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Field Effect Modulation of Electrocatalytic Hydrogen Evolution at Back-Gated Two- Dimensional MoS₂ Electrodes

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ABSTRACT: Electrocatalytic activity for hydrogen evolution at monolayer MoS₂ electrodes can be enhanced by the application of an electric field normal to the electrode plane. The electric field is produced by a gate electrode lying underneath the MoS₂ and separated from it by a dielectric. Application of a voltage to the back-side gate electrode while sweeping the MoS₂ electrochemical potential in a conventional manner in 0.5 M H₂SO₄ results in up to a 140-mV reduction in overpotential for hydrogen evolution at current densities of 50 mA/cm². Tafel analysis indicates that the exchange current density is correspondingly improved by a factor of 4 to 0.1 mA/cm² as gate voltage is increased. Density functional theory calculations support a mechanism in which the higher hydrogen evolution activity is caused by gate-induced electronic charge on Mo metal

centers adjacent the S vacancies (the active sites), leading to enhanced Mo-H bond strengths. Overall, our findings indicate that the back-gated working electrode architecture is a convenient and versatile platform for investigating the connection between tunable electronic charge at active sites and overpotential for electrocatalytic processes on ultrathin electrode materials.

Previously, we have reported field effect modulation of outer-sphere electrochemistry at two-dimensional (2D) semiconductors,¹⁻³ such as monolayer MoS₂ and 5-nm-thick ZnO films grown by atomic layer deposition (ALD). In these experiments, the 2D material is supported on a dielectric such as SiO₂ with a backside gate electrode, forming a metal-oxide-semiconductor (MOS) heterostructure, as shown in Figure 1a. The backside gate may be a true metal electrode or, because of convenience, a heavily-doped Si substrate. Application of a back-gate voltage V_{BG} between the gate and an electrical contact to the 2D semiconductor simultaneously shifts the conduction and valence band edges and accumulates or depletes charge carriers in the semiconductor; this is the conventional field effect employed in silicon field effect transistors (MOSFETs).⁴ In some sense this field effect modification of the 2D working electrode is akin to chemical doping in that the offset between the Fermi level (E_F) and the band edges is controllably changed (as in n-doping or p-doping). However, the field effect is distinctly different from chemical doping in that (1) it is electronically controlled, continuously variable, and easily reversible; (2) it is the band edges that shift in response to the field, not E_F , which means that the positions of these edges with respect to redox couples in solution are changed, which in turn implies that the heterogeneous electron transfer rate constants can be tuned.

Figure 1. (a) Cross-sectional view of MoS₂ working electrode and (b) 3D structure of the back-gated electrochemical flow cell (not to scale) with the electrical/electrochemical configuration. The inset optical image in (b) shows a plan view of a MoS₂ electrode. The symbols used in the schematics are as follows: working electrode potential (V_W), source-to-drain bias (V_{SD}), and back-gate bias (V_{BG}).

We have shown that field effect modulation of the band edges and carrier concentration in monolayer MoS₂ and ultrathin ZnO can control heterogeneous charge transfer kinetics between the 2D material and simple, outer-sphere redox couples in electrolyte on the “front” side of the semiconductor. These initial experiments demonstrated the concept of field effect modulation of outer-sphere electrochemistry.^{1–3} Here, we take the next step and demonstrate that field effect modulation can modify the rate of an inner-sphere, electrocatalytic reaction, namely the hydrogen

evolution reaction (HER) on MoS₂. Prior reports by others have demonstrated that both polymorphs of MoS₂ (metastable, metallic 1T and semiconducting 2H) are catalytically active for HER.^{5–14} The activity of 2H MoS₂, our focus here, derives from coordinatively unsaturated Mo active sites, *i.e.*, Mo centers adjacent S vacancies or at exposed crystal edges. Consequently, S vacancy (active site) formation is a commonly adopted strategy to activate electrocatalysis on MoS₂,^{7,15} though heteroatom doping is also employed.^{16–18}

