Electronic Supplementary Information (ESI)

Engineering the nanostructure of a polymer-nanocomposite film containing Ti-based core-shell particles to enhance dielectric response

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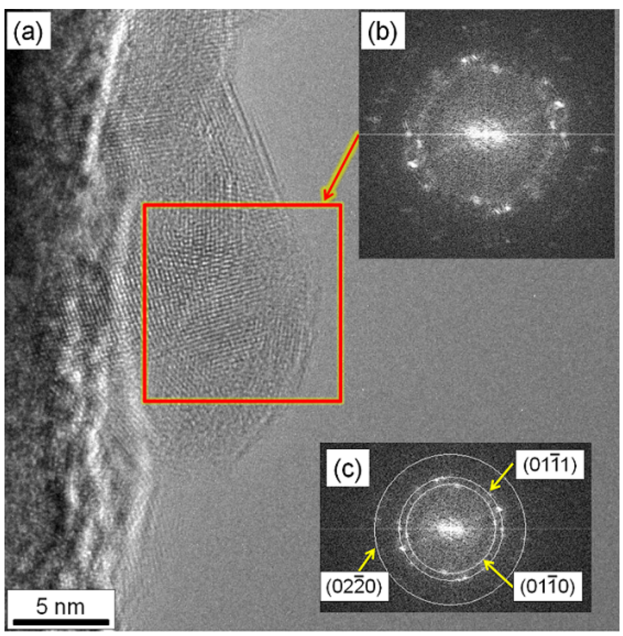

Figure S1: (a) High-resolution transmission electron microscopy (HRTEM) image of a Ti-nanoparticle protruding into the vacuum, (b) the corresponding fast Fourier transform (FFT) from the highlighted square region, and (c) analysed FFT showing the three circles along which most of the spots lie.

Figure S1(a) is a high-resolution transmission electron microscopy (HRTEM) image of a Ti-nanoparticle protruding into the vacuum. The corresponding fast Fourier transform

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(FFT) from the highlighted region is shown in Figure S1(b). An analysis of the FFT in Figure S1(b) showed that most of the spots were traced by three circles as shown in Figure S1(c) and corresponded to $(01\bar{1}0)$, $(01\bar{1}1)$, and $(02\bar{2}0)$ Ti lattice planes. Regions of crystalline and amorphous nature can be seen near the edge of the nanoparticle. Such Ti-nanoparticles were considered qualitatively similar to the Al-nanoparticles[1] that oxidised to form an oxide-shell around the metal-core.

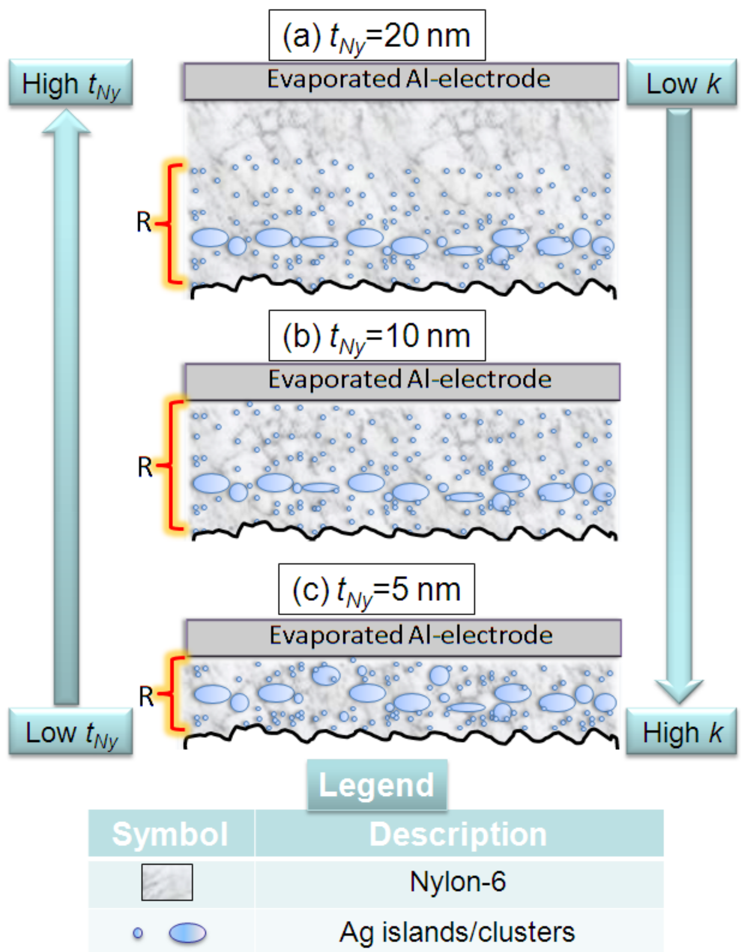
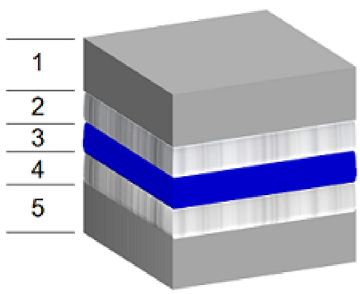


