**Abstract:** To find an effective alternative to scarce, high-cost noble platinum (Pt) electrocatalyst for hydrogen evolution reaction (HER), researchers are pursuing inexpensive and highly efficient materials as an electrocatalyst for large scale practical application. Layered transition metal dichalcogenides (TMDCs) are promising candidates for durable HER catalysts due to their cost-effective, highly active edges and Earth-abundant elements to replace Pt electrocatalysts. Herein, we design an active, stable earth-abundant TMDCs based catalyst, $\text{WS}_{(1-x)}\text{Se}_x$ nanoparticles-decorated onto a 3D porous graphene/Ni foam. The $\text{WS}_{(1-x)}\text{Se}_x$/graphene/NF catalyst exhibits fast hydrogen evolution kinetics with a moderate overpotential of $\sim$93 mV to drive a current density of 10 mA cm$^{-2}$, a small Tafel slope of $\sim$51 mV dec$^{-1}$, and a long cycling lifespan more than 20 h in 0.5 M sulfuric acid, which is much better than $\text{WS}_2$/NF and $\text{WS}_2$/graphene/NF catalysts. Our outcomes enabled a way to utilize the TMDCs decorated graphene and precious-metal-free electrocatalyst as mechanically robust and electrically conductive catalyst materials.

**Keywords:** hydrogen evolution reaction; electrocatalysts; electrocatalytic activity; TMDC

1. Introduction

Water splitting is widely considered to be an effective route for renewable, clean, and efficient energy production from the abundant water on Earth. Electrocatalytic or photocatalytic water splitting into oxygen and hydrogen may potentially address the global environmental pollution and energy crisis [1,2]. Platinum (Pt) has proved to be a most efficient hydrogen evolution reaction (HER) catalyst, however, it has low appeal to use in industrial applications due to its high cost and scarcity [3]. The development of an inexpensive, Earth-abundant, highly active, and acid-stable material to use as an electrocatalyst is a grand challenge. In recent years, tremendous effort has
been made to develop efficient HER catalysts from Earth-abundant materials with lots of active edges to replace Pt, such as transition-metal-based oxides/hydroxides, non-oxides, including metal based sulfides [4–6], selenides [7–9], carbides [10,11], phosphides [12,13], borate [14], phosphate [15], and their alloys. However, so far most of the catalysts exhibit inferior efficiency compared to Pt, while many processes involve complicated material synthesis and multiple steps, which may result in the increase of cost and further limit potential applications. Graphene is a well-known material, and it has potential for use in various electrocatalyst applications, which include supercapacitor, HER, and DSSCs [16,17]. Recently, tungsten disulfide (WS₂), which is from the family of transition metal dichalcogenides (TMDCs), has been studied elaborately as an electrocatalyst due to its high electrocatalytic properties [18]. Various studies have been done to promote the electrocatalytic activity of WS₂ with the combination of highly conductive materials, such as macro- and meso-porous carbon materials, gold (Au), and carbon paper in a hybrid nature for oxygen and hydrogen evolution reactions (OER and HER). Davodi and co-workers [19,20] reported the nitrogen doped multi-walled carbon nanotube (MWCNT) and Ni@γ-Fe₂O₃/MWCNTs functionalized with nitrogen-rich emeraldine salt for alkaline HER and OER processes. Luo et al. also demonstrated Fe₃O₄@NiFe₂O₄ core–shell nano-heterostructures toward the OER with an overpotential −410 mV@1 mA cm⁻² and Tafel slope of 48 mV dec⁻¹ [21]. Zhou et al. [22] used 3D hybrids of WS₂/graphene/Ni foam as a catalyst in HER application and observed the low overpotential of −119 mV@10 mA cm⁻², the small Tafel slope of −43 mV dec⁻¹, and the large cathodic current density. Recently, Zhou et al. has reported ternary tungsten sulfoselenide (WS₂(1−x)Se₂x) particles with a 3D porous metallic NiSe₂ foam to have excellent catalytic performance with −88 mV@10 mA cm⁻² of overpotential, 46.7 mV dec⁻¹ of Tafel slope, and 214.7 µA cm⁻² of exchange current density [23]. Our group has recently demonstrated a facile way to prepare a MoS₂ QDs film using a solution process and WS₂/CoSe₂ heterostructure for HER applications [24,25]. Moreover, ternary alloys of MoS₂(1−x)Se₂x and WS₂(1−x)Se₂x were synthesized as an electrocatalyst for HER by a sputtering-CVD process with the overpotentials of −141 and −167 mV to drive 10 mA cm⁻² and Tafel slopes of 67 and 107 mV dec⁻¹, respectively [26].

