



Article Enhanced Hydrogen Evolution Reaction in Surface Functionalized MoS₂ Monolayers

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Abstract: Monolayered, semiconducting MoS₂ and their transition metal dichalcogenides (TMDCs) families are promising and low-cost materials for hydrogen generation through electrolytes (HER, hydrogen evolution reaction) due to their high activities and electrochemical stability during the reaction. However, there is still a lack of understanding in identifying the underlying mechanism responsible for improving the electrocatalytic properties of theses monolayers. In this work, we investigated the significance of controlling carrier densities in a MoS₂ monolayer and in turn the corresponding electrocatalytic behaviors in relation to the energy band structure of MoS₂. Surface functionalization was employed to achieve p-doping and n-doping in the MoS₂ monolayer that led to MoS₂ electrochemical devices with different catalytic performances. Specifically, the electron-rich MoS₂ surface showed lower overpotential and Tafel slope compared to the MoS₂ with surface functional groups that contributed to p-doping. We attributed such enhancement to the increase in the carrier density and the corresponding Fermi level that accelerated HER and charge transfer kinetics. These findings are of high importance in designing electrocatalysts based on two-dimensional TMDCs.

Keywords: surface functionalization; hydrogen evolution reaction; doping; MoS₂ monolayer

1. Introduction

Hydrogen (H₂) is emerging to be an essential energy solution for a next-generation and sustainable energy system that can replace fossil fuels due to its clean, renewable, and affordable characteristics [1,2]. Nevertheless, the majority of hydrogen fuels is produced from fossil fuels by reforming procedures. In order to avoid fossil fuels in hydrogen production, a number of hydrogen production methods are in development, especially in eco-friendly ways. One environment-friendly method to produce H_2 is by electrochemically evolving H₂ by water splitting using sunlight or electricity generated by wind turbines or solar cells [3]. Splitting water molecules into hydrogen occurs by electrochemical hydrogen evolution reaction (HER, $2H^+ + 2e^- \rightarrow H_2$) on the surface of the catalyst's electrodes, and the efficiency of hydrogen production can be increased by decreasing the overpotential needed to drive the hydrogen evolution reaction (HER) [4]. Current hydrogen production from water splitting generally relies on noble metal catalysts. In particular, platinum (Pt)based catalysts are known to display an excellent catalytic performance with its balanced hydrogen adsorption/desorption energy, small overpotential, and long cycling stability in terms of favorable HER behavior. However, due to high cost and limited supply of platinum, extensive efforts have been paid to seek high efficiency and cost-effective nonnoble metal alternatives such as transition metal sulfides and oxides, nickel alloys, and so forth [5].

Molybdenum disulfide (MoS_2), which is mostly studied among a hexagonally packed layered structure of transition metal dichalcogenides (TMDCs), has been considered to be



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). a promising candidate for catalyzing electrochemical hydrogen production from water due to its relatively low cost, its element abundance in earth, high catalytic activity, and good electrochemical stability [6–8]. Up to now, numerous studies have focused on improving the catalytic performance of MoS_2 by increasing the concentration of exposed sulfur edges (catalytic active sties) and constructing the hierarchical morphology and structure of MoS_2 [1,4,9–12]. In particular, the MoS_2 monolayer shows a dramatic increase in catalytic performance compared to its bulk counterpart, which can be attributed to the large density of unsaturated molybdenum in basal planes and edge sites as well as lower internal resistance than its bulk counterpart, that subsequently lead to efficient charge transfer kinetics [13,14].

Due to its semiconducting nature, the HER behaviors of the MoS₂ monolayer can be significantly affected by the change in energy level of MoS₂, which can then lead to different charge transport kinetics. Simultaneously, controlling the energy level of the MoS₂ monolayer can result in different HER behavior by modifying the charge exchange process between the electrocatalyst and protons as well as the charge transfer dynamics between the electrode and the electrocatalyst [5,14]. Consequently, the changes in the electronic band structure of the MoS₂ monolayer can strongly affect the overall electrocatalytic performance of MoS₂ catalysts. However, so far, relatively little attention has been paid to methods that modify the electrocatalytic performance of the MoS₂ monolayer and to the role of the modulation of energy level of MoS₂ in HER.

