

## Supporting information

### Conductive polymer nanocomposites with hierarchical multi-scale-structure via self-assembling carbon-nanotubes on graphene on polymer-microspheres

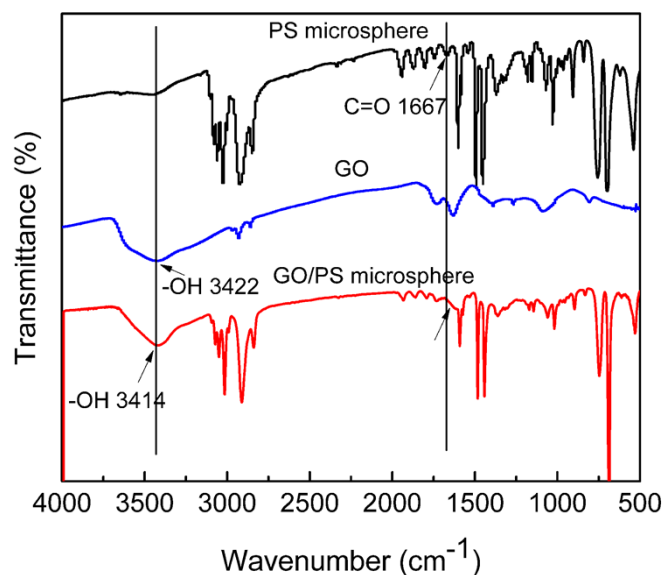


Figure 1S FTIR spectra of PS microsphere, GO and GO/PS microsphere.

The C=O peak of PVP at 1667 cm<sup>-1</sup> appearing in the PS microsphere corresponds to the water-soluble PVP grafted on PS microspheres surface. The C=O in PVP can act as the donor site of hydrogen-bonding to combine with -OH (3422 cm<sup>-1</sup>) of GO sheets. In the FTIR spectrum of GO/PS microsphere, the C=O peak of PVP and -OH peak of GO sheets both obviously shift toward low frequency, indicating the presence of the hydrogen-bonding interaction between PS microspheres and GO sheets.

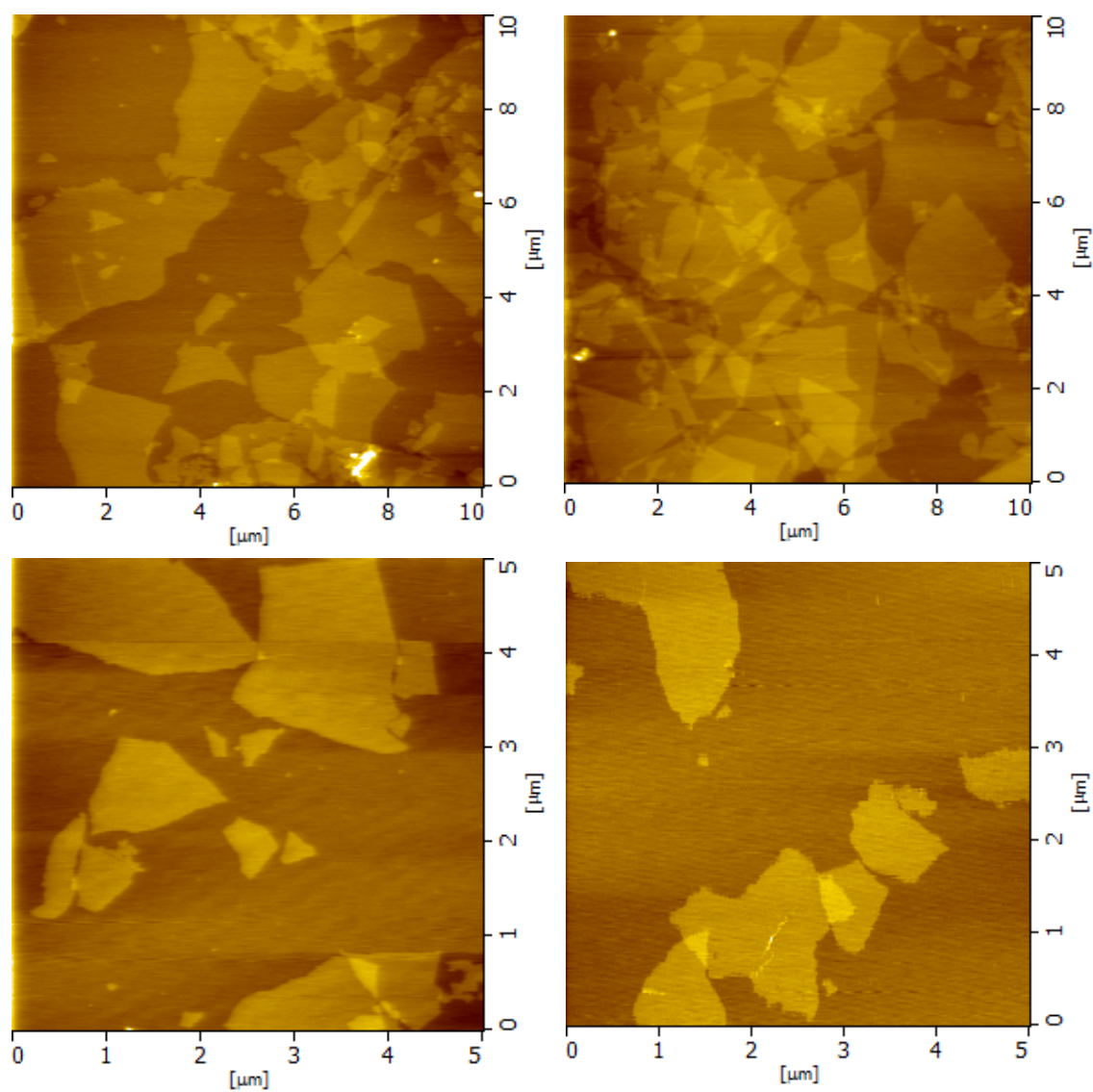


Figure 2S AFM images of GO sheets on a mica substrate, which are used for the plot of histograms.

