Electronic Supplementary Information (ESI) for

“Ultralow Percolation Threshold and Enhanced Electromagnetic Interference Shielding in Poly(l-lactide)/Multi-Walled Carbon Nanotubes Nanocomposites with Electrically Conductive Segregated networks”

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1. Transcrystals in S-PLLA/MWCNTs composites

S-1
The cryo-fractured surface of the S-PLLA/MWCNTs composites was etched in a water-methanol (1/2 v/v) solution containing 0.025 mol/L sodium hydroxide to remove the amorphous regions of the PLLA matrix, and finally coated with a layer of platinum in a vacuum chamber before the SEM observation. Fig. S1 shows the crystalline morphology of the S-PLLA/MWCNTs composites with 0.6 vol. % MWCNTs. It can be found that the transcristalline layers and spherulites range in the H-PLLA phase. The transcrystals which was formed by the nucleating effect of MWCNTs were surrounded with the L-PLANT phase. The formation of the transcrystals was thought to enhance the Young’s modulus and tensile strength of S-PLLA/MWCNTs composites.

Fig. S1 Crystalline morphology of the S-PLLA/MWCNTs composites with 0.6 vol. % MWCNTs.

2. Nonisothermal crystallization behavior of the S-PLLA/MWCNTs composites
The nonisothermal crystallization behavior of the samples was performed by a differential scanning calorimeter (NETZSCH DSC-214) in a dry nitrogen atmosphere. For each measurement, about 5 mg sample was placed in an aluminum pan, which was first heated from 25 to 190 °C at a heating rate of 10 °C/min and held for 5 min to remove thermal history, then cooled down to 25 °C at a cooling rate of 10 °C/min, and finally reheated to 190 °C at a heating rate of 10 °C/min. The degree of crystallinity ($X_c$) was evaluated according to the Eq. S1 from the second heating curve.\(^{S1}\)

$$X_c = \frac{\Delta H_m - \Delta H_c}{w_f \Delta H_m^o}$$

where $\Delta H_m$, $\Delta H_c$, $w_f$ and $\Delta H_m^o$ were the measured enthalpies of melting, the measured enthalpies of cold crystallization, the weight percent of PLLA matrix and the melting enthalpies of 100 % crystalline PLLA of 93.7 J/g,\(^{S2}\) respectively.

Fig. S2 shows the non-isothermal crystallization of the L-PLANT, R-PLLA/MWCNTs and S-PLLA/MWCNTs composites. The L-PLANT composites have only one thermal transition upon heating, i.e. glass transition at ~ 60 °C, indicating that no crystallization for L-PLLA happens during the processing. However, both the R-PLLA/MWCNTs and S-PLLA/MWCNTs composites exhibit multiple transitions upon heating: a glass transition temperature ($T_g$) of ~ 60 °C, a cold crystallization peak ($P_{cc}$) of ~115 °C and a melting peak ($P_m$) of ~170 °C. The crystallinity of the composites was also calculated and showed in Fig. S2b and c. The crystallinity of all the tested S-PLLA/MWCNTs composites was less than 7 %, while the tested R-PLLA/MWCNTs composites had more than 13 % crystallinity. The reasons are that the MWCNTs show high nucleating effect...
on H-PLLA crystallization but no nucleating effect on L-PLLA crystallization (Fig S2a). The nucleating effect on H-PLLA crystallization is also retarded by the confined distribution of MWCNTs in L-PLLA phase for the S-PLLA/MWCNTs composites. Furthermore, the crystallinity of the R-PLLA/MWCNTs composites increases at low MWCNTs loadings (0, 0.2 and 0.6 vol. %) and then decrease at high MWCNTs loadings (0.8 vol.%). The results are attributed to the crystallization confinement probably happening at the higher concentration of MWCNTs.

![DSC and heating curves](image)

**Fig. S2** DSC and heating curves of the L-PLANT (a), R-PLLA/MWCNTs (b) and S-PLLA/MWCNTs (c) composites with different MWCNTs loadings.

**References**
