

Engineering Hexagonal/Monoclinic WO₃ Phase Junctions for Improved Electrochemical Hydrogen Evolution Reaction

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Cite This: <https://doi.org/10.1021/acsaem.2c01383>

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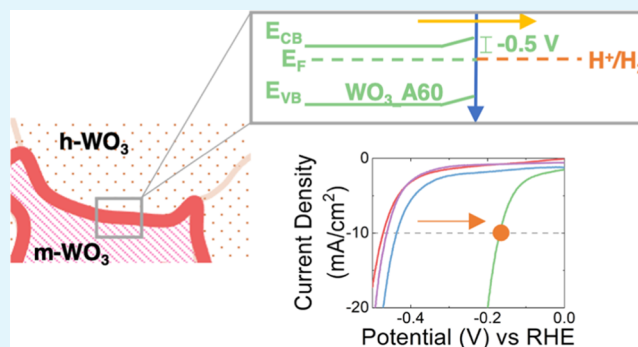
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ABSTRACT: Electrochemical hydrogen evolution reaction (HER) is one of the most promising green methods used to produce renewable and sustainable energy. The development of a highly efficient Pt-free electrocatalyst for HER is a crucial point for the ecosustainability and cost reduction of this method. Herein, WO₃ nanorods were synthesized by a hydrothermal method and calcinated in air at 400 °C for different times (30, 60, and 90 min). Experimental investigation involved SEM, TEM, XRD, and electrochemical analyses such as linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and Mott Schottky analysis. Calcination at 400 °C induces a peculiar crystal phase transition driven by the formation of hexagonal/monoclinic WO₃ phase junctions. The best HER performance (170 mV overpotential for 10 mA/cm²) is obtained when WO₃ nanorods show comparable volumes of hexagonal and monoclinic phases (after 60 min annealing). The effect of phase junction on HER catalysis sustained by WO₃ nanorods is investigated in detail, opening the route of efficient, Pt-free catalysts for HER application.

KEYWORDS: hydrogen evolution reaction, WO₃, electrocatalyst, phase junction, band bending, Pt-free catalyst



1. INTRODUCTION

The finite supply of fossil fuels, the climate change, and the growing world energy demand inspire the scientific community for developing renewable and sustainable energy sources, among which H₂ attracts a lot of awareness. One of the most promising green methods to produce highly pure H₂ on a large scale, with zero carbon emission, sustainability, recyclability, and ecofriendliness is water electrolysis through hydrogen and oxygen evolution reactions at the cathode and anode, respectively.^{1–3} The most active catalysts for the hydrogen evolution reaction (HER) are Pt-based materials, but the large-scale application with these catalysts is limited by the low availability and high cost of Pt;^{4,5} indeed, several earth-abundant transition metal-based electrocatalysts have been studied for HER, both in acidic and alkaline media, such as transition-metal oxides.^{6–9} Among them, WO₃ has emerged as a favorable material thanks to its large availability and advantageous properties.^{10–15}

Indeed, WO₃ is an *n*-type semiconductor with abundant reserves, high electrochemical stability in acidic environments, tunable band gap, and good proton conduction; unfortunately, as a semiconductor, it has poor electron transport ability and few active sites hindering high HER performances.^{4,16,17} These negative aspects can be strongly reduced by an effective strategy using nanostructures, with high surface-to-volume ratio and low resistance to further improve the electrochemical

properties, of WO₃ as cathodes for HER. WO₃ nanostructures can be effectively synthesized by hydrothermal,¹⁸ sputtering,¹⁹ thermal evaporation,²⁰ sol-gel,²¹ and electrodeposition²² methods. Nevertheless, in its pristine form, nanostructured WO₃ does not give excellent HER performances, as the atomic hydrogen adsorption free energy (ΔG_H) on the W site is high, leading to a poor HER activity, as explained by Sabatier's principle, for which ΔG_H close to zero gives better catalytic performances.^{4,23,24} Many efforts have been made with the aim of modulating the WO₃ electronic structure, such as decoration with Pt clusters,^{25,26} the embedding of W-based compounds on conductive supports such as reduced graphene oxide (RGO)¹⁷ and carbon nanotubes (CNTs),¹¹ and the realization of heterostructures by coupling WO₃ with other transition-metal oxides.^{27–29} Although these solutions are effective for enhancing the HER activity, their exploitation on a large scale is limited by the complex synthesis and assembly processes.

The crystal phase of WO₃ can also play a pivotal role. The hexagonal structure of WO₃ seems to be the most performing for electrochemical applications due to the favorable H⁺ intercalation–release pathways,³⁰ while the monoclinic phase

