Supplementary Information

Robust and Efficient Charge Storage by Uniform Grafting of TEMPO Radical Polymer around Multi-Walled Carbon Nanotubes

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Experimental

Synthesis of the end-modified radical polymer (3): Monomer **2** (100 mg, 0.2 mmol) and Grubbs' 2nd generation catalyst (8.6 mg, 0.01 mmol) was dissolved in 2 mL of anhydrous dichloromethane. The reaction mixture was stirred at room temperature for 10 min, and then the terminating agent, 1-but-2-en-1,4-diyl-4-bis(perfluorophenyl)dibutanedioate,[S1] (18.6 mg, 0.03 mmol) was added to the mixture. The reacted solution was poured into methanol to form precipitate. The precipitate was collected by a glass filter and dried under vacuum to yield the end-modified radical polymer **3**. GPC ($CHCl_3$, polystyrene standard): M_n = 5800, M_w/M_n = 1.1. IR (KBr, cm^{-1}): 1738 ($\nu_{C=O}$), 1192 (ν_{C-O}).

Preparation of the amino group-modified MWNT (5)[S2]: MWNTs were refluxed in concentrated H_2SO_4/HNO_3 (v/v = 3:1) at 70°C to yield carboxylated MWNTs **4**. The yielded **4** was washed with deionized water, dried, and then refluxed with $SOCl_2$ for 24 h. $SOCl_2$ was removed from the mixture by evaporation. To the residue were added $NH_2(CH_2)_3NH_2$ (0.89 g) and toluene. The mixture was stirred for 24 h at 70 °C. The resulting mixture was washed with ethanol and deionized water on a membrane filter (0.2 μm) to yield the amino group-modified MWNT **5**. The product **5** was characterized by the X-ray photo electron spectroscopy (XPS). Fig. S3 shows peaks corresponding to amino, amide, carbonyl, and carboxyl groups of **5** in the N_{1s} and C_{1s} region, which was determined from fitting to Gaussian-Lorentzian shape peaks.

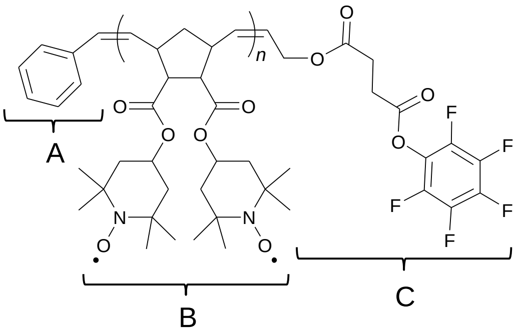
Preparation of the radical polymer-grafted MWNTs via the "grafting to" method (1): The amino group-modified MWNT **5** (10 mg), the end-modified radical polymer **3** (125 mg), *N,N*-dicyclohexylcarbodiimide (DMAP) (5.2 mg) and *N,N*-dimethyl-4-aminopyridine (3.1 mg) were dispersed in 10 mL of DCB. The mixture was stirred for 3h at room temperature. The resulting mixture was filtrated and washed with chloroform several times on a membrane filter. The grafting amount of **3** in **1** was 30 wt% determined from the TGA analysis (Fig. S4). The grafting density of **3** on MWNTs was estimated to be 0.26 chains/nm^2.

Synthesis of the norbornene-modified MWNT (6): Norbornene-modified macroinitiator **6** was synthesized by a literature procedure[S3] with slight modification. A suspension of MWNTs (20 mg) in tetrahydrofuran (THF) (60 ml) was sonicated for 10 min using the prove type sonicator. To the dispersion were added activated molecular sieves (4A) and 5-norbornene-2-methanol (0.8 mL, 6.6 mmol). The mixture was heated at 65 °C. To the mixture were slowly added a solution of dimethyl acetylenedicarboxylate (DMAD) (2 mL, 16.6 mmol) in THF and DMAP

(2.4 g, 19.8 mmol) during 36 h. To the reaction mixture was added 5-norbornene-2-methanol (3 ml), and then the resulting mixture was stirred at 65^{o}C for another 4 h. The mixture was cooled at room temperature, and then centrifuged at 15000 rpm for 10 min. The supernatant was discarded and the residue was dispersed in DMF for 5 min using the prove type sonicator. The same sequence was repeated twice with DMF and acetone used as solvents. The norbornene-modified MWNT **6** was dried under vacuum for 6 h. The grafting amount was 28 wt% determined from TGA analysis in Fig. S5.

