Computation and Investigation of Two-Dimensional WO₃·H₂O Nanoflowers for Electrochemical Studies of Energy Conversion and Storage Applications

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ABSTRACT: The aim of this study is to prepare a two-dimensional (2D) WO₃·H₂O nanostructure assembly into a flower shape with good chemical stability for electrochemical studies of catalyst and energy storage applications. The 2D-WO₃·H₂O nanoflowers structure is created by a fast and simple process at room condition. This cost-effective and scalable technique to obtain 2D-WO₃·H₂O nanoflowers illustrates two attractive applications of electrochemical capacitor with an excellent energy density value of 25.33 Wh kg⁻¹ for high power density value of 1600 W kg⁻¹ and good hydrogen evolution reaction results (low overpotential of 290 mV at a current density of 10 mA cm⁻² with a low Tafel slope of 131 mV dec⁻¹). A hydrogen evolution reaction (HER) study of WO₃ in acidic media of 0.5 M H₂SO₄ and electrochemical capacitor (supercapacitors) in 1 M Na₂SO₄ aqueous electrolyte (three electrode system measurements) demonstrates highly desirable characteristics for practical applications. Our design for highly uniform 2D-WO₃·H₂O as catalyst material for HER and active material for electrochemical capacitor studies offers an excellent foundation for design and improvement of electrochemical catalyst based on 2D-transition metal oxide materials.

1. INTRODUCTION

In order to overcome the fossil fuels crisis and global warming, it is necessary to provide new, sustainable energy storage and conversion applications.¹ Transition metal oxides (TMOs) have been studied widely during the past few decades in various areas of energy storage, especially batteries and supercapacitor electrodes which enhance the energy density to provide high performance.²³⁴ Currently, with the appearance of two-dimensional (2D) nanomaterial, there are many types of 2D materials being applied for both energy storage, especially batteries and supercapacitors and conversion (electrocatalyst—hydrogen evolution reaction).⁵⁻¹⁰ In this condition, the 2D structures of transition metal oxides are attractive due to abundant reserves, ease of synthesis, large surface area, and high-exposure active sites and short ions diffusion distance.¹¹⁻¹⁴ Herein, in this report, 2D-WO₃·H₂O with nanoflowers structure is synthesized, studied, and introduced as a good TMO material for dual applications of energy storage and conversion.

Hydrogen production from water splitting through electrocatalysis process has been determined as a clean and sustainable energy source with very high gravimetric power and energy density, zero carbon dioxide emission, and renewability.¹⁵⁻¹⁸ Among various hydrogen production technologies, water splitting by electrocatalytic process is considered as a green way to product hydrogen gas with a simple system, low cost, and abundant raw electrolyte (the pollution water can be used as electrolyte for hydrogen production).¹⁹⁻²¹ Herein, the hydrogen reaction is one of the two halves of two reactions in water splitting electrode reactions by the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), at the anode and at the cathode, respectively, which can be storage separately for further applications.²²⁻²⁴ Traditionally, the noble metal family, especially platinum (Pt), is the best choice for electrocatalyst with strongest reaction kinetics, with lower overpotential and Tafel slope, a mandatory requirement for HER.²⁵⁻²⁷ But the noble metal family faces a major problem of high price, shortage and high cost to treat after release,²⁸,²⁹ so that scientists have been studying ways to replace them by the other low-cost and abundant materials. Currently, transition metal oxide materials have been increasing as promising candidates for HER studies due to good performance, low cost, earth-
Table 1. Lattice Constants

| WO₃·H₂O  | a (Å) | b (Å) | c (Å) | α  | β  | γ  |
|-----------|-------|-------|-------|----|----|----|
| GGA       | 5.3444| 10.2471| 5.0485| 90.000| 91.8493| 90.000|
| HSE06     | 5.3041| 10.2219| 5.0124| 90.000| 91.4884| 90.000|
| experiment | 5.289 | 10.711 | 5.133 | NA | NA | NA |
| experiment | 5.2516| 10.4345| 5.1380| NA | NA | NA |

abundance, and easy synthesis. Recent advances in transition metal oxide materials have shown that two-dimensional transition metal oxides, especially 2D-WO₃·H₂O, would be promising, inexpensive alternatives to high-cost materials for electrochemical catalyst application.

