WO$_{3-x}$ Nanoplates Grown on Carbon Nanofibers for an Efficient Electrocatalytic Hydrogen Evolution Reaction

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ABSTRACT: The search for non-noble metal catalysts with high activity for the hydrogen evolution reaction (HER) is crucial for efficient hydrogen production at low cost and on a large scale. Herein, we report a novel WO$_{3-x}$ catalyst synthesized on carbon nanofiber mats (CFMs) by electrospinning and followed by a carbonization process in a tubal furnace. The morphology and composition of the catalysts were tailored via a simple method, and the hybrid catalyst mats were used directly as cathodes to investigate their HER performance. Notably, the as-prepared catalysts exhibit substantially enhanced activity for the HER, demonstrating a small overpotential, a high exchange current density, and a large cathodic current density. The remarkable electrocatalytic performances result from the poor crystallinity of WO$_{3-x}$, the high electrical conductivity of WO$_{3-x}$, and the use of electrospun CNFs. The present work outlines a straightforward approach for the synthesis of transition metal oxide (TMO)-based carbon nanofiber mats with promising applications for the HER.

KEYWORDS: two-dimension, carbon nanofibers, electrocatalysis, hydrogen evolution, WO$_{3-x}$

1. INTRODUCTION

As a green fuel of the future, hydrogen has the potential to become an exceptional substitute for traditional fossil fuels. As is well-known, water electrolysis is an essential strategy to generate hydrogen. To accomplish the efficient electrochemical splitting of water for various applications, active electrochemical catalysts for the hydrogen evolution reaction (HER) are crucial. To date, various catalysts have been explored for such applications. Although some precious metals (e.g., platinum) have been shown to be efficient for the HER, their scarcity and high cost impede their practical applications on a large scale. Therefore, developing nonprecious metal catalysts has been widely investigated. Metal oxides, metal sulfides, metal borides, metal phosphides, metal carbides, and metal selenides are typical candidates for water splitting. Currently, because of their abundance, stability, and accessibility, transition metal oxides (TMOs), including tungsten oxides, molybdenum oxides, and cobalt oxides, have attracted considerable attention. Notably, it has been reported that oxygen vacancies in TMOs are critical for the efficient production of hydrogen. These vacancies provide active sites for the catalysts, which increase its conductivity and raise its electrocatalytic performance. Hence, TMOs with a large number of oxygen vacancies are excellent candidates for use in the HER because of their active and metallic nature. Among the various TMO catalysts for the HER, transition metal (e.g., Mo and W) oxides have recently been given added attention. For example, Wu et al. prepared metallic WO$_2$-carbon mesoporous nanowires (MWCNMs) by calcination of WO$_2$-ethylenediamine hybrid precursors. The products showed superior electrocatalytic activity and stability compared to the WO$_2$ porous nanowires. The enhancement of the HER performance was primarily attributed to the presence of a large number of oxygen vacancies, which have been shown to act as active sites for the HER. In addition, Jin and Shen reported nanoflower-like metallic MoO$_2$ electrocatalysts on nickel foam (NF). In this case, the NF-supported MoO$_2$ also exhibited excellent performance for hydrogen generation; indeed, the onset overpotential was reported to be only 10 mV. Therefore, transition metal (e.g., Mo and W) oxides are promising candidates as electrocatalysts for the HER.

Because of the strong metal–metal bonding in the crystal structures of tungsten suboxides and dioxides and the various oxygen vacancy defects in their lattices, WO$_2$ and WO$_{3-x}$ possess metallic conductivity (e.g., the conductivity of WO$_2$ is $\sim$350 S cm$^{-1}$) and are thus expected to have high potential activity. However, until now, it has been challenging to synthesize these metallic TMOs supported on highly conductive substrates with nanostructures containing a high number of active sites and a larger specific area because of the...
complicated synthetic process and/or the instability of the products.\textsuperscript{15,19} Polymer binders such as Nafton are widely employed to immobilize electrocatalysts on the electrodes for applications or measurements.\textsuperscript{20} However, polymer binders may reduce the catalytic efficiency of the electrochemical catalysts because they reduce the permeability of gas and block the active sites. Therefore, avoiding the use of polymer binders in the preparation of electrocatalysts is preferred. Moreover, because of their high conductivity and large specific area, electrospun carbon nanofiber mats synthesized from polycrylonitrile (PAN) nanofibers have been widely employed as substrates for HER catalysts.\textsuperscript{21}

