Piezoelectric Energy Harvesting from Two-Dimensional Boron Nitride Nanoflakes

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ABSTRACT: Two-dimensional (2D) piezoelectric hexagonal boron nitride nanoflakes (h-BN NFs) were synthesized by a mechanochemical exfoliation process and transferred onto an electrode line-patterned plastic substrate to characterize the energy harvesting ability of individual NFs by external stress. A single BN NF produced alternate piezoelectric output sources of ~50 mV and ~30 pA when deformed by mechanical bendings. The piezoelectric voltage coefficient (g31) of a single BN NF was experimentally determined to be 2.35 × 10⁻¹¹ V·m·N⁻¹. The piezoelectric composite composed of BN NFs and an elastomer was spin-coated onto a bulk Si substrate and then transferred onto the electrode-coated plastic substrates to fabricate a BN NFs-based flexible piezoelectric energy harvester (f-PEH) which converted a piezoelectric voltage of ~9 V, a current of ~200 nA, and an effective output power of ~0.3 μW. This result provides a new strategy for precisely characterizing the energy generation ability of piezoelectric nanostructures and for demonstrating f-PEH based on 2D piezomaterials.

KEYWORDS: flexible energy harvester, piezoelectric, two-dimensional boron nitride, self-powered nanogenerator, boron nitride nanoflake, flexible electronics

1. INTRODUCTION

Energy harvesting based on piezoelectric nanostructures from ambient and tiny mechanical stimulations has provided a breakthrough of flexible self-powered systems.¹⁻⁹ Piezoelectric nanogenerators constructed by transferring one-dimensional (1D) nanowires with a noncentrosymmetric structure (e.g., ZnO,²,⁴ ZnSnO₃,¹⁰ CdTe,¹¹ BaTiO₃,¹² and PMN-PT¹³ nanowires) have been extensively studied for flexible and wearable energy harvesting/sensing applications owing to their excellent piezoelectricity and mechanical flexibility. In addition, new approaches that demonstrate vertical or lateral configurations have enabled highly efficient flexible nanogenerators.¹⁴⁻¹⁸ Recently, two-dimensional (2D) piezoelectric nanostructures such as hexagonal boron nitride (h-BN),¹⁹⁻²¹ molybdenum sulfide (MoS₂),²⁰,²²,²³ and tungsten diselenide (WSe₂)²⁰,²⁴ have been examined for energy conversion because they have excellent flexibility compared with the traditional 1D piezoelectric nanostructures.²⁵

A number of 2D layered bulky materials, including h-BN, MoS₂, WSe₂, and many transition-metal dichalcogenides (TMDCs), have centrosymmetric crystal structures, whereas, when thinned into a single layer, they show different symmetries. Unlike graphene, in which all atoms are identical and have a center of symmetry, the inversion symmetry is broken in monolayer h-BN, MoS₂, WSe₂, and TMDCs; this behavior causes a strong piezoelectricity.²⁶⁻²⁸ Recently, experimental observation of the intrinsic piezoelectricity indicated that the piezoelectric coefficients of the 2D nanostructures were 2.9 × 10⁻¹⁰ C·m⁻¹ (ε₃₁ for MoS₂)²² and 3.26 ± 0.3 pm·V⁻¹ (d₃₁ for WSe₂)²⁴ by using piezoresponse force microscopy, which enables an expanded study of 2D materials in a variety of piezoelectric applications.

h-BN is typically a nonconductor (a wide-band semiconductor), the bandgap of which is reportedly 5.3–5.9 eV. The remarkable advantages of h-BN are excellent mechanical properties, high thermal conductivity, chemical inertness,
nontoxicity, environmental safety, and so forth. Mele et al. reported theoretically the existence of piezoelectricity in planar BN nanotubes owing to the polarization of the B−N chemical bond in terms of geometric phase.28 Although reports have revealed that h-BN shows a piezoelectric response when subjected to external deformation, there are still limitations on previous characterizations of the energy harvesting ability of 2D h-BN. Moreover, the product yields of monolayer h-BN are scarce because of the limited fabrication methods adopted, which restricts actual applications.

This study is of great significance for its first attempt to measure the piezoelectric voltage coefficient of a single BN nanoflake (NF) and to evaluate the energy harvesting ability of 2D h-BN. Moreover, the product yields of monolayer h-BN are scarce because of the limited fabrication methods adopted, which restricts actual applications.

