Supplementary Information

Preparation of graphene oxide nanosheets (GONS)

Graphene oxide nanosheets (GONS) were prepared from purified natural graphite powder using an improved Hummer's method reported by Marcano et al.[1] Briefly, 1 g of graphite flakes and 6 g of $KMnO_4$ were added into a 135 ml:15 ml mixture of H_2SO_4/H_3PO_4. The resulting mixture was stirred at 50°C for 12 h. Afterwards, the mixture was cooled down to room temperature and then poured onto a mixture of 200 ml of ice and 1 ml of 30% H_2O_2. The graphite oxide was washed and centrifuged with water, HCl, and ethanol sequentially and the supernatant was decanted. The remaining solid was filtered over a PTFE membrane (0.45 µm pore size) and vacuum dried overnight at room temperature (Figure S1:A1).

Preparation of functionalized graphene oxide nanosheets (FGONS)

In a typical procedure,[2, 3] 4 ml of oxalyl chloride $(COCl)_2$ was added drop-wise to a homogenous suspension of 100 mg of graphene oxide in 100 ml of dimethylformamide (DMF) at 0°C under nitrogen. The resulting mixture was initially stirred at 0°C for 2 h followed by two more hours at room temperature. Subsequently, in order to remove the excess $(COCl)_2$, the mixture was heated to 70°C overnight under stirring. Thereafter, the intermediate product (i.e., acyl-chloride functionalized GONS) was washed with anhydrous toluene three times. Finally, the acyl-chloride functionalized GONS was re-dispersed in 40 ml of DMF and allowed to react with 40 mg of 3,5-di(trifluormetyl)-aniline in the presence of 1.5 ml of triethylamine (Et_3N) at 130°C for 72 h under nitrogen.

After the reaction was complete, the solution was cooled to room temperature, and then poured into 300 ml of anhydrous ether to precipitate the product. The resulting mixture was filtered through a 0.2-mm pore-size membrane and washed thoroughly with DMF, ethyl alcohol, and deionized (DI) water, sequentially. The 3,5-di(trifluormetyl)-aniline-functionalized graphene oxide nanosheets (FGONS) were collected from the membrane and vacuum-dried overnight (Figure S2:A2).

