



# One-step chemical transformation synthesis of CoS<sub>2</sub> nanosheets on carbon cloth as a 3D flexible electrode for water oxidation

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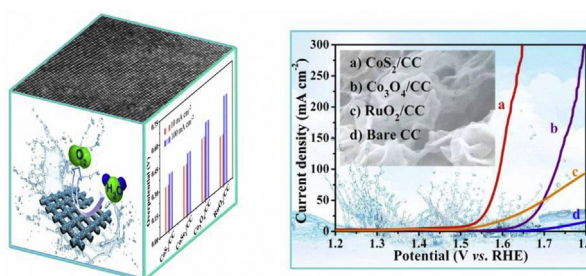
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## HIGHLIGHTS

- Co<sub>3</sub>O<sub>4</sub>/CC precursor was acquired through a facile route.
- CoS<sub>2</sub>/CC was synthesized by one-step chemical transformation strategy.
- CoS<sub>2</sub> nanosheets supported on CC possess good conductivity and large surface area.
- CoS<sub>2</sub>/CC as a 3D flexible electrode shows a sparkly OER performance in basic media.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Keywords:

Cobalt sulfide  
Nanosheets  
Electrocatalyst  
Oxygen evolution reaction

## ABSTRACT

Water electrolysis is an important way to gain pure hydrogen, while it is restricted by the sluggish kinetics of oxygen evolution reaction. To improve hydrogen production capability, it is critical to search for low-cost, earth-abundant, and superior catalytic activity materials as electrocatalysts for water oxidation. Herein, one-step chemical transformation strategy is utilized to synthesize cobalt sulfide nanosheets supported on the carbon cloth through the sulfuration process of the Co<sub>3</sub>O<sub>4</sub> precursor. The catalyst exposes abundant active sites and facilitates charge transfer, which is beneficial to water oxidation. In alkaline electrolyte, the catalyst as a non-noble metal electrode exhibits sparkly performance for water oxidation. To achieve current densities of 10 and 100 mA cm<sup>-2</sup>, the overpotentials as low as 291 and 364 mV are demanded, respectively. Moreover, cobalt sulfide nanosheets on the carbon cloth manifest a small Tafel slope of 69 mV dec<sup>-1</sup> and robust long-term durability. In addition, this one-step chemical transformation strategy can be utilized to synthesize cobalt selenide nanosheets on the carbon cloth, providing an orientation for developing other binder-free electrocatalysts for water oxidation.

## 1. Introduction

The depletion of carbon-based fuels and its negative influence on the global environment have stimulated increasing researchers to develop more advanced energy. Hydrogen, clean, renewable and high-energy, is considered as the perfect alternative to fossil fuels. Water electrolysis, cathodic hydrogen evolution reaction (HER) and anodic

oxygen evolution reaction (OER), is a facile, efficient, and attractive way to obtain highly pure hydrogen [1–4]. In general, it is easy to achieve the hydrogen evolution because it is just a two electron-transfer reaction. While the oxygen evolution, a four electron-proton coupled reaction, demands a large oxidation overpotential to overcome the high reaction barriers during the catalytic process [5–7]. More significantly, OER is also a core process associated with energy conversion and

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storage systems, including solar water-splitting devices, regenerative fuel cells, and metal-air batteries. Hence, it is still an arduous challenge for water electrolysis and other related energy systems on account of the dull dynamics of OER. Currently, ruthenium (Ru) and iridium (Ir) oxides are reported to be the state-of-the-art catalysts toward OER while the less reserves and high cost restrict their applications on a large scale. Moreover, it is proved that these noble metal catalysts can be easily oxidized and dissolved in electrolyte [8,9]. Therefore, it is critical to develop effective, robust, and cheap OER electrocatalysts. Recently, numbers of researches based on earth-abundant metals (Fe, Co, Ni), including their chalcogenides [10–13], phosphides [14–16], hydroxides [17–19], oxides [20–22], and phosphates [23–25], have demonstrated that they possess the brilliant OER performance. Although attractive achievements have been gained in pursuing the alternative materials, the efficient and low-cost OER materials are still restricted for extended periods of time.

Co-based compounds have superior catalytic activities due to their exceptional electronic configuration, which have attracted enormous attention to energy-related applications, such as OER [26–28], HER [29,30], batteries [31–33], supercapacitors [34], photovoltaics [35], and so on [36]. In particular, a series of Co-based chalcogenides have been illustrated to possess a superior catalytic performance toward water oxidation. For example, Hao et al. developed N-enriched CoS<sub>2</sub> catalyst, which required a low overpotential of 240 mV to achieve 10 mA cm<sup>-2</sup> for water oxidation in alkaline media [37]. Liu et al. prepared CoSe<sub>2</sub> microsphere electrocatalysts *via* one-step selenylation process, which showed remarkable OER catalytic activity with a Tafel slope of 79 mV dec<sup>-1</sup> and excellent stability [11]. Liu et al. synthesized CoS<sub>2</sub> nanosheets supported on Ti mesh by electrodeposition, which displayed the sparkly OER performance with a low overpotential of 430 mV for 100 mA cm<sup>-2</sup> [38]. These nanostructured Co-based chalcogenides may act as promising substitutes for the noble metal electrocatalysts toward OER. However, more effort is still demanded to enhance the electrocatalytic activity of Co-based chalcogenides for water oxidation.

