An energy scavenging nanogenerator using a piezoelectric zinc oxide (ZnO) nanowire was developed in 2006 and, since, many studies have explored applications such as piezoelectric field-effect transistors, force/pressure sensors, and resonators. The advantage of the piezoelectric nanodevice is that electrical energy can be generated by a variety of external stimuli, including body movement, vibrations, and hydraulic or air forces, resulting in a wireless self-powered system. Our previous work has demonstrated that transparent flexible (TF) nanogenerators with piezoelectric ZnO nanorods can be driven directly by pushing or bending the TF nanogenerator itself. Such TF nanogenerators have garnered a great deal of attention because of the potential they present for new types of energy harvesting technology, such as nanogenerator-equipped flags that are charged by wind, or nanogenerator-embedded touch screens, in which a touching action is used for operating the display as well as self-charging. Furthermore, these devices can lead to new applications such as deformable mobile electronics or tactile skin sensors that can simultaneously detect position and pressure. However, since the TF nanogenerators are designed using indium tin oxide (ITO) electrodes to create a transparent device, the ITO-based nanogenerators have limited flexibility due to the ceramic structure of the ITO, and defects can easily be introduced if the device is overflexed.

Conventionally, metallic or metal oxide thin films have been used for transparent conductors in optical devices including light-emitting diodes and photovoltaics. These transparent conducting films, however, have limited use in flexible optoelectronics due to their mechanical brittleness, chemical instability, and high cost (they often include noble or rare metals). As a workaround, carbon nanotube (CNT) films, which have good optical, mechanical, and electrical properties, have been developed for many flexible optical devices. However, some unfavorable characteristics, such as the difficulty in separating metallic and semiconducting CNTs, diameter-dependent electrical properties, and significant roughness, have greatly hindered the performance and development of further applications for CNT-based devices.

Graphene is a 2D material with extraordinary electrical and mechanical properties. Graphene sheets have extremely high mobility (as high as 26000 cm² V⁻¹ s⁻¹) at room temperature and high mechanical elasticity (elastic modulus of about 1 TPa) based on the carbon–carbon covalent bonds, favorable for use in unique applications in the fields of nanoelectronics and spintronics. In particular, graphene, with a high optical transmittance and high chemical stability, provides an attractive building block as a window material for optoelectronic devices. Historically, graphene sheets have been prepared using mechanical exfoliation, ultrasonic cleavage of graphite, chemical oxidation of graphite, or epitaxial growth on silicon carbide. These methods are, however, delicate and time-consuming, or have provided the graphene sheets with low optical and electrical quality (e.g., about 2 kΩ at 70% transmittance) due to the poor interlayer junction contact resistance and the structural defects formed during the vigorous exfoliation and reduction process.

Recently, our group developed a direct synthesis method of producing large-scale graphene sheets with high-quality optical and electrical properties using chemical vapor deposition (CVD). Such high-quality, large-area, and cost-effective graphene sheets are expected to provide an excellent platform for emerging TF devices. Here, we report on the first use of the CVD-grown large-scale graphene sheets as transparent electrodes to realize fully rollable transparent (RT) piezoelectric energy harvesting nanodevices (termed “nanogenerators”). To complete the integrated graphene-based nanogenerator, we first fabricate a
A heterogeneous 3D nanostructure consisting of 1D ZnO nanorods on a 2D graphene electrode.

Large-scale graphene sheets were prepared using CVD on a nickel (Ni)-coated SiO$_2$/Si wafer (Fig. 1a). The graphene-grown 4$'$SiO$_2$/Si wafer was cut to the size required for its purpose (here, about 2 cm $\times$ 2 cm). The graphene sheet was separated from the underlying Ni layer using a Ni etchant (trascene). The separated floating graphene sheet was then transferred to a flexible polymer substrate using the fishing method (Fig. 1b). The transferred graphene sheet was used as the platform for the growth of ZnO nanorods, which are synthesized at 95 °C using the aqueous solution method (Fig. 1c). The field-emission scanning electron microscopy (FE-SEM) image in Figure 1c shows vertically well-aligned ZnO nanorods on graphene. Such a low-temperature fabrication method for the 3D heterogeneous nanostructure (1D semiconducting ZnO nanorods on a 2D metallic graphene electrode) can provide no significant thermal interdiffusion among the layers of Ni, graphene, and ZnO as well as no thermal damage to the graphene-transferred plastic substrate. In addition, the 3D heterogeneous nanostructure can be a promising building block for graphene-based TF electronics with a cost-effective and continuous fabrication process, which offers multifunctional applications. A graphene-based nanogenerator was completed by integrating the 3D heterogeneous nanostructure with the other graphene sheet (as a top electrode), as shown in Figure 1d. In the case of ITO-based nanogenerators, many line defects were visible to the human eye on the ITO electrodes after rolling on an 8 mm diameter pen. However, we could not see any big defects on the graphene-based nanogenerators after rolling on the same pen. This structural stability will be further discussed and investigated.