2. EXPERIMENTAL SECTION

2.1. Preparation of BN NFs. For mechanochemical exfoliation of BN, 2 g of micron-sized h-BN powder (Kojundo Korea) and a 2 M aqueous NaOH solution (Junsei Chemical) were put together with 8 mm steel balls in a steel jar and subjected to milling in a planetary mill (P100, KM Tech, Korea) at 600 rpm for 24 h with a ball-to-powder ratio of 50:1. The milled product was rinsed several times until the pH was near neutral with HCl solution (Sigma-Aldrich) and deionized (DI) water to remove by-products such as Fe3+. The resultant was dried in an oven and then dispersed in isopropyl alcohol (IPA, Merck) at a concentration of 0.5 mg/mL, followed by sonication for 1 h. Finally, the BN NFs were obtained by centrifugation (Supra 22K, Hanil Science Industrial, Korea) for 30 min at a speed of 2000 rpm.

2.2. Material Characterization. The surface functional groups were investigated using a Fourier transform infrared (FT-IR) spectrometer ( Nicolet 6700, Thermo Fisher Scientific, USA) in an attenuated total reflectance mode. The zeta potential of BN NFs dispersed in IPA was detected using an ELSZ-1000 (Otsuka Electronics, Japan). The crystallographic structure of the powders was analyzed by X-ray diffraction (XRD; MiniFlex600, Rigaku, Japan) with Cu Kα radiation (λ = 1.54 Å). The specific surface area of the raw BN powder and BN NFs was measured by the Brunauer–Emmett–Teller method (BET; ASAP2020, Micromeritics Inc., USA).
The morphology of BN NFs was observed using transmission electron microscopy (TEM; JEM-2100F, JEOL, Japan). The thickness and lateral size of BN NFs were investigated by atomic force microscopy (AFM; NX20, Park Systems, Korea), with the sample prepared by transferring the NFs on a mica substrate.

2.3. Fabrication Process for a Single BN NF on a Plastic Substrate. An electrode layer (Au, 100 nm) was deposited onto a flexible plastic substrate (polyimide, 125 μm) and patterned using a standard microfabrication procedure to form electrode lines and pads. A thin chromium layer (<10 nm thickness) was also deposited onto the electrode line-coated plastic substrate to avoid the problem of charging under the FIB-Pt deposition process. Subsequently, a drop of a solution of well-distributed BN NFs in ethanol and DI water was transferred to the electrode line-coated plastic substrate. To connect both ends of the selected single BN NF with the Au electrode lines, in situ Pt deposition was conducted by employing the FIB process. Cu wires were affixed to the electrode pads using an Ag-based conductive epoxy to detect the electric signals produced from the single BN NF. The single BN NF on the plastic substrate suffered a high electric field of ~5 MV cm⁻¹ for 3 h at 120 °C; as a result, the surface of the single BN NF was electrically poled in plane.

2.4. Fabrication Steps for BN NFs-Based f-PEH. To demonstrate a flexible energy device made of 2D piezoelectric BN NFs, we used the well-known nanocomposite-based generator (NCG) fabrication technique. First, a pure polydimethylsiloxane (PDMS) elastomer, to serve as a dielectric layer, was prepared using a base (Sylgard 184, Dow Corning) and a hardener in the ratio of 10:1; subsequently, PDMS as a dielectric layer was spin-casted onto a bulk substrate at 1500 rpm for 30 s. A 50 μm thick PDMS was cured at 85 °C for 10 min in an oven. Next, the piezoelectric nanocomposite (p-NC) composed of inorganic piezoelectric BN NFs and organic elastomers at a ratio of 5 wt % was coated onto the PDMS-coated bulk substrate with the same coating/curing conditions. A pure PDMS was also placed onto p-NC as the top dielectric layer; subsequently, the fully hardened three layers were sliced into areas of 3 × 3 cm². For the fabrication of f-PEHs, the BN NFs-based piezoelectric rubber was peeled off from the bulk substrate and inserted into the two transparent electrode (indium tin oxide)-coated plastic substrates (polyethylene terephthalate). The top and bottom electrodes were connected with a high-voltage source meter and poled with a high voltage from 0.5 to 2 kV for ~12 h to enhance the piezoelectric effect.

2.5. Measurement of the Harvested Output Signals. A customized bending machine was used to repeatedly deform the single BN NF on the plastic substrate and f-PEHs with various displacements and strain rates. The electrical output signals generated from the single BN NF and f-PEHs during periodic mechanical deformations were measured and simultaneously recorded by means of a precise electrometer unit. To avoid disturbance from any external source, a Faraday cage was used during the process of measuring the output signals produced from the energy harvesters.

