1. Introduction

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Recently successful fabrication of ferroelectric flexible nanocomposites has gained vast research interest for their substantial application in low-power, flexible and wearable electronic systems [1-2]. Ferroelectric substances are a kind of material possessing spontaneous polarization in the absence of external electric field which can be altered by application of external electric field. They are also responsive to their structural deformation. They have been widely used for their spontaneous polarization along with their sensitivity in electric, magnetic and optical fields [3-4]. Due to having such features, they have been used extensively for fabrication of capacitors, non-volatile memory, thermistors, light detectors, modulators, trans-polarizers, actuators, filter devices etc. [5]. In this regard, polymer based flexible ferroelectric substances have become well accepted [6]. Polyvinylidene fluoride (PVDF) is basically an electroactive, thermoplastic, fluropolymer possessing many tremendous features like piezo, pyro and ferroelectric properties [7-9]. Such superior qualities have made it an optimistic material for various microelectronic devices [10]. But being a polymer substance, PVDF is a high resistive material along with heavy dielectric loss which creates an obstruction in the path of their device fabrication [11]. So improvement of ferroelectric quality and dielectric permittivity of PVDF without compromising its mechanical flexibility has become the key to successful fabrication of devices [12 – 13]. In this regard, incorporation of various materials in nanoparticle form has become popular choice of researchers to overcome the obstacle. Incorporation of nanofillers to a very certain fraction, improves conductivity abruptly known as percolation threshold [14]. But at the same time, inclusion of nanofillers deteriorates mechanical flexibility of those nanocomposites. Also, relative increase in dielectric loss makes the fabricated device less efficient. So lowering of percolation threshold value becomes necessary to maintain device efficiency along with good conductivity and mechanical flexibility. Recently, conducting nanofillers with high aspect ratio has been added for lowering of percolation threshold by modulating interfacial characteristics of host polymers [15]. One dimensional nanostructures like carbon nanotube (CNT) is capable of lowering percolation threshold greatly but at the expense of agglomeration due to high Van der Waals attraction force which is an obstacle in the path of well dispersion of CNT [16]. Lot of ceramic materials like $BaTiO_3$, $SrTiO_3$ can be used to achieve high dielectric constant but mechanical flexibility. In this regard, fabrication of tri-phase composite is emerging as an alternative to achieve high dielectric permittivity along with conductivity and low dielectric loss.

