Supporting Information

Noncovalent dispersion of multi-walled carbon nanotubes with poly(*tert*-butyl methacrylate) modified hyperbranched polyethylene for flexible conductive film

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1. Chemicals and methods

1.1 Chemicals

HBPE-*g*-P*t*BMA (Mn=145.1 kg/mol, PDI=2.8) was synthesized according to the literature [1]. The FT-IR spectrum of HBPE-*g*-P*t*BMA was shown in Fig. S1a, and ascribed as follow [1]: 2978, 2927, 2855 cm^{-1} (v_{C-H}, -CH$_2$-, -CH$_3$), 1725 cm^{-1} ($\tau_{C=O}$, -C=O-R), 1461 cm^{-1} (δ_{C-H}, -CH$_2$-, -CH$_3$), 1393, 1368 cm^{-1} ($\delta_{(S, C-H)}$, -CH$_3$), 1252 cm^{-1} (v_{C-O}, -(C=O)-O) and 1139 cm^{-1} (v_{C-O}, R-C-O-). Multi-walled carbon nanotubes (MWCNTs) (diameter=6-9 nm, length=5 μm, purity >95% carbon) and glass wool (98%) were purchased from Sigma Aldrich. The Raman spectrum of MWCNTs was shown in Fig. S1b, and ascribed as follow [2]: 1341 cm^{-1} (D band) and 1580 cm^{-1} (G band). Chloroform (CHCl$_3$, AR) was purchased from Sinopharm Chemical Reagent Co., Ltd.

1.2 Dispersion of MWCNTs by HBPE-*g*-P*t*BMA in CHCl$_3$

MWCNTs (4.0 mg) were dispersed employing a certain amount of HBPE-*g*-P*t*BMA in 4.0 mL CHCl$_3$ by ultrasonication at 35 °C for 1.0 h [3, 4]. The MWCNTs dispersion was then left undisturbed for 24 h. To remove the bundled MWCNTs, the supernatant of MWCNTs/HBPE-*g*-P*t*BMA dispersion was filtrated through glass wool (0.1 g) packed in a 5.0 mL syringe [5]. The obtained stable MWCNTs dispersion was utilized for lateral analysis. Typically, for TGA measurement, 0.8 mL of the stable MWCNTs/HBPE-*g*-P*t*BMA dispersion was transferred into a TGA sample pan in batches. After evaporating most of the CHCl$_3$ in the TGA pan at room temperature, the resultant mixture together with the pan were dried under vacuum at 35 °C for 24 h. Finally, the dried MWCNTs/HBPE-*g*-P*t*BMA was subjected to TGA measurements directly. For TEM and SEM analysis, 20.0 μL of the MWCNTs dispersion was dropped onto the copper grid and silica wafer respectively after proper dilution.

1.3 Preparation of HBPE-*g*-P*t*BMA/MWCNTs/PET conductive film

The conductive film was prepared by spin-coating (200 RPM, 120 s) the stable MWCNTs/HBPE-*g*-P*t*BMA dispersion (50 μL, 455 mg/mL, HBPE-*g*-P*t*BMA/MWCNTs=2/1, wt/wt) onto the PET substrate. The resultant film was dried at room temperature for 24 h. Then, two pieces of copper foils were pasted at the edge of the film for electronic properties study.

1.4 Measurements

Fourier transform infrared spectrum (FT-IR) was recorded on Nicolet 5700. Raman spectrum was recorded on LabRAM HR Evolution (Horiba) with a laser power of 150 mW through a 50× objective. Thermo gravimetric analysis (TGA) was performed on TA-Q500 (Mettler-Toledo) at a heating rate of 10 °C/min in nitrogen atmosphere. UV-vis spectra were recorded on UNICO UV-3802. Scanning electron microscope (SEM) images were taken using Hitachi SU-8010 SEM. Transmission electron microscopy (TEM) images were taken using Hitachi HT-7700 TEM. The thickness of the conductive film were measured by using TT240 eddy current thickness meter from ten different places. The conductivity of the prepared film was measured in SB1002A/2 four-probe conductivity meter based on equation (S1) obtained from the operation manual.

$$\rho_F = \frac{\Pi}{\ln 2} \times \frac{V}{I} \times d$$

Equation (S1). ρ_F: the specific resistance; I: the current applied in the four-probe conductivity meter; V: the voltage measured in the four-probe conductivity meter; d: the thickness of the conductive film and π: constant (3.14).

