Electronic Supporting Information file

Controlled Oxidative Cutting of Carbon Nanotubes Catalysed by Silver Nanoparticles

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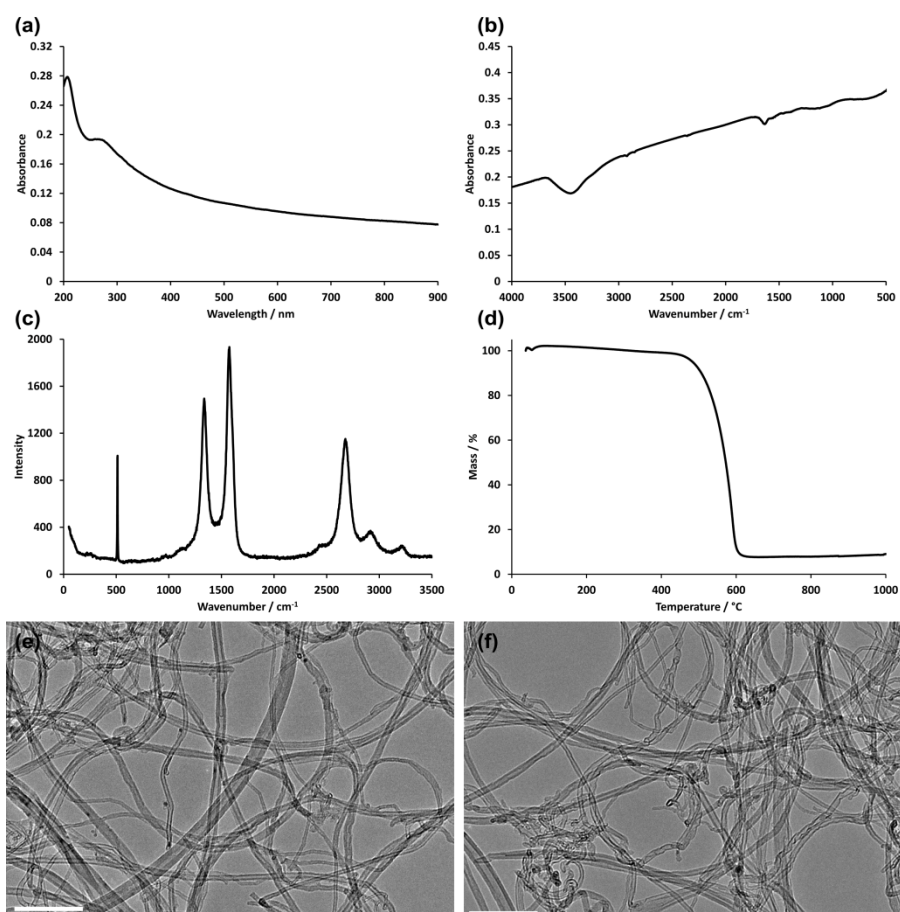## S1.   Cutting CVD MWNT using literature protocols

Characterisation of CVD MWNT

UV-vis (H$_2$O): λ_{max}/nm 264.0.
IR (KBr): ν/cm^{-1} 1384 ($\nu_{C=C}$), 1633 ($\nu_{C=C}$).
TGA (air): T$_{ox}$/°C 589, M$_{1000}$/wt% 8.4.
TEM (200 keV): L$_{NT}$/nm 3251 ±1600 (851-7000 nm), d$_{NT}$/nm 14.4 ±6.0 (5.6-27.1 nm).
Raman (532 nm): ν/cm^{-1} 1335.7 ±3.8 (D), 1576.2 ±1.7 (G), I$_D$:I$_G$ = 0.791 ±0.020.

Figure S1. Spectroscopic, gravimetric and microscopic analysis of as-received CVD MWNT: (a) UV-vis spectroscopy demonstrating a characteristic π-plasmon absorbance at 264 nm indicating a high level of conjugation; (b) IR spectroscopy indicating a broad stretching vibration due to aromatic C=C bonds at 1633 cm^{-1}; (c) Raman spectroscopy showing the initial degree of disorder by comparison of D and G bands at 1336 and 1576 cm^{-1} respectively (sharp peak at 520 cm^{-1} corresponds to silicon from the sample support); (d) thermogravimetric analysis showing a single oxidation feature at 589°C and (e,f) TEM where all nanotubes extend beyond the limits of the frame due to extreme length(scale bars are 100 nm).

Method 1: Chemical oxidation using H₂SO₄/HNO₃

CVD MWNT (25 mg) were suspended in a mixture of concentrated sulphuric acid (75 mL) and concentrated nitric acid (25 mL) with ultrasonication for 24 hr. The suspension was then diluted with deionised water (500 mL) and the solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with aqueous sodium hydroxide (1M, 50mL) and copious deionised water and dried *in vacuo* to yield a black solid (23.0 mg, 7% mass loss).

Raman (532 nm): ν/cm^{-1} 1341.2 ±4.0 (D), 1574.3 ±7.0 (G), I_D:I_G = 0.881 ±0.030.
TEM (200 kV): L_{NT}/nm 478 ±243 (180-1300 nm).

Method 2: Chemical oxidation using "piranha"

CVD MWNT (25 mg) were suspended in a mixture of sulphuric acid (96%, 25 mL) and hydrogen peroxide (30%, 5 mL) and stirred at 70°C for 9 hr. The suspension was diluted in deionised water (500 mL) and the solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with copious deionised water until the filtrate exhibited a neutral pH. The black solid was then washed with ethanol (25 mL) and dried *in vacuo* to yield a black solid (22.4 mg, 10% mass loss).