Currently, TMO materials also have been studied in electrochemical energy storage applications which include batteries and supercapacitors. As a new energy storage field, supercapacitors are highly attractive for their rapid charge–discharge capability and long life cycle. In comparison with various types of materials for supercapacitor electrodes, TMOs are good candidates with many advantages, such as improving the performance by Faradaic reaction at the electrode layer during the charge–discharge process, easy scaling, and sustainability. Among various types of TMO materials, tungsten oxide is an excellent choice for a high-exposure active surface, strong durability, and low cost, which are suitable for supercapacitor electrode and the negative electrode of water splitting.

In this work, to widen the field research of WO₃·H₂O as a promising material for various applications, we introduce an excellent method to synthesize 2D-WO₃·H₂O. Herein, 2D-WO₃·H₂O was prepared by a fast and simple wet chemical method to obtain a two-dimensional nanostructures which is considered as a versatile active material for energy conversion of hydrogen evolution reaction and energy storage of supercapacitors applications. Furthermore, the complex devices which combine the supercapacitors and hydrogen evolution/oxygen evolution reaction provide an excellent idea for future electrochemical models. Finally, in this report, we will discuss how new computational and experimental techniques were combined with strategies on the understanding of electrochemical capacitor and HER kinetics with the situation of 2D-WO₃·H₂O nanoflowers.

2. RESULTS AND DISCUSSION

2.1. Computational Results of WO₃·H₂O Nanoflowers.

2.1.1. Computational Details. The crystalline structure of WO₃·H₂O nanoflowers is the orthorhombic. To well understand the orthorhombic WO₃·H₂O structure, morphology, and electronic properties, herein, the density functional theory (DFT) calculations were studied by Vienna ab initio Simulation Package (VASP) code. Furthermore, the investigation of the electron–ion interactions and electronic exchange correlations was carried out by the projector augmented-wave potentials (PAWs) and the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional. For comparison purposes, GGA and HSE06 methods were used to reduce the self-interaction error. More importantly, this selectively adds an energy correction to localized electron states such as d or f orbitals that the self-interaction is notably large. Then, the conjugate gradient diagram was chosen in order to optimize all atomic positions and lattice constants until the force components on each atom have the order of 10⁻⁴ eV Å⁻¹. The kinetic energy of the plane-wave basis set cutoff is set as 400 eV to ensure the exactitude of the simulation results. We used the bulk supercell of WO₃·H₂O containing 28 (W/O/H) atoms, which correspond to 4 WO₃·H₂O units. Herein, for the WO₃·H₂O supercell, the numbers of K-mesh were (4 × 2 × 4).

2.1.2. Crystal Structure. The optimized lattice constants of WO₃·H₂O were obtained from our DFT calculations are shown in Table 1; experimental values are included for comparison. The stable structure of WO₃·H₂O calculated using the GGA method show the lattice parameters values of a ≈ 5.3444, b ≈ 10.2471, and c ≈ 5.0485 Å, which corresponded correctly with published data of WO₃·H₂O X-ray diffraction (JCPDS Card No.43-0679) and the American Mineralogist Crystal Structure Database (AMSD Card 0005199). According to the results described in Table 1, the functional GGA and HSE06 provide accurate description of the lattice parameters of WO₃·H₂O.

Herein, the crystal structure of WO₃·H₂O sheets is made by the basic structural unit of a [WO₅−H₂O] octahedron with the location of W at the center of an octahedron and connection to six oxygen atoms by a W–O covalent bond. The sheets are stacked in the direction of [010] with the intercalation with each other by a hydrogen bond (O–H–O) which forms a three-dimensional network structure. Protons (hydrogen atoms) are marked in green, red for oxygen ions, and yellow for tungsten ions and also WO₆ octahedral.

