Electronic Supplementary Information

Functionalized Single walled Carbon Nanotube Containing Amino Acid Based Hydrogel: A hybrid Nanomaterial

Subhasish Roy and Arindam Banerjee*

Subhasish Roy and Prof. Arindam Banerjee,

Department of Biological Chemistry,

Indian Association for the Cultivation of Science, Jadavpur,

Kolkata-700 032, India

Fax: +91-33-2473-2805

E-mail: bcab@iacs.res.in

Experimental Section.

General Methods and Materials.

9-fluorenylmethyl Choloroformate (Fmoc-Cl) and L-Phenylalanine were purchased from local chemical SRL. 1, 4-dioxane, sodium carbonate and other chemicals were purchased from Merck.

Synthesis of Fmoc-Phe-OH.

Synthesis of Fmoc-Phe-OH and characterization have been described elsewhere (see Electronic Supplementary Information of S. Roy and A. Banerjee, *Soft Matter,* 2011, **7**, 5300-5308).

Measurements.

UV-Vis-NIR spectroscopic analysis.

A Cary Varian 5000 spectrophotometer was used for the UV-Vis-NIR study.

Atomic Force Microscopic Study.

Morphologies of the reported hydrogel were investigated using atomic force microscope (AFM). AFM studies were done by placing a small amount of diluted gel and also the diluted SWCNT-gel hybrid materials of the corresponding compounds on a mica foil and then it was dried by slow evaporation. The material was then allowed to dry in vacuum at 30 °C for 2 days. Images were taken by an AUTOPROBE CP base unit, di CP-II instrument, model no. AP-0100.

Transmission Electron Microscopy.

Transmission electron microscopic (TEM) experiments were carried out to investigate the morphology of the hydrogel and the morphology of the hybrid hydrogel. TEM images were recorded on a JEM 2010 electron microscope at an accelerating voltage of 200 KV.

Field Emission Scanning Electron Microscopy (FE-SEM).

Morphologies of the *f*-SWCNT containing hydrogel materials have been investigated by FE-SEM. For the FE-SEM study, the hybrid gel material has been dried and coated with platinum. Then the micrographs have been taken in a SEM apparatus (JEOL microscope JSM-6700F).

X-ray diffraction study.

X-ray diffraction study of the xerogel was done by placing it on a XRD plate. The *f*-SWCNT containing hydrogel was dried to get solid materials and then it has been placed on a XRD plate. Experiments were carried out by using an X-ray diffractometer (Bruker D8 Advance) with a parallel beam optics attachment. The instrument was operated at a 35 kV voltage and 30 mA current using Ni-filtered CuKa radiation and the instrument was calibrated with a standard silicon sample before use. Samples were scanned from 5º to 45º (2θ) at the step scan mode (step size 0.03°, preset time 2s) and diffraction patterns were recorded using a scintillation scan detector.

Rheology.

Rheological experiments were performed with an AR 2000 advanced rheometer (TA Instruments) with cone plate geometry in a Peltier plate. The plate diameter has 40 mm, with a cone angle of 4 degrees.

Raman spectroscopy.

Raman spectroscopic analysis was performed with a micro-Raman spectrometer HORIBA Jobin Yvon (LABRAM HR 800) by means of Red light (633 nm).

Conductivity Mesurements (*I-V*).

A thin film of *f*-SWCNT-hydrogel hybrid nanomaterials was prepared on glass substrate using spin coater for electrical conductivity measurements. The film was well dried in *vacuum* for 3 days. The current-voltage (*I-V*) analysis were carried out using Ag electrodes in coplanar configuration using a Keithley model 6517A Electrometer at 26° C. The thickness of the film was analyzed using a surface profilometer (STYLUS, Model No. DEKTAK 6M), and it was found to be uniform in thickness (with an average thickness of 7000 Å). Electrical conductivity was measured putting the point I =11.9 $\times 10^{-4}$ A, V= 4.95 V from I-V curve (Figure S6) using the following equation: $\sigma = 1/\rho = l/RA = L \times I/V \times A$ (where A = 38.5 $\times$ 10^{-4} cm^2 and the length between the two electrode is 0.5 cm), where R stands for electrical resistivity, I the current, L the length, V the voltage, and A the cross-sectional area.

