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Dielectric and piezoelectric augmentation in self-poled magnetic Fe₃O₄/poly(vinylidene fluoride) composite nanogenerators

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Abstract

One major discipline of contemporary research in energy harvesting and conversion aims in developing lead-free, biocompatible, easily scalable, flexible and high power-density nanogenerators via utilizing poly(vinylidene fluoride) as an electroactive host-network due to its large breakdown strength, interesting polyelectrolyte electrical order and thermoplastic nature. In this work, surface-functionalized magnetite nanoparticles (MNP) of two different size having exotic electret and size-dependent magnetic properties are mixed with PVDF gel to fabricate self-poled composite piezoelectric films, which can obstruct electromagnetic interference also for smart device applications. A four-fold enhancement of its polar β-phase is verified from XRD and Raman spectra against incorporation of Fe₃O₄. Dielectric analysis suggests higher dielectric constant and lower dissipation for the films with tiny MNP embedded in PVDF. The observations are duly validated from first principles studies. The physisorption process is recognized via geometrical optimization of Fe₃O₄/PVDF composite structure and significant amount of charge-transfer is demonstrated by the Mulliken charge-analysis. Open-circuit voltage and short-circuit current attain enhancement up to an order due to adequate ion-dipole and dipole-dipole interactions between the polar nanoscopic surface of Fe₃O₄ and PVDF. Finally, the nanogenerators are employed to light up commercial LEDs.

1. Introduction

The ever-increasing demand of energy in the midst of over-population, industrial uprising, depletion of fossil fuels and environmental hazards such as global warming concerning overuse of conventional energy-sources seems to be a potential threat to civilization. As a result, the thrust in materials research and nanotechnology has bent to the development of renewable alternate energy-sources such as solar, thermal, sonic, mechanical, geothermal, wind and fusion-energy. Eco-friendly energy harvesting and storage using mechanical vibrations or biomechanical movements have been rapidly explored in recent times for development of self-powered wearable & portable electronic devices [1–3] and piezo-/pyro-/triboelectric nanogenerators [4–10]. Recent progress on modulation of the triboelectric surface charge density in polymers by low-energy Helium irradiation/implantation, contact electrification-induced charge transfer and power generation from solid-liquid or liquid-liquid interfaces, and development of integrated piezo photo-transistor & organic field-effect transistors is also noteworthy [11–15]. In this regard, poly(vinylidene fluoride) (PVDF), a highly non-reactive and purely thermoplastic fluoropolymer and its copolymers are the most extensively studied material [16–19]. Pure PVDF in general is a semi-crystalline mixture of five different polymorphs viz., α, β, γ, δ, and ε-phases [20]. Among these, α, β, and γ-phases are predominant and important in technological application point of view. The α-phase has a semi-helical alternate trans-gauche (TGTG) conformation, which although is the most abundant and thermodynamically favourable polymorph, is insignificant in electronic applications due to non-polar nature. Contrarily, β, γ, and δ-phases are polar and thereby electroactive due to parallel alignment of the dipoles. Among all polar phases, the pseudohexagonal β-phase with all-trans (TTTTT) conformation holding high
spontaneous polarization and remarkable piezo-, pyro- and ferroelectric properties is given paramount importance in development of easily scalable polymer-based nanogenerators with high power-density. While handling multi-phase PVDF for such applications, the main challenge is to improve the proportion of β-counterpart. This can be achieved by mainly three ways: (a) mechanical: by application of stress/tension via stretching, bending, twisting or pressing [21]; (b) high electric field poling [22]; and (c) chemical: by adding suitable filler materials [23], that can enhance the mechanical, electrical, thermal or optical properties of PVDF via appropriate ion-dipole or dipole-dipole interactions. The third process is not only cost-effective, but also concerns development of advanced multifunctional nanomaterials, which is noteworthy in materials researchers’ perspective.