3. RESULTS AND DISCUSSION

Figure 1a shows the fabrication procedure for the preparation of BN NFs by the ball-milling method with the assistance of an hydroxide. This process involving chemical exfoliation and mechanical shear forces allows to improve the output of NFs and to prevent the agglomeration between the particles. The h-BN monolayer has a honeycomb lattice structure constructed of boron (B) and nitrogen (N) atoms in an ordered mode. As shown in the schemes of Figure 1b, by the mechanical force along the horizontal direction, the inversion symmetry of the h-BN layer is broken which causes a nonzero dipole moment in the strain direction; this behavior leads to the generation of a piezoelectric potential. The raw h-BN powder had characteristic hexagonal diffraction peaks at 26.7, 41.6, 43.9, 50.2, and 55.1: these peaks are indexed to the (002), (100), (101), (102), and (004) planes, respectively, with the lattice constants of a = 0.2504 nm and c = 0.6661 nm (ICDD card 01-073-2095). No impurity peaks observed in Figure 1c indicate that the produced BN NFs are chemically pure. The relatively high intensities of the (002) and (004) peaks compared to the raw BN powder show that the exfoliation
The morphology of BN NFs was investigated by using TEM and AFM. As seen in the TEM image [Figure 1e(i)] and the height profiles (Figure S1) of BN NF using AFM, the BN NFs have an average lateral size of ~0.82 μm and a thickness of ~25 nm; these values were taken from the statistical data of 60 NFs. The selected-area electron diffraction (SAED) pattern [the inset of Figure 1e(i)] of BN NFs indicated the typical sixfold symmetry with [0001] viewing zone axis which means that BN NFs maintain the hexagonal lattices during the harsh exfoliation processes. Figure 1e(ii,iii) shows the high-resolution TEM images obtained from the surface and the edge region of a single BN NF, respectively. From the profiling results (the insets) of the TEM contrast intensity recorded along the red dotted lines, fringe separation and interlayer distance were found to be ~0.25 and ~0.33 nm, respectively. By the geometrical relationship, the spacing between B and N atoms was estimated to be ~1.43 Å; this value agrees well to the length of the B–N bond of 1.44 Å.33,36

The FT-IR spectra (Figure 1d) of both raw BN and BN NFs show the E\textsubscript{1u} mode (B–N stretching: in-plane ring vibration) around 1348 cm\(^{-1}\) and the A\textsubscript{2u} mode (B–N bending: out-of-plane vibration) around 790 cm\(^{-1}\). In addition, the BN NFs have an additional peak at 1190 cm\(^{-1}\) different from the raw BN powder, which is due to the B–O deformation caused by the hydroxylation of the BN NFs.33,35 The zeta potentials of raw BN and BN NFs dispersed in IPA solution were 3.23 and -61.4 mV, respectively. A newly appeared B–O deformation peak in the FT-IR spectra and the highly negative zeta potential are due to the hydroxyl groups attached to the planes and the edge sites of the BN NFs.

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To evaluate the piezoelectric output performance of an individual BN NF under mechanical deformation conditions, we demonstrated a single BN NF connected to the electrode pads on a plastic substrate and explored the power generation from the single NF. Figure 2a(i) shows the fabrication design used to characterize the intrinsic piezoelectricity of a single BN NF: these procedures were detailed in the Experimental Section. The right panels of Figure 2a show the scanning electron microscopy (SEM) images and the photograph of a single BN NF on a plastic substrate (5 × 5 cm\(^2\)), respectively, in which both edges of the single NF (lateral size of about 1 μm) were connected with the electrode lines by FIB-Pt deposition. When the single BN NF was periodically bent along the direction indicated in Figure 2a(ii), the output signals were measured with open-circuit voltage (\(V_{oc}\)) and short-circuit current (\(I_{sc}\)) signals, as shown in Figure 2b,c. During the mechanical bendings with a strain of 0.283% which corresponds to the induced force of 17 μN with an elastic modulus of 865 GPa at a strain rate of 2.32%·s\(^{-1}\), a single BN NF at an electrode gap of 800 nm generated piezoelectric outputs of ~50 mV and ~30 pA; these values were obtained from the top surface of the single BN NF and can be converted to a piezoelectric voltage coefficient (\(g_{31}\)) of 2.35 × 10\(^{-3}\) V·m·N\(^{-1}\). The piezoelectric properties of BN NFs are expected to be improved by optimizing the exfoliation processes because the piezoelectric outputs of the 2D piezoelectric nanomaterials depend on the number of atomic layers. According to the reported results, the odd-layer sheets show intrinsic piezoelectricity owing to the inversion symmetry; on the contrary, the piezoelectricity disappeared for even-layer samples and the bulk three-dimensional form with a centrosymmetric structure.25,38,39 We also performed a verification process, the so-called switching polarity test, to verify that the measured tiny electricity originated from the piezoelectricity of the single BN NF. The alternate electric signals measured in response to the bending and releasing in a forward connection (left signals of Figure 2b,c) were inverted in reverse connection (right signals). As a result, we checked that the detected electric...
Figure 4. (a) Output voltage and current values measured from f-PEH as a function of an applied poling voltage. (b) Measured load voltage and current under various external resistors in the range from 100 kΩ to 1 GΩ. (c) Effective output power calculated by multiplying load voltage and current. (d,e) Open-circuit voltage of the f-PEH stressed by a bending machine with varied displacements (d) and strain rates (e). (f) Mechanical stability test results of the fabricated f-PEH under repeat bending up to 5000 cycles.