In this work, we investigated the influence of the surface-chemistry on the modulation of the charge carrier density of the MoS₂ monolayer associated with Fermi level position and the corresponding electrocatalytic behaviors. To demonstrate a clear relationship between the surface chemistry, fermi-level position, and corresponding HER performance, a self-assembled monolayer (SAM) was employed to effectively donate and withdraw electrons from the MoS_2 monolayer. We found that the surface modification to the MoS_2 monolayer effectively modulated charge carrier density and the resulting Fermi-level position, which was confirmed through Raman and photoluminescence (PL) measurement as well as electrical measurement by fabricating back-gated field-effect transistors (FETs). The catalytic performance of the surface modified MoS₂ monolayer was measured by contact with the Ti/Au electrode with on-chip device configuration and exposing the MoS₂ surface only to the electrolyte. We demonstrated efficient catalytic activities of the MoS_2 monolayer when the Fermi-level of MoS_2 shifted upward, which was observed through improved onset potential, decreased overpotential, and decreased Tafel slope. We attributed such enhancement to the higher density of free carriers that translated into higher conductivity and better charge transfer kinetics. These findings present an important pathway toward designing catalysts based on TMDC monolayers.

2. Results and Discussion

Monolayer MoS₂ was directly grown on a 300 nm SiO₂/Si substrate using our thermal chemical vapor deposition (CVD) method [15,16], as shown in Figure S1a, and the resulting optical image of MoS₂ is shown in Figure S1b. In order to find whether the synthesized MoS₂ was monolayered, Raman and PL analysis was conducted as shown in Figure S2. Figure S2a shows the two characteristic Raman peaks measured around 383 cm⁻¹ and 402 cm⁻¹, corresponding to in-plane (E^{1}_{2g}) and out-of-plane (A_{1g}) vibrational modes, respectively. The difference between the two modes was found to be around 19 cm⁻¹, which confirmed that the synthesized MoS₂ was single-layered [17]. We also measured PL as shown in Figure S2b, and the distinct strong PL emission was measured, which corresponded to the direct bandgap nature of a single-layer MoS₂. In order to investigate the influence of the charge carrier density of the MoS₂ monolayer on the electrocatalytic behaviors, the well-known SAM surface functionalization technique was employed in this study. Octadecyltrichlosilane (ODTS, electron withdrawing) and (3-Aminopropyl)triethoxysilane (APTES, electron donating) organic molecules were used as they can effectively tune the carrier concentrations, electrical, and optical properties of TMDC monolayers and other

nanomaterials [18–20]. The surface functionalization of the as-grown MoS₂ monolayers with ODTS and APTES was performed in a hexane solution containing the functionalized organic molecules in an argon-filled glove box as shown in Figure 1a,b. Note that SAM molecules donate and withdraw electrons through built-in molecular dipoles [19]. The charge transfer from and/or to organic molecules then effectively modulates the charge carrier densities of the MoS₂ monolayer, which then results in the rise and/or lower Fermi energy level as shown in Figure 1c. Compared to pristine MoS₂, the Fermi-level of APTES-functionalized MoS₂ was shifted upward, while it shifted downward for ODTS-functionalized MoS₂, and the changes in the carrier density and Fermi level are supported in the next paragraphs. It should be highlighted that the SAM technique is effective and a nondestructive method of changing carrier concentrations of the MoS₂ monolayers.



Figure 1. (a) A schematic illustration of the surface functionalization of either ODTS (Octadecyltrichlosilane) or APTES ((3-Aminopropyl)triethoxysilane) in a hexane solution. (b) ODTS and APTES molecules that withdraw and donate electrons from the MoS_2 monolayer. (c) Energy band diagram of MoS_2 monolayer depicting the change in the Fermi-level upon surface functionalization with either ODTS or APTES.