Preparation of the radical polymer grafted MWNTs via the "grafting from" method (7): To a dispersion of **6** (10 mg) in 10 mL of anhydrous dichloromethane was added a solution of Grubbs' 2nd generation catalyst (10.2 mg, 0.012 mmol). The mixture was then stirred for 3h at room temperature. To the reaction mixture was added the monomer **2** (147.2 mg, 0.3 mmol). The mixture was stirred for 15 h at room temperature to yield the radical polymer grafted MWNT **7**. The product **7** was washed with chloroform for three times on a membrane filter. The grafting amount of the radical polymer was 28 wt% determined from the TGA analysis in Fig. S5.

Molecular weight of typical example of 3



Formula weight: A = 90.12, B = 490.63, C = 310.17

GPC ($CHCl_3$, polystyrene standards): M_n = 5,800 g mol^{-1}

Calculated and measured molecular weight of **3** were described as follows (Fig. S1);

4-mer: *m/z* = (90.12 + 490.63· 4 + 310.17) g/mol; M_{peak} = 2363 g/mol (calc.), 2363 g/mol (measured)

8-mer: *m/z* = (90.12 + 490.63· 8 + 310.17) g/mol; M_{peak} = 4325 g/mol (calc.), 4333 g/mol (measured)

10-mer: m/z = (90.12 + 490.63· 10 + 310.17) g/mol; M_{peak} = 5307 g/mol (calc.), 5319 g/mol (measured)

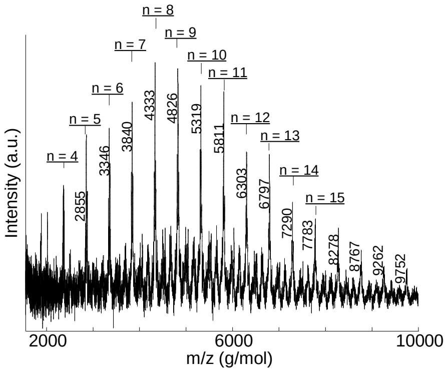


Fig. S1 MALDI-TOF mass spectrum of the end-modified radical polymer **3**.

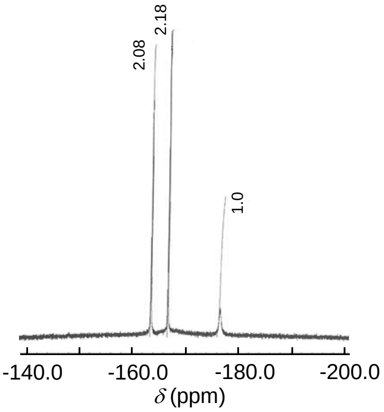


Fig. S2 ^{19}F-NMR spectra of the end-modified radical polymer **3**

XPS spectra for amino group-modified MWNTs

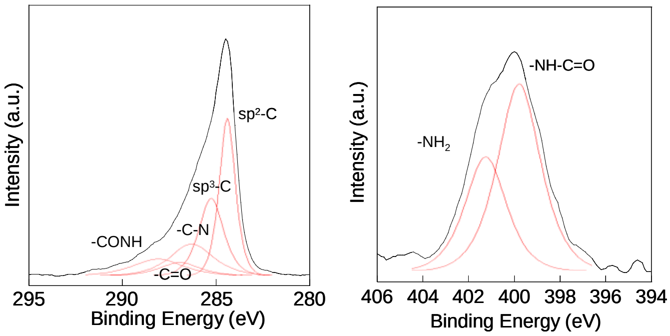


Fig. S3 XPS spectra of **5** (a) N_{1s}, (b) C_{1s} region.

Determination of grafting density of 3 on MWNTs in 1

Considering that the residues of **5** and **1** was attributed to the MWNTs and was determined to be 72 and 50 wt% from TGA analysis at 550 °C, respectively (Fig. S4), the grafting density of **3** on MWNTs in **1** was calculated as follows.

Assume that *a*, *b*, c, and *d* wt% of MWNTs, alkylamine group, alkylcarboxylic acid group, and 10-mer of **3**, respectively. Since the residue of **5** was 72 wt%, Eq. (1) is given.

$$a / (b + c) = 72 / (100\text{-}72) \tag{1}$$

Similarly, since the residue of **1** was 50 wt%, Eq. (2) is given.

$$a / (b + c + d) = 50 / (100\text{-}50) \tag{2}$$

Then, Eq. (1) and (2) provided Eq. (3).

$$a / d = 50 / 30 \tag{3}$$

Given that a 10-mer of **3** was grafted to the *x* carbon atoms of MWNTs in **1**,

$$\begin{aligned} x &= [\mathrm{C}] / [\text{10-mer of } \mathbf{3}] \\ &= (a / 12) / (d / 4990) \end{aligned} \tag{4}$$

Eq. (3) and (4) gave $x = 690$. Assuming that the MWNTs are consisted of 6 layers of graphene sheets according to the fact that the average diameter of MWNTs was 10 nm, we may regard that 21% of the total number of carbon atoms *x* is at the outermost surface of MWNTs. Consequently, a 10-mer of **3** per 145 carbon atoms was grafted on the surface of **1**, giving the grafting density of 0.26 chains/nm^2.