Figure S2: A schematic representation of the cross-sections of PNC films showing the relative positions of the region, R, in which the near-percolation effect operates at various thicknesses of the nylon-6 (Ny) layer: (a) t_{Ny}=20 nm, (b) t_{Ny}=10 nm, and (c) t_{Ny}=5 nm. The thickness of the deposited Ag in all PNCs is 5 nm.

Figure S2 is a schematic representation of the cross-sections of PNC films showing the relative positions of the region, R, in which the near-percolation effect operates at various thicknesses of the nylon-6 (Ny) layer. The nominal thickness of the deposited Ag in all PNCs is 5 nm. At t_{Ny}=20 nm in Figure S2(a), R is relatively far from the Al-electrode and the volume fraction v_f of Ag in the 20 nm thick nylon-6 layer might be so small (or nil) so that it may be considered as a discrete, insulating layer, thereby limiting the overall enhancement in k, as seen previously in Ag-PNCs.[2] When t_{Ny} is reduced to 10 nm or 5 nm, the region R becomes sufficiently close to the Al-electrode to form a near-percolating network, as seen in Figure S2(b) or (c). At these thicknesses, the nylon-6 layer ceases to be a discrete, insulating layer that separates the Al-electrode from the rest of the PNC film. Therefore, the thickness of the nylon-6 layer and the percolative nature of the nanocomposite film are in an inverse relationship. It is important to note that the thickness of the nylon-6 layer should not be reduced to such an extent that the dielectric starts percolating, in which case the dielectric loss will be relatively and eventually unacceptably high.



Layer	Material	t (nm)	$\dot{t}$ (nm/s)
1	Al (electrode)	40	0.5
2	Nylon-6	Variable	0.1
3	Ti	Variable	Variable
4	Nylon-6	Variable	0.1
5	Al (electrode)	40	0.5

Figure S3: A schematic of alternate layers of metal and polymer.

The overall fraction of Ti and Ag present in the various PNC systems studied are summarised in Table S1.

Table S1: The various PNC systems with the fraction of Ti and Ag in each system.

PNC system	**Ti fraction**	**Ag fraction**
$Ti_{0.5}$-Ny_{20}	0.11 & 0.2	-
$Ti_{0.1}$-Ny_{10} & $Ti_{0.5}$-Ny_{10}	0.33	-
$Ti_{0.1}$-Ny_{5}	0.5	-
$Ti_{0.1}$-Ny_{10}	0.33	-
Ag+$Ti_{0.1}$-Ny_{5}	0.25	0.25
Ag+$Ti_{0.1}$-Ny_{10} & Ag+$Ti_{0.5}$-Ny_{10}	0.17	0.17

TEM

The TEM samples were simultaneously produced in parallel by depositing the PNC directly on two types of grids: a 400-mesh Cu grid with a continuous C film and a 200-mesh Cu grid. The C film on the grid provided a support structure on which the PNC film grew and facilitated plan-view TEM, STEM, and SAED, whereas the PNC that grew over the edges of the Cu only grid allowed high-resolution imaging of the Ti-based core-shell nanoparticles. The area of the PNC under investigation was always chosen such that it was sufficiently far away from the mesh to minimise any background data from the Cu grid. The Al electrodes used for dielectric measurements were not deposited on the TEM grids.

Impedance spectroscopy

The dielectric properties of the PNCs were studied using a Solartron SI 1260 impedance analyzer operating at 1 kHz. Simple parallel-plate capacitors were formed from the PNC multilayer films by evaporating Al (40 nm thick) on both sides of the PNC. All PNC-based capacitors were dried at 40 ^{0}C for 20 hours to negate any water vapour effects immediately before dielectric characterisation. The thicknesses of the PNC films were measured using a DekTak 6M profilometer (Veeco Instruments, Inc), and k was estimated directly from the impedance data.

References

(1) A. Mahadevegowda, N. P. Young and P. S. Grant, *Nanotechnology*, 2014, **25**, 475706.

(2) A. Mahadevegowda, N. P. Young and P. S. Grant, *JPCS*, 2014, **522**, 012041.