

## Supporting Information

### **Wall- and Hybridisation-Selective Synthesis of Nitrogen-Doped Double-Walled Carbon Nanotubes**

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## General Methods

**Synthesis:** Compound **1** was synthesised according to reported procedures,<sup>[1]</sup> however additional purification was carried out. Compound **1** was first dissolved in CHCl<sub>3</sub>, the solution was passed through an alumina pad and the solvent was evaporated. Then, the compound was reprecipitated from CH<sub>2</sub>Cl<sub>2</sub> upon the addition of *n*-hexane, washed with *n*-pentane until the obtained solid was white and then it was dried under vacuum.

**Preparation of N-SWNT@SWNT analytical samples:** SWNT (NanoCarbLab) were annealed in air at 540 °C for 10 minutes (weight loss ~40%). The SWNT (2.8 mg) and N-PAH feedstock (**1**) (2 mg) were sealed in a pyrex ampule under reduced pressure (10<sup>-6</sup> mbar). The ampule was heated at 120 °C for 3 days. The sample was washed with chloroform (25 mL) to remove material from the outside. A small sample was sonicated in iso-propanol and deposited on a lacy carbon TEM grid for analysis at 100 kV

**Preparation of N-SWNT@SWNT bulk samples:** The SWNTs were synthesized by a method called enhanced-direct-injection-pyrolytic-synthesis (eDIPS) using ferrocene as catalyst.<sup>[2]</sup> The average diameter of the SWNTs is 1.4-1.7 nm. To open the SWNTs, the SWNT buckypaper was burned in air at 500 °C for 30 min. Then the opened SWNT buckypaper (1.3 mg) and **1** (2.0 mg) were sealed together in a quartz tube with the inner diameter of 8 mm under reduced pressure (2.2x10<sup>-6</sup> mbar). In order to fill the **1** inside the SWNTs, the sealed quartz tube was heated at 300 °C for 3 days. Then the sample was taken out and cleaned with chloroform thoroughly, and the obtained sample is named as **1**@SWNT. To transform the **1** molecules (inside the SWNTs) into N-doped inner carbon nanotubes, the **1**@SWNT samples from the same branch were annealed separately at 1200, 1300, and 1400 °C for 2 hours. The annealed samples were marked with **N-SWNT@SWNT** followed by their annealing temperature.

**HR-TEM** imaging was carried out on a JEOL 2100F TEM equipped with an Oxford Instruments X-rays detector at 100 kV (point resolution 0.19 nm, pressure ~10<sup>-8</sup> Pa, spot size 3 nm). EDX spectra were recorded for small bundles of SWNTs (3-10 nanotubes) filled with filled with the molecules.

**Raman:** The samples were measured by a Raman spectrometer (Horiba Jobin Yvon, LabRAM HR800) in ambient conditions with a 568 nm laser for excitation. The slit width was set at 200 μm and a X50 objective was used, thus the spectral resolution was ~2 cm<sup>-1</sup>. For ease of comparison, all the spectra were normalized to the intensity of the G<sup>+</sup>-band.

**XPS:** To obtain the information of the nitrogen dopants, the samples were probed with monochromatic AlKα radiation (1486.6 eV) by a hemispherical SCIENTA RS4000 photoelectron analyser (E/ΔE~1×10<sup>4</sup> at 125 eV). The samples were put on a vertical copper holder, which was mounted on a manipulator attached with a resistive heating system that allows annealing up to 1000 K. The experimental chamber had a base pressure of 8 × 10<sup>-10</sup> mbar. In order to remove any remaining impurities, the samples were firstly outgassed

*in-situ* at 400 K for 12 hours. All XPS measurements were carried out at room temperature. The nitrogen to carbon ratio was calculated via the area analysis of N<sub>1s</sub> and C<sub>1s</sub>.