Raman (532 nm): ν/cm^{-1} 1345.6 ±1.8 (D), 1581.7 ±2.6 (G), I_D:I_G = 0.863 ±0.038.
TEM (200 kV): L_{NT}/nm 1127 ±862 (100-4300 nm).

Method 3: Chemical oxidation using KMnO₄

CVD MWNT (25 mg) were suspended in a mixture of aqueous potassium permanganate (0.3 M, 20 mL) and aqueous sodium hydroxide (0.1M, 10 mL) with ultrasonication for 20 min before stirring at reflux for 40 min. To the stirred solution was added sodium hydrogen sulphite (0.7 g) and sulphuric acid (1M, 0.1 mL) and the mixture was stirred under reflux for a further 19 hr. The solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed sequentially with sodium hydroxide (0.01M, 50 mL), hydrochloric acid (5M, 50 mL) and copious deionised water and finally dried *in vacuo* to yield a black solid (2.0 mg, 92% mass loss).

Raman (532 nm): ν/cm^{-1} 1345.6 ±1.3 (D), 1579.4 ±1.5 (G), I_D:I_G = 1.185 ±0.050.
TEM (200 kV): L_{NT}/nm 1254 ±986 (180-5070 nm).

Method 4: Air oxidation catalysed by NiONP

CVD MWNT (25 mg) were suspended in nitric acid (3M, 53 mL) with ultrasonication for 15 min and stirred at reflux for 5 hr. The black solid was collected by vacuum filtration (0.5 μm pore size PTFE membrane), washed sequentially with deionised water (50 mL), sodium hydroxide (1M, 50 mL), hydrochloric acid (1M, 50 mL) and copious deionised water to yield a black solid (24.5 mg, 2% mass loss). To the black solid suspended in ethanol (5 mL) was added an aqueous solution of nickel(II) sulphate hexahydrate (0.085M, 5 mL) and the mixture stirred vigorously while an aqueous solution of potassium borohydride (0.085 M, 5 mL) was injected and stirred for a further 50 min. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with deionised water (200 mL) and dried at 120°C in air for 2 hr. The black solid was heated in air to 400°C at a rate of 10°C min^{-1} and held at 400°C for 1 hr. A flow of argon was introduced and the sample was heated to 900°C at a rate of 10°C min^{-1} and held at 900°C for 2 hr before cooling to room temperature. The black powder was suspended in sulphuric acid (5M, 1 mg mL^{-1}) with sonication for 15 min before the solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed sequentially with aqueous sulphuric acid (1M, 500 mL) and copious deionised water and dried *in vacuo* to yield a black solid (4.0 mg, 84% mass loss).

Raman (532 nm): ν/cm^{-1} 1337.2 ±4.6 (D), 1573.2 ±6.6 (G), I_D:I_G = 0.956 ±0.050.
TEM (200 kV): L_{NT}/nm 787 ±586 (80-3450 nm).

Method 5: Air oxidation catalysed by in situ AgNP

CVD MWNT (25 mg) were suspended in nitric acid (5M, 50 mL) and stirred at reflux for 5 hr. The suspension was diluted with deionised water (300 mL) and solid collected by vacuum filtration (0.5 μm pore size PTFE membrane), washed sequentially with sodium hydroxide (1M, 50 mL), hydrochloric acid (1M, 50 mL), deionised water (200 mL) and acetone (50 mL) and dried *in vacuo* to yield a black solid (24.2 mg, 3% mass loss). The nanotubes were suspended in an aqueous solution of silver nitrate (0.005 M, 1.42 mL) and the suspension stirred at 40°C for 90 min, before the mixture was dried completely at 100°C for 90 min to yield a black solid (21.6 mg). The composite material was heated under a flow of argon to 300°C at a rate of 3°C min^{-1} and held at 300°C for 3 hr, before cooling to room temperature under argon. The sample was then heated under argon to 350°C at a rate of 3°C min^{-1} and air was then flowed across the sample at 350°C for a further 100 min before cooling in air. The nanotube sample was then sonicated in nitric acid (2M, 1 mg mL^{-1}), the black solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with copious deionised water and dried *in vacuo* to yield a black solid (12.0 mg, 52% mass loss).

Raman (532 nm): v/cm^{-1} 1337.6 ±4.1 (D), 1579.3 ±10.6 (G), I_D:I_G = 0.814 ±0.070.
TEM (200 kV): L_{NT}/nm 1353 ±1446 (200-8600 nm).

Method 6: Air oxidation catalysed by ex situ AgNP

To silver nitrate (153 mg) in ethanol (30 mL) was added dropwise dodecanethiol (0.1 mL) and the combined mixture stirred for 10 min at room temperature. To this was added dropwise a saturated solution of sodium borohydride in ethanol (60 mL) and the combined mixture vigorously stirred at room temperature for 2 hr. To the mixture was added acetone (100 mL) and the solution stored in the freezer at -20°C overnight affording a solid precipitate which was collected by vacuum filtration (0.5 μm pore size PTFE membrane), washed sequentially with toluene (10 mL), acetone (200 mL), methanol (200 mL) and dried *in vacuo* to yield a brown solid (171 mg).