WO₃·H₂O crystallizes in the orthorhombic Pnma space group. The crystal structure of 2D-WO₃·H₂O nanosheets (Figure 1) is made by the basic structural unit of a [WO₅−H₂O] octahedron, with the location of W atom in the center of an octahedron which connected to six oxygen atoms by a W–O covalent bond. There is a spread of W–O bond distances ranging from 1.753 to 1.943 Å. The six corners are made by six oxygen atoms of the octahedron can be classified into three types: (1) the oxygen atom (O₁) locate in H₂O, (2) two vertices of the octahedron is made by one another oxygen atom (O₂), and (3) four locations at four corners of the same plane are four oxygen atoms (O₃) and form a rectangle perpendicular to the [010] direction. The O₁ atom at the upper vertex of the octahedron bond shares corner mode with four O₂ atoms to four adjacent the octahedron with the upper vertex as the O₂ atom, respectively. Herein, the three-dimensional network structure is made from sheets intercalating with each other by a hydrogen bond (O₁–H···O₂) and stack in the direction of [010].

2.1.3. Electronic Structures. Density of states (DOS) and electronic band structure bands of WO₃·H₂O are calculated with the functional GGA and HSE06. The results are presented in Figures 2 and 3. The energy band gap of WO₃·H₂O has been calculated by the following equation: Eₐ = Eₖ–CB (where Eₖ and E₄CB respectively represent potential energy of valence band (VB) and conduction band (CB)). WO₃·H₂O has relatively small band gap and is widely studied. The calculated electronic density of states DOS of WO₃·H₂O using GGA method is shown on the right-hand side in Figure 2 with
the atom and decomposed DOS including O(p), W(s), W(p), and W(d). The calculated band gap energy using GGA (Figure 2) is found to be direct with a value of 1.442 eV at the Γ point, larger than the experimental values of 2.17 eV and smaller than the estimated value of 2.5 eV for WO₃·H₂O spherical particle. This result can be acceptable due to the exchange correlation (xc) functionals are needed to satisfy the agreement between the calculated and experimental band gaps of 2D-WO₃·H₂O nanosheets. The study of the calculation of electron DOS for 2D-WO₃·H₂O nanosheets using the HSE06 method is shown on the right-hand side in Figure 3 with the atom and decomposed DOS including O(p), W(s), W(p), and W(d). The energy bands following the HSE06 method can be also classed into three groups: (1) states lower than $-2.1$ eV below the Fermi level, originating from the overlap by the oxygen O(p) orbitals and the tungsten W(p) and W(d); (2) states from $-2.1$ to 0 eV, mainly formed by the oxygen O(p) orbitals; and (3) bands above the Fermi level of predominantly tungsten W(d) character and overlapped by O(p) orbitals. It can be understood that the deep-lying valence bands between 2.318 and 7.221 eV are due to the overlapped by the O(p) orbitals and W(d) orbitals.

By DFT simulation, WO₃·H₂O has the estimated band gap around 2.17 eV that corresponds to the experimental value (Figure 7), which was favorable not only for electrocatalyst but also for electrochemical capacitor. HSE06 method is appropriate functionals to understand the geometrical structure and electronic properties of 2D-WO₃·H₂O.

2.2. Structure and Morphology Characterizations.

The crystal structure of the prepared sample 2D-WO₃·H₂O nanoflowers was identified by XRD measurement, which is shown in Figure 4. It can be seen that the XRD spectrum of 2D-WO₃·H₂O in Figure 4a shows the narrow peaks which reflect the good crystallinity and high-quality orthorhombic phase (JCPDS Card No. 43-0679). The diffraction peaks of 2D-WO₃·H₂O corresponding to the hexagonal plane with the (020), (111), (040), (200), and (002) main planes at angles at around 16.3, 25.4, 33.2, 34, and 34.8°, which are associated with JCPDS Card No. 43-0679. Raman spectra in Figure

![Figure 1. Crystal structure of tungsten trioxide hydrate, WO₃·H₂O. Hydrogen atoms are illustrating in green, oxygen ions in red, and tungsten ions and also WO₆ octahedron in yellow color.](image1)