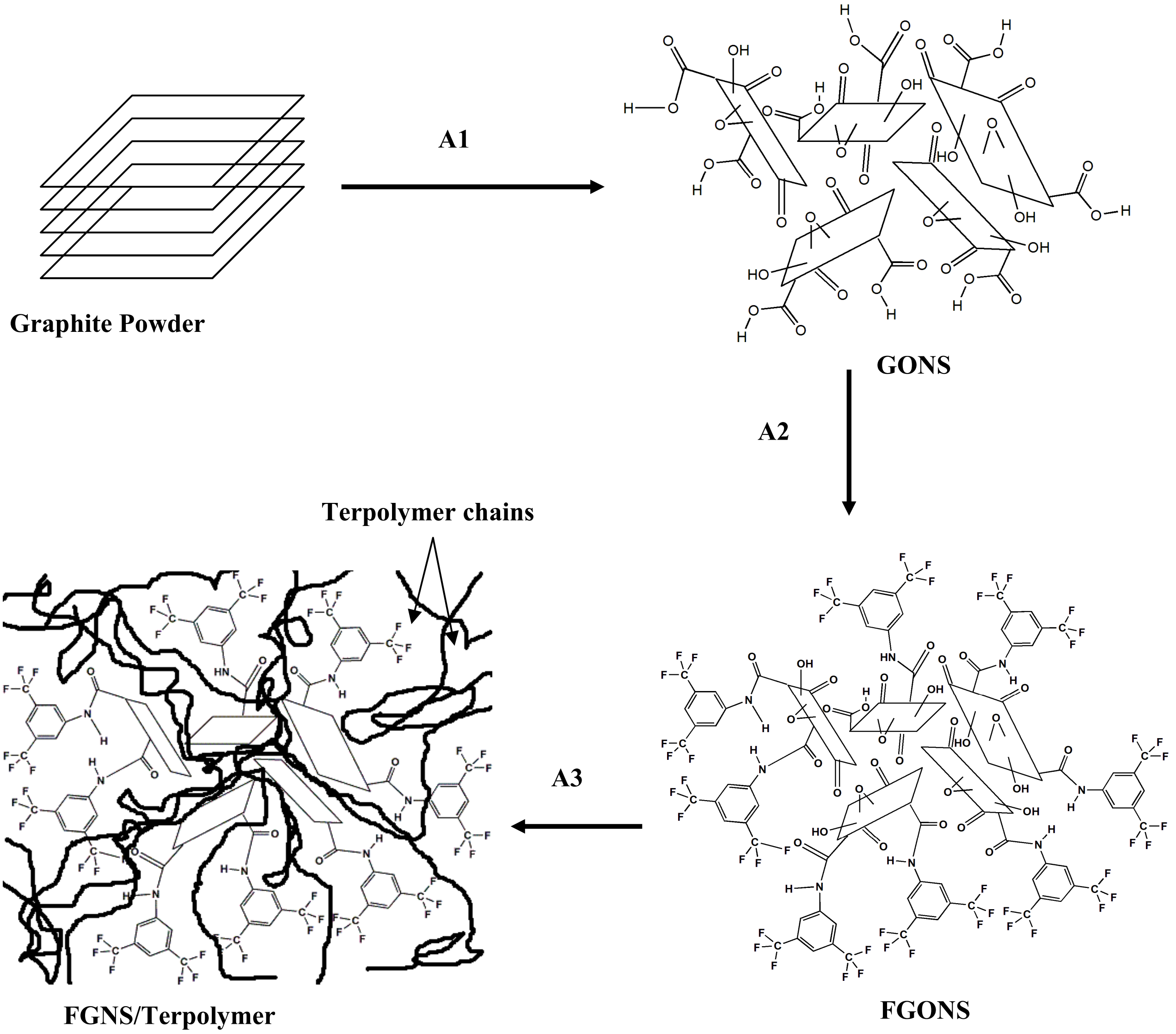

Figure S1: Schematic representation of the preparation of GONS (A1), FGONS (A2), and FGNS/terpolymer (A3).

Characterization of functionalized graphene oxide nanosheets (FGONS)

Figure S2 shows the ^{1}H-NMR spectra of the GONS and GONS functionalized by 3,5-di(trifluormetyl)-aniline (FGONS). Two new proton peaks (a: 7.902 ppm and b: 7.199 ppm) appeared in the NMR spectrum of the FGONS attributed to the protons from 3,5-di(trifluormetyl)-aniline indicating that the GONS were successfully functionalized by 3,5-di(trifluormetyl)-aniline[4]. This finding was further supported by an FT-IR analysis on the GONS and FGONS as shown in Figure S3.

The characteristic IR absorption peaks of GONS included the C=O (carboxylic acid) peak stretching from 1700 to 1740 cm^{-1} and the broad O–H peak stretching from 2500 to 3300 cm^{-1}.[2] After the GONS were functionalized by 3,5-di(trifluormetyl)-aniline, the O–H peak became significantly weaker as the carboxylic acid groups (consisting of –OH and C=O groups) on the GONS reacted with 3,5-di(trifluormetyl)-aniline forming an amide bond.[5] Also, new IR absorption peaks appeared at 3000 to 3100 cm^{-1} (C–H stretching) and 1400 to 1600 cm^{-1} (C=C stretching), which are characteristic peaks of aromatic compounds. [5] Also, IR absorption peaks at 1500 to 1700 cm^{-1} and 1000 to 1400 cm^{-1} were observed which were attributed to the C=O (amides I&II) and C–F stretching, respectively.[2, 4] Hence, according to NMR and FT-IR analyses, GONS were successfully functionalized by 3,5-di(trifluormetyl)-aniline leading to uniform dispersion in a hydrophobic polymer matrix.