Prior to this work, the field effect has been reported to improve HER activity at back-gated *multilayer* MoS₂ electrodes.¹⁹ However, in that work (see also a related paper on gated multilayer VSe₂²⁰), the enhanced HER activity was attributed to increased conductivity of the multilayer MoS₂ (20–30 nm thick) upon gating and not to any changes in the intrinsic reactivity of the active sites. Herein, we demonstrate by a combination of experiment and density functional theory (DFT) calculations that field effect enhancement of HER activity on *monolayer* MoS₂ occurs by a different mechanism, namely the gate-induced charging of the localized Mo d-states at the active (S-vacancy) sites, and the resultant increase of the Mo-H binding energy. In this mechanism, the increase in HER activity is due to an increase in the intrinsic reactivity of the active sites in monolayer MoS₂ on applying a positive gate bias V_{BG} . Experimentally, we achieve a 140-mV decrease in η at 50 mA/cm² and a 4-fold increase in the exchange current density i_0 by varying V_{BG} . We systematically eliminate the possibility that the enhancement in i_0 and the decrease in η are due to changes in the MoS₂ conductivity or the resistance of the electrical contacts to MoS₂. Further, using DFT, we demonstrate that the charging of the Mo centers at the active sites leads to a 140% increase in the Mo-H bond energy, which provides a clear explanation for the enhanced HER activity. We believe these experiments and associated theoretical calculations open up new

possibilities for investigating and understanding electrocatalysis at 2D materials, as we describe below.

Monolayer MoS₂ was synthesized by chemical vapor deposition (CVD) at 850 °C following a modification of previously reported methods.^{21,22} Large monolayer flakes that are desirable for back-gated electrocatalysis experiments were characterized by atomic force microscopy (AFM), Raman spectroscopy, and photoluminescence and confirmed the 2H phase (Figure S2). After the transfer of a monolayer of MoS₂ onto SiO₂/p-Si back gates, fabrication of MoS₂ electrodes was accomplished in a series of steps including photolithography, plasma etching, e-beam evaporation of Ti/Au metal contacts, and SiO₂ passivation (see the Supporting Information for details of synthesis and device fabrication). The two Ti/Au contacts (source and drain) were made to the front-side of MoS₂ and the completed structure in Figure 1a can thus be viewed as a FET. From the MoS₂ sheet conductance-gate voltage (G_S - V_{BG}) characteristics, Figure S5, we confirmed the n-type behavior of MoS₂ with an on/off current ratio of $\sim 10^4$ and a FET electron mobility of $\sim 22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which further confirmed that the monolayer MoS₂ was the 2H phase.

To perform electrochemical measurements, a molded polydimethylsiloxane (PDMS) block with an embedded 200- μm wide microfluidic channel was assembled onto a MoS₂ electrode, Figure 1b. Integration of this flow cell structure facilitated forced convection of electrolyte, thereby minimizing mass transport effects on voltammetry and helping to sweep away gas bubbles generated on the MoS₂ working electrode. Figure 2a displays our principal results, namely the polarization curves in flowing 0.5 M H₂SO₄ upon sweeping the MoS₂ working electrode potential V_W while applying a constant V_{BG} . At $V_{BG} = 0 \text{ V}$, the HER overpotentials ($\eta = |V_W - U^0|$) at current densities of 10 and 50 mA/cm² were 294 and 474 mV, respectively. These η values at

$V_{BG} = 0$ V are comparable to those previously reported for HER on monolayer MoS₂.^{7,15,23,24} As V_{BG} increased from 0 V to +100 V at 20 V intervals, η progressively decreased to 184 mV (at 10 mA/cm²) and 334 mV (at 50 mA/cm²), respectively (Table 1), indicating an overall improved catalytic activity for HER. Negative V_{BG} , on the other hand, suppressed HER on back-gated MoS₂, resulting in an increased η . The effect of V_{BG} on HER activity was reversible, *i.e.*, switching of V_{BG} to higher and lower values produced corresponding voltammograms that retraced themselves. As a control, we tested back-gated working electrodes in which MoS₂ was replaced with graphene, Figure 2a. We observed no significant HER activity for back-gated graphene at any value of V_{BG} (Figure S7), consistent with expectations. We also verified that the observed shift in η was not a result of the ohmic drop across the MoS₂ working electrode. To check that, we measured the sheet resistance of MoS₂ electrodes simultaneously during the electrochemical measurement (Figure S6a). The calculated in-plane polarization at varying V_{BG} and V_W was always smaller than 11 mV (Figure S6b) and accounted for less than 1% of the overall polarization (*i.e.* η) at current densities of 10 and 50 mA/cm² (Figure S6c). Therefore, it is clear that the reduced η did not result from changes in the in-plane ohmic losses.

