Extended Abstracts of the 2012 International Conference on Solid State Devices and Materials, Kyoto, 2012, pp442-443

# Highly Sensitive Stretchable Free-standing Power Generators with Modified Graphene Electrodes

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## 1. Introduction

The power generation performance and commercialization of piezoelectric power generators with a thick and rigid template are limited, because they are usually operated in a low magnitude and frequency situation with very minute and irregular mechanical energy sources from the living environment, such as body movement, air flow, hydraulic pressure and acoustic vibrations, which are mostly of low magnitude and low frequency [1–3]. Therefore, developing free-standing type piezoelectric energy harvesters with high performance and stretchability is extremely important. The atomically layered structure of two-dimensional graphene sheets with high mechanical elasticity (elastic modulus of about 1 TPa) and high transparency can be used to prepare fully flexible and rollable transparent piezoelectric power generators. Moreover, although large-scale graphene grown by the chemical vapor deposition (CVD) method shows outstanding uniformity and good electrical properties, the enhancement of the electrical mobility of CVD-based graphene is required for it to be used as an electrode material for high performance stretchable transparent piezoelectric power generators. In this work, we report a new type of stretchable transparent free-standing power generator (FPG) using an organic piezoelectric material consisting of poly(vinylidene fluoride trifluoroethylene) [P(VDF-TrFE)] sandwiched with mobility-modified CVD-grown graphene electrodes by ferroelectric polarization into P(VDF-TrFE). This new type of generator has a very high sensitivity and mechanical durability with fully flexible, rollable, stretchable, foldable, and twistable properties.

## 2. Experimental

Growth of graphene sheets : To grow the graphene sheets, a Cu foil was placed in a rapid thermal CVD chamber and the temperature was increased from room temperature to 1000 °C with a 10 standard cubic centimeters per minute (sccm) flow of $H_2$ (1 Torr). When the temperature reached 1000 °C, the Cu foil was annealed for 30 min to clean its surface by the reduction of copper(II) oxide and grow the grain size. The synthesis of the graphene sheets was achieved with a mixture of $CH_4$ (20 sccm) and $H_2$ (10 sccm) for a growth time of 30 min (1 Torr). After the growth was completed, the gas supply was terminated and the chamber was cooled to below 100 °C at a cooling rate of 160 °C $min^{-1}$.

Fabrication of P(VDF-TrFE) thin films : The piezoelectric material P(VDF-TrFE) (70/30) was purchased from Piezotech S.A. A solution of P(VDF-TrFE)(20 wt%) dissolved in N-N dimethylformamide (DMF) solvent was spun on the graphene electrode to a layer thickness of 2 μm, followed by drying at 60 °C to remove the DMF solvent. Next, this layer was maintained at 140 °C for 2 hr and then naturally cooled down to room temperature in nitrogen ambient, in order to enhance the crystallinity of the ß phase.

## 3. Results

The transparent, mechanically durable, and high carrier mobility properties of graphene made it a promising material for us as an electrode material for the FPG in this work. Interestingly, it was found that the ferroelectric remnant polarization of P(VDF-TrFE) affects the electrical properties of the graphene sheet. The carrier type, carrier concentration, and mobility of graphene are investigated before and after poling at room temperature by Hall-effect measurements. The electrical properties of the three monolayer graphene sheet with non-poled P(VDF-TrFE) shows p-type conduction with a carrier mobility of 748 $cm^2V^{-1}s^{-1}$ and a sheet carrier density of 3.84 x 1013 $cm^{-2}$. When the ferroelectric P(VDF-TrFE) is poled in both directions, it dopes the graphene with either electrons or holes. We observed the change of the charge carrier mobility in the graphene sheets depending on the direction of the applied electric field, as shown in **Figure 1**. On the application of an electric field of - 100 MV/m, the graphene sheets exhibited a carrier mobility of 822 $cm^2V^{-1}s^{-1}$, which is approximately 10 % higher than that of graphene with non-poled P(VDF-TrFE). On the other hand, on the application of an electric field of + 100 MV/m, the graphene sheets exhibited a carrier mobility of 665 $cm^2 V^{-1} s^{-1}$, which is approximately 10 % lower than that of graphene with non-poled P(VDF-TrFE). Proposed mechanism details will be discussed in the presentation.