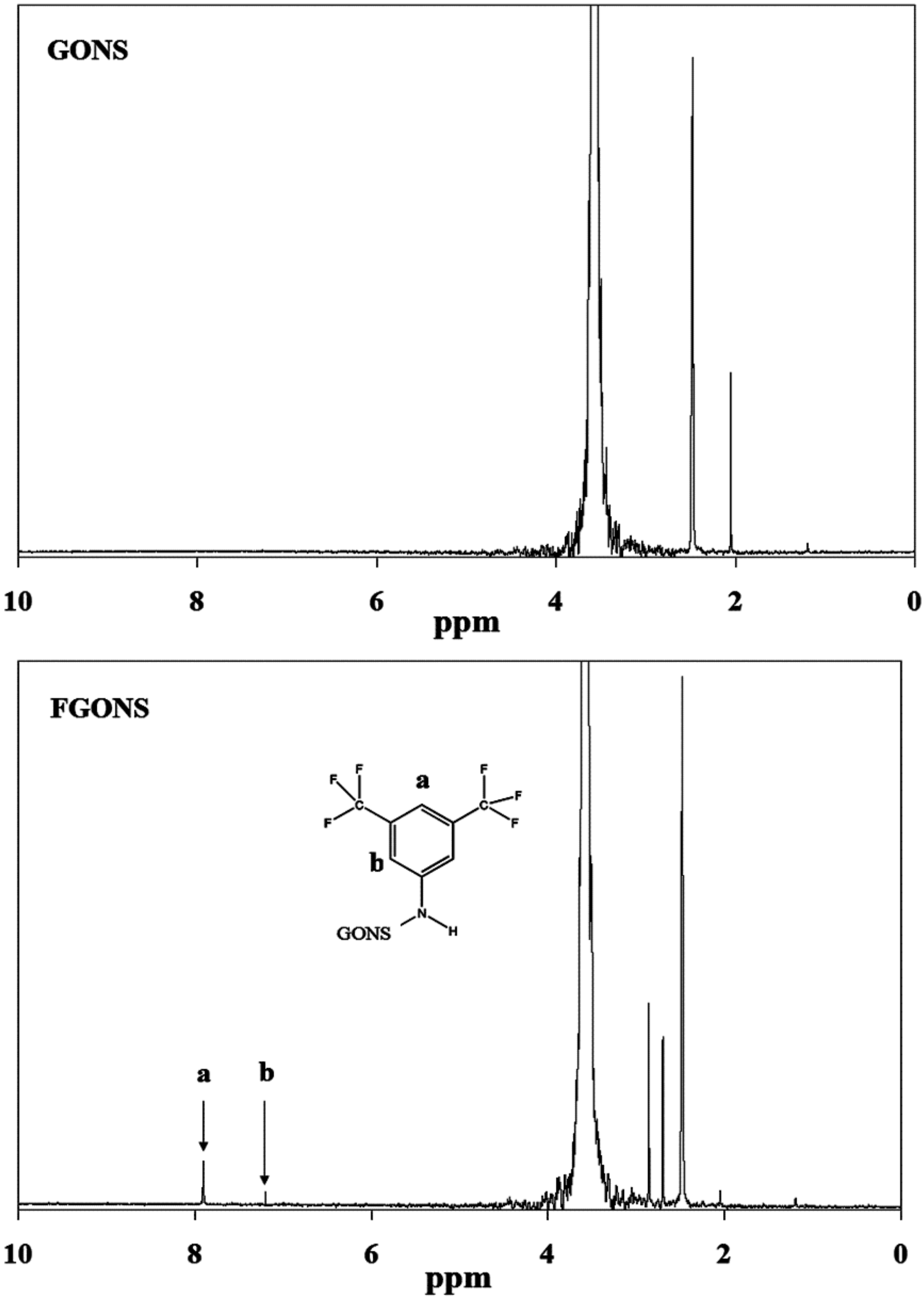

Figure S2: ^{1}H-NMR spectra of GONS and FGONS.