2. Calculating the concentration of HBPE-*g*-P*t*BMA/MWCNTs dispersion

Firstly, the pristine MWCNTs, HBPE-*g*-P*t*BMA, and HBPE-*g*-P*t*BMA/MWCNTs dispersion with a mass ratio of HBPE-*g*-P*t*BMA/MWCNTs=2.0 were analysized by TGA independently. As shown in Fig. S2a, pristine MWCNTs almost showed negligible mass lose even at 600 °C. In contrast, HBPE-*g*-P*t*BMA and HBPE-*g*-P*t*BMA/MWCNTs dispersion showed three stages of weight lose at about 150 °C, 250 °C and 400 °C respectively. It was noted that the TGA curves of four indivudially prepared TGA samples of HBPE-*g*-P*t*BMA/MWCNTs dispersion with the same mass ratio of HBPE-*g*-P*t*BMA/MWCNTs almost overlaped before 500 °C. However, they showed different mass residues after 500 °C, which

might because of the system error. Then, the average concentration of MWCNTs in $CHCl_3$ was calculated to be 455 mg/L based on the TGA date at 600 °C according to the equation (S2).

$$\begin{cases} m_3 = m_1 + m_2 \\ \\ m_3' = a \times m_1 + b \times m_2 \end{cases} \Rightarrow \quad m_1 = \frac{m_3' - b \times m_3}{a - b} \quad \quad m_2 = \frac{a \times m_3 - m_3'}{a - b}$$

Equation (S2). Equation employed to calculate the exact mass of MWCNTs in the dispersion based on the TGA data. m_1: the unknown initial weight of MWCNTs; m_2: the unknown initial weight of HBPE-*g*-P*t*BMA; m_3: the initial weight of HBPE-*g*-P*t*BMA/MWCNTs mixture determined by TGA; m_3': the final weight of HBPE-*g*-P*t*BMA/MWCNTs mixture at 600 °C determined by TGA; a: the weight percentage of MWCNTs at 600 °C determined by TGA; b: the weight percentage of HBPE-*g*-P*t*BMA at 600 °C determined by TGA.

Secondly, the HBPE-*g*-P*t*BMA/MWCNTs dispersion with known concentration (455 mg/L) was subsequently diluted to six samples with concentration varied from 1 to 10 μg/mL and their UV-vis spectra were recorded (Fig. S2b). Then, their absorbance at 600 nm were plotted against their corresponding concentration. The specific extinction coefficient of MWCNTs in $CHCl_3$ was then calculated to be 0.0648 L·cm^{-1}·mg^{-1} after linear fitting (Fig. S2c). The UV-vis spectra of HBPE-*g*-P*t*BMA/MWCNTs dispersion with mass ratio of HBPE-*g*-P*t*BMA/MWCNTs varied from 0 to 5.0 were recorded after proper dilution (Fig. S2d) and their concentration were then calculated based on their absorbance at 600 nm and the specific extinction coefficient obtained above.
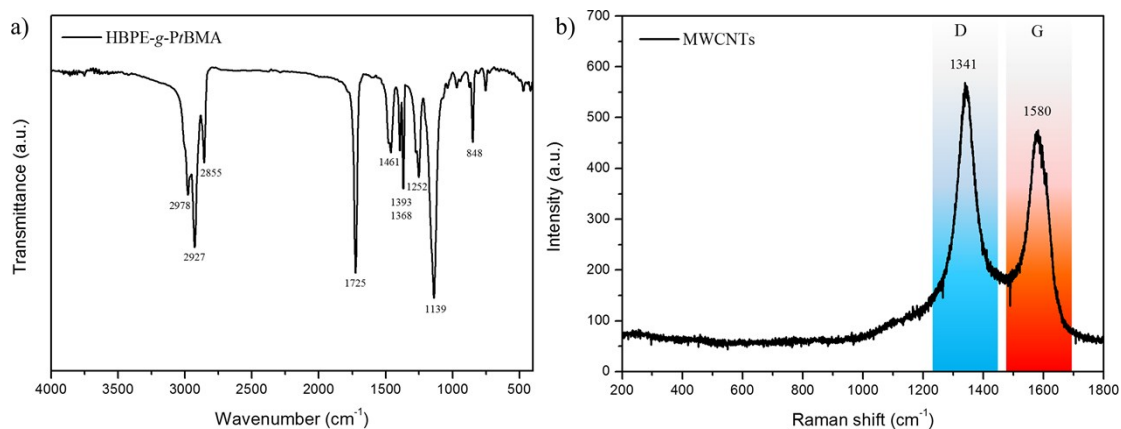
3. Figures

