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# Novel $\text{Co}_x\text{S}_y/\text{WS}_2$ nanosheets supported on carbon cloth as efficient electrocatalyst for hydrogen evolution reaction

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## ABSTRACT

To maximum the activity of transition metal sulfides for hydrogen evolution reaction (HER), two strategies usually have been adopted including designing unique nanostructures and integrating other metal element. Herein,  $\text{Co}_x\text{S}_y/\text{WS}_2$  nanosheets supported on carbon cloth ( $\text{Co}_x\text{S}_y/\text{WS}_2/\text{CC}$ ) have been fabricated via a facile hydrothermal process. The cross-linked structures composed of  $\text{Co}_x\text{S}_y/\text{WS}_2$  nanosheets uniformly cover on the surface of CC, which may expose abundant active sites for HER and accelerate charge transfer rate. The molar ratio of  $\text{Co}_x\text{S}_y$ -incorporating has been investigated in detail. The molar ratio of  $\text{W}/\text{Co} = 1/3$  (noted as  $\text{Co}_x\text{S}_y/\text{WS}_2/\text{CC}-3$ ) has been proved to have unique spherical  $\text{Co}_x\text{S}_y/\text{WS}_2$  nanostructure, which may further expose more active sites for HER. Electrochemical measurements demonstrate that  $\text{Co}_x\text{S}_y$ -incorporating can enhance HER activity and conductivity compared with  $\text{WS}_2/\text{CC}$ . In addition,  $\text{Co}_x\text{S}_y/\text{WS}_2/\text{CC}-3$  exhibits the best HER activity, smallest charge transfer resistance and excellent stability than the counterparts, implying that the degree of  $\text{Co}_x\text{S}_y$ -incorporating may impact the HER activity of  $\text{WS}_2$ . The mechanisms of  $\text{Co}_x\text{S}_y$ -incorporating on enhancing HER activity of  $\text{WS}_2$  have been discussed. It may offer a promising way to design transition metal sulfides-based electrocatalysts for HER by non-precious metal incorporating.

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## Introduction

Electrochemical water splitting to produce  $\text{H}_2$  and  $\text{O}_2$  has been acknowledged as efficient and clean route to provide sustainable hydrogen energy as an ideal energy carrier to replace fossil

fuels [1–5]. In recent years, continuous researches have been conducted to design effective non-precious metal-based materials for HER alternative to precious Pt-based catalysts [6–10]. Transition metal sulfides (TMDs) have emerged as attractive candidates and  $\text{MoS}_2$  has been regarded as representative one [8,11–13]. As a typical earth-abundant TMD material,  $\text{WS}_2$  is

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also attractive as HER electrocatalyst [12,13]. However, the limited surface area with few active sites on edges, semi-conductivity and aggregation of two dimensional (2D) materials can inhibit the further enhancement of HER activity of WS<sub>2</sub>.

Currently, many researches have focused on tackling these issues of WS<sub>2</sub>, such as metallic nanosheets [14], nanoribbons [15], reduced graphene oxides hybrids [16] or N-incorporated nanosheets [17]. However, more novel strategies are still required. On basis of theoretical calculations over past few years, the chemical-inert basal plane of TMDs can be activated by metal doping [18–20]. It has been proved that Co doping in MoS<sub>2</sub> can intrigue the intrinsic catalytic activity of MoS<sub>2</sub> by generating more active sites as well as improving the conductivity of semi-conductive MoS<sub>2</sub> [21–25]. However, few studies have ever focused on application of Co<sub>x</sub>S<sub>y</sub>-incorporating on WS<sub>2</sub>.

Very recently, carbon cloth (CC) has been emerged as ideal substrate with excellent conductivity, good flexibility and chemical stability to satisfy harsh industrial conditions [26,27]. Particularly, the unique three-dimensional (3D) framework of CC cannot only provide abundant pathways for faster electron transfer process, but also contribute to better dispersion of active components and enhanced catalytic efficiency [28,29]. Therefore, it is promising to utilize CC as support to integrate 2D TMD materials and form hierarchical 3D electrodes for hydrogen production.

