# Supporting Information

# Defining the role of nanonetting in the electrical behaviour of composite nanofiber/nets

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### Properties of the starting solutions.

Two molecular weights, 600 and 1000 kDa, have been investigated, and two concentrations (1.5 and 3.5 wt%) of MWCNTs have been analysed. PEO concentration has been kept fixed at 5 wt%, more details about the selection of the polymer concentration are available in the following. The list of resulting solutions investigated in this work is reported in Table S-1, indicating their composition, the electrical conductivity, and the average viscosity,  $\eta$ .

The name of each solution has the general structure PEOA\_B, where A stands for the polymer molecular weight and B indicates the weight percentage of MWCNTs added into the solution. The name of nanocomposite samples after electrospinning are PEOA@V, where A

refers to the polymer as before and V is the working voltage applied during the electrospinning step.

PEO is a non-electrically conducting material, so using a higher molecular weight causes only a slight change of  $\sigma_{sol}$ , as shown in Table S-1, while the introduction of MWCNTs induces significant changes of  $\sigma_{sol}$ . At a fixed loading of MWCNTs, the value of  $\sigma_{sol}$  is almost the same for the two molecular weights: this can be explained considering that the contribution of the polymer is quite small.

The effects of both the filler and the Mw are quite noticeable on the average viscosity of the solution, whose values are reported in Table S-1. Indeed,  $\eta$  increases when using a higher Mw, and a further increase is caused by the addition of MWCNTs. According to the literature, solutions whose average shear viscosity belongs to the range between 0.02 and 300 Pa·s are well suited for electrospinning [1S]. For values below this range, nanofibers with several defects, as beads, are formed, while for too high values severe difficulties arise in managing the highly viscous solution during the process. Based on the obtained values of the average apparent viscosity, all the solutions are well suited for electrospinning from this viewpoint.

 Table S-1. The names and the main properties of the examined PEO-based solutions are

 listed.

Solution name	Mw	MWCNT	$\sigma_{sol}$	η
	[kDa]	[wt%]	[µS/cm]	[Pa·s]
PEO600	600	0	4.2	23.8
PEO600_1.5	600	1.5	203	/
PEO600_3.5	600	3.5	405	68

PEO1000	1000	0	12.6	44.9
PEO1000_1.5	1000	1.5	240	/
PEO1000_3.5	1000	3.5	420	138

#### Raman spectroscopy

A deeper investigation was performed, using Raman spectroscopy, on the nanocomposite nanofibrous materials made starting from PEO1000 solution and processed at 18 kV. The collected Raman spectra are shown in Fig. S-1. The green and blue curves refer to the samples containing 1.5 and 3.5 wt% of MWCTNs, respectively.



**Figure S-1.** Raman spectra of nanofiber mats containing 1.5 wt% and 3.5 wt% of MWCNTs.

MWCNTs are confirmed to be present into the nanocomposite, by the D, G and the G' bands in the spectra. The D band, which is present in all graphite-like carbons, originates from structural defects and, in MWCTNs-based composites, can be related to the stress induced on the carbon nanotubes by the hosting polymer when strong chemical-physical interaction is established among them. Increasing the amount of MWCNTs from 1.5 wt% to 3.5 wt% into the nanocomposite, the position of the D peak moves slightly to lower wavenumbers (from 1352 to 1348 cm<sup>-1</sup>), which is in line with an increase of the stress induced by interaction with MWCNTs [2S]. The other peaks refer to the PEO matrix. In particular, inplane CH deformations can be associated to the peak at 1122 cm<sup>-1</sup>,at 1465 cm<sup>-1</sup> CH<sub>2</sub> bending is visible, whereas at 2876, 2940 and 3074 cm<sup>-1</sup> bands are present that can be assigned to C-H stretching modes [3S].

#### Selection of PEO concentration

To select the PEO concentration, two water based solutions were prepared adding PEO with 1000 kDa molecular weight at two different concentrations, i.e. 3 and 5 wt%. To those solutions two concentration on MWCNTs were added, i.e. 1.5 and 3.5 wt%. Samples were processed by Electrospinning using the following parameters: voltage at 23 kV, flow rate at 0.1 ml/h, working distance at 150 mm.

In Fig. S-2 the obtained nanofibers are analysed by FESEM. The results show that the average diameter of the nanofibers increases while increasing the polymer concentration, and slightly decreases for increasing content of MWCNTs into the composite. It is interesting to notice that nano-fiber/nets do not form when the low PEO concentration (i.e. 3 wt%) is used. For this reason we decided to analyse 5 wt% PEO only in the article.

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**Figure S-2** FESEM images of nanofiber mats obtained from 1000 kDa PEO at two different concentrations: 3 wt%, reported on the right column, and 5 wt% on the left column. The evolution of the nanofibers diameters increases with the Mw and it slightly decreases with MWCNTs concentration. NFN is well visible when 5 wt% PEO is used, while NF are obtained using a 3wt%.

## Compared analysis of NF (PEO600) and NFN (PEO1000) morphologies

The FESEM characterizations of PEO600 and PEO1000 samples containing MWCNTs are reported in Figure S-3(a) and S-3(b), respectively. For both the two sets of samples, the

diameters of the nanofibers reduce when MWCNTs are added: the higher the MWCNTs concentration (i.e., 3.5 vs. 1.5 wt%) the lower the diameter, and a slight decrease is also caused by using higher voltages (i.e., 23 than 18 kV). For PEO1000 samples, starting from 1.5 wt% MWCNTs processed at 18 kV, the typical arrangement of nano-netting appears (Figure S3b), while no nanonet is observed for PEO600 samples (Fig. S-3(a)), no matter the voltage and the concentration of MWNTs. The nanofiber/nets are denser in the PEO1000 composite systems having a higher content of MWCNTs (Fig. S-3(b)-iii and S-3(b)-iv), and for increasing values of the working voltage (Fig. S-3(b)-ii and S-3(b)-iv). Starting from PEO1000@18 samples with at least a concentration of MWCNTs to 3.5 wt%, the nanofiber/net morphology becomes more complex, since very small size beads are present along the nanonets (see Figure S3b). Moreover, by increasing the amount of MWCNTs, not only the density of nanonet increased, but the density of nanobeaded-nanonet increased as well (see Figure S3b-ii).

Comparing PEO600 to PEO1000 samples it is possible to notice that PEO1000@18 (left column of Fig. S-3(b)) are less dense (or more porous) than samples the corresponding PEO600 having the same content of MWCNTs; while the behaviour is the opposite for the PEO1000@23 samples.

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**Figure S-3** In (a) and (b) FESEM images of samples PEO600 and PEO1000 respectively, with different concentrations of MWCNTs. Two values are reported for each PEO Mw, i.e. 1.5 and 3.5 wt%, in the upper and lower line respectively of each picture. Morphology is investigated as function of voltage: pictures refers to 18 kV in the left column and 23 kV in the right column. Processing the 5PEO\_1000 with MWCNTs nanonetting appears, as highlighted in b).

#### References

- [1S] Wendorff JH, Agarwal S. Electrospinning: Materials, Processing and Applications.Hoboken, NJ USA: Wiley. 2012
- [2S] Chipara DM, Macossay J, Ybarra AVR, Chipara AC, Eubanks TM, Chipara M. Raman spectroscopy of polystyrene nanofibers—Multiwalled carbon nanotubes Composites Appl. Surf. Sci. 2013; 275: 23– 27
- [3S] Socrates, G. Infrared and Raman Characteristic Group Frequencies: Tables and Charts. Hoboken, NJ USA:Wiley. 2001