Previously many filler-materials having ferroelectric/piezoelectric characteristics and mechanically robust 1D morphologies such as nanorod or aligned fiber structure have been incorporated in different members of the PVDF-family i.e., polymers of vinylidene fluoride (VDF), trifluoroethylene (TrFE), tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE) etc to boost up electromechanical response. Among them, binary oxides/chalcogenides (ZnO, ZnS, CdS), normal & relaxor ferroelectric all-inorganic perovskites (BaTiO3, BiFeO3, ZnSnO3, PbTiO3, and solid solutions of similar materials), organic/hybrid perovskites (CH3NH3PbX3; X = Cl, Br, I), carbon nanotubes (CNT), graphene oxide (GO) & reduced graphene oxide (rGO), Ag-nanoparticles etc have been used vigorously in this regard, which delivered interesting outcomes [24-35]. Im and Park recently developed mechanically robust Fe3O4/PVDF nanofibers to fabricate triboelectric nanogenerators using magnetite as an electret filler [10]. An electret is a dielectric material holding a quasi-permanent electrical charge i.e., the time-constant of the charge-decay is quite longer than the timescale associated with the concerned experiments [36]. Naturally, electrets can enhance the dielectric and electroactive properties of the system by accomplishing a temporal storage of charge. Moreover, Fe3O4 has very consistent size-dependent magnetic properties. Bulk magnetite with an inverse-spinel cubic crystal structure: (Fe3+)3[Fe2+Fe3+]6(O2-)14 holds a ferrimagnetic alignment of magnetic dipoles, due to coexistence of an antiferromagnetic superexchange interaction and a predominant ferromagnetic double-exchange interaction between particular cationic coordinations through the overlapping oxygen orbitals [37, 38]. As the crystallite size decreases below 30 nm, thermal fluctuations play a major role to develop a superparamagnetic response. Polymer-based nanogenerators with embedded magnetic nanoparticles within; can shield electromagnetic interference from the mobile and telecommunication networks, which is highly required in modern smart electronic devices. In this work, first surface-functionallized magnetite nanoparticles (MNPs) of two different sizes with distinct magnetic properties are synthesized and studied. Then an optimized 5 wt% of MNP is incorporated in PVDF matrix followed by duly investigated structural and electrical properties of the composite films. A profound improvement in polarization is demonstrated both from dielectric spectroscopy and first principles calculations. Finally, piezoelectric nanogenerator devices are fabricated to verify the enhancement of the electroactive β-phase and piezo-performance and thereby employed to light up commercial LEDs.

2. Methods & enumeration

2.1. Materials

Analytical grade reagents are purchased and used without further purification. Solvents required for polyol synthesis are ethylene glycol (EG), diethylene glycol (DEG) & polyethelene glycol (PEG). The principle precursors viz., ferric chloride hexahydrate (FeCl3.6H2O), anhydrous sodium acetate (CH3COONa) and hydrated disodium (∆-) tartrate [(CHOHCOONa)2.2H2O] with ≥99.5% purity are bought from SIGMA-ALDRICH. PVDF powder and N,N-dimethylformamide (DMF), used to prepare nanogenerator devices, are also received from the same supplier. Deionised water (~18.2 MΩ) and absolute ethanol from Merck are used for washing.

2.2. Synthesis and fabrication of device

Water-dispersible MNP are synthesized by a facile solvothermal approach. FeCl3.6H2O, (CHOHCOONa)2.2H2O, CH3COONa and PEG-6000 are mixed vigorously by magnetic stirring at 75 °C in a polyol medium. After thorough mixing and ultrasonication for an hour, the homogeneous dirty yellow solution is poured into a teflon lined hydrothermal autoclave and placed in a hot-air oven. Two different size of Fe3O4 nanoparticles are prepared principally by controlling crystal growth using the surfactant cum coating agents: PEG-6000 & disodium tartrate and varying other experimental conditions. The details regarding amount of precursors and synthesis protocol are given in table 1. After the specific reaction-time, the autoclave is taken out and allowed natural cooling. A thorough washing using ethanol & deionized water and vacuum-drying at 60 °C for 5 h produce fine Fe3O4 powder samples.
Table 1. Details of Fe$_3$O$_4$ synthesis.

