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# Oxygen vacancy improves the hydrogen evolution reaction property of $WO_{3-x}$ nanosheets

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ABSTRACT

$WO_{3-x}$ nanosheets are at the first time reported on Ni foam (NF) directly without the binder. Due to low electron conductivity of $WO_{3-x}$, NF as the substitute is a better choice to improve performances of $WO_{3-x}$ nanosheets electrodes. On the other hand, $WO_{3-x}$ with unsaturated valence annealed at 400 °C in $Ar/H_2$ can increase the defect and improve the performances of hydrogen evolution reaction (HER). As catalyst for HER, $WO_{3-x}$/NF exhibits better catalytic activity and stability than $WO_3$/NF with overpotentials of 175 mV and 260 mV at the current densities of 10 mA $cm^{-2}$ and 50 mA $cm^{-2}$, respectively. In addition, $WO_{3-x}$/NF has superior durability and stability for 105 h in the long-term electrochemical process. This study provides a new direction in the design and development of transition metal oxides (TMOs) as high activity HER catalysts for practical applications.



## 1. Introduction

With the increase of energy consumption and environmental problems, it is imperative to find low-cost, large-scale production and environmentally friendly energy sources [1–3]. As we all know, Hydrogen energy is the most potential for development of the clean energy [4–6]. Electrolytic water is an important method to produce hydrogen, but HER without effective catalysts has high overpotentials and low reaction kinetics that seriously restricts its development [7,8]. Therefore, the development of HER catalysts which are highly efficient, noble-metal-free and durable to produce hydrogen is the key factor for large-scale application of hydrogen energy.

As reported, Shen et al. has prepared $MoO_2$ nanoflowers with a overpotential of ≈ 55 mV at a current density of 10 mA $cm^{-2}$, indicating the catalyst has an excellent HER electrocatalytic property and durability [9]. Other related reports have also appeared, such as NiO [10,11] and $Co_3O_4$ [12,13]. These results can be well demonstrated that transition metal oxides (TMOs) can be the attractive electrocatalyst candidates due to their diversity and potential stability [14]. At the same time, according to the "volcano" relation model [15], TMOs show high promise as good catalysts, such as $WO_{3-x}$ [16–18]. On the one hand, W and Mo atoms belong to the same group, and their oxides have the same distorted rutile crystal structure [9,19,20]. So they should have the similar catalytic activity. On the other hand, Wu et al. has reported $WO_2$-carbon mesoporous nanowires with a superior performance for HER [21]. Therefore, $WO_{3-x}$ as catalysts for HER is feasible.

However, due to the low electron conductivity [22,23], most of TMOs often form a Schottky barrier at the interface of catalyst–support electrode and catalyst–electrolyte leading to a higher overpotential [24], so it is necessary to develop $WO_{3-x}$ with high electron conductivity. NF with 3D frame structures as conductive substrate is a good choice to improve the matter. As we all know, there have been no previous reports of $WO_{3-x}$ nanostructures grown directly on 3D NF through simple, inexpensive hydrothermal approach.

Herein, we present our recent achievement that $WO_{3-x}$ nanosheets have grown on NF directly without the binder. As catalyst for HER, it shows a good durability and stability, which only needs overpotential of about 175 mV at the current density of 10 mA $cm^{-2}$.

## 2. Experimental section

### 2.1. Synthesis of $WO_{3-x}$ nanosheets

NF was cleaned by ultra-sonication with ethanol and deionized water for several times, respectively. 0.5 g ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40} \bullet XH_2O$) was dissolved in 35 mL deionized water, and the mixture was stirred to obtain a homogeneous solution at room temperature. Next the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave, and the already processed NF was placed vertically in the autoclave. Then

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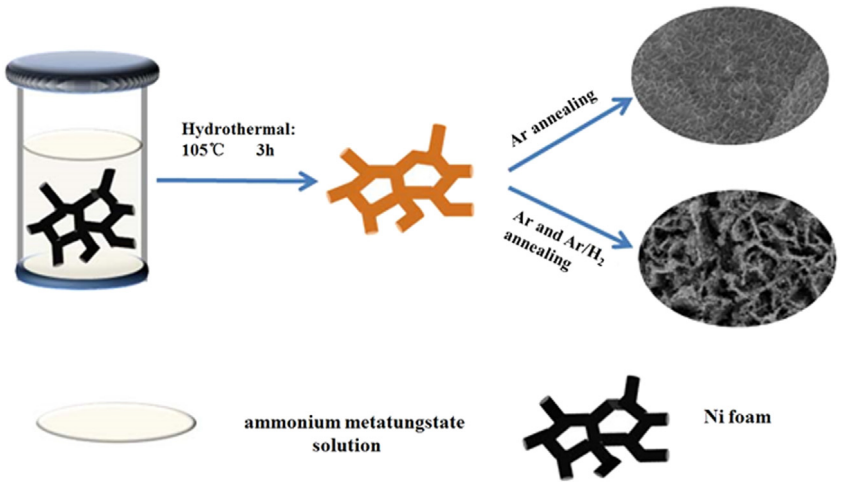


