



WO₃-Based Materials as Electrocatalysts for Hydrogen Evolution Reaction

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Environmental pollution and energy shortage make the development of clean energy more and more urgent. As a kind of clean renewable energy, hydrogen has attracted more attention recently. WO₃-based materials have emerged as one of the most promising candidates for electrocatalytic hydrogen evolution reaction (HER) due to their attractive electrocatalytic activity, low cost, as well as electrochemical durability. In this minireview, we systematically provide an overview of WO₃-based materials applied for HER, including pure WO₃, doped WO₃, and WO₃-based composite materials. Furthermore, the strategies to enhance their electrocatalytic performance are summarized and discussed, such as morphological engineering, doping, as well as compositing with other materials. Finally, the limitation and challenges of WO₃-based materials for HER and their prospects for future research are proposed. We believe that this minireview will be favorable for scientists to seek more promising HER electrocatalysts.

Keywords: tungsten oxide, doping, composites, electrocatalyst, hydrogen evolution reaction

INTRODUCTION

Nowadays, the discovery and use of fossil fuels (such as coal and petroleum) have made great contributions to the development of human society (Wang Y. et al., 2018; Hao et al., 2019; Liu G. L. et al., 2020; Ma et al., 2020; Yu et al., 2020). However, the fast development of human society brought excessive emission of carbon dioxides and overuse of non-renewable resources, resulting in many serious problems, such as global warming, climate change, sharp decline in energy reserves, and so on (Liu G. et al., 2019; Zhao et al., 2019; Wang W. et al., 2020; Zou et al., 2020).

Recently, a series of renewable energy resources such as wind energy, solar energy, tidal energy, and hydropower have been intensively studied and emerged as alternatives for fossil fuels (Peng et al., 2017; Liu G. et al., 2018). Meanwhile, electrochemical energy store (Guo et al., 2019; Wang F. et al., 2018; Wang et al., 2019e; Wang R. et al., 2020; Liu Y. et al., 2019; Yuan et al., 2019; Li M. et al., 2020; Song et al., 2020; Sui et al., 2020), electrocatalysis (Chen et al., 2019a; Li Y. et al., 2019; Wang et al., 2019c, Wang et al., 2019d; Xiao et al., 2019), and other new energy technologies have also developed rapidly in recent years (Ma et al., 2013, 2017; Zhang et al., 2014, 2018; Cheng et al., 2019; Li Y. et al., 2019; Zheng et al., 2020). It is worth noting that hydrogen fuel is of great concern because of its high energy density and abundant natural resources. Moreover, the product of hydrogen combustion is water, which is pollution-free and can effectively reduce the emission of greenhouse gases and toxic gases (Yu et al., 2019).

At present, the production of hydrogen by electrochemical water splitting has caught extensive attention because of its simple and flexible operation (Zou and Zhang, 2015). However, hydrogen production is hindered by the high overpotential of the hydrogen evolution reaction (HER) and the low hydrogen production rate (Lei et al., 2020). Therefore, in order to overcome these defects and promote the production of H₂, it is urgent to introduce efficient electrocatalysts. Platinum is acknowledgedly regarded as one of the best electrocatalysts for HER (Ma et al., 2019); nevertheless, further application is limited by its high price. Therefore, it is necessary to explore proper non-noble metals for electrocatalytic hydrogen evolution.

As a transition metal oxide, tungsten oxide (WO₃) is expected to be a hopeful candidate to substitute Pt as an electrocatalyst for efficient HER due to its outstanding redox capability, low cost, and high stability (Chandrasekaran et al., 2019; Wang et al., 2019b). Hence, more and more attention has been paid to investigating WO₃-based materials for electrocatalytic HER. For example, Chen Y. et al. (2018) reported an article about crumpled graphene/tungsten disulfide/tungsten trioxide with high electrocatalytic HER performance. And recently, Tian et al. (2019) reported unique highly dispersed Pt atom clusters on WO₃@CFC (carbon fiber cloth) as superior electrocatalysts for HER. Furthermore, Huang et al. (2019) gave a comprehensive review on recent progress in WO₃-based materials as photoanodes for water oxidation. However, to the best of our knowledge, a critical review that exclusively puts a spotlight on WO₃-based materials for electrocatalytic HER has not been reported.

