PIEZOELECTRIC MATERIALS BASED ON MODIFIED PVDF AND PAN FOR ENERGY HARVESTING AND SENSING

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by

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Dedicated to my grandparents

Sh. Sudarshan Kaur and Late S. Harjit Singh

CERTIFICATE

This is to certify that the thesis titled '**Piezoelectric materials based on modified PVDF and PAN for energy harvesting and sensing',** being submitted by **Ms. Gurneet Kaur** to the **Indian Institute of Technology Delhi** for the award of degree **Doctor of Philosophy**, is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and fulfilled the requirements for the submission of thesis, which has attained the standard required for a Ph.D. degree of this Institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

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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% $^oC^{-1}$ for 30–60 ^oC and 2% $^oC^{-1}$ 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.

सार

एकीकृत इलेक्ट्रॉनिक्स के साथ पहनने योग्य वस्त्रों का स्वास्थ्य देखभाल, मनोरंजन, फिटनेस और फैशन उद्योगों में कई उपयोग होते हैं। पीजोइलेक्ट्रिक नैनोजेनरेटर और कैपेसिटिव सेंसर को आसानी से पहनने योग्य वस्तुओं के साथ एकीकृत किया जा सकता है। पीजोइलेक्ट्रिक नैनोजेनरेटर सरल आर्टिकुलर गतियों से मिलीवाट में ऊर्जा निकाल सकते हैं, जबकि पीजो-कैपेसिटिव सेंसर शरीर के जोड़ों के विस्तार और लचीलेपन की गतिविधियों, शरीर के तापमान और स्वास्थ्य देखभाल अनुप्रयोगों के लिए दबाव को समझ सकते हैं।

पॉली (विनाइलिडीन फ्लोराइड) (पीवीडीएफ) आधारित पीजोइलेक्ट्रिक नैनोजेनरेटर, हालांकि लचीले होते हैं, खराब खिंचाव और यांत्रिक स्थिरता प्रदर्शित करते हैं। यह मानव कलात्मक गतियों से उत्पन्न होने वाली बार-बार होने वाली विकृतियों से ऊर्जा संचयन के लिए उनके अनुप्रयोग को सीमित करता है। पीवीडीएफ-पीयू नैनोफाइबर में थोड़ी मात्रा में पॉलीयुरेथेन (पीयू) को मिलाकर पीवीडीएफ के पीजोइलेक्ट्रिक प्रभाव को बढ़ाने के साथ-साथ उपरोक्त मुद्दों को दूर करने के लिए एक सरल और लागत प्रभावी दृष्टिकोण का उपयोग किया गया था। पीवीडीएफ में 21% पीयू की उपस्थिति इलेक्ट्रोएक्टिव चरणों को 46% तक बढ़ा सकती है, जैसा कि एफटीआईआर द्वारा मापा गया है, डी33 मान 3.02 से 7.064 pmV^{-1} तक बढ़ सकता है और स्ट्रेचेबिलिटी में 90% तक सुधार हो सकता है।

स्ट्रेचेबल पीजोइलेक्ट्रिक नैनो-जेनरेटर (S-PENG) डिवाइस विकसित करने के लिए, 100% स्ट्रेन पर 4.5-गेज फैक्टर के साथ स्ट्रेचेबल इलेक्ट्रोड को पॉली (3,4-एथिलीनडाइऑक्सीथियोफीन): पॉली (स्टाइरीन सल्फोनेट) (पीईडीओटी): ग्राफीन नैनोप्लेट्स की स्पिन-कोटिंग द्वारा निर्मित किया गया

था। $PVDF_{79}PU_{21}$ नैनोफाइबर आधारित S-PENG ने चक्रीय विरूपण के दौरान क्रमशः 3.8 V, 0.65 μA और 0.48 μWcm^{-2} के पीक ओपन सर्किट वोल्टेज, शॉर्ट सर्किट करंट और पावर घनत्व का उत्पादन किया। डिवाइस ने कम से कम 2000 चक्रों तक विद्युत और यांत्रिक दोनों स्थिरता दिखाई। इसे पहनने योग्य वस्तुओं के साथ एकीकृत करके घुटने, कोहनी और पैर से संबंधित विभिन्न मानव जोड़ संबंधी गतिविधियों के लिए इसके प्रदर्शन का प्रदर्शन किया गया। S-PENG से उत्पन्न ऊर्जा कैपेसिटर को केवल 100 सेकंड में ~650 mV तक आसानी से चार्ज कर सकती है। डिज़ाइन किए गए एस-पीईएनजी ने सरल मानव गतियों से ऊर्जा संचयन में काफी संभावनाएं दिखाईं।

पीजो-कैपेसिटिव सेंसर के रूप में $PVDF_{79}PU_{21}$ नैनोफाइबर के प्रदर्शन ने 8 kPa दबाव उत्तेजनाओं के लिए 0.3 kPa^{-1} की उत्कृष्ट संवेदनशीलता के साथ मल्टीमॉडल प्रतिक्रिया दिखाई, 0-40% चक्रीय तनाव के लिए 0.5-0.75 के बीच एक अच्छा गेज कारक (GF), और 30-60 ^oC के लिए 0.8% $^oC^{-1}$ और 60-100 ^oC के लिए 2% $^oC^{-1}$ की उच्च संवेदनशीलता। इनका उपयोग 0.9% $^oC^{-1}$ की संवेदनशीलता के साथ 37 से 40 ^oC की सीमा में मानव शरीर के तापमान को मापने के लिए किया जा सकता है। $PVDF_{79}PU_{21}$ नैनोफाइबर आधारित पीजो-कैपेसिटिव सेंसर के प्रोटोटाइप को उच्च संवेदनशीलता के साथ विस्तार और लचीलेपन की गतिविधियों को मापने के लिए शरीर के विभिन्न हिस्सों से जोड़ा गया था, जिसने पहनने योग्य सेंसर के रूप में इसकी महान क्षमता को दिखाया।

