

Electronic Supplementary Information

Functionalized multi-walled carbon nanotubes in an aldol reaction

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Synthesis of 5: To a stirring solution of (2*S*, 4*R*)-di-*tert*-butyl 4-hydroxypyrrolidine-1,2-dicarboxylate (0.19 g, 0.65 mmol) in dry CH₂Cl₂ (10 mL), glutaric anhydride (0.15 g, 1.30 mmol) and DMAP (15 mg, 0.10 mmol) were added consecutively. The reaction mixture was left stirring at room temperature for 72 h. The solvent was removed in vacuo and the product was purified by column chromatography with CH₂Cl₂/CH₃OH 9/1 as the eluent, to afford **5**¹ (0.20 g, 77 %). [α]_D²⁰ = -37.9 (*c* = 1.0, CH₂Cl₂); ¹H NMR (200 MHz, CDCl₃) δ (ppm) 6.98-6.55 (br s, 1H), 5.35-5.17 (m, 1H), 4.33-4.09 (m, 1H), 3.71-3.43 (m, 2H), 2.41-2.21 (m, 5H), 2.19-1.97 (m, 1H), 1.96-1.77 (m, 2H), 1.41 (s, 18H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 177.9, 172.6, 171.8, 154.2, 81.8, 80.8, 72.1 (73.0), 58.6, 52.1 (52.4), 36.8 (35.7), 33.3 (33.1), 28.5, 28.2, 28.1, 19.9; MS 402 (M+H⁺, 21).

Synthesis of 8: A solution of proline derivative **5** (0.10 g, 0.25 mmol) in MeOH/EtOH (1:1) (10 mL) was treated with an ethereal solution of TMSCHN₂ at 0 °C until yellow colour persisted. The reaction mixture was left stirring for 1 h at room temperature. The reaction was then quenched with a few drops of acetic acid until the yellow colour disappeared. The solvent was removed in vacuo and the crude product was used in the next reaction as it is. The above crude mixture was diluted in CH₂Cl₂ (5 mL) and trifluoroacetic acid (5 mL) was added. The mixture was stirred at room temperature for 18 h. After removal of the solvent and the excess of TFA under reduced pressure, the crude residue was purified by column chromatography on silica gel using CH₂Cl₂/CH₃OH 8/2 as the eluent, yielding the product (55 mg, 62% for the two steps). [α]_D²⁰ = -6.9 (*c* = 1.0, CHCl₃); ¹H NMR (200 MHz, CDCl₃) δ (ppm) 9.13-9.08 (br s, 1H), 5.45-5.25 (m, 1H), 4.71-4.37 (m, 1H), 3.86-3.41 (m, 5H), 2.61-2.23 (m, 6H), 2.01-1.79 (m, 2H), 1.45 (s, 1H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 173.6 (173.5), 172.3 (172.2), 171.7 (171.6), 162.8 (q, *J* = 73 Hz), 116.6 (q, *J* = 289 Hz), 72.5 (72.2), 58.8 (59.0), 51.7 (51.6), 51.4 (51.3), 34.3 (34.9), 32.8 (33.0), 27.7 (29.7), 19.6 (20.0); ¹⁹F NMR (188 MHz, CDCl₃) δ (ppm) -9.27 (s, CF₃); MS 260 (M+H⁺, 32).

Synthesis of 11: To a stirring solution of 2-(2-benzyloxy)ethoxy)ethanol (0.56 g, 2.85 mmol) in dry CH₂Cl₂ (15 mL), glutaric anhydride (0.65 g, 5.70 mmol) and DMAP (175 mg, 1.40 mmol) were added consecutively. The reaction mixture was left stirring at room temperature for 72 h. The reaction mixture was diluted with CH₂Cl₂ (15 mL) and washed with aq. NaOH 1N (40 mL). The aqueous layer was acidified with HCl 1N (pH=1). The product was extracted CH₂Cl₂ (3 x 35 mL). After removal of the solvent, the crude product was used without purification at the next step.