In this minireview, we will give a comprehensive description of WO₃-based materials, mainly including stoichiometric WO₃, non-stoichiometric WO_{3-x}, doped WO₃, and WO₃-based composite materials with their application in the field of electrocatalytic HER in recent years. Their micro/nanostructures and electrocatalytic performances for HER are systematically summarized, as shown in **Supplementary Table S1**. Furthermore, we also present some rational proposals to facilitate breakthroughs in the future. We hope that this minireview could draw more attention to WO₃-based electrocatalysts and boost their practical applications.

NANOSTRUCTURED TUNGSTEN OXIDE

Stoichiometric WO₃

In recent years, the electrocatalytic performances of WO₃ have been greatly enhanced by utilizing nano/micrometer-sized WO₃, mainly due to their high surface area to volume ratio. The nanostructured stoichiometric WO₃ with different morphologies as electrocatalysts for HER includes nanorods (Ham et al., 2010), nanowires (NWs) (Phuruangrat et al., 2010), nanoplates (Hu et al., 2015; Nayak et al., 2017), nanoparticles (Ganesan and Gedanken, 2008), and so on.

For example, Ham et al. (2010) developed a facile hydrothermal method to prepare monoclinic WO₃ (m-WO₃) nanoplates and nanorods (**Supplementary Figures S1A,B**). The cyclic voltammetry results show the decent stability of m-WO₃ nanoplates and nanorods for HER (**Supplementary Figures S1C,D**). When they are tested at -0.2 V in 1 M H₂SO₄, m-WO₃ nanoplates and nanorods shows cathodic current densities of 17.58 and 23.86 mA cm⁻², respectively (**Supplementary Figure S1E**), and the Tafel slopes of m-WO₃ nanoplates (122 mV dec⁻¹) or nanorods (113 mV dec⁻¹) are lower than those of commercial bulk m-WO₃ (135 mV dec⁻¹), indicating superior performances for HER (**Supplementary Figure S1F**). Phuruangrat et al. (2010) employed a novel microwave-assisted hydrothermal (MH) method to fabricate 1D hexagonal WO₃ NWs (*hex*-WO₃). The as-synthesized *hex*-WO₃ samples display different morphology and sizes when the MH time was adjusted from 3 to 12 h (**Supplementary Figures S2A-D**). The specific activity for HER of *hex*-WO₃ NWs fabricated by MH at -0.1 V is far higher than that of *hex*-WO₃ NWs fabricated by conventional hydrothermal method (CH) and commercial WO₃ (**Supplementary Figure S2E**). Furthermore, the Tafel slope and the exchange current density of *hex*-WO₃ NWs by MH are 116 mV dec⁻¹ and 6.61 mA cm⁻², respectively, elucidating better electrocatalytic kinetics of *hex*-WO₃ than those of commercial WO₃ (157 mV dec⁻¹ and 0.27 mA cm⁻²) (**Supplementary Figure S2F**). The performance enhancement of *hex*-WO₃ NW samples can be attributed to their high aspect ratio and crystallinity.

