Electrochemical Hydrogen Evolution over Hydrothermally Synthesized Re-Doped MoS₂ Flower-Like Microspheres

Juan Aliaga 1,*, Pablo Vera 1, Juan Araya 2, Luis Ballesteros 3, Julio Urzúa 4, Mario Farías 5, Francisco Paraguay-Delgado 6, Gabriel Alonso-Núñez 5, Guillermo González 7 and Eglantina Benavente 1,*

1 Departamento de Química, Universidad Tecnológica Metropolitana, Las Palmeras 3360, Ñuñoa, Santiago, Chile; p.vera1@gmail.com
2 Centro de Investigaciones Costeras de la Universidad de Atacama (CIC-UDA), Universidad de Atacama, Copiapó 485, Copiapó, Chile; juan.araya@uda.cl
3 Instituto de Ciencias Químicas Aplicadas, Universidad Autónoma de Chile, El Llano Subercaseaux 2801, San Miguel, Chile; luis.ballesteros@uautonoma.cl
4 Departamento de Ciencias Farmacéuticas, Facultad de Ciencias, Universidad Católica del Norte, Casilla 1280, Antofagasta, Chile; j.urzuahumada@gmail.com
5 Centro de Nanociencia y Nanotecnología, Universidad Nacional Autónoma de México, Ensenada C. P. 22860, Mexico; francisco.paraguay@cimav.edu.mx
6 Departamento de Física de Materiales, Centro de Investigación Materiales Avanzados S.C., Miguel de Cervantes 120, CP 31136, Chihuahua, Mexico; francisco.paraguay@cimav.edu.mx
7 Departamento de Química, Facultad de Ciencias, Universidad de Chile, Las Palmeras 3425, Santiago, Chile; ggonzale@uchile.cl

* Correspondence: jaliaga@utem.cl (J.A.); Ebenaven@utem.cl (E.B.)

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Abstract: In this research, we report a simple hydrothermal synthesis to prepare rhenium (Re)-doped MoS₂ flower-like microspheres and the tuning of their structural, electronic, and electrocatalytic properties by modulating the insertion of Re. The obtained compounds were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Structural, morphological, and chemical analyses confirmed the synthesis of poorly crystalline Re-doped MoS₂ flower-like microspheres composed of few stacked layers. They exhibit enhanced hydrogen evolution reaction (HER) performance with low overpotential of 210 mV at current density of 10 mA/cm², with a small Tafel slope of 78 mV/dec. The enhanced catalytic HER performance can be ascribed to activation of MoS₂ basal planes and by reduction in charge transfer resistance during HER upon doping.

Keywords: molybdenum disulfide; rhenium doping; hydrothermal synthesis; HER; hydrogen evolution reaction

1. Introduction

The use of hydrogen (H₂) as fuel has gained significant importance. Hydrogen is a source of clean energy obtained at convenient cost by the water electrolysis process [1,2]. This process has proven to be one of the most efficient methods for hydrogen production; however, the use of high-cost and scarce precious metal (Pt, Pd) materials, which have excellent electrocatalytic performances, hinders their large-scale application. In this context, several earth-abundant catalytic alternatives have been investigated, including, for example, phosphide-based materials [3], transition metal monopnictides [4], metal carbides [5], and transition metal dichalcogenides [6], among others. Molybdenum disulfide...
(MoS\textsubscript{2}), one of the most earth-abundant transition metal dichalcogenides, has been extensively researched as a low-cost electrocatalyst for hydrogen evolution reaction (HER) [2,7]. Theoretical and experimental studies have demonstrated that the edges of the semiconducting 2H-MoS\textsubscript{2} are the catalytically active sites toward HER, while the basal planes are inert [8,9]. Most strategies to improve HER performance of MoS\textsubscript{2} electrocatalysts are consequently focused on phase, defects, and heterostructure engineering to maximally expose edge sites and to activate the basal plane [7,10,11]. Doping with non-metallic or transition metals atoms into the MoS\textsubscript{2} structure activates both edges and basal plane, improving the electronic mobility, charge transportability, and catalytically active surface area, therefore enhancing HER activity of the material [12–15]. In this sense, rhenium doping has been proposed to tune the electronic structure and polymorphic phases and to activate the basal planes of MoS\textsubscript{2} [16–19]. It has been demonstrated that a low concentration Re (n-type) doping induces broader valence bands and electron accumulation close to the Fermi level in MoS\textsubscript{2} fullerenes, resulting in a better HER performance [20].

