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Double-segregated carbon nanotube/polymer conductive composites as candidates for liquid sensing materials

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Experimental

10 UHMWPE was from Beijing No. 2 Auxiliary Agent Factory (Beijing, China). PMMA (SUMIPEX MH) was from Sumitomo Chemical Corporation (Singapore). CNTs with diameters of 20–40 nm and lengths of 10–20 mm were kindly supplied by Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). For electrical conductivity measurements using a Keithley 4200SCS apparatus, silver paste was attached to the surface of each sample to ensure good contact of the sample surface with the electrode. In the liquid sensing test, the sample with dimensions of $0.5\times5\times12$ mm^3 was quickly immersed into the good organic solvents at room temperature, and the resistivity

15 was real time recorded using a Keithley 4200SCS apparatus. For the long-term operational stability measurement, the immersion was carried out in chloroform for 900 s under controlled temperatures at 25 °C. For the drying procedure, the samples were lifted up and remaining solvent drops were wiped off at air and room temperature for 900 s. The conductivity of samples was stable during the long-term operational stability measurement. The solvents (chloroform. dimethyl formamide, toluene and acetone) were all purchased from Chengdu Kelong Chemical Reagent Factory (Chengdu, China) and were used as received. Transmission electron microscopy (TEM)

20 observation was performed on an FEI Tecnai F20, with an accelerating voltage of 200 kV. The sample section for TEM observation was obtained using a Leica EMUC6/FC6 microtome, whose thickness was ~80 nm. For optical microscopy observations made using an Olympus BX51, the specimens were cut into films with a thickness of 15 μm, using a microtome.

Reproducibility of liquid sensing property

25 **Table S1** Original conductivity and responsivity for the double-segregated CNT/PMMA/UHMWPE composites filled with 0.5 vol.% CNTs during 9 immersion-drying runs in chloroform .

Immersion-drying run	1st	2nd	3rd	4th	5th	6th	7th	8th	9th
Original conductivity (S/m)	0.83	0.21	0.22	0.21	0.19	0.21	0.22	0.22	0.23
Responsivity ($\times10^4$%)	4.7	6.8	10.6	11.7	12.8	13.2	13.4	13.9	14.6

Table S1 displays the detailed quantitative data related to the reproducibility of liquid sensing property during 9 immersion-drying runs. Apparently, the original conductivity of samples only decreased from 0.83 S/m to 0.2 S/m after solvent swelling and etching the double-segregated conductive network. More interestingly, the double-segregated composite still had a high responsivity of ~14.6×10^4%. These

30 results both indicate that our double-segregated composites possess an outstanding reproducibility of liquid sensing properties.

Affinity of PMMA for solvents

Table S1 Solubility parameters of solvents, PMMA and χ_{12} Flory–Huggins interaction parameter.

Solvent/polymer	$\delta_T/$ $(Jcm^3)^{1/2}$	$\delta_d/$ $(Jcm^3)^{1/2}$	$\delta_p/$ $(Jcm^3)^{1/2}$	$\delta_h/$ $(Jcm^3)^{1/2}$	$V_{mol}/$ (cm^3mol^{-1})	$\chi_{12[PMMA]}$
Chloroform	18.95	17.80	3.10	5.70	79.70	0.34
Toluene	18.16	18.00	1.40	2.00	106.30	0.70
DMF	24.86	17.40	13.70	11.30	76.95	0.22
Acetone	19.93	15.50	10.40	7.00	73.52	0.15
PMMA	22.20	17.00	5.80	9.20	—	—

As shown in Table 1, Flory–Huggins interaction parameter χ_{12} values were calculated with eqn (1):

$$\chi_{12} = \frac{V_{mol}(\delta_{Tpol} - \delta_{Tsol})^2}{RT} \tag{1}$$

where V_{mol} is the molar volume of the solvent, T is the temperature, R is the ideal gas constant, and δ_{Tpol} and δ_{Tsol} are the solvent and polymer global solubility parameters, respectively. According to other literature,[1, 2] the smaller χ_{12} indicates the larger the swelling of CNT/PMMA phase, corresponding to an increase of CNT gaps and consequently the higher responsivity. The affinity of PMMA for chloroform and toluene obtained from χ_{12} (Table S1) is correlated with that of responsivity. However, for acetone and DMF, the correlation cannot be well expressed, which may originate from the significant δ_p difference between solvents and PMMA.

Electronic supplementary information reference

1. J. B. Lu, J. F. Feller, B. Kumar, M. Castro, Y. S. Kim, Y. T. Park and J. C. Grunlan, *Sens. Actuat. B*, 2011, **155**, 28-36.
2. J. B. Lu, B. J. Park, B. Kumar, M. Castro, H. J. Choi and J. F. Feller, *Nanotechnology*, 2010, **21**, 255501-255510.