Electronic Supplementary Information (ESI)

Effect of γ -PVDF on Enhanced Thermal Conductivity and Dielectric Property of Fe-rGO

incorporated PVDF Based Flexible Nanocomposite Film for Efficient Thermal

Management and Energy Storage Applications

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1. Experimental Section

1.1. Preparation of graphene oxide (GO)

We have synthesized graphene oxide (GO) by oxidizing natural graphite following modified Hummer method.¹ Briefly, 8 g graphite powder and 4 g NaNO₃ were well mixed followed by the addition of 368 ml concentrated H_2SO_4 (98%) in an ice bath. After that, mixture was stirred uniformly followed by sonication for 1 h. Then, KMnO₄ (48 g) was added to the mixture under stirring condition below 20 °C temperature. The solution mixture was stirred for 24 h at room temperature. After that ice cold distill water (1000 ml) was added to the mixture with constant stirring. Ultimately, 30% H_2O_2 was added drop wise until the color of the mixture transferred to bright yellow and continued the stirring for another 1 h. The mixture was left for overnight and then filtered, washed by centrifugation for several times using 5% HCl and distilled water until the solution became neutral. Lastly, the oxidized graphite was washed many times with ethanol and dry in vacuum oven at room temperature for 3 days to obtain the final product.

1.2. Synthesis of Fe-rGO

Fe and/Fe-oxide contain reduced graphene oxide (Fe-rGO) was prepared by reducing GO using iron powder and HCl.² Firstly, the prepared GO (0.5 mg/ml) was dispersed in 200 ml distilled water and ultrasonicated (OSCAR Model PR-250; Ultrasonic Power, Frequency 25 kHz, diameter of Probe Tip is 6 mm) for 1h. Next, 2 g of Fe powder was added to the suspended GO and ultrasonicated for 1h. Later, 50 ml of HCl solution (35%) was added in the suspended mixture of GO and Fe powder and stirred for 2h at 50 °C temperature. The resulting solution was centrifuged and the residue was washed with distilled water (to maintain pH \approx 7) and ethanol for several times. Finally, the obtained black solid was dried in vacuum oven at 90 °C for 24 h. We

assume that during the reduction process, some Fe and/or Fe-oxides particles have been present into the surface of rGOs as confirmed by EDAX (Fig. S9A) and XPS analysis. We assume that, Fe not only reduced the GO to rGO, but also remain present in rGO as an impurity. Some Fe particles were present in the rGOs as Fe and/ or Fe-oxides as confirmed from XPS (Fig. S1C and D), EDAX (see Fig. S9), X-ray mapping (Figs. S3 and S5) study. Mixture of Fe and/ or Feoxides containing rGO is referred as Fe decorated rGO (Fe-rGO) in the manuscript.

2. Results and Discussion

2.1. Verification of GO and Fe-rGO

A high intense peak at $2\theta \approx 10.50^{\circ}$ and a small broadened peak at $2\theta \approx 23.29^{\circ}$ was observed in XRD (Fig. S1A) signifying the formation of GO and Fe-rGO, respectively.² A less intense peak (due to very less amount of Fe atom, ≈ 1.2 atomic percent) at $\approx 35.69^{\circ}$ can be indexed to (110) plane of Fe₂O₃ (JCPDS card No- 01-073-0603). That peak may also be attributed to (311) plane of Fe₃O₄ (JCPDS card No- 01-074-1910) since both the planes have nearly same diffraction angles. Raman spectra (inset in Fig. S1A) illustrates that, the G and D band of GO were appeared at 1591 cm⁻¹ and 1353 cm⁻¹, and for Fe-rGO those are appeared at 1583 cm⁻¹ and 1343 cm⁻¹ respectively. In case of Fe-rGO, both the bands are shifted towards the lower frequency probably due to the recovery of the hexagonal network of carbon atoms with defects. The (I_D/I_G) was increased from 0.93 to 1.10 (GO to Fe-rGO) is due to the decrease in average size of the sp² domain during reduction of GO.²⁻⁴



Fig. S1. (A) X-ray diffraction patterns of GO and Fe-rGO and (B) FTIR spectra of graphite, GO and Fe-rGO in the region of 4000–600 cm⁻¹. (C) XPS survey spectra and (D) (deconvoluted) C1s spectra of GO and Fe-rGO respectively. Inset of Fig. 2A and C represents the Raman spectra and energy spectra of Fe_{2p} (showing oxidation state and satellite formation), respectively.

