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Tunable piezoelectric nanogenerators using flexoelectricity of well-ordered hollow 2D MoS2 shells arrays for energy harvesting

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\textbf{ABSTRACT}

Piezoelectric two-dimensional (2D) transition-metal dichalcogenides such as molybdenum disulfide (MoS\textsubscript{2}) have recently attracted significant attention owing to their applicability for fabrication of flexible power generators. In this study, novel piezoelectric nanogenerators (PNGs) consisting of 2D piezoelectric MoS\textsubscript{2} shells are fabricated where an Al\textsubscript{2}O\textsubscript{3} thin layer deposited on the surface of polystyrene (PS) beads is used to avoid collapse of the spherical MoS\textsubscript{2} shells under the high growth temperature. In addition, the MoS\textsubscript{2} shell size is controlled by adjusting the PS bead size and the effects of the MoS\textsubscript{2} shell size on power generation characteristics are investigated. Our PNG based on the piezoelectric MoS\textsubscript{2} shells produces a peak output voltage of approximately 1.2 V at a pressure of 4.2 kPa. The minimum pressure for power generation by tapping is 0.3 kPa. This novel method is very promising for development of the next-generation PNGs based on 2D semiconductor piezoelectric materials.

1. Introduction

Highly entangled networks based on hollow two-dimensional transition-metal dichalcogenide (2D TMD) shells have attracted significant attention owing to their very large surface areas and lower densities those of solid spheres. The hollow spheres are widely employed as catalysts, health monitoring materials, chemical sensors, pressure sensors, piezoelectric nanogenerators (PNGs), and energy storage materials [1–5]. In fact, 2D TMD in film form has been applied to various applications such as nanogenerator [6]. Here they showed remarkable piezoelectric properties in TMD with a mono-layer and odd layers. However, nanoshell arrays based on 2D TMD has not been reported because of its difficulties in fabrication. Both sides of thin TMD shells were functionalized with various materials using the voids on the thin shells. The shell-based networks can exhibit significant changes under physical stress on the shell surface.

Among their applications, energy harvesting, a technology used to convert the abundant wind, solar heat, and geothermal energies into electrical energy, attracted significant attention owing to the need for power supplies of various wearable devices as well as the exhaustion of the traditional carbon energy. The current battery models would not be suitable for wearable devices in the future owing to their limited lifetimes and environmental and weight issues. Particularly, PNGs can overcome the limitations of current battery models by efficiently converting mechanical energy into electrical energy [6–12]. In previous studies, PNGs based on vertically grown piezoelectric nanowires were used for detection of small forces such as the movement of insects and human breathing [13–15]. In addition, piezoelectric textiles with nanowires [16], nanotubes [17,18], nanopillars [19], and nanoparticles [20,21] were utilized to improve the characteristics of PNG devices. Recently, 2D piezoelectric materials with hollow shell structures attracted significant attention owing to their strain sensitivity and excellent power generation properties. For example, symmetry-controlled Pb(Zr,Ti)O\textsubscript{3} and ZnO shells were utilized for bending and tapping PNGs, respectively [5,22]. However, as top and bottom electrodes on ferroelectric and piezoelectric materials were still required for the fabrication of PNG devices, the external forces for power generation could not be efficiently applied to the piezoelectric material, which hindered the detection of small forces. In case of TMD materials, nanogenerator by effectively transferring external forces to the sample applying top-top
configuration of two electrodes on the sample surface was reported [23].

In a recent study [24], S. Datta et al. theoretically investigated the response of a polymerized shell to external mechanical forces, in which the thin shells isotropically shrunk under a small pressure and were buckled by localized indentation under a high pressure above a threshold value. The internal atoms of the buckled shell experienced strain gradients. A flexoelectric contribution in accordance with the instantaneous polarization of the dielectrics owing to the strain gradient emerged inside the shells [25,26]. The buckling phenomenon increases the piezoelectric effect. However, no extensive studies have been carried out on nanogenerators for energy harvesting using buckled flexoelectric shells.