Non-stoichiometric WO_{x<3}

The performances of tungsten oxide can also be adjusted and controlled by defects in its architecture (Royer et al., 2014; Zheng et al., 2017). Several oxygen-deficient WO_{x<3} nanomaterials have been reported to promote the electrocatalytic HER efficiencies, such as mesoporous WO_{2.83} (Cheng et al., 2018), WO_{3-x}/Ni foam (NF) (Yi et al., 2018), and monoclinic WO_{3-x} (Sharma et al., 2019). For instance, Zheng et al. (2017) synthesized two-dimensional WO₃ nanosheets with rich O vacancies via a liquid exfoliation method. The structure of the O vacancies model was built based on WO₃ (010) ($\sqrt{2} \times \sqrt{2}$) R45° slab with the surface of all terminal oxygen atoms as well as one bridging oxygen atom removed (**Figure 1A**). At 10 mA cm⁻², the overpotential of as-synthesized sample is 38 mV and the Tafel slope is also 38 mV dec⁻¹, which is close to the optimal performances of benchmarking electrochemical catalyst Pt/C (**Figure 1B**). Unique

O vacancies were verified by density-functional-theory (DFT) calculation on WO₃ to bring in gap states around the Fermi level, which obviously increased hydrogen absorption and reduced H₂ adsorption free energy (ΔG_{H^*}) (Figure 1C).

Hetero-atom Doped WO₃

Besides the method of introducing O vacancies in WO₃, hetero-atom doping with a metallic element is also an efficient way to promote electron transfer and shorten proton diffusion paths.

In 2014, Xie et al. (2014) reported nanostructured Ta-doped WO₃ as an efficient electrocatalyst for HER. The as-prepared Ta-doped WO₃ NWs show excellent performance. Later, metallic element doping in WO₃ for electrocatalytic HER was further developed, and the mechanism was demonstrated by Chandrasekaran et al. (2019). They prepared Mn-doped WO₃ and V-doped WO₃ via the hydrothermal route, and the particle sizes are 50–70 and 20–30 nm, respectively (Figure 1D). The electrochemical results indicate that the V-doped WO₃ (3 wt.% denoted as VW-S2) exhibits the optimal performance for HER. The overpotential of VW-S2 at 10 mA cm⁻² is 38 mV versus the reversible hydrogen electrode (RHE) (Figure 1E). Moreover, the Tafel slope is 41 mV per decade, which is lower than that of Mn-doped WO₃ (MW-S2) (68 mV dec⁻¹) and undoped WO₃ (121 mV dec⁻¹), close to the benchmarking Pt/C (32 mV dec⁻¹) (Figure 1G). Additionally, the value of free energy ΔG_{H^*} under the circumstances shown in Figure 1F is ideal (0.08 eV at O_b sites), which gains significant reduction (Figure 1H). DFT calculation indicates that band gap reduction in WO₃ is on account of V doping, resulting in great conductivity, and the high HER activity could be ascribed to the V element bonding with terminal oxygen in the lattice of WO₃.

WO₃-BASED BINARY COMPOSITES

To further enhance electrocatalytic properties for HER, WO₃ has been composited with other materials, such as carbon (Wondimu et al., 2018a,b), metals (Li W. et al., 2019; Tian et al., 2019), and metal-based compounds (Yang et al., 2016; Shang et al., 2017).

WO₃/Carbon Composites

Carbon materials are often utilized as conductive materials due to their superior electronic conductivity and outstanding chemical durability (Wu et al., 2019). Hence, compositing WO₃ with carbon materials is an efficient way to improve the HER performances (Wondimu et al., 2018a,b; Hu et al., 2019). For example, Wondimu et al. (2018a) developed novel electrocatalyst tungsten oxide NWs with rich O vacancies supported by nitrogen doped-reduced graphene oxide (N-rGO) (denoted as WO_xNWs/N-rGO), which exhibits better HER performance than Fe-WO_xP/rGO approaching to Pt/C. The overpotential as well as the Tafel slope are only 40 mV at 10 mA cm⁻² and 38.2 mV dec⁻¹, respectively, which are close to the state-of-the-art Pt/C. The superior performance could be mainly put down to O vacancies and the network between the WO_xNWs and N-rGO.

