



# Carbon nanofibers as nanoreactors in the construction of PtCo alloy carbon core-shell structures for highly efficient and stable water splitting



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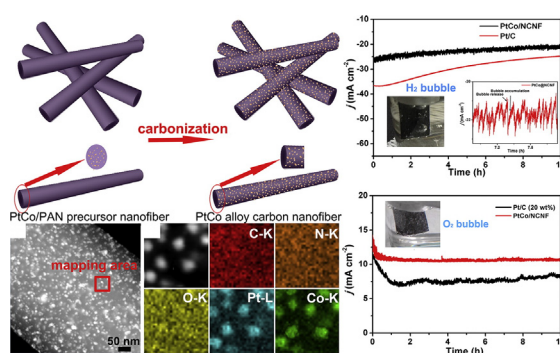
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## HIGHLIGHTS

- PtCo alloy carbon core-shell nanostructures with nitrogen doping were synthesized.
- Carbon nanofibers served as nanoreactors.
- The PtCo alloy carbon exhibits high HER and OER activity and high stability.
- The OER activities originate from the conductivity of NCNF and the PtCo alloy.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 23 May 2016

Received in revised form 5 July 2016

Accepted 8 July 2016

Available online 14 July 2016

### Keywords:

PtCo alloy

Carbon nanofibers

Nanoreactors

Hydrogen evolution reaction

Oxygen evolution reaction

## ABSTRACT

Carbon nanofibers served as nanoreactors for the design and construction of PtCo alloy carbon core-shell nanostructures with nitrogen doping (PtCo/NCNF) through a combination of electrospinning and nitrogen doping treatments. The PtCo/NCNF hybrid consists of PtCo alloy nanoparticles surrounded by a few of N-doped carbon layers, demonstrating a typical core-shell structures. The PtCo/NCNF hybrid can both served as electrode materials for electrocatalytic water splitting including hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). For the HER performance, the PtCo/NCNF exhibits very small onset potential of 20 mV, an overpotential of 50 mV at a  $j$  (vs RHE) = 10 mA cm<sup>-2</sup> and Tafel slope of 30 mV dec<sup>-1</sup>. The PtCo/NCNF hybrid also exhibits high OER activity with an onset potential of 310 mV, an overpotential of 400 mV at a  $j$  of 10 mA cm<sup>-2</sup> and a small Tafel slope of 76 mV dec<sup>-1</sup>. The high catalytic activities of PtCo alloy for HER and OER originate from the 3D hierarchical structures, well-dispersed PtCo alloy, high conductivity of NCNF, protection from the carbon-encapsulated structure, and the introduction of nitrogen.

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## 1. Introduction

Water splitting has been hailed as a promising candidate to meet the increasing demands for clean and sustainable energy on the global scale. Electrocatalytic water splitting consists of the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) [1]. One of the

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important approaches is to develop highly efficient and durable electrocatalysts that can substantially expedite the kinetics of HER and OER process [2,3]. Therefore, to improve the energy efficiency, an high-performance electrocatalyst is essential for reducing the overpotentials of electrodes, promoting the reaction kinetics, and enhancing the specific activity. However, compared to the HER, the OER process is harsh and kinetically sluggish because of its thermodynamically and kinetically demanding process involving four sequential proton-coupled electron transfer steps and the oxygen-oxygen bonding formation [3]. The four sequential proton-coupled electron transfer steps for OER process leads to slower kinetics and relatively higher overpotentials [2–5]. Co-based electrocatalysts, such as CoP, Co<sub>3</sub>O<sub>4</sub> and CoS<sub>2</sub> have been known as active OER catalysts, and considerable efforts has been made to develop advanced Co-based nanostructures for improving the OER activity and stability [6–11].

Notwithstanding significant progress, there are only a few catalysts that are able to catalyze both HER and OER process. Recently, a type of precious-metal alloy with transition metal (Co, Mn, etc.) [12,13] and nonmetal catalyst (graphitic carbon, N-doped graphitic carbons, etc.) [14] have been employed as an effective co-electrocatalyst for HER or OER. In this regard, it is of great interest to introduce a certain amount of Pt into Co phase to generate PtCo alloy for the overall water splitting. The PtCo alloy exhibits good catalytic activity along with good durability due to the modification of the Pt electronic structure. Wang and co-workers reported cobalt-embedded N-doped carbon nanotubes (CNTs), exhibiting both high oxygen reduction reaction (ORR) and OER activity [14]. The high catalytic activity of cobalt-embedded N-doped CNTs is thought to be facilitated by the combination of the embedded cobalt, the N-doped carbon, and the CNTs substrate. It is reported that metal embedding has been found to be conducive to protecting the metal nanoparticles from dissolution, migration, detachment and coalescence by the electrolyte, resulting in high long-term stability [15].

Recently, Du et al. group have reported the novel fabrication of carbon nanofibers (CNF) supported noble metal nanoparticles, transitional metal dichalcogenides nanoplates and core-shell nanostructures [15–18]. The nanocrystal/carbon nanofibers systems exhibit superior electrocatalytic activity for water splitting. Three-dimensional (3D) nanomaterials with hierarchical structure have been widely designed for the electrochemical reactions, such as HER, OER and ORR [19–22]. Compared with bulk solid structures, the complex hierarchical structures endow materials with high specific surface areas, which can facilitates diffusion of active species and accelerates subsequent surface reactions [20–22]. The one-dimensional (1D) nanostructures of CNF can provide more contact surfaces between supported catalysts and electrolyte. The interconnected 3D architecture of CNF induces large interfaces and interstices of the electrolyte and the nanocrystal surfaces, which provide rapid electron transport and fast gas diffusion [20,22]. In addition, the 3D architecture of CNF also can promote the release of evolved gas bubbles, which are benefit for the electrode kinetics and catalytic performance [23]. Meanwhile, the introduction of nitrogen into carbon material not only can promote electronic transfer but also provide more active sites for both the OER and ORR [24–26]. It is of great interest to fabricate hierarchical 3D structures integrated with PtCo alloy and CNF, serving as promising materials for both HER and OER in electrocatalytic water splitting.

