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Piezo devices using poly(vinylidene fluoride)/reduced graphene oxide hybrid for energy harvesting

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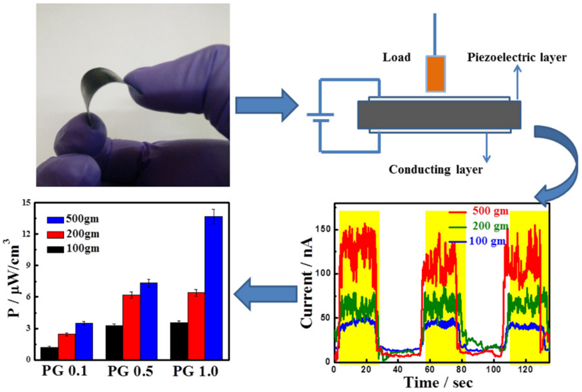
GRAPHICAL ABSTRACT



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ABSTRACT

Harvesting of energy, the continuous human effort throughout history, or reclaim energy from mechanical stress is presented in this work. Reduced graphene oxide, homogeneously dispersed in poly(vinylidene fluoride), induces the electroactive phases in the polar polymer. Good dispersion arising from better interactions between 2-D nanofiller and polymer chain is revealed through transmission electron microscopy and spectroscopic measurement. The induction of electroactive phases in polymer in the presence of nanofiller has been confirmed through structural, spectroscopy and thermal studies. Electroactive phases is confirmed through FTIR peaks at 840 cm^{-1} for β/γ phase and 884 cm^{-1} band for γ-peak in nanohybrid against 796, 876 and 975 cm^{-1} absorption peaks for α-phase in pure PVDF. Morphological alteration (both surface and bulk) reaffirms the change of phases in the nanohybrid vis-à-vis pure polymer. Quantification of different phases has been made, in the presence of varying content of graphene, which is directly reflected in their properties. Greater mechanical and thermal stability of the nanohybrid help promoting this class of hybrid material for device application. Devices have been fabricated to understand the piezoelectric responses from the hybrid materials and output electrical signals (both voltage and current) are measured under mechanical stress applied from a motor driven mechanical setup. Both output voltage and current significantly increase either with greater applied load or graphene content in hybrid primarily due to higher strain produce or better induction of piezo phase, respectively. Moderately high electrical power density up to 14 μW/cm^3 is measured from the device made of the hybrid material, suitable for a number of low power consuming electronic self-power devices and wireless sensors.

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1. Introduction

Poor power density of primary batteries is amongst the core issues of the leading pacemaker manufacturer over the years since its inception where conventional power sources are not a good fit either for medical ground or durability until lithium battery with high energy density was introduced [1–3]. A pacemaker produces electric impulses that are considerably more powerful than the stimulus itself. During cardiac contraction, a small fraction of the energy is released which can be reused as pulse energy, turning the receiver, *i.e.*, the patient into his supplier. This idea started with the quest for powering medical implants from the human body itself. Advancement in micro-fabrication and ultra low-power electronics techniques are now empowering a large range of miniaturized implantable systems for sensing, health monitoring and deficiency treatments [4,5]. Nanodevices and nanosystems usually function at a very low power which falls in the vicinity of nW to μW. Thus, if a small portion of such mechanical vibration could be converted into electrical energy which should be enough to energize low-power biomedical devices [6]. Mechanical or vibrational stress is one of the most abundant energies available in our surroundings that can be reprocessed. It can be from a moving object, a vibrating structure or vibration induced by water flow or air. Mechanical waste energies are commonly harvested through vibration-to-electricity conversion [6–8]. Waste energy harvesting is primarily recognized for low power generations, so its main applications are for low-power electronic devices only. However, the latest advancement in the field of energy harvesting is also useful for large scale applications [9]. Vibration-to-electricity conversion can be achieved by three simple transduction principles, including electromagnetic [10–12], electrostatic [13], and piezoelectric [14,15] transductions.