According to the carbothermic reduction theory of WO\textsubscript{3}, the formation of tungsten carbides follows the sequence WO\textsubscript{3} → WO\textsubscript{1−x} → W → W\textsubscript{2}C.\textsuperscript{22} Generally, a high carbon excess condition is required to generate both W and W\textsubscript{2}C.\textsuperscript{22,23} The formation of WO\textsubscript{1−x} is more favorable at lower carbon excess conditions than the formation of W and W\textsubscript{2}C.\textsuperscript{24,25} Therefore, the desired material can be crafted in a favorable manner by changing the amount of thermally active carbon around WO\textsubscript{3} during the fabrication process. With relatively less active carbon, WO\textsubscript{3} is prone to partially reduce to give WO\textsubscript{1−x}.\textsuperscript{26,27} In fact, reducing the amount of thermally active carbon or increasing the amount of WO\textsubscript{3} are both viable approaches to increasing the amount of WO\textsubscript{3} are both viable approaches to the desired material can be crafted in a favorable manner by changing the amount of thermally active carbon around WO\textsubscript{3} during the fabrication process. With relatively less active carbon, WO\textsubscript{3} is prone to partially reduce to give WO\textsubscript{1−x}.\textsuperscript{26,27} In fact, reducing the amount of thermally active carbon or increasing the amount of WO\textsubscript{3} are both viable approaches to increases the catalytic e

2. EXPERIMENTAL SECTION

2.1. Preparation of PAN nanofiber mats and tungsten chloride hydrate containing PAN FMs. Polycrylonitrile nanofiber mats (PAN FMs) were prepared via an electrospinning technique. PAN powder (1.28 g) was dissolved in 10 mL of dimethylformamide (DMF, 99.5%, from Aldrich) under magnetic stirring until a homogeneous solution was obtained. The mass ratio of PAN in the DMF solution was 12%. The solution was transferred to a syringe with a stainless copper needle at the tip. The needle was connected to a high voltage power supply. The fixed voltage was set to 12 kV, and the needle-to-collector distance was 12 cm. The flow rate was set to 0.01 mL min\textsuperscript{−1}. The electrospinning procedure was performed at room temperature. The electrospun nanofiber mats were collected on a piece of aluminum foil. The W-PAN FMs were synthesized by adding additional tungsten chloride powder (WC\textsubscript{4}, 99.80%, from Aldrich) to the as-mentioned PAN/DMF solution by electrospinning under the same conditions. The concentration of WC\textsubscript{4} is based on the weight of the PAN powder.

2.2. Fabrication of carbon nanofibers, preoxidized W-PAN, and W-CNF nanofiber mats. The as-collected electrospun PAN FMs and W-PAN FMs were peeled off the aluminum foil, cut into pieces, and placed into a chemical vapor deposition (CVD) furnace for heat treatment. The nanofiber mats were heated from room temperature to 230 °C in air at a rate of 5 °C min\textsuperscript{−1} and maintained at that temperature for 4 h for stabilization. The furnace was then heated to 800 °C at a rate of 5 °C min\textsuperscript{−1} under Ar flow (100 sccm) and maintained at this temperature for an additional 6 h for graphitization. Finally, the samples were cooled to room temperature under an Ar atmosphere. The synthesized products are denoted as W-X-CNFs, where X is the weight percent of tungsten to PAN powder in the W-PAN precursor.\textsuperscript{25} Preoxidized W-PAN nanofiber mats were prepared as follows: the samples were heated from room temperature to 230 °C in air at a rate of 5 °C min\textsuperscript{−1}, maintained at this temperature for 4 h for stabilization, and then cooled to room temperature.