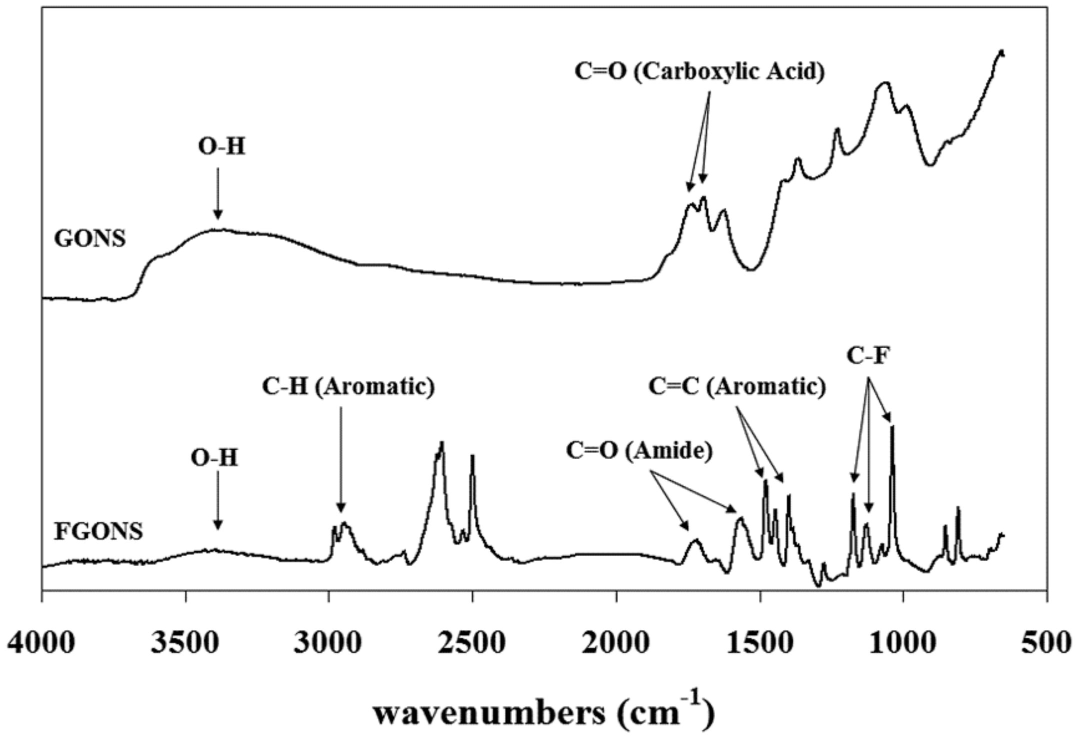

Figure S3: FTIR spectra of GONS and FGONS.

Preparation of functionalized graphene nanosheet (FGNS)/terpolymer nanocomposite films

The FGNS/terpolymer nanocomposite samples were prepared by an improved method combining solution-casting and hot-pressing techniques.[6, 7] Appropriate amounts of the FGONS and terpolymer were dissolved in DMF under sonication (100 W for 30 min). Then, 0.2 ml of anhydrous hydrazine was added to the solution which was stirred at 80°C for 24 h in order to reduce functionalized graphene oxide nanosheets (FGONS) to functionalized graphene nanosheets (FGNS) in-situ (Figure S1:A3).[8] Subsequently, the resulting FGNS/terpolymer solution was stirred another 2 h at 120°C to remove the excess amount of hydrazine. Finally, the FGNS/terpolymer solution was re-sonicated and poured into a glass Petri dish and vacuum-dried at 90 °C for 8 h to form a solution-cast film. To improve the uniformity of the FGNS/terpolymer nanocomposite film, several solution-cast films were stacked together and hot-pressed at 200°C for 30 min. The thicknesses of the resulting films were between 100 and 200 μm.