Increasing the number of active sites by nanostructuring is an efficient strategy to improve the electrocatalytic performance for OER, and the surface morphology of Co-based chalcogenides plays a critical role in the catalytic performance [39]. Currently, two-dimension (2D) materials have gained extensive attention in various fields, especially in electrocatalytic application [40]. A series of 2D nanosheets, including CoS<sub>2</sub>, Co<sub>3</sub>S<sub>4</sub>, and CoSe<sub>2</sub>, performed superior OER properties than corresponding bulk materials [38,41,42]. The 2D materials possess superior merits with the larger surface area and better electroconductivity that can expose more active sites and accelerate charge transfer, which contributes to accelerate reaction kinetics for water oxidation [43]. Moreover, growing the catalyst on the conductive substrates (such as Ni foam, Ti mesh, Cu foam, carbon cloth, and so on) as the 3D flexible electrode is another confirmed efficient approach to improve the electrical conductivity [12,44–46]. More significantly, the Co-based chalcogenides directly supported on the current-collecting substrates not only avoid the negative effect of inactive binder, but also prevent the excessive aggregation of 2D nanosheets during the fabrication procedure of the flexible electrode [47].

By integrating the aforementioned design principles, we fabricate CoS<sub>2</sub> nanosheets firmly anchored on carbon cloth (CC) (CoS<sub>2</sub>/CC) using one-step convenient chemical transformation method *via* a low-temperature sulfuration of the Co<sub>3</sub>O<sub>4</sub>/CC precursor. It is noteworthy that CoS<sub>2</sub> 2D nanosheets can expose more catalytic active sites and facilitate electron transfer, which is more favorable for the enhancement of the OER performance. As expected, the CoS<sub>2</sub>/CC material is a highly sparkly catalyst for OER with a low overpotential, small Tafel slope, and robust durability under alkaline condition. It is highly expected that chemical transformation method could be expanded to prepare other 2D nanosheets anchored on CC.

## 2. Experimental

### 2.1. Materials and chemical reagents

Carbon cloth (CC) was purchased from CeTech Co., Ltd. (Taiwan, China). Nafion (5 wt%), cetyltrimethyl ammonium bromide (CTAB, AR), sodium borohydride (NaBH<sub>4</sub>, AR), selenium powder (Se, AR), and ruthenium oxide (RuO<sub>2</sub>) were supplied from Aladdin Industrial Co., Ltd. (Shanghai, China). Cobaltous sulfate heptahydrate (CoSO<sub>4</sub>·7H<sub>2</sub>O, AR) and sulfur powder (S, AR) were obtained from Chengdu Kelong Industrial Co., Ltd. (Chengdu, China). All chemical reagents were used directly without further treatment. The ultrapure water with a specific resistance of 18.2 MΩ cm was utilized through all the experiments.

### 2.2. Characterization

The morphological structures of samples were carried out using a field-emission scanning electron microscope (FESEM, INSPECT F50, FEI, USA) and a transmission electron microscope (TEM, G2 F20, FEI, USA). The elemental mapping analysis was performed using energy dispersive spectroscopy (EDS, X-MAX50, Oxford, UK). X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo, USA) was used to analyze the chemical compositions of the samples. X-ray diffraction (XRD, Bruker, Germany) patterns were carried out from 10° to 80° with Cu Kα source radiation. The N<sub>2</sub> adsorption-desorption of CoS<sub>2</sub> powder scraped off from the surface of the CoS<sub>2</sub>/CC electrode was carried out using Brunauer-Emmett-Teller (BET) measurement (Micromeritics, ASAP2460, USA). The Raman spectrum was acquired on a Raman spectrometer (Renishaw, InVia, UK) from 100 to 1000 cm<sup>-1</sup> with 532 nm laser under ambient conditions. The loading mass was determined on a coupled plasma-optical emission spectrophotometer (ICP-AES, Agilent, USA).

### 2.3. Fabrication of the Co<sub>3</sub>O<sub>4</sub>/CC precursor

Commercial carbon cloth (CC) (1.5 cm × 1.0 cm) was immersed with concentrated HNO<sub>3</sub>, ethanol, and ultrapure water for each 10 min under ultrasonication, thus the clean CC was obtained. The Co<sub>3</sub>O<sub>4</sub>/CC precursor was synthesized according to the reported literature with some minor modification [48,49]. CoSO<sub>4</sub>·7H<sub>2</sub>O (562 mg) and CTAB (500 mg) were dissolved in 25 mL ultrapure water under magnetic stirring, which was named as solution A. After stirring for 10 min, CC was put into solution A followed by continuously stirring for 20 min. NaBH<sub>4</sub> (100 mg) was dissolved in 10 mL ultrapure water, which was designated as solution B. Next, solution B was dropwise dipped into solution A. After reacting for 5 min, CC was washed with ethanol for 5 times and dried at room temperature. Finally, the above sample was annealed in air at 450 °C for 2 h to obtain the Co<sub>3</sub>O<sub>4</sub>/CC precursor for further work.

### 2.4. Synthesis of the CoS<sub>2</sub>/CC and CoSe<sub>2</sub>/CC catalysts

To obtain the CoS<sub>2</sub>/CC catalyst, a low-temperature sulfuration method was employed in this system. In detail, Co<sub>3</sub>O<sub>4</sub>/CC and sulfur powder were placed in the backward position and upstream site of porcelain boat, respectively. During the sulfuration process, the temperature of the tube furnace was quickly elevated to 450 °C in 30 min, and maintained for 120 min in N<sub>2</sub> atmosphere. The CoS<sub>2</sub>/CC catalyst was obtained after cooling down naturally. The loading mass density of CoS<sub>2</sub> catalyst on the CC was ~0.98 mg cm<sup>-2</sup>.

The synthetic process of CoSe<sub>2</sub>/CC catalyst is similar to the fabrication of CoS<sub>2</sub>/CC, except that sulfur powder was replaced by selenium powder.

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