Received: May 5, 2022

Accepted: July 13, 2022

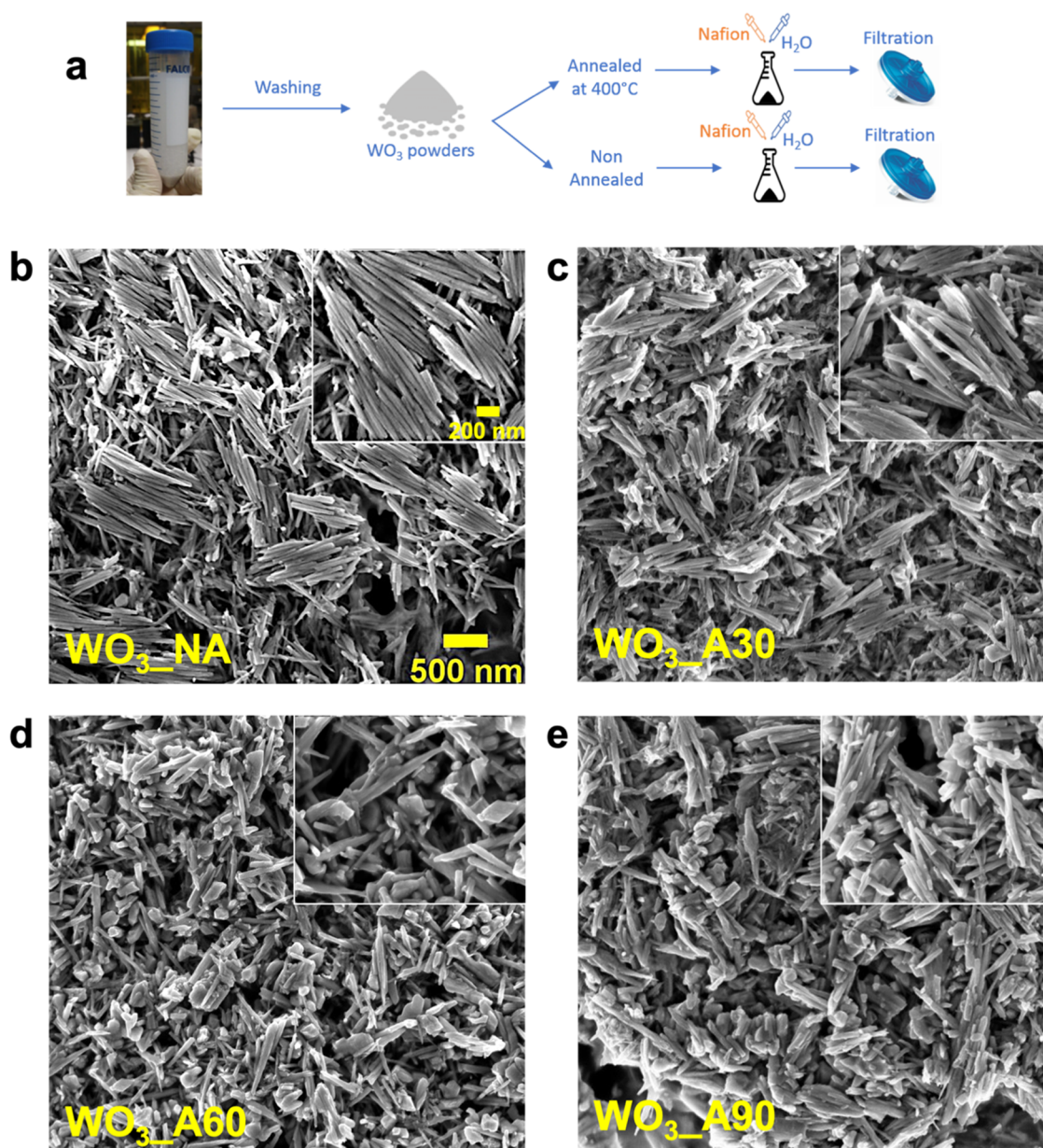


Figure 1. (a) WO_3 powder extraction, annealing, and filtering; low- and high- (inset) magnification SEM images of (b) WO_3 _NA-, (c) WO_3 _A30-, (d) WO_3 _A60-, and (e) WO_3 _A90-based electrodes. Markers in (a) are valid for all relative images.

is more stable at room temperature.³¹ The mixed hexagonal–monoclinic WO_3 -based heterostructure has been recently shown to enhance the photoelectrochemical ability by means of a Z-scheme in energy bands, promoting electron–hole pair separation.^{32,33} Such a heterostructure can be extremely interesting for HER as the hexagonal–monoclinic interface can act as an active site for H^+ adsorption thanks to the formation of an electron reservoir promoting the catalytic and electrical properties.

Here, we report a low-cost and simple hydrothermal synthesis of a WO_3 -based hexagonal–monoclinic phase junction heterostructure with excellent HER performances, evidenced by detailed structural and electrochemical characterization. A comprehensive description of the HER mechanism at the interface of the phase junction is also provided.

2. EXPERIMENTAL SECTION

2.1. Synthesis of WO_3 Nanorods. Hexagonal WO_3 nanorods are synthesized by using hydrothermal synthesis, as reported in our previous work.³⁴ WO_3 powder (Figure 1a) is obtained by centrifugation (6000 rpm for 10 min), followed by washing with ethanol and water several times, and finally drying on a hot plate for 1 h in air at 70 °C (denoted as WO_3 NA). Some samples underwent a calcination process on a hot plate at 400 °C for 30, 60, and 90 min (denoted as WO_3 A30, WO_3 A60, and WO_3 A90, respectively).

2.2. Preparation of Electrodes. The obtained WO_3 -based nanostructures were used for the realization of different pastes (20 mg of nanostructure powder, 0.1 mL of Nafion, and 2 mL of deionized water, with subsequent filtration by a 1.2 μm filter), as shown in Figure 1a. Electrodes are produced by drop-casting the obtained WO_3 -based pastes on graphene paper substrates (GP, 2 \times 1 cm^2 , Sigma Aldrich, 240 μm thick). The masses of the electrode (substrate + WO_3 nanostructures) and the bare substrate were measured by a Mettler Toledo MX5 microbalance (sensitivity: 0.01 mg).