Materials and Methods

P(VDF–TrFE–CFE) terpolymer was supplied from Piezotech, France. All of the reagents were obtained from Sigma–Aldrich and Fisher Scientific and used as-received. Surface modification of the GONS was characterized by a Varian MercuryPlus 300 ^{1}H-NMR (300 HZ, DMSO-d_6) and a Bruker TENSOR series FTIR spectrometer. The morphology of the FGNS was investigated using a LEO EM-912 transmission electron microscope operated at 120 kV. The samples were prepared by dipping a Formvar-carbon coated grid into a diluted solution of FGNS in DMF. The dielectric properties of the FGNS/terpolymer nanocomposites were measured using an Agilent E4980A LCR meter at room temperature with an Agilent 16451B dielectric test fixture. Three specimens were measured for each sample and the average results were reported. Mechanical properties were characterized by a dynamic mechanical analyzer (DMA Q800) from TA Instruments at room temperature according to the ASTM standard for polymeric thin films (ASTM D882). Three specimens were measured for each sample and the average results were reported.

The electromechanical response of the FGNS/terpolymer nanocomposite films was measured using a Matsusada AMS-10B2 high voltage amplifier. Three specimens were measured for each type of FGNS/terpolymer nanocomposite film with varying FGNS loading levels and the average results were reported. Carbon paste electrodes (CPEs) were applied on both sides of the nanocomposite film for strain characterization (Figure

S4). The transverse strain ($S_{33} = (S_{final}–S_{initial}) / S_{initial})$) in the direction parallel to the applied electric field was measured using a high speed laser triangulation sensor (MICROTRACK LTC-025-02, MTI Instruments). The films were uniaxially stretched (20% strain, 50°C) and then annealed at 95°C for 6 h prior to electromechanical characterization to improve the electromechanical response.[9, 10]

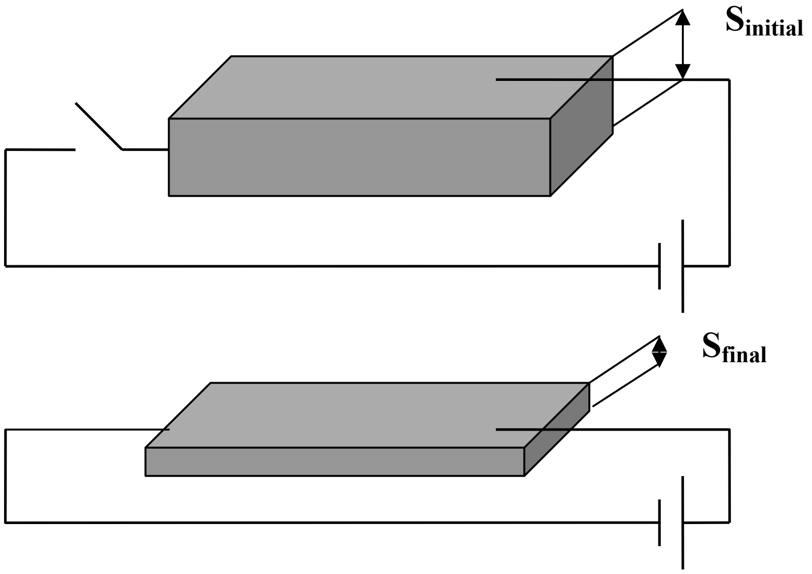

Figure S4: Schematic representation of the set-up utilized to measure the electromechanical performance of FGNS/terpolymer nanocomposites.

