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

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Abstract: Controlled nitrogen-doping is a powerful methodology to modify the properties of carbon nanostructures and produce functional materials for electrocatalysis, energy conversion and storage, and sensing, among others. Herein, we report a wall- and hybridisation-selective synthetic methodology to produce double-walled carbon nanotubes with an inner tube doped exclusively with graphitic sp²-nitrogen atoms. Our measurements shed light on the fundamental properties of nitrogen-doped nanocarbons opening the door for developing their potential applications.
Controlled substitutional nitrogen-doping is a powerful methodology to modify the properties of carbon nanostructures.[1-14] The synthesis and characterisation of nitrogen-doped fullerenes, carbon nanotubes, graphene and graphene nanoribbons have revealed that nitrogen-doped carbon nanostructures are promising materials for electrocatalysis,[2-9, 11, 13-14] energy conversion and storage,[2, 4-7, 10, 13-14] and sensing,[13-14] among others. The synthesis of nitrogen-doped nanocarbons still presents challenges for controlling: (i) the inclusion percent and the distribution of nitrogen within the graphitic lattice; (ii) the bonding of the nitrogen atoms, as principally three types of nitrogen (pyridinic, graphitic, and pyrrolic) can exist; (iii) wall-selectivity, in the case of layered nanocarbons (e.g. double-walled and multi-walled carbon nanotubes, or stacked layers of graphene). Among the above-mentioned challenges, wall-selectivity has received little attention[15-17] and provides numerous opportunities for establishing and understanding the fundamental properties of nitrogen-doped nanocarbons and for developing their potential applications.[3]
Scheme 1. Synthetic approach for the preparation of coaxial N-SWNT@SWNT.
Herein, we report a wall- and hybridisation-selective synthetic methodology to produce double-walled carbon nanotubes (DWNT) with an inner tube doped exclusively with graphitic nitrogen atoms (Scheme 1). Such coaxial carbon nanotubes have been prepared in two steps by using a nitrogen-rich polycyclic aromatic hydrocarbon, namely dicyanopyrazophenanthroline 1, as feedstock and empty single-walled carbon nanotubes (SWNT) as reaction vessels. Firstly, dicyanopyrazophenanthroline 1 is sublimed into the internal cavity of SWNT. Then, the filled SWNTs (1@SWNT) are exposed to an electron beam or thermally treated so the encapsulated dicyanopyrazophenanthroline 1 converts into a nanotube to produce DWNT with an inner nanotube doped with nitrogen (N-SWNT@SWNT). The graphitic nitrogen content in the inner tube can be controlled with the annealing temperature to reach values up to 100%, as demonstrated by a combination of Raman spectroscopy, high-resolution transmission electron microscopy (HR-TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray photoemission spectroscopy (XPS) and cyclic voltammetry.

Dicyanopyrazophenanthroline 1 was selected as feedstock because of the high C/N ratio (16/6), the fact that all the nitrogen atoms are already incorporated in the π framework as sp² or sp nitrogen; and its ability to sublime. Dicyanopyrazophenanthroline 1 was synthesised following a reported procedure¹⁸ and then to ensure a high level of purity it was further purified by chromatography on alumina and reprecipitation (see experimental procedures in supporting information).
Opened SWNT were filled with 1 by heating a mixture of the compound with SWNT in $10^{-6}$ mbar vacuum at 120 °C. HR-TEM imaging confirmed that the molecules become encapsulated inside the SWNT, yielding $1@\text{SWNT}$ (Figure 1). The molecules of 1 are disordered within the cavity of the SWNT, although in some areas, the molecules appear to stack within the nanotube cavity (Figure 1 top zoomed image). Extended exposure to the electron beam resulted in the transformation of the molecules within the nanotube into a new nanotube, thus forming a DWNT ($\text{N-SWNT}@@\text{SWNT}$). The formation of $\text{N-SWNT}@@\text{SWNT}$ is evidenced by the presence of long continuous structures coaxial to the external tube, terminated with internal caps (Figure 1 bottom zoomed image).