To a stirring solution of the crude product (0.15 g, 0.48 mmol) in dry CH₂Cl₂ (10 mL), (*S*)-Boc-3-aminopyrrolidine (0.08 mL, 0.48 mmol), WSCI (0.10 g, 0.53 mmol), HOBt (0.07 g, 0.53 mmol) and triethylamine (0.07 mL, 0.53 mmol) were added and the reaction mixture was left stirring at room

temperature for 20 h. The reaction mixture was diluted with CH₂Cl₂ (10 mL) and washed with aq. HCl (1N, 10 mL), brine (10 mL), aq. NaOH (1N, 10 mL) and brine (10 mL). After drying over Na₂SO₄ and filtration, the solvent was removed in vacuo. The crude mixture was used in the next step.

To a stirring solution of the crude product in absolute ethanol (10 mL), 10% Pd/C was added and the reaction mixture was left stirring under H₂ atmosphere for 16 h. After filtration over Celite, the solvent was removed under vacuo. The crude mixture was purified by column chromatography with CH₂Cl₂/CH₃OH 95/5 as the eluent, to afford the product. $[\alpha]_D^{25} = -4.5$ ($c = 1.0$, EtOH); ¹H NMR (200 MHz, CDCl₃) δ (ppm) 6.72 (br s, 1H), 4.41-4.17 (m, 3H), 3.72-3.01 (m, 10H), 2.34 (t, $J = 6.8$ Hz, 2H), 2.18 (t, $J = 7.1$ Hz, 2H), 2.07-1.67 (m, 3H), 1.40 (s, 9H), 1.17 (t, $J = 7.0$ Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ (ppm) 173.3, 172.3, 154.5, 79.5, 72.2, 68.9, 63.1, 61.4, 58.1, 48.5 (49.2), 43.6 (43.9), 34.8, 33.1, 28.4, 20.9, 18.2; MS 260 (M+H⁺, 32); HRMS exact mass calculated for [M+H]⁺ (C₁₈H₃₂O₇N₂)⁺ requires m/z 388.2210 found m/z 388.2221.

References

1. E. Bellis and G. Kokotos, *Tetrahedron*, 2005, **61**, 8669.

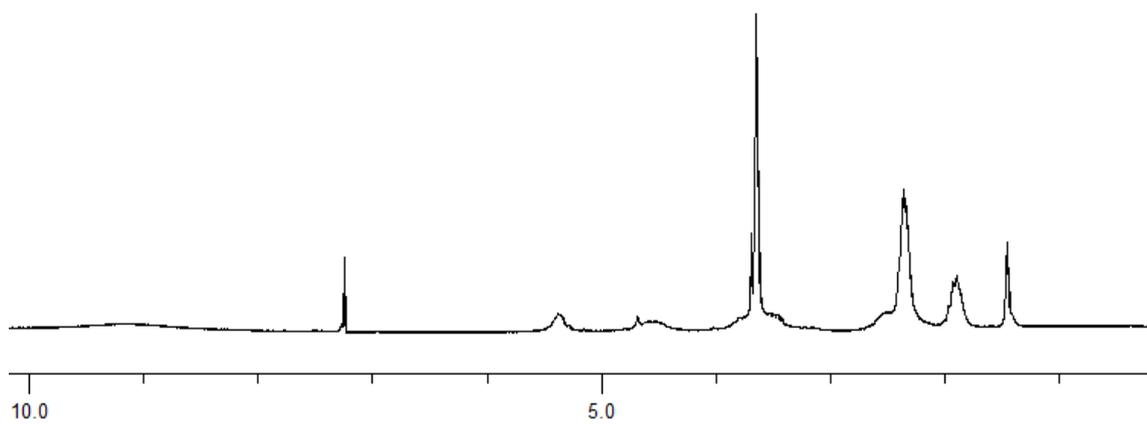


Fig. S1 ^1H NMR spectrum of compound **8**.