In this study, PNG devices based on 2D piezoelectric hollow MoS2 shells with multi-layer atomic structures were fabricated by simply coating the MoS2 precursor on sacrificial polymer spherical beads and subsequent thermal decomposition processes. Although the piezoelectricity of multilayer TMD is very small [27], it has been reported that piezoelectric properties are exhibited in a multilayer structure according to the staking modes [28]. We also investigated the effects of the PNG device by the MoS2 shell sizes. A maximum generated voltage of 1.2 V was observed with polarity characteristic, which indicating the piezoelectricity of the PNG devices based on MoS2 with a shell size of 1 μm. In addition, enhancement in power generation and hysteresis behavior owing to the buckling phenomenon were observed for the PNG based on the MoS2 shells with diameters of 1 μm. Furthermore, a theoretical analysis of the strain behavior with the increase in the diameter was carried out using the finite-element method (FEM), which was consistent with the experimental results.

2. Experimental

2.1. Synthesis of hollow MoS2 shell films using solution process

For the fabrication of PNG devices based on MoS2 shells, a monolayer or multilayer of carboxylated polystyrene (PS) beads was placed on a solid substrate such as a SiO2 surface. A mixture of the PS sphere solution, we was able to remove completely thin Al2O3 layer during the etching process by using interconnection windows. Subsequently, the PS beads were removed through these interconnection windows. In addition, a MoS2 shell uniform film over a large area (2 × 2 cm2) was synthesized to demonstrate the industry-scale application, as shown in Fig. S3 in Supplementary Information. As shown in Fig. 2c, the microstructures of the MoS2 shells with diameters of 500 nm were analyzed using field-emission transmission electron microscopy (FE-TEM). The shells prepared for the FE-TEM observation were dispersed in ethanol by ultrasonication, and the solution was then dropped on a TEM grid. As shown in Fig. 2c-i, the MoS2 shell had a uniform wall thickness with a spherical shape. In Fig. 2c-ii, the thickness of the MoS2 shell is approximately 10 nm with 15 layers and the spacing between layers is 0.66 nm, which is similar to the known lattice spacing of bulk MoS2 (~0.61 nm, 2H molybdenum disulfide, JCPDF # 06-0097). The selected-area electron diffraction (SAED) pattern in Fig. 2c-ii shows four intense diffraction rings. The lattice distances obtained from the radii of the measured rings were 0.26, 0.22, 0.15, and 0.13 nm, which correspond to 2H–MoS2 (101), (103), (008), and (201), respectively. The fabricated MoS2 shell film with a shell diameter of 500 nm is presented in Fig. 2d-i. The MoS2 shells were hexagonally close-packed, and their spherical structures were maintained. The MoS2 shell film was then transferred to a polyethylene-terephthalate (PET) substrate using the PMMA-assisted wet transfer method for application of our MoS2 film to flexible power generators. As shown in the FE-SEM image of the MoS2 shell multilayer film on the PET substrate after the transfer (Fig. 2d-ii), the MoS2 shell structure slightly changed into a hexagonal shape after the transfer, compared to the MoS2 shells maintaining their spherical shapes before the transfer. However, the cross-sectional observation shows that the spherical shape of the MoS2 shell is retained, as shown in Fig. S5 in Supplementary Information. In addition, according to the TEM image of synthesized MoS2 shells (Fig. S12 in Supplementary Information), the thickness of MoS2 shells is almost similar regardless of MoS2 shell diameter. This is closely related to the attraction force between the solution and shell surface during MoS2 growth process. As our synthesis method enabled fabrication of a MoS2 shell thin film on a flexible substrate such as PET, this method may pave the way for the fabrication of flexible TMD-based devices with superior physical durability and flexibility.