Figure 2. (a) Polarization curves and (b) corresponding Tafel plots of 0.5 M H₂SO₄ solution on a back-gated MoS₂ electrode at different back-gate biases V_{BG} . Results on Pt and graphene electrodes are included for comparison. The polarization curves are iR-corrected for solution resistance. All the electrochemical measurements were performed at a working electrode potential scan rate of 50 mV/s and an electrolyte volumetric flow rate of 10 μ L/min.

Table 1. Overpotential, Tafel Slope, and Exchange Current Density at Varying Back-Gate Biases

V_{BG} (V)	η at 10 mA/cm ² (mV)	η at 50 mA/cm ² (mV)	Tafel Slope (mV/dec)	i_0 (mA/cm ²)
-40	396	532	164	0.030
-20	352	502	130	0.032
0	294	474	115	0.034
20	266	442	113	0.047
40	254	424	111	0.054
60	230	388	106	0.067
80	211	365	105	0.098
100	184	334	100	0.122

The polarization curves in Figure 2a were converted into corresponding Tafel plots, Figure 2b, to assess the reaction mechanism. Tafel slopes (b) and exchange current densities (i_0) were obtained by fitting the plots to $\eta = b (\log(i_w) - \log(i_0))$. As expected, a Tafel slope of 115 mV/decade is observed for HER on MoS₂ at $V_{BG} = 0$ V, consistent with ~120 mV/decade that others have reported for monolayer MoS₂ on Si/SiO₂.⁹ The Tafel slope gradually decreases to 100 mV/decade with increasing V_{BG} , while it increases to 164 mV/decade at negative V_{BG} . It is widely accepted that HER on MoS₂ follows the Volmer-Heyrovsky mechanism, where $H^+ + e^- \rightleftharpoons H_{ads}$ (Volmer) and $H^+ + e^- + H_{ads} \rightleftharpoons H_2$ (Heyrovsky) are the elementary steps.²⁵ Tafel slopes of ~120 mV/decade or larger suggest that the Volmer reaction, namely the coupled adsorption and charge transfer step, limits the overall reaction rate.²⁶ The slight decrease in the Tafel slope indicates that there is likely not a significant change in the reaction mechanism upon varying V_{BG} . However, the exchange density i_0 increases by a factor of 4 from 0.034 to 0.122 mA/cm² as V_{BG} increases to +100 V, Table 1 and Figure 3. These i_0 values obtained on back-gated MoS₂ are among the highest

reported to date,^{7-9,11} and the considerable increase in i_0 suggests substantially enhanced catalytic activity at equilibrium.

Figure 3. Exchange current density i_0 as a function of the back-gate induced charge carrier density, Δn_{BG} . The x-axis is quoted in electrons / cm^2 and electrons/S vacancy.

With more than a 100 mV shift in η at 10 mA/cm^2 and a 4-fold increase in i_0 , it is reasonable to conclude that the overall HER activity of monolayer 2H MoS₂ is improved by the field effect. In order to clarify the mechanism for enhanced activity, DFT calculations were performed. The Mo centers adjacent to S vacancies on the MoS₂ basal plane are considered to be the active sites for HER.⁷ X-ray photoelectron spectroscopy (XPS) analysis of the CVD monolayer MoS₂ used in this study indicate that there are ~6% S vacancies (Figure S3) that function as active sites. We therefore constructed a monolayer MoS₂ surface comprised of 5.5% S vacancies to serve as a model for DFT calculations, as shown in Figure 4a. The creation of S vacancies within the MoS₂ surface resulted in the formation of mid-gap electronic states (see Figure 4b and S9)

comprised predominantly of localized Mo d-states that favorably bind protons.⁷ To model the electrostatic doping effect of the back-gate bias on these mid-gap states, we charged the model substrate with extra electrons corresponding to the excess electron densities obtained experimentally (see Supporting Information for further details on the computational methods used). Excess electron densities of nearly $1 \times 10^{13} \text{ cm}^{-2}$ as calculated by $\Delta n_{BG} = C_{SiO_2} \times V_{BG}$ (C_{SiO_2} is the specific capacitance of 300 nm SiO₂, measured to be $\sim 15 \text{ nF/cm}^2$, Figure S8), are induced experimentally at $V_{BG} = +100 \text{ V}$. Figure 4c displays the DFT-calculated electron density difference map corresponding to the difference in charge density at $V_{BG} = +100 \text{ V}$ ($\Delta n_{BG} = 10^{13} \text{ cm}^{-2}$) versus that at 0 V ($\Delta n_{BG} = 0$). From this figure, it is evident that the excess electron density induced upon the application of V_{BG} is concentrated on the Mo atoms near the S vacancy site. This accumulation of excess electron density on the Mo centers in turn leads to a downward shift of the mid-gap states closer to E_F as V_{BG} is increased from 0 to +100 V as shown in Figure 4b. This downward shift of the energy levels is in agreement with expectations based on the known operating principles for field effect devices.