2.3. Characteristics. The morphology evolution of the prepared samples was observed by JSM-6700F field-emission scanning electron microscopy (FE-SEM; JEOL, Japan) at an acceleration voltage of 3 kV and by JSM-2100 transmission electron microscopy (TEM; JEOL, Japan) at an acceleration voltage of 200 kV. X-ray photoelectron spectra of the products were recorded using an X-ray photoelectron spectrometer (Kratos Axx Ultra DLD) with an aluminum (mono) K\textsubscript{r} source (1486.6 eV). The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images, STEM mappings, and line-scan energy-dispersive X-ray spectroscopy (EDX) images were recorded by a STEM (Tecnai G2 F30 S-Twin, Philips-FEI) at an acceleration voltage of 300 kV. The X-ray diffraction (XRD) patterns of the products were obtained on a diffractometer (Bruker AXS D8) using a Cu K\textsubscript{r} radiation source (λ = 0.15418 nm) with a 2θ scan from 10° to 80° with a step size of 0.02°.

2.4. Electrochemical measurements. The HER performance of the electrodes was measured in a 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte solution. The electrolyte was purged with nitrogen for at least 30 min before each test, and a nitrogen environment was maintained at all times to eliminate dissolved oxygen in the solution. Commercial Pt/C (Johnson-Matthey, 20 wt %) was cast on a glassy carbon disk of 3 mm diameter with a catalyst loading of 0.21 mg cm\textsuperscript{−2}. The samples were cut into 1 × 1 cm\textsuperscript{2} squares and fixed with a Teflon electrode clamp to be used directly as the working electrode. A Pt mesh was used as the counter electrode, and a saturated calomel electrode (E\textsubscript{RHE} = E\textsubscript{(RHE)} = E\textsubscript{(SCE)} + 0.265 V after calibration) was used as the reference electrode. All electrochemical measurements were performed on a CHI660E workstation (Shanghai Chenhua, Shanghai). Linear sweep voltammetry was conducted beginning at +0.3 V and ending at −0.5 V with a scan rate of 5 mV s\textsuperscript{−1}. The polarization curves were obtained after ir-compensation. Electrochemical impedance spectroscopy (EIS) was performed at a constant −0.25 V vs RHE while sweeping the frequency from 5 to 20 MHz with a 10 mV AC dither. The chronoamperometric response was obtained under a static overpotential of 0.215 V vs RHE. Current measurements were standardized through the catalyst’s geometry and all potential values were plotted with reference to the reversible hydrogen electrode (RHE).

3. RESULTS AND DISCUSSION

According to the above discussions, we propose a facile method for the fabrication of WO\textsubscript{1−x} on the surface of carbon nanofibers (Figure 1). First, W composites were homogeneously dispersed on PAN nanofibers by an electrospinning
method. Then, after being preoxidized in air for 4 h, W composites became uniformly distributed on the surface of the nanofibers and reacted with oxygen, forming evenly distributed WO₃ nanoparticles (NPs). It was expected that additional W in the precursor would lead to more WO₃ NPs on the nanofiber surface. Carbon reduces WO₃ to W₂C on the surface when the clusters eventually forms a WO₃ van der Waals forces. In this case, the lateral growth of the sites and attract neighboring nanoparticles to form clusters via van der Waals forces. In this case, the lateral growth of the clusters eventually forms a WO₃ nanoplate on the surface of the CNFs.³⁰

Figure S1a displays the TEM image of preoxidized W-PAN nanofibers with minute WO₃ nanoparticles uniformly distributed on their surface. In the XRD results of preoxide W-PAN nanofibers (Figure S1b), three strong peaks present at 26.3°, 33.6°, and 54.8° can be attributed to the (200), (220), and (420) planes, respectively, which are characteristic of cubic WO₃ because of an inadequate reduction process. Some WO₃ nanoparticles possibly act as nucleation sites and attract neighboring nanoparticles to form clusters via the CNFs.³⁰

As shown in Figure 2, W₂C and WO₃ were prepared on carbon fiber mats (CFMs) to different extents. The CFM

Figure 2. SEM images of (a) W-10-CNFs; (b) W-20-CNFs; (c) W-30-CNFs; (d) high-angle annular dark field (HAADF) STEM images of W-20-CNFs. Inset contains the elemental maps obtained from the mapping area in image d.