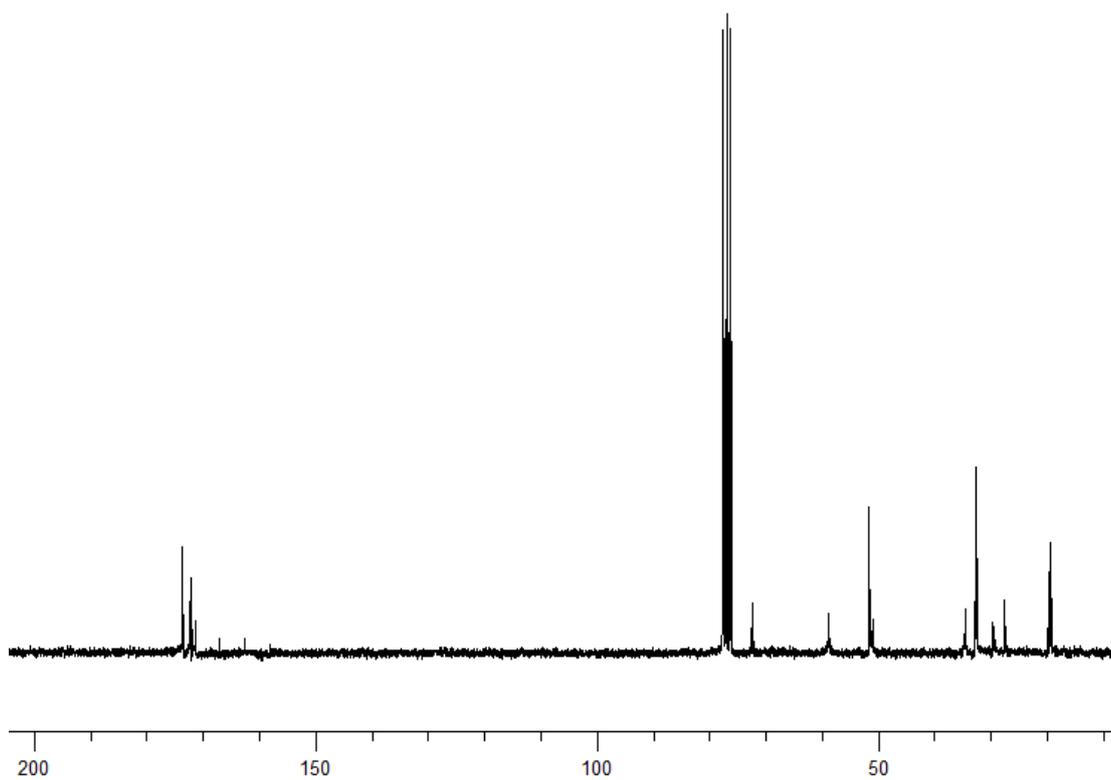


Fig. S2 ^{13}C NMR spectrum of compound **8**.