IR (KBr): v/cm^{-1} 1541, 1559, 1653, 1699, 2326, 2336, 2356 and 2364.
UV/vis (toluene): λ_{max}/nm 435.0.
TEM (200 kV): d_{NP}/nm 7.3 ±1.7 (4.7-11.5 nm).

CVD MWNT (20 mg) was dispersed in concentrated hydrochloric acid (20 mL) with ultrasonication for 30 min. The nanotube suspension was then diluted with water (200 mL), the solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed sequentially with water (500 mL) and acetone (100 mL) before being dried *in vacuo*. To the resulting carbon nanotube powder (10 mg) was added a suspension of the silver nanoparticles (10 mg) in dichloromethane (10 mL) and the mixture was sonicated for 30 min. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with dichloromethane (10 ml) and dried *in vacuo*.

TGA (air): T_{ox}/°C 472, M_{1000}/wt% 29.0.

The carbon nanotube composite material was heated in air at 480°C for 7 min resulting in a 32% reduction in mass. The resultant black powder was suspended in nitric acid (2M, 0.5 mg mL^{-1}) with ultrasonication for 30 min. This suspension was then diluted with water (50 mL), the solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed sequentially with water (20 mL) and acetone (20 mL) and dried *in vacuo* to yield a black solid (1.2 mg, 88% mass loss).
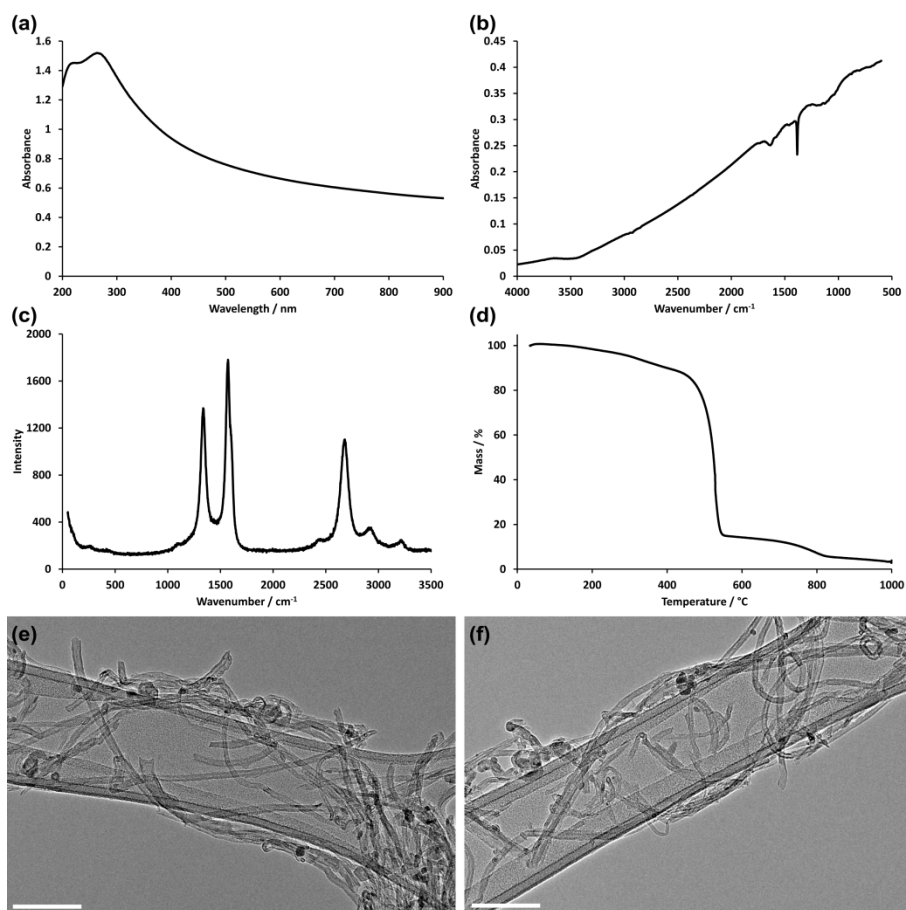
UV-vis (H$_2$O): λ/nm 264.3.
IR (KBr): v/cm^{-1} 1384 ($v_{C=C}$), 1636 ($v_{C=C}$).
TGA (air): T_{ox}/°C 528, M_{1000}/wt% 3.3.
TEM (200 kV): L_{NT}/nm 634 ±436 (125-2330 nm), d_{NT}/nm 12.4 ±3.7 (6.9-26.8 nm).
Raman (532 nm): v/cm^{-1} 1336.2 ±1.5 (D), 1571.6 ±2.3 (G), I_D:I_G = 0.801 ±0.028.

Figure S3. Spectroscopic, gravimetric and microscopic analysis of CVD MWNT subsequent to cutting by air oxidation catalysed by *ex situ* AgNP: (a) UV-vis spectroscopy showing a clear π-plasmon absorbance at 264 nm which has not shifted relative to Figure S1 inferring no considerable change in conjugation; (b) IR spectroscopy with insignificant changes in functionalisation and a slightly stronger band due to nanotube $\upsilon_{C=C}$ stretching vibrations at 1384 cm^{-1}; (c) Raman spectroscopy indicates a negligible difference I_D:I_G ratio compared to the nanotubes prior to oxidation which infers minimal sidewall damage; (d) thermogravimetric analysis showing a reduced oxidation temperature of 528°C and 3 wt% residual catalyst remaining; and (e,f) TEM showing visibly shorter carbon nanotubes with comparable morphology to those prior to oxidation (scale bars are 100 nm).