Recently, many efficient strategies to increase the number of active edge sites with large surface areas, high porosity, and better intrinsic electrical conductivity or the contact between the catalyst and the electrode were adopted to increase the electrocatalytic activity of electrode material. Herein, we utilized a 3D porous structure nickel (Ni) foam (NF) as a highly conductive skeleton, and produced WS₂/NF, WS₂-decorated graphene/NF, and WS₂(1−x)Seₓ nanoparticles-decorated graphene/NF catalysts for HER applications. The obtained electrodes exhibited low overpotentials of −145, −115, and −93 mV vs. RHE for WS₂/NF, WS₂/Graphene/NF, and WS₂(1−x)Seₓ/Graphene/NF, respectively, at 10 mA cm⁻². The small Tafel slope was obtained for WS₂(1−x)Seₓ/Graphene/NF (51 mV dec⁻¹) as compared to the WS₂/NF and WS₂/graphene/NF (62 and 63 mV dec⁻¹, respectively).

2. Experimental Details

2.1. Synthesis of Graphene/NF, WS₂/Graphene/NF, and WS₂(1−x)Seₓ/Graphene/NF

Initially, the Ni foam (NF) was cleaned with ultrasonic baths of acetone, ethanol, and deionized water, baked at 120 °C for 5 min, and then annealed with a hydrogen (H₂)/argon (Ar) (30/50 sccm) environment at 900 °C for 30 min in a quartz tube furnace to clean the surface of the Ni foam without breaking the vacuum. Then to prepare the graphene on NF, the mixture of H₂/Ar/methane (CH₄) flow (H₂/Ar/CH₄ = 50:100:50 sccm) was maintained for 30 min. Subsequently, the H₂/CH₄ flow gas channel was shut off, and then rapidly cooled to room temperature in Ar environment. Furthermore, prepared graphene/NF was used as substrate for the growth of WS₂ and WS₂(1−x)Seₓ.

For WS₂ growth, ammonium tetra-thiotungstate ((NH₄)₂WS₄) (Sigma Aldrich, 99.97%) was used as the main source material. First, a precursor of (NH₄)₂WS₄ (0.2 g) was dissolved in N,N-Dimethylformamide (DMF) (20 mL), and then the solution was sonicated for 30 min. The 3D graphene/Ni foam was immersed into the prepared (NH₄)₂WS₄ solution and then baked at 100 °C.
for 30 min. Finally, synthesized films were placed in an annealing chamber and heated up to 450 °C for 30 and 45 min in a sulfur or sulfur/selenium environment to form WS₂/NF, WS₂/graphene/NF, and WS₁₋ₓSeₓ/Graphene/NF. The gas flow Ar/H₂ flux (50/50 sccm) was maintained, and the pressure of chamber was kept at 2 × 10⁻² Torr. The same quantity of sulfur/selenium (0.3/0.3 g) powder was used.

2.2. Electrochemical Measurements

The electrochemical measurements were conducted in a three-electrode setup with a Biologic SP-300 workstation. The polarization curves were collected using a linear sweep voltammetry (LSV) with a scan rate of 10 mV/s⁻¹ in 0.5 M H₂SO₄ electrolyte at room temperature. For the LSV measurement, a saturated calomel reference electrode (SCE) was used as the reference electrode. WS₂(30 min)/NF, WS₂(45 min)/NF, WS₂/graphene/NF, and WS₁₋ₓSeₓ/graphene/NF were used as the working electrode. Also, a graphite rod was used as the counter electrode. All LSV measurements were probed in terms of SCE and then converted to a reversible hydrogen electrode (RHE) scale with the help of the following equation: E(RHE) = E(SCE) + E°(SCE) + 0.059 pH. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a potentiostatic mode with a frequency range from 0.01 Hz to 100 kHz under an amplitude of 10 mV. All the LSV polarizations were recorded after the ohmic drop iR correction. The stability measurement was examined using a chronoamperometric analysis.

