We developed a three-dimensional spring-type piezoelectric energy harvester using a dip-coating method and multi-directional electrode deposition. The energy harvester consists of a bilayered structure composed of a surface electrode and a ferroelectric polymer, on a conventional spring which has two roles – the core electrode and the mechanical substrate for the ferroelectric polymer. The energy harvester generated an output voltage of up to 88 mV as a function of cycling compression stress, which leads to a piezoelectric constant of 28.55 pC N$^{-1}$ for unpoled P(VDF-TrFE) films. Since the spring structure significantly decreases the resonance frequency of the harvester, the spring-type energy harvester can effectively generate electricity using low-frequency vibration energy abundant in the nature.

Vibration-based energy harvesting (VEH) devices have attracted great interest for use as sustainable and clean electric power supplies for wireless sensor networks that enable health monitoring of important infrastructures such as power plants, bridges and remote power grids.\(^1\)\(^-\)\(^3\) Since there are abundant vibration sources with a low frequency (between 1 and 200 Hz) in nature,\(^4\) low frequency vibrations are of high interest and are targeted in VEH device design for a wide range of potential applications.\(^5\)\(^-\)\(^10\) Several approaches exist to convert vibrations to electrical power including electromagnetic, electrostatic and piezoelectric conversion, among which piezoelectric energy harvesting systems (PEHSs) have received the most attention. This is because they directly convert mechanical energy into electricity, leading to a simpler device design in comparison to other mechanisms, which require complex geometries and numerous additional components.\(^1\)

However, PEHSs are facing challenges such as low output power and high resonance frequency.\(^6\) As the resonant frequency is usually higher than the vibration frequency with the highest amplitude in the environment when PEHSs are scaled down to micron size, they suffer from low output power because energy harvesters generate the maximum power at the resonance frequency.\(^11\) The most commonly adopted ways to reduce the resonance frequency of the harvester are 1) to add a mass to the harvester\(^12\) or 2) to use a spring structure or equivalent that can decrease the overall system stiffness. We came up with the idea of a spring-type structure, which can significantly decrease the resonance frequency toward 1 kHz or less as compared with a beam-type structure with the same weight. Furthermore, our idea can be applied to existing spring structures in automobiles, bridges or even in mattress, which enables us to convert otherwise wasted volume and energy into useful ones. However, in fabricating a spring-type piezoelectric energy harvester, there are processing challenges such as conformal coating of piezoelectric material onto a substrate with a complex geometry, and uniform electrode deposition to ensure maximum contact with the deposited piezoelectric materials.

Here, we report the way we addressed the processing challenges of spring-type piezoelectric energy harvesters, namely a combination of dip-coating method and multi-directional electrode deposition, and measured the output voltage as a function of cycling compression stress without an external poling process.

The method and preparation for fabricating the spring-type energy harvesters are described as follows. Firstly, poly(vinylidene fluoride trifluoroethylene) (P(VDF-TrFE)) solution, a spring and a low speed motor were prepared. The spring was commercially available (Seoul Spring, Inc.), with a wire diameter of 0.97 mm, an outer spring diameter of 11.55 mm and a length of 40 mm. The spring had 10 turns. The spring constant was measured by placing a mass of 500 g at the end of the spring. The precursor solution was prepared by dissolving 15 wt% P(VDF-TrFE) (VDF:CH$_2$–CF$_2$, 75:25) in methyl ethyl ketone solvent (MEK).\(^1\) The iron spring was immersed in the solution for 30 s. The spring was then withdrawn from the solution at a speed of 0.3 mm s$^{-1}$. The coated P(VDF-TrFE) was left to dry for 1 h in vacuo (less than 1 kPa). To obtain the optimum thickness, we repeated the above
measured the average thickness of 6.43 μm on the Fe plate using the dip-coating method from which we estimated the deviation of 0.508 μm. Lastly, we conducted FTIR spectroscopy (FTIR, Bruker Optiks IFS66V S$^2$-spectroscopy and Hyperion 3000) analyses to identify the crystalline phases and the structure of the P(VDF-TrFE) films deposited on the Fe substrate.

In order to simplify the optimization of the dip-coating process, we used a model system that has a 99.9% Fe substrate with a flat geometry on which we deposited P(VDF-TrFE) by a dip-coating method. We measured the deposition rate by monitoring the thickness after each coating cycle which was verified by scanning electron microscopy (SEM, Hitachi S-4800, operating voltage: 10 kV). Then, we performed X-ray diffraction (Rigaku D/MAX-2500 at a scanning velocity of 1°/min and using the 0/2θ scan at 40 kV and 300 mA) and Fourier transform infrared spectroscopy (FTIR, Bruker Optiks IFS66V S$^2$-spectroscopy and Hyperion 3000) analyses to identify the crystalline phases and the structure of the polymer chains. Lastly, we conducted P-E hysteresis loop measurements (Radiant Technologies RT-66A Standardized Ferroelectric Test System with tungsten probe tip (cat-whisker, T20-7A)) to measure the remnant polarization and the coercive field, which allowed us to predict the piezoelectric properties of the P(VDF-TrFE) films deposited on the Fe substrate.