S2.   Cutting CVD MWNT using *ex situ* metal nanoparticles

Synthesis of gold, copper and palladium nanoparticles

AuNP

To a solution of tetrachloroauric acid trihydrate (79 mg, 0.2 mmol) in deionised water (30 mL) was added a colourless solution of tetraoctylammonium bromide (219 mg, 0.4 mmol) in dry toluene (60 mL) to give a biphasic solution. Upon addition of dodecanethiol (48 μL, 0.2 mmol) in toluene (5 mL) a slight yellow colour was observed. A solution of sodium borohydride (76 mg, 2 mmol) in deionised water (30 mL) was added dropwise and the reaction mixture turned dark brown. The mixture was left stirring at room temperature for 20 hr. The organic layer was separated and washed repeatedly with water before being dried over sodium sulphate and filtered through cotton wool. The solvent was removed *in vacuo* and the dark solid dissolved in toluene (3 mL) and precipitated by the addition of ethanol (350 mL) at -18°C for 20 hr. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane) to yield dark brown solid nanoparticles (42 mg).

IR (KBr): v/cm^{-1} 1466, 1632, 2851, 2872, 2921 and 2956.
UV/vis (toluene): λ_{max}/nm 522.8.
TEM (200 kV): d_{NP}/nm 2.2 ±0.7 (1.2-4.4 nm).

CuNP

To a solution of copper nitrate hemipentahydrate (279 mg, 1.2 mmol) in deionised water (120 mL) was added a colourless solution of tetraoctylammonium bromide (4.36 g, 8.00 mmol) in dry toluene (320 mL) to give a biphasic solution. Upon addition of dodecanethiol (432 μL, 1.8 mmol) in toluene (5 mL) a slight yellow colour was observed. A solution of sodium borohydride (752 mg, 20 mmol) in deionised water (100 mL) was added dropwise and the reaction mixture turned dark brown. The mixture was left stirring at room temperature for 20 hr. The organic layer was separated and washed repeatedly with water before being dried over sodium sulphate and filtered through cotton wool. The solvent was removed *in vacuo* and the dark solid dissolved in toluene (3 mL) and precipitated by the addition of ethanol (350 mL) at -18°C for 20 hr. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane) to yield dark brown solid nanoparticles (119 mg).

IR(KBr): v/cm^{-1} 1425, 1470, 2850, 2874, 2919 and 2955.
UV/vis (toluene): λ_{max}/nm 279.0.
TEM (200 kV): d_{NP}/nm 2.6 ±1.4 (0.8-10.0 nm).

PdNP

To a solution of potassium tetrachloropalladate (150 mg, 0.46 mmol) in deionised water (25 mL) was added a colourless solution of tetraoctylammonium bromide (375 mg, 0.69 mmol) in dry toluene (125 mL) to give a biphasic solution. Upon addition of dodecanethiol (110 μL, 0.46 mmol) in toluene (5 mL) a slight yellow colour was observed. A solution of sodium borohydride (175 mg, 4.6 mmol) in deionised water (10 mL) was added dropwise and the reaction mixture turned dark brown. The mixture was left stirring at room temperature for 20 hr. The organic layer was separated and washed repeatedly with water before being dried over sodium sulphate and filtered through cotton wool. The solvent was removed *in vacuo* and the dark solid dissolved in toluene (3 mL) and precipitated by the addition of ethanol (350 mL) at -18°C for 20 hr. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane) to yield dark brown solid nanoparticles (105 mg).

IR(KBr): v/cm^{-1} 1465, 2342, 2360, 2851, 2870, 2921 and 2956.
UV/vis (toluene): λ_{max}/nm 420.1.
TEM (200 kV): d_{NP}/nm 1.2 ±0.3 (0.6-1.7 nm).

Preparation of nanoparticle-nanotube composites

CVD MWNT (10 mg) were added to a suspension of metal nanoparticles (10 mg) in dichloromethane (10 mL) and the mixture was sonicated for 30 min. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with dichloromethane (10 mL) and dried *in vacuo* to yield a black solid (9, 19 and 15 mg for composites of CVD MWNT and Au, Cu and PdNP respectively).
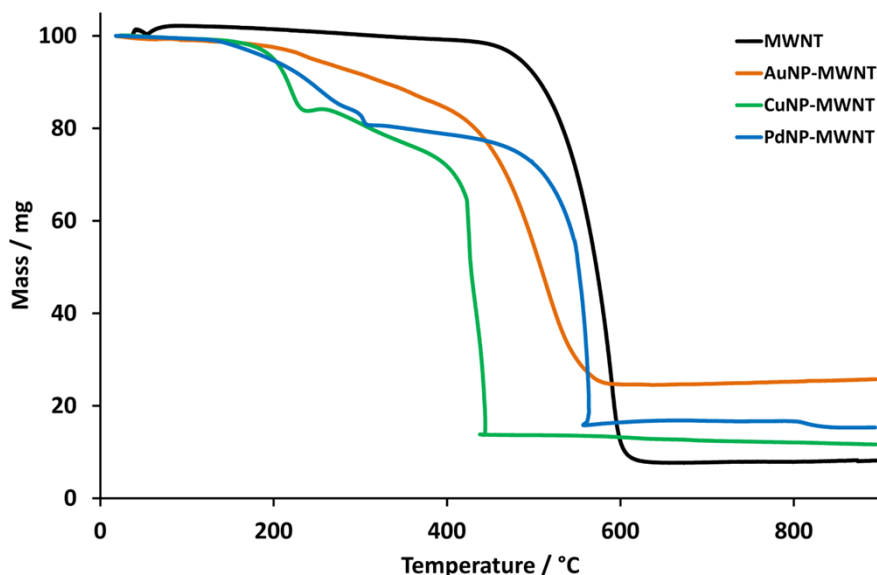
Figure S4. Thermogravimetric analysis of the composite materials comprising of gold (orange), copper (green) and palladium (blue) metal nanoparticles on CVD MWNT (black); showing the reduced oxidation temperature of each composite material relative to as-received MWNT.

