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Full Length Article

# Facile synthesis of mesoporous $WS_2$ for water oxidation

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ABSTRACT

Mesoporous transition metal disulfide $WS_2$ are facilely grown on the Ni foam substrate with 3D nanoflowers morphology and large surface area. The as-obtained $WS_2$/Ni exhibit high performances for water oxidation in 1.0 M NaOH solution, which are much superior to those of the state-of-the-art $RuO_2$/Ni and previously reported oxygen evolution catalysts. The $WS_2$/Ni electrocatalyst manifests the high performance, displaying a very low overpotential of 0.335 V at 20.0 mA $cm^{-2}$ and much improved durability. The facile and controllable synthesis is promising for the rational design of electrocatalyst for the renewable energy conversion.

## 1. Introduction

Electrocatalytic water oxidation is a very important reaction in electrochemistry and it is expected to play a crucial role in the clean energy conversion [1–3]. The thermodynamic potential of 1.23 V versus the reversible hydrogen electrode involves the transfer of four electrons and requires high energy input to overcome the high energy barrier [4–6]. So far, various electrodes (e.g., Ni, $RuO_2$, $IrO_2$, perovskites, and layered double hydroxides) have been frequently used were mainly based on and mixed metal oxide system [7–10]. $RuO_2$ is known to be the most active metal oxide for water oxidation according to the theoretical "volcano plot" [3,4]. The high activity of $RuO_2$ for OER has been ascribed to its optimal binding energy to the reaction intermediates, and relatively low reduction/oxidation potentials [7,11]. However, Ru metal suffers from the limited existence, instability and corrosion under oxygen evolution conditions [12–14]. Therefore, it is imperative to develop alternative electrode materials composed of widely available elements with the enhanced electrochemical performance and stability for water oxidation.

Layered chalcogenide metal disulfides (e.g., $MoS_2$ or $WS_2$) have been studied as high-performance electrode materials for water splitting [15–17] and energy storage [16] because of its better electrical conductivity, its-Pt like behavior and higher electrochemical activity [15,18]. Different nanostructured metal disulfides have been designed to increase the number of exposed active edge sites, showing much improved activity. However, these materials still face the challenges of poor electrical conductivity, high overpotential, difficulty in the oxidation of water at high current density and poor durability. Moreover, some synthesis procedures of the materials are still time-consuming, costly, and difficult in controlling the morphology and the composition [17,23]. To overcome these issues, it is ideal to directly grow metal disulfides to the class of conductive and porous substrates. Zhang et al. conducted a pioneered work and developed an epoxide-assisted sol-gel method for the synthesis of $Ni_3S_2$ nanorod with good performances in alkaline solution [19]. Recently, we grew the unregularly $MoS_2$ microsphere on Ni foam and it displayed much better performance and stability than the commercial $RuO_2$ [20]. Nevertheless, the structure of metal sulfides is still less controllable and there is still large space to improve the performance. Herein, we report a simple method to controllably grow mesoporous transition metal disulfide $WS_2$ nanoflower arrays on the 3D conductive Ni foam as binder-free and high-performance electrode materials for water oxidation.

## 2. Experimental section

### 2.1. Synthesis of $WS_2$ on Ni foam

The chemicals are purchased from Sigma-Aldrich and American Elements. The source and purity are depicted in the Sporting Information. Polycrystalline $WS_2$ were fabricated using solid state method [16,17]. W (99.9%) and S (99.999%) were mixed through the appropriate stoichiometric ratios at the stirring rate of 1200 rpm for 12 h, and then heated in sealed evacuated silica tubes at a rate of 1 °C $min^{-1}$ to 600 °C from room temperature and kept at 600 °C for 120 h. After that, the growth of $WS_2$ nanoflowers on the clean Ni foam (the treatment details are described in Supporting Information) was