This work studies the influence of rhenium incorporation under hydrothermal conditions in the electrocatalytic behavior of Re-doped MoS\textsubscript{2} for HER in acidic media. The Re-doped MoS\textsubscript{2} samples were prepared by a direct in situ sulfurization of ammonium molybdate and ammonium perrhenate by thiourea, using a simple hydrothermal process. A pristine MoS\textsubscript{2} material for direct comparison was also synthesized by the same method. Herein, we show morphological, structural, electronic, and electrocatalytic effects of a hydrothermal Re doping on MoS\textsubscript{2}, where the HER performance is tuned by the amount of Re doping.

2. Results

2.1. Characterization of the Catalyst

2.1.1. Scanning Electron Microscopy Analysis

SEM measurements were carried out to characterize the morphology of all samples. SEM images of all samples showed an overall flower-like similar morphology, both in the undoped and Re-doped MoS\textsubscript{2} samples (Figure 1).

![Figure 1](image-url)
These flower-like particles are composed of disordered nanosheets, which project their edges perpendicularly from the surface of a hierarchical structure. For the pristine MoS$_2$ sample (Figure 1a), an agglomeration of sphere-like particles with sizes ranging from 1.0 to 3.0 µm is observed. With increasing Re content in the samples, a decreasing size of the MoS$_2$ hierarchical structures is observed, with no perceptible changes in their morphology (Figure 1a–c). As it can been seen in Figure 1c,d, more discrete particles are observed for samples with higher rhenium content, with an average diameter of 1.63 µm for the 39.2% Re-doped MoS$_2$ sample (Figure 1d). Higher magnification of the nanosheets reveals the Re-doped samples to have a smaller lateral size than that of the undoped sample, with the smallest size for the 39.2% Re-MoS$_2$ sample (Insets Figure 1a–d). Similar trends have been observed for solvothermal MoS$_2$, and MoSe$_2$ materials doped with Cu, Ru, and V [14,21,22].

2.1.2. X-ray Diffraction Analysis

XRD was utilized to analyze the structural features of rhenium doping in all samples. As observed in Figure 2, the XRD profiles of pristine and doped samples look very similar, showing a single-phase with four reflections at approximately 2θ = 14.3, 33.2, 39.5, and 58.7° corresponding, respectively, to (002), (100), (103), and (110) planes of 2H-phase MoS$_2$ polytype (JCPDS 37–1492) [19,23]. Dominance of 2H-MoS$_2$ diffraction peaks makes it difficult to determine the presence of the 1T$_d$-ReS$_2$ phase (which has a particularly disordered lattice structure) in all XRD sample patterns [23]. Although the Re-doped MoS$_2$ and pristine MoS$_2$ XRD profiles shown in Figure 2 look very similar, even with increasing rhenium content, they reveal a broadening of the (002) peaks and a gradual decrease of the I(002)/I(100) diffraction peaks ratio (2.2, 1.9, 1.3 for pristine MoS$_2$, 14.7% Re–MoS$_2$, and 27.7% Re–MoS$_2$, respectively). This result indicates a concomitant decrease of the aligned (002) planes with increasing rhenium content in the samples, which is in agreement with similar MoS$_2$ materials with disordered structures [24]. Sample 39.2% Re–MoS$_2$, which presents the highest proportion of rhenium, shows the most amorphous structure, with a broad bulge in the 33–45° range, associated with merging of (100) and (103) planes, and by the presence of a low-intensity and shifted (110) peak (Inset Figure 2) [25].

