

**Electronic Supplementary Information**

**Flexible piezoelectric energy harvesters using different architectures of  
ferrite based nanocomposites**

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### **E.1. Synthesis of ZF (spherical particle) (ZF-s)**

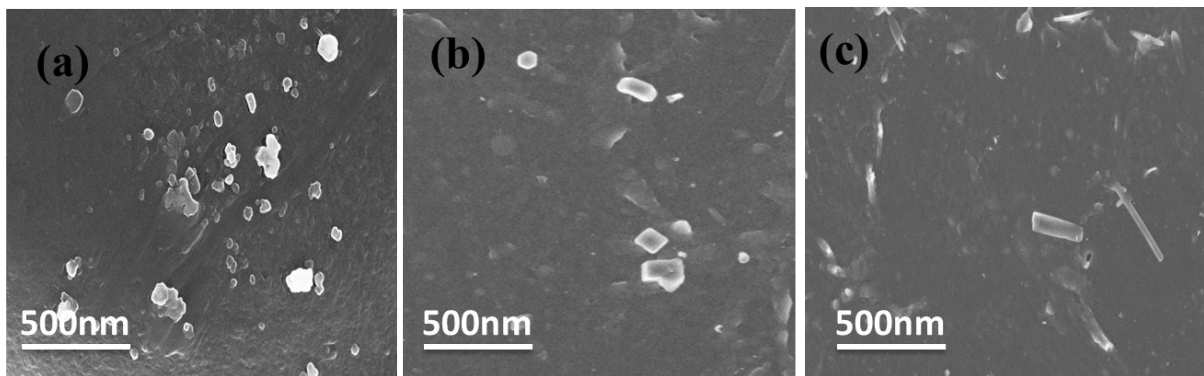
Zinc Ferrite (ZF) nano particles were synthesized by one step hydrothermal technique from their Nitrate salt solution ( $Zn^{2+}/Fe^{3+}$  was 1:2 mole ratio, 1.49 g of Zinc Nitrate Hexahydrate and 4.04 g of Iron (III) Nitrate Nonahydrate) using 50 ml Ethylene Glycol (Merck,  $\geq 99.0\%$ ) as media and 3ml of Poly(ethylene glycol)-400 (Merck, 99.5%) as chelating agent to prevent the aggregation of the nanoparticles. Nitrates solution were ultra-sonicated for 1h and then the suspension was transferred into a stainless-steel Teflon lined autoclave for hydrothermal treatment and the cup was sealed and maintained at  $150^{\circ}C$  for 10 h. The resulting dark brownish precipitate was collected by centrifugation twice (Remi, PR-24 model, 10,000 rpm for 15 mins each times) after cooling to room temperature, washed with water (400 ml of DI water was in total) and absolute Ethanol (Merck,  $\geq 99.9\%$ , used as solvent) alternatively for five times (8 ml of Ethanol used for each step). The precipitate was further dried in an oven at  $60^{\circ}C$  overnight.

### **E.2. Synthesis of ZF nanocube (ZF-c)**

ZF-c has been synthesized by following Oleate precursor route. Detailed procedure was described by D. Maity and coworkers.<sup>S1r</sup> In brief, first Sodium Oleate was synthesized using 4 g of Sodium Hydroxide (Merck Emplura,  $\geq 97\%$ ), 20 ml of Oleic Acid (Merck, 99.5%) and 200 ml Ethanol (Merck,  $\geq 99.9\%$ , used as solvent). Then Iron and Zinc Oleate was synthesized using this 12 gm Sodium Oleate, 4.04 gm Iron and 4.04 gm Zinc Nitrate respectively in refluxing condition (25 ml double distilled water, 75 ml of Ethanol and 100 ml of Hexane (Merck, 97%) were mixed together for each metal oleate synthesis and refluxed at  $70^{\circ}C$  for 4 h). Further, ZF was synthesized from two metal oleates (2:1 mole ratio, 0.25 mmol Iron (III) Oleate and 0.125 mmol Zinc Oleate) in excess Oleic Acid (0.25 mmol, 72  $\mu$ l) and 6 ml of 1-Octadecene (Sigma-Aldrich,  $\geq 95\%$ ) as solvent through solvothermal technique at  $300^{\circ}C$  for 3 h. At the end of the reaction, the solution was cooled down, the precipitate was

separated by precipitation-redispersion method by dissolving first in minimum amount of Chloroform (MerckEmplura,99.9%) and then Ethanol to further precipitate the nanoparticles. The procedure was carried out twice, washed thoroughly for five times using 40 ml of Ethanol and dried at 80°C overnight.