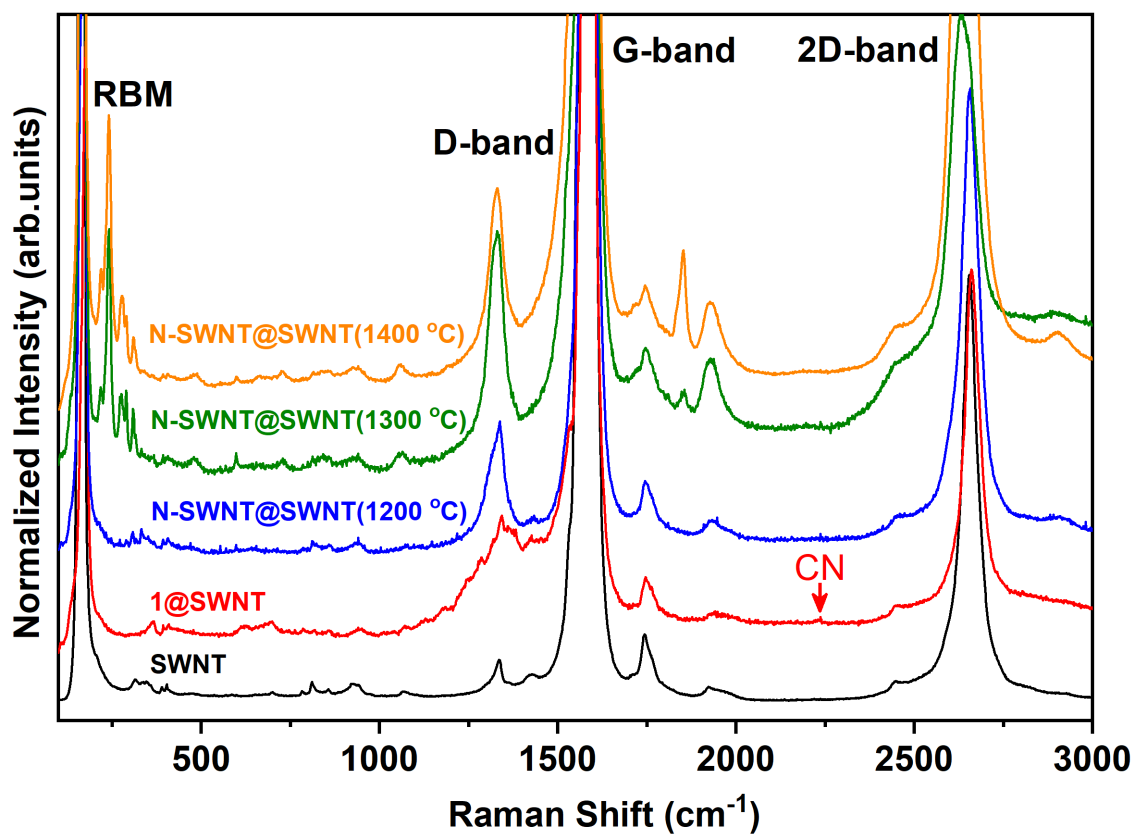
**Electrochemistry:** The electrochemical properties of SWNT, **N-SWNT@SWNT** (1300 °C) and **N-SWNT@SWNT** (1400 °C) were evaluated in a three-electrode cell which is composed of a glassy carbon rotating disk electrode (RDE, Tacussel, France), as support for the deposition of catalyst inks, a SCE reference electrode and a Pt wire auxiliary electrode. The whole characterizations were conducted with a SP-300 bipotentiostat (Biologic Instruments) electrochemistry workstation equipped with an additional current booster and a built-in electrochemical impedance spectroscopy (EIS) analyzer. The materials were dispersed in DMF (0.4 mg mL<sup>-1</sup>) and drop cast (50 uL) onto RDE. The ORR performance was tested in O<sub>2</sub>-saturated 0.1 M ultrapure KOH (99.99 %, Sigma-Aldrich) solution.

Koutecky-Levich (K-L) equation:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{0.62nFC_0(D_0)^{2/3}v^{-1/6}\omega^{1/2}} + \frac{1}{nFkC_0}$$