Herein, inspired by the superiority of PtCo alloy, N-doped carbon and enhanced durability of metal embedding, the CNF were used as a nanoreactor to synthesize PtCo alloy carbon core-shell nanostructures with nitrogen doping (PtCo/NCNF) through a combination of electrospinning and nitrogen doping treatments. Small sized PtCo alloy carbon core-shell nanoparticles were uniformly dispersed throughout the whole CNF. The PtCo/NCNF hybrid consists of PtCo alloy nanoparticles surrounded by a few of N-doped carbon layers, demonstrating a typical core-shell structures. The PtCo/NCNF hybrid can both served as electrode materials for HER and OER. For the HER performance, the novel nanomaterials exhibit very small onset potential of

20 mV, overpotentials at a  $j$  (vs RHE) of 10 mA cm<sup>-2</sup> of 50 mV and Tafel slope of 30 mV dec<sup>-1</sup>, which are better than the commercial Pt/C (20 wt%) catalysts (onset potential of 27 mV and overpotentials at a  $j$  (vs RHE) of 10 mA cm<sup>-2</sup> of 59 mV) and PtCo/NCNF without NH<sub>3</sub> treatment (onset potential of 34 mV and overpotentials at a  $j$  (vs RHE) of 10 mA cm<sup>-2</sup> of 68 mV). In addition, the PtCo/NCNF hybrid also exhibits high OER activity with an onset potential of 310 mV, an overpotential of 400 mV at a  $j$  (vs RHE) of 10 mA cm<sup>-2</sup> and a small Tafel slope of 76 mV dec<sup>-1</sup>, which are also better than PtCo/CNF (onset potential of 340 mV, an overpotential of 520 mV at a  $j$  (vs RHE) of 10 mA cm<sup>-2</sup> and Tafel slope of 83 mV dec<sup>-1</sup>). The PtCo/NCNF membrane can be directly used as electrodes for HER and OER, demonstrating superior stability in acid and alkaline conditions after continuous operation for 10 h. The high catalytic activities of PtCo alloy for HER and OER originate from the 3D hierarchical structures, well-dispersed PtCo alloy, high conductivity of CNF, protection from the carbon-encapsulated structure, and the introduction of nitrogen.

## 2. Experimental

### 2.1. Materials

Chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 99.9%) and dimethylformamide (DMF, 99.5%) were procured from Shanghai Civi Chemical Technology Co., Ltd. Cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) and potassium hydroxide (KOH) were supplied by Aladdin Co., Ltd. Polyacrylonitrile (PAN,  $M_w \approx 1.4 \times 10^5$ , copolymerized with 10 wt% methyl acrylate) was purchased by Sinopec Shanghai Petrochemical Co., Ltd. Ultrapure water (Milli-Q) was used throughout the experiments. All were used as received without further purification.

In a typical procedure, 0.15 g of CoCl<sub>2</sub>·6H<sub>2</sub>O and 0.15 g of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O were co-dissolved in 22 mL of a PAN/DMF solution with a mass fraction of 10% PAN. Thereafter, the homogeneity of the three-component mixture was obtained by vigorously stirring of the mixture at 80 °C for 3 h. Afterward, the mixture was transferred to a syringe with a stainless copper needle at the tip. The needle was connected to a high voltage power supply to get a voltage of 15 kV, the needle-to-collector distance was about 12 cm, and the flow rate of the precursor solution was 0.6 mL h<sup>-1</sup>.

Under these conditions, the homogeneous PtCo/PAN nanofibrous membrane were obtained at room temperature. The direct growth of the PtCo/NCNF hybrid was carried out in a home-built chemical vapor deposition (CVD) furnace. The as-collected PtCo/PAN nanofibrous mats were placed in a ceramic boat located at quartz tube in the center of the heating zone of the furnace. Next, the PtCo/PAN nanofibrous mats were heated in air from room temperature at a temperature ramp of 5 °C min<sup>-1</sup> to 230 °C and maintained for 6 h. After the stabilization process, the nanofiberous mats were continue to heat up with the feeding of Ar (150 sccm) at ambient pressure. When the temperature reached 400 °C, the NH<sub>3</sub> (10 sccm) gas was introduced. After 2 h, the NH<sub>3</sub> gas was then turned off, while the furnace temperature was heated up to 1000 °C and the temperature was held constant for 8 h. The samples were cooled to room temperature naturally under the protection of flowing Ar. For reliable comparison, the PtCo/CNF, NCNF and CNF were prepared similarly as a control.

### 2.2. Characterization

Field-emission scanning electron microscopy (FE-SEM) images were recorded on the JSM-6700F (JEOL, Japan) at high vacuum with an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM) and selected-area electron diffraction (SEAD) were taken using a JSM-2100 transmission electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. The high-angle annular dark field scanning TEM (HAADF-STEM), STEM mapping, and line-scan energy dispersive X-ray spectroscopy (EDX) were taken with a STEM (Tecnai G2 F30S-Twin, Philips-FEI) operating

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