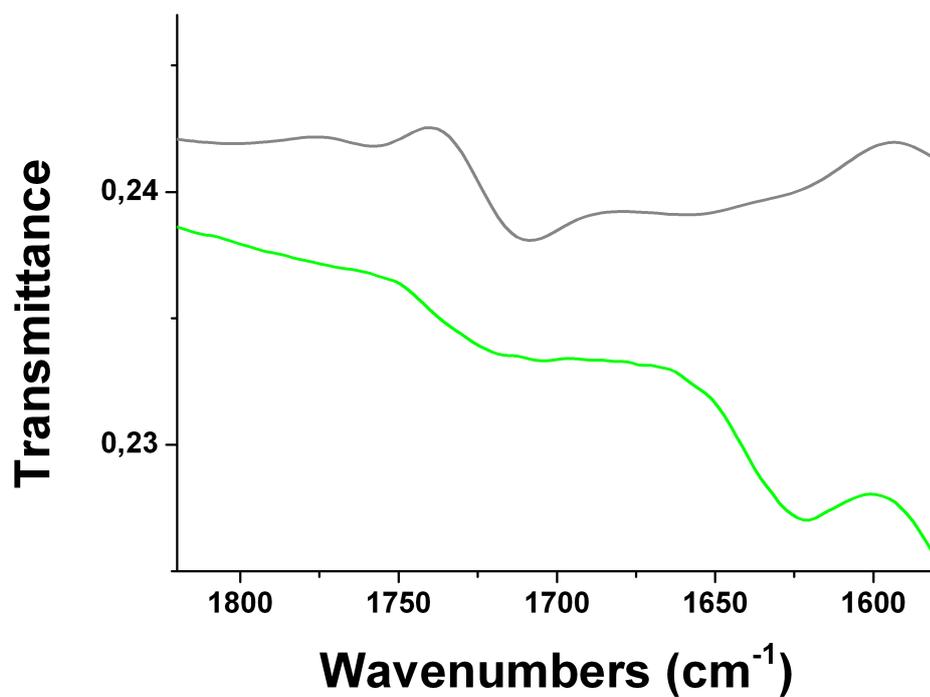


Fig. S3 ATR-IR spectra of oxidized MWCNTs **1** (gray) and MWCNT-based material **10** (green).

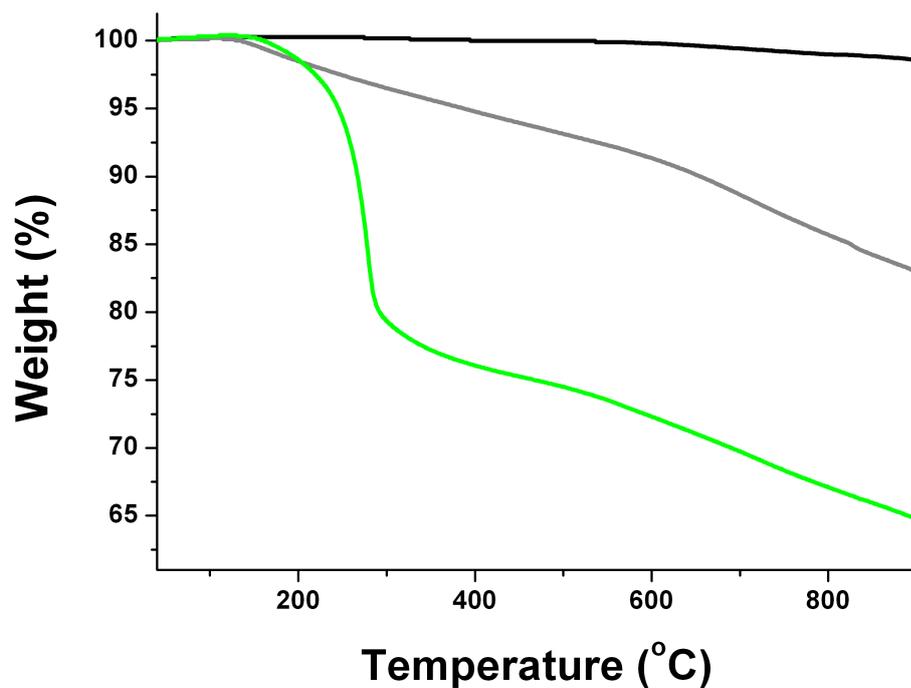


Fig. S4 Thermographs of pristine MWCNTs (black), oxidized MWCNTs **1** (gray) and MWCNT-based material **10** (green), obtained under nitrogen atmosphere.