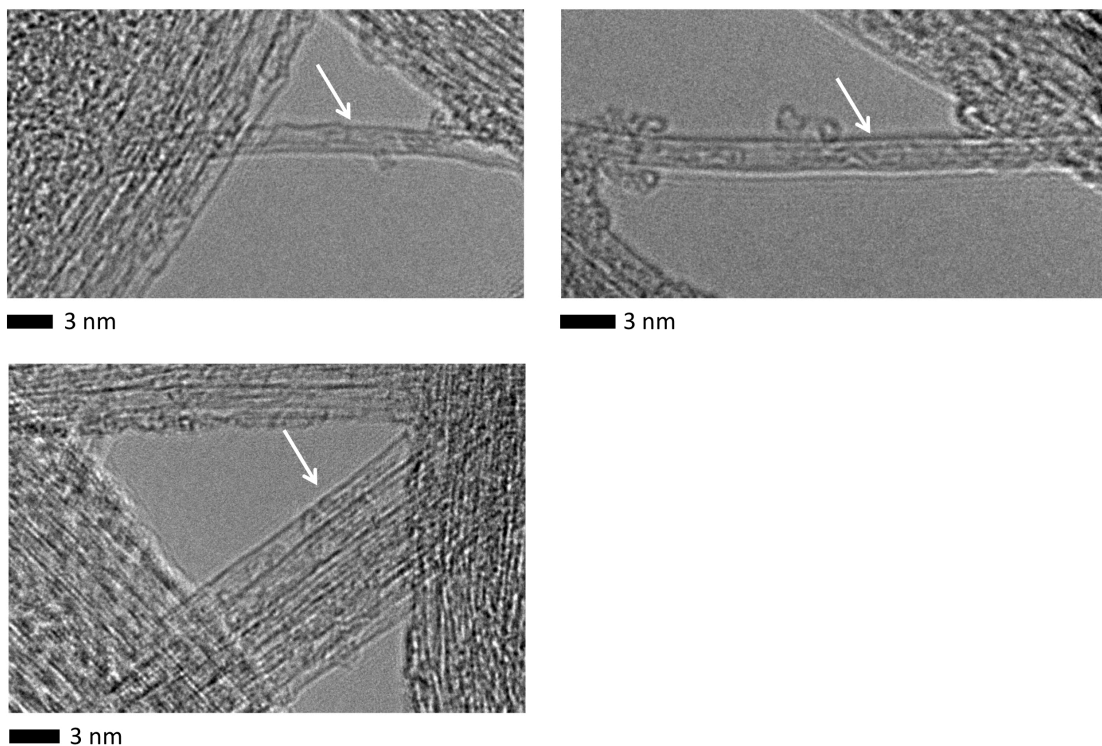
where  $n$  is the electron transfer number,  $F$  is the Faraday constant (96485 C mol<sup>-1</sup>),  $C_0$  and  $D_0$  are the bulk concentration and diffusion coefficient of O<sub>2</sub> in electrolyte ( $C_0$ , 8.4 x10<sup>-7</sup> mol cm<sup>-3</sup>;  $D_0$ , 2 x 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup> in 0.1 M KOH),  $\nu$  is the kinematic viscosity of the electrolyte (0.008977 cm<sup>2</sup> s<sup>-1</sup> in 0.1 M KOH),  $\omega$  is the angular velocity (rad s<sup>-1</sup>),  $j_K$  is the kinetic-limiting current density, and  $k$  is the electron-transfer rate constant.

**Calculations:** The calculations were computed at the tight-binding DFTB-D3 level with the OB3 parameter set with the software DFTB+ version 18.2. For the DWNT models unit cells of 0.428 and 0.856 nm were used. Geometry optimizations were performed with 256 k points in 1D reciprocal space, while the DOS were computed with 1024 k points and a broadening of 0.01 eV. The electronic temperature of electronic smearing was in all cases 100 K. The orbitals were computed with a  $\Gamma$ -point calculation on a 13.7 nm cell with the same N doping. In addition to the presented results, models with the (8,0)@(18,0) and different N distributions, were also computed yielding similar general results.