with a diameter of 200–300 nm is a three-dimensional substrate commonly employed in the electrocatalytic field. Figure 2a–c displays a distinct transition of the main morphology from nanoparticles of W₂C to nanoplates of WO₃. Figure 2b is a typical transitional period in which W₂C nanoparticles and WO₃ nanoplates coexist. By comparing the nanoplates in parts b and c of Figure 2, it can be seen that the size of the WO₃ nanoplates increases as the W content increases. In addition, the size of the nanoplates also markedly increases. WO₃ nanoplates were evenly dispersed onto almost every carbon nanofiber in the present work. Thus, a high electrocatalytic performance for the HER was expected because of several WO₃ active sites and the large specific surface area of the three-dimensional CFM.

A representative TEM image of a typical specimen (W-10-CNFs) is shown in Figure 3a. As seen, there are a large number of W₂C nanoparticles evenly distributed on the CNF substrate. The corresponding high-resolution TEM (HRTEM) image of a W₂C nanoparticle shows that the lattice spacing is 0.277 nm, which can be ascribed to the (101) plane of hexagonal W₂C. A representative TEM image of another typical specimen (i.e., W-20-CNFs) exhibits that the as-prepared WO₃ nanomaterials are rectangle-like nanoplates with edge lengths of 200–300 nm on the rough surface of the CNFs. Figure 3d displays the high-resolution TEM image of a representative single WO₃ nanosheet from Figure 3c. As seen, the nanosheet is comprised of both amorphous and crystalline areas. The crystalline area has lattice spacings of 0.368 and 0.325 nm, which can be attributed to the peaks located at 24.1° and 27.4°, respectively, in the XRD pattern. The discontinuous crystalline area suggests poor crystallinity of the single nanoplate and suggests that several catalytically active sites could be exposed on the basal plane. In this regard, oxygen vacancies have been shown to act as active sites in TMOs for the HER. sixty-three. For this reason, the additional oxygen vacancies in amorphous WO₃ produce electrocatalytically active sites, which can enhance its performance for the HER. The crystalline area may benefit the electrochemical stability for the reaction, and the amorphous area is beneficial for the high electrocatalytic activity in acidic electrolytes. Spatially resolved W, C, and O elemental mapping obtained from the area in Figure 2b exhibits even distribution of W and O on the nanosheet, which suggests that the nanoplates consist of W and O (Figure 2d).

To further investigate the morphology of the W-20-CNFs, TEM and STEM analyses were conducted (Figure 4). Figure 4a shows a high-resolution TEM image of a carbon nanofiber with W-20-CNFs. As seen, there exist some nanoparticles with a lattice spacing of 0.266 nm, which can be ascribed to the spacing of the (101) plane of W₂C. The STEM-EDX mapping images of a single nanofiber confirm the existence and even distribution of W, C, and O. As shown in Figure 4d, the chemical composition was further confirmed by line-scan energy-dispersive X-ray (EDX) analysis on the backbone, which gives the relative intensities of the C, W, and O elements. As seen, the intensity of O is much lower than those of W and C, demonstrating that the nanoparticles distributed on the
The TEM and STEM results of W-30-CNFs are shown in Figures S4 and S5; it can be seen that the nanoplates on the W-30-CNFs and W-20-CNFs have the same crystalline structure and composition. In addition, there are still some W2C nanoparticles on the nanoﬁbers of W-30-CNFs (Figure S5c), which are consistent with the XRD results (Figure 5f). To calculate the \( x \) value of the WO\(_{3-x} \) nanoplate, EDX analyses were conducted on the single nanoplates and the \( x \) values of W-20-CNFs and W-30-CNFs are determined as 1.64 and 1.53, respectively (Figure S4).