Figure 2a shows the transparency of the graphene sheet transferred to a polyethylene naphthalate (PEN) substrate. The transferred graphene sheet presented about 75% transmittance at a wavelength of 550 nm. As previously reported, our CVD-grown graphene sheet showed excellent electrical properties, including a sheet resistance of 200 $\Omega$ per square and a carrier mobility of 1760 cm$^2$/V$\cdot$s$^{-1}$ with a sheet carrier density of $1.77 \times 10^{13}$ cm$^{-2}$. In addition, the Raman spectrum measured for our graphene sheet on SiO$_2$ showed a strongly suppressed defect-related D-band peak (see the Supporting Information, Fig. S1). This suppressed D-band peak verifies the overall good quality of the graphene sheets created using the CVD method.

An atomic force microscope (AFM) image of a graphene sheet on PEN shows some intrinsic and extrinsic ripples (Fig. 2a inset). Even considering these ripples, the surface morphology is smooth [root-mean-square (RMS) roughness = 3.41 nm for a 3 $\mu$m $\times$ 3 $\mu$m area]. If we exclude the ripples, the RMS roughness is only 0.374 nm (see the dotted square box in the inset of Fig. 2a). Such a smooth surface morphology might be favorable to the growth of other nanostructures. Furthermore, the hexagonal atomic structure of graphene might be able to provide a building platform for the epitaxial growth of other hexagonal nanostructures such as ZnO.
We investigated the in situ electrical stability of the transferred graphene sheet under mechanical bending, as shown in Figure 2b. To release the stress and strain concentration at the gripping region, we set up an initial position with an orientation angle of about 20°. The radius of curvature (ρ) of the maximum-bent film was 4 mm. The bending rate was about 0.5 Hz and several cycles (80 s for one cycle) were performed. The two representative results (indicated by the red and blue circles in Fig. 2b) were presented in the graph. The two-probe resistance of the graphene sheets after bending was perfectly recovered, and the variation in resistance during the bending was less than 100 Ω. The stable electrical characteristic of a graphene electrode under the bending tests is attributed to the high mechanical strength (elastic modulus of 0.5–1 TPa and fracture strength >100 GPa)\textsuperscript{[20,35,36]} and the thin thickness (t\textsubscript{c}) of the graphene electrode. When t\textsubscript{c} is much smaller than ρ, the peak strain (ε) is given by the simple expression \( \varepsilon = \frac{t_c}{2\rho} \times 100 \% \).\textsuperscript{[17]

For the graphene electrode with a radius of curvature of 4 mm, the peak strain is \( \sim 10^{-5} \% \), which is about 100 times smaller than the peak strain of the 80-nm-thick ITO (\( \sim 10^{-3} \% \)). These optical and electromechanical properties of our CVD-grown graphene therefore strongly indicate the tremendous potential for use of these graphene sheets as fully RT electrodes in various flexible electronics.

Given the favorable surface morphology and the atomic structure of graphene sheets, we successfully fabricated 1D ZnO nanorods on the 2D graphene sheets (Fig. 3a). The vertically aligned ZnO nanorods were well grown on the graphene sheets with a density of about 20 μm\textsuperscript{-2}. The length was about 2 μm and the diameter was below 100 nm. The ZnO nanorods grown on the graphene layer are single-crystalline, as shown in the high-resolution transmission electron microscopy (HR-TEM) image (Fig. 3b) and fast Fourier transformation (FFT) patterns (Fig. 3c and 3d). A lattice spacing between adjacent lattice planes is 0.26 nm, indicating the preferential growth of ZnO nanorods along the [001] c-axis orientation. The crystalline lattice of the graphenes is also visible under HR-TEM. The lattice spacing of 0.34 nm in the graphenes is in good agreement with the interplanar distance of (002) graphite. The HR-TEM results suggest that single-crystalline ZnO nanorods have an epitaxial relation to the graphene layer. Concrete results and mechanism regarding the epitaxial growth of ZnO on the graphene are outside the scope of the current work and are currently being investigating.

The ZnO/graphene 3D heterojunctions were further investigated using micro energy-dispersive X-ray spectroscopy (μ-EDS). The point-focused μ-EDS profile from the point marked as O\textsubscript{1} shows intense Zn and O peaks with no carbon (C) or Ni-related peaks as shown in Figure 2S. The μ-EDS profile from the point marked as O\textsubscript{2} (ZnO/graphene interface) shows the co-existence of Zn, O, C, and Ni peaks, which might be attributed to the resolution limit of the μ-EDS equipment or to the atomic diffusion of Ni atoms toward the graphene layer during the CVD growth of graphene at high temperature. Point O\textsubscript{3} shows only a Ni component. Given these μ-EDS results, it appears that the ZnO nanorods were successfully grown on the graphene sheet without any significant interdiffusion among the layers of ZnO, graphene, and Ni due to the low growth temperature of the ZnO nanorods.

