Highly Active Tungsten Oxide Nanoplate Electrocatalysts for the Hydrogen Evolution Reaction in Acidic and Near Neutral Electrolytes

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ABSTRACT: An efficient, cost-effective, and earth-abundant catalyst that could drive the production of hydrogen from water without or with little external energy is the ultimate goal toward hydrogen economy. Herein, nanoplates of tungsten oxide and its hydrates (WO₃·H₂O) as promising electrocatalysts for the hydrogen evolution reaction (HER) are reported. The square-shaped and stacked WO₃·H₂O nanoplates are synthesized at room temperature under air in ethanol only, making it as a promising green synthesis strategy. The repeated electrochemical cyclic voltammetry cycles modified the surface of WO₃·H₂O nanoplates to WO₃ as confirmed by X-ray photoelectron and Auger spectroscopy, which leads to an improved HER activity. Hydrogen evolution is further achieved from distilled water (pH 5.67) producing 1 mA cm⁻² at an overpotential of 15 mV versus the reversible hydrogen electrode. Moreover, WO₃·H₂O and WO₃ nanoplates demonstrate excellent durability in acidic and neutral media, which is highly desirable for practical application. Improved hydrogen evolution by WO₃(200) when compared to that by Pt(111) is further substantiated by the density functional theory calculations.

INTRODUCTION

Rapid depletion of fossil fuels and ever-increasing energy demand prompt the researchers to explore clean, renewable, sustainable, and environmentally friendly energy sources.¹ On that prospect, hydrogen is considered as an efficient, earth-abundant, and renewable clean energy carrier that has potential to play a major role. Hydrogen can be produced through electrochemical water splitting with zero emission of CO₂, to play a major role. Hydrogen can be produced through earth-abundance of these noble metals are the major hindrance for their practical utilization. High cost and poor earth-abundance of these noble metals are the major hindrance for their practical utilization. Therefore, it is indispensable to develop noble metal-free HER catalysts which are not only efficient but also earth-abundant, low cost, and stable in the electrolyte which is being used. Several noble metal-free electrocatalysts, particularly Mo- and W-based materials, have been reported recently and have been reckoned to be promising. In particular, chalcogenides such as MoS₂,⁸⁻¹² WS₂,¹³⁻¹⁶ WSe₂,¹⁷ and MoSe₂,¹⁷ have been successfully investigated as cost-effective potential substitution to the noble metal-based catalysts in acidic solutions. Although several chalcogenides have been studied for the HER in acidic media, little emphasis has been directed toward metal hydroxides and/or oxides and/or in neutral media.

Hydrogen evolution in neutral electrolyte solutions is desirable for practical applications. Thus, 0.1 M acetate buffer solution (pH 4.5) and phosphate buffer solution (PBS, pH 7) have been used as electrolytes for hydrogen evolution by Andreiadis et al.¹⁸ with a cobalt-based complex and Karunadasa et al.¹⁹ with a molybdenum-oxo-complex, respectively. Helm et al. also demonstrated hydrogen production using nickel complexes in both aqueous and acidic electrolytes.²⁰ The synthesis of these metal complexes is not only complex but also involves multiple steps and several chemicals. However, the stability of these complexes for long-term uses is an issue. Therefore, it is of immense importance to explore suitable...
inorganic electrocatalysts for hydrogen generation in neutral media.

Here, competent HER activity of tungsten trioxide (WO3) nanoparticles is demonstrated in acidic and neutral electrolytes, and compared with standard platinum on carbon (Pt/C) catalysts. Coincidently, WO3 was obtained by electrochemical surface oxidation of WO3·H2O nanoparticles through repeated electrochemical cyclic voltammetry (CV) cycles for the first time. The electrochemically surface-modified WO3·H2O exhibits a performance similar to WO3 obtained separately by annealing WO3·H2O nanoparticles under air at 400 °C. It is noteworthy that WO3·H2O nanoparticles were synthesized at room temperature using only ethanol as a solvent thus excluding the use of corrosive HCl or HNO3 along with other organic chemicals previously reported for the synthesis of hydrated WO3.21–24 To demonstrate the potential of the present electrocatalysts, we further demonstrate hydrogen evolution in a neutral medium (distilled water; pH, 5.67) and their remarkable stabilities in acidic and neutral electrolytes. The superior HER activity of WO3 when compared to that of Pt is additionally supported by reaction energetics obtained by the density functional theory (DFT) calculations.