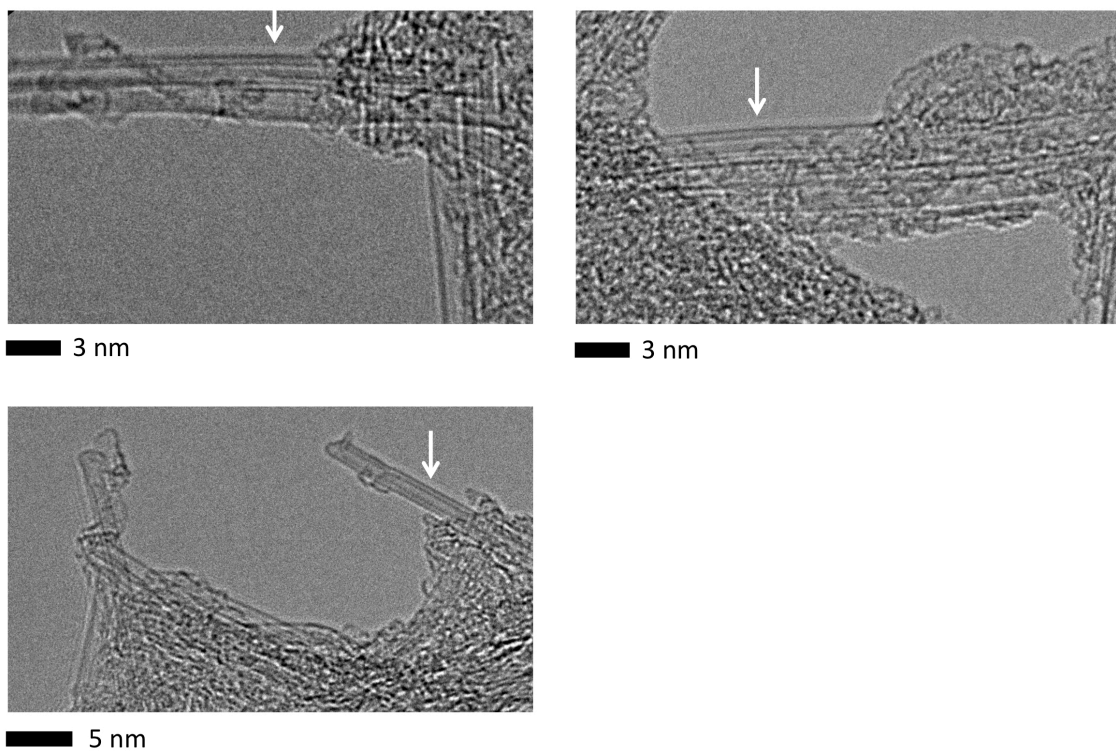


**Figure S1.** Zoomed resonant Raman spectra of 1@SWNT annealed at different temperatures, showing the presence and the disappearance of the signals of 1.