Figure 4. (a) Schematic of the S vacancy site (denoted by red dotted circle) created on model MoS₂ surface used for DFT calculations (b) Computed band structures of MoS₂ surface with 5.5 % S vacancy at different induced charges varying from $\Delta n_{BG} = 0$ ($V_{BG} = 0$ V) to $\Delta n_{BG} = 10^{13} \text{ cm}^{-2}$ ($V_{BG} = 100$ V). The band structure at $V_{BG} = 0$ V is shown in red. (c) Charge density difference map (isosurface value = 0.0002 e-/Bohr^3) of monolayer MoS₂ with 5.5 % S vacancy showing the positive difference in electron density at an induced charge carrier density of 10^{13} cm^{-2} versus that at no excess charge density. The maps show localization of excess charge on the Mo atoms near the sulfur vacancy denoted by red circle.

The binding energy of atomic hydrogen (ΔE_H) to an electrode surface has been shown to be a good descriptor for trends in HER activity.⁵ Thus, we calculated ΔE_H for the binding of

hydrogen to the S vacancy site at charge densities corresponding to the applied back-gate voltages. As shown in Figure 5a, ΔE_H becomes significantly more exothermic at higher Δn_{BG} . Importantly, this stronger H binding provides a clear rationale for higher activity of adsorption-limited HER on MoS₂; increased ΔE_H lowers the activation energy for the Volmer step and leads to a higher fraction of hydrogenated active sites, *i.e.*, equilibrium is shifted in favor of H_{ads}.

In keeping with this analysis, we observed an exponential dependence of the experimental i_0 on the calculated ΔE_H values as shown in Figure 5b. This exponential increase is expected as i_0 is an exponential function of the activation barrier for the rate-limiting Volmer step.^{27,28} The Figure 5b trend is also consistent with previous reports that show i_0 increases exponentially with ΔE_H for electrocatalysts that lie on the right side of the i_0 vs. ΔE_H “volcano plot”, that is those that bind hydrogen weakly ($\Delta E_H > -0.2$ eV).^{5,28–30} Thus, the detailed DFT calculations reported here strongly support a mechanism in which the gate-induced charge enhances the intrinsic activity of the MoS₂ active sites, in particular by stabilizing H_{ads}.

Figure 5. (a) Hydrogen adsorption energies (ΔE_H) as function of induced excess electron density (Δn_{BG}) for values ranging from 0 to 10^{13} cm^{-2} (b) Experimentally determined exchange current densities i_0 for hydrogen evolution on back-gated monolayer MoS_2 versus calculated ΔE_H .

The results reported here are distinctly different than previous work reported on field effect modulation of HER at multilayer (30-nm thick) MoS_2 , which indicate that the decrease in η with applied gate voltage is the result of conductance changes across the MoS_2 flake, *i.e.*, to changes in the ohmic transport of charge from the contacts to the catalytic interface.¹⁹ As mentioned above, using methods that we have previously reported¹ we categorically rule out the possibility that the changes in η are due to in-plane transport effects or to contact resistance.^{9,19} The changes in η that we observe are instead due to changes in inherent catalytic activity of monolayer MoS_2 . This is a

distinctly different mechanism from that proposed previously. Moreover, it does not seem likely that appreciable gate-induced enhancement of S-vacancy activity could be observed in 25-30 nm thick multilayer MoS₂ due to electrostatic confinement and screening of the gate-induced charge at the MoS₂/gate dielectric interface. For example, we estimate the Thomas-Fermi screening length in MoS₂ at $\Delta n_{BG} = 10^{13} \text{ cm}^{-2}$ to be approximately 1-3 nm, smaller than the 25-30 nm thickness of multilayer MoS₂.