**RESULTS AND DISCUSSION**

**Structural Analysis.** The structural analysis of the as-synthesized samples was carried out by powder X-ray diffraction (XRD) as shown in Figure 1. The diffraction features of the precipitate formed at room temperature (Figure 1a) are readily indexed to the orthorhombic WO3·H2O with lattice parameters \( a = 5.25 \) Å, \( b = 10.7 \) Å, and \( c = 5.11 \) Å, which are in good agreement with those of JCPDS file no. 00-043-0679 \( (a = 5.24 \) Å, \( b = 10.7 \) Å, and \( c = 5.12 \) Å). The XRD pattern (Figure 1b) of WO3·H2O annealed at 400 °C for 2 h under air matches that of monoclinic WO3 with lattice parameters \( a = 7.3 \) Å, \( b = 7.51 \) Å, and \( c = 7.71 \) Å (JCPDS file no. 01-083-0951, \( a = 7.3 \) Å, \( b = 7.54 \) Å, and \( c = 7.69 \) Å). No other phases and/or impurities such as WO3·2H2O and WO3·0.33H2O were found in any of these samples indicating the phase-pure product. The XRD analysis suggests that the WO3·H2O powder formed at room temperature is completely phase-transformed to WO3 upon annealing at 400 °C for 2 h under air.

**Thermal Stability.** Complete conversion of WO3·H2O to WO3 upon annealing was further confirmed by thermogravimetry (TG) analysis. Figure 2 shows the TG and its derivative plot of WO3·H2O nanoparticles in a temperature range of 26–800 °C at a heating rate of 10 °C min⁻¹ under air. A major weight loss of 7.2% occurred up to 230 °C matches the theoretical value of 7.2% confirming the phase transformation of WO3·H2O to WO3.25 The subsequent weight loss of 1.1% between 230 and 400 °C is believed to be due to the final water decomposition in the crystallization of minor amorphous contents. The TG analysis corroborates the XRD results on the complete phase transformation of WO3·H2O to WO3 under air at 400 °C for 2 h (Figure 1).