![Figure 2. DOS and electronic energy band structures of WO₃·H₂O by using GGA method.](image2)
4b show the crystalline of 2D-WO₃·H₂O with two major characteristic potenti and sharp peaks around 640 and 944 cm⁻¹, which illustrate the crystalline nature phase of metal oxide. The board peak located at 640 cm⁻¹ corresponds to the stretching mode of the bridging ν(O−W−O) bond of the layer of the octahedral, sharing four equatorial oxygen atoms which suggest the exhibition of WO₃·H₂O nanoparticles thickness and hydration level. The strong peak at around 944 cm⁻¹ indicates the terminal bond of double-bond character belong to oxygen atom ν(W=O). The N₂ adsorption−desorption isotherm (Figure 4c) and pore-size distribution (Figure 4d) were measured on the basis Brunauer−Emmett−Teller (BET) theory. From the Figure 4c, the specific surface area of 2D-WO₃·H₂O with nanoflowers structure obtains a value of 2.3 m² g⁻¹, indicating a good 2D structure. The increase of the high relative pressure region of the N₂ isotherm in Figure 4c illustrates the existence of macropores. The large open hysteresis loop of P/P₀ from 0.45 to nearly 1 indicates the existence of mesopores in the samples. Moreover, the plot of the N₂ isotherm at a low ratio of P/P₀ < 0.45 indicates the micropores. In summary, the WO₃·H₂O nanoflowers have a 2D plates structure containing micropores, macropores, and also mesopores. Figure 4d shows the pore-size distribution based on the Barrett−Joyner−Halenda analysis from N₂ adsorption−desorption isotherm. Herein, the distribution of pores via adsorption average pore with (4 V/A by BET) around 22.45 nm. The good BET results of 2D-WO₃·H₂O with the large open hysteresis loop indicate the high surface active sites for fast redox reaction which serve perfectly for electrode materials for energy storage and conversion. Further, the X-ray photoelectron spectroscopy (XPS) for identifying the chemical states of 2D-WO₃·H₂O nanoflowers was carried out and showed in Figure 4e,f. As seen in Figure 4e, the W 4f spectra show two major peaks at 35.2 and 37.4 eV which can be assigned to W 4f₅/₂ and W 4f₇/₂, respectively, for tungsten oxide which corresponds to the W⁶⁺ oxidation state of W. The O 1s spectra in Figure 4f show two convoluted peaks at 531 and 532.7 eV are assigned to metal oxide (W=O) and hydroxide groups (-OH) which confirm the hydrated WO₃. The relatively high binding energy peak of the hydroxide group (-OH) corresponds to the hydrated phase in the material.

The morphology of 2D-WO₃·H₂O nanoflowers sample was measured by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively. Panels a and b of Figure 5 show the SEM images of 2D-WO₃·H₂O at different magnification. The thin nanoflowers were found with the highly uniform size and square shape, which gather into a flower morphology. Panels c−e of Figure 5 illustrate clearly the TEM image of stacked 2D-WO₃·H₂O in according with the SEM images. At high-resolution TEM (HRTEM) in Figure 6a−c, the 2D-WO₃·H₂O nanoflowers show the lattice spacing approximately 0.27 nm, which corresponds to (021) plane. Moreover, the TEM mapping of 2D-WO₃·H₂O confirms the stacked nanoflower with the attribution of tungsten and oxygen elements (Figure 6c−f).

The UV−vis absorption spectroscopy in Figure 7a shows the optical respose of 2D-WO₃·H₂O in the UV region. The Tauc optical band gap (Eᵥ) value of 2D-WO₃·H₂O nanoflowers were calculated from the absorption plots and given in equation: (αhv)² = B(hv − Eᵥ), where h is the energy of the incident photon and B is an energy-independent constant. Eᵥ was found to be 2.17 eV (Figure 7b) on the basis of the Tauc plot and the UV absorption spectra.