To our knowledge this is the first report of field-effect modulation to change the intrinsic activity of electrocatalytic sites on ultrathin, back-gated electrodes. To be clear, by “field-effect modulation” we mean the back-gating method we have employed here, not the normal double-layer charging that occurs in conventional electrochemical experiments. It is important to note that the back gate provides a degree of freedom that is not generally available in conventional electrocatalysis experiments. In a conventional electrocatalysis experiment, double-layer charging of active sites surely occurs but there is no ability to reversibly change the degree of charging independent of the electrochemical potential. With the back gate on sufficiently thin electrocatalyst layers, the amount of charge in the active sites is independently controlled and the impact on the overpotential can then be assessed directly and immediately, as demonstrated here.

There are other reports of electronic modification of gas-phase heterogeneous catalysts that have intriguing analogies to our experiments.^{31,32} An example is the use of voltage-controlled Schottky junctions to manipulate electronic occupation in thin catalytic layers grown on doped semiconductors.³² However, the use of an intervening dielectric in the platform we describe here can dramatically boost accumulated charge concentrations and provides flexibility in 2D electrode design as the alignment of the electrode band edges with the substrate is not a primary consideration.

The back-gated platform described here offers ample opportunities for further investigations of electrocatalysis at 2D electrodes for several reasons. First, the advent of ALD and 2D materials synthesis provides a rich palette of ultra-thin materials that can be coupled to gate/dielectric stacks and implemented as back-gated working electrodes. Second, the continuous, reversible electrostatic doping that is achieved in this platform can be a powerful complement to chemical (*e.g.*, heteroatom) doping strategies for optimizing 2D electrocatalysts. It will be interesting to understand in what ways electrostatic doping and chemical doping are similar or dissimilar. Third, as noted above, the independent control of electrode charging afforded by the back gate portends important opportunities to understand the differences in active site promotion by field-effect versus double-layer charging.

We note that the electrode architecture we have presented here is not fully optimized. For example, switching to high dielectric constant insulators, such as HfO₂, offers the possibility of simultaneously decreasing the required gate voltages and increasing the gate-induced carrier densities up to 10^{14} cm^{-2} . Preliminary computational results suggest a nearly 10-fold stronger hydrogen binding ($\Delta E_H = -146 \text{ meV}$) at such induced carrier densities, which should further enhance the utility of this platform for understanding HER (and other reactions) at ultrathin electrodes.

ASSOCIATED CONTENT

Supporting Information

Materials; synthesis of monolayer MoS₂; device fabrication; characterization: AFM image and Raman, photoluminescence, and XPS spectra of MoS₂; electrical and electrochemical measurements: sheet conductance of MoS₂ as a function of V_{BG} (without electrolyte), sheet resistance of MoS₂ measured in electrolyte simultaneously during electrochemical measurements,

calculated in-plane polarization of a MoS₂ electrode, polarization curves on a back-gated graphene electrode, determination of back-gate dielectric capacitance; computational methods.

The Supporting Information is available free of charge on the ACS Publications Website.

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Notes

The authors declare no competing financial interests.

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Table of Contents

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Supporting Information

Field Effect Modulation of Electrocatalytic Hydrogen Evolution at Back-Gated Two-Dimensional MoS₂ Electrodes

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S1. Materials

Sulfuric acid (H_2SO_4 , 95-98%, ACS grade), was purchased from BDH ARISTAR. Water used to prepare aqueous solutions was purchased from Fisher Chemical. P-type highly boron doped silicon wafers with thermally grown 300-nm-thick SiO_2 ($\text{SiO}_2/p\text{-Si}$), used in both chemical vapor deposition (CVD) and device fabrication, were purchased from Silicon Valley Microelectronics. Molybdenum oxide (MoO_3 , 99.97%), sulfur powder (99.98%), molybdenum sulfide powder (particle size $< 2\mu\text{m}$, 99%), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 98%, reagent grade), and poly(methyl methacrylate) (PMMA, molecular weight: 350 kDa) were purchased from Sigma-Aldrich. Polydimethylsiloxane (PDMS) precursor and its curing agent (Sylgard 184 silicone elastomer kit) were purchased from Dow Corning. Ag/AgCl reference electrodes (CHI111P) were purchased from Fisher Scientific. Graphite rods (99.95%) with a diameter of 1.0 mm used as counter electrodes were purchased from Sigma-Aldrich. CVD monolayer graphene grown on Cu foil was purchased from Graphene Square Inc. (Seoul, South Korea).