N_2 Adsorption study.

Nitrogen sorption isotherms were obtained using a Beckmann Coulter SA3100 surface area analyzer at 77 K.

Energy Minimized Structure.

We have studied the energy optimized electronic structures of the gelator molecule (Fmoc-Phe-OH) by employing the density functional theory (DFT) with hybrid function B3LYP using 6-31+G (d, p) basis set for all these elements involved. The B3LYP function is a hybrid function, which contains the Becke three-parameter exchange and Lee–Yang–Parr correlation function. All calculations have been performed in the Gaussian 03 suite of quantum chemistry program.

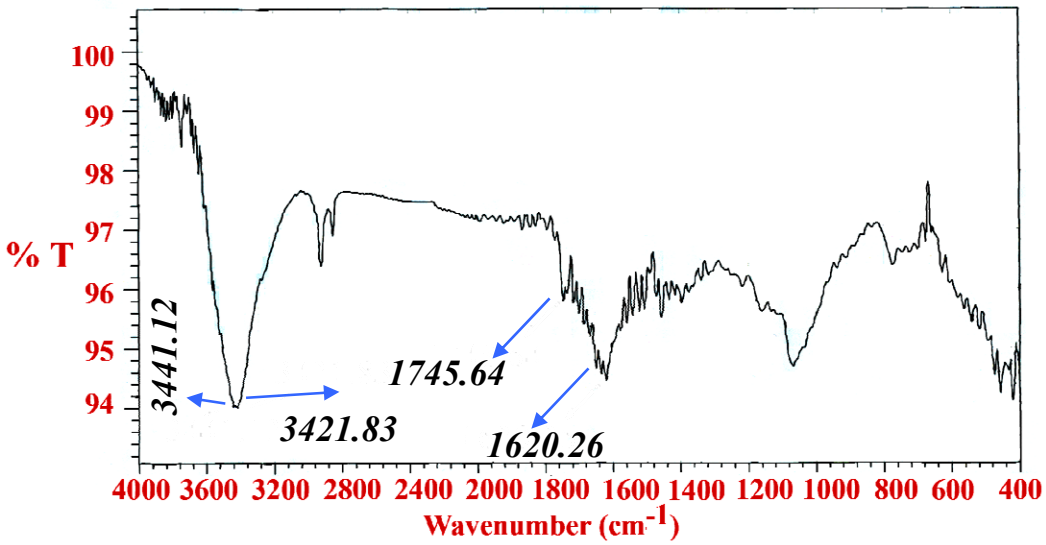

Fig. S1 FT-IR spectroscopic analysis of functionalized SWCNT.