Not only could the rGO assist the WO₃-based materials to be more excellent and efficient, but also other carbon

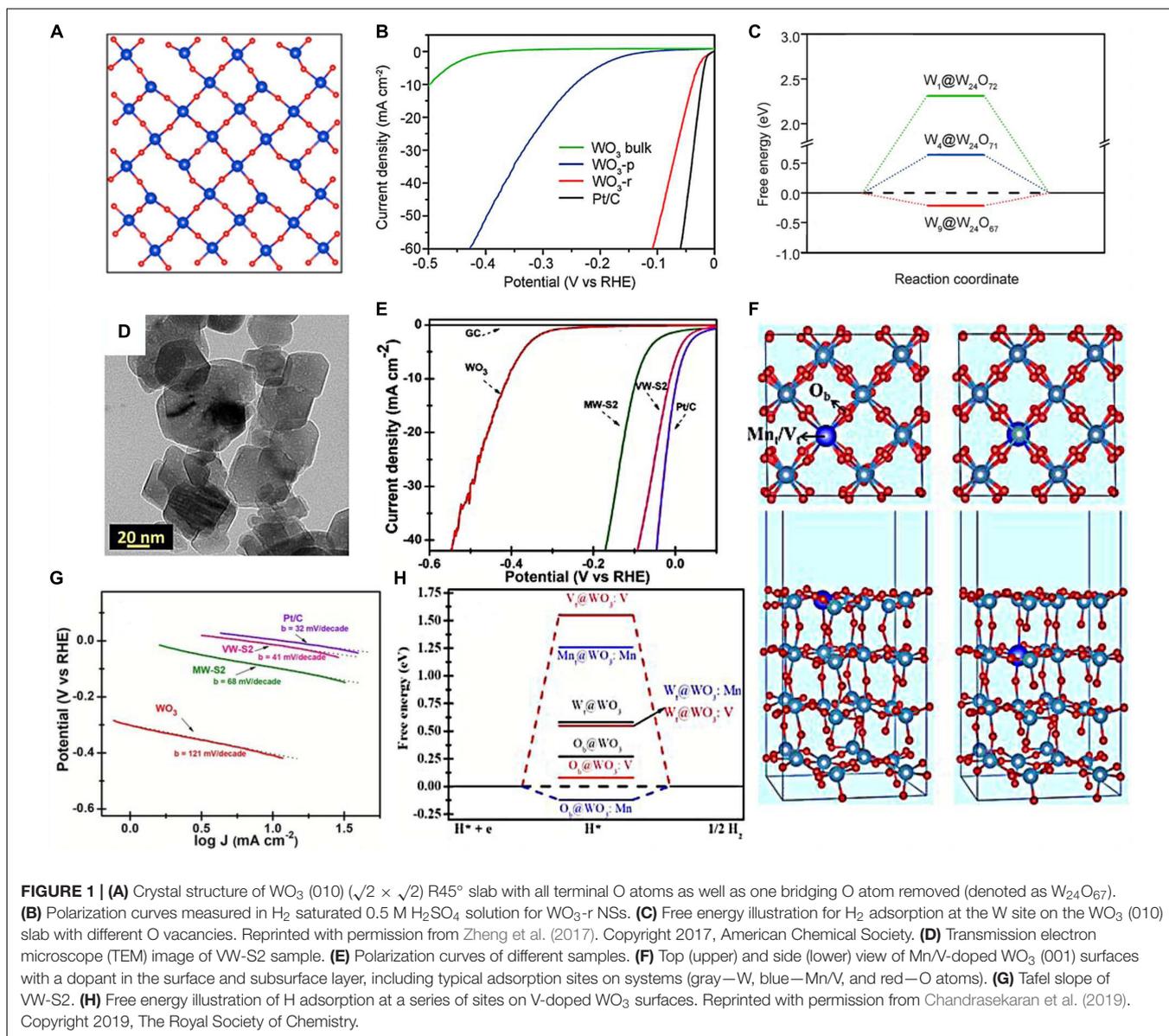
materials could increase the conductivity and further enhance the electrocatalytic properties for HER, such as WO₃/C (Zheng and Mathe, 2011), WO₃/Carbon nanotube (CNT) (Chekin et al., 2013), and WO_{3-x}@nitrogen-doped carbon (NC) (Chen J. et al., 2018). More details on the electrocatalytic performances could be found in Supplementary Table S1.