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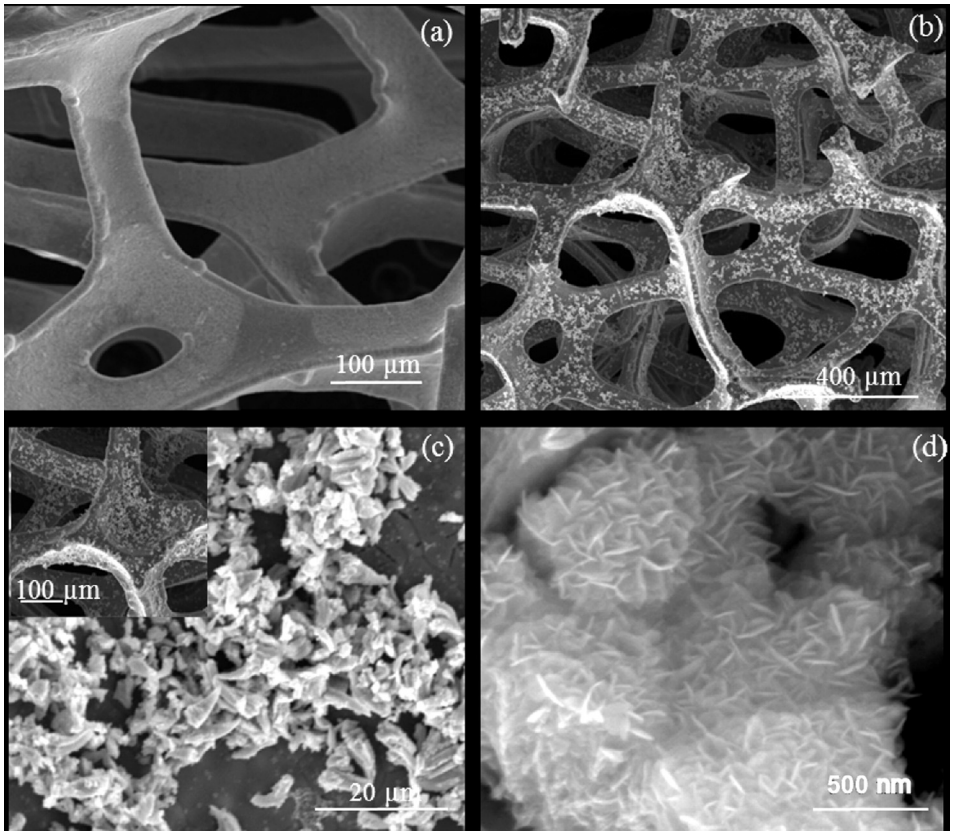


**Fig. 1.** Scanning electron microscopy (SEM) images of the treated Ni foam substrate (a), $WS_2$ assembled on the Ni foam (b–d, the Inset in Fig. 1c is the large area of the as-obtained $WS_2$ on Ni foam).

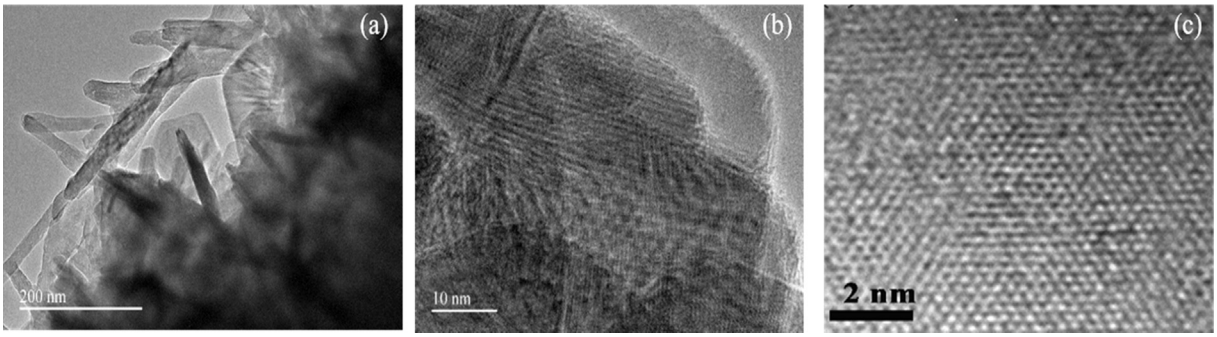


**Fig. 2.** Transmission electron microscopy (TEM) and high-magnification TEM images of the $WS_2$ powders scratched down from the Ni foam substrate.

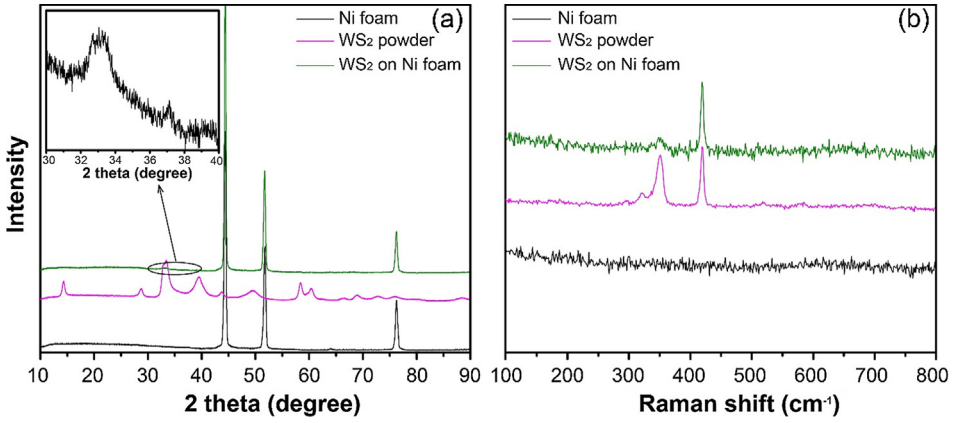


**Fig. 3.** XRD (a) and Raman (b) analysis of the Ni foam substrate, the $WS_2$ powder, the as-obtained $WS_2$/Ni electrode.