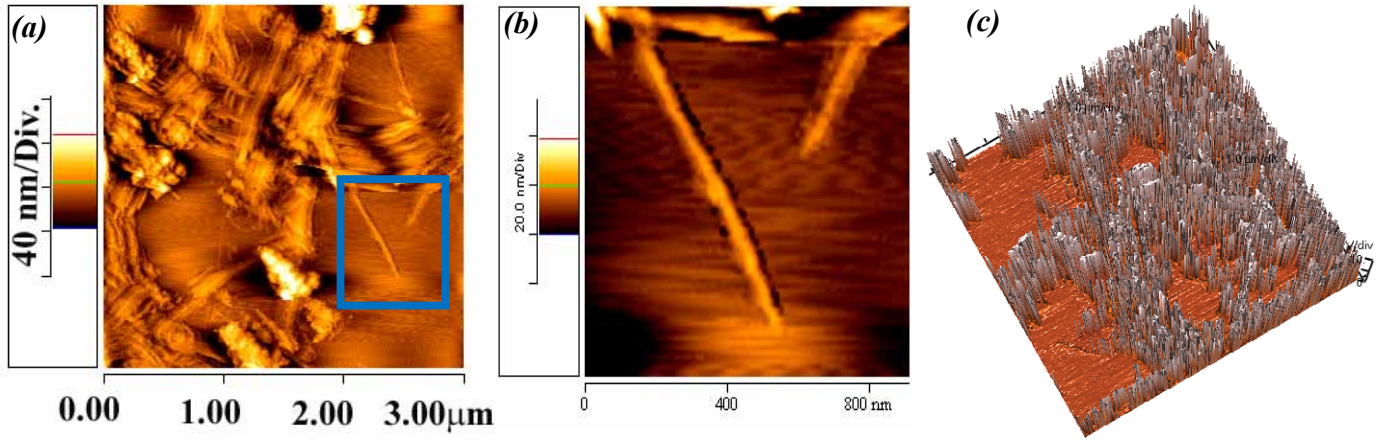

Fig. S2 (a) (b) and (c) are the Atomic Force Microscopic images of the *f*- SWCNT**.**

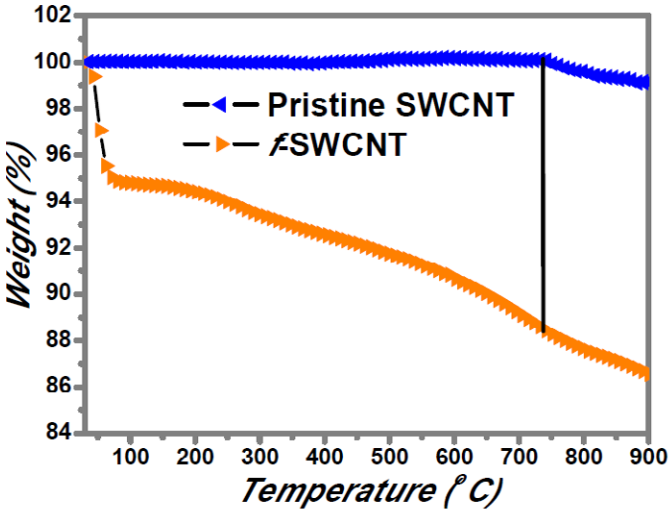

Fig. S3 Thermogravimetric analysis (TGA) analyses of pristine SWCNT and *f*-SWCNT**.** TGA analyses have clearly suggested that the functionalized single walled carbon nanotube contains 12.5 % functionalization with respect to the pristine single walled carbon nanotube.

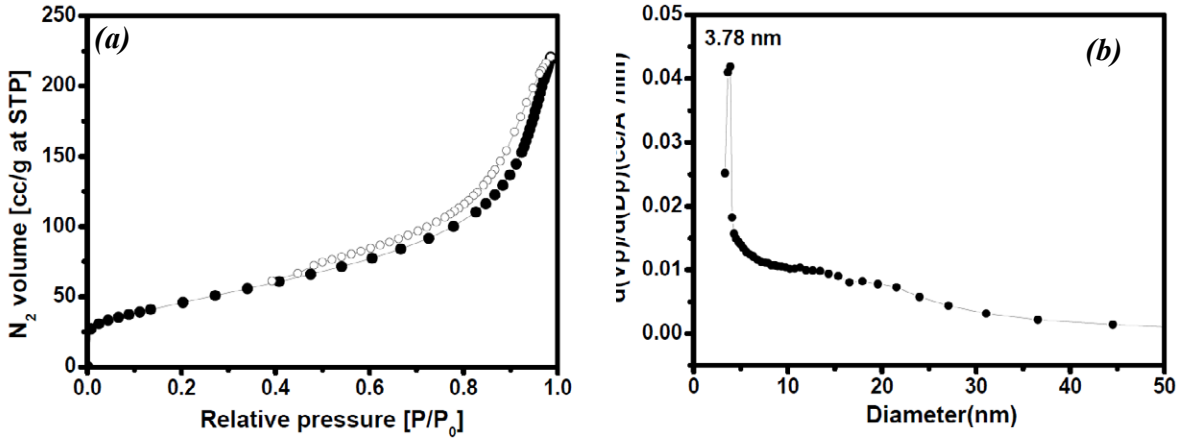

Fig. S4 (a) N_2 adsorption-desorption isotherm of *f*-SWCNT calcined at 77 K, and (b) the respective pore size distribution.