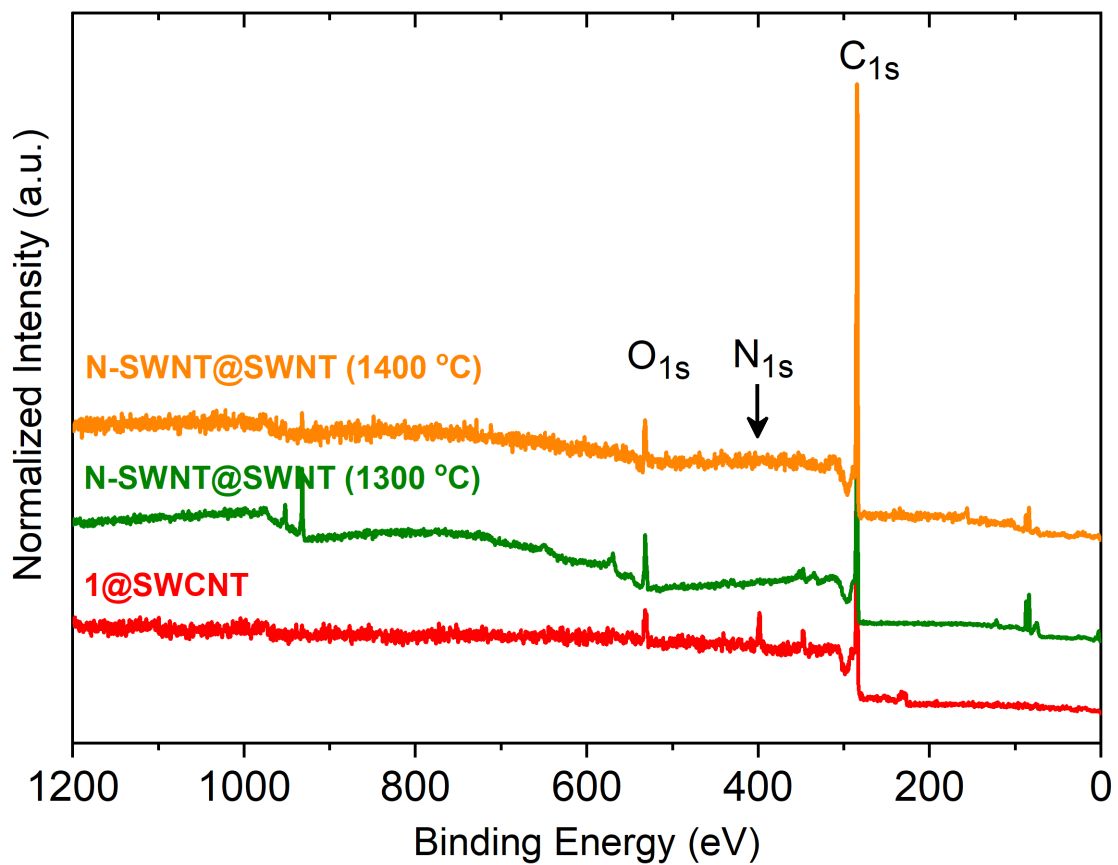




**Figure S2.** HR-TEM images of 1@SWNT. Arrows indicate the presence of molecules of 1 in the SWNT cavities.



**Figure S3.** HR-TEM images of N-SWNT@SWNT. Arrows indicate the presence of coaxial internal carbon nanotubes.

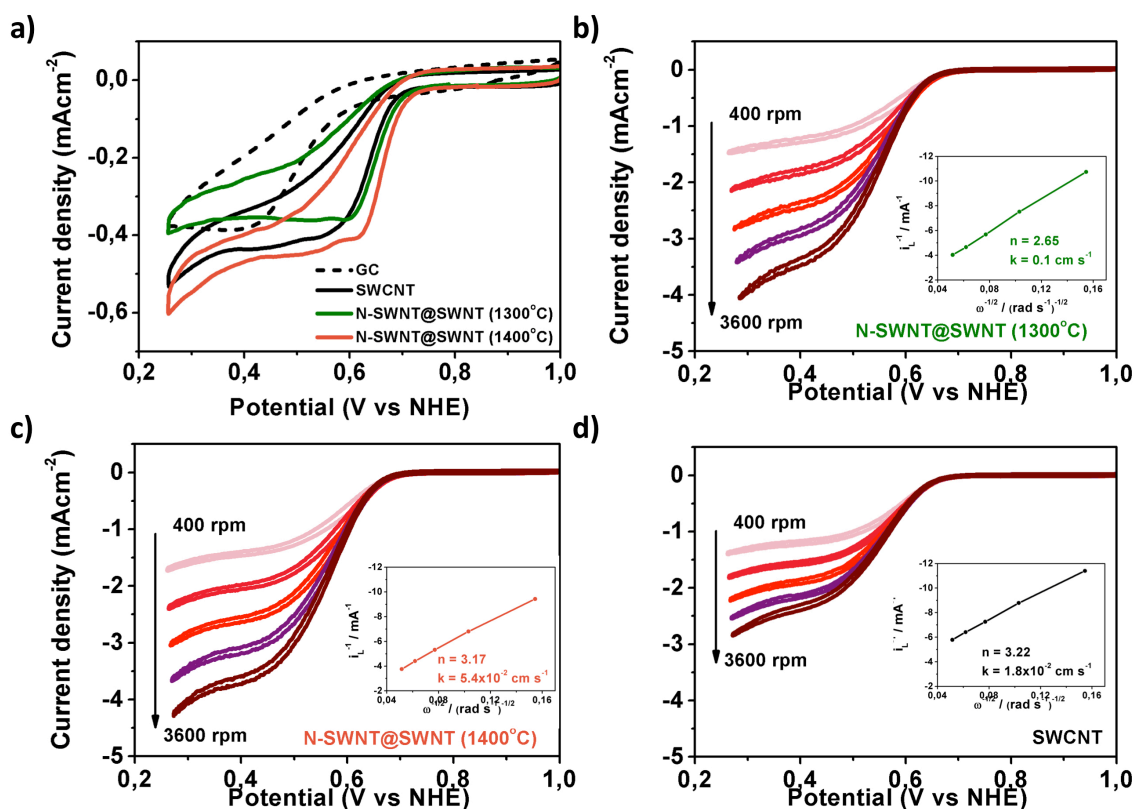


**Figure S4.** Complete XPS spectra of 1@SWNT annealed at different temperatures.

DWNT have been predicted to show an intertube distance slightly superior to the interlayer distance of graphite.<sup>[3]</sup> Using this model, the system (9,0)@(18,0) was found as a representative model for the experimental systems. Geometrically, the ratio of atoms is 2/1 for (18,0)/(9,0) giving a 1/3 ratio for the inner tube with respect to the DWNT. Table S1 provides estimates of the concentration of N on the inner SWNT with different macroscopic fillings estimated with a (9,0)@(18,0) DWNT model and the N concentration measured experimentally (~0.8 %). The computed concentration values refer to the parts of the sample that are effectively DWNTs. For instance, in the 50 % filling regime estimated from models of 1@(18,0), only half of the tubes would be filled yielding DWNTs. Those DWNTs would have a 4 % of N in the inner SWNT which is equivalent to 3.4 nitrogen atoms per nm.