![Figure 2. X-ray diffraction patterns of pristine MoS$_2$, 14.7% Re-doped MoS$_2$, 27.7% Re-doped MoS$_2$, and 39.2% Re-doped MoS$_2$ samples. Inset shows the (110) peak of all samples.](image)

2.1.3. Raman Spectroscopy Analysis

Raman spectroscopy was utilized to characterize crystal phase and structural features of Re-doped MoS$_2$ samples. As shown in Figure 3, Raman spectra of all samples display the typical two main lines of 2H-MoS$_2$, corresponding to out-of-plane A$_{1g}$ mode, and an in-plane E$_{12g}$ mode, observed at approximately 409–400 cm$^{-1}$ and 382–371 cm$^{-1}$, respectively [23,26]. By the increase of rhenium...
content, a remarkable line broadening is observed in the first-order Raman signals. The disordered layered arrangement in the Re-doped MoS$_2$ samples agrees with the broadening of the lines and with the aspect ratio intensity of these peaks ($A_{1g}:E_{2g}^{1}$) in all samples [26,27]. This has also been correlated with incorporating substitutional Re into the MoS$_2$ structure [23,27]. Additionally, the intensity of the broadened band in the region between 100 and 250 cm$^{-1}$ can also be attributed to Re content in the samples [28]. In this sense, the rhenium content could affect this Raman region through formation of a ReS$_2$ single phase (ReS$_2$ Raman active strongest vibrations are located in the range of 120 to 240 cm$^{-1}$) [29,30] by inducing changes in the MoS$_2$ phase (from 2H to 1T/1T$_d$) [16,18,31] or by defect-induced scattering of the MoS$_2$ small/disordered particles (low-frequency defect-activated modes) [26,28,32]. The overlapping frequencies of these variables preclude a particular identification for the origin of these bands.

![Figure 3. Raman spectra of pristine MoS$_2$, 14.7% Re-doped MoS$_2$, 27.7% Re-doped MoS$_2$, and 39.2% Re-doped MoS$_2$ samples.](image)

**2.1.4. Scanning Transmission Electron Microscopy Analysis**

High-resolution transmission electron microscopy was used to characterize the microstructure of Re-doped MoS$_2$ samples. Figure 4a shows the border of a flower-like particle of the 14.7% Re-doped MoS$_2$ sample. As can be seen, it confirms that the flower-like particles are composed of an agglomeration of few MoS$_2$ layers, whereas Figure 4b shows the detail of a few MoS$_2$ stacked layers in the same sample, which are composed of about 10 atomic layers. Further, a layer spacing of 0.66 nm can be observed, corresponding to the (002) crystalline plane of 2H-MoS$_2$ [21]. The most noticeable difference between the pristine MoS$_2$ and Re-doped MoS$_2$ samples is the curvature associated in the latter (Figure S1). Figure 4c shows a c-axis view of the same sample (14.7% Re-MoS$_2$). A d-spacing of 0.27 nm is evident, which can be assigned to the (100) plane of hexagonal MoS$_2$. A high-angle annular darkfield-scanning transmission electron microscopy (HAADF-STEM) image of the same sample reveals insertion of rhenium atoms in MoS$_2$ layers (Figure 4d), and its homogeneous distribution over the structure is corroborated by elemental mapping (Figure 4e).
Figure 4. High-resolution TEM (HRTEM) images of 14.7% Re-doped MoS$_2$ particle (a) border of the particle, (b) detail of the previous image, (c) c-axis view of the particle, (d) (HAADF-STEM) image of the same sample c, (e) HAADF element mapping images of Mo, Re, and S of the Re-doped MoS$_2$ particle.