Fig. S1 a) FT-IR spectrum of HBPE-*g*-P*t*BMA and b) Raman spectrum of pristine MWCNTs.
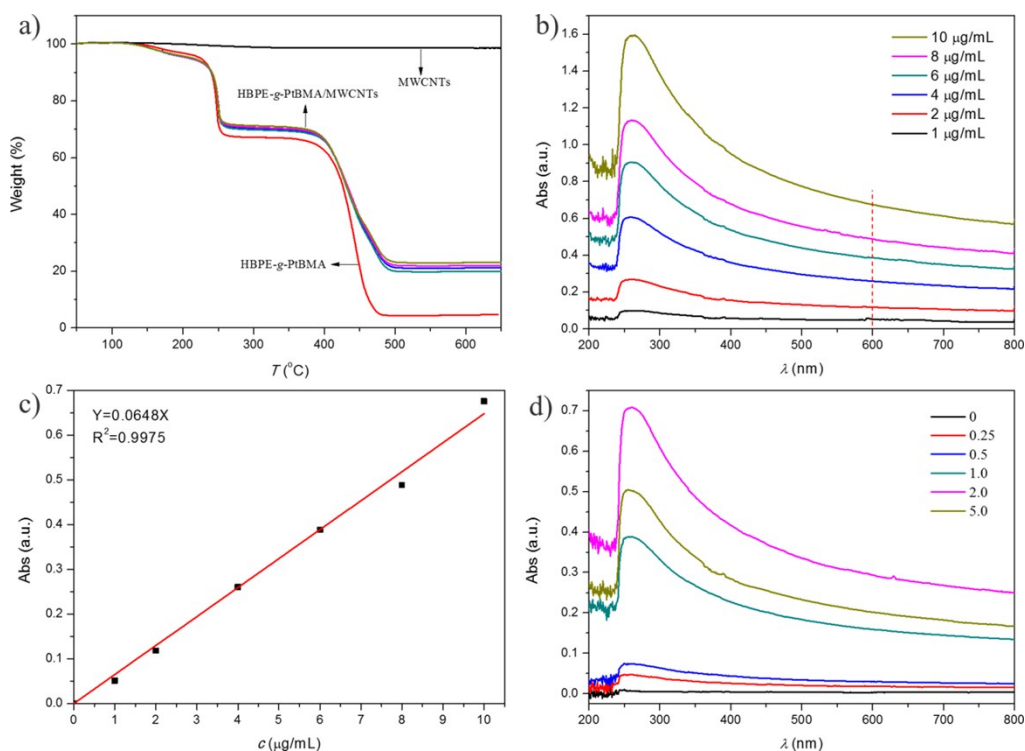
Fig. S2. a) TGA curves of HBPE-*g*-P*t*BMA, pristine MWCNTs and four individually prepared HBPE-*g*-P*t*BMA/MWCNTs dispersion with the same mass ratio of HBPE-*g*-P*t*BMA/MWCNTs=2.0. b) UV-vis spectra of HBPE-*g*-P*t*BMA/MWCNTs dispersion (HBPE-*g*-P*t*BMA/MWCNTs=2:1 wt/wt) with concentration of MWCNTs varied from 1 to 10 μg/mL; c) Linear fitting curve of the absorbance of MWCNTs in CHCl$_3$ at 600 nm against their concentration and d) UV-vis spectra of HBPE-*g*-P*t*BMA/MWCNTs dispersion with mass ratio of HBPE-*g*-P*t*BMA/MWCNTs varied from 0 to 5.0.
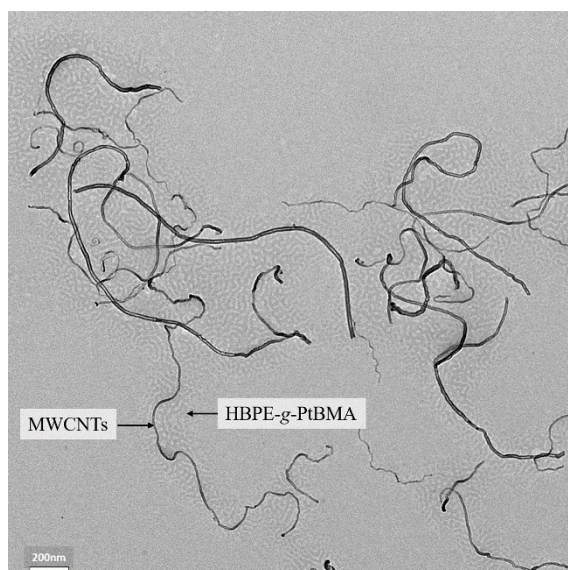
Fig. S3. Magnified TEM image of HBPE-*g*-P*t*BMA/MWCNTs dispersion with mass ratio of HBPE-*g*-P*t*BMA/MWCNTs=2.0.
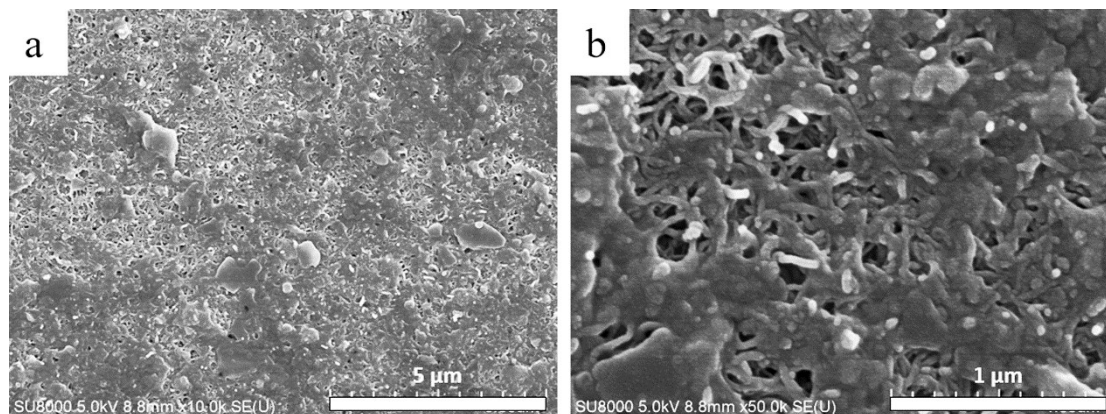