Table S1. Thermogravimetric analysis of composite materials comprising of metal nanoparticles on CVD MWNT showing the oxidation temperature (T_{ox}), the reduction in oxidation temperature relative to as-received CVD MWNT (ΔT_{ox}) and the metal loading (M) as measured *via* TGA by mass remaining at 900°C (corrected by subtracting the residual metal from nanotube synthesis).

Material	T_{ox} / °C	ΔT_{ox} / °C	M / wt.%
AuNP–CVD MWNT	512	−77	17
CuNP–CVD MWNT	439	−150	3
PdNP – CVD MWNT	559	−30	7

Cutting carbon nanotubes using metal nanoparticles

The carbon nanotube composite material (10 mg) was heated in air for 5 min at 515, 440 or 560°C for Au, Cu and PdNP respectively. The resultant black powder was suspended in nitric acid (2M, 0.5 mg mL^{-1}) by ultrasonication for 30 min. This suspension was then diluted with water (50 mL), the solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed sequentially with water (20 mL) and acetone (20 mL) and dried *in vacuo* to yield a black solid (8.4, 6.3 and 5.2 mg for composites of CVD MWNT and Au, Cu and PdNP respectively).
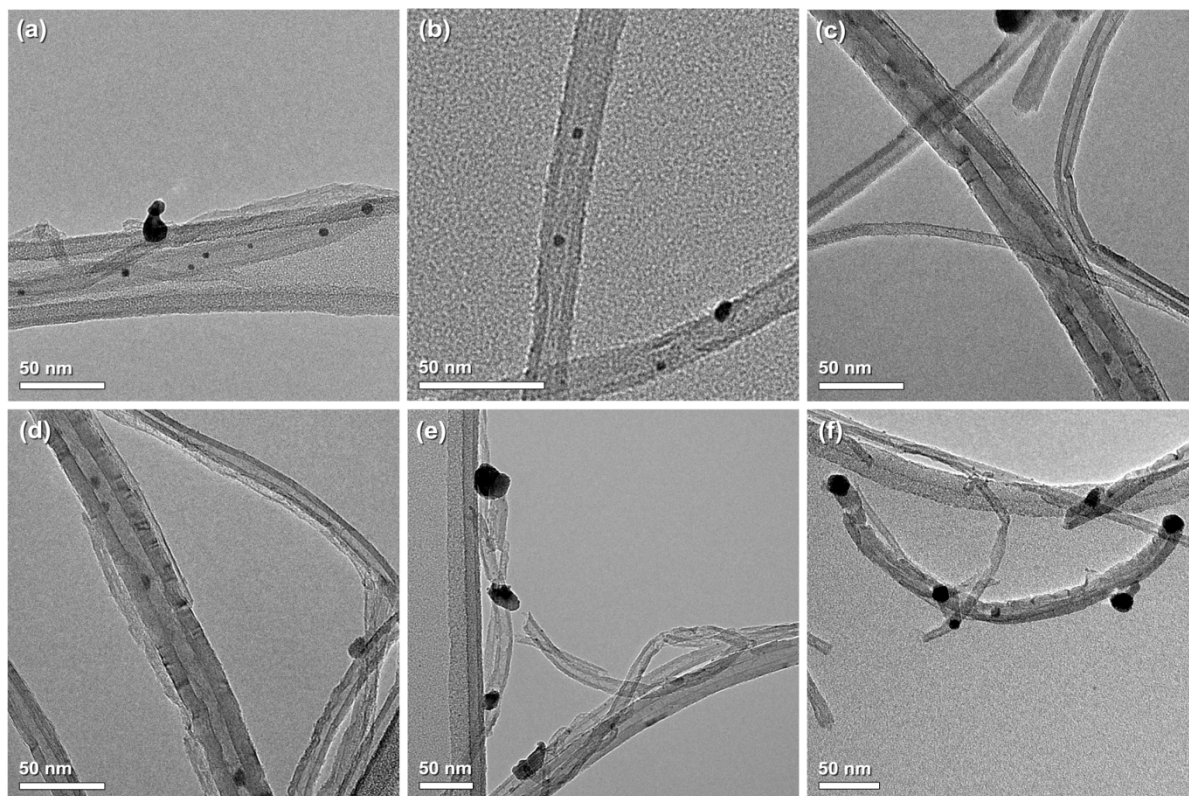
Figure S5. Transmission electron micrographs showing CVD MWNT subsequent to air oxidation in the presence of (a, b) gold, (c, d) copper and (e, f) palladium nanoparticles.

