Performance Piezoelectric Nanogenerator

Ju-Hyuck Lee, and Sang-Woo Kim*

In this work, a sulfur (S) vacancy passivated monolayer MoS2 piezoelectric nanogenerator (PNG) is demonstrated, and its properties before and after S treatment are compared to investigate the effect of passivating S vacancy. The S vacancies are effectively passivated by using the S treatment process on the pristine MoS2 surface. The S vacancy site has a tendency to covalently bond with S functional groups; therefore, by capturing free electrons, a S atom will form a chemisorbed bond with the S vacancy site of MoS2. S treatment reduces the charge-carrier density of the monolayer MoS2 surface, thus the screening effect of piezoelectric polarization charges by free carrier is significantly prevented. As a result, the output peak current and voltage of the S-treated monolayer MoS2 nanosheet PNG are increased by more than 3 times (100 pA) and 2 times (22 mV), respectively. Further, the S treatment increases the maximum power by almost 10 times. The results suggest that S treatment can reduce free-carrier charge by sulfur S passivation and efficiently prevent the screening effect. Thus, the piezoelectric output peaks of current, voltage, and maximum power are dramatically increased, as compared with the pristine MoS2.

Scavenging electrical energy from mechanical energy sources wasted in nature has attracted great attention for powering portable devices with low power consumption and developing self-powered electronics. Considerable scientific efforts to fabricate high performance piezoelectric nanogenerators (PNGs) based on piezoelectric nanostructures are being expanded toward realizing electronic components for transparent flexible self-powered electronic skins, sensors, switches, etc. Recent studies have reported the strong piezoelectric properties of atomic layered transition-metal dichalcogenides (TMD) materials with an applied external force due to their broken inversion symmetry. In previous studies, most of the 2D TMD materials exhibit piezoelectric properties, unlike its bulk parent crystal. Remarkably, the calculation of the piezoelectric coefficient for monolayer TMD such as MoS2, WSe2, etc. according to density-functional theory revealed that the monolayer structure exhibits a stronger piezoelectric coupling.
PNG consisting of monolayer MoS₂ nanosheet and Au electrode on polyethylene terephthalate (PET) substrate. Figure S1 (Supporting Information) shows the device fabrication process of the MoS₂ piezoelectric nanogenerator. In our experiment, monolayer MoS₂ nanosheet was synthesized using the CVD method on sapphire substrate, and then transferred to PET using a polymer-assisted wet transfer method. Grown MoS₂ nanosheet is a large-area monolayer and is clearly shown in Raman mapping results. (Figure S2, Supporting Information). To measure the piezoelectric response, Cr/Pd/Au (1/20/50 nm) electrodes were deposited on the transferred monolayer MoS₂ with a channel of 100 µm width and 100 µm length. Figure 1b shows a photographic image of the flexible MoS₂ piezoelectric nanogenerator device, and an optical microscope image of the optimized channel (inset). Figure 1c shows the results of Raman analysis carried out before and after S-treatment to confirm the layer and crystalline change of MoS₂ samples. The frequency difference between out-of-plane (A₁₈g) and in-plane (E₁₂g) phonon modes depends on the number of layer of MoS₂. The frequency difference between E₁₂g and A₁₈g was 19 cm⁻¹. This means that the pristine MoS₂ and S-treated MoS₂ clearly show monolayer quality. After the additional S-treatment process, there is no peak shift or peak intensity difference. This result indicates that the additional S-treatment process does not change the layer and crystallinity of monolayer MoS₂. To confirm the observation of the piezoelectric property of the pristine and S-treated monolayer MoS₂ nanosheet, PFM analysis, one of the methods that can detect the characteristics of piezomaterial,[11] was performed. Figure S3 (Supporting Information) shows a schematic illustration of the PFM measurement set up, and the detailed measurement method of lateral PFM. We prepared the synthesized pristine and S-treated monolayer MoS₂ nanosheet on sapphire substrate. In order to apply an external electric field laterally through the MoS₂ samples, two lateral electrodes were deposited onto both edges of the MoS₂ nanosheet. Figure 1d shows the piezoresponse as a function of the magnitude of the applied external bias for the pristine and S-treated monolayer MoS₂ nanosheets and the α-quartz, revealing a distinct piezoresponse from the S-treated MoS₂ nanosheet when compared to that of the α-quartz and the pristine monolayer MoS₂ nanosheet, which increases as the applied bias increases. Since the piezoelectric coefficient, d₁₁, of the quartz is known to be ≈2.3 pm V⁻¹, it can be used to calibrate the piezoresponse that was obtained. We calculated the piezoelectric coefficient d₁₁ based on the slope of the lateral PFM results. The obtained piezoelectric coefficients of pristine and S-treated monolayer MoS₂ nanosheets are 3.06 ± 0.6 and 3.73 ± 0.2 pm V⁻¹, respectively. These results clearly show that the piezoproperty of our S-treated monolayer MoS₂ nanosheet sample was almost close to the theoretical value, compared to the pristine samples. This means that the S-treatment process enhanced the piezoelectric characteristic of the S-treated
monolayer MoS₂ nanosheet, compared to that of the pristine monolayer MoS₂ nanosheet.