| Sl. No. | EG + DEG (ml) | FeCl$_3$.6H$_2$O (g) | Disodium tartrate (g) | Sodium acetate (g) | PEG– 6000 (g) | Reaction temperature (°C) | Growth time (h) | Average size (d) of MNP from FESEM micrograph (nm) |
|---------|---------------|----------------------|----------------------|-------------------|---------------|--------------------------|----------------|----------------------------------|
| 1       | 40 + 10       | 1.20                 | 0.10                 | 4.00              | 1.00          | 200                      | 24             | 147.2 ± 2.9                      |
| 2       | 10 + 40       | 1.00                 | 0.50                 | 3.00              | 4.00          | 180                      | 8              | 17.3 ± 2.4                       |
1.50 g commercial PVDF powder and 75 mg magnetite are mixed in a 20 ml solution made of 12 ml acetone and 8 ml DMF and put to magnetic stirring at 85 °C for 2 h. The mixture is carefully transferred onto glass-slides to form thin self-poled homogeneous layers, followed by an overnight vacuum-drying at 80 °C in absence of any prior mechanical disturbance. The bare PVDF film is labelled as S1, whereas composite PVDF films with 5 wt% Fe₃O₄ comprising large and tiny nanoparticles are labelled as S2 & S3 respectively. Finally, the dry films are snatched out of the slides and used to fabricate flexible stand-alone nanogenerators by attaching thin aluminium electrodes in both sides with copper wire contacts.

2.3. Experimental techniques
X-ray diffraction data of MNPs and composite films are acquired using a Rigaku Miniflex powder x-ray diffractometer; operated at 40 kV – 15 mA with 0.5° min⁻¹ scanning speed & 0.02° step-size. A ZEISS Sigma field emission scanning electron microscopy (FESEM) system equipped with a 5 kV electron-gun and 400 k x maximum zoom is used to explore the size-distribution & surface-morphology of the MNPs and quality of the composite films. Finger-print vibrational modes are further detected in Raman spectra collected from a WITec ALPHA300 RS confocal spectrometer in backscattering configuration. A solid-state Nd:YAG laser (532 nm) is used as the excitation source and laser-power is kept limited to 10 mW to avoid oxidation of the embedded MNPs. A 20X Zeiss achromatic objective with 600 groove/mm grating is used to capture data. 10 spectral acquisitions each having 10 s of integration-time are averaged to collect the final spectra having minimal background noise. An Agilent precision impedance analyzer with an operating range of 40 Hz–110 MHz and 42 V maximum bias is used to record impedance spectra. Ag electrodes are deposited in both sides of the films to form a MIM geometry compatible for dielectric analysis. Electroactive response of the as-fabricated piezoelectric nanogenerators is studied by employing a KEYSIGHT InfiniiVision DSOX2012A digital storage oscilloscope.

2.4. Computational details
Within the density functional theory (DFT) framework, as implemented in the well-known Vienna *ab-initio* simulation package (VASP) [39, 40]; projector augmented wave (PAW) technique [41] is employed to describe the individual electron-ion interactions. The exchange-correlation terms are entreated with the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functionals for both DFT and DFT + U approach [42]. The value of U is set to 3.50 eV for the strongly correlated Fe 3d electrons, as suggested in previous reports [43, 44]. The PBE + D2 force field (Grimme’s) method is used for dispersive force corrections [45]. During the geometrical optimization of pristine Fe₃O₄ and PVDF, the first Brillouin zone (BZ) is sampled with a Γ-centered k-point mesh of (6 × 6 × 6) and (3 × 8 × 1) respectively. But, in case of the sufficiently large Fe₃O₄/PVDF composite system, a smaller (1 × 1 × 1) k-mesh is used. All first principles calculations are carried out in spin unrestricted manner. The conventional inverse spinel cubic cell of pristine Fe₃O₄ is used for the theoretical calculations. The lattice parameter is optimized to a = 8.398 Å. For the orthorhombic structure of β-PVDF, optimized lattice-parameters are: a = 8.336 Å, b = 4.910 Å and c = 2.583 Å. To entreat the composite system, the monomer unit of PVDF is placed on the intense (311) diffraction-plane of Fe₃O₄. A vacuum slab of 20 Å length is placed along ‘c’-direction to circumvent the interactions among periodic images. The plane-wave basis set having a cut-off energy of 600 eV is applied and the structures are allowed to be completely relaxed until the energy convergence criterion of 10⁻⁵ eV atom⁻¹ is reached. To calculate charge on individual atoms, Mulliken population analysis is executed using CASTEP (Cambridge Serial Total Energy Package) code [46], taking linear combination of atomic orbitals. During this calculation, Vanderbilt ultrasoft pseudopotential [47] is used and a k-mesh of (1 × 2 × 1) has been chosen.

