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MoS_2 Nanogenerators: Harvesting Energy from Droplet Movement

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ABSTRACT

Presently, the efforts to produce electricity from a ubiquitous source is gaining tremendous importance, as it would be a way to significantly reduce our carbon footprint. Energy harvesting devices that are able to convert energy from our surroundings into electricity are required in the age of the Internet of Things (IoT) in order to power multiple sensors. Water is a promising clean energy source that is abundantly available. An attractive way to harvest the kinetic energy of the movement of water into electricity, using low-dimensional materials such as graphene, has been previously reported. This method is promising for powering a wearable sensor as it could transform the energy directly without any large turbine. However, up until recently, the output voltage of such graphene nanogenerators was limited to 100 mV. In this article, we demonstrate the utilization of a single-layer MoS_2 nanogenerator, which is capable of generating a high output voltage of over 5 V from the motion of water droplets. The large output voltage was caused by the high resistance of a single-layer MoS_2 film. We also demonstrated the output voltage and current alteration by using a chemical dopant. The output current was significantly improved by exposing the MoS_2 nanogenerator with an n-type dopant diethylenetriamine (DETA). Moreover, the output voltage and current were multiplied about three times when three identical MoS_2 nanogenerators were arranged in parallel and series, respectively, showing the potential for MoS_2 nanogenerators to be scaled up.

INTRODUCTION

A new method to scavenge energy from a clean energy source could help us to achieve the goal of zero-carbon emissions at a global scale. Water covers seventy percent of the earth's crust and conserves a large amount of energy in its dynamic forms. However, conventional hydropower systems require a massive water reserve, making their availability limited to specific areas. A study by Král and Shapiro theoretically showed direct electricity generation from the movement of liquid on the surface of a carbon nanotube (CNT) film. The water that flows across the CNT layer could drag the free carriers in the CNT layer [1]. Just two years after the aforementioned groundbreaking theoretical work, Ghosh et al. experimentally demonstrated the generation of electricity from the movement of water by using a CNT film [2]. Several millivolts of generated voltage were produced from a CNT film inside a tube filled with running ionic liquid. This finding shows promising potential for development into a self-powered system to power wearable IoT sensors in the future.

Recently, voltage generation using the movement of water droplets on the surface of 2-dimensional (2D) graphene was also reported [3]. When the droplet was dragged on graphene's surface, it generated voltage on the order of tens of millivolts. The output voltage resulting from droplet movement was too small for driving silicon-based electrical components. Generally, output voltage of over 1 V is needed to run those components. Even though several engineering attempts have been reported to improve the output voltage of graphene nanogenerators, the reported values are still below 500 mV [4–6].

The low voltage generated from graphene nanogenerators is due to the small sheet resistance property of gra-