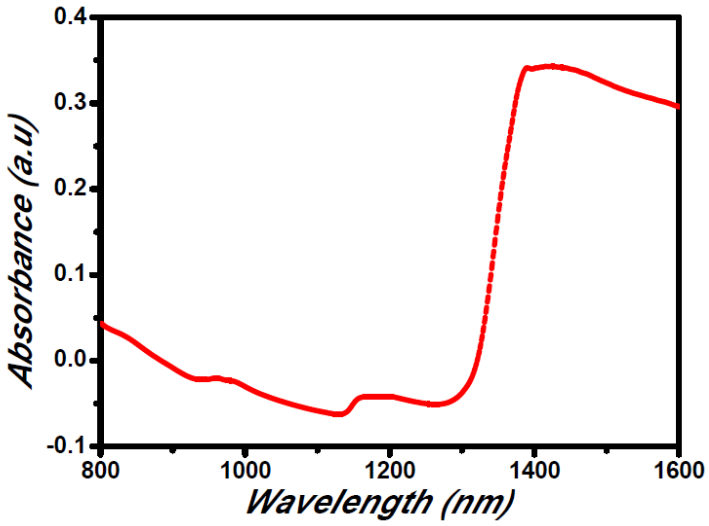

Fig. S5 Vis-NIR profile of the hydrogel-functionalized hybrid nanomaterial.

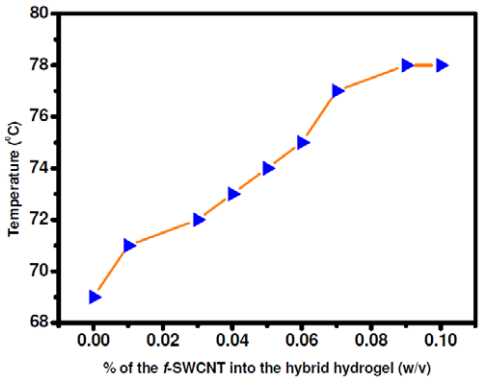

Fig. S6 Concentration dependent T_{gel} profile obtained from varying amount of *f*-SWCNT incorporated into the hybrid hydrogel keeping the gelator concentration constant (0.5 % w/v).