WO₃/Metal-Based Material Composites

Besides carbon materials, construction of WO₃ with metal and metal-based materials is regarded as another effective way to enhance the charge transfer and promote the synergistic effect between them (Wang et al., 2019a,b). Up to now, many metal-based materials have been composited with WO₃, such as Pt (Li W. et al., 2019; Tian et al., 2019), Ag (Ma et al., 2019), WX₂ (X = S) (Yang et al., 2016; Shang et al., 2017), Se (Fominski et al., 2016), and Al₂O₃ (Zou et al., 2019). For instance, Yang et al. (2016) *in situ* synthesized WO₃·2H₂O/WS₂ hybrid electrocatalyst for HER with superior electrocatalytic properties through a facile anodizing treatment. Furthermore, to minimize the use of precious metals, Tian et al. (2019) fabricated an effective low-Pt electrocatalyst with high oxygen vacancies in WO₃@CFC (carbon fiber cloth) denoted as Pt/def-WO₃@CFC. Firstly, the WO₃ nanoplates were grown on carbon fiber cloth through a hydrothermal method, followed by heat treatment under the atmosphere of 5 vol.% H₂ and 95 vol.% Ar to produce O vacancies on WO₃. And the Pt/def-WO₃@CFC was obtained after Pt nanoclusters dispersed on the defect of WO₃ via thermal reduction (Figure 2A). The lattice fringe spacing are 0.374 and 0.365 nm, corresponding to the (002) and (020) planes of WO₃, respectively (Figure 2B). And the spherical aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image shows that the number of O vacancies is relatively low (Figure 2C). But after the loading of Pt, an obvious decrease in intensity is seen with a reduction in the electron spin resonance (ESR) peak, indicating the substitution of O vacancies by Pt clusters. The HER performance shows a Tafel slope of 61 mV dec⁻¹ and an overpotential of 42 mV at 10 mA cm⁻² in 0.5 M H₂SO₄ (Figure 2D), which are comparable to those of the state-of-the-art commercial Pt/C catalyst (η_{10} = 34 mV, Tafel slope = 46 mV dec⁻¹). And it is worthy to mention that the activity of low-Pt catalyst Pt/def-WO₃@CFC is 3.3 times that of commercial Pt/C, which could be attributed to the synergistic effect between the Pt and defective WO₃ (Figure 2D). Pt atoms are tightly tied in the position of O vacancies, hindering their aggregation or growing during the period of hydrogen evolution, which definitely reveals the significant functions of defect-rich nanostructures (Chen et al., 2019b; Zhu et al., 2019).

Others

Besides the above mentioned, there are still some WO₃-based composite electrocatalysts with enhanced HER performance. The electrocatalyst SiO₂/WO_{3-x} nanofacets calcined *in situ* at 500°C for 5 h (denote as 500-5) by Ketpang et al. (2013) exhibits an overpotential of 170 mV owing to the interaction between them. And nano-zeolite with 3 wt.% WO₃ prepared via the work of Anis and Hashaikeh (2018) is also a promising candidate for HER with a lower Tafel slope of 31.9 mV dec⁻¹ due to the high



surface areas and decent durability brought by zeolites. However, their specific mechanisms need deep insight on the assistance of DFT calculation.