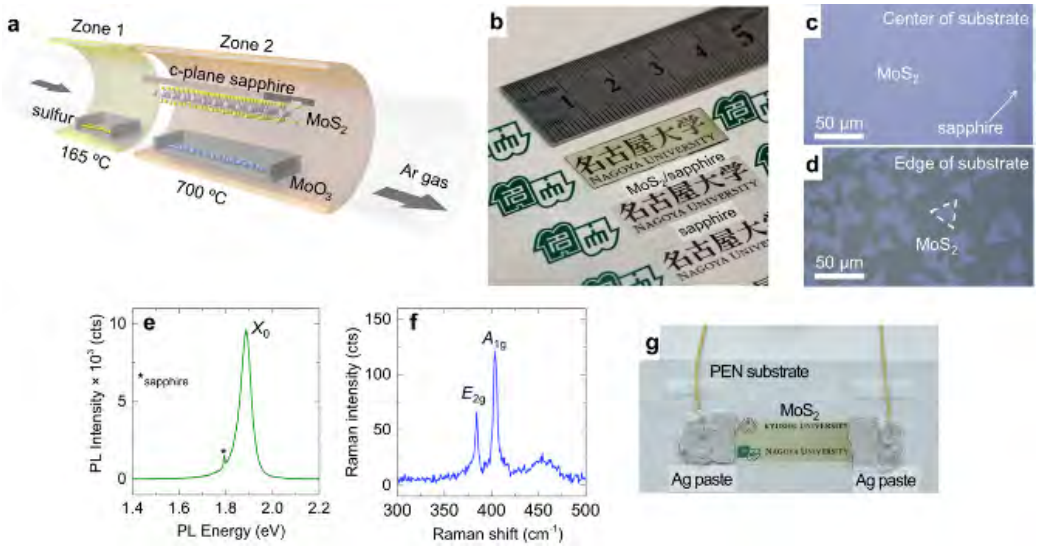

Fig. 1: (a) Schematic view of the large-area MoS_2 CVD setup. (b) Photograph of the as-grown MoS_2/sapphire and bare sapphire. Optical microscope images of MoS_2 on sapphire in the (c) center and (d) at the edge of the sapphire substrate. (e) PL and (f) Raman spectroscopy spectra of a single-layer MoS_2 film. (g) Photograph of a MoS_2 nanogenerator connected with wires [9].

phene [3]. The usage of semiconducting 2D materials, such as single-layer MoS_2, is predicted to be an excellent means to produce high generated voltage from the movement of droplets. An attempt to use a multilayer MoS_2 film has been reported, yet the recorded output voltage was just below one millivolt [7]. The low output voltage was presumably caused by the high number of layers of MoS_2 produced by sulfurization of the Mo thin film. This trend was also observed in graphene nanogenerators, where thicker graphene produced much less voltage than a single-layer graphene nanogenerator [8]. Thus, large-area, single-layer MoS_2 film is ultimately needed to improve the output voltage of the nanogenerators. However, the study of single-layer MoS_2 for harvesting electricity from the movement of droplets is still lacking due to the difficulty of producing centimeter-scale single-layer MoS_2 films.Here, we introduce a single-layer MoS_2 nanogenerator with a large output voltage of over 5 V from the movement of 1 M of aqueous NaCl across its surface [9]. We employed the chemical vapor deposition (CVD) method to produce centimeter-scale single-layer MoS_2 as the active layer of the nanogenerator. The observed high output voltage originated from the high resistance of single-layer MoS_2. We also fabricated MoS_2 nanogenerators on various substrates, where the polymer substrate gave the MoS_2 nanogenerator the largest output voltage. Moreover, we also report the chemical doping feasibility of our MoS_2 nanogenerator by using the DETA molecule as n-type dopant. This strategy is promising because it could boost the output current with a simple doping process. Our MoS_2 nanogenerator is also highly scalable, as both the output voltage and current could be multiplied by arranging nanogenerators in series and parallel, respectively. The nanogenerators could harvest electricity from undulating sea waves as well, reflecting the broad potential applications of MoS_2 nanogenerators.

SYNTHESIS, CHARACTERIZATION, AND FABRICATION OF CENTIMETER-SCALE SINGLE-LAYER MoS_2 NANOGENERATORS

The CVD method was used to produce a centimeter-scale single-layer MoS_2 film. C-plane sapphire was chosen as the growth substrate because of its symmetry with the crystal structure of MoS_2, which resulted in high layer controllability of MoS_2. Figure 1(a) shows the schematic view of the CVD setup with two furnaces, where the respective temperatures of the furnaces could be controlled independently [9]. In the center of furnace 1, the MoO_3 precursor powder (0.1 mg) was placed in a ceramic boat and the growth substrate was positioned on top of the MoO_3 powder. The sulfur precursor powder was placed in furnace 2. Ar gas was used as the carrier gas with a flow-rate of 20 sccm throughout the CVD process. The temperature of furnace 1 and 2 were ramped up to 700 ˚C and 165 ˚C, respectively. After the furnaces reached the set temperature, their temperatures were held for 3 minutes. The sample was then taken out from the CVD system after it naturally reached room temperature.