Pulses were introduced from the piezoelectric effect of the single BN NF.

To fabricate f-PEH devices by adopting 2D piezoelectric BN NFs, we used the widely used NCG fabrication technique with a spin-coating process. Figure 3a presents the schemes involving the fabrication procedures of BN NFs-based f-PEHs, which were detailed in the Experimental Section. The thick piezoelectric rubber layer formed from the BN NFs that were embedded in the polymeric matrix was inserted between two transparent electrode-coated plastics (see the actual fabricated f-PEH in the right panel of Figure 3a) and mechanically bent by a bending machine at a precise displacement and strain rate. As shown in Figure 3b,c, the fabricated flexible energy harvester with a real area of 3 × 3 cm² converted V_friends of ∼9 V and I_friends of ∼200 nA from the repeated mechanical deformations created by bending with 5 mm displacement at a strain rate of 5 cm·s⁻¹. From the switching polarity test results, we verified that the recorded peaks truly originated from piezoelectric energy harvesting by the f-PEH.

We also characterized the dependence of the output performance on the poling process with an induced high voltage from 0.5 to 2.0 kV. The as-fabricated f-PEH without the poling process showed a negligible output (V_friends < 1 V and I_friends < 10 nA), whereas the piezoelectric output values of the poled f-PEHs were improved, as shown in Figure 4a. To determine the instantaneous power of BN NFs-based f-PEHs, the load voltage (V_L) and current (I_L) were measured with load resistors ranging from 100 kΩ to 1 GΩ (Figure 4b). The load voltage of a resistor slowly increased to 10 MΩ and then rapidly rose with increasing resistance; on the contrary, the load current through the resistor gradually decreased. Consequently, by multiplying V_L and I_L under different resistances, we found an effective power with different loads and a maximum value of ∼0.3 µW at an external load of around 200 MΩ (see Figure 4c). Figure 4d shows the measured output voltage of BN NF-based f-PEHs when subjected to bending deformation, with the displacement varying from 1 to 5 mm at a fixed strain rate of 5 cm·s⁻¹. From these results, the values of the electric potential difference can be improved by the degree of deformation. To investigate the strain rate dependence of the f-PEHs on output performance, the produced output voltage peaks were recorded during periodic bending, with the strain rates ranging from 1 to 5 cm·s⁻¹ at a consistent displacement of 5 mm (see Figure 4e). Because the rapid bending deformation enhances the charges that contribute to the output signals because of fast electron flows, the f-PEHs deformed by fast bending can provide superior performance compared to the output generated by slow bending. We performed the mechanical durability test of an f-PEH during 5000 repeat bending cycles with a displacement of 5 mm at a strain rate of 5 cm·s⁻¹. As shown in Figure 4f, the BN NF-based f-PEH is mechanically stable and maintains the amplitude of the electrical output peaks.

4. CONCLUSIONS

In summary, we adopted a mechanochemical exfoliation process to achieve 2D h-BN NF with an average lateral size of ∼0.82 µm and a thickness of ∼25 nm. To characterize the energy harvesting ability of the synthesized single BN NF, we used the simple transfer and FIB-Pt deposition processes and demonstrated the single BN NF on a flexible substrate, which produced alternate piezoelectric output signals of ∼50 mV and ∼30 pA under repeated mechanical bendings. A piezoelectric rubber, by dispersing the BN NFs into an elastomer matrix, was inserted between two transparent electrode-coated flexible substrates to fabricate f-PEHs: the harvested V_friends and I_friends reached up to ∼9 V and ∼200 nA, respectively. An effective output power was calculated at ∼0.3 µW by using load voltage and current values with various external resistors. Our technology allows the precise characterization of energy generation from piezoelectric nanostructures and provides an innovative progress toward the realization of 2D piezoelectric nanomaterial-based f-PEHs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b12187.
AFM topography image of the BN NFs and statistical data obtained from the selected 60 BN NFs (PDF)

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Notes

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