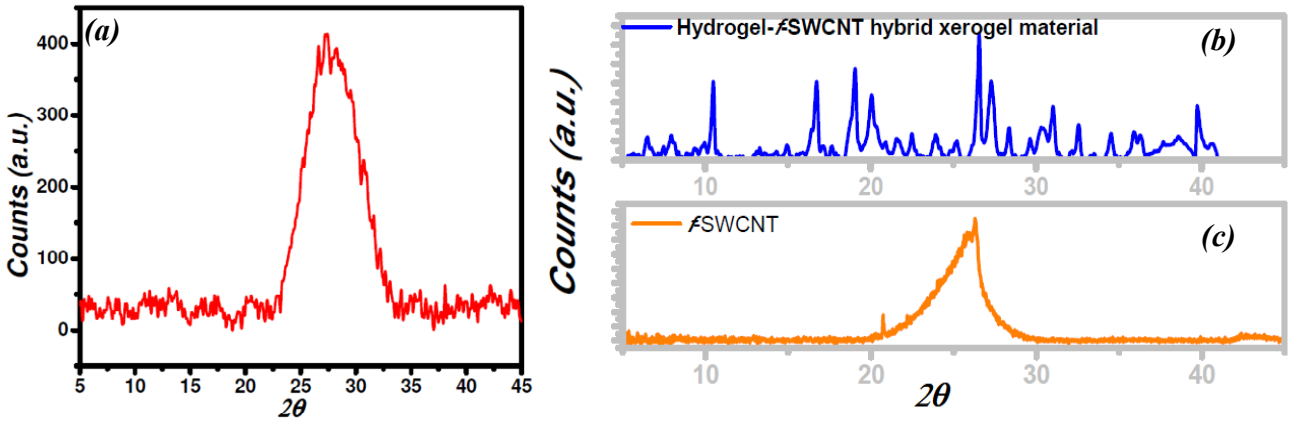

Fig. S7 X-ray diffraction patterns of (a) wet hybrid hydrogel containing *f*-SWCNT, (b) *f*-SWCNT containing hybrid xerogel material and (c) only *f*-SWCNT.

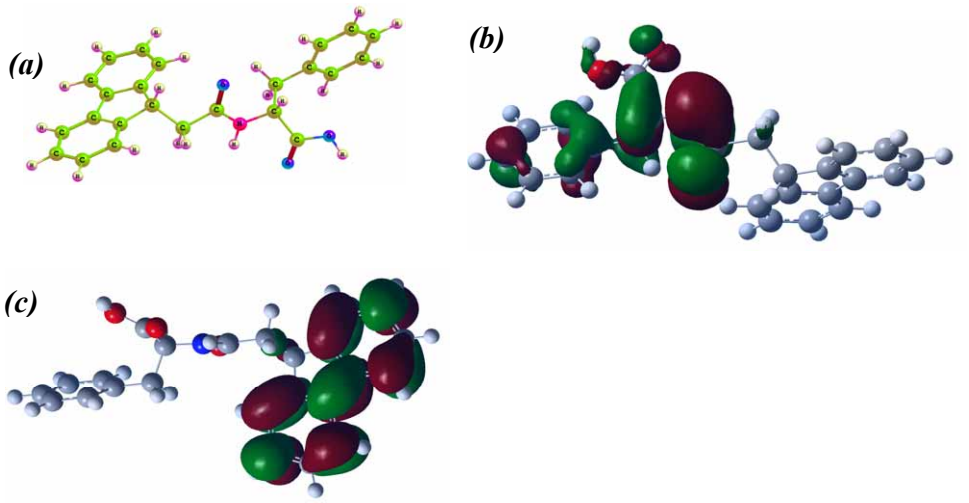

Fig. S8 (a) B3LYP/6-31+G** energy minimized structure, (b) HOMO and (c) LUMO structures of Fmoc-Phe-OH.

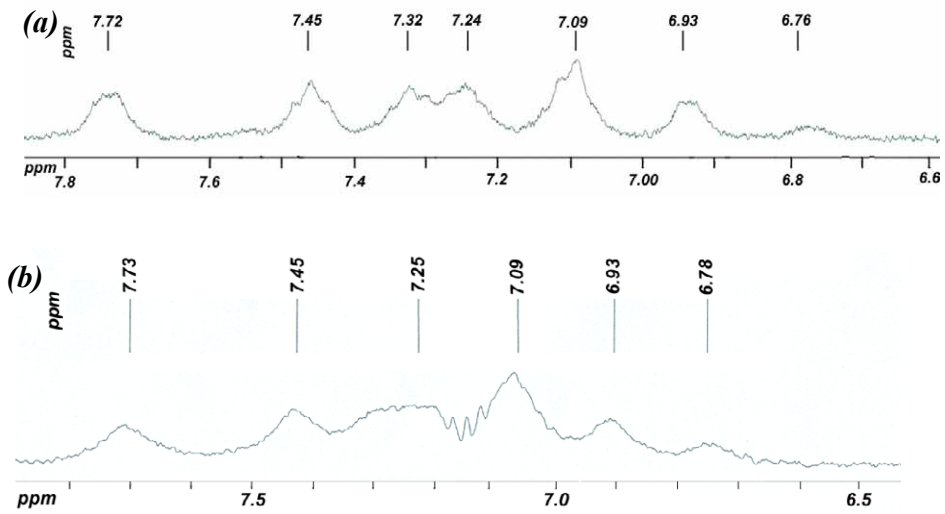

Fig. S9 (a) ^{1}H NMR spectrum of the hydrogelators near to hydrogel state in D_2O and (b) ^{1}H NMR spectrum of the *f*-SWCNT containing hydrogelators near to hydrogel state in D_2O.