To better illustrate the chemical states of O, C, and W on the surface of the resulting samples, XPS analyses of a typical sample (i.e., W-20-CNFs) were conducted. The weak peak at \( \sim 170 \text{ eV} \) can be ascribed to the binding energy of S 2p. All the spectra were calibrated using the C 1s peak of carbon present at 284.50 eV. As shown in Figure 5c, there are two W states after deconvolution and each state is a pair of doublets. The peaks located at 35.2 (W 4f\(_{7/2}\)) and 37.0 eV (W 4f\(_{5/2}\)) correspond to the W\( \text{–O} \) bond of WO\(_{3-x} \). Compared with the W 4f binding energy in WO\(_3\), there is a red-shift in the binding energy of W, indicating that WO\(_3\) has been partially reduced and that oxygen vacancies are present in WO\(_{3-x} \).6 In addition, oxygen vacancies in tungsten oxides were also evidenced by their strong vis/NIR absorption.6,11 As can be seen in Figure S8, compared with W-10-CNFs, W-20-CNFs and W-30-CNFs show a big absorption tail in the range of 460–800 nm, strongly demonstrating the existence of a large amount of oxygen vacancies. Meanwhile, the energy bands at approximately 31.4 (W 4f\(_{7/2}\)) and 33.4 eV (W 4f\(_{5/2}\)) correspond to the W\( \text{–C} \) bond, with good correspondence to the binding energy of W2C.32 For the O 1s spectra, the distinct peak at 531.1 eV is further separated into two peaks at 531.1 and 530.4 eV, which correspond to the C\( \equiv \text{O} \) and W\( \text{–O} \) bonds, respectively.33 Here, the C\( \equiv \text{O} \) groups are attributed to the oxygen-containing groups on the surface of the carbon nanoﬁbers.33,34 The C 1s spectra show a distinct peak at 284.7 eV, corresponding to graphitized carbon.34 The other two weaker peaks located at 286.1 and 289.5 eV are attributed to the W\( \text{–C} \) and C\( \equiv \text{O} \) bonds, respectively.33,34

XRD analysis was performed to investigate the crystal structures of the three samples. The diffraction peaks of the W-10-CNFs are consistent with the standard pattern of hexagonal W\(_2\)C (JCPDS card no. 35-0776), indicating the high purity of the sample. The broad peaks at \( \sim 25.5^\circ \) can be ascribed to the (002) plane of the graphite layers on the carbon nanoﬁbers.34 More importantly, the result conﬁrms that the particles distributed on the surface of the W-10-CNFs are W\(_2\)C nanoparticles. Notably, one distinct peak at 13° and three distinct peaks located from 24.08° to 27.53° arise in the W-20-CNFs and W-30-CNFs, which correspond to the formation of WO\(_{3-x} \).

In this work, the catalytic performances of the W-10-CNFs, W-20-CNFs, and W-30-CNFs were evaluated in a typical three-electrode electrochemical cell employing a 0.5 M H\(_2\)SO\(_4\) electrolyte solution. Images of the cross sections were obtained because the catalysts were used directly as the working electrodes (Figure S2). The cyclic voltammetry experiments were recorded at 400 cycles to stabilize the samples and to eliminate surface contaminant.

As shown in Figure 6a, the CNFs exhibit negligible HER performance. In contrast, the W-30-CNFs catalysts show excellent HER activity with the low onset potential of 134 mV, with the current in the cathode rising rapidly under more negative potential. Moreover, in the entire potential area, overpotentials under the same current density of the W-30-CNFs are much lower than those of the CNFs, W-10-CNFs and W-20-CNFs. For instance, at a cathodic current density of 10 mA/cm\(^2\), the overpotential of the W-30-CNFs sample is 185 mV, which is lower than that of the W-20-CNFs (227 mV) and the WO\(_{3-x} \) nanoplate, EDX analyses were conducted on the single nanoplates and the \( x \) values of W-20-CNFs and W-30-CNFs are determined as 1.64 and 1.53, respectively (Figure S4).
uniformly dispersed on the CNF surface. Recent reports showed that the crystal phase fundamentally impacts the HER catalytic activity of transition metal carbide-based materials.\textsuperscript{13} As shown in the XRD patterns, the crystal phase of W\textsubscript{12}C is hexagonal, which may be the primary factor that influences HER activities.\textsuperscript{3} Compared with WO\textsubscript{3-x}, the W\textsubscript{12}C hexagonal phase may exhibit relatively lower performance for the HER because of its intrinsic nature.\textsuperscript{11,13} Hence, in the present investigations, the W content in the precursor has a significant influence on the HER performance by changing the composition and morphology of the catalysts on the CNFs. In addition, to exclude the influence of Pt particles’ dissolution from counter electrode to the real HER performance of work electrode, we chose a typical sample (W-20-CNFs) to test the HER performance after 400 cyclic voltammetry scans using carbon electrode as the counter electrode. It can be seen that the two curves overlap well and the onset potential as well as current densities at any over potentials are comparable. (Figure S7). Therefore, the influence of Pt dissolution to the work electrode is negligible.