In order to confirm and analyze the SAM functionalized-induced change of the carrier density using either ODTS or APTES, we first measured the change in the Raman and PL spectrum as they were strongly perturbed by the change in the carrier density of the MoS₂ monolayers [18]. Raman spectra of the pristine MoS₂ (pristine-MoS₂) and functionalized MoS₂ (APTES-MoS₂, and ODTS-MoS₂) were measured, which is shown in Figure 2a. We clearly observed that the A_{1g} Raman mode of the functionalized MoS₂ monolayers was dependent on the functionalized molecules, while the E¹_{2g} mode was rather unaffected by the SAM doping. As shown in Figure 2b, the A_{1g} vibrational mode of pristine was 400.2 cm⁻¹, which then increased to 401 cm⁻¹ for ODTS-MoS₂ and decreased to 399.3 cm⁻¹ for APTES-MoS₂. Moreover, it was found that the A_{1g} mode stiffened for ODTS-MoS₂ and softened for APTES-MoS₂, evidenced by the change in its linewidth. The doping-dependence of A_{1g} vibrational mode of MoS₂ can be understood as an electron–phonon coupling, in which electron doping leads to strong electron–phonon coupling, which then softens the A_{1g} vibrational mode, and the trend shown in the results were in good agreement with previous studies [21].

The functionalized MoS₂ monolayer was further characterized using PL spectroscopy. PL spectra of pristine-MoS₂, ODTS-MoS₂, and APTES-MoS₂ were obtained (Figure 2c). It was clearly noticeable that the PL spectrum of ODTS-MoS₂ was blue-shifted (6 nm), and the PL intensity was increased, while for the APTES-MoS₂, there was a decrease in the PL intensity and the red-shift (7 nm) of the peak wavelength. Furthermore, the full-width at half-maximum (FWHM) of the PL peak of the ODTS-MoS₂ layer was decreased, while it was largely increased for APTES-MoS₂. These trends of changes in the PL of the MoS₂ layer upon surface functionalization can be attributed to the change of carrier concentrations: more electrons in the MoS₂ monolayer decrease the radiative recombination rates of exciton and makes recombination of trions dominant, and these results are consistent with previous reports that measured the carrier density-dependent PL of MoS₂ [22].



Figure 2. Raman and photoluminesence characterization of MoS₂ monolayer functionalized with ODTS and APTES. (**a**) Raman and (**c**) PL spectra taken from pristine and surface functionalized MoS₂. (**b**) Raman peak (E12g mode and A1g mode) shift and (**d**) PL peak shift (primary axis) and full width at half maximum (secondary axis) with respect to the functionalized molecules.

In order to characterize the SAM functionalization-induced change in the charge carrier density and the corresponding Fermi level, electrical properties of MoS₂ FETs were measured for the pristine and modified MoS₂ FETs. The devices employed for this study was fabricated using photolithography, followed by the deposition of Ti/Au (5/45 nm) electrode layers as shown in Figure 3a. Figure 3b shows the representative drain-source current, I_{ds} , versus gate voltage, V_g , on a logarithmic scale (transfer curve) at a drainsource voltage of $V_{ds} = 0.1$ V. We could easily notice that the APTES-MoS₂ device showed noticeably high on-current and conductance compared to the pristine-MoS₂ device, while low on-current and conductance was measured for the ODTS-MoS2 device. These trends of conductance with respect to the SAM functionalization were in good agreement with Figure S3, which shows the representative drain-source current versus drain-source voltage at varying gate voltages (output curve). In addition, it was found that the threshold voltages were negatively shifted for APTES-MoS₂ devices, while threshold voltages shifted toward more positive voltages for ODTS-MoS₂. For statistical analysis of the devices, the resulting statistical chart of 10 control devices are shown in Figure 3. The results presented in the transfer and output curves demonstrate that SAM functionalization is effective in donating electrons (APTES) and withdrawing electrons (ODTS) from the MoS₂ monolayer and consequently changes the Fermi energy level of the MoS_2 monolayer. To further analyze and compare the change in the free carrier density, we calculated and compared the amount of change in carrier density when MoS2 devices were functionalized with SAM using the electrical results shown in Figure 3b and the parallel-plate capacitor model, $N_{doping} = \frac{C|\Delta V_{th}|}{e}$, where *C* is the capacitance of the HfO₂ gate oxide layer (309.9 nF/cm²), ΔV_{th} is the change in the threshold voltage of the functionalized devices with respect to the pristine device, and e is the elementary charge. The N_{doping} was calculated to be

 3.874×10^{12} and 2.905×10^{12} cm⁻² for the APTES-MoS₂ device and ODTS-MoS₂ device, respectively, and was consistent with previously reported results [18,23–25]. Therefore, it is evident from the shift of threshold voltages and change in the carrier density that the SAM functionalization-induced doping of MoS₂ was successfully employed, which consequently affected the Fermi energy level of theMoS₂ monolayers.