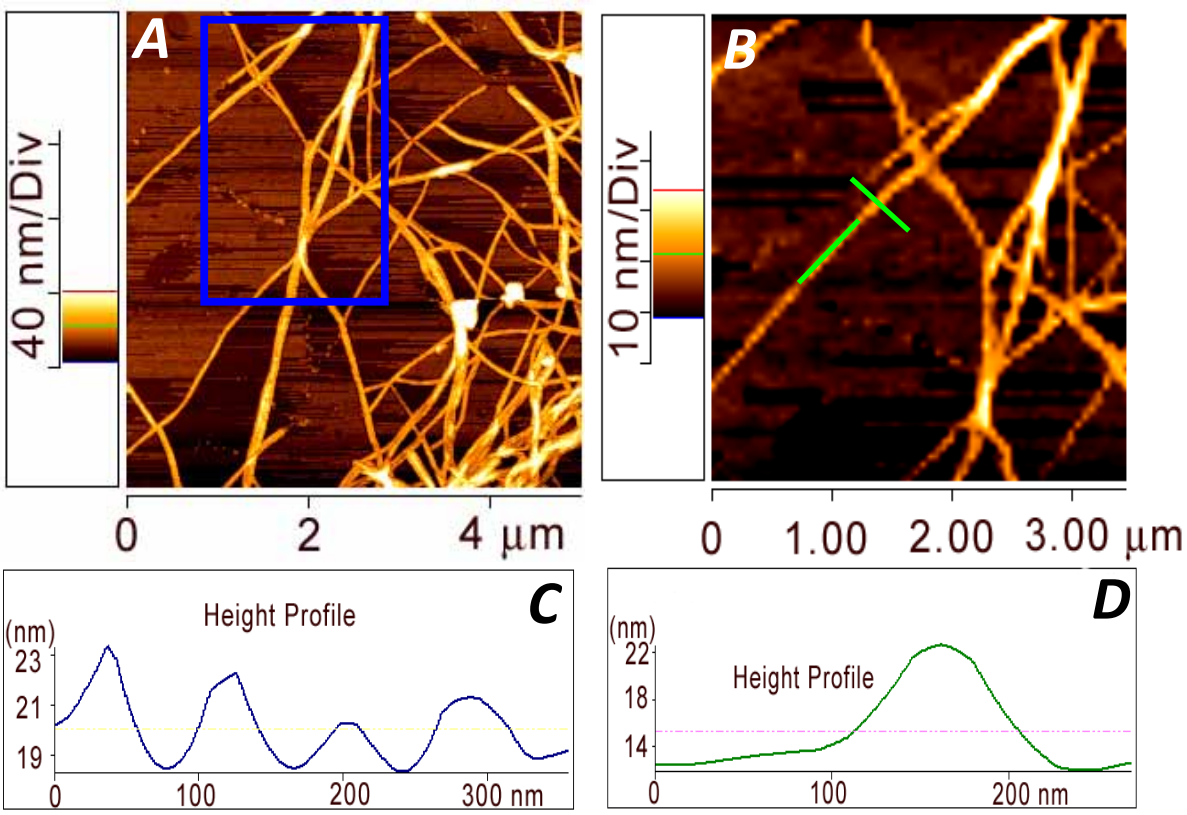

Fig. S10 (A) Atomic force microscopic analysis of the hydrogel showing the cross-linked nanofibrillar pattern, (B) Enlarged view of the Fig. A (selected area marked in the Fig. S6 A) showing the helical nature of the hydrogel nanofibers and (C) and (D) are the height profile of the helical nanofibers.