Table S2. Raman analysis of CVD MWNT after oxidative treatment with gold, copper and palladium nanoparticles showing the percentage increase in $I_D:I_G$ ratio upon oxidation. A correlation between oxidation temperature (Table S1) and $\Delta(I_D:I_G)$ indicates that catalysis at higher temperature generally introduces a greater number of nanotube defects.

Material	D / cm⁻¹	G / cm⁻¹	$I_D:I_G$	$\Delta(I_D:I_G)$ / %
CVD MWNT	1335.7±3.8	1576.2±1.7	0.791±0.020	-
AuNP–CVD MWNT	1340.2±1.7	1578.2±3.0	0.867±0.045	+9.6
CuNP–CVD MWNT	1341.3±3.5	1576.7±1.5	0.828±0.123	+4.7[a]
PdNP–CVD MWNT	1343.8±2.6	1580.2±1.7	0.908±0.045	+14.8
[a] Values within standard deviation of measurements in triplicate				

S3. Cutting CVD MWNT using *ex situ* silver nanoparticles

Table S3. Commercial suppliers of the carbon nanotubes used in this study.

| Carbon nanostructure	Synthesis method	d_{NT} / nm	Commercial name	Commercial Supplier
CoMoCAT SWNT	CVD	0.7±0.1	6,5-SWeNT	Sigma Aldrich, UK
HiPCO SWNT	CVD	1.0±0.1	HiPCO SWNT	Unidym Inc., CA, USA
AD SWNT1	AD	1.3±0.1	Helix SWNT	Helix Materials Solutions, TX, USA
AD SWNT2	AD	1.3±0.1	P2 SWNT	Carbon Solutions Inc., CA, USA
CVD MWNT	CVD	14.4±6.0	PD30L520 MWNT	Nanolab, MA, USA
AD MWNT	AD	19.0±5.8	MER MWNT	MER Corporation, AZ, USA
CVD GNF1	CVD	96±32	PR24 GNF	Applied Sciences, OH, USA
CVD GNF2	CVD	115±37	PR19 GNF	Applied Sciences, OH, USA

Experimental procedure

Carbon nanostructures (20 mg) were dispersed in concentrated hydrochloric acid (20 mL) using an ultrasonic bath at room temperature for 30 min. The nanotube suspension was then diluted with water (200 mL), collected by vacuum filtration (0.2 μm pore size PTFE membrane) and washed sequentially with water (500 mL) and acetone (100 mL) before being dried *in vacuo*. To the resulting black powder (10 mg) was added a suspension of dodecanethiolate-stabilised silver nanoparticles (10 mg) in dichloromethane (10 mL) and the mixture was sonicated for 30 min. The solid was collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed with dichloromethane (10 mL) and dried *in vacuo*. The composite material was heated in air at a prescribed temperature until approximately 30% mass loss was observed (see Table S4 for details). The resultant black powder was suspended in nitric acid (2M, 0.5 mg mL^{-1}) with ultrasonication for 30 min. This suspension was then diluted in water (50 mL), the solid collected by vacuum filtration (0.2 μm pore size PTFE membrane), washed sequentially with water (20 mL) and acetone (20 mL) and dried *in vacuo* to yield a black solid.

Table S4. Thermogravimetric analysis for various carbon nanostructures showing the oxidation temperature (T_{ox}), the change in oxidation temperature facilitated by pre-formed silver nanoparticles (ΔT_{ox}) and the loading of silver nanoparticles. Experimental heating conditions, temperature (T_{exp}) and duration, are also described for each carbon nanostructure.

Carbon nanostructure	T_{ox} / °C	ΔT_{ox} / °C	Ag / wt.%[a]	T_{exp} / °C	Duration / mins
CoMoCAT SWNT	563	−84	20.7	480	14
HiPCO SWNT	499	−56	6.2	440	14
AD SWNT1	457	−31	12.2	425	14
AD SWNT2	725	−108	42.4	620	7
CVD MWNT	589	−117	20.6	480	7
AD MWNT	727	−111	36.3	600	10
CVD GNF1	761	−263	22.0	440	35
CVD GNF2	733	−250	29.7	440	28