S2. Synthesis of Monolayer MoS_2

Monolayer MoS_2 was synthesized by CVD using MoO_3 and sulfur as precursors in a horizontal hot-wall reactor system (PlanarTECH, Planar GROW-5S). In a typical CVD growth, an alumina boat (50 mm $\times$ 12 mm $\times$ 10 mm) containing 0.5 mg MoO_3 powder was placed at the center of the hot-wall furnace. Another alumina boat of same size, holding 200 mg sulfur powder, was placed upstream of the furnace, 25 cm away from the furnace center. A receiving substrate ($\text{SiO}_2/p\text{-Si}$, 30 $\times$ 30 mm²) was mounted face-down on the MoO_3 -containing boat. At room temperature, the quartz tube was first pumped down to vacuum and then purged by flowing Ar gas at a flow rate of 500 sccm for about 10 min until the pressure reached 760 torr again.

After purging, the furnace temperature was ramped to 850 °C in 30 min and was kept at 850 °C for 15 min, while the flow rate of Ar gas was held at 67.5 sccm. At 850 °C furnace temperature, the temperature of sulfur precursor was measured to be approximately 300 °C. After growth, the furnace was first naturally cooled to 650 °C and then was moved to the downstream side to cool the receiving substrate rapidly to room temperature.

Figure S1. Schematic illustration of the CVD setup used in this study

S3. Device Fabrication

The fabrication process was described in detail in our prior work.^{1,2} Briefly, the as-grown MoS₂ was spin-coated with PMMA and the resulting PMMA film holding MoS₂ flakes was separated from the growth substrate by etching the interfacial SiO₂ layer with KOH solution (aqueous, 30 wt%) and then transferred onto a SiO₂/p-Si substrate that is used as the dielectric/back gate stack. After removing PMMA with acetone, the MoS₂ flake with a desirable size and minimal cracks was patterned into a rectangular stripe by selective O₂ plasma etching following photolithography. Another step of photolithography was carried out before e-beam evaporation of Ti/Au (3 nm/ 30 nm) metal contacts on MoS₂. To prevent electrochemical reactions from occurring on the surface of Au, a layer of 30 nm thick SiO₂ was e-beam evaporated on top of the peripheral metal area of MoS₂, with the help of a shadow mask. After

lift-off, the fabricated MoS₂ working electrode was ready to assemble with a molded PDMS microfluidic flow cell. Similarly, graphene electrodes were prepared through these steps described above, except the etchant solution used to separate the PMMA film holding graphene from Cu foil in the transfer step was 100 g/L ammonium persulfate aqueous solution. Pt electrodes were prepared via photolithography and e-beam evaporation of Ti/Pt (3 nm/ 50 nm) on SiO₂/p-Si wafers.

The master mold for PDMS microfluidic channels (200-μm wide, 50-μm tall) was fabricated on a 4-inch Si wafer with a negative photoresist, SU8 2050 (MicroChem), via photolithography.² PDMS precursor mixed with its curing agent (10:1 by weight) was poured onto the master mold and cured at 70 °C in an oven for 3 to 4 h. The cured PDMS was cut into separate blocks where the inlet and outlet holes were made with 1- and 3-mm diameter punch tools, respectively. A molded PDMS flow cell was bonded onto a back-gated MoS₂ electrode substrate through a condensation reaction with SiO₂ at 120 °C, following O₂ plasma treatment of the bonding surfaces² (note that MoS₂ was covered by a shadow mask in this O₂ plasma treatment).

S4. Characterization

Raman and photoluminescence spectra were obtained with a 532 nm laser using a confocal Raman spectrometer (Witec Aphas300R). Atomic force microscopy (AFM) images were collected in the contact mode on a scanning probe microscope (Bruker Nanoscope V Multimode 8). X-ray photoelectron spectroscopy (XPS) measurements were carried out in ultra-high vacuum (10⁻⁷ pascal) with an Al Kα X-ray monochromatic source (1486.6 eV) on a PHI VersaProbe III scanning XPS Microprobe.

Figure S2. (a) Optical image of CVD grown MoS₂ supported on SiO₂/p-Si substrate; (b) AFM image obtained at the edge of a MoS₂ flake; The inset of (b) shows the height profile measured along the white line; (c) Raman and (d) photoluminescence spectra collected on the large MoS₂ flake in (a).