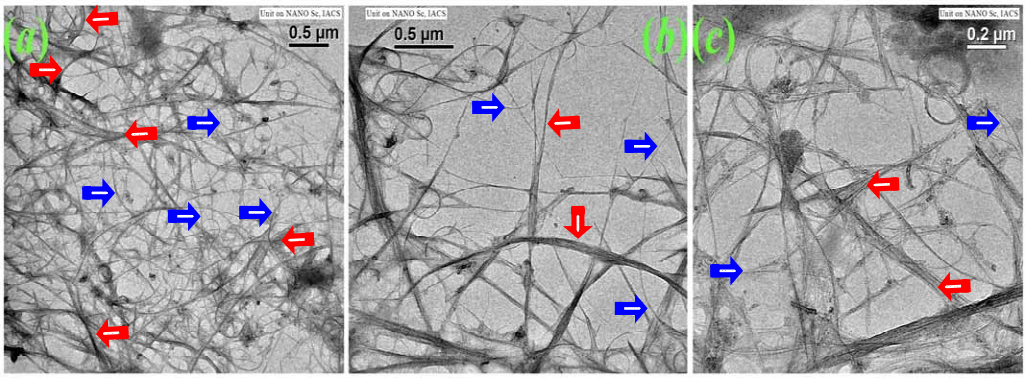

Fig. S11 Transmission electron microscopic (TEM) analysis of the hydrogel containing functionalized SWCNT at different position of the grid. This Fig. shows the presence of both nanotape type as well as nanofibrillar morphologies indicating successful incorporation of *f*-SWCNT into the hydrogel based nanofibrillar system.

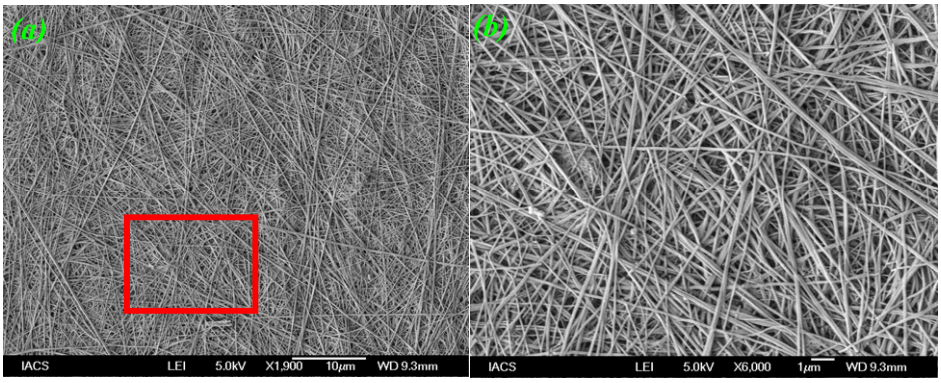

Fig. S12 (a) Field-Emission Scanning electron microscopic (FE-SEM) analysis of the hydrogel containing functionalized SWCNT and (b) Enlarged view of the selected area.

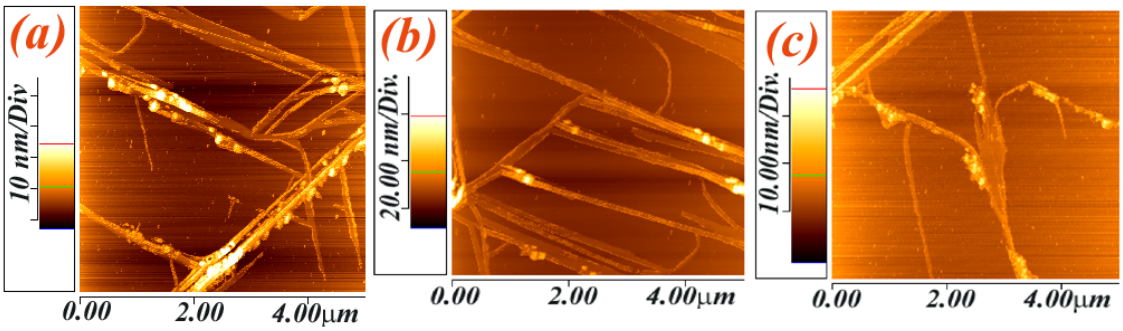

Fig. S13 Atomic force microscopic (AFM) analysis of the hydrogel containing functionalized SWCNT.