Macroscopic filling	%N (inner SWNT)	[N] / L (atoms / nm)
100%	2.42%	2.0
75%	2.96%	2.5
50%	4.03%	3.4
25%	7.26%	6.1

**Table S1.** Nitrogen concentrations at the inner tube and per axial unit length with different macroscopic fillings.



**Figure S5.** a) CVs of a bare GC electrode, SWNT, **N-SWNT@SWNT** (1300 °C), **N-SWNT@SWNT** (1400 °C) under static conditions. CVs at different rotating rates and (the insets) corresponding Koutecky–Levich plots, electron transfer numbers and electron-transfer rate constants of b) **N-SWNT@SWNT** (1300 °C), c) **N-SWNT@SWNT** (1400 °C) and d) SWNT modified GC electrodes. The potentials presented are referred to as normal hydrogen electrode (NHE). (electrolyte: O<sub>2</sub>-saturated 0.1 M KOH aqueous solution, potential sweep rate: 10 mV s<sup>-1</sup>).

	$E$ (V vs NHE) @ 1 mAcm <sup>-2</sup>	$n$	$k$ (cm s <sup>-1</sup> )
SWNT	0.564	3.22	1.8 x 10 <sup>-2</sup>
<b>N-SWNT@SWNT</b> (1300 °C)	0.580	2.65	1.0 x 10 <sup>-1</sup>
<b>N-SWNT@SWNT</b> (1400 °C)	0.685	3.17	5.4 x 10 <sup>-2</sup>

**Table S2.** Potentials ( $E$ ), number of electrons ( $n$ ) and heterogenous electron transfer constant ( $k$ ) of **SWNT**, **N-SWNT@SWNT** (1300 °C), **N-SWNT@SWNT** (1400 °C).

In order to consider relevant electronic scenarios for DWNTs, we have considered two different DWNT models with qualitatively different electronic properties: 1) (8,0)@(17,0) which is a semiconductor DWNT with a diameter of 1.33 nm and 2) (9,0)@(18,0) which is a semimetallic DWNT with 14.1 nm. Four different degrees of doping were computed: 0, 1, 2 and 4 N per unit cell in both cases. For clarity, the N doping values in different units are found in Table S3.

	atoms of N / Unit cell	%N (inner SWNT)	[N] / L (atoms / nm)
(8,0)@(17,0)	1	3.1%	2.3
(8,0)@(17,0)	2	6.3%	4.7
(8,0)@(17,0)	4	12.5%	9.3
(9,0)@(18,0)	1	2.8%	2.3
(9,0)@(18,0)	2	5.6%	4.7
(9,0)@(18,0)	4	11.1%	9.3

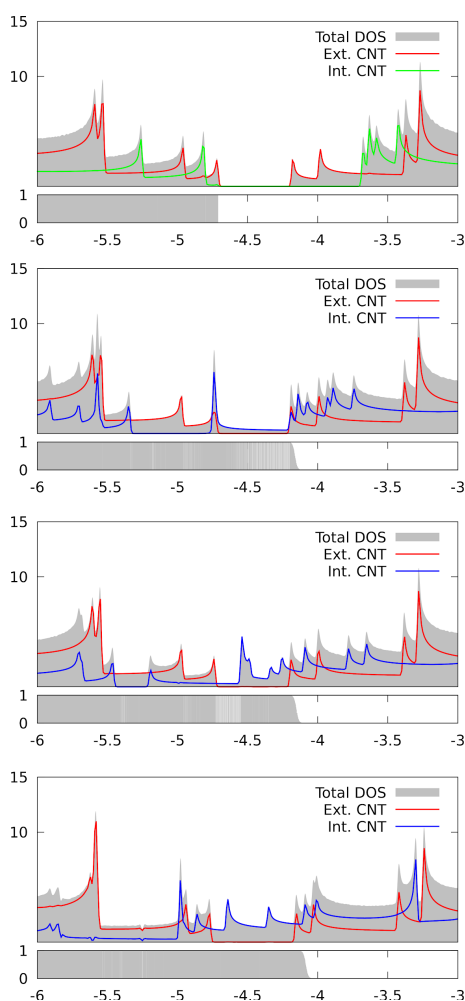
**Table S3.** Nitrogen concentrations at the inner tube and per axial unit length with different model N concentrations.