Field-emission scanning electron microscopy (FE-SEM) was used for structural analysis and microstructural characterization of various MoS2 shell films. Fig. 2a and b show FE-SEM images of the single- and multilayer MoS2 shells with diameters of 350 nm, respectively. These images show that the MoS2 shells maintained the spherical shape after the MoS2 shell growth, and that the MoS2 shell size was similar to those of the PS beads. In addition, a MoS2 shell uniform film over a large area (2 × 2 cm2) was synthesized to demonstrate the industry-scale application, as shown in Fig. S3 in Supplementary Information. As shown in Fig. S3, the microstructures of the MoS2 shells with diameters of 500 nm were analyzed using field-emission transmission electron microscopy (FE-TEM). The shells prepared for the FE-TEM observation were dispersed in ethanol by ultrasonication, and the solution was then dropped on a TEM grid. As shown in Fig. 2c-i, the MoS2 shell had a uniform wall thickness with a spherical shape. In Fig. 2c-ii, the thickness of the MoS2 shell is approximately 10 nm with 15 layers and the spacing between layers is 0.66 nm, which is similar to the known lattice spacing of bulk MoS2 (~0.61 nm, 2H molybdenum disulfide, JCPDF # 06-0097). The selected-area electron diffraction (SAED) pattern in Fig. 2c-ii shows four intense diffraction rings. The lattice distances obtained from the radii of the measured rings were 0.26, 0.22, 0.15, and 0.13 nm, which correspond to 2H–MoS2 (101), (103), (008), and (201), respectively. The fabricated MoS2 shell film with a shell diameter of 500 nm is presented in Fig. 2d-i. The MoS2 shells were hexagonally close-packed, and their spherical structures were maintained. The MoS2 shell film was then transferred to a polyethylene-terephthalate (PET) substrate using the PMMA-assisted wet transfer method for application of our MoS2 film to flexible power generators. As shown in the FE-SEM image of the MoS2 shell multilayer film on the PET substrate after the transfer (Fig. 2d-ii), the MoS2 shell structure slightly changed into a hexagonal shape after the transfer, compared to the MoS2 shells maintaining their spherical shapes before the transfer. However, the cross-sectional observation shows that the spherical shape of the MoS2 shell is retained, as shown in Fig. S5 in Supplementary Information. In addition, according to the TEM image of synthesized MoS2 shells (Fig. S12 in Supplementary Information), the thickness of MoS2 shells is almost similar regardless of MoS2 shell diameter. This is closely related to the attraction force between the solution and shell surface during MoS2 growth process. As our synthesis method enabled fabrication of a MoS2 shell thin film on a flexible substrate such as PET, this method may pave the way for the fabrication of flexible TMD-based devices with superior physical durability and flexibility.

X-ray photoelectron spectroscopy (XPS) was employed for a surface compositional analysis of the MoS2 shell thin film. Fig. 3a shows Mo 3d and S 2p core-level XPS of the transferred MoS2 shell thin film. Mo 3d5/2 and Mo 3d3/2 peaks are observed at binding energies of 232.48 and 229.28 eV, respectively, in the Mo core spectrum. In the S 2p core-level spectrum, S 2p3/2 and S 2p1/2 peaks are observed at 163.28 and 162.18 eV, respectively [30]. Here, all the collected XPS spectra were calibrated with C 1s peak located at 284.48 eV. In addition, in the core-level XPS of Mo 3d, S 2p, and Al 2p (Fig. S6 in Supplementary Information), the Al element corresponding to Al2O3 deposited on the PS beads by the ALD completely vanished in the KOH solution during the transfer process. This implies that Al2O3 was effectively removed inside MoS2 shell and that only the MoS2 shell-based thin film remained. The structure of the MoS2 shell thin film was also investigated by X-ray diffraction (XRD), as shown in Fig. 3b. The four peaks at 14.07, 32.64,
Fig. 1. Schematic of the fabrication of the PNG devices based on the MoS$_2$ shells. (a) Deposition of the Al$_2$O$_3$ layer on the PS bead film by ALD. (b) Spin coating of (NH$_4$)$_2$MoS$_4$ as a precursor for the MoS$_2$ growth on the PS beads with the Al$_2$O$_3$ layer. (c) Growth of the MoS$_2$ layer and removal of the PS beads through the thermal annealing. (d) Transfer of hollow MoS$_2$ nanoparticles onto the flexible PI substrate and fabrication of the electrode on the hollow MoS$_2$ shells.

Fig. 2. SEM images of the hollow MoS$_2$ shell films. SEM images of the (a) single layer of MoS$_2$ shells (the inset shows a high-resolution image of the single layer of MoS$_2$ shells) and (b) multilayer MoS$_2$ shell films. (c) TEM image of the (i) MoS$_2$ shell with a diameter of 500 nm, (ii) corresponding high-resolution image, and (iii) SAED pattern. (d) MoS$_2$ shell films with shell diameters of 500 nm (i) before and (ii) after the transfer onto the PI substrate.
44.71, and 58.20° were assigned to (002), (100), (006), and (110) reflections (2H–MoS2, #JCPDF 06-0097), respectively. The signal marked as * originated from the PS beads, as shown in Fig. S7 in Supplementary Information. The magnitude of the (002) reflection increased with the size of the shell. For the MoS2 shells with diameters of 350, 500, and 1 μm, the d-spacings corresponding to the MoS2 (002) reflection are 0.6251, 0.6286, and 0.6306 nm, obtained using the Bragg’s equation, respectively. The distance between Mo and Mo decreases with the decreased in the diameter of the MoS2 shell. This indicates that a large strain emerges in the MoS2 shells with a small curvature. Further, Raman spectra were acquired at a laser excitation wavelength of 514 nm under ambient conditions to investigate the structural characteristics of the MoS2 shell thin films. Fig. 3c shows the Raman spectra of the thin films based on the MoS2 shells with various sizes under the 514-nm laser excitation. (d) Raman spectrum A1g and E12g peak positions of the MoS2 shell-based thin films with various shell sizes.