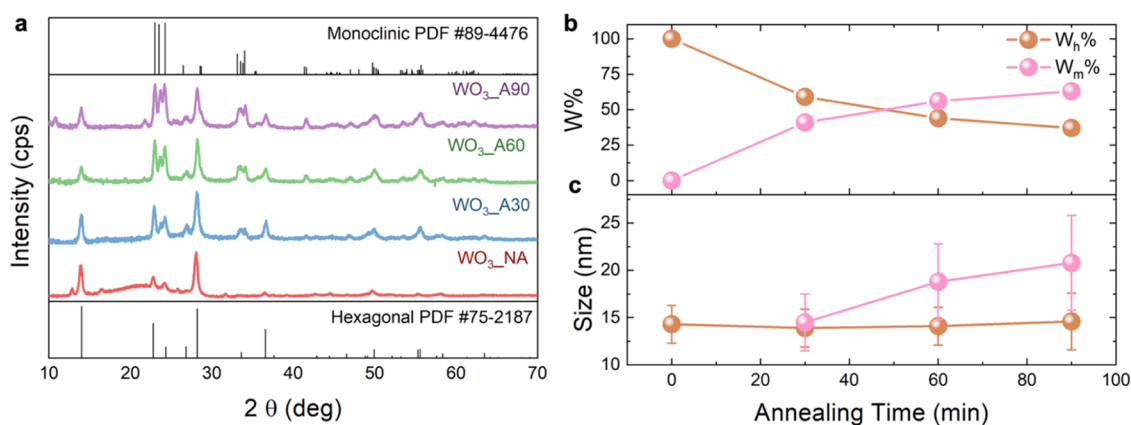


Figure 2. (a) XRD patterns of WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 powders, compared with pure hexagonal and monoclinic WO₃ XRD patterns; (b) weight ratio (W%) and (c) crystallite sizes of h-WO₃ and m-WO₃ (brown and pink spheres) as a function of annealing time for WO₃-based powders.

2.3. Characterization. The morphological analyses were carried out by a scanning electron microscope Gemini Field Emission SEM Carl Zeiss SUPRATM 25 (FEG-SEM, Carl Zeiss Microscopy GmbH, Jena, Germany) in lens mode and a transmission electron microscope (JEOL, JEM-ARM200F) operated in TEM mode. The film structure was analyzed through XRD using a SmartLab Rigaku diffractometer, at grazing incidence of 0.5°, equipped with a rotating anode of Cu K α radiation operating at 45 kV and 200 mA. The scans were acquired from 10° to 70° with steps of 0.02°. The electrochemical measurements were performed at room temperature by using a potentiostat (VersaSTAT 4, Princeton Applied Research, USA) and a three-electrode setup, with a graphite rod electrode as the counter electrode (to avoid any Pt contaminations), a saturated calomel electrode (SCE) as the reference, and WO₃ onto GP as the working electrode, in 1 M H₂SO₄ supporting electrolyte.

2.4. Electrochemical Measurements. Electric current values were normalized to the geometrical immersed surface area of each electrode. The measured potential versus SCE was converted into the reversible hydrogen electrode (RHE) according to the Nernst equation:^{28,35}

$$E'_{\text{RHE}} = E_{\text{SCE}}^{\ominus} + E_{\text{SCE}} \times 0.059 \times \text{pH} \quad (1)$$

where E_{SCE}^{\ominus} is the standard potential of SCE at 25 °C (0.241 V), and E_{SCE} is the measured potential versus SCE. The HER activities of various WO₃-based electrodes were investigated using linear sweep voltammetry (LSV), recorded at 5 mV/s from -0.2 to -0.8 V versus SCE. Electrochemical impedance spectroscopy (EIS) was performed from 100 kHz to 0.1 Hz in a potentiostatic mode, with an AC voltage of 5 mV at the potential (vs SCE) of 10 mA/cm² in the LSV curves. The double-layer capacity (C_{dl}) was determined from the cyclic voltammetry (CV) curves, recorded at different scan rates (5 to 100 mV/s) from -0.2 to -0.3 V versus SCE. All the obtained potentials vs RHE are manually corrected by iR_{u} compensation as follows:

$$E_{\text{RHE}} = E'_{\text{RHE}} - iR_{\text{u}} \quad (2)$$

where i is the electrode current, and R_{u} [ohms] is the uncompensated resistance, measured by EIS.¹ The Mott-Schottky analyses were carried out from -0.2 to -1.6 V versus SCE at 1000 Hz frequency.

3. RESULTS AND DISCUSSION

3.1. Morphological Characterization. Figure 1b–e shows the low- and high- (inset) magnification SEM images of WO₃_NA-, WO₃_A30-, WO₃_A60-, and WO₃_A90-based electrodes, which appear composed of oddly aligned nanorods (0.5–1 μm long and 50 nm large; see inset in Figure 1) stacked on top of each other until they form a homogeneous

and very porous film, which does not change by the thermal treatment, as also reported in the literature.³²

A change in the phase structure of WO₃-based nanostructures during annealing processes was analyzed as a function of annealing time. Figure 2a shows the XRD patterns of WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 powders compared with the XRD patterns of hexagonal (PDF #89-4476) and monoclinic (PDF #75-2187) WO₃, respectively. The XRD pattern of WO₃_NA shows typical diffraction peaks related to the hexagonal crystal structure, which appear at $2\theta = 14.00^\circ, 24.36^\circ, 26.84^\circ, 28.22^\circ, 33.62^\circ, 36.58^\circ,$ and 49.95° as expected, indicating the pure hexagonal phase in as-prepared WO₃ nanorods.³⁴ Besides the abovementioned diffraction peaks, with the increasing of annealing time, peaks clearly related to the monoclinic crystal structure appear ($2\theta = 23.00^\circ, 23.50^\circ, 24.28^\circ, 33.12^\circ, 33.54^\circ, 33.84^\circ, 34.04^\circ, 49.74^\circ,$ and 55.71°) with the increasing intensity, suggesting the coexistence of hexagonal and monoclinic WO₃ phases (h-WO₃ and m-WO₃) in WO₃_A30, WO₃_A60, and WO₃_A90 powders. Therefore, according to the XRD results shown in Figure 2a, h-WO₃ starts to change phase toward m-WO₃ as soon as the annealing process begins.