We computed the difference in Mulliken charges for both SWNTs in the system and the charge difference between both SWNTs in the system, which in the case of null charge transfer would be 0. These charges provide an approximated measure of the degree of charge transfer in the DWNT system and show how the presence of N induces one order of magnitude larger charge transfer from the internal to the external tube compared to the pristine system (Table S4). Doping can also be quantified by comparing the position of the Fermi energy (Table S4). The filling of a SWNT by a SWNT involves a small yet noticeable effect ( $\leq 27$  mV). In contrast, N doping induce a much larger effect in both our models systems ranging from 162 mV, for a metallic external SWNT, to 301 mV, for a semiconducting external SWNT.

	atoms of N / Unit cell	%N	[N] / L (atoms / nm)	InterTube Charge Transfer / Unit cell (e-)	Fermi Energy ( eV)	Rel. Potential (mV)
(17,0)	0	NA	NA	NA	-4.45	0
(8,0)@(17,0)	0	NA	NA	0.01	-4.45	7
(8,0)@(17,0)	1	3.1%	2.3	-0.14	-4.16	291
(8,0)@(17,0)	2	6.3%	4.7	-0.16	-4.16	291
(8,0)@(17,0)	4	12.5%	9.3	-0.25	-4.15	301
(18,0)	0	NA	NA	NA	-4.47	0
(9,0)@(18,0)	0	NA	NA	-0.02	-4.44	27
(9,0)@(18,0)	1	2.8%	2.3	-0.13	-4.31	162
(9,0)@(18,0)	2	5.6%	4.7	-0.22	-4.29	180
(9,0)@(18,0)	4	11.1%	9.3	-0.29	-4.29	181

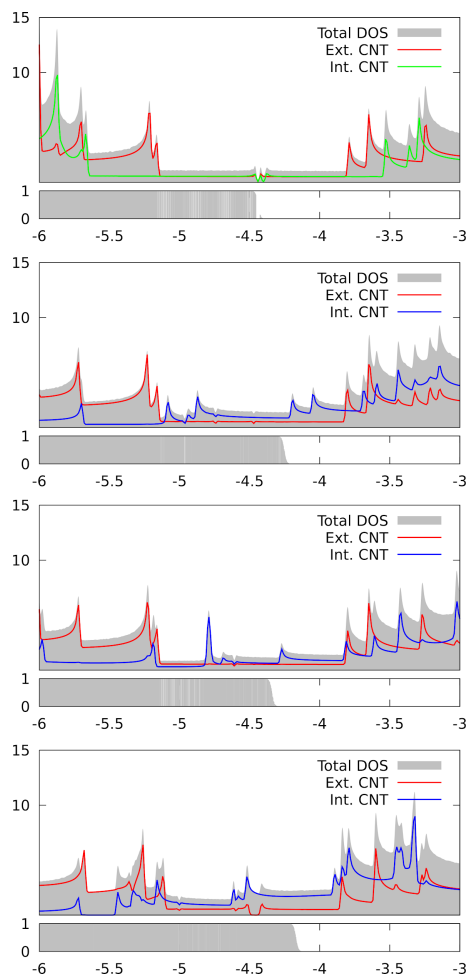
**Table S4.** Intertube charge transfer, Fermi energy and relative chemical potentials versus nitrogen concentrations. Negative charges indicate the partial electron transfer from the internal to the external tube.

The (8,0)@(17,0) is semiconducting, Figure S6, with a band gap defined by the external tube: (17,0) SWNT. The effect of the N doping in graphitic sites adds extra electrons to the system in comparison to the pristine system effectively n-doping the DWCNT. The (8,0)@(17,0) gets transformed from a semiconductor DWCNT, at zero doping, to a metal due to the graphitic N. Comparing the Density of States (DOS) and the projected density of states of the (8,0)@(17,0) system it can be seen that the DOS corresponding to the outer SWNT is basically unchanged for all systems. In contrast, large alterations are found for the doped (8,0) system DOS. This analysis also shows how the electron doping is also populating the unoccupied states of the external tube, (17,0), namely on the region of the first van Hove singularity of the virtual states.



**Figure S6.** Density of States (DOS) for pristine (8,0)@(17,0) and doped systems with 1N, 2N and 4N per unit cell from top to bottom. The total DOS is in grey, as the electron occupancies (from 0 to 1), the projected density of states for the outer SWNT, in red, and for the internal SWNT for the undoped systems, in green, and in blue for the nitrogen-doped systems. **All energies in eV.**