2.1.5. X-Ray Photoelectron Spectroscopy

The chemical states, phase, and composition of the Re-doped MoS$_2$ samples were characterized by X-ray photoelectron spectra (XPS) measurements (Figure 5). Figure 5a shows the XPS survey spectra of all samples, indicating the presence of O, Mo, C, S, and Re on the surface. Binding energies (BEs) of all peaks were calibrated on the C–C bond of C 1s at 284.5 eV (Figure S2). Figure 5b–d shows Mo 3d, S 2p, and Re 4f high-resolution spectra of pristine MoS$_2$, and of 14.7%, 29.7%, and 39.2% Re-doped MoS$_2$ samples. A typical doublet Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$ with binding energies in agreement for the presence of Mo$^{4+}$ in MoS$_2$ is shown in Figure 5b [27]. Samples 14.7% Re-doped MoS$_2$ and 29.7% Re-doped MoS$_2$ show an upshift of 0.5 eV in comparison to the pristine MoS$_2$, with peaks located at approximately 229.7 and 232.8 eV for the Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively, in both samples. The binding energy
upshift for the same samples is also observed in the S 2p region (Figure 5c). These results, together with those of HAADF-STEM analysis, confirm a substitutional n-type Re doping on the MoS$_2$ structure and are consistent with previously synthesized Re-doped MoS$_2$ materials [33]. The sample with the highest amount of rhenium (39.2% Re-MoS$_2$) shows the most broadened spectra, having an additional low-energy component obtained by the deconvolution of the Mo 3d and S 2p spectra (Figure 5b,c), which suggests the presence of two kinds of molybdenum species [19]. This component at low binding energy can be considered as a contribution of structural defects or due to disordered structures close to the metastable 1T-MoS$_2$ configuration among a 2H-MoS$_2$ phase [19]. Figure 5d shows the Re 4f$^{7/2}$ and 4f$^{5/2}$ binding energy peaks for the 14.7%, 29.7%, and 39.2% Re-doped MoS$_2$ samples, which confirms the presence of Re$^{4+}$ in all the Re-doped samples [30]. This points out that rhenium atoms are immobilized as Re$^{4+}$ (as rhenium sulfide) in the MoS$_2$ structure. The binding energies and element analysis results of the samples are summarized in Table 1.

![Figure 5](image-url)

**Figure 5.** X-ray photoelectron spectra (XPS) spectra of Re-doped MoS$_2$ and pristine MoS$_2$. (a) Survey XPS of all samples, high-resolution XPS core-level of (b) Mo 3d, (c) S 2p, and states of (d) Re 4f and Mo 4p.

**Table 1.** Binding energies (eV) of core electrons of the pristine MoS$_2$ and Re-doped MoS$_2$ samples.

| Sample          | Mo 3d$_{5/2}$ | S 2p$_{3/2}$ | Re 4f$^{7/2}$ | Composition               |
|-----------------|---------------|--------------|---------------|---------------------------|
| Pristine MoS$_2$| 229.3         | 161.8        | -             | MoS$_{1.64}$             |
| 14.7% Re-doped MoS$_2$ | 229.7         | 162.6        | 42.4          | Mo$_{0.85}$Re$_{0.15}$S$_{1.76}$ |
| 27.7% Re-doped MoS$_2$ | 229.7         | 162.5        | 42.2          | Mo$_{0.72}$Re$_{0.28}$S$_{1.73}$ |
| 39.2% Re-doped MoS$_2$ | 229.8, 228.8  | 162.8, 161.7 | 42.7, 41.6    | Mo$_{0.61}$Re$_{0.39}$S$_{1.83}$ |
2.2. Hydrogen Evolution Reaction (HER) Performance of Pristine MoS$_2$ and Re-doped MoS$_2$ Samples