**Morphology and Microstructure.** The morphology and microstructure of the as-synthesized orthorhombic WO3·H2O and monoclinic WO3 were examined in detail using field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), respectively. Figure 3a, b shows the FESEM images of WO3·H2O nanoparticles at different magnifications synthesized by mixing WCl6 in ethanol at room temperature. These nanoparticles were found to be square-shaped, highly uniform, and stacked. The length/width of these nanoparticles was measured to be 100 nm with a thickness <30 nm, measured from the magnified SEM image (shown as an inset in Figure 3b). Figure 3c presents a TEM image of stacked WO3·H2O nanoparticles in accordance with the FESEM images. The high-resolution TEM (HRTEM) image of a WO3·H2O nanoplate shows a lattice spacing of 3.5 Å corresponding to the (111) plane as shown in Figure 3d. Additional TEM images (Figure S1, Supporting Information) clearly depict the stacked arrangement and thickness of individual WO3·H2O nanoparticles. The powder XRD pattern (Figure 1a) of WO3·H2O nanoparticles also shows maximum intensity for the same (111) plane indicating their growth direction. The regular spot selected area diffraction (SAED) pattern (inset of Figure 3d) obtained from the WO3·H2O nanoplate confirms its single crystalline nature. Although synthesis of WO3·H2O nanoparticles has been reported earlier,21,23,24 they were of much larger sizes and synthesized at a higher temperature than the room temperature used in the present work. In particular, Huang et al.23 synthesized rectangular slab-like WO3·H2O of size 2–3 µm by taking Na2WO4 and HCl at 70 °C for 10 h and Kalantar-zadeh et al.24 reported hydrated WO3 platelets of 0.2–0.5 µm size obtained at 80 °C for 6 h using 0.5 M HNO3. Recently, Guo et al. reported
orthorhombic WO$_3$·H$_2$O nanoplates of size >200 nm by the hydrothermal method at 100 °C for 10 h. The formation of nanosized WO$_3$·H$_2$O plates (∼100 nm) is thus attributed to the lower synthesis temperature (room temperature) employed in the present work. Figure 3e,f shows the FESEM images of stacked WO$_3$ nanoplates at different magnifications obtained by annealing WO$_3$·H$_2$O nanoplates at 400 °C for 2 h under air. The annealing not only produced phase-pure WO$_3$ but also resulted in nanoplates to be separated in the stack as shown in Figure 3f. A TEM image of WO$_3$ nanoplates is shown in Figure 3g, which reveals the formation of gap between consecutive nanoplates (marked by arrows) and voids (marked by a circle) in the nanoplates. The formation of gaps and voids in WO$_3$ nanoplates is due to the annealing of WO$_3$·H$_2$O nanoplates at a higher temperature (400 °C). In WO$_3$·H$_2$O, water molecules are present between layers of WO$_6$ octahedral units and the W−OH$_2$ bond is weak. Thus, water molecules in WO$_3$·H$_2$O nanoplates are evaporated upon annealing as confirmed from the mass loss (Figure 2) forming gaps between nanoplates and voids in the resulting WO$_3$ nanoplates. The HRTEM image of a WO$_3$ nanoplate shows a lattice spacing of 3.8 Å, corresponding to the (002) plane of monoclinic WO$_3$. The regular spot SAED pattern (inset of Figure 3h) confirmed the single crystalline nature of the WO$_3$ nanoplates. In addition, the elemental energy dispersive X-ray (EDX) mapping of WO$_3$·H$_2$O and WO$_3$ nanoplates was performed (Figure S2, Supporting Information) in a FESEM which shows a uniform distribution of W and O throughout the sample.

**Electrocatalytic HER Study.** The electrochemical HER performance of WO$_3$·H$_2$O and WO$_3$ nanoplates was examined by linear sweep voltammetry (LSV), CV, and chronoamperometry in a highly acidic (0.5 M H$_2$SO$_4$) electrolyte. Figure 4a presents the LSV plots for the HER in 0.5 M H$_2$SO$_4$ at 1 mV s$^{-1}$ with WO$_3$·H$_2$O and WO$_3$ nanoplates along with Pt/C and glassy carbon electrodes (GCE) for comparison. An overpotential of 147, 73, and 24 mV was measured to obtain 10 mA cm$^{-2}$ with WO$_3$·H$_2$O, WO$_3$, and Pt/C, respectively. An 73 mV overpotential with WO$_3$ nanoplates was found to be smaller than that reported for several nonnoble metal electrocatalysts including Ni$_2$P (117 mV), MoS$_2$/Au (226 mV), MoS$_2$ (190 mV), WS$_2$ (233 mV), and other electrocatalysts (Table S1, Supporting Information). Moreover, a similar superior HER activity was reported by Phuruangrat et al. with hexagonal WO$_3$ nanowires synthesized by the microwave-assisted hydrothermal method. This suggests WO$_3$ as a potential HER electrocatalyst. The cyclic stability of WO$_3$·H$_2$O and WO$_3$ nanoplates was tested by performing CV for 4000 cycles in 0.5 M H$_2$SO$_4$ at 100 mV s$^{-1}$ (Figure S3, Supporting Information). A slight
positive current on Pt/C, WO3·H2O, and WO3 prior to onset potential of the HER (Figure 4a) was found to disappear after CV cycles, which is believed to be due to oxidative surface cleaning and surface oxidation of hydroxide. Furthermore, the HER current density of WO3·H2O was found to be significantly increased (Figure S3a) with repeated CV cycles toward the value of WO3 nanoplates (Figure S3b), which is attributed to surface oxidation of WO3·H2O to WO3 (discussed later). A smaller increase in the HER current density for WO3 nanoplates (Figure S3b) can be termed to surface cleaning during CV cycles and conversion of surface hydroxide to oxide. Figure 4b shows the Tafel plots of the electrocatalysts from which a slope was measured. The Tafel slopes (and exchange current densities) were measured to be 43.9 mV dec⁻¹ (6.1 mA cm⁻²), 39.5 mV dec⁻¹ (12.58 mA cm⁻²), and 29 mV dec⁻¹ (17.78 mA cm⁻²) for WO3·H2O, WO3, and Pt/C, respectively, in the first cycle. The Tafel slope and exchange current density were, respectively, smaller and larger with WO3 nanoplates than those of several other chalcogenides reported recently (Table S1, Supporting Information) for the HER. After 4000 CV cycles, the Tafel slope was found to be further decreased while the exchange current density increased for WO3·H2O (Table 1). The estimated Tafel slopes suggested the Volmer–Tafel HER mechanism of these electrocatalysts. The superior HER activity of W-based hydroxide and oxide to that of other recently studied materials (Table S1, Supporting Information) makes it a potential candidate for hydrogen generation.