In nanogenerators, the contact between a ZnO nanorod and a top electrode should have a Schottky barrier to generate a cumulative current output, supposing that the electrons generated from ZnO nanorods are transported to the top electrode.\textsuperscript{[1–4]} The ZnO nanorods grown on graphene sheets in our experiments were oriented along the c-axis, as described previously.\textsuperscript{[8,34]} The (001) and (00\textsubscript{2}) facets of ZnO are terminated with zinc and oxygen, respectively, and a nonsymmetrical Schottky contact usually appears at one end in transport measurement.\textsuperscript{[48]} The work function of graphene electrodes is usually between 4.4–4.7 eV.\textsuperscript{[39,40]} The work function of our graphene electrode was measured to be 4.53 eV according to UV photoemission spectroscopy (UPS); see the Supporting Information, Figure S3. Since the electron affinity of ZnO is 4.1–4.35 eV,\textsuperscript{[41]} a Schottky contact is formed at the interface between graphene and a ZnO nanorod.

We measured the current output generated from the graphene-based nanogenerator using graphene sheets as the top and bottom electrodes by applying the pushing force (1 kgf) to the top of the nanogenerator in the vertical direction. Figure 4 exhibits the current density generated by the graphene-based nanogenerators. The output current density was approximately 2 μA cm\textsuperscript{-2}. In spite of the high sheet resistance of the graphene top electrode (about 200 Ω, which is much larger than that of the commercially available ITO on plastic substrates, which is 60–80 Ω), the output currents were successfully and clearly detected. Moreover, the output current peaks were sharp and narrow. According to the previous work,\textsuperscript{[3]} quick release and fast transport of the electrons generated by piezoelectricity can produce a significant large electric current pulse. Thus, we suggest that the clear observation of the output current with the high on/off ratio from the graphene-based nanogenerators is attributed to the high carrier mobility (\( \mu_c = 1760 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \)) of the graphene electrodes (note \( \mu_c = 20–40 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \) for ITO on plastic substrates). We believe that the current output level could be improved by increasing the work function and reducing the...
resistance of graphene electrodes via the controlled doping process, and these possibilities are being explored by our group.\[42\]

To verify that the measured signal was generated by the graphene-based nanogenerators rather than the measurement system, we performed the “switching-polarity” tests and “linear superposition” tests.\[38\] When the current meter was forward connected to a graphene-based nanogenerator, a positive current pulse was recorded during the pushing (before 50 s in Fig. 4a). When the current meter was reverse connected (after 50 s in Fig. 4a), the current pulses were reversed. The output current density for both connecting conditions was almost the same. In the linear superposition tests, the output current of the nanogenerators was enhanced by connecting them in parallel. The output current was approximately the sum of the output currents of the individual nanogenerators (data not shown).

We further explored the output currents before and after the rolling of the graphene-based nanogenerator. The inset in Figure 4b presents the rolling of the graphene-based nanogenerator on the 8-mm-diameter pen. Notably, there were no differences in the output currents measured from the graphene-based nanogenerator before and after the device was rolled several times on the pen (see Fig. 4b). We attribute this stable and reliable output current to the mechanical and structural strength of the graphene-based nanogenerators. Figure 5a and 5b shows the FE-SEM images for the ZnO nanorods on graphene (the lower part of the device) and the graphene top electrode (the upper part in the device), respectively, after the rolling of the device on the pen. Although some ZnO debris, which may have originated from the large ZnO rods (as defects) and the damaged ZnO nanorods, was found on the surface of the graphene top electrode, the number of ZnO nanorods on the graphene top electrode (Fig. 5b) is much smaller compared with the number of ZnO nanorods on the graphene electrode in the lower part of the device (Fig. 5a) after rolling.