[a] Metal loading is corrected to account for residual metal content associated with carbon nanotube synthesis catalyst.
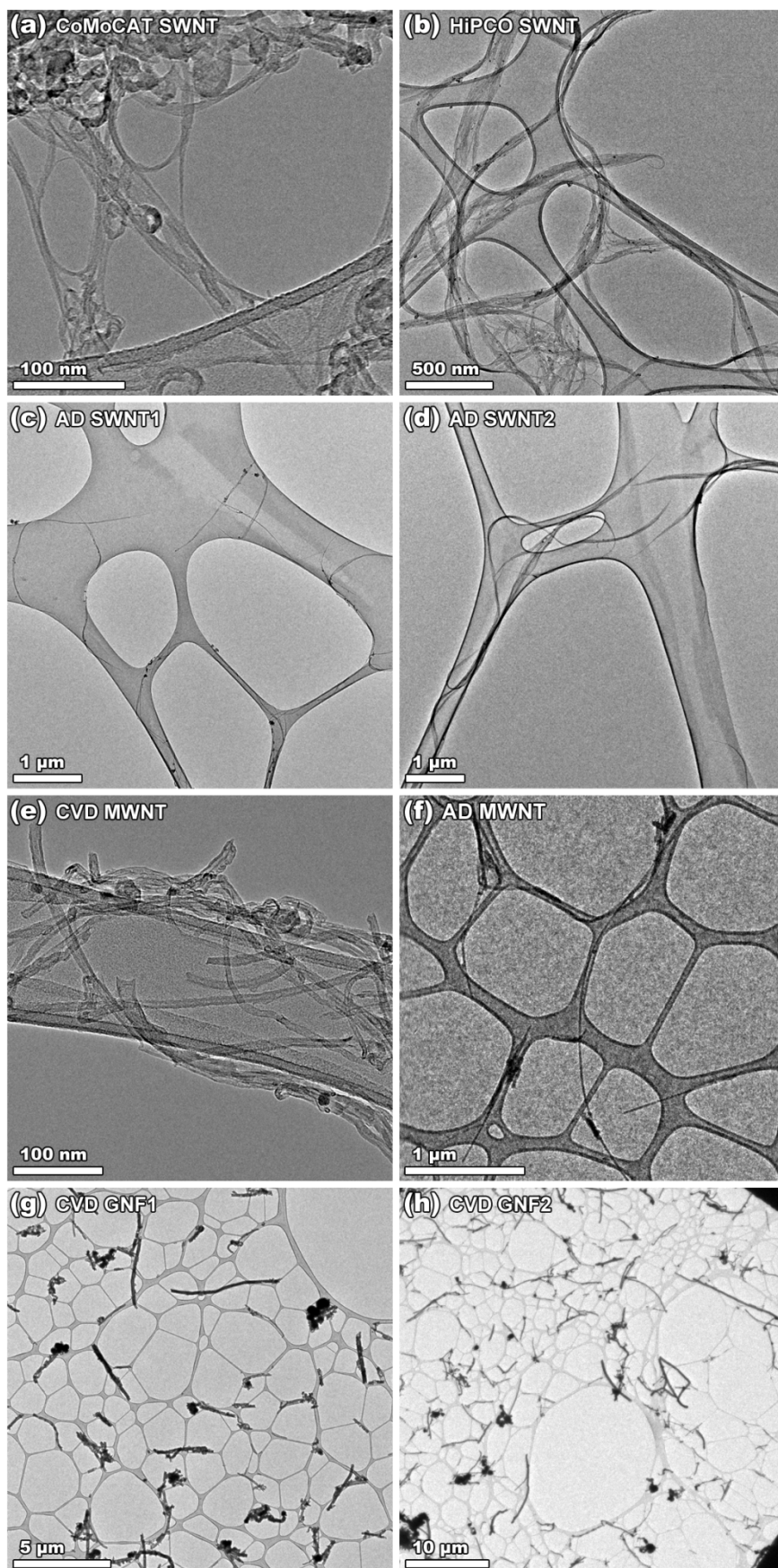
Figure S6. Transmission electron micrographs showing each carbon nanostructure subsequent to silver nanoparticle-catalysed oxidation.

Table S5. Raman analysis for various carbon nanostructures including the absolute change in I_D:I_G ratio subsequent to cutting using pre-formed silver nanoparticles.

Carbon nanostructure	D / cm^{-1}	ΔD / cm^{-1}	G / cm^{-1}	ΔG / cm^{-1}	I_D:I_G	ΔI_D:I_G
CoMoCAT SWNT	1303.2±1.5	+1.4	1578.7±3.1	−6.0	0.113±0.011	+0.034
HiPCO SWNT	1320.2±0.9	+2.5	1577.7±2.3	0.0	0.159±0.006	+0.009[a]
AD SWNT1	1329.2±1.7	+4.0	1581.2±1.5	+3.5	0.038±0.003	+0.008
AD SWNT2	1338.7±2.3	+0.5	1586.2±0.9	+1.0	0.016±0.002	-0.004
CVD MWNT	1335.7±3.8	+0.5	1576.2±1.7	−4.5	0.791±0.020	+0.010[a]
AD MWNT	1346.8±0.0	-1.5	1577.2±1.7	-2.0	0.147±0.012	+0.005[a]
CVD GNF1	1335.2±0.9	+1.5	1563.6±2.3	−0.5	0.225±0.049	+0.104
CVD GNF2	1337.2±2.3	+8.4	1564.1±2.3	+7.3	0.154±0.038	+0.051

[a] Values within standard deviation of measurements in triplicate

Raman spectroscopy of AgNP/CVD MWNT composite material prior to catalytic oxidation in air
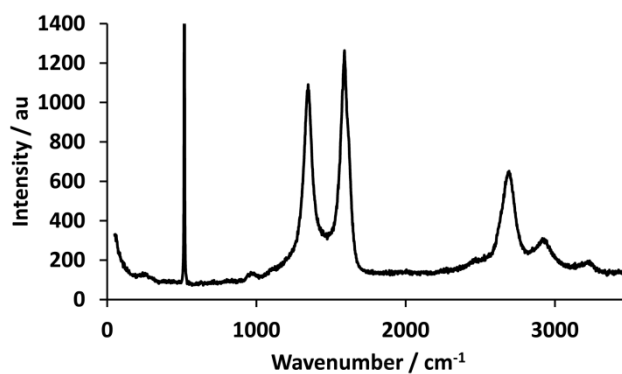
Figure S7. Raman spectrum of the composite material comprising silver nanoparticles deposited on CVD multi-walled carbon nanotubes. The I_D:I_G ratio of 0.895 (± 0.021) shows a 13% increase relative to CVD MWNT prior to silver nanoparticle deposition. This enhancement of the D band has been attributed to selective interactions between silver nanoparticles and nanotube defect sites.[S1]