To understand the better HER performance of WO3 than that of WO3·H2O, the electrochemical active surface area (ECSA) was calculated from the electrochemical double layer capacitance measurement using eq 1.

\[
\text{ECSA} = \frac{C_{dl}}{C_s}
\]

where \(C_{dl}\) is the electrochemical double layer capacitance and \(C_s\) refers the specific electrochemical double layer capacitance of an atomically smooth surface (typically 15–50 μF cm⁻²). In the present case, the value of \(C_s\) is 30 μF cm⁻² for all the electrodes in 0.5 M H2SO₄ electrolyte. \(C_{dl}\) was calculated by measuring the CVs at different scan rates in the nonfaradaic region. Figure 5a,b shows the CVs at different scan rates in the potential range of 0.54–0.84 V vs the RHE (nonfaradaic region) in 0.5 M H2SO₄ solution with (a) WO3·H2O and (b) WO3 nanoplates. (c) Capacitive currents measured at 0.7 V vs the RHE as a function of scan rates with WO3·H2O and WO3 nanoplates. (d) Nyquist plots of WO3·H2O and WO3 nanoplates at 0.06 V (vs RHE) before and after the stability test and the inset shows the equivalent circuit diagram used to fit the experimental data.

| catalysts   | electrolyte         | overpotential (mV at 10 mA cm⁻² vs RHE) | Tafel slope (mV dec⁻¹) | exchange current density (A cm⁻²) |
|-------------|---------------------|----------------------------------------|------------------------|----------------------------------|
| WO3·H2O (1st LSV) | 0.5 M H2SO₄          | 147                                    | 43.9                   | 6.11 × 10⁻³                      |
| WO3 (1st LSV)    | 0.5 M H2SO₄          | 73                                     | 39.5                   | 12.58 × 10⁻³                    |
| WO3·H2O (4001st LSV) | 0.5 M H2SO₄        | 66                                     | 34.8                   | 14.2 × 10⁻³                     |
| WO3 (4001st LSV)  | 0.5 M H2SO₄          | 70                                     | 38.53                  | 12.82 × 10⁻³                    |
| Pt/C             | 0.5 M H2SO₄          | 24                                     | 29                     | 17.78 × 10⁻³                    |
| WO3·H2O (1st LSV) | distilled water      | 55.7                                   | 0.02 × 10⁻⁵            |                                  |
| WO3 (1st LSV)    | distilled water      | 31.1 at 1 mA cm⁻²                       | 51.59                  | 0.021 × 10⁻⁵                    |
| WO3·H2O (10001st LSV) | distilled water    | 177 at 1 mA cm⁻²                       | 32                     | 0.032 × 10⁻⁵                    |
| WO3 (10001st LSV) | distilled water      | 193 at 1 mA cm⁻²                       | 47.73                  | 0.052 × 10⁻⁵                    |