HER catalytic activity for the pristine MoS$_2$ and the Re-doped MoS$_2$ samples is shown in Figure 6. As depicted in the electrochemical linear sweep voltammetry (LSV) in Figure 6a, the pristine MoS$_2$ sample exhibits an overpotential of 326 mV at a current density of 10 mA/cm$^2$ in agreement with similar MoS$_2$ materials reported in the literature [34]. Although doping by rhenium clearly improves the catalytic performance of MoS$_2$, it is the sample with the lowest rhenium content (14.7% Re-doped MoS$_2$) that shows the highest activity among all samples towards HER, with a small overpotential of 210 mV observed at a current density of 10 mA/cm$^2$. Considering the similar crystallinity and nanosheet arrangement between the pristine MoS$_2$ and 14.7% Re-doped MoS$_2$ sample, the superior catalytic activity of the doped sample must necessarily arise from doping, rather than from textural effects of rhenium over morphology. A decay in HER performance for samples with higher Re-doping content (39.2% Re-MoS$_2$ and 27.7% Re-MoS$_2$) is also evident, and this trend has been previously observed for transition metal doping in MoS$_2$ materials [16,35]. Thus, the Re atoms do not function as active sites; rather, they activate the Mo$_2$ basal planes. Tafel plots of all samples were derived from LSV curves to characterize their intrinsic reaction kinetics (Figure 6b). As can be seen, 14.7% Re-doped MoS$_2$ exhibits the smallest Tafel slope (78 mVdec$^{-1}$), indicating a faster reaction rate in comparison with that of the pristine MoS$_2$ sample (102 mVdec$^{-1}$). Re atomic doping increases the Tafel slope of samples, as summarized in Table 2. These results indicate that HER of 14.7% Re-doped MoS$_2$ sample proceeds via a Volmer–Heyrovsky mechanism, where a proton fast discharge is followed by a rate-limiting electrochemical desorption step [36]. Figure 6c shows electrochemical double-layer capacitance (C$_{dl}$) measured from cyclic voltammograms of Figure S3, considering its linear proportional relationship with the electrochemical active surface area (ECSA). As expected, 14.7% Re-doped MoS$_2$ shows the highest C$_{dl}$ of all samples, being approximately three times higher than that of the pristine MoS$_2$ sample, suggesting a greater availability of active sites in Re-doped MoS$_2$ sample. Higher ECSA in Re-doped MoS$_2$ samples can be explained by the increase of catalytically active sites in basal planes, in agreement with previous results obtained in similar Re-doped MoS$_2$ materials [16]. Electrochemical impedance spectroscopic (EIS) measurements were conducted to elucidate the electrode kinetics upon HER. The observed diameters of semicircles in Nyquist plots (Figure 6d) correlate with the charge transfer resistance (R$_{ct}$) at the solid–liquid interphase. As can be seen in Figure 6d, the sample with minor rhenium content (14.7% Re-MoS$_2$) displayed lower impedance than that of the pristine MoS$_2$ sample. This demonstrates that low Re-doping on MoS$_2$ decreases charge-transfer resistance in this material and enhances its catalytic activity in HER. The stability of the 39.2% Re-doped MoS$_2$ sample was investigated by a continuous cyclic voltammetry (CV). A similar polarization curve after 1000 cycles was observed in comparison to the initial curve in Figure S4, indicating the long-term stability of 39.2% Re-MoS$_2$ sample, with only slight activity degradation at the end of the cycling.

Experimental results indicate formation of 2H MoS$_2$ phase with Re substitutional n-type doping, where Re doping allows tuning of morphological, structural, and electronic properties of MoS$_2$ during hydrothermal synthesis. Although it has been found that hydrothermal synthesis of MoS$_2$ doped with Re induces 2H-1T phase transformation [18], we cannot specifically identify this phase transformation in our results due to special features of MoS$_2$ synthesized under solvothermal conditions. These include easy oxidation of samples in environmental conditions during Raman acquisition (Figure S5) [31]; difficulty in identifying the 1T/2H phase of few-layered MoS$_2$ materials in TEM [37]; and existence of molybdenum polysulfides (considering solvothermal synthesis conditions) for XPS [38]. Our electrocatalytic results show that low Re doping improves overall HER catalytic activity of MoS$_2$ due to the creation of new catalytically active sites in basal planes, and by decreasing charge transfer resistance in the doped material. This result agrees with n-type Re doping in MoS$_2$, where the presence of extra states close to the Fermi energy is correlated with an increase of HER activity and with longer Mo-S bond length [16]. The catalytic active sites in our hydrothermal Re-doped MoS$_2$ samples should correspond to activated sulfur atoms (Re-S$^+$-Mo) in the basal plane of MoS$_2$ [15,35]. This can explain...
the lower HER performance of higher rhenium content samples, where there is a decrease of Re–S*–Mo by formation of Re–S bonding.

Figure 6. Electrocatalytic performance of Re-doped MoS$_2$ and pristine MoS$_2$. (a) Linear sweep voltammetry (LSV) curves, (b) Tafel plots, (c) electrochemical double layer capacitance ($C_{dl}$), and (d) electrochemical impedance spectroscopy (EIS) plots.