Herein, we report that a facile hydrothermal synthesis has been used to prepare Co<sub>x</sub>S<sub>y</sub>-incorporated WS<sub>2</sub> nanosheets supported on carbon cloth (Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC). For comparison, the pure WS<sub>2</sub> nanosheets based on CC (Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC) has also been fabricated. XRD and XPS show the formation of Co<sub>x</sub>S<sub>y</sub>-incorporated WS<sub>2</sub>/CC. EDX spectra and HR-TEM image further confirm that the hybrid crystal of Co<sub>x</sub>S<sub>y</sub> has been successfully incorporated into WS<sub>2</sub> nanosheets. Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub> nanosheets show cross-linked structure and uniformly cover on the surface of CC, which may avoid severe aggregation, facilitate charge transport and expose much more active sites for HER. The degree of Co<sub>x</sub>S<sub>y</sub>-incorporating has also been investigated by changing molar ratio of W/Co in precursor (low degree: 6/1, 3/1; middle degree 1/3; high degree: 1/6) and marked by Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-1, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-2, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-4. The middle degree of Co<sub>x</sub>S<sub>y</sub>-incorporating of Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3 shows unique sphere-like structure of Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub> nanosheets, which may further enhance the surface area to provide more catalytic active sites for HER. Electrochemical measurements show that the HER performances of Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC is better than that of WS<sub>2</sub>/CC, demonstrating that Co<sub>x</sub>S<sub>y</sub>-incorporating can intrigue the intrinsic HER activity and improve the conductivity of WS<sub>2</sub>. In addition, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3 exhibits the best HER activity, smallest charge transfer impedance and excellent stability than other Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC, suggesting that the middle degree of Co<sub>x</sub>S<sub>y</sub>-incorporating may lead to maximum HER activity. The non-precious metal incorporating may offer a novel strategy to design TMD-based electrocatalysts for hydrogen production.

## Experimental

Prior to the typical experiment, carbon cloth (CC, thickness: 0.35 mm, surface density: 189 g m<sup>-2</sup>) was treated in acid,

acetone and ethanol under sonication for 30 min consecutively. Then it was under hydrophilic treatment by concentrated nitric acid (20 mL) in a Teflon-lined stainless steel autoclave at 80 °C for 6 h, followed by washing with water and dried at vacuum of 40 °C.

In a typical synthesis, oxalic acid (1.20 g), thioacetamide (1.80 g) and ammonium metatungstate (0.17 mg) were uniformly mixed with deionized water (30 mL). Then the solution was transferred to Teflon-lined stainless steel autoclave added with pre-treated CC and maintained at 200 °C for 24 h. The final product were rinsed with water and dried in vacuum, which was marked by WS<sub>2</sub>/CC. In order to investigate the degree of Co<sub>x</sub>S<sub>y</sub>-incorporating, cobalt acetate was added into the mixture by changing molar ratio of W/Co (low degree: 6/1, 3/1; middle degree 1/3; high degree: 1/6). The corresponding products were marked by Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-1, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-2, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-4, respectively. For comparison, the Co<sub>x</sub>S<sub>y</sub>/CC was also fabricated under the same condition without W precursor (ammonium metatungstate). The catalyst loading of Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-1, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-2, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3, Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-4, Co<sub>x</sub>S<sub>y</sub>/CC and WS<sub>2</sub>/CC is 12.8 mg/cm<sup>2</sup>, 15.3 mg/cm<sup>2</sup>, 13.6 mg/cm<sup>2</sup>, 3.9 mg/cm<sup>2</sup>, 1.1 mg/cm<sup>2</sup> and 3 mg/cm<sup>2</sup>, respectively.

X-ray diffraction (XRD, X'Pert PRO MPD, Cu KR) was conducted with 2θ range from 5° to 70°. X-ray photoelectron spectrum (XPS, VG ESCALAB MK II, Al Ka of 1486.6 eV) was performed to identify the valence states of main elements of Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3. Scanning electron microscopy (SEM, Hitachi, S-4800) was utilized to investigate the morphology of all samples. X-ray fluorescence elemental analysis (EDX) was undertaken on a representative area of the samples. Transmission electron microscopy (TEM, FEI Tecnai G2) and high-resolution transmission electron microscopy (HR-TEM) were used to investigate the crystal structure of Co/WS<sub>2</sub>/CC-3.

Electrochemical measurements were carried out in a standard three-electrode configuration (Gamry Reference 600 Instruments, USA). All as-synthesized samples were used as working electrodes, with platinum gauze as counter electrode and an Ag/AgCl as reference. 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as electrolyte (degassed by N<sub>2</sub> in advance). Linear sweep voltammetry (LSV) was performed with a scan rate of 5 mV s<sup>-1</sup> (with iR correction). Electrochemical impedance spectroscopy (EIS) measurements were employed at -0.32 V (vs. Ag/AgCl) with frequency from 10<sup>5</sup> Hz to 10<sup>-2</sup> Hz and an AC voltage of 5 mV. The long-term stability of Co<sub>x</sub>S<sub>y</sub>/WS<sub>2</sub>/CC-3 was evaluated by chronoamperometry under -0.34 V (vs. Ag/AgCl) in 10<sup>4</sup> s. The potentials conversion from vs. Ag/AgCl to vs. RHE is as follows:

$$\text{pH (0.5 M H}_2\text{SO}_4) = 0.16$$

$$E (\text{Ag/AgCl (saturated KCl)}) \text{ vs. } E (\text{RHE}) = 0.197 \text{ V}$$

$$E (\text{vs. RHE}) = E (\text{vs. Ag/AgCl}) + 0.197 \text{ V} + (0.0591 \text{ V}) \text{ pH} = E (\text{vs. SCE}) + 0.21 \text{ V}$$

$$\text{Overpotential } \eta = E (\text{vs. RHE}) - 1.23 \text{ V} = E (\text{vs. SCE}) - 1.02 \text{ V}$$

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