### Table 1. HER Performance of WO3·H2O and WO3 Nanoplates in Different Electrolytes

- **catalysts**
- **electrolyte**
- **overpotential (mV at 10 mA cm⁻² vs RHE)**
- **Tafel slope (mV dec⁻¹)**
- **exchange current density (A cm⁻²)**
nanoplates at different scan rates (10–100 mV s\(^{-1}\)) in 0.5 M H\(_2\)SO\(_4\) electrolyte, respectively. The capacitive currents for WO\(_3\), H\(_2\)O and WO\(_3\) nanoplates at 0.7 V versus the reversible hydrogen electrode (RHE) were plotted as a function of scan rates (Figure 5c) and their slope is known as \(C_\text{dl}\) The ECSA (and \(C_\text{dl}\)) of WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates was measured to be 1.0 \(\text{cm}^2\) (0.03 mF) and 2.83 \(\text{cm}^2\) (0.085 mF), respectively. The larger ECSA of WO\(_3\) nanoplates clearly indicates more active sites in them, which resulted in higher HER performance compared to that of WO\(_3\)-H\(_2\)O nanoplates. Furthermore, the specific activity (SA) of WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates was calculated to compare their intrinsic catalytic performance by normalizing the HER current density to the specific surface area (Figure S4, Supporting Information) as per eq \ref{eq:SA}.\(^{35,36}\)

\[
\text{SA} = \frac{j}{10 \times m \times S_{\text{BET}}} \tag{2}
\]

where \(SA\) stands for specific activity (mA cm\(^{-2}\)), \(j\) refers to the current density (mA cm\(^{-2}\)) at 0.35 V (vs RHE), \(m\) stands for the catalyst loading mass (28.57 mg cm\(^{-2}\)), and \(S_{\text{BET}}\) is the Brunauer-Emmett-Teller surface area (m\(^2\) g\(^{-1}\)). The SA values normalized to the specific surface area were calculated to be 2.58 and 5.38 in magnitude for WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates, respectively. This further confirms the higher HER performance of WO\(_3\) nanoplates. The electrochemical impedance spectroscopy (EIS) study was carried out to understand the charge transfer behavior at the electrode/electrolyte interface. Figure 5d shows the Nyquist plots of WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates before and after 4000 CV cycles at an applied potential of 0.06 V versus the RHE in 0.5 M H\(_2\)SO\(_4\). All the EIS spectra show semicircles and straight lines in the high-frequency and low-frequency regions, respectively. The diameter of the semicircles infers to the charge-transfer resistance (\(R_Q\)) at the electrode/electrolyte interface. A smaller semicircle confirms superior performance of the electrode because of a smaller \(R_Q\). The \(R_Q\) values for WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates were measured to be 9.3 and 5.5 \(\Omega\), respectively, by fitting the experimental data with an equivalent circuit model shown as an inset in Figure 5d. As expected, the \(R_Q\) value decreased to 4.6 and 4.8 \(\Omega\) for WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates, respectively, after 4000 cycle CV test. A smaller \(R_Q\) further validates an increased current density with the electrocatalysts after the stability test.

The quantitative estimation of hydrogen evolution was finally performed with WO\(_3\) nanoplates using a gas chromatograph. The hydrogen generation rate was found to increase and reach 20.4 mmol cm\(^{-2}\) in 10 h (Figure 6) with WO\(_3\) nanoplates at −0.76 V versus the RHE in 0.5 M H\(_2\)SO\(_4\). The repeated 4000 CV cycles (Figure S3, Supporting Information) and hydrogen generation for 10 h suggests the good stability of WO\(_3\)-H\(_2\)O and WO\(_3\) for the HER.