Table 2. Summary of electrochemical measurements of pristine MoS$_2$ and Re-doped MoS$_2$ samples.

| Sample               | Onset Potential (mV) | $\eta_{10}$ (mV) | Tafel Slope (mVdec$^{-1}$) | Rct ($\Omega cm^2$) |
|----------------------|-----------------------|------------------|-----------------------------|---------------------|
| Pristine MoS$_2$     | 203                   | 326              | 102                         | 32.58               |
| 14.7% Re-doped MoS$_2$ | 123                  | 210              | 78                          | 7.77                |
| 27.7% Re-doped MoS$_2$ | 164                  | 285              | 97                          | 17.45               |
| 39.2% Re-doped MoS$_2$ | 244                  | 379              | 132                         | 157.86              |
| Pt/C 10%             | 20                    | 42               | 32                          | -                   |

3. Materials and Methods

3.1. Chemicals

All chemical reagents used in the experiments were obtained from commercial sources as guaranteed grade reagents. Thiourea CH$_4$N$_2$S (molecular weight 76.12 g/mol, purity $\geq$ 99.0%), ammonium molybdate (NH$_4$)$_2$MoO$_4$ (molecular weight 196.01 g/mol, purity $\geq$ 99.98%), ammonium perrhenate NH$_4$ReO$_4$ (molecular weight 268.24 g/mol, purity $\geq$ 99.0%), and Pt/C 10% (molecular weight 195.08, purity 9.8–10.2%) were purchased from Sigma-Aldrich. All chemical reagents were of analytical grade and utilized without any further purification.

3.2. Synthesis of Re-Doped MoS$_2$ and Pristine MoS$_2$

The synthesis of Re-doped MoS$_2$ consists in the hydrothermal treatment of 1.0 to 2.0 mmol (NH$_4$)$_2$MoO$_4$, 6.0 mmol CH$_4$N$_2$S, and 0.2 to 1.0 mmol NH$_4$ReO$_4$ (Table 3). This mixture was dissolved
in 18 mL of deionized water, placed into a Teflon-lined 20 mL stainless steel autoclave, and heated in an electric oven for 24 h at 180 °C. The obtained product, a black powder, was washed several times with ethanol and dried in vacuum overnight. The as-prepared samples were annealed by heating at 10 °C per min rate in a conventional tube furnace under Ar flow (20 sccm) up to 400 °C for 2.0 h. The same procedure was used to prepare pristine MoS\(_2\) as the control experiment, but without adding NH\(_4\)ReO\(_4\).

| Sample             | (NH\(_4\))\(_2\)MoO\(_4\) | (NH\(_4\))ReO\(_4\) | CH\(_4\)N\(_2\)S |
|--------------------|---------------------------|----------------------|------------------|
| Pristine MoS\(_2\) | 2.0 mmol                  | -                    | 6.0 mmol         |
| 14.7% Re-doped MoS\(_2\) | 1.8 mmol                 | 0.2 mmol             | 6.0 mmol         |
| 27.7% Re-doped MoS\(_2\) | 1.5 mmol                 | 0.5 mmol             | 6.0 mmol         |
| 39.2% Re-doped MoS\(_2\) | 1.0 mmol                 | 1.0 mmol             | 6.0 mmol         |

3.3. Characterization Techniques

X-ray diffraction (XRD) measurements of the samples were gathered in a Bruker diffractometer model D8 (Bruker, Billerica, USA) using the Cu K\(_\alpha\) radiation (40 kV, 30 mA) with a wavelength of 0.154 nm. Crystalline phases were identified using standard JCPDS files. Raman spectroscopy measurements were collected at room temperature. Samples were measured using a confocal WITec alpha300 system instrument (WITec, Ulm, Germany) equipped with a 100× objective and 300 lines/mm grating. Measurements were performed using a green (532 nm) laser excitation wavelength. The Si Raman band at 520 cm\(^{-1}\) was used as a reference for the calibration of the Raman shift. Field-emission scanning electron microscopy (SEM) micrographs were obtained in an SEM LEO 1420VP, Oxford Instruments, equipped with an energy-dispersive X-ray spectroscopy (EDS) system (Oxford Instruments, Oxford, UK). Transmission electron microscopy (TEM) in STEM mode was conducted using a JEOL 2000FS (JEOL, Peabody, MA, USA) operating at 200 kV. The analysis of images was carried out using the Digital Micrograph Gatan™ software. X-ray photoelectron spectra (XPS) of both catalysts were carried out in a SPECS GmbH custom-made system using a PHOIBOS 150 WAL hemispherical analyzer and a μ-FOCUS 500 X-ray source (SPECS, Berlin, Germany). All data were acquired using monochromated Al K\(_\alpha\) X-rays (1486.6 eV, 110 W), a pass energy of 50 eV, and high-intensity lens mode. The charge referencing was done against adventitious carbon (C 1s 284.5 eV). Spectra were presented without smoothing, and a Shirley-type background was subtracted. Fits of the experimental peaks were obtained using combinations of Gaussian/Lorentzian lines with a 70/30 proportion using CasaXPS from Casa Software Ltd. The effective atomic concentrations were corrected according to sensitivity factors.