3.2. Output voltage of PNGs based on MoS2 shell thin films

Fig. 4 shows real-time monitoring of the output voltages generated by external tapping motions using power generators based on MoS2 shell thin films with different shell sizes. The device was fabricated by depositing Au/Cr electrodes on the MoS2 shell thin film. At a pressure of 3 kPa applied on top of the MoS2 shell thin film, the open-circuit output voltages of MoS2 based-devices with different shell sizes are shown in Fig. 4a. Output voltages of 0.001, 0.18, and 1.15 V were measured at 350, 500, and 1 μm, respectively. In the measurement of output voltage and current (Fig. S9 in Supplementary Information), the direction of the signal changed when the direction of the electrode was switched between forward and reverse. This polarity property suggests that the signal originated from the piezoelectric effect of the MoS2 shell thin film. Compared to that of films, the developed voltage in the shell is a very large number in spite of multi-layered-polycrystalline. This performance improvement is believed to be due to relaxation of clamping effects by substrates, preferred orientation of nanoshell by well-ordered arrangement [29], and buckling effect due to the flexibility of the shell. Additionally, we measured the output voltages of the devices based on the MoS2 shell thin films with various shell sizes according to the external resistance (Fig. S10 in Supplementary Information) and calculated the power density as a function of the calculated external resistance (Fig. 4b). Here, the power of MoS2 shell thin films with various sizes was calculated using the following formula.

\[
P = \frac{1}{T} \int \frac{V(t)^2}{R} dt
\]

where T is the period of the mechanical movement, \( V(t) \) is the real-time output voltage, and R is the external resistance. The calculated maximum power densities of the MoS2 shell thin films with shell sizes of 350 nm, 500 nm, and 1 μm were 0.002, 1.45, and 8.07 μW/m², respectively. A linear relationship was observed between the shell diameter and power density.
In order to investigate the changes in the piezoelectric properties with the force magnitude, the applied pressure was swept from 0.2 to 3.6 kPa for the MoS$_2$ shell thin films with the shell diameters of 350 nm, 500 nm, and 1 μm (Fig. S11 in Supplementary Information). For the 350- and 500-nm shell thin films, the output voltages linearly increased with the force magnitude and linearly decreased without hysteresis when the force magnitude was decreased. However, the increase and decrease were nonlinear with respect to the magnitude of the force for the 1-μm MoS$_2$ shell film and a hysteresis behavior was observed below the pressure of 4 kPa. These nonlinear properties and the hysteresis behavior could be attributed to the buckling in the shells with thin walls. The buckling, leading to a significant change in shell volume, is a peculiar phenomenon observed in elastic structures with thin walls [33]. One or more indentations of spherical plastics were observed during the buckling process, and the threshold pressure for shell buckling is closely related with the diameter of the shell [25]. The MoS$_2$ shells with diameters of 350 and 500 nm exhibited linear behaviors with the variation in the pressure, while nonlinear changes with the variation in the pressure and hysteresis were observed for the 1-μm shells. This implies that the shells with diameters of 350 and 500 nm were exposed to the forces below the threshold pressure, while the shells with the diameters of 1 μm experienced forces above the threshold pressure. Therefore, active buckling occurred only in the 1-μm MoS$_2$ shells. It led to the nonlinear changes and hysteresis and is considered to be a major factor significantly improving the power generation. The decreased restoring force by the buckling is also attributed to the origin of the hysteresis characteristic according to the external force [32]. SEM was also utilized for the characterization of the morphology of MoS$_2$ shell-based films to confirm the stability of shells under electrical power generating process (Fig. S14 in Supplementary Information). SEM images of MoS$_2$ shell-based films with 350 nm and 1 μm shows that MoS$_2$ shells still have the shell structure after 10$^3$ tapping tests.

