Supplementary Information for:

Carbon nanotube functionalization as a route to enhancing the electrical and mechanical properties of Cu-CNT composites

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Structural Properties

The stability of a Cu-fCNT composite is determined using a combined analysis of the interfacial strength τ and matrix internal surface energy γ .¹ The interfacial strength is defined as:

$$\tau = -\frac{E_{comp} - E_{matrix} - E_{CNT}}{A_{int}},\tag{1}$$

where E_{matrix} , E_{CNT} and E_{comp} are the total energies of the metal matrix, CNT and composite, respectively. The interfacial area, A_{int} , is the sum of the lateral surface area of the CNT $((2\pi(\bar{r}+t)l)$ and its two end areas $(4\pi(\bar{r}_l + \bar{r}_r)t)$. The average radius of the CNT (\bar{r}) was determined as a geometric average of distances between the axis of the tube and all carbon atom positions, whereas the radius of the left(right) end $(r_{\bar{l}(r)})$ of the tube considers only the position of the C atoms at the left(right) end. The thickness of the CNT, t, is equal to $2r_C$, where r_C is the van der Waals radius of a carbon atom (1.7 Å).

The matrix internal surface energy is defined as:

$$\gamma = -\frac{E_{matrix} - \sum_{\alpha=1}^{N} E_{atom,\alpha}}{A_{cavity}},$$
(2)

where A_{cavity} is the internal surface of the matrix cavity formed by the CNT and $E_{(atom,\alpha)}$ is the total atomic energy of a Cu bulk atom.

The distortion in the carbon network caused by the functionalization of the CNTs and embedding them in the Cu matrix is quantified using the coefficient of variation of the CNT radius, CV, which is defined as the ratio of the standard deviation to the mean of the CNT radius.²

The separation distance between the CNT backbone and the surrounding Cu matrix, $(\langle d_{min}^{Cu-CNT} \rangle)$, is calculated as an arithmetic mean of the minimal separation distance between all C and Cu atoms from the first layer around the CNT. In the case of Cu-nCNT composites, the N atoms were also included.

Elastic Properties

The elastic stiffness of the Cu-fCNT composites was estimated by calculating Young's modulus along the \hat{z} (longitudinal) axis of the supercell. The equilibrium structures of the Cu-fCNT composites were subjected to a uniaxial elongation of l_c (Δl_c) along the nanotube symmetry axis as schematically presented in the inset of Fig.3 and the resulting stress tensor was determined. The Young's modulus was calculated using the following expression:

$$Y = \frac{\sigma_{ii}}{\varepsilon_{ii}},\tag{3}$$

where ε_{ii} is the normal strain defined as $\varepsilon_{ii} = \frac{\Delta l_c}{l_c}$, and σ_{ii} is the corresponding stress component of the stress tensor.

Electronic and Transport Properties

The electrostatic difference potential was calculated as the difference between the electrostatic potential of the self-consistent valence charge density and the electrostatic potential from a superposition of atomic valence densities.

The transmission coefficients, $T(\epsilon, U)$, of electrons with energy ϵ incident in the central scattering region constituting the device under a bias voltage U, was calculated using the following expression:

$$T(\epsilon, U) = G(\epsilon)\Gamma_l G^{\dagger}(\epsilon)\Gamma_r, \qquad (4)$$

where $G(\epsilon)$ is the Green's function of the central region and $\Gamma_{l(r)}$ is a matrix accounting for the coupling of the central region to the left (right) electrode.

In order to visualise the local charge transmission, the transmission coefficient $T(\epsilon, U)$ can be split into local bond contributions t_{ij} :³

$$T(\epsilon, U) = \sum_{ij} t_{ij}(\epsilon, U).$$
(5)

The electrical current through the device under non-equilibrium conditions was calculated using the Landauer-Büttiker formula:

$$I(U) = \frac{2e}{h} \int_{-\infty}^{+\infty} T(\epsilon, U) \left(f_l \left(\epsilon - \mu_l \right) - f_r \left(\epsilon - \mu_r \right) \right) d\epsilon,$$
(6)

where $\mu_{l(r)} = \epsilon_F \pm eU/2$ is the electrochemical potential of the left (right) electrode, and $f_{(l(r))}$ is the corresponding Fermi-Dirac electron distribution. ϵ_F is the Fermi energy. Inelastic scattering effects, e.g. electron-phonon coupling, were not considered. However, as our previous work has shown,¹ the calculated values are in qualitative agreement with electrical measurements of the composite material.