TGA analysis of MWNTs

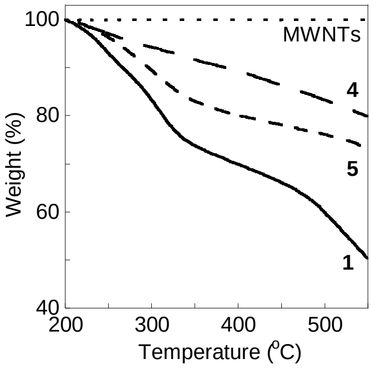


Fig. S4 TGA of MWNTs, **4**, **5**, and **1**.

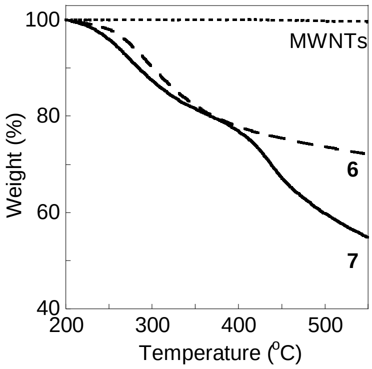


Fig. S5 TGA of MWNTs, **6**, and **7**.

TEM images of the radical polymer-grafted MWNTs 7 synthesized by the “grafting from” method.

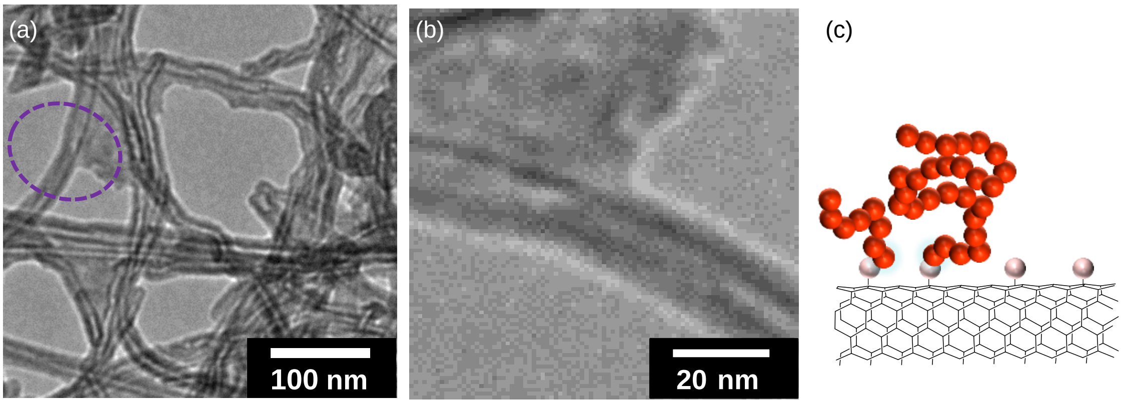


Fig. S6 TEM image of the **3**-grafted MWNT **7** *via* the “grafting from” method. (a) Overview, (b) a magnified image, and (c) schematic illustration of **7**. TEM images show that the radical polymer was attached inhomogeneously on MWNTs.

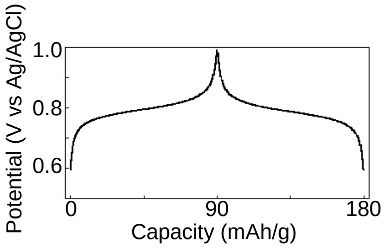


Fig. S7 Charging-discharging curve of **1**.

Reference

[S1] A. E. Madkour, A. H. R. Koch, K. Lienkamp, and G. N. Tew, *Macromolecules*, 2010, **43**, 4557-4561.

[S2] S.W. Lee, B.-S. Kim, S. Chen, Y. Shao-Horn, P.T. Hammond, *J. Am. Chem. Soc.*, 2009, **131**, 671.

[S3] D. Izuhara, T. M. Swager, *Macromolecules* 2009, **42**, 5416.