3. Results and discussion

3.1. Structural characterization of Fe₃O₄ nanospheres and Fe₃O₄/PVDF nanocomposite
XRD pattern of the two samples of magnetite; acquired in a 2θ range: 15°–80° are shown in figure 1. All the diffraction peaks are duly indexed from the JCPDS card no. 85-1436. Absence of any additional peak confirms purity of phase. The vast change in the full width at half maximum (FWHM) clearly depicts the difference in crystallite-size. FESEM images of the two sample are given in figure 2; which show formation of nanospheres. From a Voigt fit of particle-size distribution, average size (d) of the spherical nanoparticles is determined. Diameter of the nanospheres, d = 147.2 and 17.3 nm for the two samples respectively. Using XRD data, the crystallite-size (L) of MNPs can also be calculated employing the well-known Scherrer’s equation:

\[
L = \frac{K\lambda}{\beta \cos \theta}
\]
where $K$ is the geometrical shape-factor; having a typical value of 0.89 for spherical morphology, $\lambda$ is the wavelength of incident X-ray; which is 1.5406 Å for Cu $K_{\alpha}$ source used here, $\beta$ = FWHM of the Bragg-peak and $\theta$ is the angle of diffraction measured in degree. Considering the three most intense peaks of Fe$_3$O$_4$ viz., (311), (440) and (220); average values of $L$ for the two samples turn out (89.2 ± 1.4) and (11.1 ± 5.7) nm respectively. The significantly small crystallite size compared to the particle-sizes obtained from FESEM hint at the polycrystalline nature of the as-prepared samples.

Magnetite has very interesting and regular size-dependent magnetic properties, which has been explored elsewhere in detail [48]. Bulk magnetite or sufficiently large nanoparticles possess typical ferrimagnetism; whereas tiny nanoparticles demonstrate superparamagnetic nature. The principle reason is the size-dependence of the so-called blocking temperature given by,

$$T_B = \frac{K_{\text{eff}} V}{k_B \ln \left( \frac{t_m}{\tau_0} \right)}$$

where $K_{\text{eff}}$ = effective anisotropy energy density, $V$ = particle-volume, $k_B$ = Boltzman constant, $t_m$ = time of measurement and $\tau_0$ = characteristic attempt period of the material. As the particle-size decreases below 30 nm, thermal fluctuations reorient the magnetic dipoles via jumping through the anisotropic energy-barrier rapidly through the course of measurement. So, if the temperature at which experiments are conducted is greater than $T_B$ (which is quite small for tiny nanoparticles), the net magnetic moment averages to zero indicating superparamagnetic behavior. The ferri-/superparamagnetic nature of MNPs can be conclusively determined.

Figure 1. X-ray powder diffraction pattern of the pure Fe$_3$O$_4$ nanoparticles of two different size. The orange and purple curve represent the respective large and tiny nanoparticles. The immense difference between the FWHM for the respective samples demonstrate variation in size.

Figure 2. (a) and (b) FESEM micrographs of the large and tiny Fe$_3$O$_4$ nanoparticles. Frequency versus particle-size plot is fitted using a Voigt probability distribution function to extract average size ($d$).
either from M–H hysteresis pattern or from the area-fraction between quadrupole splitting and magnetic hyperfine interaction in Mössbauer spectra [48–50]. Here from the information regarding size of nanoparticles and crystallites, we urge to conclude, Sample—1 & 2 hold ferrimagnetic and superparamagnetic properties respectively, which can revoke electromagnetic interference if incorporated in smart electronic gadgets.

The successful formation of Fe$_3$O$_4$/PVDF nanocomposite is verified from XRD and Raman spectra respectively, see figure 3. Although pure PVDF (S1) mainly consists of the non-polar $\alpha$-phase, the enhancement of the electroactive $\beta$-phase in S2 and S3 due to incorporation of MNPs is substantial [51]. XRD patterns detect respective Bragg planes in the semicrystalline composite, whereas Raman spectrum is capable of detecting the fingerprint modes of lattice-vibration and can quantitatively be employed to identify the amount of $\beta$-phase in the system. The Bragg planes and phonon-modes detected in the material and corresponding phases are enlisted in tables 2 and 3. Among all, Raman bands at 843 ($\beta$) and 795 cm$^{-1}$ ($\alpha$) are the most intense & significant ones and their intensities can be used to determine the relative proportion of the corresponding phases [52–54].