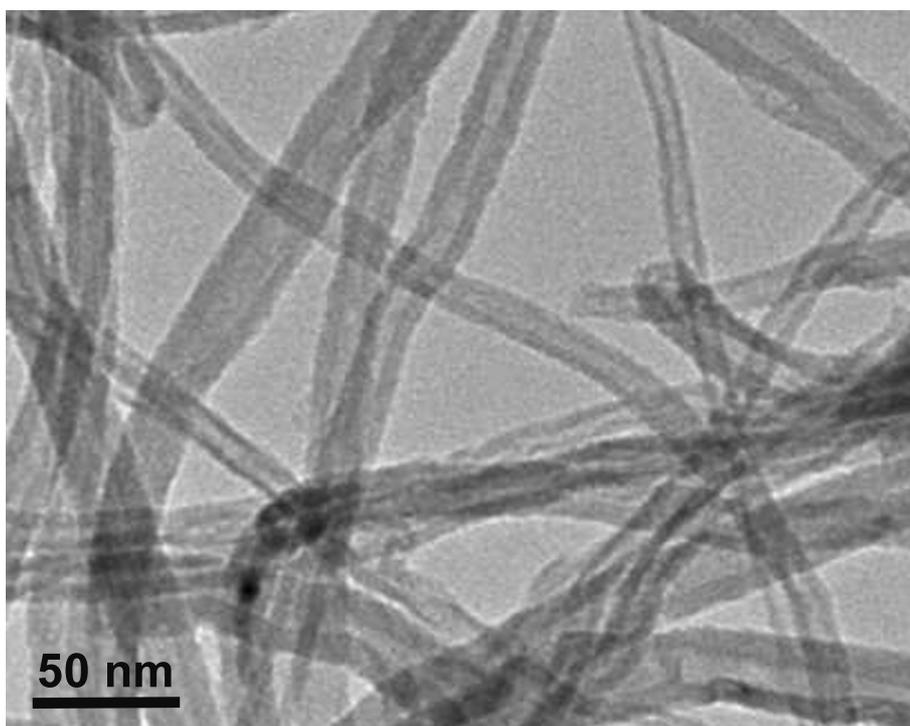


Fig. S5 Representative TEM image of MWCNT-based material **10**.

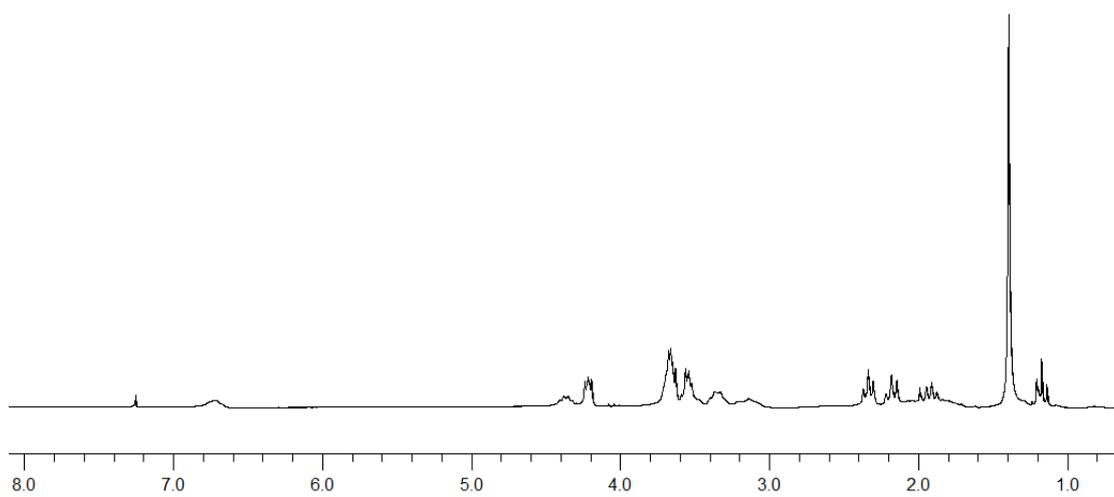


Fig. S6 ^1H NMR spectrum of compound **11**.