By using the RIR method, the weight ratio (W%) of h-WO₃ and m-WO₃ ($W_{\text{h}}\%$ and $W_{\text{m}}\%$, respectively) in WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 powders can be calculated (details are reported in the Supporting Information), and Figure 2b shows the obtained values for $W_{\text{h}}\%$ and $W_{\text{m}}\%$ as a function of annealing time. The intensities of m-WO₃ peaks increase gradually with the increasing annealing time, starting from 0 W% for the WO₃_NA sample until reaching 63 W% for the WO₃_A90 sample. A full phase transition into the monoclinic phase does not occur in our samples, as longer times or higher temperatures are needed, as expected.³² In fact, annealing conditions were chosen to allow a careful modification of hexagonal/monoclinic volume ratio, greatly useful for HER optimization. The size of the h- and m-WO₃ submicrometer crystallites can be calculated by using the Scherrer equation³⁶ (details are reported in the Supporting Information), which are reported in Figure 2c as a function of the annealing time (error bars are reported for each measurement). It is worth to note that the thermal treatment affects the m-WO₃ crystallite size, which increases with the annealing time. However, h-WO₃ crystallite size does not

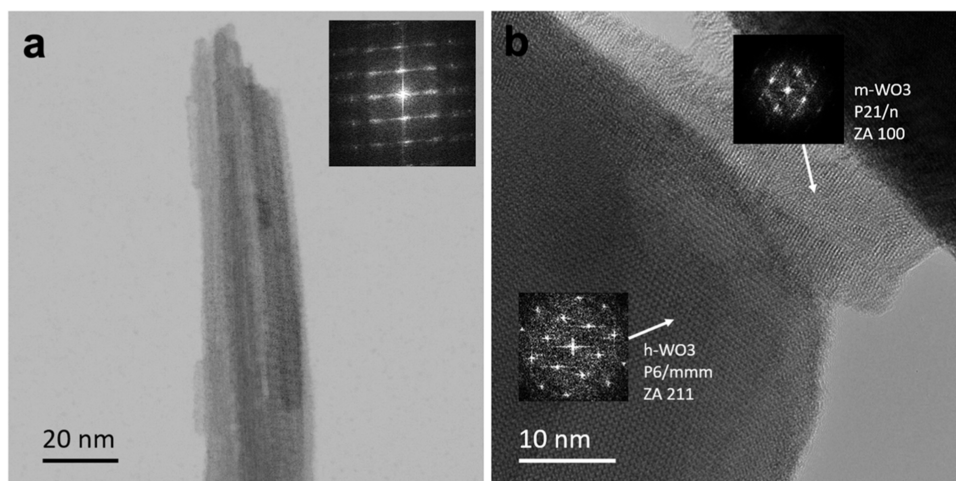


Figure 3. (a) TEM bright-field image of a single nanorod, composed of aligned nanoneedles. (b) High-resolution TEM image which confirms the presence of the h-/m-WO₃ phase junction. Inset: (a) FFT of Figure 3a; (b) FFT of h- and m-WO₃.

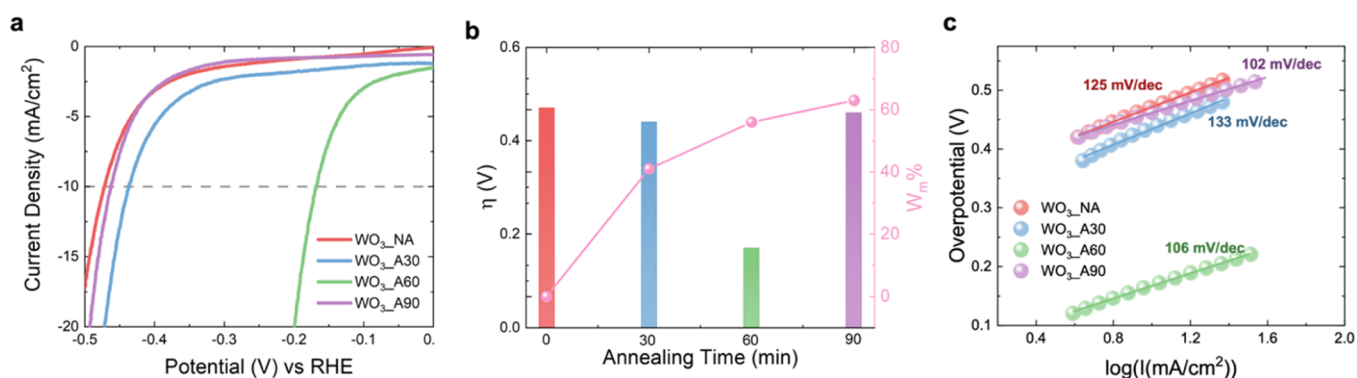


Figure 4. (a) LSV curves, (b) η and $W_m\%$ as a function of annealing time, and (c) Tafel plots related to the WO₃_NA (red), WO₃_A30 (blue), WO₃_A60 (green), and WO₃_A90 (violet) electrodes. The dashed line in (a) indicates the current density of 10 mA/cm².

depend on the annealing time. The observed reduction of $W_m\%$ with annealing suggests a decrease of h-WO₃ crystallite density.

TEM analyses were performed to investigate the morphology and crystal structure of single nanorods. Figure 3a reveals that each nanorod is composed of a bundle of smaller needles (about 10 nm large) probably stuck together during the hydrothermal synthesis. These needles are well-aligned with each other, with the main dimension along the *c*-axis, as shown by the fast Fourier transforms (FFTs) in the inset. Interestingly, the high-resolution micrograph of a WO₃ nanoneedle (Figure 3b) clearly shows a phase junction among the hexagonal and monoclinic structures (confirmed by the respective FFTs in the insets). Such evidence confirms the presence of h-/m-WO₃ phase junctions in the WO₃_A60 powder, as expected from the XRD results.