WO₃-BASED TERNARY COMPOSITES

Recently, WO₃-based ternary composite electrocatalysts for HER receive more and more attention due to the great synergy effect between the components (Choudhary et al., 2017; Chen Y. et al., 2018). For instance, Lv et al. (2018a) synthesized WO₃/C@CoO on NF observed as octopus tentacles via facile hydrothermal treatment as well as following thermal treatment. As shown in **Figure 2E**, a CoO NWs precursor grows on NF after hydrothermal treatment. The SEM and TEM images (**Figures 2F–H**) showed the

morphology of the WO₃/C@CoO nanostructure. When it is measured as an electrocatalyst for HER, the overpotential at 10 mA cm⁻² is tested as 55 mV (**Figure 2I**). The Tafel slope is 115 mV dec⁻¹ (**Figure 2J**), which is smaller than that of argon-treated WO₃/C@CoO/NF (122 mV dec⁻¹) and CoO NWs (132 mV dec⁻¹). And the outstanding HER stability is still maintained after 2,000 cycles (**Figure 2K**). The excellent electrocatalytic performance is mainly due to the distinctive structure and robust synergistic effect among WO₃, CoO, and NF. Another ternary CoSe₂/WSe₂/WO₃ hybrid NWs on carbon cloth (CC) were synthesized by Lv et al. (2018b). The high performance indicates the significant functions of unique nanostructure and strong synergistic effects, which prompts Ar/H₂-treated WO₃/C@CoO/NF and CoSe₂/WSe₂/WO₃ NWs/CC to become remarkable electrocatalysts for HER (Du et al., 2018).