A photograph of as-grown MoS_2 on a 3 × 1 cm sapphire substrate and a bare sapphire substrate is shown in Fig. 1(b). The as-grown sapphire substrate appears yellowish due to the presence of single-layer MoS_2. Figures 1(c) and 1(d) show the optical microscope images of MoS_2 on the center and at the edge of the substrate. The MoS_2 film covered the sapphire entirely, and the triangular shape at the edge of the substrate reflects the good crystallinity of the MoS_2 grain. Furthermore, the strong photoluminescence spectrum and A_{1g} and E_{2g} peak Raman shift separation of 19 cm-1 from the sample indicated the formation of single-layer MoS_2, as shown in Figs. 1(e) and 1(f) [10, 11]. The large-area single-layer MoS_2 films then were transferred into different substrates in order to make a nanogenerator. The MoS_2 films were transferred by using polystyrene (PS) thin film for support. PS thin film was chosen because its high surface energy allowed the MoS_2 film to be delaminated from a sapphire substrate efficiently, using water [8]. A single-layer MoS_2 film, which was supported by the PS film, was placed onto the target substrate. After removing the residual water, the PS film was removed by immersing it into warm toluene. Finally, silver paste was applied on both ends of the MoS_2 film to form the electrode, as shown in Fig. 1(g).

ELECTRICITY GENERATION BY DROPLET MOVEMENT ON A MoS_2 NANOGENERATOR

The experimental setup is schematically drawn in Fig. 2(a). A MoS_2 nanogenerator was placed on the stage with an inclined angle of 45 degrees. Then, several droplets of 50 μL 1 M NaCl were dropped onto the MoS_2 nanogenerator. Figures 2(b) and 2(c) show the generated voltage and current from the movement of droplets on the hydrophobic MoS_2 surface. Each droplet could produce a voltage of over ~6 V [9]. The movement of droplet also generated a current of ~5 nA. Fig. 2d shows the figure-of-merit of electricity generation by using a 2D material nanogenerator. The generated voltage exhibited here is marked as the highest value, as compared to reports of other 2D material-based nanogenerators.

We also investigated the performance of a MoS_2 nanogenerator with different substrates to study the effect of the underlaying substrate of MoS_2 on energy conversion capabilities. Figures 3(a) and 3(b) show the voltage and current generated from the movement of droplets on MoS_2 with SiO_2/Si, sapphire, and polyethylene naphthalene (PEN) substrates. The MoS_2 nanogenerator fabricated on a PEN substrate had the highest voltage and current, as compared to the others fabricated on SiO_2/Si and sapphire substrates. We found that higher MoS_2

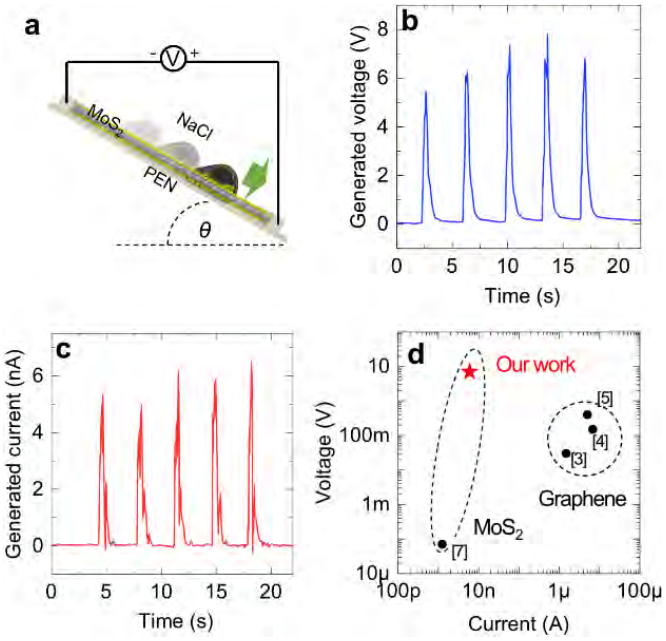

Fig. 2: (a) Schematic diagram of the experimental setup to measure the electricity generation from the movement of droplets on the MoS_2 surface. Typical (b) voltage and (c) current responses to the movement of 1 M NaCl on the MoS_2 surface. (d) Comparison of voltage and current generation of a 2D material-based nanogenerator [9].

