Abstract

Title: "Investigation of dielectric and optical properties of perovskite materials with possible applications in promising energy harvesting"

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With the pace of modernization, harvesting renewable energy is not an option, it is the ultimate future not only to cope with the day-by-day increasing power need but also to address various severe challenges such as depletion of fossil fuels, alarming increasing rate of environmental pollution, etc. In recent years, the Internet of Things (IoTs) and sensors have brought a revolution in the field of microelectronics. These sensors construct the pillar to maintain our modern life-style and require minimal power to run. Acquiring abundant mechanical energy from our day-to-day life in the form of human motion, acoustic noise, and vibration and converting it to an electrical signal can be an optimum option to power these low-powered sensors. Solar energy is another source of sustainable energy. Harvesting solar and mechanical energy both in a sole unit can serve the purpose on a large scale. Besides, energy harvesting, energy storage is another global concern nowadays. Integrating energy harvesting and storing in a single unit is the new trend.

Organic-inorganic hybrid perovskites have gathered immense attention among recent years owing to their synthesis simplicity, fascinating photovoltaic property, tunable band gap, long carrier diffusion length, etc. In this dissertation, I have synthesized propylammonium lead halide ($C_3H_7NH_3PbX_3$, X = I, Br) via sol-gel method that exhibits excellent stability in the presence of moisture, UV light and temperature. $C_3H_7NH_3PbI_3$ possesses rod-like structure with an optimal band gap of ~ 2.38 eV. An extensive analysis on frequency dependent dielectric properties of $C_3H_7NH_3PbX_3$ over $273\ K \leq T \leq 373\ K$ are performed. $C_3H_7NH_3PbBr_3$ shows giant dielectric constant with an appreciable conductivity. The individual contribution of grain and grain boundary over the total impedance of $C_3H_7NH_3PbI_3$ has been resolved with Maxwell-Wagner equivalent circuit model from the suppressed semicircles appear in the nyquist plots at each temperature. The depressed nature of the semicircles and the asymmetric behaviour of the imaginary part of electric modulus confirm the non-Debye type nature of the samples which varies with the temperature rise. The overall conductivity of the samples has been analysed in detail employing Jonscher's power law. We fabricated a UV photodetector using $C_3H_7NH_3PbBr_3$ that yields significant output.

Polyvinylidene difluoride (PVDF) is one of the most promising ferroelectric polymers due to its cost effectiveness, easy synthesis process and flexibility. The major demerit of this polymer is the dominance of non-polar α phase within it whereas polar β phase plays the key responsibility toward ferroelectricity. To bring out the dominance of β phase within it, assisting external filler is the most convenient methods. We incorporated $C_3H_7NH_3PbI_3$ in PVDF in different wt% by the method of electrospinning to prepare flexible, homogeneous. These nanofibers possess an improved degree of crystallinity with the successful conversion of non-polar phase to polar phase content. We fabricated lightweight, flexible, self-powered piezoelectric nanogenerator that is observed to generate 60 V open circuit voltage (V_{OC}), 27.5 μA short circuit current (I_{SC}), and 9.81 mW/m^2 power under periodic hammering with a free hand. Voltage generation of this nanogenerator scavenging mechanical energy from various sources is also detected. This device exhibits remarkable mechano-sensitivity (~ 6.3 V/N in the low applied force region and 12.12 V/N in the higher applied force region) with superior energy conversion efficiency ~ 42.03 %. The flexibility along with ultra-sensitivity of this power generator initiates its utility as wearable nano sensors. Moreover, the ultrafast capacitor charging ability of the nanogenerator assures its potential as a nano-tactile sensor. The optimal energy band gap and photoactive nature of the $C_3H_7NH_3PbI_3$ @PVDF composite confirm its efficacy as a photodetector/diode. Therefore, the proposed $C_3H_7NH_3PbI_3$ @PVDF composite enables to design a multifaceted device that can perform separately/simultaneously as mechanical energy and solar energy harvester.

Next, we synthesized different self-poled, flexible films of the same perovskite incorporated PVDF composite in larger proportions than that of nanofibers. The inclusion of $C_3H_7NH_3PbI_3$ in PVDF induces significant enhancement of the ferroelectric phase content i.e β phase ~ 66.7 % of the film. The piezoelectric energy harvester (PEH) fabricated using this film generates ~ 80 V open circuit voltage and 17.8 mA/cm^2 short circuit current under hammering with free hand. The flexibility of PEH provides an added advantage for the film to be used as wearable bio-sensor. Moreover, the photo response of the photodetector made of the aforesaid composite is remarkable enough to serve as a piezo-active photo-detector.

Despite exhibiting high piezoelectric response, the aforesaid OIHPs contain toxic lead , though in a very limited proportion along with polymer capping. Here, we synthesized oxide perovskite, $NdMnO_3$, via sol-gel method. We designed piezo nanogenerator using $NdMnO_3$@PVDF films that exhibited significant response of V_{OC} (~50 V) and I_{SC} (~30 μA) under periodic dynamic strain. The output response assures its utility in internet of things (IoTs). The generated energy was stored in commercially available capacitors and was sufficient to glow several green and blue LEDs. The incorporation of sol-gel driven $NdMnO_3$ nanoparticle in PVDF results in enormous β phase formation ~ 89.71 % along with significantly high V_{OC}. To establish the additive contribution of $NdMnO_3$ nanoparticle to the piezoelectric effect, a separate experimental protocol has been designed and perfomed which also supports the piezoeffect of $NdMnO_3$ nanoparticle even though no such experimental support is reported in the literature. This may occur due to the interface mediated strain induced into $NdMnO_3$ nanoparticle making it piezoactive material as it is embedded within PVDF. Moreover degredation of a dye by piezocatalysis exhibited by this film make it a multifunctional composite. The potential self-charging piezoelectric supercapacitor using the same composite as a separator has also been explored which demonstrates energy storing behaviour under the periodic mechanical deformation. The areal capacitance is significant 41.37 mF cm^{-2} and 99% of capacitance retention after 2000 cycles. The study of the overall performance of the device opens a window for fabrication of self-powered piezoelectric wearable devices in union with supercapacitor.

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