3.2. Electrochemical Characterization. Figure 4a shows the iR_u -corrected LSV curves reported versus the RHE scale (eqs 1 and 2) of WO₃_NA-, WO₃_A30-, WO₃_A60-, and WO₃_A90-based electrodes, at a scan rate of 5 mV/s. All the polarization curves show a similar trend, with an initial current density plateau, followed by a rapid increasing current density, evidencing a more and more pronounced H₂ production. WO₃_NA and WO₃_A90 electrodes (red and violet curves, respectively) show almost overlapping polarization curves by revealing a similar HER behavior. The WO₃_A30 electrode polarization curve (blue curve) shows a little improvement in terms of current density produced at a fixed potential. The

WO₃_A60 electrode (green curve) shows an excellent polarization curve with a strong current density at a moderately low negative potential, revealing a very good electrocatalytic HER activity. In detail, the overpotential at 10 mA/cm² (η) of the WO₃_A60 electrode is 170 mV, whereas WO₃_NA, WO₃_A30, and WO₃_A90 electrodes show η values of about 460 mV (η values are listed in Table S1). The supremacy of HER performance of the WO₃_A60 electrode can also be appreciated by its current at an overpotential of 170 mV (10 mA/cm²), which is 10 times higher than that of WO₃_NA, WO₃_A30, and WO₃_A90 electrodes at the same overpotential. The annealed series from 30 to 90 min was experimentally reproduced two times, confirming the best outcomes for 60 min annealing.

The η and crystal phase mixture trends as a function of the annealing time are reported in Figure 4b. By increasing $W_m\%$ up to 56%, η decreases to its minimum value (170 mV for WO₃_A60). A further increase of $W_m\%$ (63%) leads to a worsening of the HER catalytic activity, which becomes comparable to that of the fully hexagonal phase. Such a behavior clearly indicates that a mixture of phases is better than a single phase. While it is clearly established that a fully hexagonal phase is much better than a fully monoclinic one,^{10,15} here, we demonstrate that when the hexagonal and monoclinic phases coexist to a comparable extent, the highest HER performance is obtained.

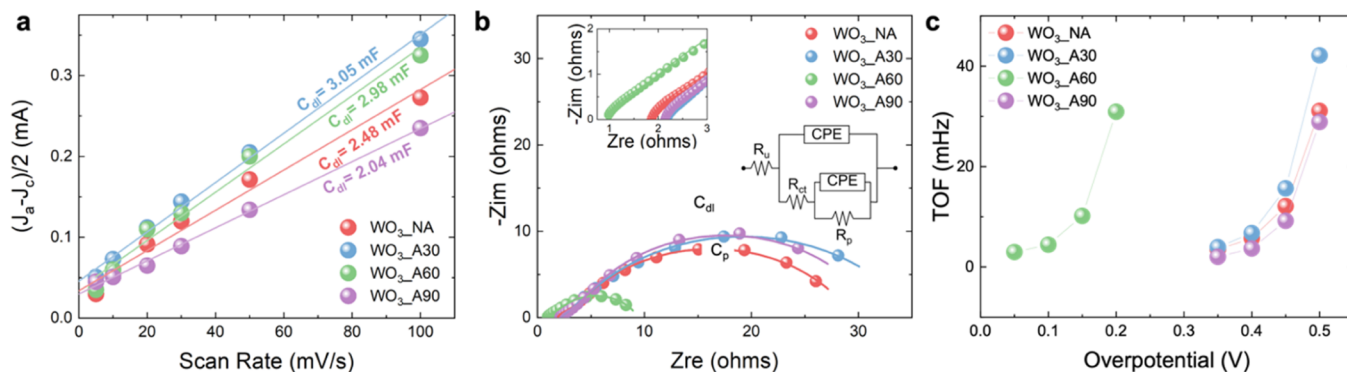


Figure 5. (a) Plot of $(J_a - J_c)/2$ recorded at -0.25 V vs the scan rate (solid sphere) and related linear fits (solid line). (b) EIS analyses and (c) TOF as a function of the overpotential of WO_3 _NA (red), WO_3 _A30 (blue), WO_3 _A60 (green), and WO_3 _A90 (violet) electrodes. Inset: Armstrong and Henderson equivalent circuit and the magnification of the high-frequency region.

To deepen such experimental evidence, we analyzed the kinetics of HER in our samples. Figure 4c shows the Tafel plot and the relative linear fit of WO_3 _NA, WO_3 _A30, WO_3 _A60, and WO_3 _A90 electrodes (filled circle curves and solid lines, respectively) obtained from the polarization curves of Figure 4a (details are reported in the Supporting Information). All Tafel plots show the same slope, in the range of 100–130 mV/dec (values are listed in Table S1). A slightly lower Tafel slope seems to be related to a higher monoclinic volume ratio, even if the variation among all samples is fairly limited. The lack of variation in the Tafel slope is an index of the same HER mechanism, regardless of the hexagonal and monoclinic contents in WO_3 . The Tafel slope is strictly related to the rate-determining step (RDS) among the elementary characteristic steps through which HER occurs.³⁷ According to Tian et al., the HER process in an acidic environment occurs through the combinations of the following steps, namely, the Volmer, Tafel, and Heyrovsky equations, respectively:³⁷



where * denotes the active adsorption site. In detail, the HER occurs through a Volmer–Tafel or a Volmer–Heyrovsky mechanism, depending on the electrode material. Moreover, the Tafel slope around 118 mV/dec is typically related to the HER for which the Volmer process acts as the RDS.³⁷ Such a situation describes all our WO_3 -based electrodes, for which the HER process is limited by the H^+ adsorption process on the electrode surface. Such evidence is not in contrast with the variation of the $W_{\text{h}}\%/W_{\text{m}}\%$ ratio, as this last parameter fairly regards the bulk material, while the H adsorption process occurs at the surface.