In the finger print region of FTIR spectra (Fig. S1B) the spectrum of the graphite is featureless, while the presence of absorption bands at 1054 cm⁻¹ (C–O–C stretching vibration of epoxy groups), 1228 cm⁻¹ (C–OH stretching vibration), 1412 cm⁻¹ (C–O–O deformation), 1613 cm⁻¹ (O–H bending of C–OH), 1730 cm⁻¹ (carbonyl or carboxyl stretching vibration) and a broad peak at 3361–3100 cm⁻¹ (stretching vibrational modes of hydroxyl group) are the indication of formation of GO. In addition, peaks in the region of 1060–1015 cm⁻¹ in the GO are assigned to – CH–OH groups, due to the oxidation of graphite and from the bulk graphite.^{5,6} After the

reduction, the absorption peak intensity of the oxygen containing functional groups remarkably decreases as compared to that of GO, indicating effective reduction has been occurred in presence of Fe/HCl. The intensity of O1s in rGO is reduced compared to the GO as confirmed from XPS study (shown in Fig. S1C and D). The increasing trend of C/O ratio from GO (2.0) to rGO (6.9) is the indication of formation of rGO. XPS survey scans spectra (Fig. S1C) also reveals the same characteristic result for the confirmation of reduction of oxygen percent from GO to Fe-rGO. The five different peaks have been observed at 283.7, 285, 286.2, 287.7 and 288 eV both in GO and rGO which are the corresponding values of the sp²C, sp³C, -C-O, -C=O and -COO- groups, respectively.² The intensities of C1s spectra is drastically increased in Fe-rGO compared to the GO after the reduction. Fig. S1D shows that, the sp² C peak intensity increases and sp³ C peak intensity decreases in case of Fe-rGO compared to that of GO. The oxygen functionalities are drastically reduced and most of the conjugated type rGO network has been restored after the reduction of GO. The narrow XPS spectrums of Fe-rGO (inset in Fig. S1C) are the indication of Fe_{2p} that reveals Fe can exists (≈ 1.2 atomic percent) in different oxidized forms. A very less intense peaks at 707 eV, and a more intense peaks at 710.6 and 724.1 eV are assigned to Fe, Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively. Thus, we assume that the Fe/Fe-oxides particles are incorporated in rGOs surface during the reduction. The charge transfer satellite also occurred for Fe 2p_{3/2} at 719.9 eV with the formation of different oxide states of Fe (II and III) in the Fe-rGOs.^{7,8} The sheets like structure and Fe-oxides particle are visible in FE-SEM (Fig. S2A) and HR-TEM (Fig. S2B) images confirmed the formation of Fe-rGO. The distribution of O, C, F and Fe atoms in Fig. S8 and EDAX analysis of these atoms in Fig. S9B clearly indicate the presence of Fe-oxides in the nanocomposite. The SAED patterns of Fe-rGO also support the decoration of Fe-oxides particles on the surface of rGO as shown in inset of Fig. S2B.



Fig. S2. FESEM image of (A) shows wrinkled (yellow dotted circular line) type of morphology of rGO and (B) HRTEM image of rGO shows the presence of Fe-oxides (red dotted circular line) particles. The inset of Fig. B shows the SAED patterns of Fe-rGOs.



Fig. S3. FE-SEM image of (A) Fe-rGO with X-ray mapping shows the distributions of (B) C atoms, (C) O atoms and (D) Fe atoms respectively.

2.2. Evidence of γ-phase formation

The crystalline γ -phase can be confirmed from FTIR and XRD studies were given in Fig.



Fig. S4. (A) FTIR spectra and (B) X-ray diffraction patterns of Fe-rGO/PVDF nanocomposite film at different Fe-rGO loadings.

The relative proportion of γ -phase has been calculated by the following equation:^[9]

$$F_{(\gamma)} = \frac{\chi_{(\gamma)}}{\chi_{(\alpha)} + \chi_{(\gamma)}} = \frac{A_{(\gamma)}}{(K_{(\gamma)}/K_{(\alpha)})A_{(\alpha)} + A_{(\gamma)}}$$
(1)

where, A_{α} and A_{γ} signify the absorption intensity of α and γ -phases (at 764 and 833 cm⁻¹), respectively. X_{α} and X_{γ} are the corresponding crystallinities of α and γ - phases, respectively. K_{α} and K_{γ} are the corresponding absorption co-efficient having the values of 0.365 and 0.150 μ m⁻¹, respectively.⁹

S2.



Fig. S5. (A) Relative proportion of γ -phase (%) formation for PVDF and Fe-rGO/PVDF nanocomposite at different Fe-rGO loadings calculated using the above equation 1. (B) Raman spectra of Fe-rGO and 1.5Fe-rGO/PVDF nanocomposite in the region of 1000–2000 cm⁻¹.

We see that, the relative proportion of γ -phase gradually increases with the increasing of Fe-rGO loading (Fig. S5A).

Raman spectra (Fig. S5B) confirmed the interaction between Fe-rGOs and PVDF. The value of G band is shifted towards right from 1583 cm⁻¹ to 1599 cm⁻¹ (3.0 Fe-rGO/PVDF) nanocomposites. In another side, the I_D/I_G ratio slightly decreases (from 1.10 to1.04) with respect to Fe-rGO, is the indication hexagonal network structure restoration in the nanocomposites. Because of the presence of $-CH_2-/-CF_2-$ dipoles in PVDF the charge dissimilarity has been occurred where some $-CH_2-/-CF_2-$ dipoles are attract/repelled, providing the formation of γ -phase.