To investigate characteristic change after the S-treatment process, PL, XPS, and KPFM were performed. Figure 2a indicates the intrinsic S vacancy commonly observed in CVD-grown monolayer MoS₂, and S atoms filled into the vacancy positions by the S-treatment process. In order to analyze the characteristic difference between pristine and S-treated monolayer MoS₂ nanosheet by the additional S-treatment process, low temperature PL measurement was performed at 80 K. Figure 2b shows that two prominent absorption peaks can be identified at 1.89 and 1.98 eV in the spectra of both pristine MoS₂ and S-treated MoS₂. These two resonances have been established to be the direct excitonic transition and the spin–orbital splitting of the valence band of MoS₂. Their energy difference is due to the spin–orbital splitting of the valence band, and the two resonances are known as A₁ and B₁ excitons, respectively. However, the PL peak intensity of S-treated MoS₂ is higher than that of pristine MoS₂. This PL modulation results is due to change between the exciton PL and trion PL, depending on the carrier density in monolayer MoS₂.²⁷,²⁸ It is known that control of the carrier density is an effective method to tune the optical properties of TMDs.²⁹–³¹ Owing to the natural n-type doped property, there is tightly bound trion (negatively charged exciton) formation on MoS₂,²⁹ therefore, the PL intensity of MoS₂ is mostly weak. After S-treatment, excessive electrons are captured to make bonding between S atom and S vacancy site, which decreases the free carrier density of MoS₂. Thus, the PL process is switched from trion recombination to exciton recombination, and dramatically enhances the PL intensity of monolayer MoS₂.²⁷,²⁸ Also, the carrier density changes before and after S-treatment calculated using a field effect transistor are discussed below.

XPS measurement can show the S vacancy passivation phenomenon by the additional S-treatment process. Figure 2c shows that the stoichiometry of pristine monolayer MoS₂ nanosheet as determined by XPS appears to be ≈1.8:1 (S/Mo).
This would be consistent with the presence of S vacancies. On the other hand, the S/Mo ratio of S-treated MoS2 shows 2:1. This means that pristine monolayer MoS2 nanosheet becomes stoichiometric MoS2 nanosheet due to S vacancies becoming filled with S atoms by the S-treatment process, as shown in Figure 2d. Also, the binding energy of S-treated MoS2 shifts to low binding energy, compared to that of the pristine MoS2. This binding energy shift is related to the Fermi level of MoS2, and is discussed below.

Figure 3 shows the surface potential and carrier density difference between the pristine and S-treated monolayer MoS2 nanosheet. Figure 3a,b shows the KPFM measurement results of pristine and S-treated monolayer MoS2 nanosheet, respectively. The work function of pristine monolayer MoS2 nanosheet measured 5.07 ± 0.2 eV, and that of S-treated monolayer MoS2 nanosheet measured 5.52 ± 0.2 eV. Based on these KPFM results, Figure 3c shows a schematic of the Fermi level change of pristine and S-treated monolayer MoS2 nanosheet. The additional S-treatment process increased the work function by ≈0.4 eV. This means that the Fermi level of S-treated monolayer MoS2 shifted toward the intrinsic Fermi level. These results are consistent with the XPS results shown in Figure 2c,d. Since the binding energy of core-levels detected in XPS is referenced to the Fermi level of the system, the shift of 0.4 eV to lower binding energy can be attributed to a 0.4 eV shift in the Fermi level position closer to the valence band edge, and not to the existence of a new chemical state.[32]

