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# $NiCoSe_{2-x}$/N-doped C mushroom-like core/shell nanorods on N-doped carbon fiber for efficiently electrocatalyzed overall water splitting

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## ABSTRACT

Developing stable and efficient bifunctional catalysts for overall water splitting is a critical step in the production of renewable energy sources. Here we report a stable and highly active electrocatalyst comprised of $NiCoSe_{2-x}$/N-doped carbon mushroom-like core/shell nanorods on silk-derived carbon fiber through one step selenization. The unique one-dimensional nanorod structure facilitates the charge transport, and the N-doped carbon shell also increases the electrical conductivity, resulting in a remarkable enhancement of the catalytic activity. The N-doped carbon shell also functions as a protection layer. The composite catalyst therefore exhibits outstanding OER and HER performance, it can also stably drive the overall water splitting at a low cell voltage of 1.53 V in base solution. The present work provides an efficient strategy for the fabrication of stable and active electrocatalysts with earth-abundant elements.

## 1. Introduction

The development of clean and renewable energy sources holds the promise for the solution of environmental contamination and energy crisis [1–3]. Hydrogen has been recognized as the center of newly emerged hydrogen economy, and water electrolysis is the most efficient way for the clean and sustainable production of hydrogen when coupled with renewable solar and wind [4–7]. Water electrocatalysis is an uphill process and consisted of two half reactions including the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), with the latter more challenging [8,9]. Up to date, the best electrocatalysts for the HER and the OER are noble Pt and Ir-based compounds, respectively [10,11]. However, the high cost of noble metals limits their industrial applications. It is important to develop active electrocatalysts using earth-abundant elements [12,13].

Much effort has been made for the development of transition metal-based electrocatalysts [14–16]. Of a particularly, Ni and Co based nanomaterials show outstanding catalytic activity toward HER, OER and even overall water electrolysis [17–19]. Recently, transition metal selenides (TMSs) have been demonstrated to be very active electrocatalysts in HER and OER. However, many TMSs are unavoidable to be oxidized in base electrolyte, or corroded in acidic media, and hence serve as the precatalyst for the catalytic reaction [20]. In addition, the vast majority of existing TMSs are unsuitable for use in the same electrolyte because of the mismatch of pH ranges in which the electrocatalysts are both stable and sufficiently active. It is therefore important to develop new strategies to fabricate these high-performance materials.

Most recently, nickel cobalt diselenide has been reported to be active for HER [21,22], but with few report on OER probably because of the stability issue. It has been shown that carbon-based materials can not only increase the catalysts stability but also contributed to the catalytic reaction [23–26].

In this work, to solve the mentioned concerns on the catalyst stability and further improve the performance, we developed a facile on-step selenization method to synthesize a core/shell nanorod structure with the nickel-cobalt diselenide nanorod core

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protected by N-doped carbon shell on silk-derived carbon fiber. The core/shell nanorod on carbon fiber can directly be employed as the binder-free electrode to drive overall water splitting, with the cell voltage as low as 1.53 V at 10 mA cm$^{-2}$. The present work demonstrates an efficient route for the development of robust bifunctional electrochemical catalysts of water splitting.

## 2. Experimental methods

### 2.1. Chemicals and materials

Acetone, alcohol, deionized water and N,N-Dimethylformamide were purchased from Hangzhou Gaojing Fine Chemical Industry Co., Ltd. (Zhejiang China). Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Nickle nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and selenium powder were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai China).

### 2.2. Preparation of the $NiCoSe_{2-x}$/NC precursor

Silk was cleaned in acetone, alcohol, deionized water by ultrasonication and dried in vacuum at 60 °C overnight. Then, 1 g of clean silk was immersed in a deep-red solution containing 1.16 g of $Ni(NO_3)_2$, 1.16 g of $Co(NO_3)_2$ and N,N-dimethylformamide. After 24 h, the silk was picked up and dried at 60 °C overnight. The above immersing-drying process was repeated to ensure enough metal salts are loaded onto the silk.

### 2.3. Synthesis of $NiCoSe_{2-x}$/NC nanomushroom arrays grown on the silk-derived carbon fibers

The selenization process was conducted in a tube furnace. An alumina boat loaded with the silk and precursor was placed in the center of a quartz tube, and another alumina boat loaded with 0.3 g of Se powder was placed at the upstream side in the tube with the distance of 26 cm from the silk boat. The silk boat was heated to 230 °C from room temperature at the rate of 5 °C/min and maintained for 3 h at 230 °C in air. Then Ar gas (150 sccm) was introduced and the temperature was ramped to 900 °C and kept for 3 h. For comparison, $Ni_3Se_4$ and CoSe were prepared with the same method.