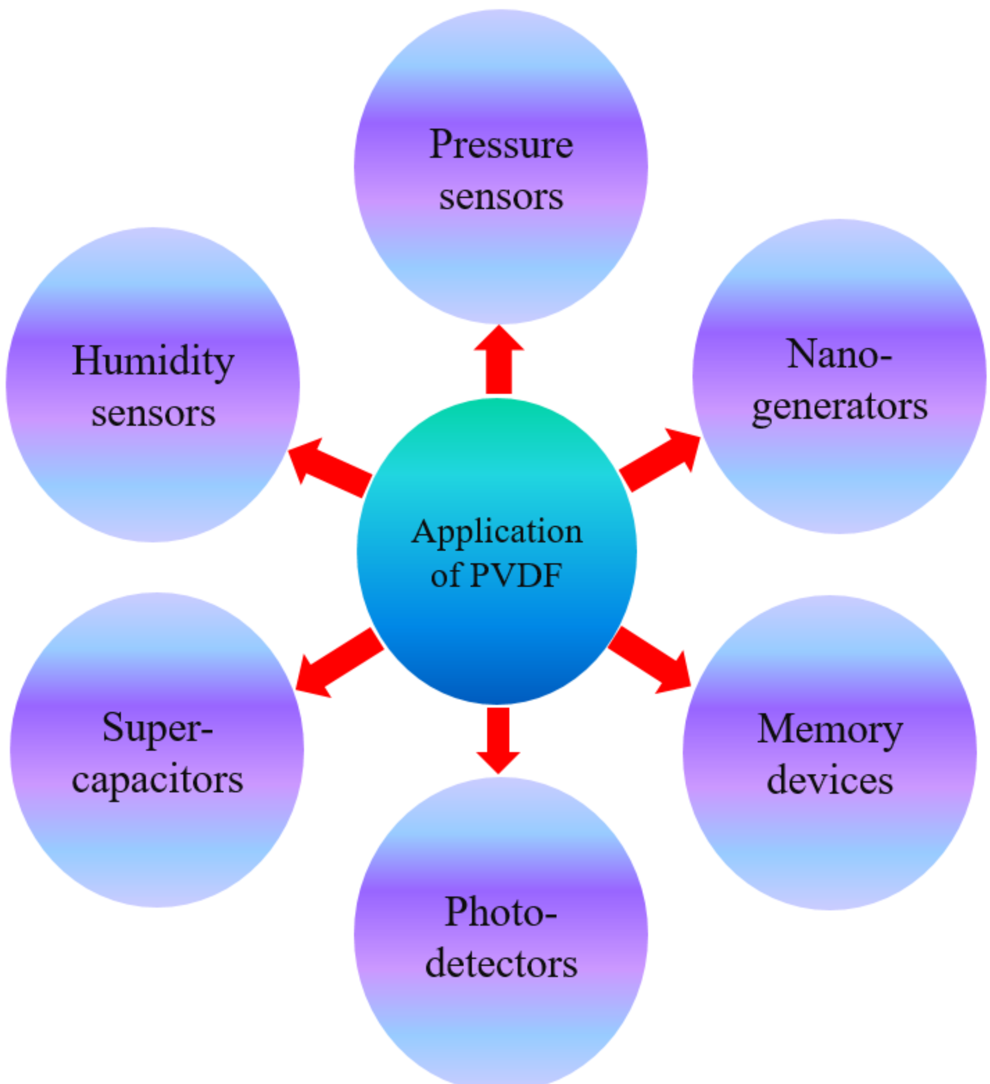

Fig. 1.1 Various applications of PVDF and its composites

Reduced graphene oxide (rGO) or graphene oxide (GO) is a tremendous filler material as enforcement to modulate ferroelectric and dielectric properties of many host materials [17 – 19]. It is a two dimensional hexagonal sheet of sp^2 hybridized carbon atoms similar to graphene but additionally containing oxygen functional groups like hydroxile (-OH), carbonyl (C=O), alkoxy (C-O-C), carboxylic acid (-COOH) and other oxygen functional groups [20]. It has garnered excessive interest in recent times due to possessing many tremendous characteristics like enormous mechanical strength, very high conductivity and carrier mobility, excellent thermal conductivity, good optical transparency, huge specific surface area etc. [21-24]. GO has specific surface area ~ 2600 – 3200 m^2/gm, which can modulate surface polarization and dielectric permittivity of host polymers greatly [25]. Besides, zinc oxide (ZnO) is a well-known piezoelectric material is being used excessively to improve ferroelectric and piezoelectric properties of many host materials for energy conversion and storage devices [26-27]. In ZnO, Zn^{2+} and O^{2-} ions are bonded tetrahedrally to form ZnO_4 group in such a way that the bond along c-axis is relatively longer compared to other 3 bonds resulting in generation of permanent electric dipole moment. Thus ZnO doped nanocomposites can exhibit enhanced ferroelectric characteristics along with better dielectric performance [28 - 29]. So incorporation of ZnO along with GO in PVDF host may be a fruitful triple phase composite for device applications. Moreover, ZnO present there helps in further reduction of GO to rGO through coulomb interaction and also prevents agglomeration [30]. Therefore, development of suitable tri-phase ferroelectric composite by modulating interfacial characteristics can be beneficial for future polymer based dielectric and ferroelectric device applications.