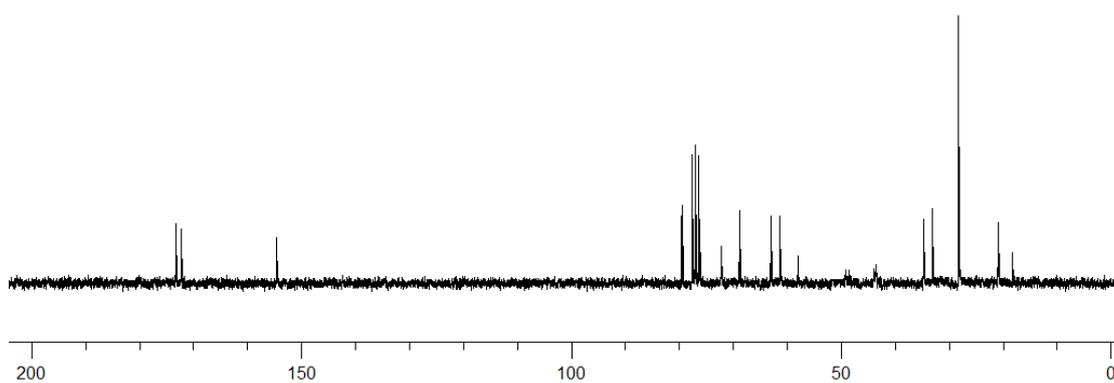


Fig. S7 ^{13}C NMR spectrum of compound **11**.

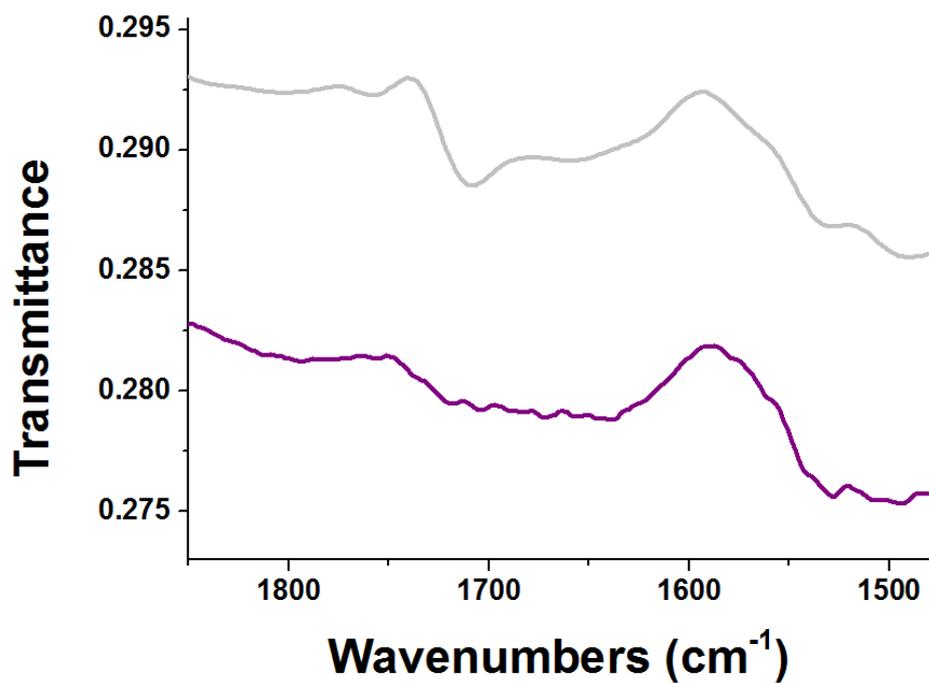


Fig. S8: ATR-IR spectra of oxidized MWCNTs **1** (gray) and MWCNT-based material **13** (purple).