The energy harvester developed here consists of a conventional spring with a bi-layered structure, composed of a surface electrode and a ferroelectric polymer, of which a schematic and actual image along with its circuit are shown in Fig. 1. The spring has two roles, one as the core electrode and other as the mechanical substrate for the ferroelectric polymer. The ferroelectric polymer is then coated on the Pt surface electrode. When the spring is vertically pressed, the amplitude of the shear stress on the surface is considerably larger than the vertical stress. Therefore, it is expected that the spring-type energy harvester will efficiently convert the mechanical energy into electricity via the piezoelectric effect and the amplified conversion of applied vertical stress into internal shear stress.

Fig. 2a shows the tilted-view SEM image of P(VDF-TrFE) coated on the Fe plate using the dip-coating method from which we measured the average thickness of 6.43 μm with a standard deviation of 0.508 μm. The P(VDF-TrFE) films went through three iterative dip-coating processes. It should be noted that we were not able to measure well-defined P-E hysteresis loops from the single and double coated films. We think it is due to the poor interface between the electrode and P(VDF-TrFE) based on the shape of the P-E hysteresis loops. However, as shown in Fig. 2d, we could measure reliable P-E hysteresis loops from the triple coated film.

In the XRD pattern (see Fig. 2b), the P(VDF-TrFE) film showed a peak in intensity at 2θ = 19.95°, which stems from the reflections of (110) and (200) crystal planes, and represents the ferroelectric β phase. Bulk P(VDF-TrFE) has peaks in intensity at 2θ = 19.5° for the (200) reflection and at 2θ = 19.8° for the (110) reflection, and these two Bragg peaks overlap due to the fact that their natural width (Δ2θ = 0.5°) is larger than the distance (0.3°) between the (110) and (200) peaks that are associated with the ferroelectric β phase. No peak was observed near 2θ = 18° which is related to the paraelectric phase.

Fig. 2c shows a FTIR spectrum of PVDF-TrFE film deposited on the Fe plate. Absorption bands at 844, 880, 1076, 1119, 1170, 1287, 1400 and 1430 cm$^{-1}$ were observed in the IR spectra, and are related to the crystalline-phase spectra. However, the bands at 844, 880, 1076, 1119, 1170, 1400 and 1430 cm$^{-1}$ for the crystalline phase overlap with the broad disordered-phase bands in this region. The 1287 cm$^{-1}$ peak does not overlap with any disordered-phase band and is assigned to the sequences of four or more trans isomers. Although 844 and 880 cm$^{-1}$ peaks for the crystal phase overlap with the disordered-phase band, the crystal-phase bands contribute to the peaks more than the disordered-
phase band, and the peaks are assigned to the sequences of three or more *trans* units and *trans* sequences, respectively.\textsuperscript{19,20} Both XRD and FTIR results confirmed that the P(VDF-TrFE) film contains a ferroelectric $\beta$ phase.

Subsequently, $P$–$E$ hysteresis loops were measured to check the ferroelectric properties of the P(VDF-TrFE) films deposited on the Fe substrate (model system), which are related to the piezoelectric properties via permittivity and an electromechanical coupling coefficient.\textsuperscript{21} Remnant polarization ($P_r$) of 16.4 $\mu$C cm$^{-2}$ and a coercive field value of 19.4 MV m$^{-1}$ were measured ($P_r$ values reported in the literature\textsuperscript{22–24} are between 5 and 15 $\mu$C cm$^{-2}$). The results show that the P(VDF-TrFE) films on iron as a model system using the dip-coating method contain a ferroelectric $\beta$ phase and have well-defined ferroelectric properties.

Based on the process optimization results from the model system, we applied the same processing recipe to the spring structure, which has a more complicated geometry than the Fe plate. Fig. 3a shows the schematic of the resulting spring-type energy harvester under an applied vertical force of up to 17.4 N, which we measured from the displacement (24 mm) and the spring constant (725.9 N m$^{-1}$). We were able to collect the output voltage signals from the energy harvester using a digital oscilloscope. As shown in Fig. 3b, the spring was cyclically compressed within the range 16–33 mm. The average displacement of the spring length was 15.92 mm under applied vertical force while the period of displacement was 0.507 s. The output signal showed a more complicated shape than the displacement curve did, which comes from the fact that it consists of signal induced by piezoelectricity and noise from other sources (see Fig. 3c). As such, we applied a Fourier transform method to extract the signal induced by piezoelectricity of which details can be found in the supplementary information. We obtained an effective piezoelectric constant of 28.55 pC N$^{-1}$, which is large if we consider the fact that the spring has not been poled by an externally applied voltage (poled P(VDF-TrFE) has piezoelectric coefficients of $-31.6$ (d$_{33}$), 10.2 (d$_{31}$) and $-36.0$ (d$_{15}$) pC N$^{-1}$, respectively).\textsuperscript{25,26} Although the self-poling effect was observed in the P(VDF-TrFE) thin films deposited on transparent polymer substrates,\textsuperscript{27} this alone cannot account for such a high piezoelectric coefficient without external poling. Another possible reason is that the P(VDF-TrFE) film is exposed to a greater in-plane stress than the vertical stress through thickness because the P(VDF-TrFE) film coated on the spring is stretched out when the spring is deformed.\textsuperscript{14}