The HER activity was further evaluated by calculating the ECSA parameter, as described in the Supporting Information. Figure S1 shows the CV curves recorded in a nonfaradic region, between -0.3 to -0.2 V versus SCE, at different scan rates ranging between 5 and 100 mV/s of (a) WO_3 _NA, (b) WO_3 _A30, (c) WO_3 _A60, and (d) WO_3 _A90 electrodes. Figure 5a shows the plot of $(J_a - J_c)/2$ recorded at -0.25 V from the CV curves of Figure S1 versus the scan rate (red, blue, green, and violet solid spheres) and the related linear fits (red, blue, green, and violet solid lines) which allow defining C_{dl} at -0.25 V.³ The ECSA parameter is defined (details in the

Supporting Information). The C_{dl} and ECSA values are listed in Table S1. The C_{dl} (ECSA) values are comparable for the WO_3 electrodes with an intermediate *m*- WO_3 content (3.05 mF (102 cm²) and 2.98 mF (100 cm²) for WO_3 _A30 and WO_3 _A60, respectively), while they are slightly lower for the WO_3 electrodes with the prevalence of a hexagonal or monoclinic crystalline phase (2.48 mF (83 cm²) and 2.04 mF (68 cm²) for WO_3 _NA and WO_3 _A90, respectively). The slightly higher C_{dl} and ECSA values for WO_3 _A60 are not high enough to explain its excellent catalytic HER activity. Thus, further in-depth electrochemical analyses were carried out.

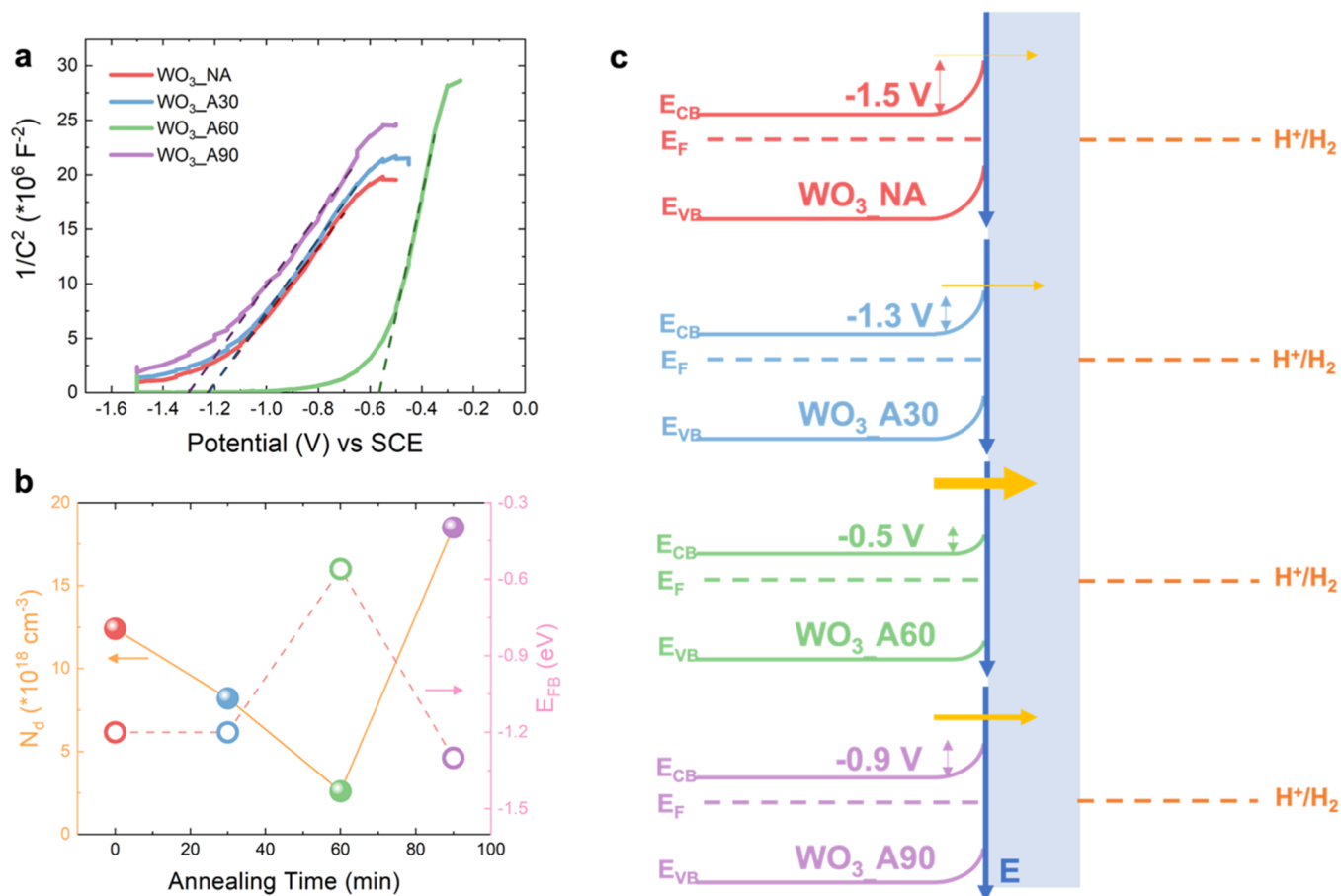
The charge transfer kinetics occurring at the interface between the electrolyte and the WO_3 -coated electrode was investigated by using EIS analysis. Figure 5b shows the Nyquist plot for all the WO_3 -based electrodes (solid spheres). All the EIS spectra exhibit a hint of a very small (inset of Figure 5b) and a large semicircle in the higher and lower frequency regions, respectively. The impedance data were interpreted and fitted (solid line in Figure 5b) using the equivalent circuit of Armstrong and Henderson reported in Figure 5b. R_{u} represents the uncompensated resistance used in eq 2 for the iR_{u} correction of the LSV current, R_{ct} represents the charge transfer resistance related to the substrate electrode reaction, R_{p} is related to the mass charge resistance of the intermediate H_{ads} on the surface of the catalytic material which is also called *pseudo-resistance*, and C_{dl} and C_{p} are constant phase capacitances, which represent the double-layer capacitance and pseudo-capacitance (at η), respectively, and are described by pre-exponential (P_{dl} and P_{p}) and exponential (n_{dl} and n_{p}) factors.³⁸ All fit values are reported in Table 1. P_{dl} and n_{dl} are similar for all WO_3 -based electrodes as well as P_{p} and n_{p} . The R_{ct} values are similar to each other, regardless of the crystal phase composition of WO_3 nanostructure-based electrodes, confirming that the substrate role is the same as well as the substrate coverage for all WO_3 -based electrodes. The sum of R_{ct} and R_{p} represents the total faradaic resistance of the