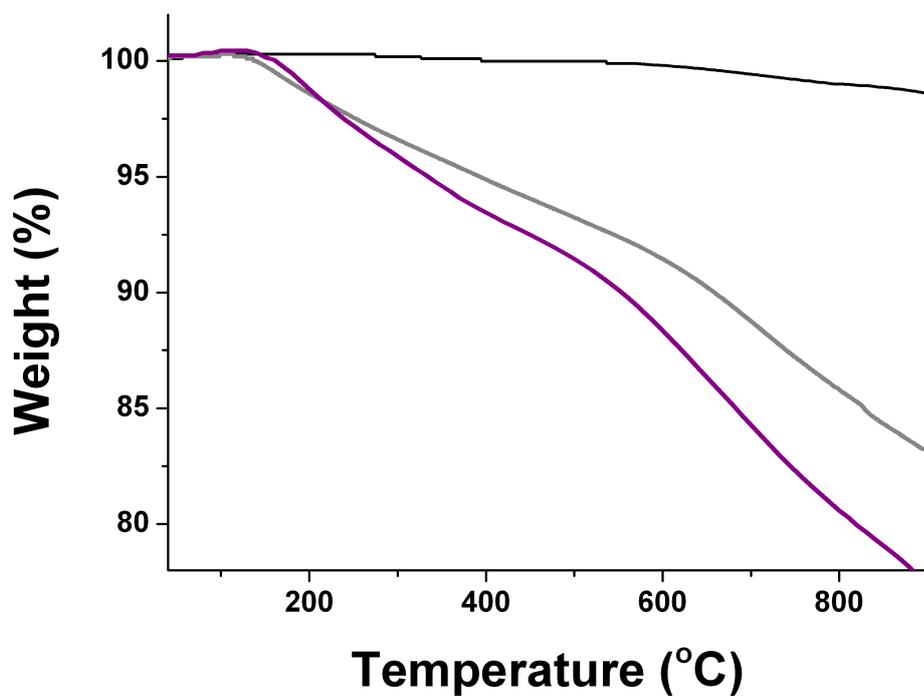


Fig S9 Thermographs of pristine MWCNTs (black), oxidized MWCNTs **1** (gray) and MWCNT-based material **13** (purple), obtained under nitrogen atmosphere.

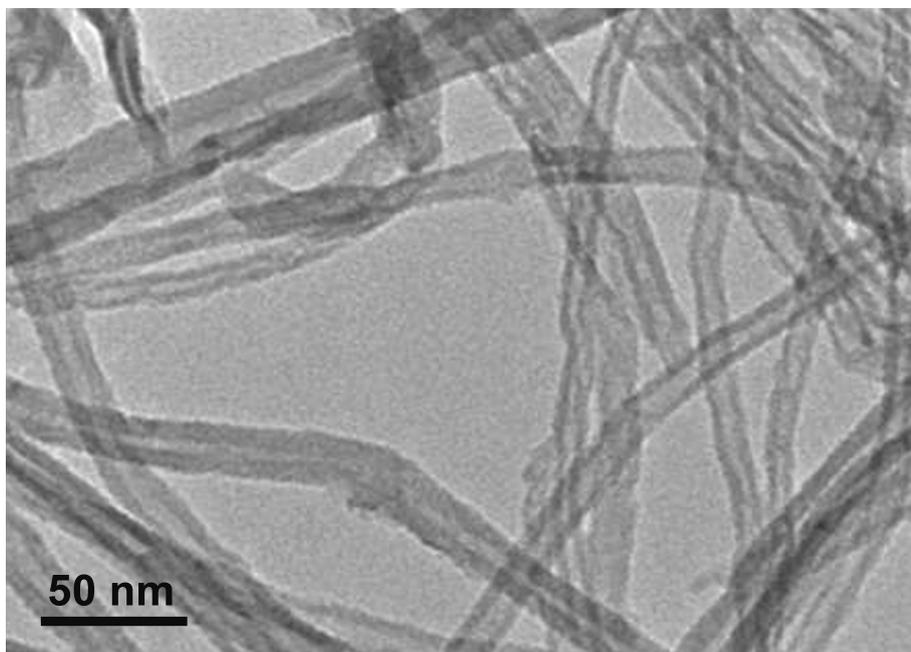


Fig. S10 Representative TEM image of MWCNT-based material **13**.