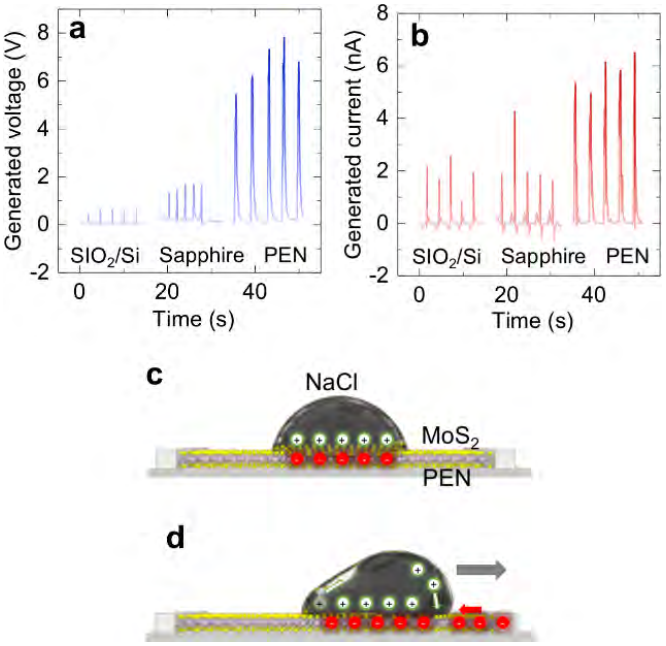

Fig. 3: Dependency of the generated (a) voltage and (b) current on different underlying substrates for a MoS_2 nanogenerator. Working mechanism of the liquid-MoS_2 film at (c) the steady- and (d) the dynamic-state. [9].

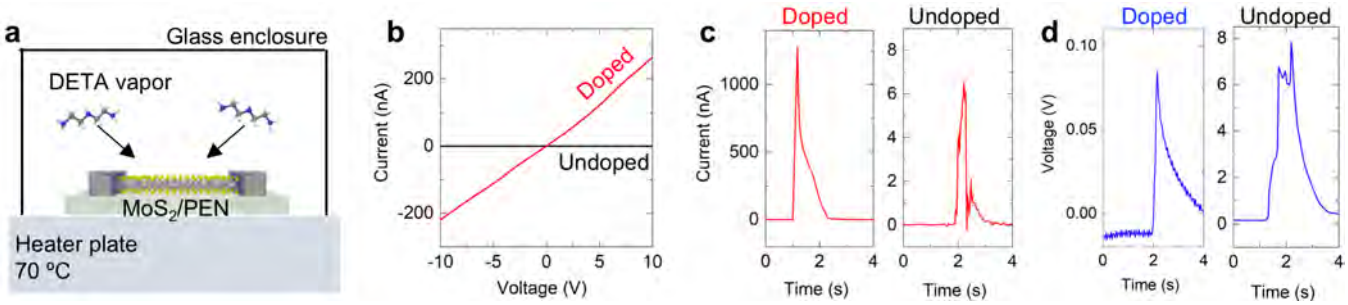

Fig. 4: (a) Schematic illustration of the DETA doping procedure of MoS_2 nanogenerators. *I-V* curves of MoS_2 nanogenerator (a) before and (b) after doping process. Measured output (c) current and (d) voltage of the DETA doped and pristine MoS_2 nanogenerators.

film sheet resistance gave a higher generated voltage. The measured sheet resistance of MoS_2 on PEN, sapphire, and SiO_2/Si substrates were 3009, 1870, and 329 MΩ sq^{-1}, respectively. These results are in agreement with the relationship between high sheet resistance and high generation voltage reported previously [3, 8, 12]. Interestingly, the MoS_2 nanogenerator fabricated on a PEN substrate also gave the highest generated current over the other substrates even though it has the largest resistance. A polymer substrate, such as PEN, is more effective to absorb positive ions onto the surface, resulting in larger electric double layer (EDL) formation [6, 13]. Larger EDL formation tends to generate larger currents.

The mechanism of electricity generation from the movement of droplets on a MoS_2 nanogenerator is mainly due to the interaction of ions in ionic liquid with the MoS_2 surface. The Na^+ ions (white dots) are absorbed onto MoS_2 surface, and Cl- tends to be repelled away from the MoS_2 surface [14, 15]. As illustrated in Fig. 3(c), the EDL is naturally formed at the interface of the MoS_2 surface and ionic liquid upon dropping the ionic liquid. At this steady-state stage, the potential difference across the interface of the MoS_2 surface and ionic liquid results in no electricity generation. At the dynamic state, as the droplets slide on the MoS_2 surface, the new Na^+ ions at the front-end of the droplets are absorbed on the MoS_2 surface. To counter these ions, electrons (red dots) are drawn from the right-hand side electrode to the newly formed interface between the MoS_2 surface and the front-end of the droplets, as illustrated in Fig. 4b. At the rear-end, the absorbed Na^+ ions leave the MoS_2 surface and give the electrons to the MoS_2 layers. These charging and discharging activities occur with the movement of the droplets on the MoS_2 surface.