The current density, j, was calculated as a ratio of the electrical current I, to the average cross-sectional area $\bar{A} = V/l_c$, where V is the volume of a system and l_c is the z-dimension of the model.

The differential conductance can be also calculated from the current:

$$\delta G = \frac{dI(U)}{dU}.\tag{7}$$

Finally, the change in the resistance of the Cu-fCNT system with respect to the pure Cu-CNT system was calculated as:

$$\Delta R = \frac{R_{Cu-fCNT} - R_{Cu-CNT}}{R_{Cu-CNT}},\tag{8}$$

where R is expressed as 1/G(U). The conductance, G(U) was obtained directly from the transmission, $T(\epsilon, U)$:

$$G(U) = G_o Tr[T(\epsilon, U)] \tag{9}$$

and $G_o = 2e^2/h$ is is the unit of quantum conductance.

Spin polarization has only a negligible impact on the transport properties of all Cu-

fCNT systems. Due to computational constraints, spin-orbit coupling was only assessed for the carpet systems. It was also found to have a negligible impact on their transport properties.



Figure S1: a) Schematic representation and (b) photograph of the experimental setup used to synthesize the CNT carpets.



Figure S2: (a)-(b) Cross-sectional and (c)-(d) end views of as-made N-doped CNT carpets indicating a high density and very uniform alignment of MWCNTs. End view of the CNT carpets shows iron catalyst in some of the CNT hollow cores.



Figure S3: Photograph of the Webb 134 Red Devil high vacuum furnace used for heat treatment of the CNT carpets.



Figure S4: Thermogravimetric analysis of (a) as-made N-doped CNTs and (b) heat treated N-free CNTs. Vacuum heat treatment at 2000 °C improves the degree of graphitisation. Sample in (b) has a higher oxidation temperature than sample in (a) which indicates a high graphitisation level (low defect concentration). The residual weight (amount of material left after oxidation) of N-free CNTs is lower because some of the catalyst (iron) was evaporated out of the material at 2000 °C.



Figure S5: Raman spectra of as-made N-doped CNTs (a) before and (b) after nitrogen removing vacuum heat-treatment of up to 2000 °C. D and G indicate the defect-induced and graphitic vibration bands respectively. The average intensity ratio (I_D/I_G) of the defect-induced band (D) to the graphitic vibration band (G) was reduced from 0.86 to 0.32 after heat treatment.



Figure S6: Left: Atomistic side and cross-sectional views of fully optimized Cu-n(10,10)@(5,5) system. For clarity, some layers of Cu atoms in the side view are drawn with different degrees of transparency. Supercells are marked by grey lines. Right: The cross-sectional views of the composites containing oxygenated and aminated DWCNTs.



Figure S7: Projected density of states (PDOS) of Cu-CNT composite systems containing (a) a SWNT and (b) a DWNT. ϵ_F is the Fermi energy. Inset: DOS projected on atoms at the side interface.



Figure S8: Projected density of states (PDOS) of Cu-OO-CNT composite systems containing different amounts of oxygen. ϵ_F is the Fermi energy.



Figure S9: Projected density of states (PDOS) of (a) Cu-O-(6,4), (b) Cu-N-(6,4), and (c) Cu-n(6,4) composite systems. EF is the Fermi energy.



Figure S10: Current density as a function of applied voltage for composites containing (a) different types of pure Cu-CNT composites and (b) different concentration of nitrogen atoms in Cu-N-(5,5) composites, including aggregates. Inset: The relative change in differential conductance of Cu-N-(5,5) composites with respect to the undoped system. (c) Change in resistance of Cu-N-(5,5) composites with applied voltage.



Figure S11: Cross-sectional (perspective) and longitudinal (side) views of the transmission pathways in Cu-N-(5,5) composites. The left figure shows transmission pathways as a function of magnitude where the thickness and the colour of an arrow represents the relative local transmission component (t) with respect to the maximum value (t_{max}) . The colour of an arrow on the right figure indicates the magnitude of the local flow. The positions of the nitrogen atoms are also shown on the right figure. In both figures, an arrow is only drawn when its magnitude is at least 5% of the maximum local transmission.