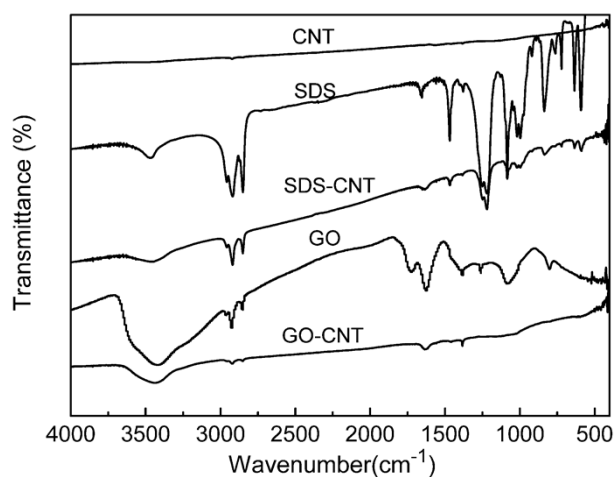


Figure 3S FTIR spectra of CNT, SDS, SDS-CNT, GO and GO-CNT.

SDS-CNT and GO-CNT were collected from aqueous suspensions of SDS-CNT and GO-CNT via filtration and water washed respectively. The characteristic bands from SDS and GO are also present in SDS-CNT and GO-CNT, indicating that SDS and GO have strongly adsorbed on CNT surface. As a result, the hydrophilic functionalities of CNT surface greatly increase.

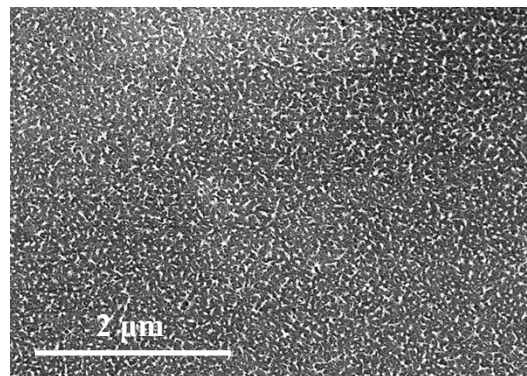


Figure 4S SEM image of cross-sections of PS film from hot-pressing of PS microspheres.

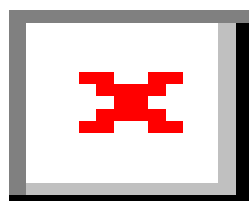
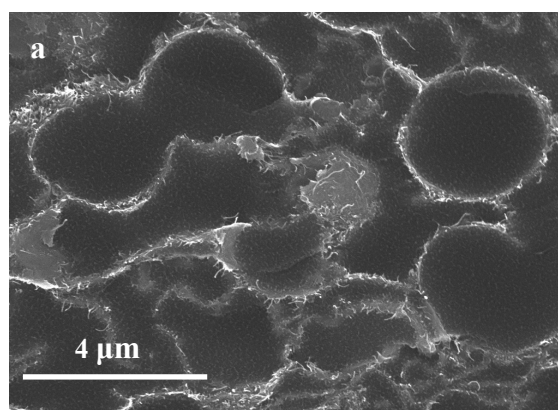


Figure 5S SEM images of cross-sections of RGO-CNT/PS CPC film at a low (a) and a high (b) magnifications, respectively.

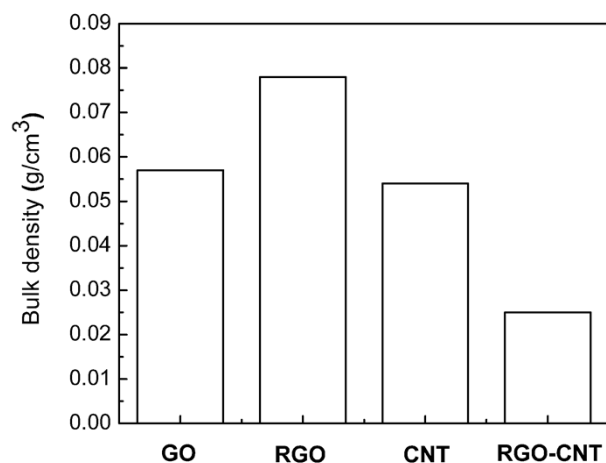


Figure 6S Bulk density of GO, RGO, CNT and RGO-CNT.

**Table 1S Mechanical properties of PS and its nanocomposites**

Samples	Tensile strength (MPa)	Tensile modulus (MPa)
PS	15.5±2.1	1860±62
1 vol% SDS-CNT/ PS	26.1±1.3	2090±55
2 vol% SDS-CNT/ PS	17.0±0.8	1910±34
1 vol% RGO-CNT/ PS	15.7±1.5	2670±28
2 vol% RGO-CNT/ PS	16.3±0.6	2320±23

The tensile strength and tensile modulus of the samples were measured on an Instron universal testing machine 4302 (with a 500N load cell and pneumatic side-action grips) at room temperature with gauge length of 20 mm and a tensile rate of 5mm/min according to ASTM D882. Four parallel measurements were carried out for each sample.