### 2.4. Electrochemical measurements

Electrochemical measurements were carried out using an electrochemical work station (Ivium A88441). All of the measurements were performed using a three-electrode cell with an Ag/AgCl electrode as the reference. A platinum net and a graphite rod were used as the counter electrode in OER and HER tests, respectively. The samples were cut into regular flakes (0.9 cm × 0.6 cm) and the mass is 5.76 mg. The total loading of $NiCoSe_{2-x}$ is about 4.54 mg calculated according to the SEM-EDS results. The samples were directly used as the binder-free working electrode and 0.5 M $H_2SO_4$ and 1.0 M KOH were used as the electrolytes. Linear sweep voltammetry (LSV) was performed at scan rate of 0.2 mV/s to obtain the polarization curves. Cyclic voltammetry (CV) was carried out from −0.244 V to 0.556 V with the scan rate of 0.5 mV/s. Electrochemical impedance spectroscopy (EIS) was employed when the working electrode was biased at a constantly value of −0.23 V *vs.* reversible hydrogen electrode (RHE) while sweeping the frequency from 5 MHz to 10 MHz.

### 2.5. Characterizations

The structures of the synthesized samples were characterized by field emission scanning electron microscopy (FE-SEM) under the accelerating voltage of 3 kV (ULTRA55, ZEISS, Germany). Transmission electron microscopy (TEM) was carried out on a JSM-2100 (JEOL, Japan) and the high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images as well as the line-scan energy dispersive X-ray spectroscopy (EDX) were conducted on a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at the accelerating voltage of 300 kV. X-ray diffraction (XRD) patterns were recorded on Bruker Axs D8 Discovery instrument with a Cu K$\alpha$ line. The chemical state of elements was analyzed on X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD) under the Al K$\alpha$ source (1486.6 eV).

## 3. Results and discussion

Fig. 1 shows the schematic illustration of the fabrication of $NiCoSe_{2-x}$/N-doped C (denoted as $NiCoSe_{2-x}$/NC) nanomushroom arrays on the silk-derived carbon fibers as advanced electrocatalysts for water splitting. The XRD patterns of $NiCoSe_{2-x}$/NC, CoSe and $Ni_3Se_4$ are revealed in Fig. 2a. The as-prepared $NiCoSe_{2-x}$/NC is indexed to hexagonal phase (PDF#65-7038), while the CoSe and $Ni_3Se_4$ belong to hexagonal and monoclinic phase, respectively. The broad peak at 24.2° marked by green triangle is assigned to the (002) plane of graphitized carbon. Raman analysis (Fig. 2b) was further confirmed the existence of graphitized carbon with obvious D and G peak located at 1331 and 1572 cm$^{-1}$, respectively [27]. It is clear that the peaks of $NiCoSe_{2-x}$/NC are not the simple superimposition of $Ni_3Se_4$ and CoSe, in addition, the intense bonds of $NiCoSe_{2-x}$/NC which located at the 459 cm$^{-1}$ and 657 cm$^{-1}$ have a smaller blue shift comparing to those of CoSe. The possible reason is that the Ni atom instead of Co atom causing the new chemical bond [22,28].

The morphology of the prepared samples was characterized by SEM as shown in Fig. 3. The $NiCoSe_{2-x}$/NC displays uniform nanorods with mushroom-like morphology vertical to the carbon support (Fig. 3a and d). The cross-section view image (Fig. S1) reveals that the length and the diameter of the nanorod are 0.535 μm and 0.105 μm, respectively. The SEM images of the $Ni_3Se_4$ (Fig. 3b and e) and CoSe (Fig. 3c and f) indicate the both the $Ni_3Se_4$ and CoSe show polyhedron morphologies and are homogeneously distributed on the silk-derived carbon fibers. The results of SEM-EDS elemental mapping indicate the existence of Ni, Co and Se with the ratio of about 1:1.19:1.55 for the $NiCoSe_{2-x}$/NC sample (Fig. S2 and Table 1).

The mushroom-like morphology of the vertical $NiCoSe_{2-x}$/NC nanorod was further confirmed by TEM characterization in Fig. 4a. The measured the length and the diameter of the nanorod is about 0.534 μm and 0.108 μm (Fig. S3), in good agreement with the SEM results. High resolution TEM images in Fig. 4b and c shows the nanorod has a core/shell structure. The thickness of the carbon shell is about 13.56 nm. The measured distance of the lattice fringe is 0.367 nm and 0.323 nm, corresponding to the (002) plane of graphitized carbon and the (100) plane of hexagonal $NiCoSe_{2-x}$. Besides, the lattice d-spacing in Fig. 4c and d is measured to be 0.216 nm and 0.285 nm, assigned to the (102) and (101) planes of the hexagonal phase $NiCoSe_{2-x}$, respectively. The selected-area electron diffraction (SAED) pattern image exhibits bright spots (Fig. 4e), suggesting the single crystallinity of the as-synthesized $NiCoSe_{2-x}$ rather than the mixed phase of CoSe and $Ni_3Se_4$. The patterns are assigned to the (100), (102) and (002) planes of hexagonal $NiCoSe_{2-x}$. The elemental composition was first analyzed by TEM-EDX elemental mapping of the selected area in Fig. 4a (green square). The results show the existence of Ni, Co and Se with the atomic ratio of about 1:1.01:1.63, as well as C and N (Fig. S4).

Scanning transmission electron microscopy (STEM) and EDX mapping were used to characterize the elements distribution