Exchange current density ($j_0$) is a vital measure of the HER performance of electrocatalysts by providing insight into their inherent activities. Typically, $j_0$ is deemed to be proportional to the active area on the catalyst’s surface.\textsuperscript{1,36} As shown in Table 1, the $j_0$ value calculated from the Tafel plot for the W-30-CNFs is 0.239 mA cm\textsuperscript{-2}, which is much higher than that for the W-10-CNFs (0.122 mA cm\textsuperscript{-2}) and W-20-CNFs (0.186 mA cm\textsuperscript{-2}). Further, the highest exchange current density for the W-30-CNFs is ascribed to both the high number of active sites on the WO\textsubscript{3-x} nanolayers and the discontinuous crystallization on its basal plane. To estimate the effective surface area of the catalysts, one alternative method is to calculate the double layer capacitance ($C_\text{dl}$). To this end, CV plots were constructed under a potential range of 0.1–0.2 V vs RHE at scan rates of 0.5–5 mV s\textsuperscript{-1} without the presence of a faradic current (Figure S3). The $C_\text{dl}$ values of the electrodes containing different samples were calculated and are listed in Table 1. The $C_\text{dl}$ of the W-30-CNFs is 711 mF cm\textsuperscript{-2}, which is 1.78 and 1.21 times larger than the values for the W-10-CNFs (399 mF cm\textsuperscript{-2}) and W-20-CNFs (587 mF cm\textsuperscript{-2}), respectively. These data indicate that the W-30-CNFs possess a larger electrocatalytic effective surface area than the other two materials. The increase in the $C_\text{dl}$ values demonstrates an increased number of active sites, which enhances the HER performance of the catalysts.

To investigate the kinetics of the electrode in the HER, electrochemical impedance spectroscopy (EIS) measurements were conducted. Figure 6c displays the Nyquist plots of various catalysts at $\eta = 100$ mV. No Warburg impedance is observed, indicating that the reaction is kinetically controlled. The emergence of only one semicircle in the plot indicates that the equivalent circuit is characterized by only one time constant.\textsuperscript{5} Therefore, one simple equivalent electrical circuit for the HER can be used for its description. With respect to the solution resistance ($R_\text{s}$), the value for all electrodes is $\sim$3 $\Omega$. It is worth noting that the charge transfer resistance ($R_\text{ct}$) among these catalysts is quite different. The value of $R_\text{ct}$ for the W-30-CNFs electrodes is $\sim$15 $\Omega$, which is conspicuously smaller than the values for the W-10-CNFs (ca. 170 $\Omega$) and W-20-CNFs (ca. 85 $\Omega$). As is well-known, $R_\text{ct}$ is strongly associated with the kinetics of the HER, with a low $R_\text{ct}$ value reflecting a higher electrocatalytic activity of the corresponding electrode.\textsuperscript{35,38}

Clearly, the W-30-CNFs possess an optimal electrocatalytic performance relative to the other electrodes. As discussed
above, WO_{3-x} possesses many oxygen vacancy defects that can enhance the conductivity of the catalyst and decrease the charge transfer resistance.\(^{31}\) Therefore, by increasing the amount of WO_{3-x} in the catalysts, the corresponding \(R_t\) values decrease, which is evident from a comparison of the \(R_t\) values for the W-10-CNFs, W-20-CNFs, and W-30-CNFs materials.