Figure 3. (a) XRD pattern and (b) Raman spectra of the composite films. Peaks/bands corresponding to particular phases of PVDF and Fe$_3$O$_4$ are designated. Compared to pure PVDF (S1), the $\beta$-signatures are found to uprise along with the magnetite peaks in S2 and S3.

3.2. Dielectric analysis of bare PVDF and Fe$_3$O$_4$/PVDF nanocomposite

All dielectric materials develop polarization in presence of an external electric field and/or mechanical strain. The piezoelectric deformation varies linearly with polarization, and the polarization is again proportional to the dielectric constant. Hence, piezoelectric performance can be roughly estimated from the dispersion of dielectric constant without application of an external bias, as a higher deformation energy should be induced for a larger dielectric constant. Therefore, a thorough dielectric analysis of all the samples is performed to find out the nature of frequency-dispersions of various quantities e.g., impedance ($Z = |Z|e^{j\psi} = Z' + jZ''$, $j = \sqrt{-1}$),
admittance ($Y$), dielectric constant ($\varepsilon_r$) and dielectric loss ($D$), see figure 5. In ac impedance spectroscopy, the dielectric constant is obtained from the capacitive dispersion using the formula,

$$\varepsilon_r = \frac{\varepsilon}{\varepsilon_0} = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} (3)

where $C$ is the capacitance of the MIM structure, $d =$ thickness of the film, $\varepsilon_0 =$ permittivity of vacuum $= 8.854 \times 10^{-12}$ F m$^{-1}$ and $A$ is the effective electrode area. The dielectric constant is quite steady throughout moderate frequencies, unless at the high frequency region ($>10$ MHz), where traps, defects and

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Table 2. X-ray diffraction peaks and corresponding phases.

| $2\theta$ | Bragg planes | Assigned phases |
|----------|--------------|-----------------|
| 17.99°   | (100)        | $\alpha$-phase (PVDF) |
| 19.90°   | (110)        | $\alpha$-phase (PVDF) |
| 26.56°   | (021)        | $\alpha$-phase (PVDF) |
| 39.03°   | (002)        | $\alpha$-phase (PVDF) |
| 20.28°   | (200) and (110) | $\beta$-phase (PVDF) |
| 18.45°   | (020)        | $\gamma$-phase (PVDF) |
| 19.09°   | (002)        | $\gamma$-phase (PVDF) |
| 18.29°   | (111)        | Fe$_3$O$_4$ |
| 29.98°   | (220)        | Fe$_3$O$_4$ |
| 35.45°   | (311)        | Fe$_3$O$_4$ |

Table 3. Raman modes of vibration and corresponding phases.

| Raman shift ($cm^{-1}$) | Modes of vibration | Assigned phases |
|-------------------------|---------------------|-----------------|
| 276                     | CF$_2$ twisting/wagging | $\alpha$-phase (PVDF) |
| 413                     | CF$_2$ rocking       | $\alpha$-phase (PVDF) |
| 609                     | CF$_2$ scissoring    | $\alpha$-phase (PVDF) |
| 795                     | CH$_2$ rocking      | $\alpha$-phase (PVDF) |
| 511                     | CF$_2$ scissoring    | $\beta$-phase (PVDF) |
| 843                     | CH$_2$ rocking      | $\beta$-phase (PVDF) |
| 1272                    | C-C symmetric stretching & scissoring | $\beta$-phase (PVDF) |
| 485                     | CF$_2$ scissoring    | $\gamma$-phase (PVDF) |
| 812                     | CH$_2$ wagging       | $\gamma$-phase (PVDF) |
| 881                     | C-C symmetric stretching | Multiple phases of PVDF |
| 1077                    | C-C symmetric and asymmetric stretching | Multiple phases of PVDF |
| 1172                    | CH$_2$ wagging       | Multiple phases of PVDF |
| 1429                    | CH$_2$ scissoring    | Multiple phases of PVDF |
| 670                     | Fe–O stretching and bending ($A_{1g}$ peak) | Fe$_3$O$_4$ |