### E.3. Results and discussion (supplementary)

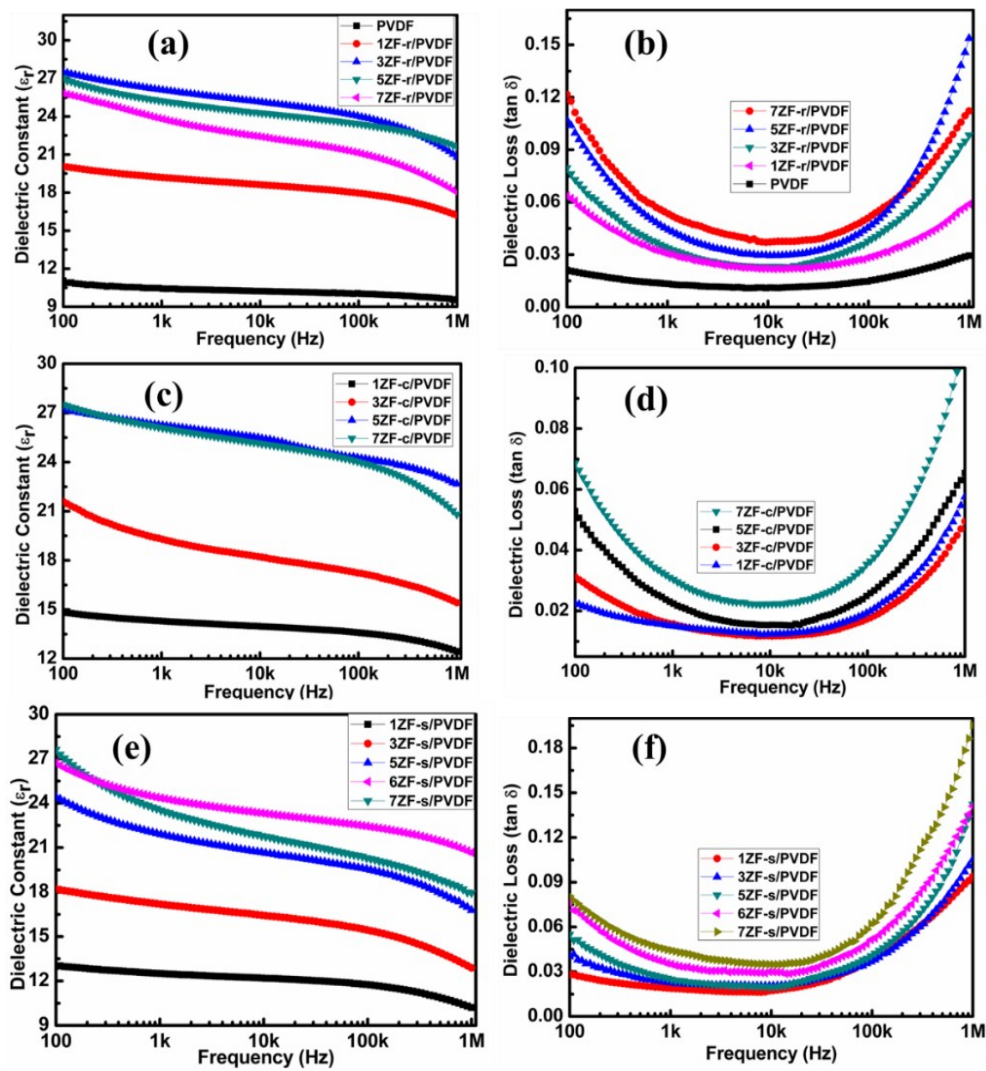


**Fig.S1a-c** FESEM micrograph of **a.** spherical, **b.**cube and **c.** rod, shaped ZF- PVDF composites

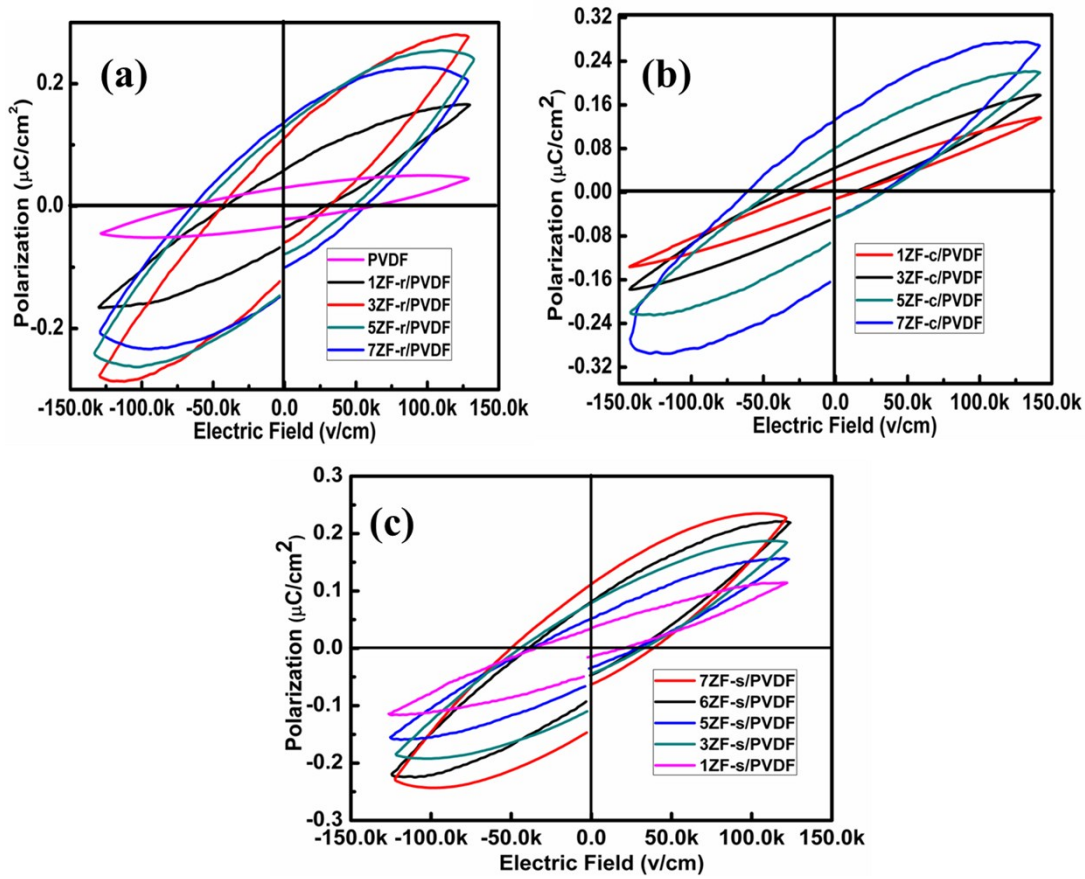
As observed in **Fig. S1a-c**, ZF-r nanostructures were well-dispersed in the PVDF matrix under the low doping concentration. The *'inplane'* orientation of the nanorods also was exhibited in **Fig. S1c**. The spherical shaped nanostructures are more prone to agglomerate compared to other two shaped ZFs which may due to maximum surface energy of this particular structure.

The variation of dielectric constant and associated tangent loss of composites with increment in filler concentration in polymer matrix was investigated (showed in **Fig. S2 a-f**) to determine the dielectric percolation threshold. The improvement in dielectric permittivity followed a similar trend of  $\beta$  phase, i.e., improved linearly with increase in filler concentration, reached to its highest value (for rod at 3wt%, for cubic at 5wt% and for spherical at 6wt% ZF incorporation) and then decreased. The tangent loss values varied with nanoparticle concentration within the measured frequency range. Although the value of

tangent loss was very high for rod shaped structure based composite compared to other structures, but at lower filler concentration the value is in permissible limit. But after reaching the maximum value, the formation of conducting network through the tunnelling of electrons from one ZF surface to its closer one, adversely affected the dielectric loss of composite.<sup>S2r-S4r</sup> Comparing above results, incorporation of low weight fraction rod shaped ZF nanostructure in PVDF matrix is the best choice for fabrication of high dielectric composite.