Determination of the Percolation Threshold

The percolation threshold was determined according to Equation (1):

$$\varepsilon = \varepsilon_m \left\{ (f_c - f) \big/ f_c \right\}^{-q} \quad (1)$$

where ε_m is the dielectric constant of the insulating matrix, q is a critical exponent (~1 for a three-dimensional composite), and f_c is the electrical percolation threshold. [11, 12] As shown in Figure S5, the f_c=0.58 and q=1.05 values were determined by linearly fitting the experimental dielectric constant data measured at 1 kHz (shown in Figure 3b) into Equation (1). The critical exponent q was close to 1, a value predicted for three-dimensional composites. According to percolation threshold theory, the dielectric loss increases significantly when the volume fraction of nanofillers approaches the percolation threshold due to the formation of conductive paths. [11, 12] As depicted in the right inset of Figure 3 (a), the dielectric loss values started to increase rapidly at FGNS volume concentrations higher than 0.55% which is in good agreement with percolation threshold value calculated from equation (1).

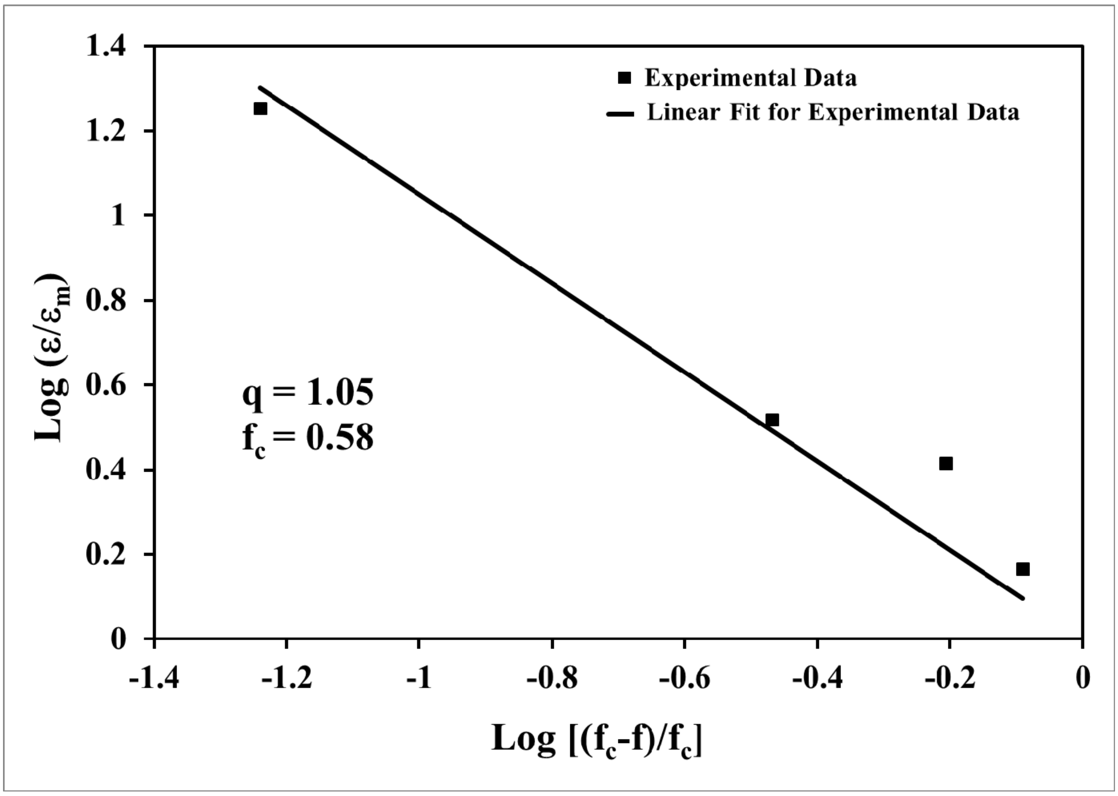

Figure S5: The determination of electrical percolation threshold based on a linear fitting of the experimental dielectric constant data acquired at 1 kHz.

References

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