Figure S3. High-resolution X-ray photoelectron spectra of CVD monolayer MoS₂ flakes and bulk MoS₂ powder: (a) Mo 3d states and (b) S 2p states. The high-resolution Mo 3d and S 2p peaks shown in (a) and (b) were used to calculate the S/Mo ratios. The S vacancy concentration of CVD monolayer MoS₂ samples was estimated to be ~6% by comparing the S/Mo atomic ratio of CVD monolayer MoS₂ to that of bulk MoS₂ powder.

Figure S4. (a) and (b) X-ray photoelectron spectroscopy (XPS) survey spectra taken from 0 to 700 eV; (c) and (d) Mo 3d raw XPS spectra and fitted curves; (e) and (f) S 2p raw XPS spectra and fitted curves. (a), (c) and (e) are for CVD monolayer MoS₂ samples on SiO₂/Si. (b), (d) and (f) are for bulk MoS₂ powder on conductive aluminum foil tape.

S5. Electrical and Electrochemical Measurements

The electrical and electrochemical configuration used in experiments is shown in Figure 1b. To obtain MoS₂ sheet conductance as a function of back-gate bias V_{BG} without electrolyte, Keithley 2400 and 2611 source meters were used to apply V_{BG} and source-to-drain bias V_{SD} , respectively, while measuring currents. To perform electrochemical experiments while testing sheet conductance of MoS₂, an Ag/AgCl reference electrode and a graphite rod counter electrode were introduced to the setup. The Ag/AgCl (filled with 1 M KCl) reference electrode was plugged into a Luggin capillary (filled with 0.5 M H₂SO₄) whose tip was placed at the outlet of the flow cell. The graphite counter electrode was inserted 3 to 5 mm away from the outlet. The MoS₂ working electrode was aligned in the microfluidic channel and placed ~100 μ m away from the outlet, as shown in Figure 1b. During the sweep of working electrode potential, the source metal contact on the MoS₂ working electrode was grounded while a 5 mV bias was applied at the drain metal contact. The reaction current was obtained by adding up the currents measured at both source and drain contacts (detailed explanation can be found in our prior reports^{2,3}). We used four source meters (Keithley 2400, 2611, 2612 and 236) to apply potentials and measure currents and data were collected with an in-house LabView program. The working electrode potential V_W was iR corrected to account for ohmic losses in the electrolyte using the same method as reported before,² where a value of 211 mS/cm found in the literature⁴ was used as the bulk conductivity of 0.5 M H₂SO₄. All the electrical and electrochemical measurements were conducted in ambient environment at room temperature.

Figure S5. Sheet conductance, G_S , of a representative MoS₂ electrode (50×50 μm²) measured by applying a constant source-to-drain bias, $V_{SD} = 10$ mV, while sweeping back-gate bias V_{BG} from -100 to +100 V at a sweep rate of 2V/s. The blue and gray plots are shown in semilog and linear scale, respectively. The sheet conductance was obtained without any electrolyte or encapsulation layer on top of MoS₂. The field effect electron mobility μ was calculated using the following equation: $\mu = \frac{dG_S}{dV_{BG}} \cdot \frac{1}{C_{BG}}$, where C_{BG} is the specific capacitance (capacitance per unit area) of 300-nm-thick SiO₂ dielectric layer, which was estimated to be 15 nF/cm² via displacement measurements (see Figure S8). The slope of the red dashed line shown here was used as $\frac{dG_S}{dV_{BG}}$ to calculate μ .

Figure S6. (a) Sheet resistance, R_s , of a back-gated MoS₂ electrode ($50 \times 50 \mu\text{m}^2$) simultaneously obtained during sweep of working electrode potential V_W in 0.5 M H₂SO₄ at different back gate biases V_{BG} (Note that a source-to-drain bias $V_{SD} = 5 \text{ mV}$ was applied to measure R_s); (b) corresponding in-plane polarization calculated (The method used to calculate in-plane polarization was described in detail in our previous report.³); (c) percentage of in-plane polarization to overall polarization at current density $i_w = 10$ and 50 mA/cm^2 as a function of applied back-gate bias V_{BG} .

Figure S7. Polarization curves obtained in flowing 0.5 M H₂SO₄ on a back-gated graphene electrode (50×50 μ m²) at varying back-gate biases V_{BG} . The inset optical microscopy image shows a plan view of a back-gated graphene electrode. The scan rate of the working electrode potential is 50 mV/s and the volumetric flow of the electrolyte is 10 μ L/min.