The HER investigation was further extended to a neutral medium using normal distilled water (pH 5.67). Figure 7a–c shows the LSV, Tafel, and chronoamperometry plots of WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates in water. The HER was found to begin at ~0.5 V versus the RHE (−0.076 V vs saturated calomel electrode (SCE)) during the cathodic scan and HER current sharply increased below 0 V versus the RHE (−0.576 V vs SCE) in the presence of the catalyst, as shown in Figure 7a. As expected, WO\(_3\) exhibited a higher HER activity in the neutral medium as well. The obtained HER current of 1.0 mA cm\(^{-2}\) at the overpotential of 15 mV in the first cycle is significantly lower than recently reported electrocatalysts studied in the PBS electrolyte.\(^{18,37}\) The Tafel slopes (and exchange current densities) of 49.75 mV dec\(^{-1}\) (1.0 mA cm\(^{-2}\)) and 43.43 mV dec\(^{-1}\) (1.15 mA cm\(^{-2}\)) were measured for WO\(_3\)-H\(_2\)O and WO\(_3\) nanocubes in the first cycle, respectively. The repeated CV cycles showed an increase in the HER current density of WO\(_3\)-H\(_2\)O to the value obtained for WO\(_3\) nanoplates in water as well (Figure S5a,b, Supporting Information). After 10 000 CV cycles, LSV collected with WO\(_3\)-H\(_2\)O and WO\(_3\) nanoplates revealed improved performance, that is, a higher current density (3.6 mA cm\(^{-2}\) at 15 mV overpotential for both WO\(_3\)-H\(_2\)O and WO\(_3\) nanocubes), smaller Tafel slope (30.0 mV dec\(^{-1}\) for WO\(_3\)-H\(_2\)O and 41.98 mV dec\(^{-1}\) for WO\(_3\)), and higher exchange current density (1.5 mA cm\(^{-2}\) for WO\(_3\)-H\(_2\)O and 1.1 mA cm\(^{-2}\) for WO\(_3\)) as shown in Figure S6 (Supporting Information) and Table 1. Similar to the HER study in acidic electrolyte, a higher positive current was found with WO\(_3\)-H\(_2\)O than with WO\(_3\) nanoplates prior to the onset of HER (Figure 7a), which is due to the oxidation of surface hydroxide. However, after repeated CV cycles, the positive current prior to the onset of the HER remained (Figure S6, Supporting Information), which suggests that further study is needed to understand this behavior. The chronoamperometry measurement further confirmed excellent stability of the electrocatalysts as studied for 20 h without a decrease in current (Figure 7c). The quantitative hydrogen generation was also measured using gas chromatography and was found to be 550 \(\mu\)mol cm\(^{-2}\) in 10 h with WO\(_3\) nanoplates at −0.42 V versus the RHE (or −1.0 V vs SCE) in distilled water (Figure 7d).

**Surface Composition.** Improvements in the HER performance of WO\(_3\)-H\(_2\)O after repeated CV cycles is attributed to its surface modification to WO\(_3\). The change in the surface composition was confirmed by X-ray photoelectron spectroscopic (XPS) and Auger electron spectroscopic (AES) measurements. Figure 8 shows the W 4f and O 1s region XPS spectra of WO\(_3\)-H\(_2\)O, WO\(_3\)-H\(_2\)O after repeated CV cycles (in 0.5 M H\(_2\)SO\(_4\)), and WO\(_3\). The W 4f binding energy positions are well-matched to the literature values.\(^{38,39}\) The two O 1s XPS peaks at ~530.5 and ~531.7 eV are assigned to oxide and surface hydroxide, respectively.\(^{58}\) The W and O atomic compositions estimated using CasaXPS software are presented in Table 2, which clearly indicate the change in the surface composition of WO\(_3\)-H\(_2\)O to WO\(_3\) after CV cycles. Figure S7 (Supporting Information) shows the AES spectra of WO\(_3\)-H\(_2\)O, WO\(_3\)-H\(_2\)O after CV cycles (in 0.5 M H\(_2\)SO\(_4\)), and WO\(_3\). The surface composition (Table 2) measured by AES correlates the XPS results and confirmed the surface oxidation of WO\(_3\)-H\(_2\)O.
to WO$_3$ during electrochemical CV cycles. This signifies the important role of room temperature synthesized WO$_3$·H$_2$O nanoplates for the HER. However, the XRD pattern (not shown) of WO$_3$·H$_2$O after CV cycles showed no change in its phase, thus indicating the surface modification only.