EFFECT OF N-TYPE DOPING ON MoS_2 NANOGENERATORS

To further investigate the influence of sheet resistance with electricity generation, we performed a doping procedure on a MoS_2 nanogenerator by using a chemical dopant. We used a chemical doping technique because of its doping efficacy on 2D materials, such as graphene or MoS_2 [16, 17]. The n-type dopant diethylenetriamine (DETA) was used to alter the sheet resistance of MoS_2. Fig. 4(a) schematically illustrates the doping process where a MoS_2 nanogenerator fabricated on a PEN substrate was exposed to DETA vapor. The MoS_2 nanogenerator was placed inside a petri dish enclosure, surrounded by ~300 µL of DETA solution. The vaporization of DETA occurred at a temperature of 70 °C for 30 minutes. After being exposed to the DETA vapor, the MoS_2 nanogenerator then was washed by distilled water three times to remove excess DETA molecules on the MoS_2 surface. Fig. 4(b) shows the *I-V* characteristic of the MoS_2 nanogenerator before and after the DETA doping procedure. The current of the MoS_2 nanogenerator was greatly enhanced due to DETA molecule exposure. The sheet resistance of the MoS_2 nanogenerator after the DETA doping procedure was about 16 MΩ sq^{-1}, which is a hundred times smaller than the undoped one. The reduction of sheet resistance is presumably due to the electron transfer from the DETA molecules to the single-layer MoS_2 surface.

Next, we measured the electricity generated from the movement of droplets on doped and undoped MoS_2 nanogenerators. The experimental setup was similar to the one previously explained in Fig. 2(a). Figure 4(c) shows the voltage generated from the movement of droplets on undoped and doped MoS_2 nanogenerators. An improvement in generated current was observed in the doped MoS_2 nanogenerators. The doped MoS_2 nano-

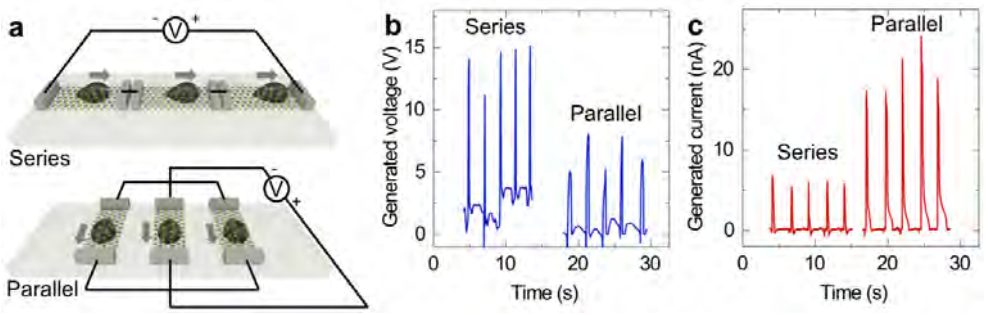

Fig. 5: (a) Schematic illustration of the (top) series and (bottom) parallel connections of three MoS_2 nanogenerators. Measured output (b) voltage and (c) current of the integrated three MoS_2 nanogenerators in series and parallel connections [9].

