Abstract

Wearable textiles with integrated electronics have numerous uses in the healthcare, entertainment, fitness, and fashion industries. Piezoelectric nanogenerators and capacitive sensors can easily be integrated with wearables. Piezoelectric nanogenerators can extract energy in milliwatts from simple articular motions, whereas piezo-capacitive sensors can sense body joint's extension and flexion movements, body temperature, and pressure for healthcare applications.

Poly(vinylidene fluoride) (PVDF) based piezoelectric nanogenerators, though flexible, exhibit poor stretchability and mechanical stability. This limits their application for harvesting energy from repeated deformations arising from human articular motions. A simple and cost-effective approach was used to overcome the above issues while simultaneously enhancing the piezoelectric effect of PVDF by mixing a small amount of polyurethane (PU) in PVDF-PU nanofibers. The presence of 21% of PU in PVDF could enhance the electroactive phases by up to 46% as measured by FTIR, increase in d_{33} value from 3.02 to 7.064 pmV^{-1} and improved stretchability to 90%

For developing a Stretchable Piezoelectric Nano-Generator (S-PENG) device, stretchable electrodes with 4.5-Gauge factor at 100% strain were fabricated by spin-coating of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS): graphene nanoplates on a pre-strained PU substrate. $PVDF_{79}PU_{21}$ nanofiber based S-PENG produced peak open circuit voltage, short circuit current and power density of 3.8 V, 0.65 µA and 0.48 μWcm^{-2}, respectively, during cyclic deformation. The device showed both electrical and mechanical stability for at least 2000 cycles. Its performance was demonstrated for various human articular motions related to knee, elbow and foot by integrating it with wearables. The generated energy from the S-PENG could readily charge capacitors up to ~650 mV in just 100 s. The designed S-PENGs showed great potential in harvesting energy from simple human motions.

The performance of $PVDF_{79}PU_{21}$ nanofibers as piezo-capacitive sensors showed multimodal response with excellent sensitivity of 0.3 kPa^{-1} for up to 8 kPa pressure stimuli, a good gauge factor (GF) ranging between 0.5-0.75 for 0-40% cyclic strain, and high sensitivities of 0.8% $^{o}C^{-1}$ for 30–60 ºC and 2% $^{o}C^{-1}$ for 60–100 ºC. They could be used for measuring human body temperature in the range of 37 to 40 °C with a sensitivity of 0.9% $°C^{-1}$. The prototypes of $PVDF_{79}PU_{21}$ nanofiber based piezo-capacitive sensors were attached to different body parts to measure extension and flexion movements with high sensitivity, which showed its great potential as a wearable sensor.

Poly(acrylonitrile) (PAN) has a greater dipole moment (3.5 D) than poly(vinylidene fluoride) (PVDF), therefore, it has a strong potential for use as piezoelectric nanogenerators and pressure sensors. However, due to strong dipole-dipole repulsion, the nitrile groups are difficult to align in a zig-zag configuration resulting in reduced ability of the system to convert mechanical energy into electrical energy. To address this issue, ZnO nanoparticles (ZnP) and ZnO nanowires (ZnW) were incorporated in PAN films. Due to the strong interaction of ZnO nanostructures with PAN, the dipole-dipole repulsion reduced resulting in increased zigzag conformation of PAN. Compared to ZnP, ZnW was found to show better alignment of PAN nitrile groups and faster relaxation of

dipoles after removal of stresses. Without any external poling, PAN, ZnP-PAN, and ZnW-PAN films based piezoelectric nanogenerators could generate 27.6, 79.3 and 86.3 mW/m^2 of power, respectively. The incorporation of 5wt% ZnP and ZnW also significantly improved the pressure sensitivities of the devices to 0.9 $fFPa^{-1}$ and 1.1 $fFPa^{-1}$, respectively, as compared to 0.1 $fFPa^{-1}$ for pristine PAN film.

Further, these ZnO nanostructures of different aspect ratios were incorporated to PAN nanofibers to improve the zigzag conformation. ZnW-PAN nanofibers exhibited significantly better piezoelectric properties resulting in devices with higher power density by 46% than those based on ZnP-PAN nanofibers and by 578% compared to those with PAN nanofibers. Further, the use of ZnW-PAN nanofibers in a sensor device could show higher pressure sensitivity as well. This enhancement in properties was attributed to the effect of morphology of ZnO nanostructures, which resulted in higher zig-zag content of PAN in the presence of ZnWs.

Thus, using ZnO nanostructures, PAN based piezoelectric devices with enhanced properties could be developed.