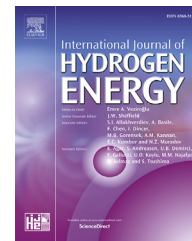




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# Cellulose nanocrystals (CNC) derived Mo<sub>2</sub>C@sulfur-doped carbon aerogels for hydrogen evolution

Xuelin Kong<sup>a,b</sup>, Shuai Chen<sup>d</sup>, Yihui Zou<sup>a</sup>, Shaoyi Lyu<sup>b</sup>, Xilin She<sup>a</sup>, Yun Lu<sup>b,e,\*</sup>, Jin Sun<sup>a</sup>, Huawei Zhang<sup>f</sup>, Dongjiang Yang<sup>a,c,\*\*</sup>

<sup>a</sup> Collaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, Institute of Marine Biobased Materials, School of Environmental Science and Engineering, Qingdao University, Qingdao, 266071, PR China

<sup>b</sup> Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing, 100091, PR China

<sup>c</sup> Queensland Micro- and Nanotechnology Centre, School of Natural Sciences, Griffith University, Nathan, Brisbane, QLD, 4111, Australia

<sup>d</sup> State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Science, Taiyuan, 030001, PR China

<sup>e</sup> University of Natural Resources and Life Sciences Vienna, Department of Chemistry, Division of Chemistry of Renewable Resources, Konrad-Lorenz-Strasse 24, A-3430, Tulln, Austria

<sup>f</sup> College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, 266590, PR China

## ARTICLE INFO

### Article history:

Received 29 November 2017

Received in revised form

10 January 2018

Accepted 13 January 2018

Available online xxx

### Keywords:

Cellulose nanocrystals

Sulfur doping

Aerogels

Mo<sub>2</sub>C

HER

## ABSTRACT

Hydrogen evolution reaction (HER), is considered as an ideal alternative approaches to settle the energy crisis. Therefore, we need to explore efficient and stable non-Pt-based electrocatalysts for hydrogen production from water electrolysis. In this work, S-doped ultra-fine molybdenum carbide anchored on cellulose nanocrystals (CNC) derived carbon composite aerogels (Mo<sub>2</sub>C@S-CA) were synthesized for HER by a simple one-step carbonization method, utilizing inorganic-organic hybrid ammonium molybdate/CNC (AMM/CNC) as precursor. The obtained Mo<sub>2</sub>C@S-CA aerogels can not only provide plenty of active sites, but also accelerate the hydrogen release from the reaction surface of the electrocatalysts. The as-synthesized catalysts exhibit superior HER activity with a small overpotential value of 176 mV vs. RHE at 10 mA cm<sup>-2</sup> and excellent long-term stability after 10,000 cycles in 0.5 M H<sub>2</sub>SO<sub>4</sub>. These superb properties make the catalyst be a promising electrocatalyst for the HER. This work highlights the importance of biomass-derived multifunctional value-added composite aerogels in enhancing the electrolysis of water.

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\* Corresponding author. Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing, 100091, PR China.

\*\* Corresponding author. Collaborative Innovation Center for Marine Biomass Fibers, Materials and Textiles of Shandong Province, Institute of Marine Biobased Materials, School of Environmental Science and Engineering, Qingdao University, Qingdao, 266071, PR China.

E-mail addresses: [y.lu@criwi.org.cn](mailto:y.lu@criwi.org.cn) (Y. Lu), [d.yang@qdu.edu.cn](mailto:d.yang@qdu.edu.cn) (D. Yang).

<https://doi.org/10.1016/j.ijhydene.2018.01.072>

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## Introduction

Currently, hydrogen production via electrochemical hydrolysis has drawn substantial focus. Because hydrogen ( $H_2$ ) is a renewable, environmentally carbon-free fuel, settling the twin matters of consumption of conventional fossil fuel and greenhouse gas ( $CO_2$ ) emissions [1–4]. There is no doubt that hydrogen is widely believed to be a promising candidate for taking the place of traditional petroleum fuels in the future [2,5]. Though, Pt-based noble metals catalysts show the superb catalytic activity for hydrogen evolution reaction (HER) [6]. Their expensive price and deficiency limit scalable industrial applications of Pt-based electrocatalysts [7,8]. It is urgent to find cheap and sustainable catalysts to take the place of precious metal materials for HER application.

Recently, a wide variety of 3d transition metals (TMs) and derivative components have been investigated and developed intensely.  $WS_2$ ,  $WO_2$ ,  $MoO_2$ ,  $MoB$ ,  $MoP$ ,  $MoS_2$ ,  $MoSe_2$ , and  $Mo_2C$  have been exploited as promising candidates for Pt-based catalysts [9–13]. Among the above catalysts,  $Mo_2C$  has attracted considerable attention owing to their Pt-like characteristics. To further improve the HER performance,  $Mo_2C$  composites were inlaid on conductive nanocarbon substrates, including graphene, carbon nanotubes (CNTs) and carbon black [14–18], which can not only fabricate a great deal of active sites but also prevent Mo-based compounds from aggregating [19]. However, the complicated manufacturing technologies, high costs precursors, especially non-renewability restrict the large-scale industrialization of these conductive nanocarbon supports [20–24].