3. Results and Discussion

Initially, the graphene was grown on a 3D NF using a chemical vapor deposition (CVD), as reported previously [27]. WS₂ was further grown by a hydrothermal process using an (NH₄)₂WS₄ precursor on 3D graphene with NF. To improve the crystalline quality, the film was further annealed at 500 °C in a sulfur environment at 30~45 min to form WS₂ nanoparticle-decorated graphene on NF (WS₂/graphene/NF). To form WS₁₋ₓSeₓ nanoparticles-decorated graphene on NF (WS₁₋ₓSeₓ/graphene/NF), a CVD deposited film was annealed at 450 °C in a sulfur and selenium environment at 30 min, respectively, to form WS₁₋ₓSeₓ onto graphene. The schematic representation is given in Figure 1.

![Figure 1. Schematic preparation process of graphene and the WS₁₋ₓSeₓ/graphene/NF catalyst.](image)

The surface morphological analysis was performed using a field emission scanning electron microscopy (FESEM) and a high-resolution transmission electron microscopy (HRTEM). Figure 2a–d shows the typical FESEM images of graphene, WS₂/NF, WS₂/graphene/NF, and WS₁₋ₓSeₓ/graphene/NF, respectively, and its insets show the higher magnification images. The bare NF (Figure 2a) is composed of lots of pores with sizes in tens to hundreds of micrometers, which will lead to somewhat irregular and uneven film growth which will be beneficial to enhance the HER property. From the FESEM image (Figure 2b), the regular deposition of graphene onto NF is observed with different thicknesses on the curvature of the foam. The larger area FESEM images of WS₂/NF, WS₂/graphene/NF, and WS₁₋ₓSeₓ/graphene/NF are provided in Figure S1. Wrinkles and ripples of graphene are spotted, which might be contributed to the differences in thermal expansion coefficients between the graphene and the Ni substrate [28]. The direct synthesis of WS₂ on NF,
for comparison, showed agglomerated small spherical granules with a non-uniform shape on the surface of the NF due to their curvature nature (Figure 2c). The nanoparticles with different sizes, due to agglomeration, were observed for WS$_2$/graphene/NF from the low and higher magnification FESEM images (Figure 2d). In the case of WS$_{1-x}$Se$_x$/graphene/NF, the stacked nano-plate-like agglomerated grains were observed as shown in Figure 2e. The elemental composition of WS$_{1-x}$Se$_x$ alloys were determined by the energy dispersion spectra (EDS) as presented in Figure S2 (WS$_{1-x}$Se$_x$—W: 32.0%, S: 16.3%, C: 4.8%, and Se: 8.0%). Ni signals are ascribed from the NF substrate. The elemental mapping images of WS$_2$ and WS$_{1-x}$Se$_x$ layers are provided in Figures S3 and S4, and it confirms the homogeneous spatial distribution of W, S, C, and Se on the whole surface. The HRTEM studies were performed to reveal the layer structure of the prepared films. From the HRTEM images (Figure 3a), the multilayer of graphene was identified. In Figure 3b, WS$_{1-x}$Se$_x$ and graphene are shown with yellow and red boxes, respectively.

Figures 2 and 3 suggest the expose of active edge sites at the surface of WS$_{1-x}$Se$_x$/graphene/NF particles as reported in previous literature [23,29]. The WS$_{1-x}$Se$_x$ nanosheets, with an interlayer separation of 0.64 nm, were grown intimately on the graphene/NF substrate, which are also beneficial to enhance a HER reaction.
Raman spectroscopy was further used to characterize the formation of graphene, WS$_2$/NF, WS$_2$/graphene/NF, and WS$_{1-x}$Se$_x$/graphene/NF. From the spectrum of graphene/NF (Figure 4a), the principle bands of graphene, such as G band (1577 cm$^{-1}$), 2D band (2706 cm$^{-1}$), and D band (1364 cm$^{-1}$) were exhibited due to defects in the carbon lattice [30]. For WS$_2$/NF, two prominent Raman peaks originated at 350.1 and 420.5 cm$^{-1}$ correspond to the E$_{2g}$ and A$_{1g}$ modes, respectively [31]. In the case of WS$_2$/graphene/NF, E$_{2g}$ and A$_{1g}$ modes (351.6 and 420.5 cm$^{-1}$) for WS$_2$, two sharp peaks for graphene (G band: 1577.8 cm$^{-1}$ and 2D band: 2699.8 cm$^{-1}$) are shown [32,33]. In addition to the above peaks, a low intensity E$_{1g}$ mode peak was observed at 250.6 cm$^{-1}$, corresponding to WSe$_2$ [34] for WS$_{1-x}$Se$_x$/graphene/NF. Our results also confirm the formation of both WS$_2$ and WSe$_2$ on porous graphene foam. Furthermore, the observed Raman results are well consistent with previously reported results of a WS$_2$ and WSe$_2$ materials system [34].