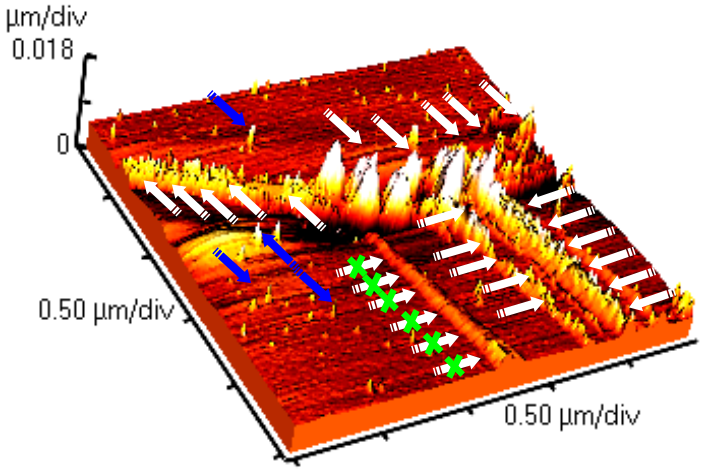

Fig. S14 Atomic force microscopic topology analysis showing the presence of bare gel nanofibers, 1D array of regularly aligned *f*-SWCNTs on the surface of the nanofibers and only functionalized CNTs. The white arrows indicate the 1D alignment of *f*-SWCNTs on gel nanofibers, while the white arrow with a centrally located cross indicates the only gel nanofibers and the blue arrow indicates the presence of only functionalized CNTs.

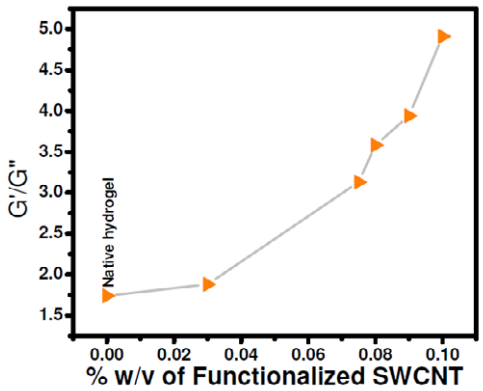

Fig. S15 G′/ *G*′ vs. % w/v of functionalized SWCNT present into the hydrogel system.

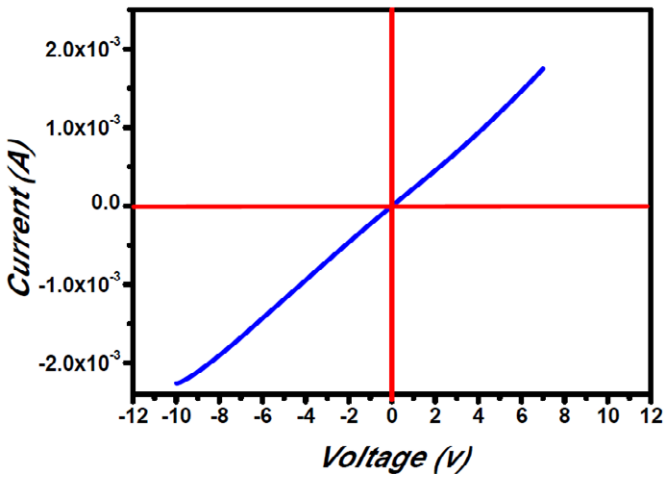

Fig. S16 *I-V* profile of the functionalized SWCNT containing hybrid hydrogel based nanomaterial.