Table 1. EIS Parameters of WO_3 _NA, WO_3 _A30, WO_3 _A60, and WO_3 _A90 Electrodes

	P_{dl} ($\times 10^{-3}$)	n_{dl}	P_{p} ($\times 10^{-3}$)	n_{p}	R_{u} (ohm)	R_{ct} (ohm)	R_{p} (ohm)
WO_3 _NA	1	0.7	4	0.7	1.9	2.3	25.4
WO_3 _A30	3	0.7	5	0.7	2.2	2.3	31
WO_3 _A60	0.4	0.8	5	0.7	2	1.2	7.3
WO_3 _A90	1	0.7	2	0.7	2.1	2.7	27

Table 2. Comparison between the Electrochemical HER Parameters for WO₃-Based Nanostructures Reported in the Literature and Our Data

	η (mV)	Tafel slope (mV/dec)	C_{dl} (mF)	ECSA (cm ²)	TOF@ η (mHz)	ref
WO _{3-x} nanoplates on carbon nanofibers	185	89				11
WO ₃ @NPRGO	225	87				17
WO ₃ ·H ₂ O nanoplates	300	97				39
Ag-WO ₃	207	52.4	54.92			40
WS ₂ -WC-WO ₃	312	59	11.8	295	20	28
WS ₂ /WO ₃ heterostructure	395	50				29
h-WO ₃ /m-WO ₃ nanorods	170	106	2.98	100	15	our work

**Figure 6.** (a) Mott–Schottky plot and (b) related donor concentration (N_d) and flat-band potential (E_{FB}) of WO₃_NA (red), WO₃_A30 (blue), WO₃_A60 (green), and WO₃_A90 (violet) electrodes; (c) scheme of the relative position of energy levels and band bending related to the H⁺/H₂ energy level at the semiconductor–liquid interface for each WO₃-based electrode. The thickness of the yellow arrow denotes the magnitude of the cathodic current.

electrode at a fixed potential.³⁸ The smallest value of R_p , which results into the smallest faradaic resistance, is obtained for the WO₃_A60 electrode which possesses the highest HER activity. As R_{ct} and R_p are strictly correlated to the active Volmer, Tafel, or Heyrovsky mechanisms, the catalytic activity of the WO₃_A60 electrode can be ascribed to a more favorable H⁺ adsorption on the surface, thanks to the lowering of the total faradaic resistance of the HER mechanism, by pointing out the correlation between the H⁺ adsorption process and the phase junction formation, which depends on the m-WO₃ and h-WO₃ contents in WO₃-based electrodes.

To further study the HER activity of WO₃-based electrodes, the turnover frequency (TOF) is calculated as a function of the overpotential, as described in the Supporting Information and reported in Figure 5c. The TOF of WO₃-based electrodes at η

is about the same (the values are listed in Table S1), thus confirming that the only relevant difference in the HER activity between the WO₃-based electrodes is the potential at which the HER starts.

The electrochemical HER parameters of the WO₃_A60 electrode are reported in Table 2 for a comparison with the data reported in the literature for WO₃-based electrodes. Our electrode shows the lower overpotential, confirming the promising HER performances of h-WO₃/m-WO₃ phase junction-based nanostructures. The presence of two crystal phases at comparable extents could be responsible for this advantageous performance.

3.3. Effect of the Phase Junction Formation. To better understand the effect of phase junction formation in the WO₃ HER catalytic activity, Mott–Schottky analysis was carried out,

in 1 M H₂SO₄ aqueous solution, for the study of the liquid–semiconductor interface. WO₃-based electrodes were characterized by measuring their capacitance as a function of applied potential.^{41–43} The typical Mott–Schottky plot (C^{-2} vs applied potential) is shown in Figure 6a. A linear trend from -1.1 to -0.7 V versus SCE is shown for WO₃_NA, WO₃_A30, and WO₃_A90 electrodes and from -0.5 to -0.4 V for the WO₃_A60 electrode. The flat-band potential E_{FB} and the donor density N_{d} are calculated as the x -axis intercept and slope from the linear part of the plot, as described in the Supporting Information, and are reported in Figure 6b (filled and hollow spheres, respectively).^{41–44} The minimum E_{FB} value (-0.5 V) is obtained for the WO₃_A60 electrode, for which lower N_{d} ($2.6 \times 10^{18} \text{ cm}^{-3}$) is recorded (do note the inverse Y scales for E_{FB} and N_{d} in Figure 6b). E_{FB} is related to band bending at the liquid–semiconductor interface under equilibrium conditions; so, by combining this value with the open-circuit potential (OCP) of each WO₃-based electrode (reported in Table S2), the actual band bending with respect to the H⁺/H₂ level can be defined. The results of such exercise are reported in Figure 6c. The WO₃_A60 electrode shows the lowest band bending as well as the lowest depletion region, which leads to the lowest energy barrier for electrons moving from WO₃ toward the electrolyte (depicted as the light blue region). A larger electron flux is thus expected for this sample (as drawn by the thickness of yellow horizontal arrows) in comparison to others. Lower band bending corresponds to a lower η for HER, explaining the better catalytic activity of the WO₃_A60 electrode.