In order to demonstrate the high performance of the FPG in a low magnitude and frequency situation with a very minute and irregular mechanical energy source, we compared this device with a normal power generator (NPG) with a plastic PEN substrate. When they are exposed to sound, the devices experience the sound pressure and, subsequently, a piezoelectric potential is generated across the thickness of P(VDF-TrFE). This generated piezoelectric potential drives the carriers from the electrodes to the external circuit; the output voltage and output current are measured from the FPG and NPG devices upon the application of various sound pressures.

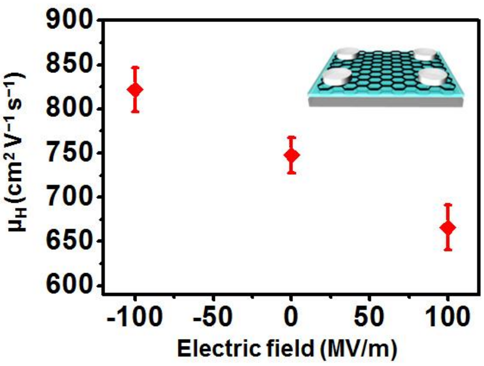


Fig. 1 Carrier mobility of graphene sheets vs. the electric field applied to P(VDF-TrFE) in poling process; the inset is a schemaic of a sample prepared for Hall Measurement.

With the exposure of the devices to sound by varying the input powers from 82 to 110 decibel (dB) at 100 Hz, the measured peak to peak output voltage of the FPG is from 50 mV to 600 mV, which shows a clear enhancement of up to about 30 times compared with that of the NPG which is from 10 mV to 22 mV (Figure 2). We clearly observed a voltage output even upon the exposure of the FPG device to sound with a low input power of 85 dB. On the other hand, we only observed noise signals upon the exposure of the NPG to sound with an input power of 85 ~ 95 dB. Hence, the clear observation of voltage output upon the exposure of the FPG device to sound with a much lower input power confirms its high performance in a low magnitude and frequency situation.

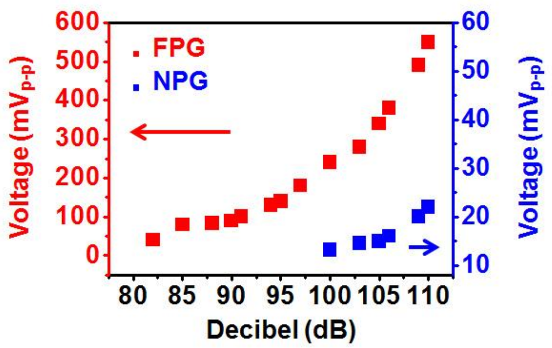


Fig. 2 Piezoelectric peak-to-peak output voltage generated from FPG and NPG under same sound wave pressure.

## 3. Conclusions

In summary, a transparent FPG with a high output performance having a thin PDMS stretchable rubber template is investigated based on the modification of the mobility of graphene electrodes by ferroelectric P(VDF-TrFE) remnant polarization. This new type of generator has stretchable, multi-shape transformable and mechanically durable properties with a very high sensitivity. We demonstrated that upon their exposure to the same input sound pressure, the measured output performance of the FPG is up to 30 times that of the NPG and that upon their exposure to an air flow at the same speed, the measured output voltage from the FPG shows a clear enhancement of up to about 8 times compared with that of the NPG. We believe that the approach described herein involving the fabrication of an FPG with graphene electrodes is very promising for harvesting energy from very minute and irregular mechanical energy sources in a living environment, such as body movement, air flow, hydraulic pressure and acoustic vibrations of low magnitude and low frequency.

## References


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