Table S1: Coefficients of variation of nanotube radius (CV) of all types of Cu-f(5,5) systems depicted in Fig.2. N is the number of O/N atoms in the supercell, whereas C is the concentration of O/N atoms relative to the number of C atoms in the nanotube. N_{agg} systems have groups/dopants located as close as possible to each other.

system	Ν	C (%)	CV
Cu-(5,5)	0	0.00	0.0211
Cu-O-(5,5)	1	1.67	0.0292
	2	3.33	0.0339
	4	6.67	0.0256
	6	10.00	0.0374
Cu-OO-(5,5)	1	3.33	0.0791
	4	13.33	0.0979
	1	1.67	0.0321
Cu-N-(5,5)	2	3.33	0.0250
	2^{agg}	3.33	0.0375
	4	6.67	0.0339
Cu-n(5,5)	1	1.69	0.0223
	2	3.45	0.0241
	2^{agg}	3.45	0.0298
	4	7.14	0.0256

Table S2: Coefficients of variation of nanotube radius (CV) of all types of Cu-f(6,4) systems considered. N is the number of O/N atoms in the supercell, whereas C is the concentration of O/N atoms relative to the number of C atoms in the nanotube.

system	N	C (%)	CV
Cu-(6,4)	0	0.00	0.0233
Cu-O-(6,4)	10	6.58	0.0437
Cu-N-(6,4)	10	6.58	0.0460
Cu-n(6,4)	10	7.04	0.0458

Table S3: Coefficients of variation of nanotube radius (CV) of all types of Cu-f(10,10)@(5,5) systems depicted in Fig.2. N is the number of O/N atoms in the supercell, whereas C is the concentration of O/N atoms relative to the number of C atoms in the nanotube. N_{agg} systems have groups/dopants located as close as possible to each other.

system	Ν	C (%)	\mathbf{CV}_{outer}	\mathbf{CV}_{inner}
Cu-DWNT	0	0.00	0.0313	0.0172
Cu-O-DWNT	1	0.56	0.0313	0.0175
	6	3.33	0.1024	0.0210
Cu-N-DWNT	1	0.56	0.0610	0.0215
	4	2.22	0.0692	0.0238
	4^{agg}	2.22	0.0980	0.0261
Cu-nDWNT	1	0.56	0.0717	0.0170
	4	2.27	0.0716	0.0210
	4^{agg}	2.27	0.0745	$0.02\overline{05}$

Table S4: Structural and electronic properties of all types of Cu-f(5,5) device systems shown in Fig.5 and Fig.S4 (b): percentage concentration of O/N per C atoms (C), coefficients of variation of nanotube radius (CV), separation distances between CNT's backbone and surrounding Cu matrix ($\langle d_{min}^{Cu-CNT} \rangle$), is the mean separation distance between the backbone of the CNT and the surrounding Cu matrix; ($\Delta \bar{V}_H$) are the electrostatic potential barriers between the metal matrix and the nanotube. N^{agg} systems have groups/dopants located as close as possible to each other. Note that the calculated CV values of the device systems differ from these of the bulk system, where Cu atoms are incorporated only around the lateral surface of the CNT.

system	C (%)	CV	$d_{min}^{Cu-CNT} > (\mathrm{\AA})$	$\Delta \bar{V}_{H}^{left}$ (eV)	$\Delta \bar{V}_{H}^{right}$ (eV)
Cu-(5,5)	0.00	0.0442	2.26	1.503	1.551
Cu-O-(5,5)	6.67	0.0519	2.36	1.588	1.598
Cu-N-(5,5)	3.33	0.0384	2.32	1.450	1.606
	3.33 ^{agg}	0.0442	2.28	1.481	1.612
	6.67	0.0495	2.35	1.538	1.597
Cu-n(5,5)	1.69	0.043	2.27	1.511	1.531
	3.45	0.085	2.23	1.490	1.523
	3.45^{agg}	0.0529	2.21	1.488	1.536
	7.14	0.0473	2.30	1.542	1.616

Table S5: Structural and electronic properties of two Cu-((5,5) carpet) systems with and without N doping. The notation is the same as in Tab.S4.

system	C (%)	CV	$\Delta \bar{V}_{H}^{left}$ (eV)	$\Delta \bar{V}_{H}^{right}$ (eV)
Cu-((5,5) carpet)	0.00	0.0295	2.757	2.799
Cu- $(n(5,5) \text{ carpet})$	7.14	0.0607	2.595	2.572

References

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