Time-dependent current density at \(\eta = 280\) mV in a 0.5 M H\(_2\)SO\(_4\) electrolyte solution was measured to evaluate the stability of the electrode. The current density of the W-30-CNFs is \(\sim 26.5\) mA cm\(^{-2}\), which is 3.1 times larger than the current density of the W-20-CNFs (8.5 mA cm\(^{-2}\)) and 6.7 times larger than that of the W-10-CNFs (4.1 mA cm\(^{-2}\)). Degradation of the current density after 12 h is negligible for every catalyst. The alternate process of bubble accumulation and release can be observed as the characteristic serrated shape of the current (inset Figure 6d). Furthermore, the durability of the catalysts, SEM images of the W-30-CNFs are shown in Figure 7a. The accelerated degradation measurement for 2000 cycles. To investigate the morphology of the sample following the stability test, SEM images of the W-30-CNFs are shown in Figure 7a. As seen, the surface structure of WO\(_3\) supplied (Figure S6). It can be seen that the morphology of the catalyst material after 2000 recycles keeps well. As discussed above, WO\(_{3-x}\) was successfully fabricated via tuning the amount of tungsten chloride. With increasing tungsten chloride in the W-PAN precursor, WO\(_{3-x}\) was synthesized in the form of nanoplates, with consequent increases in the amount of WO\(_{3-x}\) as well. The superior HER activities of the W\(_{3-x}\) nanoplates grown on CNFs are attributed to the following features: (1) Poor crystallinity of WO\(_{3-x}\) causes many defects in the lattice, leading to the exposure of more active sites. (2) WO\(_{3-x}\) possesses high electrical conductivity and thus promotes charge transfer in the HER.\(^{12,29}\) (3) The large number of WO\(_{3-x}\) nanoplates densely distributed on the carbon nanofiber surface produces numerous electrochemically active sites. (4) The electrospun CNFs can provide a large specific area that increases the contact with the electrolyte solution and enhances the conductivity of the samples.

The W-10-CNFs electrodes display the lowest performance among the three electrodes examined. This result may be caused by the intrinsic nature of hexagonal W\(_2\)C, because different phases of W\(_2\)C have a significant influence on their associated electrochemical activities.\(^{13,39}\) In addition, to the best of our knowledge, previously reported WO\(_3\) or WO\(_{2.72}\) nanostructures are mainly nanoparticles and nanotubes, which must be immobilized with a polymer binder on the electrode surface for electrochemical measurements.\(^{40}\) However, in the present work, the catalysts on the CNFs can be directly employed as the electrode. Such an approach avoids loading on the carbon gassy electrode, which will be of great benefit for large-scale syntheses and practical applications.

4. CONCLUSIONS

Novel WO\(_{3-x}\) nanoplate electrochemical catalysts were fabricated on conductive carbon nanofiber mats without the use of toxic and dangerous reactant gases. The density of the WO\(_{3-x}\) nanoplates on the surface of carbon nanofibers can be easily tailored by adjusting the initial W content in the precursor. We find that the HER activities increase as the precursor W content increases. The synthesized WO\(_{3-x}\) has poor crystalline character that exposes numerous active sites. The catalysts were used directly as binder-free cathodes in the electrochemical measurements, and all of the catalysts display high current density, low overpotential, and long-term stability for splitting water. Notably, superior HER activities can be obtained by adjusting the amount of WO\(_{3-x}\) in the products. The remarkable electrocatalytic performances resulted from the poor crystallinity of WO\(_{3-x}\) high electrical conductivity of WO\(_{3-x}\) and the use of electrospun CNFs. The present work provides a straightforward approach for synthesizing TMO-based carbon nanofiber mats that may have promising applications for the HER.

■ ASSOCIATED CONTENT

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b05245.

SEM, TEM, XRD, STEM, HRTEM, and EDX images; linear fitting of the capacitive currents of the catalysts vs scan rates; digital photo of W-30-CNFs before and after stability test; polarization curves with different counter electrodes; UV-vis diffuse reflectance spectra of the samples; table of XPS atomic concentrations of the samples (PDF).

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Notes

The authors declare no competing financial interest.

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