**DFT Study.** The mechanism of hydrogen evolution was further investigated using periodic plane wave DFT calculations on the (200) plane of the P$_2_1/n$ monocline phase of WO$_3$ nanoplates as per experimental observation and their thermodynamic stability$^{40}$ and compared with those of the well-established Pt(111) catalyst.$^{41}$ The protons adsorbed on the hcp site of Pt(111) with the Pt−H bond distance of 1.912, 1.886, and 1.872 Å whereas 0.98 Å atop WO$_3$(200). The reaction coordinates for proton adsorption followed by its recombination (H $+ e^- \rightarrow H^* \rightarrow 1/2H_2$) have been reported to be the indicator of HER catalyst activity.$^{42}$ Therefore, energy landscapes indicating the above reactions were developed as shown in Figure 9. The adsorption energy of proton on

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**Figure 7.** (a) LSV, (b) Tafel plots, and (c) chronoamperometry plots of WO$_3$·H$_2$O and WO$_3$ nanoplates for hydrogen evolution in distilled water at pH 5.67. (d) H$_2$ evolution measured by a gas chromatograph at −0.76 V vs the RHE using WO$_3$ nanoplates as the electrocatalyst and distilled water as the electrolyte.

**Figure 8.** (a−c) W 4f and (a1−c1) O 1s region XPS spectra of (a) WO$_3$·H$_2$O nanoplates, (b) WO$_3$·H$_2$O nanoplates after 4000 CV cycles in 0.5 M H$_2$SO$_4$, and (c) WO$_3$ nanoplates.
Table 2. Surface Composition (Atomic Percentage) of WO₃·H₂O Nanoplates before and after CV Cycles in 0.5 M H₂SO₄ and WO₃ Nanoplates Measured by XPS and AES

| sample             | atomic % by XPS | atomic % by AES |
|--------------------|-----------------|-----------------|
|                    | W %  | O %  | W %  | O %  | W %  | O %  |
| WO₃·H₂O            | 19.83 | 80.17 | 20.9 | 79.1 |       |       |
| WO₃·H₂O after CV cycles | 24.47 | 75.53 | 22.4 | 77.6 |       |       |
| WO₃                | 23.88 | 76.72 | 25.4 | 74.6 |       |       |

Figure 9. Calculated energy landscapes of the HER on WO₃(200) and Pt(111).

Pt(111) was calculated to be −2.52 eV matching the values calculated by Nobuhara et al. Moreover, the proton adsorption energy on WO₃(200) was found to be −1.8 eV, which was lower than that of Pt, establishing the reason behind the superior HER performance of WO₃ as experimentally observed.

■ CONCLUSIONS

The present work spotlights the importance of hydroxide and oxide for the water-splitting reaction and generation of hydrogen. The inherent stability of oxides makes them highly suitable and efficient materials for the water-splitting reaction. The superior HER performance of WO₃·H₂O and WO₃ was affirmed through high hydrogen evolution current densities and smaller Tafel slopes as demonstrated here. These catalysts also exhibited excellent durability in acidic and neutral electrolytes. The synthesis of WO₃·H₂O at room temperature and its surface evolution to WO₃ during repeated electrochemical CV cycles were evidenced from surface characterization and electrochemical performances. In addition, the high hydrogen generation rate in acidic (20.4 mmol·cm⁻²·h⁻¹) and neutral (550 µmol·cm⁻²·h⁻¹) electrolytes as measured quantitatively demonstrated potential of these electrocatalysts for hydrogen generation through water splitting.

■ EXPERIMENTAL DETAILS

Chemicals. Tungsten (VI) chloride (WCl₆), platinum on carbon (Pt/C) (Sigma-Aldrich, USA), and ethanol (C₂H₅OH) and H₂SO₄ (Merck, India) were used for synthesis and activity tests. All chemicals were of analytical grade and used without further purification.