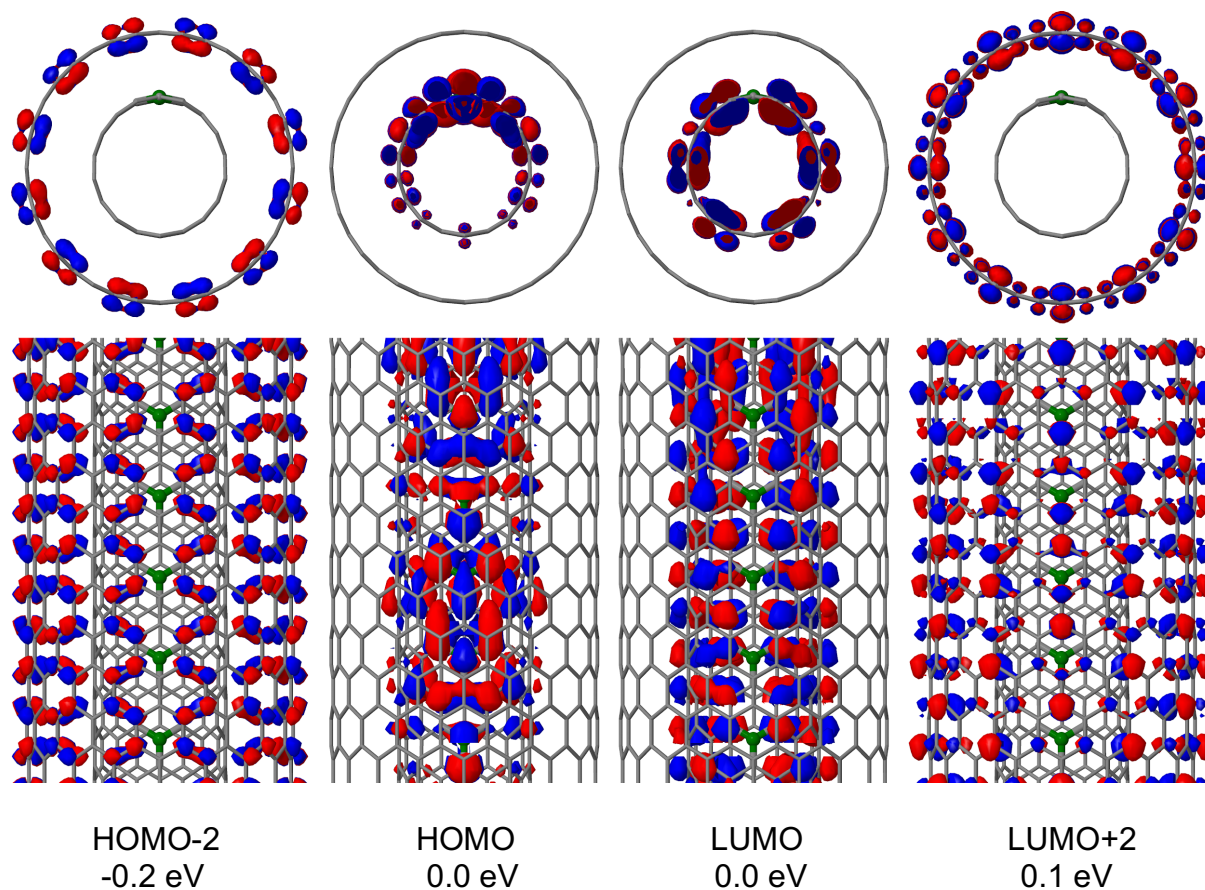
The (9,0)@(18,0) is metallic and shows a small gap near the Fermi energy that is already overcome at the electronic temperature used for the calculations (100 K). The DOS corresponding to the outer SWNT is quite similar for all systems. In addition, all doped (9,0)@(18,0) computed systems are metallic, and the extra electrons filling also virtual states of the external tube.



**Figure S7.** Density of States (DOS) for pristine (9,0)@(18,0) and doped systems with 1N, 2N and 4N per unit cell from top to bottom. The total DOS is in grey, as the electron occupancies (from 0 to 1), the projected density of states for the outer SWNT, in red, and for the internal SWNT for the undoped systems, in green, and in blue for the nitrogen-doped systems. **All energies in eV.**



Molecular orbitals were computed with a real space calculation on a 13.7 nm (9,0)@(18,0) periodic DWNT doped with 32 N atoms (2.3 N / nm doping), Figure S8. At the frontier orbitals, two different scenarios are found, in the external tube electrons and holes are completely delocalized throughout the tube length. In the internal tube, the electrons and holes are also delocalized but show larger localization near the N moieties, Figure 5. The energies for frontier levels regarding internal and external tubes are quite similar which might favour direct electron transfer.



**Figure S8.** Molecular orbitals ( $0.005 e^- / \text{\AA}^3$ ) for the (9,0)@(18,0) with 2.3 % N doping, see table 3, with relative energies for HOMO/LUMO. Nitrogen atoms are rendered in green.

## References

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- [2] T. Saito, S. Ohshima, T. Okazaki, S. Ohmori, M. Yumura, S. Iijima, *J. Nanosci. Nanotechnol.* **2008**, 8, 6153-6157.
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