To clearly understand the mechanical and structural stability of graphene-based nanogenerators under rolling, we analyzed the stress distributions for the graphene-based nanogenerator via simulation. The detailed simulation conditions are described in the Supporting Information (Fig. S4). Figure 5c shows the stress distribution of the vertically aligned ZnO nanorods between the graphene electrodes. The calculated results demonstrate that the maximum stress \(s_{\text{max}}\) for the graphene electrodes (see (i) in Fig. 5c) was about 160 MPa, which is about one over thousand (i.e., the safety factor of approximately 1000) of the fracture strength \(s_f > 100 \text{ GPa}\) of graphene.\[20,34,35\] The stress for ZnO was concentrated at the base area of the ZnO nanorods (Fig. 5c (ii)). However, the maximum stress for the ZnO nanorods was less than 30 MPa, which proves that the safety coefficient is about 10 \((\sigma_f = 200 \text{ MPa} \text{ for a ZnO nanorod})\).\[43\] Of course, since we simply designed the modeling for rolling and the fracture strength of graphene may vary with the number of graphene layers, the safety factors must be reduced. However, although we consider the reduction of the safety factors in our graphene-based nanogenerator, it is sure that the graphene-based nanogenerator is not damaged under the rolling conditions in

Figure 4. a) Current density generated by the graphene-based RT nanogenerator and switching-polarity tests. b) Output current density before (black line) and after (red line) rolling of the graphene-based nanogenerator.

Figure 5. Mechanical and structural stability of graphene-based RT nanogenerators. FE-SEM images for a) the ZnO nanorods on graphene (the lower part of the device) and b) the graphene top electrode (the upper part of the device) after rolling of the device on the pen (the scale bars in (a) and (b) indicate 10 \(\mu\text{m}\)). c) Stress distributions for the graphene-based nanogenerator under rolling. To simplify the simulation for the rolling, we assumed a cantilever bending model with a symmetric boundary condition.
this study. Thus, we definitely believe that our graphene-based nanogenerators are highly reliable and durable for external mechanical loads such as bending and rolling, resulting in a fully RT nanogenerator.

In summary, we have demonstrated the first use of CVD-grown large-scale graphene sheets as transparent electrodes for fully RT nanogenerators. To accomplish the fully graphene-based nanogenerator, we successfully fabricated a heterogeneous 3D nanostructure consisting of 1D ZnO nanorods grown epitaxially on a 2D graphene electrode with no damage using a low-temperature solution growth. Our graphene electrode, with its extremely high carrier mobility at room temperature and a Schottky contact to the ZnO nanorods, led to the realization of graphene-based nanogenerators with superior charge-scavenging performance. Furthermore, due to the outstanding mechanical properties of the graphene electrode, we created RT nanogenerators that proved to be electrically and structurally stable under external mechanical loads such as bending and rolling. Therefore, our results suggest that graphene-based RT nanogenerators are suitable for self-powered RT device applications such as flexible self-powered touch sensors, wearable artificial skins, fullyrollable display mobile devices, and battery supplements for wearable cellular phones.

**Experimental**

**Growth of Large-Scale Graphene Sheets on a Ni-Coated SiO$_2$/Si Wafer Using CVD:** A 300-nm-thick layer of Ni was first deposited on a 4°SiO$_2$/Si wafer using an electron-beam evaporator. The Ni-coated substrate was placed in a rapid thermal CVD chamber, and the temperature was increased from room temperature to 100°C in 5 min. The initial reduction of the Ni-coated substrate was carried out in a hydrogen gas flow of 45 standard cubic centimeter per minute (sccm) for 20 min at 100°C. The gas mixing ratio of C$_2$H$_2$/H$_2$ was optimized and the synthesis condition for the graphene sheets of 2/45 sccm was obtained in a growth time of 2 min. After the growth was completed, the gas supply was terminated and the chamber was cooled down to 50°C at a cooling rate of 160°C/min.

**ZnO-Nanorod-Array Growth on Graphene Transferred onto the Flexible Polymer Substrate:** Zinc acetate dehydrate (Zn(CH$_3$COO)$_2$·2H$_2$O, 0.01 M) dissolved in ethanol (100 mL) was prepared first as the seed solution, which was dropped onto the transferred graphene sheet and spin-coated at 1000 rpm for 60 s. The spin-coated graphene substrate covered with the ZnO-seed layer was then dried onto a hot template at 100°C. ZnO nanorods on the nanometer-sized ZnO-seed-coated graphene sheet were grown in a mixture solution consisting of zinc nitrate hexahydrate [Zn(NO$_3$)$_2$·6H$_2$O, 0.025 M], hexamethylenetetramine (0.025 M), and de-ionized water (250 mL). The main growth of the ZnO nanorods was undertaken at 95°C for 3 h.

**Characterizations:** The morphological and structural properties of the 3D nanostructure were examined by using FE-SEM and TEM measurements. Transmission spectra were obtained using a Varian Cary 5000 UV–vis spectrometer. We also investigated the electrical properties of the graphene sheets on PEN at room temperature using the Hall measurement system (ACCENT semiconductor UK/HL 5500PC). The surface roughness of a graphene sheet on PEN was analyzed using AFM (Dimension V, Veeco Co.) measurements. A Keithley 6485 Picoammeter was used for low-noise current measurements in order to detect currents generated by therollable piezoelectric nanogenerators.

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