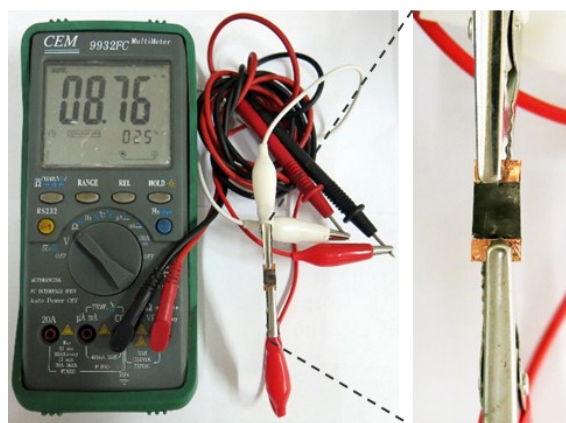Fig. S4. SEM a) and magnified SEM b) image of the conductive film.

Fig. S5. Photo of the universal resistance meter used to study the flexible properties of conductive film.

4. Reference

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3.   Z. Deng, H. Yu, L. Wang and X. Zhai, *J. Organomet. Chem.*, 2015, 791, 274-278.

4.   E. Pavoni, E. Bandini, M. Benaglia, J. K. Molloy, G. Bergamini, P. Ceroni and N. Armaroli, *Polym. Chem.*, 2014, 5, 6148-6150.

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