Figure 4. FESEM micrographs for the three films. S1 (bare PVDF) is highly uniform, whereas the composite films S2 (PVDF + 5 wt% 147.0 nm Fe$_3$O$_4$) and S3 (PVDF + 5 wt% 17.3 nm Fe$_3$O$_4$) develop some pores and channels surrounding Fe$_3$O$_4$ nanoparticles.
inherent deformations in the system cause a pseudo-increment in the dielectric constant. After magnetite incorporation, dielectric constant has enhanced up to 2 times at moderate frequencies for S3, which depicts the enhancement in the polarity. For this kind of binary systems, the dielectric constant increases mainly due to large dipole-dipole interactions. Besides, electret-doping also helps to store charge on a temporal basis, which results in a higher gain in polarization. On the other hand, dielectric loss-tangent or dissipation factor, which is a measure of relaxation loss in terms of phase-lag between the oscillating dipoles and input waveform, has also increased a bit. Hike in dielectric loss, defined as the ratio of imaginary and real parts of complex permittivity (\( \hat{\varepsilon} = \varepsilon' + j\varepsilon'' \)), given by:

\[
D = \tan \delta = \frac{\varepsilon''}{\varepsilon'}
\]

implies the incapability of the system to store electrical energy and to lose it via dissipating into heat energy. For the composite systems, generally loss increases due to less uniformity, as shown in figure 5(d). However, an identical proportion of tiny nanoparticles induce less dissipation compared to the larger particles, indicating a better dispersion in the PVDF matrix and thus better quality of the film. Hence, use of tiny nanoparticles enhances the efficiency of the system against a lower loss in dielectric relaxation.

To distinguish the resistance correlations between the dopant electret and the thermoplastic polymer-system and for developing a finer insight of the resistance-reactance correspondence, Cole-Cole plots are drawn, see figure 6. For fitting the experimental data, an equivalent circuit model is proposed including a couple of resistors (R) and constant phase-elements (Q), connected as shown in figure 6(a) \([55]\). Fe₃O₄ has a much lower resistance compared to the highly non-reactive insulator PVDF. Moreover, embedded MNPs comprise a different phase-contribution from PVDF. Hence, the proposed circuit can physically designate the nanocomposite system. Capacitive effect (C) can be correlated with Q using the relationship:

\[
C = R \left( \frac{1}{\omega} \right)^{\frac{1}{\pi}} Q^{\frac{1}{\pi}} \tag{5}
\]

where \( \alpha \) is the degree of deviation from the pure capacitive nature. In this model, frequency-dispersive complex impedance is given by,
Based on this formalism, the theoretically simulated Cole–Cole curve develops two semicircular components as shown in Figure 6(b) as an outcome of the contributions from two R–Q subsystems, here the MNPs and PVDF matrix. An absolute semicircle is only possible for an ideal Debye relaxation of non-interacting dipoles. In practice, clearly distinguishable sets of semicircles are rare and mostly the components merge altogether to generate a depressed semicircle, as discussed in Cole-Davidson and Harviliak-Negami models of dielectric relaxation \[56–58\]. Employing this circuit-model, experimental data is fitted using the EC-Lab software as shown in Figure 6(c) with satisfactory values of least-squares goodness of fit. For all samples, resistance of MNPs turn out to be a few hundreds of ohms (consistent for such a half-metallic system), whereas resistance of PVDF has the order of a few tens of MΩ. The radii of the semicircles provide a rough estimation of the overall resistance of the composite systems, which is largest for the sample S2 and smallest for S3.

### 3.3. DFT results and Mulliken charge-analysis to quantify transfer of charge

The optimized composite structure of Fe₃O₄ (311) Bragg plane (most intense in XRD patterns) and monomer unit of PVDF, i.e., vinylidene fluoride (VDF) is shown in Figure 7. The VDF unit gets bonded with the Fe₃O₄ plane via physisorption. The two Fe–F bond-lengths are 2.43 and 2.44 Å respectively. Due to the electrostatic interaction between the two constituents a considerable amount of charge-transfer and thereby development of surface-charge in the long PVDF chains are expected. To verify this proposition, Mulliken charge-analysis is employed on the Fe₃O₄ (311) plane, VDF unit and the nanocomposite structure to find out the amount of charge accumulated in particular atomic sites. By comparing this data, the transferred charge can be calculated per Fe–F bond. For long PVDF chains such bonds will form over the entire length and hence Mulliken charge per formula unit estimates its measure. The key-points are:

i. Mulliken charges are calculated for the Fe and F sites, which are engaged in the newly formed bonds. Also, the charges accumulated in the nearby atomic sites (nearest & second nearest O-sites in Fe₃O₄ and C-sites in PVDF) are provided, see table 4.