The expanded region of W4f, S2p, C, and Se3d peaks are provided in the Figure 5b–e. A sharp peak at 284 eV originated from graphene. The two principal peaks of W binding energy of 4f$_{7/2}$ and W 4f$_{5/2}$ (36.4 and 34.5 eV) doublets, which were indicative of the oxidation state of W$^{4+}$, appeared. The S 2p$_{1/2}$ and 2p$_{3/2}$ orbital peaks observed at 163.6 and 161.9 eV, respectively, indicating the S2, confirmed the WS$_2$ crystal [31,35]. The Se 3d core levels can be fitted with Se 3d$_{5/2}$ (53.8 eV) and Se 3d$_{3/2}$ (55.6 eV) corresponding to the $-2$ oxidation state of selenium [36].

**Figure 4.** (a) Raman and (b) XRD spectra of graphene/NF, WS$_2$(45 min)/NF, WS$_2$/graphene/NF and WS$_{1-x}$Se$_x$/graphene/NF.
HER activities were investigated via a standard three-electrode setup with a scan rate of 10 mV s\(^{-1}\) in 0.5 M sulfuric acid (H\(_2\)SO\(_4\)) electrolyte solution by linear sweep voltammetry (LSV) with iR correction. As expected, the commercial Pt wire exhibited the lowest overpotential, which was close to zero. The WS\(_{1-x}\)Se\(_x\)/graphene/NF catalyst can deliver an overpotential at \(-93\) mV vs. the reversible hydrogen electrode (RHE) for a geometric current density of 10 mA cm\(^{-2}\). In contrast, WS\(_2\) (45 min)/NF, and WS\(_2\)/graphene/NF exhibited inferior HER activity (\(-114\) and \(-115\) mV vs. RHE at current 10 mA cm\(^{-2}\), respectively) (Figure 6a, b). Earlier research reported that the unsaturated Se facets are highly active and improve HER activity [37,38]. Theoretical estimation supports lower Gibbs free energy for H\(_2\) adsorption onto the Se facets than the S facets [38]. Graphene is a conductive material which can increase the conduction between electrode and electrolyte and create the synergistic effect with active materials that lead to good HER properties.

The catalytic overpotential (\(-93\) mV) of the WS\(_{1-x}\)Se\(_x\)/graphene/NF was quite lower than those of the reported WS\(_2\)-based TMDCs in the literature, which include: Cobalt sulfide @WS\(_2\)/carbon cloth (CC) hybrid catalyst (\(-97.2\) mV@ 10 mA cm\(^{-2}\)) [39], WS\(_2\)/reduced graphene oxide hybrid nanosheets (\(-150 ~\sim~ 200\) mV@10 mA cm\(^{-2}\)) [40], MoS\(_2\)-WS\(_2\) (\(-129\) mV@10 mA cm\(^{-2}\)) [41], WS\(_2\)@hollow nitrogen-doped carbon nanofibers (\(-185\) mV@10 mA cm\(^{-2}\)) [42], graphdiyne-WS\(_2\) 2D-nanohybrid electrocatalysts (\(-140\) mV@10 mA cm\(^{-2}\)) [43], and Mo\(_{1-x}\)W\(_x\)S\(_2\) hollow nanospheres on an Ni\(_3\)S\(_2\) nanorod (\(-98\) mV@10 mA cm\(^{-2}\)) [44]. For comparison, graphene on NF and WS\(_2\) (annealed at 30 min in an S environment) on NF were used as electrocatalysts, and their LSV curves are provided in the supporting information Figure S6 (overpotential of \(-193\) and \(-145\) mV vs. RHE, respectively).