**Fig. 1.** The experimental synthetic steps of $WO_3$ and $WO_{3-x}$ nanosheets on nickel foam directly.

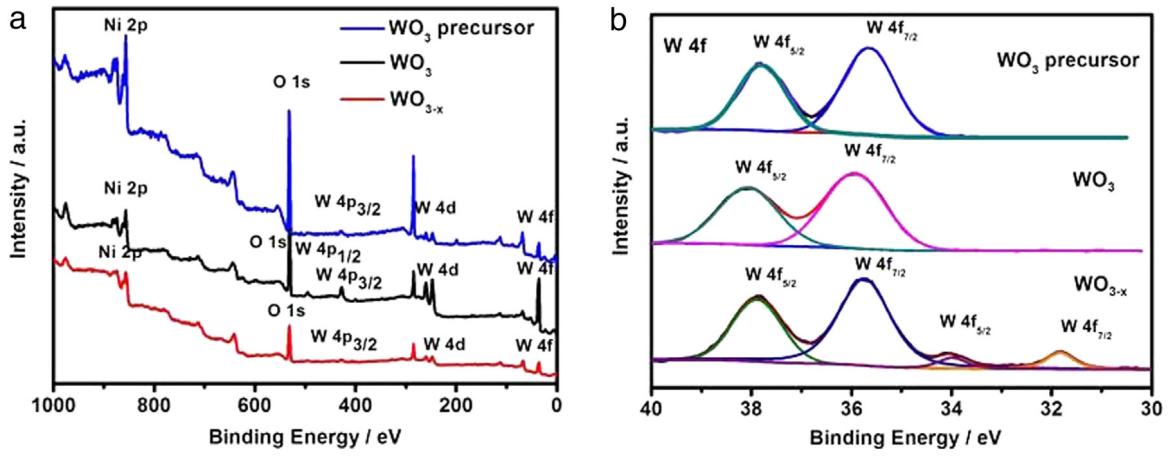


**Fig. 2.** XPS spectra of (a) Survey scan curves for $WO_3$/NF precursor, $WO_3$/NF and $WO_{3-x}$/NF. (b) W 4f peaks for $WO_3$/NF precursor, $WO_3$/NF and $WO_{3-x}$/NF.

the autoclave was put into the oven and maintained at 105 °C for 3 h. After the reaction, the NF with precursor was washed with deionized water and ethanol for several times and dried in vacuum. Finally the NF with precursor was annealed in Ar at 350 °C for 2 h and then in $Ar/H_2$ at 400 °C for 2 h.

### 2.2. Characterizations

The morphology features of the samples were observed by scanning electron microscope (SEM, Hitachi S-4800, 5 kV). Transmission electron microscopy (TEM) was carried out by a HITACHI HT7700 microscope. The samples were also analyzed by using X-ray photoelectron spectroscopy (XPS, SSI S-probe spectrometer).

### 2.3. Electrochemical measurements

Using a typical three-electrode setup to conduct the HER electrochemical measurements with $WO_3$/NF and $WO_{3-x}$/NF (1 × 1 $cm^{-2}$ about 0.5 mg), an Ag/AgCl electrode as the reference electrode, a Pt/graphite electrode as the counter electrode, respectively. Steady-state potential polarization curves were tested in 1 M KOH solution at 20 °C. Cyclic voltammetry (CV) cycle measurement was measured in 1 M KOH solution at a scanning rate of 50 mV $s^{-1}$ and linear sweep voltammetry (LSV) was conducted at a scanning rate of 5 mV $s^{-1}$. The accelerated degradation measurements were measured by conducting cyclic voltammetric (CV) sweeps between −1 and −1.2 V with a scanning rate of 50 mV $s^{-1}$ for HER in 1 M KOH at 20 °C.

## 3. Results and discussion

In order to elaborate the $WO_{3-x}$ nanosheets, the schematic illustration is provided, as shown in Fig. 1. Firstly, $(NH_4)_6H_2W_{12}O_{40}\bullet XH_2O$ as the tungsten source was put into deionized water to form the homogeneous solution. After hydrothermal reaction for 3 h, the surface of NF was covered with a thin layer of nanosheets. So the $WO_3$ precursor nanosheets were synthetized by directly growing on NF. With subsequent annealing at 350 °C in Ar for 2 h, the precursor converted into $WO_3$ nanosheets. Finally, $WO_3$ nanosheets/NF was annealed in $Ar/H_2$ at 400 °C for 2 h, and the $WO_{3-x}$ nanosheets were obtained.

It is necessary to confirm components at different steps, but the peak of NF by XRD is too much intensity to detect $WO_3$. So XPS may be a better mean to characterize the products in Fig. 2. The low-resolution XPS spectra (Fig. 2(a)) of the samples confirm the presence of W, O. In Fig. 2(b), two different peaks of the samples before annealing and annealed in Ar correspond to W $4f_{7/2}$ and W $4f_{5/2}$, respectively. These values are consistent with the $W^{6+}$ state in oxides [25–27]. So it indicates that the products before annealing and annealed in Ar are $WO_3$. After annealing in $Ar/H_2$, the two other peaks except above peaks are observed at about 33.9 and 31.5 eV, which are in accordance with $W^{5+}$ and

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