The evidence can be summarized as follows:

- (i) XRD and TEM analyses demonstrate the h-/m-WO₃ phase junction formation. $W_{\text{m}}\%$ strongly depends on the annealing time, as well as the monoclinic crystallite size;
- (ii) WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 electrodes show polarization curves with the same trend (Figure 4a), but the polarization curve of WO₃_A60 is shifted toward lower potentials by achieving lower η of 170 mV at 10 mA/cm²;
- (iii) The Tafel slopes and TOF values of WO₃-based electrodes suggest that the HER mechanism is the same, regardless of the m-WO₃ and h-WO₃ contents, and so of the phase junction formation. Moreover, the Tafel slope values suggest that the HER mechanism is limited by the H⁺ adsorption mechanism on the active material surface;
- (iv) WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 electrodes show similar C_{dl} and ECSA by ruling out the active surface role in the HER catalytic activity and in the phase junction formation;
- (v) EIS analysis shows the same quasi-negligible electrode substrate role for each WO₃-based electrode and the possibility to ascribe the superior HER activity of the WO₃_A60 electrode to a lowering of the total faradaic resistance of the HER mechanism caused by the m-WO₃ and h-WO₃ phase junction formation.
- (vi) Mott–Schottky analyses highlight the energy-level structure at the semiconductor–liquid interface, revealing the smallest band bending for the WO₃_A60 electrode, which leads to the highest cathodic current flux toward the electrolyte and so to the lowest η for the activation of the HER process.

Taking into account these considerations, a schematic representation of the correlation between the enhancement of the HER activity and the formation of m- and h-WO₃ phase (lilac and brown parts, respectively) junctions is proposed in Figure 7. The thermal treatment leads to a stable phase

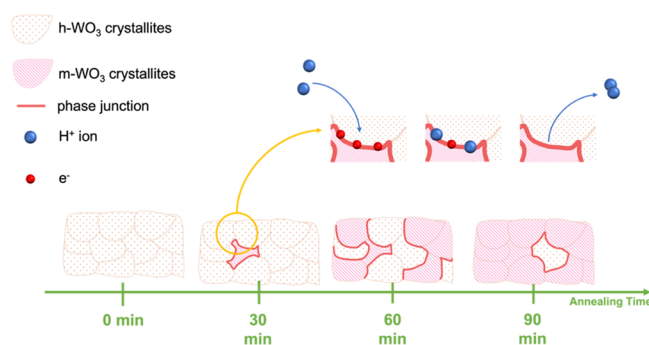


Figure 7. Schematic representation of the HER mechanism corresponding to the h-/m-WO₃ phase junction (brown and pink areas). The HER predominantly occurs at the phase junction interface (red lines), in which many electrons (red balls) are available for the adsorption of H⁺ (blue balls) and production of H₂.

junction formation corresponding to the grain boundary between h- and m-WO₃ crystallites (red lines in Figure 7) without affecting the morphology of WO₃-based nanostructures, as shown by the SEM images in Figure 1. As depicted in Figure 7, the concentration of the h-/m-WO₃ phase junctions depends on the annealing time and so on $W_{\text{h}}\%$ and $W_{\text{m}}\%$. The WO₃_A60 powder shows similar $W_{\text{h}}\%$ and $W_{\text{m}}\%$ values (see Figure 2b) and similar h- and m-WO₃ crystallites sizes (see Figure 2c), which should lead to a higher density of phase junctions. On the contrary, the WO₃_NA, WO₃_A30, and WO₃_A90 powders show a lower (or zero) phase junction density because of the prevalence of one crystal phase. At the semiconductor–liquid interface, the phase junctions affect the total band bending (Figure 6c). The lower band bending results in a higher cathodic current and hence in a higher concentration of available electrons useful to lower the total faradaic resistance. The phase junction interface becomes the main site for H⁺ adsorption and for H₂ production thanks to the largely available electrons, as shown in Figure 7. The presence of a high concentration of phase junction lowers the required potential for HER activation, and so η , confirming our experimental evidences related to WO₃_A60.

4. CONCLUSIONS

In conclusion, h-/m-WO₃ phase junction has been successfully fabricated in the hydrothermally synthesized WO₃ nanorods, annealed at 400 °C for 30, 60, and 90 min. The hexagonal and monoclinic contents strongly depend on the annealing time as well as the dimension of the as-formed monoclinic crystallites. In particular, the 60 min annealed WO₃ powders show a monoclinic content of 56% and comparable monoclinic and hexagonal crystallite sizes. This sample exhibits exceptional catalytic activity for HER in 1 M H₂SO₄ electrolyte with an overpotential of 170 mV at 10 mA/cm². The advantage of this h-/m-WO₃ combination can be ascribed to the formation of numerous phase junction interfaces at which the HER can occur faster thanks to the larger availability of electrons, as demonstrated by the Tafel, EIS, and Mott–Schottky analyses and ECSA and TOF determination. The obtained catalyst

represents a potential candidate for Pt-free electrochemical production of clean hydrogen in acid solution by paving the way to a further study and engineering of simple phase junction formation in semiconductors for Pt-free HER applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.2c01383>.

Description of the RIR method and the application of the Scherrer formula; calculation of the Tafel slope, ECSA, and TOF parameters; description of the Mott–Schottky analysis; h -WO₃ content, η , Tafel slope, C_{dl} , ECSA, and TOF of WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 electrodes; results of Mott–Schottky analyses for WO₃_NA, WO₃_A30, WO₃_A60, and WO₃_A90 electrodes; CV at different scan rates in the non-faradic region ranging between -0.3 and -0.2 V vs SCE of (a) WO₃_NA, (b) WO₃_A30, (c) WO₃_A60, and (d) WO₃_A90 (violet) electrodes (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This work was supported by programma ricerca di Ateneo UNICT 2020–22 linea 2 PIA.CE.RI “NATI4Smart Sviluppo di NANomateriali e Tecnologie Innovative per Smart detection”, and by PRIN 2017 “CLEAN-Valorizing Sustainable Plastics through a CLEver use of NANoparticles” 20174FSRZS_003.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors wish to thank G. Malandrino (University of Catania, Italy) for useful discussions and experimental XRD contribution, the Bio-nanotech Research and Innovation

Tower (BRIT) laboratory of the University of Catania (Grant no. PONa3_00136 financed by the MIUR) for the Smartlab diffractometer facility, and G. Pantè, C. Percolla, and S. Tatì (CNR-IMM Catania, Italy) for technical support.

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