2.3. Electrochemical Studies. Electrocatalytic HER measurements were studied by using glassy carbon electrode modified with 2D-WO₃·H₂O nanoflowers in 0.5 M H₂SO₄ electrolyte. Herein, the working principle of water electrolysis of metal catalyst in acidic electrolyte can be explained by the following reaction: the cathodic half-cell reaction of hydrogen evolution reaction (2H⁺ + 2 e⁻ → H₂), the anodic half-cell reaction of hydrogen oxidation reaction (H₂O → 2H⁺ + 1/2O₂ + 2e⁻), and the full cell reaction (H₂O → H₂ + 1/2O₂).

Figure 8a show the representative linear sweep voltammetry (LSV) plots of 2D-WO₃·H₂O in comparison with bare glassy carbon electrode, and Pt/C at 5 mV s⁻¹ in the voltage window of 0−0.8 V vs RHE. All measurements were converted into RHE with Ag/AgCl reference electrode. As can be seen in Figure 7a, the Pt/C shows a best overpotential value of 86 mV at current density of −10 mA cm⁻², which is known as the best material for electrocatalytic HER. The 2D-WO₃·H₂O exhibits amazing low overpotential value of 290 mV at initial time and
310 mV after stability over 30 h at the same current density of \(-10 \text{ mA cm}^{-2}\), indicating excellent strongly electrochemical durability. Figure 8b reveals that the Tafel slope following eq 1 of 2D-WO₃·H₂O was 131 mV dec\(^{-1}\) at the initial time and 138 mV dec\(^{-1}\) after 30 h, respectively, indicating a good Volmer–Heyrovsky mechanism for the HER. For further study of the transport kinetic of 2D-WO₃·H₂O, the electrochemical impedance spectroscopy (EIS) spectra were recorded and depicted in Figure 8c with the inset figure of equivalent circuit model (Randles circuit). The equivalent series resistance of 2D-WO₃·H₂O show solution resistance (R\(_S\)) around 40 Ω and charge transfer resistance (R\(_{CT}\)) of approximately 140 Ω. The low equivalent series resistance of 2D-WO₃·H₂O indicates good electrical conductivity. The stability of catalyst over the long-term operation over 30 h at overpotential of 290 mV vs RHE investigates the good catalyst durability of 2D-WO₃·H₂O, which indicates the suitability of 2D-WO₃·H₂O a catalyst for the HER.

Further, the 2D-WO₃·H₂O nanoflowers material was investigated as a promising material for electrochemical capacitor (or supercapacitor). The three electrode system for 2D-WO₃·H₂O nanoflowers working electrode in 1 M Na₂SO₄ aqueous electrolyte was investigated by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic

Figure 4. (a) XRD pattern, (b) Raman spectra, (c) nitrogen adsorption/desorption, (d) pore-size distribution, and (e, f) XPS spectra of W 4f and O 1s of WO₃·H₂O nanoflowers.
charge–discharge (GCD) measurements. As shown in Figure 9a, the CV curves at various scan rates in the range of \([10–120 \text{ mV cm}^{-1}]\), which exhibit a nonrectangular shape with Faradaic humps, indicating the combination between double layer capacitive and pseudocapacitive behavior.\textsuperscript{59,60} At various different current densities from low to high, the shape of the CV curves increase linearity, indicating the excellent behavior rate performance. Further measurement of GCD at different current densities was studied and shown in Figure 9b.