Measuring carbon nanotube length by statistical analysis of transmission electron micrographs
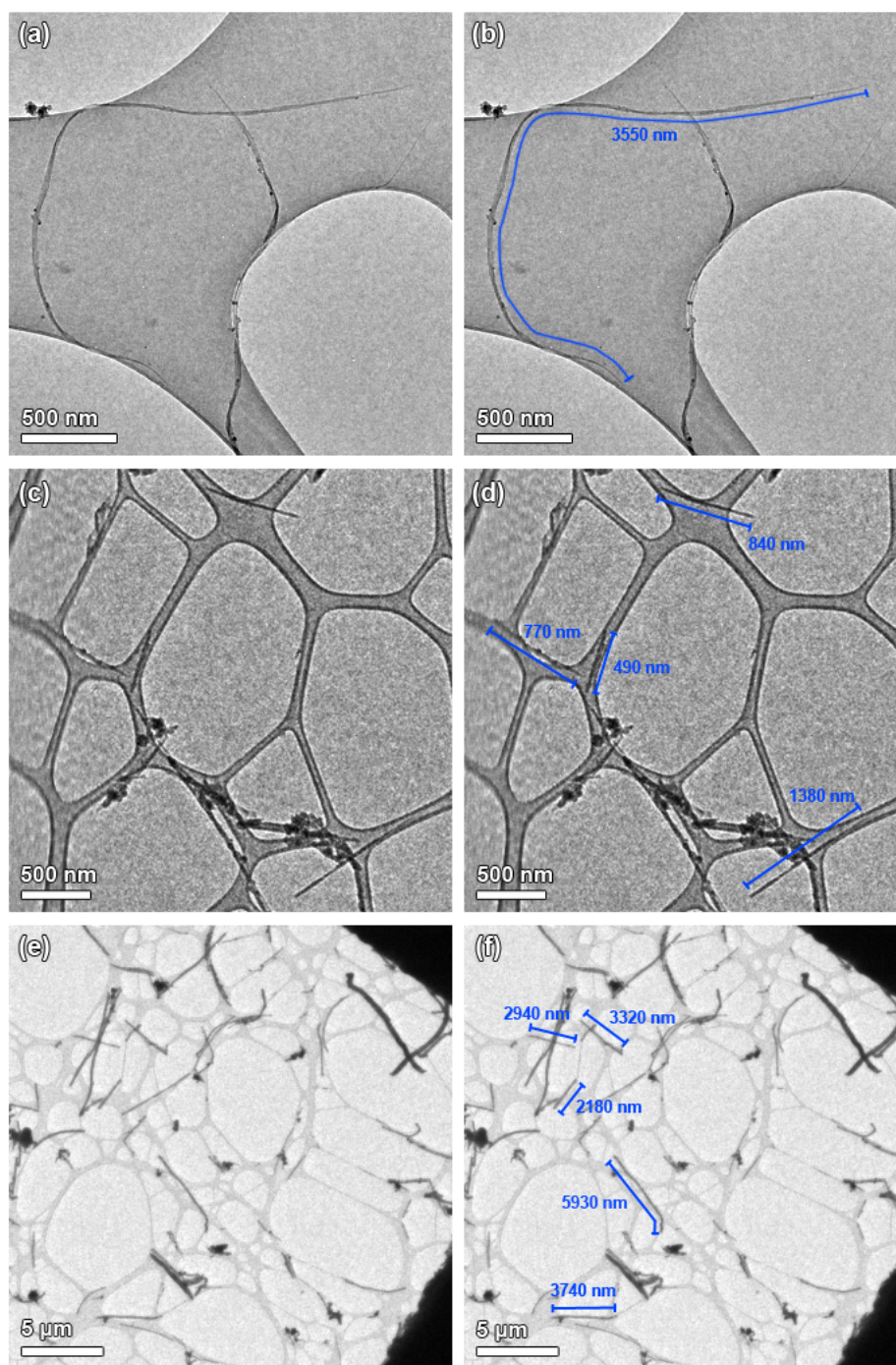
Figure S8. Representative transmission electron micrographs showing (a) AD SWNT1, (c) AD MWNT, (e) CVD GNF2 and examples of the typical procedure for measuring carbon nanotube length (b, d and f) respectively. Length analysis was completed using Gatan DigitalMicrograph software. SWNT are known to exist in bundles making measurement of individual nanotubes incredibly challenging and therefore the length of the SWNT bundles is measured here (b, where the bundle diameter is 15-30 nm), assuming that no individual nanotube can be longer than the bundle. Thus, the measurements of L_{NT} for SWNT samples do not discriminate bundles and isolated nanotubes and thus, represent the maximum length of a single nanotube within a given bundle, consistent with previous studies.[S2]

References

S1   S. Neupane, S. Khatiwada, C. Jaye, D. A. Fischer, H. Younes, H. Hong, S. P. Karna, S. G. Hirsch and D. Seifu, *ECS Journal of Solid State Science and Technology*, 2014, **3**, M39-M44.

S2   A. N. G. Parra-Vasquez, I. Stepanek, V. A. Davis, V. C. Moore, E. H. Haroz, J. Shaver, R. H. Hauge, R. E. Smalley and M. Pasquali, *Macromolecules*, 2007, **40**, 4043-4047.