In order to investigate the effect of the MoS$_2$ shell diameter on the output voltage generated from the MoS$_2$ shells, we performed finite element method (FEM) simulations and analyzed the stress distributions of the MoS$_2$ shells with various diameters of 10, 20, and 50 μm, as shown in Fig. 5a. The stress distributions were calculated under a vertical compressive force (2 × 10$^{-8}$ N/μm$^2$) applied on the MoS$_2$ shells through the polytetrafluoroethylene (PTFE) substrate, as shown in Fig. 5a–i. For reference, nodes on the lower surface of the PTFE substrate below the MoS$_2$ shells were spatially fixed. The model shape
and size variation used in the structural analysis were determined from the SEM and TEM images (Figs. 2, S5, and S12 in Supplementary Information).

It is worth noting that, according to the stress distributions in Fig. 5a, the high-stress points are concentrated mainly in the MoS2-shell/PTFE-substrate and MoS2-shell/MoS2-shell contact portions. Quantitative statistical results for the stress values corresponding to all of the calculated nodes are shown in Fig. 5b. A larger diameter of the MoS2 shell leads to larger stresses in the contact points. This tendency is more evident in the stress line profiles across the points of interest. Fig. 5c-i and 5c-ii show stress profiles along straight lines (line-A and line-B) across MoS2-shell/PTFE-substrate contact points, while Fig. 5c-iii shows the stress profile for line-C across the MoS2-shell/MoS2-shell contact portion. All of the three stress line profiles show that in the case of the larger diameter of the MoS2 shell, larger maximum stresses were observed at the contact points. As shown in Fig. 5d, this trend is more pronounced in the MoS2-shell/PTFE-substrate contact points than in the MoS2-shell/MoS2-shell contact portions. This could be explained as the vertical compressive pressure from the PTFE substrate acts primarily on top and bottom of the MoS2 shell. Consequently, at a larger diameter of the MoS2 shell, larger maximum stress is applied to a particular point of the MoS2 shell and the threshold pressure at which the buckling of the shell occurs is rather reduced. The relatively larger structural changes in the MoS2 shells with larger diameters could be a decisive contribution to the increase in the piezoelectric performance. Therefore, our simulation results show that the piezoelectric performance of the MoS2 shells can be related with the change in the maximum applied stress and buckling threshold pressure according to the diameter of the MoS2 shell.

4. Conclusion

In summary, we reported PNGs based on the 2D MoS2 shells, whose sizes were successfully controlled by adjusting the PS size. The chemical compositions and structures of the 2D hollow MoS2 shells were analyzed by XPS, Raman spectroscopy, and XRD. As PNG characteristics of the PNGs based on the MoS2 shells, the polarity and piezoelectricity were confirmed. The minimum pressure for the generation of output voltage was approximately 0.3 kPa. In addition, the output voltage of 1.2 V was measured under the pressure of 4.2 kPa. In the case of the 1-μm MoS2 shell film, the increase and decrease were nonlinear with respect to the magnitude of the force, and a hysteresis behavior was observed below the pressure of 4 kPa. In particular, high-power generation properties and nonlinear hysteresis behavior were observed for the shells with diameters of 1 μm. As the threshold pressure for buckling was in the range of applied pressures, the hysteresis in the PNG based on the 1-μm shells was observed, which was also confirmed by the FEM simulations. We believe that this synthetic method can be applied easily to a system for generating or sensing even a very small force such as insect movements due to the simplicity in our method. Considering that

Fig. 5. Finite-element method (FEM) simulation results for the MoS2 shells (hollow spheres) between the PTFE substrates. (a) Model geometries and stress distributions of the MoS2 shells with diameters of 10, 20, and 50 μm strained by the vertical compressive force. (b) Quantitative statistical results for the stress values (corresponding to all of the calculated nodes) of the MoS2 shells with various diameters of 10, 20, and 50 μm. (c) Stress profiles along (i) line-A, (ii) line-B, and (iii) line-C across the MoS2-shell/PTFE-substrate contact points. (d) Changes in the maximum stress according to the changes in the MoS2 shell diameter.
the limitations of current battery systems have been holding back the commercial applications of energy converting system, this process can be a major breakthrough toward their practical application for the future power-generators, which can be used in mechanical sensors, wireless devices, and flexible devices.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.nanoen.2019.05.017.

References