Amongst the three stated principles, piezoelectric transduction has acknowledged more interest among scientists because of its high power storage capacity and no requirement of external power sources [6,9]. Another benefit over other devices is from its micro-scale fabrication, smooth deposition techniques for thin or thick-films of piezoelectric materials especially polymers [14,16–18]. Various methods have been adopted to alter the configuration of energy harvesting device, like changing the electrode pattern, adding pre-stress to maximize the coupling and applied strain of the material, modification of piezoelectric materials, changing the poling and stress direction and tuning the resonant frequency of the device to get an efficient output. Recent research focuses on improving the effectiveness of power harvesting through various piezoelectric materials [8]. Piezoceramics are vulnerable to high frequency because it develops fatigue crack growth when exposed to cyclic loading [19] leading to a search for tough polymeric materials. Various techniques exist for harvesting energy which includes the use of electromagnetic induction [11], electrostatic generation [13], dielectric elastomers [20], and piezoelectric materials. However, piezoelectric materials have stood out because of their ability to direct conversion of applied mechanical energy into useful electric energy and the simplicity at which they can be electromechanically coupled to an external system. Another advantage of piezoelectric materials is their capacity to withstand a large amount of mechanical strain which makes them an appropriate candidate for power harvesting applications. Approximately 18 μW of power is produced when a pressure produced by a 68 kg weighing human coupled with 500 kΩ load put under the normal walking condition, showing good correlation between the analytical model and experimental data [21].

The need for creating miniaturized, self-powered devices grows with the recent advancement in electronics and computer technology. Some micro scale chips require very less power for its operation which can be provided by the energy generated from micro-scale piezoelectric power harvesters. The size of sensor, the cost of batteries and its cost of replacement can be minimized by integrating power harvesting technology with the wireless sensors [8]. To harvest mechanical energy and to achieve better conversion to electrical energy requires a system that would efficiently couple mechanical vibration or motion to a transduction mechanism.

PVDF films have electroactive properties like, piezoelectricity, pyroelectricity, ferroelectricity etc. which make them a remarkable candidate for energy harvesting applications [22]. Recently, PVDF found its increased application enormously in many fields such as in sensors, actuators, biomedicine, nonvolatile memory, nanogenerators and energy harvesting [22–25]. PVDF crystallizes generally in four types of phases namely, α, β, γ and δ. The piezoelectric properties are exhibited by the β and γ-phases [26]. The γ-phase has a higher piezoelectric coefficient than the β-phase, but the β-phase is found to be more polar [27,28]. γ-phase is more thermally stable than β-phase because of higher melting point making it appropriate for the fabrication of a thermally stable and long-lasting device [29]. However, to use PVDF in piezoelectric energy harvesting applications, many limitations have come up such as the nucleation of the γ and β-phases, mechanical stretching under electric field which makes it difficult for the generation of the batch production in the industry for device applications. Therefore, the best alternate method is to add filler into the PVDF matrix to make a nanohybrid. For improving the functionalities of PVDF, nanofillers have been used for stabilizing the γ/β-polymorphs, thus making the PVDF based nanohybrid as an improved material for piezoelectric energy harvesting. Some research groups have attempted to maximize the harvesting performance by stabilizing electroactive phases by a combination of PVDF with fillers such as graphene [30] MWCNTs [31], CTAB [32], graphene–CuS [33], nanoclay [34], graphene–ZnO [35], PMMA-RGO [36] and ferrite [37]. The choice of materials for energy harvesting is a significant step in order to achieve high efficiencies. The efficiency can be improved by increasing the value of electromechanical coupling factor (k) and mechanical quality factor (Q_M) which are the inherent properties of the piezoelectric materials [17].

Herein, we introduce a facile method to find the piezoelectricity of light weight, low-cost and flexible reduced graphene oxide/PVDF nanohybrid prepared through solution route. The nanohybrid films have shown very good piezo sensitivity against the repetitive load or external pressure. Reduced graphene oxide has been chosen as conducting fillers because of their large surface area, high aspect ratio, superior mechanical, electrical and thermal properties [38]. Owing to its high aspect ratio and excellent electrical conductivity, it is likely to form a microcapacitor if two or more graphene sheets have a compact parallel structure in the hybrid, isolated by a layer of the polymer [39]. Device has been fabricated using the hybrid piezo material and electrical output is measured under applied stress, and finally demonstrated the effect of mechanical stress to produce electricity from waste mechanical sources.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (Sigma Aldrich), graphite flakes (Sigma Aldrich, USA), sodium nitrate and potassium permanganate, Sulphuric acid (H_2SO_4), hydrogen peroxide, hydrazine hydrate, dimethyl formamide were purchased from Merck, Mumbai and were used as received.