**Figure 5.** X-ray photoemission spectroscopy scan for WS\(_{1-x}\)Se\(_x\)/graphene/NF. (a) Survey scan; (b) C, (c) W; (d) S and (e) Se binding energies.
The inherent property of catalytic activity for HER kinetics was probed by extracting the slopes from the linear regions in Tafel plots. A Tafel slope of 51 mV dec$^{-1}$ was extracted for WS$_{1-x}$Se$_x$/graphene/NF, which is close to the value of a commercial Pt catalyst, and 62 mV and 63 mV dec$^{-1}$ were obtained for WS$_2$(45 min)/graphene/NF and WS$_2$/NF, respectively (Figure 6c). The Tafel slope, 51 mV dec$^{-1}$ of WS$_{1-x}$Se$_x$/graphene/NF, was lower than those of the previously reported WS$_2$-based catalysts as well as other hybrid catalysts for HER, such as 3D WS$_2$/graphene/Ni (87 mV dec$^{-1}$) [45], nanostructured WS$_2$/CC (127–105 mV dec$^{-1}$) [46], bulk WS$_2$ and WS$_2$ nanosheets on bare oxidized carbon fiber (OCF) (149 ~99 mV dec$^{-1}$) [47], WS$_2$ @WS$_2$ nanorattles, WS$_2$ nanoflakes and bulk WS$_2$ (68, 71 and 92 mV dec$^{-1}$) [48], vertically-oriented WS$_2$ nanosheet/graphene (73 mV dec$^{-1}$) [49], WS$_2$ and WS$_{2(1-x)}$Se$_x$ nanotubes (105 and 99 mV dec$^{-1}$) [50], and monolayer of WS$_2$ and WS$_{2(1-x)}$Se$_x$ with a tunable band gap (100 and 85 mV dec$^{-1}$) [51]. Previous research demonstrated the influence of Se inclusion to create the abundant active edges which can be promote HER properties and hence to perceive the low overpotential and small Tafel slope [52].

The exchange current density ($j_0$) was found to be ~0.162, ~0.165, and ~0.274 mA cm$^{-2}$, for WS$_2$/NF, WS$_2$/graphene/NF and WS$_{1-x}$Se$_x$/graphene/NF, respectively. The observed high $j_0$ for WS$_{1-x}$Se$_x$/graphene/NF may be attributed to the large number of exposed active edge sites, good electrical conductivity, or the porous structure. The observed HER parameters for different electrodes are listed in Table 1. In acid solutions, three controlled reactions occur when hydrogen evolves on a metal chalcogenide catalyst. The overall HER reaction may proceed via a discharge step (Volmer-reaction, Equation (1)) followed by the ion-atom reaction (Heyrovsky reaction, Equation (2)) that leads to a Tafel slope of 40 mV dec$^{-1}$, or a combination reaction (Tafel-reaction, Equation (3)) that leads to a Tafel slope of 30 mV dec$^{-1}$.

\[
\text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_{ads} + \text{H}_2\text{O} \tag{1}
\]
\[
\text{H}_{\text{ads}} + \text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2 + \text{H}_2\text{O} \quad (2)
\]

\[
\text{H}_{\text{ads}} + \text{H}_{\text{ads}} \rightarrow \text{H}_2 \quad (3)
\]

From the classical theory for hydrogen evolution process, the observed Tafel slope of 36 mV dec\(^{-1}\) for Pt exposes the hydrogen production proceeds with the fast discharge step (Equation (1)) followed by the Tafel (Equation (3)) \([53,54]\). The observed intermediate Tafel slope values of 51, 62, and 63 mV·dec\(^{-1}\) (WS\(_2\)/NF, WS\(_2\)/graphene/NF and WS\(_{1-x}\)Se\(_x\)/graphene/NF, respectively) suggest that hydrogen production proceeds with the fast discharge step (equation 1) followed by the Tafel (Equation (3)) or Heyrovsky ion-atom reaction (Equation (2)) \([17,55,56]\). The observed small overpotential and Tafel slope for WS\(_{1-x}\)Se\(_x\)/graphene/NF could be attributed to the nanostructured particles on the porous substrate, which increase accessible active sites.

Table 1. Comparison of catalytic parameters of different HER catalysts.

| Catalyst                          | Overpotential (mV vs. RHE) @10 mA cm\(^{-2}\) | Tafel Slope (mV dec\(^{-1}\)) | Exchange Current Density (j\(_0\), mA cm\(^{-2}\)) |
|-----------------------------------|-----------------------------------------------|-------------------------------|-----------------------------------------------|
| Pt                                | -10                                          | 36                            | 5.98                                          |
| WS\(_2\) (45 min)/NF              | -115                                         | 62                            | 0.162                                         |
| WS\(_2\)/graphene/NF              | -114                                         | 62                            | 0.165                                         |
| WS\(_{1-x}\)Se\(_x\)/graphene/NF | -93                                          | 51                            | 0.274                                         |