**Fig.S2a-f** Variation of dielectric constant and dielectric loss of different filler fraction loaded rod, cube and spherical shaped ZF- PVDF composites



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**Fig.S3a-c** P–E hysteresis loops at 1kV electric field with addition of ZF nanostructure for all composites

In each set (described in **Fig. S3 a-c**), with the addition of filler, increment in electrical polarization was observed. But there was a threshold concentration for each set upto which this increment (3wt% (for rod shaped ZF/PVDF composite), 5wt% (for cubic shaped ZF/PVDF composite) and 6wt% (for spherical shaped ZF/PVDF composite)) was noticed. After reaching the threshold concentration, increment in  $P_r$  value and a reduction in  $P_m$  value was noticed i.e. the loops appeared more loopy in nature. This further supported our previous assumption of internal conductive pathway formation after threshold concentration which caused rapid increment in dielectric loss and the dielectric composite transformed to a conducting material.

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S2r. S. Maji, P. K. Sarkar, D. Mandal, G. Sheet, L. Aggarwal, S. K. Ghosh and S. Achary, *Phys. Chem. Chem. Phys.*, 2015, **17**, 8159-8165.

S3r. Y. Li, X. Ge, L. Wang, L. Wang, W. Liu, H. Li, R. K. Y. Li and S. C. Tjong, *Curr. Nanosci.*, 2013, **9**, 679-685.

S4r. H. J. Butt, B. Cappella and M. Kapp, *Surf. Sci. Rep.*, 2005, **59**, 1-152.