ii. The second nearest atomic sites have very small contribution to the net transfer of charge. Because of this trend, contributions from more distant atoms are neglected.

iii. By calculating the difference of charge between the final composite structure and initial state for a distinct atom, the charge-propagation is quantified.

iv. A total of 0.46e and 0.16e charge is transferred from Fe₃O₄ to PVDF via two Fe–F bonds of length 2.43 and 2.44 Å respectively.
v. This strengthens the moment of the tiny dipoles through-out the $\beta$-PVDF structure, which add up altogether and augment polarization.

### Table 4. Mulliken charge accumulation in units of electronic charge at different atomic sites.

| Bonds formed via Physisorption | Atomic sites | Structures | Transferred charge (Composite – Individual constituents) |
|-------------------------------|--------------|------------|------------------------------------------------------------|
|                               |              | Pristine Fe$_3$O$_4$ (311) plane | VDF Unit | Fe$_3$O$_4$ / PVDF Nanocomposite |
| Fe – F Bond - I (Bond-length = 2.43 Å) | Fe (Bonding site) | 0.68e | × | 0.83e | 0.15e |
|                               | Nearest O site in Fe$_3$O$_4$ | -0.65e | × | -0.64e | 0.01e |
|                               | 2nd Nearest O site in Fe$_3$O$_4$ | -0.65e | × | -0.63e | 0.02e |
|                               | F (Bonding site) | × | -0.37e | -0.31e | 0.06e |
|                               | Nearest C site in PVDF | × | -0.40e | 0.06e | -0.34e |
|                               | 2nd Nearest C site in PVDF | × | -0.60e | -0.60e | 0.00e |
|                               | Net Flow of charge from Fe$_3$O$_4$ to PVDF = $\{(0.15+0.01+0.02) - (0.06-0.34+0.00)\}$e | | | | 0.46e |
| Fe – F Bond - II (Bond-length = 2.44 Å) | Fe (Bonding site) | 0.91e | × | 1.00e | 0.09e |
|                               | Nearest O site in Fe$_3$O$_4$ | -0.56e | × | -0.55e | 0.01e |
|                               | 2nd Nearest O site in Fe$_3$O$_4$ | -0.56e | × | -0.56e | 0.00e |
|                               | F (Bonding site) | × | -0.37e | -0.34e | 0.03e |
|                               | Nearest C site in PVDF | × | 0.67e | 0.56e | -0.11e |
|                               | 2nd Nearest C site in PVDF | × | -0.85e | -0.83e | 0.02e |
|                               | Net Flow of charge from Fe$_3$O$_4$ to PVDF = $\{(0.09+0.01+0.00) - (0.03-0.11+0.02)\}$e | | | | 0.16e |

3.4. Piezo-performance of the as-fabricated nanogenerators
Against rapid finger-tapping motion, development of open-circuit voltage ($V_{OC}$) and short-circuit current ($I_{SC}$) is demonstrated in figures 8(a) and (b). The pressure exerted on the nanogenerators is limited to 35 kPa. During the press action, accumulation of electrons at the interface between the film and the electrode gives rise to the voltage peak, which immediately tries to balance the as-generated piezo-potential. As soon as an equilibrium is reached, the voltage falls as shown in figure 8(c). Due to the surface-functionalization, Fe$_3$O$_4$ nanoparticles develop a polar coating all around, which further helps to establish and strengthen ion-dipole and dipole-dipole interactions with PVDF. It favours formation of $\beta$-phase, which improves the proportion of overall polar counterpart in the system. The polarity inversion on reversing the connections prove the piezoelectric effect i.e.,...
the voltage or current development is not a result of a random mechanical disturbance or electrical impulse. Using resistors of the range 10 kΩ–120 MΩ, output voltage (V_{out}) and power density (P) changes are calculated and shown in figure 8(d) for the sample S3. Employing the maximum power transfer theorem, the internal resistance (r) of the nanogenerators can be calculated by fitting the power versus resistance data with a Voigt distribution function. Figure 8(e) depicts the consolidated data for all three samples, comparing the representative parameters of piezo-response viz., V_{OC,max}, I_{SC,max}, r, P_{max} and (I/I_o) from Raman spectra. The trend of as-calculated internal resistance for the samples are in agreement with the dielectric results. The stability and long-cycle durability of the as-fabricated devices are also satisfactory, compared to contemporary literature [26–33]. These nanogenerators can also be utilized to deliver power to electronic equipments by stabilizing the pulsed outputs by employing full-wave rectifiers & voltage regulators and finally storing the charge in high power-density electrostatic capacitors, high energy-density batteries or in supercapacitors having moderate values of both energy & power densities [59, 60].