पॉली (एक्रिलोनिट्राइल) (पैन) में पॉली (विनाइलिडीन फ्लोराइड) (पीवीडीएफ) की तुलना में अधिक द्विध्रुव क्षण (3.5 डी) होता है, इसलिए, इसमें पीजोइलेक्ट्रिक नैनोजेनरेटर और दबाव सेंसर के रूप में उपयोग की एक मजबूत क्षमता है। हालाँकि, मजबूत द्विध्रुव-द्विध्रुव प्रतिकर्षण के कारण, नाइट्राइल समूहों को ज़िग-ज़ैग कॉन्फ़िगरेशन में संरेखित करना मुश्किल होता है जिसके परिणामस्वरूप यांत्रिक

ऊर्जा को विद्युत ऊर्जा में परिवर्तित करने की प्रणाली की क्षमता कम हो जाती है। इस समस्या के समाधान के लिए, ZnO नैनोकणों (ZnP) और ZnO नैनोवायरों (ZnW) को PAN फिल्मों में शामिल किया गया। PAN के साथ ZnO नैनोस्ट्रक्चर की मजबूत अंतःक्रिया के कारण, द्विध्रुव-द्विध्रुव प्रतिकर्षण कम हो गया जिसके परिणामस्वरूप PAN की ज़िगज़ैग संरचना में वृद्धि हुई। ZnP की तुलना में, ZnW में पैन नाइट्राइल समूहों का बेहतर संरेखण और तनाव को हटाने के बाद द्विध्रुवों की तेजी से छूट देखी गई। बिना किसी बाहरी पोलिंग के, PAN, ZnP-PAN, और ZnW-PAN फिल्म आधारित पीजोइलेक्ट्रिक नैनोजेनरेटर क्रमशः 27.6, 79.3 और 86.3 mW/m2 बिजली उत्पन्न कर सकते हैं। 5wt% ZnP और ZnW के समावेश ने उपकरणों की दबाव संवेदनशीलता को क्रमशः 0.9 $fFPa^{-1}$ और 1.1 fFPa-1 तक सुधार दिया, जबकि प्राचीन पैन फिल्म के लिए यह 0.1 $fFPa^{-1}$ था।

इसके अलावा, ज़िगज़ैग संरचना में सुधार के लिए विभिन्न पहलू अनुपात के इन ZnO नैनोस्ट्रक्चर को पैन नैनोफाइबर में शामिल किया गया था। ZnW-PAN नैनोफाइबर ने काफी बेहतर पीजोइलेक्ट्रिक गुणों का प्रदर्शन किया, जिसके परिणामस्वरूप ZnP-PAN नैनोफाइबर पर आधारित उपकरणों की तुलना में 46% और PAN नैनोफाइबर वाले उपकरणों की तुलना में 578% अधिक ऊर्जा घनत्व वाले उपकरण प्राप्त हुए। इसके अलावा, सेंसर डिवाइस में ZnW-PAN नैनोफाइबर का उपयोग उच्च दबाव संवेदनशीलता भी दिखा सकता है। गुणों में इस वृद्धि को ZnO नैनोस्ट्रक्चर की आकृति विज्ञान के प्रभाव के लिए जिम्मेदार ठहराया गया था, जिसके परिणामस्वरूप ZnWs की उपस्थिति में PAN की ज़िग-ज़ैग सामग्री अधिक थी।

इस प्रकार, ZnO नैनोस्ट्रक्चर का उपयोग करके, उन्नत गुणों वाले PAN आधारित पीजोइलेक्ट्रिक उपकरण विकसित किए जा सकते हैं।

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LIST OF SYMBOLS AND ABBREVATIONS

Symbol/Abbreviation	Expanded Form/Term
R	Resistance
F_{EA}	Fraction of electroactive phase
ZnP	Zinc oxide nanoparticle
ZnW	Zinc oxide wires
ν_s	Symmetric stretching vibrations
ν_{as}	Asymmetric stretching vibrations
r_{dc}	Damping coefficient
λ	Wavenumber
V_{OC}	Open circuit voltage
I_{SC}	Short circuit current
V_{SC}	Short circuit voltage
^{o}C	Degree Celsius
ppm	Parts per million
Q	Charge
C_0	Initial capacitance
ΔC	Change in capacitance
ΔP	Change in pressure
S_P	Pressure sensitivity
GF	Gauge factor
MEV	Minimum electrospinning voltage
ν_d	poisson’s ratio of dielectric
ν_e	poisson’s ratio of electrode
l	Length
w	Width
d	Thickness
T	Temperature
S_T	Temperature sensitivity
P	Instantaneous power

P_A	Power per unit area
P_M	Power per unit gram
PU	Polyurethane
PVDF	Poly (vinylidene fluoride)
PAN	Poly(acrylonitrile)
PLLA	Poly (L-lactic acid)
DMF	N, N'-Dimethylformamide
THF	Tetrahydrofuran
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) poly (styrene sulfonate)
SDS	Sodium lauryl sulfate
FE-SEM	Field emission scanning electron microscopy
XRD	X-Ray Diffraction
NMR	Nuclear Magnetic Resonance
DSC	Differential scanning calorimeter
FTIR	Fourier transform infrared
PFM	Piezoelectric force microscopy
AFM	Atomic force microscopy
P-E Loop	Polarization-electric field hysteresis loop
CP/MAS	Cross polarization magic angle spinning
XPS	X-ray photoelectron spectroscopy
FSR	Force based resistance sensor