The GCD curves have nonsymmetrical shape and almost no voltage drop which indicate the good capacitive behavior and contribute pseudocapacitive behavior and good Coulombic efficiency. As calculated from the GCD curves, the maximum specific capacitance obtain a value of 71.25 F g\(^{-1}\) at current
density of 2 A g$^{-1}$ with good Coulombic efficiency approximately of 98.2%. Figure 9c shows the specific capacitance under high current densities from 8 to 2 A g$^{-1}$. On the basis of eq 2, at high current density of $i$, the specific capacitance still obtains a value of 25 F g$^{-1}$ with excellent Coulombic efficiency of 100% (eq 5). The 2D-WO$_3$ working electrode obtains the maximum specific capacitance of 71.25 F g$^{-1}$ at 2 A g$^{-1}$. The slight decrease of Coulombic efficiency from high to low current density maybe come from the strong Faradaic reaction at interface layer of electrode/electrolyte at low applied current. Electrochemical impedance spectroscopy is one of the critical techniques of electrochemical studies. As the Nyquist plot of 2D-WO$_3$$\cdot$H$_2$O in inset Figure 9c, the small semicircle at high frequency illustrates the charge transfer resistance while the straight line at low frequency indicates the ion diffusion from the electrolyte to the electrode layer. Typically, the equivalent resistance of the Nyquist plot obtains a low value of 19.6 $\Omega$ which indicates the good electrical conductivity of electrode material: 2D-WO$_3$$\cdot$H$_2$O. Herein, the equivalent series resistance is the combination of electrode resistance, resistance of electrolyte, and resistance of electrode/electrolyte interface. Figure 9d demonstrates the relationship between the energy density and power density (Ragone plot). From eqs 3 and 4, the maximum energy density of 2D-WO$_3$-
H2O working electrode exhibits a value of 25.33 W h kg⁻¹ at power density of 1600 W kg⁻¹. As a highest power density of 6400 W kg⁻¹, the 2D-WO₃·H₂O still obtained a good value of 8.9 W h kg⁻¹. The excellent electrochemical results of 2D-WO₃·H₂O are based on the three electrode system, making it a promising candidate for the hydrogen evolution reaction and electrochemical capacitor applications (Table 2). The hydrated WO₃ with two-dimensional structures in this report provides another perspective on the WO₃ material to diversify the studies on this interesting material, besides the previous research on anhydrous WO₃.⁶２–⁶⁷ Figure 10 illustrates an energy diagram of 2D-WO₃·H₂O (Figure 10a) and our future goal for fabrication complex devices which incorporate electrochemical capacitor and catalyst (Figure 10b).

3. CONCLUSIONS

In conclusion, we demonstrate 2D-WO₃·H₂O nanoflowers for electrochemical studies of energy conversion and storage applications. The high conductivity and two-dimensional structure of the WO₃ material enables high efficiency of exposed active sites for catalyst. Moreover, 2D-WO₃·H₂O nanoflowers electrode layers provide a large surface area for ion transport and extraction, leading to excellent electrochemical performance. This work opens up new possibilities for the application of WO₃ materials in various electrochemical devices, including electrochemical capacitors and catalysts.
transport during charge–discharge process to enhance the electrochemical behavior of supercapacitor. All of the above metrics make 2D-WO3·H2O nanoflowers attractive as a promising material for electrochemical studies for hydrogen evolution reaction and supercapacitor.

4. EXPERIMENTAL SECTION

4.1. Materials. Na2WO4·2H2O, oxalic acid (H2C2O4), poly(vinyliden fluoride) (PVDF) with MW 534,000 by GPC, and aqueous electrolyte–standard 0.5 M H2SO4 solution for HER measurement were purchased from Sigma–Aldrich. 1-Methyl-2-pyrrolidinone (C5H9NO), dimethylformamide [(CH3)2NC(O)H, DMF], and Na2SO4 were ordered from Alfa Aesar. The ultrapure water was prepared by Milipore MiliQUF system at room temperature with resistivity of 18.2 MΩ cm.

4.2. Preparation of WO3·H2O Nanoflowers. First, 50 mL of 0.2 M Na2WO4 was prepared by dissolving Na2WO4·2H2O in DI water with constant stirring to obtain a transparent solution. Then, 50 mL of 2 M HCl was dropped slowly and constantly by a 100 mL buret into the above solution with constant stirring until a yellow precipitation was obtained. Second, a certain amount of oxalic acid was added slowly into the above solution and held stable in 3 h at 90 °C. After reaction, the final yellow precipitate was collected after centrifugation and washing with DI water, ethanol, and followed by drying at 100 °C in a vacuum oven in 8 h to obtain WO3·H2O nanoflowers.