Figure S8. (a) Capacitive current density measured by sweeping back-gate bias V_{BG} applied on an Au/SiO₂/p-Si structure at different V_{BG} sweep rates; (b) Averaged capacitive current density as a function of V_{BG} scan rates in (a). A 9 mm² gold electrode was used in this measurement and it was prepared in a similar procedure as described in S3 via photolithography and e-beam evaporation of Ti/Au (3 nm/30 nm thick).

S6. Computational Methods

Spin polarized density functional theory (DFT) calculations reported herein were carried out using plane wave DFT code implemented in Vienna Ab-initio Simulation Package (VASP).⁵⁻
⁸ All of the calculations presented herein were carried using nonlocal gradient calculations using the RPBE functional within the Generalized Gradient Approximation (GGA) to determine the exchange and correlation gradient corrections.⁹ PAW pseudopotentials were used to describe the core electrons and their interaction with the valence electrons.^{10,11} An optimized lattice constant of $a = 3.19 \text{ \AA}$ was computed for the 2H phase of bulk MoS₂ which is in agreement with the experimentally determined value of $a = 3.16 \text{ \AA}$.¹² A 3x3 supercell of monolayer MoS₂ was then constructed by cleaving along the (001) plane of the 2H-MoS₂ crystal. A vacuum space of 20 $\text{\AA}$ was employed for the calculations to minimize interaction between periodic layers. This monolayer MoS₂ surface with a surface area of $79.31 \text{ \AA}^2$ was then used as the model for our calculations. An energy cutoff of 1000 eV was used to construct the plane waves for the DFT calculations. The structural optimizations were carried out until the maximum force on each of the ions was less than 0.05 eV/ $\text{\AA}$. A tolerance of 10^{-6} eV was specified for the convergence of the SCF cycle. A 3x3x1 gamma-centered k-point grid was used for structural optimizations, while a 6x6x1 k-point grid was used for energy calculations. The band structure was calculated along the high symmetry k-point path of Γ -M-K- Γ for MoS₂ with 25 intersections between each of the k-points. The S vacancy was created by removing a S atom from the pristine monolayer MoS₂ surface, thus generating a 5.55% S vacancy concentration which results in the formation of the mid-gap states shown in Figure S9 which is consistent with the states previously reported for vacancies in the monolayer surfaces of MoS₂.¹³ These mid gap states consist mainly of Mo d-states (Figure S10).

Hydrogen adsorption studies examined the binding of atomic H to the S vacancy on the MoS₂ surface as shown in Figure S11. Previous reports suggest that these S vacancies serve as the active sites for HER on MoS₂.¹³ To examine the effect of gate bias, the system was charged with excess electrons depending on the excess charge carrier density determined experimentally corresponding to the applied bias, summarized in Table S1. The hydrogen binding energy was calculated as a function charge using the following equation:

$$\Delta E_H = E(\text{MoS}_2\text{-H}) (q) - E(\text{MoS}_2) (q) - 0.5E(\text{H}_2) (q=0)$$

where $E(\text{MoS}_2\text{-H}) (q)$ is the energy of the model MoS₂ surface used with the H adsorbed on the S vacancy site at charge q , $E(\text{MoS}_2) (q)$ is the energy of the model MoS₂ used without adsorbed H at charge q and $E(\text{H}_2)$ is the energy of the hydrogen molecule.

The calculated free energies ($\Delta G_H = \Delta E_H + \Delta \text{ZPE} - T\Delta S$) are known to be good descriptors for the HER activity.¹⁵ In the present study, the changes in ZPE (ΔZPE) and $S(\Delta S)$ aren't expected to change at different charged conditions. As such, we use ΔE_H to provide the important qualitative trends as was described above.

Table S1. Number of excess electrons used to charge the system corresponding to the different voltage bias and excess charge carrier density

Back-gate voltage (V _{BG})	Excess charge carrier density (e ⁻ /cm ²)	Excess electrons added to the model system (e ⁻)
0	0	0
20	2x10 ¹²	0.016
40	4x10 ¹²	0.032
60	6x10 ¹²	0.048
80	8x10 ¹²	0.064
100	10 ¹³	0.08

Figure S9. Band structures of pristine MoS₂ with 0% S vacancy and MoS₂ with 5.55 % S vacancy showing introduction of mid-gap states at zero system charge.

Figure S10. Projected Mo d-density of states and total density of states of MoS₂ surface with 5.55% S vacancy at zero charge.

Figure S11. Hydrogen adsorption on S vacancy site.

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