-prepared POM/CPE was gently immersed in aqueous solution containing 10 mM oA (C_7H_9NO) (from Merck) and 0.5 M H_2SO_4 (from Fluka) for 15 min without any turbulence. Local dissolution of POM in the electrode surface causes interaction between the POM and oA, and consequently, on-site formation of organic-inorganic hybrid on the surface of electrode (oA-POM/CPE).

And finally, oA-POM/CPE was dipped at open circuit in a well-stirred aqueous solution in different percentages of nickel nitrate and iron nitrate. The obtained materials are named as Ni_x-Fe_y , where x and y that represent the relative amount of Ni and Fe in the molar ratios, respectively (x-y: 100-0, 75-25, 50-50, 25-75, 0-100) (Ni-Fe/oA-POM/CPE).

Characterizations

The morphology of the electrodes surface was characterized by using the FESEM, MIRA3 TESCAN electron microscope (operated at 15 kV). The overall composition (elemental analysis) and element distribution of material on the surface were analyzed in FESEM by energy dispersion X-ray spectroscopy (EDX) and elemental mapping.

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