4.3. WO3·H2O Characterization. The structures of the WO3·H2O nanoflowers was carried out by using scanning electron microscopy (FE-SEM) from Hitachi SU8000 with the high accelerating voltage of 15 kV, transmission electron microscopy from JEM-2100F with 200 kV field emission. The morphologies of WO3·H2O nanoflowers were studied by Raman spectroscopy from Jobin Yvon-Horiba (the samples were carried out by using the 520 nm line of an argon laser), X-ray diffractometry (XRD; D2 Bruker; Cu Kα tube), X-ray photoelectron spectroscopy (XPS; Escalab 250Xi, Thermo Scientific). The specific surface area and pore-size distribution of 2D-WO3 nanoflowers was carried out by porosity analyzer (Micromeritics, ASAP 2020).

4.4. Electrochemical Catalyst. In the preparation of WO3·H2O for hydrogen evolution reaction, the catalyst ink was prepared by solution casting method: 3 mg of WO3 and 1 mL of DMF were mixed together with ultrasonic in 30 min. Then, WO3·H2O ink (5 μL) was dropped onto glassy carbon electrode (3 mm in diameter) and kept naturally in hood for drying. Finally, 5 μL of 20% Nafion was covered on the glassy carbon electrode-modified with 2D-WO3·H2O.

The electrochemical studies consisting cyclic voltammetry, linear sweep voltammetry, and electrochemical impedance spectroscopy were characterized by three electrode system using Zahner Zennium electrochemical workstation (Z 2.23, Germany), where a graphite rode as counter electrode, a Ag/AgCl as reference electrode, glassy carbon electrode-modified with 2D-WO3·H2O as working electrode, and standard commercial solution 0.5 M H2SO4 acidic electrolyte. Herein, the LSV plots were measured at a scan rate of 5 mV s−1 in a range from 0 to −0.8 V vs reversible hydrogen electrode (RHE). The stability measurements of the 2D-WO3·H2O material for HER tests were studied by measuring i−t curves over 30 h at an overpotential values. The electrochemical potential was calibrated with reversible hydrogen electrode by using the Tafel plots which correspond to the inherent properties of the catalysts by using the Tafel equation:

\[ \eta = b \log j + a \]  

where \( \eta \), \( b \), \( j \), and \( a \) are the overpotential, Tafel slope, current density, and a constant, respectively.

4.5. Electrochemical Capacitor. The WO3·H2O supercapacitor electrode for three electrode system was prepared following solution casting method. The working electrodes were prepared by solution casting method: 9 mg of WO3·H2O (90%) and 1 mg of PVDF (10%) were mixed together in 0.2 mL of NMP solvent with constant stirring at 60 °C in 12 h to obtain a uniform dark yellow slurry. Then, 20 μL of this dark yellow slurry was coated onto carbon paper substrate (1 × 1 cm2) and dried at 80 °C in 2 days to obtain WO3·H2O working electrode (1 mg cm−2).

The electrochemical studies of electrochemical capacitors based on cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge–discharge were measured in three electrode system by using Zahner Zennium (version Z 2.23 from Germany) electrochemical workstation
with \( \text{WO}_3 \cdot \text{H}_2\text{O} \) working electrode, Ag/AgCl reference electrode, and platinum plate (2 × 6 cm\(^2\)) counter electrode. From the charge–discharge curves, the specific capacitances of the supercapacitor electrode \((C, \text{F g}^{-1})\) can be calculated by using the following equations:\(^{42,43}\)

\[
C = \frac{I \Delta t}{\Delta V m_{ac}}
\]

(2)

The energy density \((E, \text{Wh kg}^{-1})\) at various power density \((P, \text{W kg}^{-1})\) values can be estimated by using the following equations:\(^{42,43}\)

\[
E = \frac{C(\Delta V)^2}{2} \times \frac{1000}{3600}
\]

(3)

\[
P = \frac{E \times 3600}{\Delta t}
\]

(4)

where \(I\) (A) is the discharge current, \(\Delta t\) is the discharge time, \(\Delta V\) is the potential voltage, and \(m_{ac}\) is the weight of the active materials on working electrode (including binder).

The Coulombic efficiency can be calculated from GCD curves by following equation:

\[
\varepsilon = \frac{t_{dc}}{t_c} \times 100\%
\]

(5)

where \(t_{dc}\) is the discharge time and \(t_c\) is the charge time.

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Notes

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