3.4. Electrochemical Measurements

Electrochemical measurements were obtained with a computer-controlled Zahner IM6ex, in a standard three-electrode cell using an Ag/AgCl (in 1.0 n KCl solution) electrode as the reference electrode, a platinum wire as the counter electrode, and glassy carbon (GC) electrodes carrying the catalyst as working electrodes. The working electrode was fabricated as follows: 4 mg of catalyst and 80 µL of 5 wt% Nafion solution were dispersed in 1 mL of a solution of deionized water and ethanol (3:1 in volume ratio). After stirring by ultrasonication for 1 h, 5µL of the resulting ink was drop-casted onto the top of a glassy carbon electrode with a 3 mm diameter. The catalyst-coated GC electrode was dried at 80 °C for 2 h to yield a catalyst loading of 0.285 mg cm\(^{-2}\). Linear sweep voltammetry (LSV) with a scan rate of 2 mV s\(^{-1}\) was conducted in 0.5 M H\(_2\)SO\(_4\) (purged with Ar), without applying iR correction. To determine double layer capacitance (C\(_{dl}\)) values, cyclic voltammograms (CVs) were collected at different scan rates (50, 60, 80, 100, 120, 140, 160, 180, and 200 mV s\(^{-1}\)) in the range of potential from 0.1 to 0.2 V vs. RHE. Electrochemical impedance spectroscopy (EIS) analyses were performed at an overpotential of 200 mV (vs RHE) from 100 kHz to 0.1 Hz with the amplitude fixed at 5 mV in the same configuration. All catalysts were electrochemically cleaned by cyclic voltammetry from OPC to −0.55 V for 20 cycles at a scan rate of 10 mVs\(^{-1}\) prior to measurements.
4. Conclusions

In conclusion, hydrothermally synthesized Re-doped MoS\(_2\) materials were characterized and investigated as unsupported catalyst for HER. Re doping shows a homogeneous distribution within the catalyst structure and maintained 2H-MoS\(_2\) crystallographic phase, with no indication of minority phases. Optimization of Re-doping on the MoS\(_2\) structure enables improving its catalytic performance through activation of its basal plane for HER and by decreasing charge transfer resistance of the doped material. This result agrees with the presence of extra states close to Fermi level for n-type doping. Rhenium doping on MoS\(_2\) reduces overpotential from 326 to 210 mV at 10 mA cm\(^{-2}\) for sample with 14.7% Re.

Supplementary Materials: The following are available online at http://www.mdpi.com/1420-3049/24/4/4631/s1, Figure S1: TEM images of pristine MoS\(_2\) particle (a), and 39.2% Re-doped MoS\(_2\) particle (b); Figure S2: High-resolution spectra of C 1s of Re-MoS\(_2\) composites with different loadings of rhenium; Figure S3: Cyclic voltammograms of pristine MoS\(_2\) (a), 14.7% Re-doped MoS\(_2\) (b), 27.7% Re-doped MoS\(_2\) (c), and 39.2% Re-doped MoS\(_2\) (d) samples; Figure S4: Polarization curves of 39.2% Re-doped MoS\(_2\) sample before and after 1,000 cycles; Figure S5: Oxidation of pristine MoS\(_2\) sample in environmental conditions during Raman acquisition; Table S1: Atomic ratios of the samples derived from peak deconvolution of XPS spectra.

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