Comparing all results, the superiority of the sample S3 is conclusive. As the size of MNPs decrease, a number of positive changes occur simultaneously: (a) The surface to volume ratio, being inversely proportional to particle-diameters, hike gradually. Due to larger effective surface/interface area, greater electrostatic interaction comes into action; (b) As the size is controlled via appropriate surface-functionalization, the polar core–shell nanostructures form more homogeneous and uniform composite films, which can build up substantial spontaneous polarization, compelled by externally applied forces; and (c) Thicker hydrophilic and polar shells around the core of the nanoparticles promote development of larger surface-charge [48, 61–63]. The polar nanoscopic surface of the MNPs enhances the electroactive β-phase of PVDF and magnifies piezo-outputs. Besides, here MNPs are superparamagnetic, ideal for electromagnetic interference shielding. However, decreasing size of MNPs indefinitely approaching the quantum regime might increase the agglomeration tendency due to hydrophobic interactions and large surface-energy inside the PVDF-network, pertaining suspension of the piezo-enhancement and dielectric augmentation. Hence smaller particles can be more effective unless the films inscribe discontinuity or local accumulation of the additives. The sample (S3) is further used to light up commercially available multicoloured LEDs. A snapshot of green LEDs shining at gentle pressing on the electrode-surface is given in figure 8(f).

Figure 7. Optimized Fe$_3$O$_4$/PVDF nanocomposite structure: (a) Side view and (b) Top view. Two Fe–F bonds are seen to form in the optimized structure, having bond-lengths 2.43 and 2.44 Å respectively via physisorption and thereby charge-transfer between the Fe$_3$O$_4$ (311) plane and vinylidene fluoride (monomer) unit is promoted. Colour code of respective atoms are H: Off-white, C: Grey, F: Sky blue, Fe: Navy blue, and O: Red.
4. Conclusive remarks

Summarily, Fe₃O₄ nanoparticles of two different size having ferrimagnetic and superparamagnetic nature, are used to fabricate Fe₃O₄/PVDF nanocomposites: S2 and S3. Structural investigation is accomplished from XRD, Raman spectra and FESEM micrographs. Verification of successful formation of nanocomposite and quantitative assessment of different phases of PVDF is done from Raman spectra. Structural characterizations clearly indicate enhancement of electroactive β-phase against incorporation of Fe₃O₄ nanoparticles. Smaller nanoparticles not only form uniformly dispersed high-quality films, but also promote strong dipole-dipole interactions, which helps to attain higher dielectric constant & remnant polarization and control dielectric dissipation or polarization loss, congruent with DFT results. A significant amount of charge-transfer per formula unit is demonstrated by Mulliken charge-population analysis by virtue of physisorption-based linkage. This structural and electrical properties go in agreement with the piezo-response of the samples. Both open-circuit voltage and short-circuit current enhance upto an order compared to the neat PVDF films due to the exposure of magnetite in the system. The PVDF film with tiny nanoparticles embedded (Sample: S3) turn out to hold the most promising piezoelectric properties for nanogenerator applications. The high power-density

Figure 8. (a) Open-circuit voltage and (b) Short-circuit current for all three samples against rapid finger-tapping motion; (c) Charge gain/decay dynamics for a single finger-tap and demonstration of polarity reversal by interchanging electrode connections; (d) Output voltage and power density variation with resistance and use of maximum power transfer theorem to determine the internal resistance of the system using a Voigt fit; (e) Consolidated data and comparison of different characteristic parameters for the three nanogenerators emphasizing superiority of the sample S3; (f) Snapshot of S3 nanogenerator being employed to light up commercial LEDs.
nanogenerators are also utilized to light up commercially available LEDs by applying nominal pressure via finger-tapping.

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