Cellulose nanocrystals (CNC) have been extracted from plant cell wall by a simple acid (sulfuric acid) hydrolysis treatment with rice-like shape and high crystallinity (50–90%) [25]. And a reactive abundant sulfate ester side groups that facilitate to achieve surface functionalization of CNC, which have electrostatic attraction, coordination, and chelation with metal ions [26,27]. Furthermore, the incorporation of S not only generates plenty of exposed active sites, but also enhances the utilization efficiency of active sites to achieve high HER activity [28,29]. In this work, we use CNC as an excellent precursor for producing S-doped non-noble-metal HER electrocatalyst ( $Mo_2C@S-CA$ ) via a foolproof strategy. The strong electronic interaction between  $Mo_2C@S-CA$  networks and S atom boosts the catalytic activity [30,31]. In addition, benefiting from the 3D robust nanostructure carbon skeleton, as well as the ultrafine  $Mo_2C$  NPs, the as-prepared  $Mo_2C@S-CA$  exhibit excellent and stable electrocatalytic activity for HER (overpotential value of 176 mV at 10 mA  $cm^{-2}$  vs. RHE, good stability over 8 h during operation in 0.5 M  $H_2SO_4$ ). This work represents a low-cost green electrocatalysts with excellent performance and has provided the inspiration of the utilization of abundant biomass-derived green energy [32].

## Experimental

### Material and methods

CNC (diameter 4–7 nm, ~180 nm in length) and (2,2,6,6-tetramethylpiperidinoxy, free radical) TEMPO-mediated

oxidation CNC (TO-CNC, diameter 4–7 nm, ~160 nm in length) were lab-made from Research Institute of Wood Industry, Chinese Academy of Forestry. Ammonium molybdate ( $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ ) was purchased from Aladin Co. Nafion (5 wt%) was purchased from Sigma-Aldrich.

### Materials synthesis

Typically, 0.03089 g of ammonium molybdate was dissolved in 25 ml of CNC aqueous dispersion under magnetic stirring at room temperature for approximately 6 h until a viscous and homogeneous solution was obtained. Then the mixture solution was dispersed in distilled water, containing 0.25 wt % specimen in 1000 ml water slurry. The subsequent sonication was operated under a common ultrasonic instrument (JY99-IIID, Ningbo Scientz Biotechnology Co., Ltd., China) to prevent the biomass suspensions from flocculating into precipitate. The ultrasonic treatment was carried out in an ice/water bath. After that, the suspensions were transferred into the dialysis tubing cellulose membrane (Sigma-Aldrich), which was conducted solvent-exchange with *tert*-butyl alcohol for 24 h, the wet cellulose hybrid was poured into some plastic bottles followed by freezing at  $-78$  °C and lyophilized via a freeze-drying to assemble 3D aerogels. The as-synthesized samples were heated from room temperature to 325 °C for 1 h in the  $N_2$  flow (ramp rate: 5 °C  $min^{-1}$ ), finally the stabilized samples were carbonized at 800 °C for 1 h to obtain  $Mo_2C@S-CA$  aerogels (ramp rate: 2 °C  $min^{-1}$ ).  $Mo_2C@Carbon$  Aerogels ( $Mo_2C@CA$ ) samples were prepared by the above-mentioned process for comparison utilizing TO-CNC (cellulose  $I_\beta$ , no sulfate esters side groups, similar morphology with CNC) as the starting material.

### Structural characterization

The composition of the as-prepared materials were investigated by X-ray diffraction (XRD, Bruker D8 Adv, Germany). The microtopography of the products were characterized by field-emission scanning electron microscope (FETEM, Tecnai G2 F20, USA) and field-emission transmission electron microscope (FETEM, FEI Tecnai G20, USA). The high-resolution transmission electron microscope (HRTEM, FEI Tecnai G20, USA) and X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA) were used to study the composition of the composite catalysts. Specific surface area pore properties were measured through the Brunauer-Emmett-Teller method (Auto Chem II 2920, USA). Raman spectrum was obtained on a Raman spectrometer (Renishaw 1000 NR) with 633 nm excitation line.

### Preparation of the electrodes

3 mg as-synthesized catalysts were dispersed in 525  $\mu$ l ink, including 250  $\mu$ l deionized water, 25  $\mu$ l 5 wt% nafion, and 250  $\mu$ l ethanol. After ultrasonication for about 0.5 h, 6  $\mu$ l of the catalysts mixture ink was pipetted on the glassy carbon electrode (GCE,  $\Phi = 3$  mm) with the loading of 0.48  $mg/cm^2$ , then fully dried in the air.

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