Synthesis of WO₃·H₂O and WO₃ Nanoplates. In a typical synthesis, 40 mL (25 mM) of WCl₆ was prepared in ethanol and kept under ambient temperature (at ~30 °C) for 1 h to obtain pine green color precipitate of WO₃·H₂O nanoplates, which was washed with ethanol and dried at 60 °C for 4 h. WO₃ nanoplates were obtained by annealing WO₃·H₂O nanoplates at 400 °C in a muffle furnace for 2 h under air and cooling the furnace naturally to room temperature.

Characterization. The crystal structures of the samples were examined with a PANalytical high-resolution XRD (PW 3040/60) operated at 40 kV and 30 mA with Cu Kα X-rays (1.54 Å). TG analysis was performed with a TA Instrument (TGA Q500) under synthetic air (N₂/O₂ = 80:20) at a heating rate of 10 °C per min. The surface morphology of the as-synthesized WO₃·H₂O and WO₃ powder was examined using a Carl Zeiss SUPRA 40 FESEM. The detailed microstructures of the samples were analyzed using a Tecnai G² TEM (FEI) at an accelerating voltage of 200 kV. The surface analysis of the samples was carried out by XPS using a PHI 5000 VersaProbe II scanning XPS microprobe with a monochromatic Al Kα source (1486.6 eV). The AES measurements were performed with a scanning Auger nanoprobe (PHI 710, ULAC-PHI Inc.) equipped with a coaxial cylindrical mirror analyzer.

Electrochemical Study. The HER activity of the as-synthesized catalysts was studied using a BioLogic SP-150 potentiostat with Pt-foil as the counter electrode, SCE as the reference electrode, and a GCE coated with the catalyst as the working electrode. Prior to loading the catalyst, the GCE was cleaned by polishing with alumina powder and sonicating in distilled water and ethanol. A slurry was prepared by sonicating the catalyst powder (WO₃·H₂O or WO₃ nanoplates) in a mixture of distilled water (10 mg mL⁻¹) and one drop of diluted polytetrafluoroethylene (PTFE) (10 µL of 1% PTFE dispersion) for 30 min. Then, 50 µL of slurry was coated on the GCE by drop-cast and dried under vacuum overnight. The electrochemical measurements such as LSV and CV were carried out with a three-electrode system in 0.5 M H₂SO₄ electrolyte at a scan rate of 10⁻² V·s⁻¹. The HER study was also performed in a neutral electrolyte using distilled water (pH 5.67). The electrode potential was calibrated with respect to the RHE by using the equation, E(RHE) = E(SCE) + 0.241 + 0.0591 pH. Stabilities of the as-synthesized electrocatalysts were measured by chronoamperometry for 20 h at a selected applied potential. The hydrogen generation rate was measured using a gas chromatograph (7890B, Agilent Technologies) both in acidic (0.5 M H₂SO₄) and neutral electrolytes (distilled water, pH 5.67) at −0.36 V and −0.42 V versus the RHE, respectively.

DFT Calculations. The HER mechanism was analyzed using DFT calculations on the (200) plane of P₂₁/n monoclinic WO₃ following the experimental observation. DFT calculations were implemented with a Quantum ESPRESSO package. For optimization, a 2 x 2 surface unit cell was used with three layers while freezing bottom two layers. To avoid the interaction of the adsorbate and periodic image of the slab, a vacuum of 10 Å was incorporated. Plane wave self-consistent field calculations were carried out with the Perdew–Burke–Ernzerhof exchange–correlation functional, and ultrasoft pseudopotentials were used. For the wave functions (and charge densities), a kinetic energy cutoff of 37 Ry (370 Ry) was used. The convergence threshold of 1 x 10⁻⁴ arb units and 2 x 2 x 1 k-mesh were used for energy and Brillouin zone sampling, respectively. DFT analysis was also done with a stable (111) plane of Pt within a Pt 2 x 2 super cell. A comparative energy landscape for the reaction H⁺ + e⁻ → H₂ was developed for the synthesized catalyst and the established Pt catalyst to corroborate the difference in their activities.
**ASOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01151.

TEM images, EDX mapping, CVs, N2 adsorption–desorption isotherms, and AES spectra (PDF)

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**Notes**
The authors declare no competing financial interest.

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