Figure 3. Effect of surface functionalization on the carrier density of the MoS_2 monolayer. (a) An optical image of the field effect transistors based on the MoS_2 monolayer fabricated using photolithography. (b) Transfer curve at 0.1 V drain-source voltage acquired from the devices. (c) A change in threshold voltages for 10 control devices before and after surface functionalization. Note that threshold voltages shifted toward more negative voltages for the APTES-MoS2 devices and shifted toward more positive voltages for ODTS-MoS2 devices.

Having confirmed the changes in the carrier density and Fermi level upon surface functionalization, we now focus on elucidating the role of the carrier density in the HER catalytic behaviors of the MoS_2 monolayer. As shown in Figure 4a, the HER catalytic behaviors of the pristine and surface functionalized MoS₂ monolayers were measured by aa three electrodes system, which is the setup typically employed to measure HER catalysis [26]. A probe station was used to electrically connect the working electrode (WE), counter electrode (CE), and reference electrode (RE). Ti/Au electrodes deposited on a chip was used as the contact and current collector. Droplet of electrolyte solution $(0.5M H_2SO_4)$ was applied on the surface of MoS₂ catalysts. In order to sorely investigate the catalytic activity of the monolayered MoS_2 , we used photoresist to open the MoS_2 active sites only while the Ti/Au electrodes were covered by the photoresist, making the electrodes inert to the acid electrolyte as shown in Figure 4b. Note that this experimental design and employing an on-chip device in the electrochemical measurement made it possible to characterize 2D materials by accurately measuring the area of the active sites involved in the HER reaction [12]. Furthermore, electrochemically inert SiO_2 was used as the substrate to exclude any HER contribution from the substrate and to sorely focus on the catalytic performance of the active MoS₂.

Figure 4c shows the linear sweep curves of the pristine MoS₂ monolayer and surface functionalized MoS₂ monolayers at a scan rate of 10 mV/s. From the polarization curve, the distinctively different HER activities were noticed for the pristine and surface functionalized MoS₂ monolayers. Compared to the catalytic behavior of the pristine monolayer MoS₂, the catalytic performance was improved for APTES-MoS₂, while it deteriorated for ODTS-MoS₂, and each device performance was characterized for multiple cycles for the stability of functionalized molecules (Figure S4). The overpotential of the MoS₂ monolayers, which is measured at the catalytic current density of 10 mA/cm², were calculated to be 637 mV for ODTS-MoS₂, 445 mV for pristine-MoS₂, and 382 mV APTES-MoS₂. Likewise, as shown in Figure 4d, the Tafel slope was calculated to be 162 mV/decade for ODTS-MoS₂, and the rise of Fermi level close to the conduction band of the MoS₂ monolayer makes them favorable for H₂ production. Controlling the energy level of MoS₂

can activate or deactivate the electrochemical HER kinetics by the surface functionalization of the MoS₂ monolayer [5,14]. Furthermore, as evidenced in the output curve of Figure S3, the rise in Fermi level decreased the potential barrier between the electrode and the MoS₂ catalyst, which facilitated the charge injection from the electrode to the MoS₂ and resulted in enhanced catalytic activities of the MoS₂ monolayer [14,27]. Thus, the increase in the carrier density and the corresponding Fermi level accelerate the HER kinetics and must be considered when designing the catalysts based on 2D semiconductors.



Figure 4. Electrochemical setup for measuring the HER activity of the MoS₂ monolayers. (a) Photograph of the electrochemical device. (b) An optical microscope image of the electrochemical device. The Ti/Au electrode was covered by photoresists to make it inert to catalytic activities. (c) Polarization curves and (d) Tafel plots measured for pristine and surface-functionalized MoS₂ monolayers.