In order to compare the carrier density before and after S-treatment, we fabricated field effect transistor (FET) devices.[25,26,33–36] Figure S4 (Supporting Information) shows a schematic and the specific channel dimensions of the MoS2 transistor. The electrical characterization was performed using Keithley 4200-SCS semiconductor parameter analyzer and vacuum probe station under ≈10−5 Torr, to prevent unintentional effect from ambient atmosphere, such as oxygen or H2O molecules.[25,35,36] Figure 3d,e presents the Ids–Vgs curve of FETs made with pristine and S-treated MoS2 respectively. The gating characteristic of the pristine MoS2 device with −14.4 V threshold voltage (Vth) is a typical property of the FET device with n-type MoS2 channels.[25,26,33–36] S-treatment shifted, Vth to 7.5 V, and dramatically decreased the drain–source current (Ids). The carrier density was measured using the same condition of Vgs = 16 V and Vds = 0.5 V, the calculation method being shown in Figure S4 (Supporting Information). However, the carrier density of the pristine MoS2 device was 2.19 × 1012 cm−2, and after S-treatment decreased to 6.11 × 1011 cm−2 (Δn = 1.57 × 1012 cm−2). This phenomenon can be explained by the free carrier (electron) trap by S vacancy passivation of S atom, as mentioned above.

To investigate the piezoelectric effect of passivating S vacancy on the surface of MoS2, we fabricated PNGs and measured the piezoelectric output of pristine MoS2 before and after S-treatment. As noted above, S vacancies are considered as the cause of n-type behavior of MoS2 due to free the electrons in unsaturated Mo that do not belong to any chemical bond.[25,37] Therefore, these electrons behave as free charge carriers. A large number of free charge carriers in the pristine MoS2 have strong influence on screening the piezoelectric potential into
Here, we compared the piezoelectric output of pristine and S-treated monolayer MoS2 nanosheet. Figure 4a,b shows the piezoelectric output current and voltage responses of pristine and S-treated monolayer MoS2 nanosheet. When tensile strain is applied, positive current and output voltage are observed with increasing strain. As the strain is released from the nanogenerator, corresponding negative peaks can be observed in both the output current and voltage measurements[3] (see Figure S5 for the strain calculation, Supporting Information). The output voltage was measured with 1 GΩ of load resistance, and the short-circuit current was measured as 0.48% of strain, and 70 mm s⁻¹ (2.5 Hz) of strain rate, respectively. Figure 4a shows that the S-treated monolayer MoS2 nanosheet device generated output current around 100 pA, which is over 3 times higher than that of the pristine MoS2 (around 30 pA). In the case of output voltage, the S-treated device showed more than 2 times (22 mV) higher than that of the pristine MoS2 (around 30 mV). In the case of pristine MoS2, the switching polarity test indicates that the output current and voltage of PNGs originates from the nanogenerator, and not the measurement system noise (Figure S6, Supporting Information).[6,18] Also, there were no significant electrical outputs from bare PET substrate without a monolayer MoS2 (Figure S7, Supporting Information).[10] Figure 4c–f shows the output performance of MoS2 devices as a function of different strain rate (from 30 to 110 mm s⁻¹) at 0.48% of fixed strain. The output peak current and voltage of the pristine monolayer MoS2 nanosheet are observed from 16 to 47 pA and 8 to 12 mV, respectively (Figure 4c,e). By contrast, the output peak of the S-treated monolayer MoS2 nanosheet device reached from 30 to 240 pA and 8 to 30 mV (Figure 4d,f). Notably, the S-treated MoS2 device showed much higher output results than the pristine MoS2 device under the same bending condition. The small piezoelectric output current and voltage are dominantly attributed to the screening effect caused by free electrons due to S vacancies.[14–17] The high piezoelectric output results observed from the S-treated MoS2 are due to the passivation of native defect, such as S vacancies, presented in the pristine MoS2. Switching polarity tests were also performed to measure the current and voltage, by reversing the connection under each bending condition (Figures S8 and S9, Supporting Information). We also investigated the output peaks under 0.28–0.58% strain with a constant strain rate of 60 mm s⁻¹ bending condition. Figures S10 and S11 (Supporting Information) shows that the results reveal a similar tendency as compared with Figure 4c–f. Also note that under the fixed strain rate, the frequency decreased with increasing strain, due to the long distance movement per unit time.

Figure 4g (pristine MoS2) and 4h (S-treated MoS2) shows that to quantify the power output of the piezoelectric circuit, it is necessary to study the voltage output as a function of load resistance.[10] In both cases, the initial output voltage was ≈0 V and began to increase at 1 MΩ and began to increase at 1 MΩ. The instantaneous power was obtained from the output peak with the load resistance at 0.48% strain and 90 mm s⁻¹ of strain rate (3.2 Hz) using the electrical power equation P = V²/R. The maximum instantaneous power of pristine monolayer MoS2 nanosheet was achieved at a load resistance of 500 MΩ, and reached 0.07 pW (Figure 4g). Furthermore, the S-treated monolayer MoS2 nanosheet achieved a load resistance of 500 MΩ, and reached 0.73 pW (Figure 4h). Note that the S-treatment dramatically increased the maximum power of the MoS2 PNG by 10 times, and that the corresponding power density is 73 µW m⁻². This obtained output power was stable over time, as shown for cyclic loading up to 0.48% strain.
at 100 mm s\(^{-1}\) strain rate for 4000 cycles (Figures S12 and S13, Supporting Information). Our MoS\(_2\) PNG could also maintain good stability without any notable deterioration after more than 5 h continuous operation. The observed slight fluctuation in output may have been caused by mechanical fatigue of the PET substrate.\(^{[10]}\)

