**Printing of recyclable, flexible and transparent piezoelectric generators through SWCNT templating**

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With an increasing global population and a surge in the use of portable and wearable electronics, the demand for energy use is increasing exponentially. Advancements in miniaturised electronics are far outstripping progress in miniaturised power delivery, and thus novel and reliable energy scavenging techniques are required to power always-on, self-powered sensors and portable or wearable devices.1 Piezoelectric energy harvesting, which has the ability to convert mechanical energy (i.e., movement) to electrical energy, has been proposed as a viable technique to either supplement or replace traditional energy storage technologies. Piezoelectric materials have shown energy conversion efficiencies >35% with polymer-based materials such as poly(vinylidene fluoride) (PVDF) and other fluoropolymers allowing mechanical flexibility for wearable and implantable applications.2

Despite the promising nature of fluoropolymers, several drawbacks have limited commercial utility, most notably the energy cost in the spatial orientation of dipoles for maximised energy harvesting capabilities (a process called poling), and in processing the non-polar α phase into the polar β and semi-polar γ phases. Current poling techniques are inefficient, employing high temperatures and high electric fields under vacuum in order to achieve high energy conversion efficiencies.2 We have previously shown to eliminate this energy intensive poling process—by 3D printing poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) we have observed an enhancement in energy harvesting arising from shear-induced polarisation.3 Furthermore, recent advances in the use of engineered nanomaterials have reported enhanced polar phase fractions, although few reports have investigated energy harvesting from such nanocomposites.2

Here we present our first report in coupling shear-induced alignment of PVDF-TrFE through 3D printing with single-walled carbon nanotubes (SWCNTs) as high aspect ratio nanofillers. This technique is used as a cheap and low energy alternative to poling, which does not use high temperatures or high electric fields. The optimised devices show enhancements in polarisation with a 600% increase in the energy harvesting capability. The piezoelectricity of SWCNT/PVDF-TrFE composites produced by 3D printing is equivalent to commercial poled polymers, as measured by piezoresponse force microscopy (PFM) showing piezoelectric charge coefficients comparable to commercially available poled film. Furthermore, the potential of recycling the manufactured piezoelectric generators via green solvents and re-printing is presented as a technique to regenerate energy harvesting capabilities upon degradation.

**References**

1. Bai, Y., Jantunen, H., Juuti, J. (2018). Energy Harvesting Research: The Road from Single Source to Multisource. Adv. Mater., 30, 1707271.
2. Shepelin, N.A., Glushenkov, A.M., Lussini, V.C., Fox, P.J., Dicinoski, G.W., Shapter, J.G., Ellis, A.V. (2019). New developments in composites, copolymer technologies and processing techniques for flexible fluoropolymer piezoelectric generators for efficient energy harvesting. Energy Environ. Sci., 12, 1143-1176.
3. Shepelin, N.A., Lussini, V.C., Fox, P.J., Dicinoski, G.W., Glushenkov, A.M., Shapter, J.G., Ellis, A.V. (2019). 3D printing of poly(vinylidene fluoride-trifluoroethylene): a poling-free technique to manufacture flexible and transparent piezoelectric generators. MRS Commun., 9, 159-164