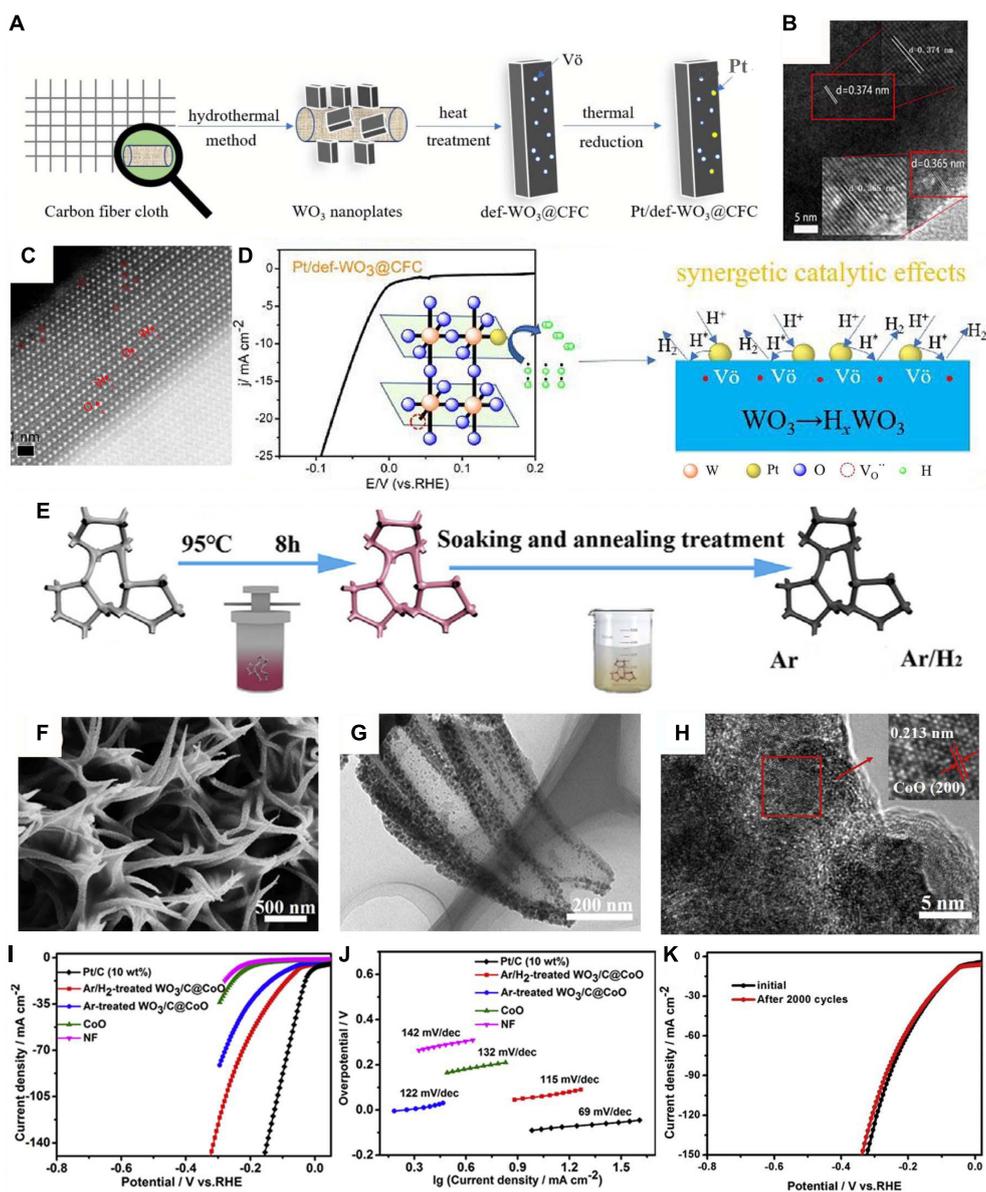


FIGURE 2 | (A) Scheme diagram for the synthetic process of Pt/def-WO₃@CFC. (B) High-resolution transmission electron microscope (HRTEM) of WO₃ NPs. (C) Spherical aberration-corrected image of Pt/def-WO₃@CFC at atomic scale. (D) Linear sweep voltammetry (LSV) curves in 0.5 M H₂SO₄ at a scan rate of 1 mV/s and the schematic model for Pt/WO₃ nanostructure with O vacancies. Reprinted with permission from Tian et al. (2019). Copyright 2019, The Royal Society of Chemistry. (E) Scheme diagram of the formation of WO₃/C@CoO/NF. (F) Scanning electron microscope (SEM), (G) TEM, and (H) HRTEM images of Ar/H₂-treated WO₃/C@CoO/NF. (I) The LSV curves and (J) the Tafel slopes of different samples. (K) The LSV curves of Ar/H₂-treated WO₃/C@CoO/NF before and after 2,000 cycles. Reprinted with permission from Lv et al. (2018a). Copyright 2018, Elsevier.

CONCLUSION AND OUTLOOKS

In summary, we briefly review the recent developments of WO₃-based materials for electrocatalytic HER. The essential synthetic methods and processes, various nanostructures, and robust performances are generally discussed. From these studies, it is clear that the strategies mentioned above are useful and meaningful for optimizing the electrocatalytic performance of WO₃. However, we should

recognize that the practical application of WO₃-based electrocatalysts for HER is still in early stage and is facing many challenges. First, the majority of works are focusing on the nanostructure morphology and electrocatalytic performances, but the understanding of mechanism is not seriously taken. Second, the latest modern characterization techniques, such as *in situ* X-ray technique, *in situ* electron microscopy, and *in situ* scanning probe technology, should be well used to explore the working mechanisms. Third,

DFT calculation is also an efficient way for us to gain insight into the nanostructure–composition–performance relationships, which may be important in the development of catalysts in the future. In addition, among these recent advances, the electrocatalysts introduced O vacancies that almost exhibit outstanding performances close to those of the benchmarking Pt/C. Decent electrical conductivity, appropriate Gibbs free energy ΔG_{H^*} , and large active surface areas will possibly render the introduction of O vacancies as a promising strategy and the orientation for better HER process. Last, the electrocatalytic stability should also be seriously considered. We hope this minireview will be helpful and will inspire more innovative ideas for WO₃-based or even transition metal oxide materials as electrocatalysts for HER.

AUTHOR CONTRIBUTIONS

YL, WZ, and SW conceived the idea. YXL and XZ wrote the draft. All authors contributed to the writing, discussion, and revision of the final version of the manuscript.

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SUPPLEMENTARY MATERIAL

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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