In summary, we have demonstrated the S vacancy passivated monolayer MoS\(_2\) PNG, and compared its properties before and after S treatment, to investigate the effect of passivating S vacancy. It is known that native S vacancies exist in the MoS\(_2\) surface, resulting in the n-type property of MoS\(_2\). As discussed above, a relatively large free-carrier density plays a crucial role in affecting the output of PNGs, so it is very important to passivate S vacancies to reduce electron concentration. We effectively passivated the S vacancies by using this S-treatment process on the pristine MoS\(_2\) surface. The S vacancy site has a tendency to covalently bond with S functional groups; therefore by capturing free electrons, S atom will form a chemisorbed bond with the S vacancy site of MoS\(_2\). S-treatment reduces the charge-carrier density of the monolayer MoS\(_2\) surface, thus the screening effect of piezoelectric polarization charges by free carrier is significantly prevented. As a result, the output peak current and voltage of the S-treated monolayer MoS\(_2\) nanosheet PNG are increased by more than 3 times (100 pA) and 2 times (22 mV), respectively. Further, the S-treatment increased the maximum power by almost 10 times. The results suggest that S-treatment can reduce free-charge carrier by S passivation, and efficiently prevent the screening effect. Thus, the piezoelectric output peaks of current, voltage, and maximum power were dramatically increased, as compared with the pristine MoS\(_2\). For practical applications including stretchable/wearable electronics, CVD-based large-area MoS\(_2\) is inevitably needed. Therefore, our results offer a new approach to enhancing the piezoelectric output of CVD-grown MoS\(_2\) for use as a promising power source of stretchable/wearable electronics.

**Experimental Section**

**MoS\(_2\) Synthesis Method:** Large-area monolayer MoS\(_2\) and S-treated MoS\(_2\) were synthesized by a CVD method using H\(_2\)S (5 sccm, 99.99%) gas and MoO\(_3\) powders (0.001 g, 99.995%) on sapphire substrate. Argon gas was used as a carrier gas with a flow rate of 200 sccm under 10 Torr. Additional S-treatment process was performed under in situ condition after the pristine MoS\(_2\) growth. After the first MoS\(_2\) growth process, H\(_2\)S gas injection was made under 1000 °C, 30 min. The synthesized monolayer MoS\(_2\) and S-treated MoS\(_2\) were transferred to the appropriate substrate by a simple wet transfer method.

**Lateral PFM Measurements:** The AFM-based investigations were carried out using an AFM (Park Systems, XE-100). The piezoelectric properties of the pristine and S-treated monolayer MoS\(_2\) samples were confirmed by PFM equipped with nonconductive silicon tips (spring constant 3 N m\(^{-1}\)) (Budget Sensors, Multi 75-G), operating in contact mode for imaging of topography and relative polarization by PFM. A lock-in amplifier (Stanford Research SR830) was used to detect the piezoresponse signal.

**Piezoelectric Output Characterizations:** Keithley 6485 Picoammeter was used for low-noise current measurements, in order to detect currents generated by the MoS\(_2\)-based piezoelectric devices. An electrometer (Keithley 6514) with 200 TΩ input impedance was used for measuring voltage signals from the device. A bending machine made by Z-Tech (Korea) was used for applying programmed driving strain inputs.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

S.A.H. and T.-H.K. contributed equally to this work. This research was financially supported by the Framework of International Cooperation Program (No. NRF-2015K2A2A7056357), the Center for Advanced Soft-Electronics as the Global Frontier Project (No. 2013M3A6A5073177) through the National Research Foundation (NRF) of Korea, and the “Human Resources Program in Energy Technology” of the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20174030201800).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

defect passivation, molybdenum disulfide, nanogenerators, piezoelectricity, sulfur vacancies

Received: January 15, 2018
Revised: February 6, 2018
Published online:

\[\text{[16]}\] X. Xue, Y. Nie, B. He, L. Xing, Y. Zhang, Z. L. Wang, Nanotechnology 2013, 24, 225501.