Recently PVDF and its copolymers are going through extensive research owing to their piezoelectric nature and their ability to convert abandoned mechanical energy into usable electric energy to power up many low power electronic gadgets [31]. PVDF and its copolymers belong to efficient piezoelectric polymer category. In spite of being a piezoelectric material with high conversion efficiency, it still lacks in delivering high output power because of random dipolar orientation of the molecules without polling and high resistive nature [32]. Moreover, high conduction loss and ferroelectric loss possess further difficulty to their energy harvesting capability [33]. Therefore, development of composite filled with conducting and polar nanofiller may be a crucial development in the path of fabrication of PVDF based composite for mechanical energy conversion with higher output. In this regard, ZnO has exhibited capability of delivering higher output power to applied mechanical forces [34]. Piezoelectric property in ZnO arises due to distorted bond length of Zn^{2+} and O^{2-} ions. Moreover, good crystalline nature and low resistivity of ZnO further improves their energy delivering capacity. But brittle nature of ZnO won't allow them to undergo enough mechanical stress for their conversion. Therefore, compositing them through flexible polymer based substances emerges as an alternative to utilize their higher power delivering ability. Recent studies have shown that PVDF based hybrid polymers loaded with ZnO nanostructure manifest conversion of mechanical energy more efficiently [35-36]. Further, incorporation of ZnO in PVDF acts as nucleating agent and enhances dielectric constant [37]. Also being a polar material itself, ZnO introduces additional charges increasing concentration of space charges at the grain boundaries [38]. This enhanced space charge accumulation at the boundaries further increases the relaxation time which is helpful in retaining the energy for longer period of time after withdrawal of external disturbance. ZnO helps improving crystallinity of PVDF and also helps in reducing its elastic modulus [39]. Therefore, presence of ZnO in PVDF seems to have improved piezoelectric as well as conducting properties of PVDF to make it a better performing composite in the field of piezoelectric energy harvesting techniques. On the other hand, GO is a material, recently has been used excessively to counter low conductivity of polymers when added to very low amount in those host polymers [40]. Therefore, existence of space charge owing to GO modified surface enhances conductivity of host matrix greatly. Insertion of GO also increases the β-phase content in PVDF due to formation of bonds between functional groups present in GO and fluorine atom in PVDF makes the composite further suitable for piezoelectric applications [41].The strong bond formed between GO and PVDF further improves the tensile strength and hardness of the composite which enables it to undergo enough mechanical stress [42]. Again, presence of ZnO helps in further reduction of GO to rGO due to electrostatic interaction between surface functional groups of GO [43]. In return, rGO helps in better dispersion of ZnO in PVDF. Therefore, introducing both ZnO and GO into PVDF host may improve energy harvesting capability of the tri-phase PVDF/ZnO/GO composite appreciably.

Beside many significant characteristics, PVDF is a polymer with reported band gap of 5.66 eV for indirect transition and 4.96 eV for direct transition [44]. This interesting optical feature helps us to think about development and improvement of PVDF based photo-sensitive composite.

Also their flexibility and transparency will assist in development of photo-detecting composite based on polymer kind of substance. But their very high band gap, high resistivity, large accumulation of charge and their low mobility causes a very little amount of generated charge carriers to reach the electrodes resulting in very low amount of photocurrent [45]. Again random orientation of molecular dipoles in organic polymers makes their response time slow apart from their low responsivity [46]. But recent development of 2D materials have the potential to overcome lot of these shortcomings by providing ultrafast detection, better conductivity, broadband detection and sensivity [47-50]. So introduction of GO into PVDF host may be a good option for modulation of transport as well as optical characteristics [51-52]. Recently GO has been used excessively to enhance responsivity and detectivity of many host materials [53]. Therefore, introduction of GO into PVDF host may improve many of its optical properties as well. Besides, being flexible polymer substance with piezoeelctric property, external mechanical stress will generate additional electric field in form of piezo-potential which provides better separation of generated charge carriers [54]. Thus in mechanically stressed condition, they are able to perform better compared to that in released situation.This makes them further useful because of their adaptability to be used in arbitrary rough surfaces. Very high band gap of PVDF makes it capable of absorbing ultraviolet (UV) radiation but with very poor efficiency because of its organic polymeric nature [55]. But ZnO is a well established UV detecting material owing to its suitable band gap (~ 3.3 eV) [56]. So inclusion of ZnO into flexiblePVDF polymer will make it a suitable composite for developing flexible UV detecting substance. Moreover, high piezoelectric nature of ZnO will produce extra piezo-potential in deformed situation which will aid in separation of UV photo generated carriers [57]. Therefore, combined effect of UV irradiation and mechanical deformation makes PVDF/ZnO composite worthy demonstrating UV piezo-phototronic effect.