In order to calculate the stress distributions on P(VDF-TrFE) film on the spring, we conducted Finite Element (FE) analysis using ABAQUS 6.11. Fig. 4 shows stress distributions on P(VDF-TrFE) film coated on the spring. FE results show that when the spring is loaded in compression, stress at the outer surface of the spring is in compression in the 2-direction but in tension in the 1-direction, where the 1- and 2- directions indicate circumferential and hoop directions respectively, as shown in Fig. 4. With thin shell theory, it is accepted that electric displacement, $q$ (Coulomb/m$^2$) for coated P(VDF-TrFE) films is related only to the normal stresses ($\sigma_{11}$ and $\sigma_{22}$) which are the components of in-plane stresses in shell elements, and it is independent of shear stress.
Therefore, $d_{31}$ is main factor on the piezoelectric behaviour of the spring-type energy harvester. For the case of using a poled piezoelectric material whose $d_{31}$ is $49 \text{ pC N}^{-1}$, it is expected that the effective piezoelectric constant would be $383 \text{ pC N}^{-1}$ for springs with 10 turns when the external electric field is zero. It means that the spring structure coated with a P(VDF-TrFE) film with 10 turns can amplify the effective load by about 7.8 times to generate piezoelectric charges, leading to a 7.8 times larger effective piezoelectric coefficient. However, as we only coated 5.5 turns in our experiment, the amplification factor is expected to reduce to 4.3 times.

Although the effective piezoelectric constant of the energy harvester was lower than the simulated result for poled P(VDF-TrFE), we believe that the spring-type piezoelectric energy harvester can be developed further due to the following reasons. First, we can enhance the output power of the spring-type piezoelectric energy harvesters by tuning the resonance frequency of the spring to the frequency of larger vibrations in the environment by increasing the outer spring diameter or number of coils in the spring. Recent studies reported that energy harvesters generate maximum power at their resonance frequency, which could be orders of magnitude greater than the power extracted at other frequencies. Secondly, from the system’s perspective, it was recently found that the maximum output power from piezoelectric energy harvesters is insensitive to the piezoelectric coefficient if one can tune the load resistance to an optimal value. Based on the arguments above, we believe that we can use the spring-type piezoelectric energy harvester without a poling process, which could simplify their applications in energy harvesting devices.

In conclusion, we developed a three-dimensional spring-type piezoelectric energy harvester, which can effectively generate electricity using low-frequency mechanical energy abundant in nature. We found that P(VDF-TrFE) films coated on an iron-based spring ($k = 725.9 \text{ N m}^{-1}$) using a dip coating method followed by multi-directional Pt electrode sputter deposition generated a voltage up to $88 \text{ mV}$ under a compressive force of $17.4 \text{ N}$, which

![Fig. 3](a) Schematic of the spring-type energy harvester under vertical stress. Plots of (b) vertical displacement of the energy harvester under cyclical compression stress, and (c) output voltage signal generated from the energy harvesters as a function of elapsed time.

![Fig. 4](a) Stress distributions on P(VDF-TrFE) shell elements (a) $\sigma_{11}$ and (b) $\sigma_{22}$. 

This journal is © The Royal Society of Chemistry 2013

RSC Adv., 2013, 3, 3194–3198 | 3197
leads to a measured piezoelectric constant of 28.55 pC N\(^{-1}\) for unpoled P(VDF-TrFE) films. We envision that our simple and effective recipe toward piezoelectric energy harvesters coated on a typical spring structure will be widely used not only in energy harvesting field but also in smart sensors and actuators.

**Acknowledgements**

This research was supported by the Mid-career Researcher Program (No. 2010-0015063) and Conversion Research Center Program (No. 2011K000674) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) and the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20103020060010) funded by the Ministry of Knowledge Economy, Korea. Work at Argonne National Laboratory (S. H. and D. K., data analysis and writing of manuscript) was supported by UChicago Argonne, a U.S. DOE Office of Science Laboratory, operated under Contract No. DE-AC02-06CH11357. J. H. acknowledges the Chung-Ang University Research Grants in 2011.

**Notes and references**