3. Materials and Methods

3.1. Synthesis of Monolayer MoS₂

The MoS₂ monolayer was directly grown on a SiO₂ (300 nm)/Si substrate using our thermal CVD process. To summarize, inside a 2-inch tube furnace, a MoO₃ precursor (0.05 mg, >99% Sigma Aldrich, Seoul, South Korea) and sulfur powders (200 mg, >99.98% Sigma Aldrich, Seoul, South Korea) on a alumina boat, which was placed on the upstream and downstream, respectively, were used to synthesize the MoS₂ monolayers. The growth substrate (SiO₂/Si) was placed faced down on the boat containing the MoO₃ precursors. The CVD furnace was heated at a rate of 18.75 °C/min up to 750 °C in an argon-filled environment, and the temperature of the furnace was maintained for 10 min for the synthesis and cooled down to room temperature.

3.2. Formation of Octadecyltrichlorosilane (ODTS) and (3-Aminopropyl)-Triethoxysilane (APTES) on a MoS₂ Monolayer

Octadecyltrichlorosilane (ODTS, Sigma Aldrich Seoul, South Korea, >90%) and (3-Aminopropyl)-triethoxysilane (APTES, Sigma Aldrich, Seoul, South Korea, 99%) were used to surface functionalize the as-grown MoS_2 in an argon-filled glove box by dipping the as-grown substrates into a 10 mL of hexane solution that contained 50 µL of ODTS or APTES. The substrates were soaked for 1 h and rinsed with hexane, followed by drying with nitrogen. The substrates were then put on a hot plate and baked at 120 °C inside a glove box.

3.3. Characterization of the Doped MoS₂

The PL and Raman measurements were performed using a 532 nm laser on a Witec Confocal Raman Spectroscopy. Laser power of 20 μ W and 1 mW were used for PL and Raman analysis, respectively. A ×50 objective lens, which corresponded to the spot size of around 1 μ m², was used.

3.4. Device Fabrication and Measurement

The polysterene (PS MW ~192,000, Sigma Aldrich, Seoul, South Korea) coated MoS₂ monolayers were detached from the growth substrate using DI water. The detached MoS₂/PS film was then transferred onto a 20 nm HfO₂/Si substrate that was used as a global back gate. The electrode pads in the MoS₂ FETs were patterned using a photolithography process and AZ 5214E MicroChem photoresist, followed by the deposition of titanium (5 nm) and gold (40 nm) layers using a thermal evaporator. After a lift-off process, another photolithography process was performed in order to open the active catalytic area in MoS₂. A semiconductor characterization system (4200-SCS, Keithley, Solon, OH, USA) was used to measure the electrical properties of MoS₂, and the catalytic activities of the MoS₂ monolayers were measured using μ AUTOLABIII. In our device measurement experimental setup, monolayer MoS₂ acts as the working electrode and the Ti/Au (5 nm/45 nm) electrode works as a current collector. Ag/AgCl and Pt wire with the diameter of 0.5 mm were used as the reference and counter electrode, respectively, and the distance between the electrodes was set to be larger than 5 mm. The active area was calculated based on the area of the triangular MoS₂ exposed through photolithography.

4. Conclusions

In summary, we investigated the role of charge carrier density associated with the Fermi energy level on the electrocatalytic behaviors of the MoS₂ monolayer. The carrier density of MoS₂ was modulated to be n-doped (APTES-MoS₂) and p-doped (ODTS-MoS₂) through the SAM doping technique, and the electrocatalytic performance was measured by fabricating an on-chip device that could accurately measure the catalytic activity of the MoS₂ monolayer. The catalytic activity of the electron rich APTES-MoS₂ was found to be enhanced, while it was deteriorated for ODTS-MoS₂, suggesting that the increase in charge carrier density associated with the upshift of Fermi-level position helps the charge transfer kinetics that lead to decreased overpotential and Tafel slope. We believe that the results presented in this work are important in designing HER catalysts based on two-dimensional TMDCs.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4 344/11/1/70/s1, Figure S1: (a) Illustration of the CVD synthesis process for a MoS2 monolayer. (b) An optical image of the as-grown MoS2 monolayers. Scale bar: 20 µm, Figure S2: (a) Raman and (b) PL spectrum of MoS2 monolayer, Figure S3: Output curves of (a) APTES-MoS2, (b) pristine-MoS2, (c) ODTS-MoS2, Figure S4: Polarization curves of (a) ODTS-MoS2 and (b) APTES-MoS2 plotted before and after 10 cycles while the electrolyte was replaced every cycle.

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