2.3. Calculation of γ crystallites size (D_{γ}) from the XRD analysis

The γ -crystallite size (D $_{\gamma}$) can be calculated from the XRD data (Fig. S6) using the method of deconvolution by the using Debye-Scherrer formula:

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{2}$$

where, *k* is the constant (0.89), λ is the wavelength (0.1540 nm) of the X-ray diffraction, β is the full width half maximum (FWHM in radian) of the intense diffraction peak and θ is the angle of diffraction. The value of (D_{γ}) gradually decreases with increasing the filler loading and obtained average values are 10.02 nm, 8.71 nm, 5.05 nm, 4.60 nm and 4.29 nm for 0.0, 0.3, 0.6, 1.5 and 3.0 loading of Fe-rGO of the nanocomposite, respectively.



Fig. S6. The curve deconvolution of XRD pattern in the 14–30° (20) range of PVDF and FerGO/PVDF nanocomposite at different FerGO loadings. The size of γ -crystallites (D_{γ}) is increases with the increasing of Fe-rGO loading is depicted within the Fig. S6.

The percentage of γ -phase increases with the decreasing crystallite size signifying the increase in surface area of the crystallites in the nanocomposite compared to that of pure PVDF. This increases the contact points between the crystallites and thus, improves the heat transfer property of the Fe-rGO/PVDF nanocomposite.



Fig. S7 DSC cooling curves of PVDF and PVDF nanocomposite at different Fe-rGO loadings.

2.4. FESEM and EDAX analysis



Fig. S8. FE-SEM image of (A) PVDF nanocomposite with X-ray mapping shows the presence and distributions of (B) F atoms (B), C atoms (C) O atoms and (D) Fe atoms (D), respectively.



Fig. S9. EDAX spectrums of 3.0Fe-rGO/PVDF nanocomposite under (A) HR-TEM and (B) FE-SEM study. It exhibits the presence of carbon (C), oxygen (O), fluoride (F) and iron (Fe) in the nanocomposite.



2.5. Ferroelectric study

Fig. S10 (A) *D-E* loops of PVDF, PVDF nanocomposite at different loadings. The Fig. (B) represents the D-E loop, shows the released energy density and energy loss density.

Table S1. The prepared Fe-rGO/PVDF nanocomposite shows high thermal conductivity

Filler in PVDF	Percent of Fillers	Thermal Conductivity (W/mK)	References
Graphene Sheet	10 wt%	0.87	[10]
Al ₂ O ₃ coated GS	40 wt %	0.58	[11]
Reduced Graphene	10 wt %	≈0.357	[12]
Functionalized graphene sheet-Nano diamond	35 wt % hybrid filler (5 wt % FGS)	0.45	[13]
Fe-rGO	3 wt%	0.89	Present Work

compared with the PVDF/graphene system published in the literature.

Table S2. T_m , T_c , ΔH_m and χ_c values of PVDF and Fe-rGO/PVDF nanocomposite film at different Fe-rGO loadings.

Fe-rGO loading	$T_{(0C)}$	$T_{\rm c}(0,\mathbf{C})$	$\Lambda H_{(1/\alpha)}$	(0/)
(wt%)	I_m (°C)	$I_c(^{\circ}\mathbf{C})$	$\Delta \Pi_m(\mathbf{J}/\mathbf{g})$	χ_c (70)
0.0	165.0	130.6	43.7	42
0.6	165.6	134.8	42.6	41
1.5	165.8	135.6	42.2	41
3.0	166.9	136.3	41.8	40

Dielectric Property		Fillers (wt%) in PVDF	References	
Constant (ɛ")	loss (ɛ")	matrix	Kererences	
57 at 1kHz	0.06	Fe-rGO	Present work	
21	0.07	BT-SAND	[14]	
11	0.07	7 wt% Graphite NS	[15]	
56	0.06	NH ₂ -GND/RGO	[16]	
58	1.5	11 wt% MgO	[17]	
21	0.7	Silver-NPs	[18]	
37	0.5	30 vol% of CBT	[19]	
52	0.10	Graphene/PANI	[20]	
pprox 20	-	20 wt% ZnO	[21]	

Table S3. The prepared nanocomposite exhibit superior dielectric property compared with

 published literature.

Table S4. The values of U_R , U_L , U_T , efficiency, D_{max} and D_r of Fe-rGO/PVDF nanocomposite film at different Fe-rGO loadings, obtained from D-E loop measurement.

Fe-	Released	Energy	Total Energy			Remnant
rGO	Energy	Loss	Density (U_T)	Efficiency	Maximum	Polarization
(wt	Density	(U_L)	$= U_R + U_I$)	$(U_R/(U_R+U_L))$	Polarization	D_r)
%)	(U_R)	(J/cm^3)	(J/cm^3)		$(D_{max}(\mu C/cm^2))$	(µC/cm ²)
, , ,	(J/cm ³)	(0,000)	()			
0.0	0.27	0.17	0.45	0.60	0.35	0.03
0.3	0.47	0.29	0.76	0.62	0.50	0.06
0.6	0.56	0.35	0.91	0.62	0.70	0.09
1.5	0.77	0.50	1.27	0.61	0.98	0.14
3.0	1.45	0.88	2.33	0.62	1.70	0.26

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