EIS was performed to study the interface reactions and electrode kinetics in HER at a frequency range from 0.01 Hz to 100 kHz. The Nyquist plots revealed the charge-transfer resistance (R\(_{ct}\)) of Pt, WS\(_2\) (45 min)/NF, WS\(_2\)/graphene/NF, and WS\(_{1-x}\)Se\(_x\)/graphene/NF. The R\(_{ct}\) value of Pt, WS\(_2\) (45 min)/NF, WS\(_2\)/graphene/NF, and WS\(_{1-x}\)Se\(_x\)/graphene/NF were approximately 0.5, 2.4, 1.1, and 0.8 Ω, respectively (Figure 6d). The lower R\(_{ct}\) value suggests a faster reaction rate between the electrode and electrolyte. The low R\(_{ct}\) value could be due to the abundance of accessible sulfur/salinization active edges on a 3D porous substrate and result in the higher HER activity.

Stability is another key factor to elucidate the performance of catalysts. For this purpose, we tested the stability of WS\(_{1-x}\)Se\(_x\)/graphene/NF electrode using potential cycling in the range from -0.5 to +0.1 V with a scan rate of 50 mV s\(^{-1}\). After a 20 h operation in a 0.5 M H\(_2\)SO\(_4\) solution, the polarization curve was little changed from the initial one, which indicated no observable degradation after long-term cycling tests (Figure 7a). The long-term electrochemical stability of this electrode was also examined. The cathodic current density for the WS\(_{1-x}\)Se\(_x\)/graphene/NF catalyst remained stable and exhibited no obvious degradation for electrolysis at a fixed overpotential of -93 mV for more than 20 h, which indicated the potential usage of this catalyst maintained its catalytic activity over a long time in the electrochemical process (Figure 7b).

![Figure 7](image-url)

Figure 7. LSV curves for WS\(_{1-x}\)Se\(_x\)/graphene/NF before and after 20 h HER performance. Time dependent current density variation of WS\(_{1-x}\)Se\(_x\)/graphene/NF catalyst at a constant applied potential of -93 mV for more than 20 h.
4. Conclusions

In summary, an effective and efficient strategy was adopted for the synthesis of WS$_2$ and ternary WS$_{(1-x)Se_x}$/graphene/NF for a robust and stable self-standing hydrogen evolving catalyst. The novel WS$_{(1-x)Se_x}$/graphene/NF catalyst showed good HER catalytic properties in acidic electrolyte with an overpotential of $-93$ mV to drive 10 mA cm$^{-2}$, a small Tafel slope of 51 mV dec$^{-1}$, and a high exchange current density with excellent long-term durability. Our results proved that Se incorporated WS$_2$/graphene/NF exhibits the highest electrocatalytic activity for HER, and it is stable in acidic media over a long period among the other electrodes due to high active edge sites and porous structures.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/8/11/929/s1, Figure S1: Low magnification of FESEM images. (a) WS$_2$(45 min)/NF; (b) WS$_2$/graphene/NF and (c) WS$_{(1-x)Se_x}$/graphene/NF. Figure S2: EDS spectrum for WS$_{(1-x)Se_x}$/graphene/NF. Figure S3: (a) FESEM image of WS$_2$/graphene/NF and its elemental mapping images of (b) Ni (c) W (d) S and (e) Se elements. Figure S4: (a) FESEM image of WS$_{(1-x)Se_x}$/graphene/NF and its elemental mapping images of (b) Ni (c) W (d) C (e) S and (f) Se elements. Figure S5: X-ray photoemission spectroscopy scan for WS$_2$(45 min)/graphene/NF. (a) survey scan; (b) C; (c) W; and (d) S binding energies. Figure S6: Linear sweep voltammetry curves of graphene/NF and WS$_2$(30 min.)/NF electrocatalyst.

Author Contributions: S.H. and K.A. initiated the study, performed the extensive experiments, and wrote the manuscript with assistance from the co-authors. D.V. analyzed the data. A.F. and R.A.A. performed extensive experiment to measure electrochemical properties. W.S. and K.-S.A. performed XPS and analyses data. S.-H.C., J.-Y.P., and J.J. participation included planning, experimental work, and discussion. All authors read and approved the final manuscript.

Acknowledgments: This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (2010-0020207, 2017R1C1B5076952), by the Nano Material Technology Development Program through the NRF funded by the Ministry of Science, ICT, and Future Planning (2016M3A7B4909994), and by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry, and Energy (MOTIE) of the Republic of Korea (20172010106080).

Conflicts of Interest: The authors declare no conflicts of interest.

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