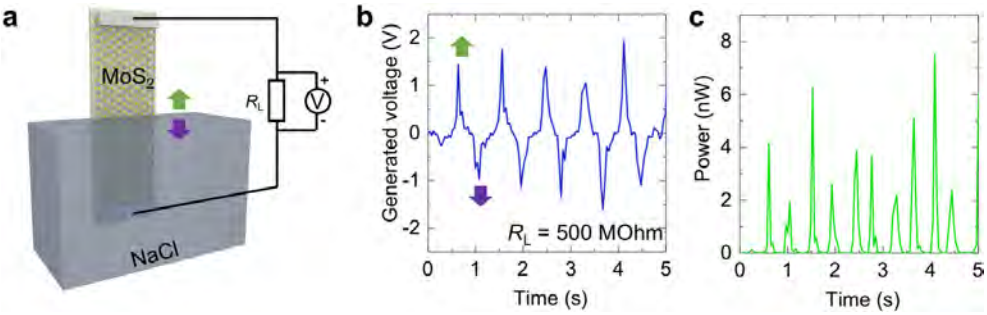

Fig. 6: (a) Schematic illustration of experimental setup for harvesting electricity from movement of sea waves by using MoS_2 nanogenerator. The output (b) voltage and (c) power harvested from an oscillating sea wave [9].

generator produced an output current reaching 1.2 μA, which is comparable to semimetallic graphene nanogenerators at the microampere level [3–5]. The lower shunt resistance in the doped MoS_2 film resulted in higher current generation as compared to the undoped film. On the other hand, the doped MoS_2 nanogenerator resulted in a lower generated voltage of only 80 mV, as shown in Fig. 4(d). A drop in generated voltage is expected from a nanogenerator with lower sheet resistance. This is the first study that has reported on how the molecular doping technique could significantly change the output voltage and current generated by the movement of droplets.

SCALABILITY AND APPLICATION OF MoS_2 NANOGENERATORS

We also studied the scalability of our MoS_2 nanogenerator by integrating several identical devices into one array. In solar cell technology, the output voltage and current can be multiplied by connecting solar cell panels in series and parallel connections, respectively [18]. We succeeded in fabricating three identical MoS_2 nanogenerators in series and parallel connections. Figure 5(a) illustrates the fabricated device where droplets were sprayed onto the device to cover all of the MoS_2 film with ionic liquid. The output voltage and current generated by the MoS_2 nanogenerators are shown in Figs. 5(b) and 5(c), respectively. The output voltage was enhanced about three times, reaching 15 V. Also, the output current showed similar behavior, as it was also improved roughly three times to 15 nA.

We also demonstrated the potential of our MoS_2 nanogenerator to harvest electricity from the kinetic energy of oscillating sea waves. The experimental setup is schematically drawn in Fig. 6(a), where the MoS_2 nanogenerator was perpendicularly fixed to a liquid surface on a beaker glass. Next, we filled the glass with simulated seawater containing 0.6 M NaCl aqueous solution until its surface reached the middle of the MoS_2 film. A series of incoming waves were generated by simply shaking the glass until the amplitude of the wave reached approximately 1 cm. Sinusoidal output voltage signals, shown in Fig. 6(b), were generated as the waves moved upward (green arrow) and downward (purple arrow). The generated voltages were about 1 V by connecting to a 500 MΩ load resistor. The converted kinetic energy of the sea wave shown in Fig. 6(c). was about 7.5 nW. The voltage generated by our MoS_2 nanogenerator was larger than other reported graphene nanogenerators, which were only able to produce 1 to 300 mV of output voltage [19–21]. This demonstration suggests some potential of our MoS_2 nanogenerator for diverse energy harvesting applications.

CONCLUSION

In this study, we experimentally demonstrated that a MoS_2 nanogenerator has the capability to convert the kinetic energy of liquids into electricity. Compared to other previously reported graphene nanogenerators, the generated voltage that resulted from the movement of liquid by our MoS_2 nanogenerator is significantly larger. The improvement in the output voltage of our MoS_2 nanogenerator is due to the high sheet resistance of the MoS_2 film and the enhanced Na^+ ion absorption of the MoS_2 layer on the PEN substrate. We also demonstrated the scalability of our MoS_2 nanogenerator, where the output voltage and current could be multiplied by arranging several identical devices in series and parallel connections, respectively. The ability to tune the output voltage and current of a MoS_2 nanogenerator was also demonstrated by a simple chemical doping procedure. Further studies are needed to find the best doping concentration in order to improve the output power of MoS_2 nanogenerators. Moreover, our MoS_2 nanogenerator is also suitable to convert various kinds of liquid dynamics, such as droplets, raindrops, and sea waves. We believe the platform and concept demonstrated in this report will be beneficial for the development of a novel energy harvester.

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