**Figure 1.** HR-TEM of $1@\text{SWNT}$ and formation of $\text{N-SWNT}@@\text{SWNT}$ over time upon exposure to the 100 keV electron beam. The zoomed images show the disordered molecules inside the cavity of the SWNT (top) and the newly formed internal nanotube (bottom).
HR-TEM imaging clearly showed the propensity of 1 to convert into a nanotube. To investigate in more detail the structural features of N-SWNT@SWNT, bulk filling and annealing experiments were carried out with SWNT with diameters 1.4-1.7 nm in order to obtain sufficient material for structural characterisation. The filling of SWNT with 1 and the transformation process of 1@SWNT into N-SWNT@SWNT by annealing at different temperatures was monitored by resonance Raman spectroscopy and the samples were further analysed by HR-TEM, energy dispersive X-ray spectroscopy (EDX) and by X-ray photoemission spectroscopy (XPS).

Figure 1 shows the Raman spectra of the pristine SWNT, 1@SWNT and N-SWNT@SWNT formed by annealing at different temperatures. In all the spectra, the G-band, D-band, 2D-band and radial breathing mode (RBM) bands typical of SWNT can be clearly observed. In the spectrum of 1@SWNT, additional Raman bands corresponding to those of the spectra of 1 were detected (Figure S1). The Raman spectra show the appearance of new bands in the RBM region, of a new D-band and of a new contribution (shoulder) in the 2D-band with the increasing annealing temperatures. In the case of the samples obtained at 1300 and 1400 °C, the new bands in the RBM region are consistent with the formation of an internal tube within the SWNT cavity (N-SWNT@SWNT). Furthermore, the Raman spectrum of 1@SWNT exhibits a nitrile band consistent with the structure of precursor 1 that disappears upon annealing (Figure S1).
Figure 2. Resonant Raman spectra of 1@SWNT annealed at different temperatures.

To confirm that the precursor molecules are inside SWNT and that the new inner nanotube grows coaxially to the host nanotube, 1@SWNT and N-SWNT@SWNT were investigated by HR-TEM. The images of 1@SWNT evidenced excellent filling rates of molecules inside the SWNT cavities (Figures 3a and S2). Also, the images of N-SWNT@SWNT samples obtained at 1300ºC and 1400ºC showed long continuous structures within the SWNT consistent with the formation of well-structure inner nanotubes (Figures 3b and S3). In addition, caps on internal nanotubes can be clearly observed similar to those formed under the electron beam. EDX provide the first evidence of incorporation of nitrogen in the nanotube with a new emerging peak of nitrogen that is not observed in the empty SWNT sample (Figure 3c).

The nitrogen inclusion percentage and bonding on 1@SWNT and N-SWNT@SWNT was investigated by XPS (Figures 3d and S4; Table 1). The N1s region of the XPS spectrum of 1@SWNT indicates a 10.6% of nitrogen present, distributed between pyridinic, nitrilic and graphitic nitrogen. The percentage of pyridinic and nitrilic nitrogen is higher than that of graphitic nitrogen, which agrees
with the structure of molecule 1. The presence of graphitic nitrogen on 1@SWNT was ascribed to the partial decomposition of 1 within the SWNT because of the high temperature used (300 °C) during the filling and cleaning processes. Importantly, the XPS spectrum of N-SWNT@SWNT obtained after annealing at 1300 °C confirms the incorporation of 0.9% of nitrogen and shows the disappearance of nitrilic nitrogen – in agreement with Raman – and a higher proportion of graphitic nitrogen versus pyridinic nitrogen. The measured nitrogen incorporation indicates 2.4% of nitrogen in the inner tube (Table 1 and Table S1), which equates to two or more nitrogen atoms per nm in length. Remarkably, the N-SWNT@SWNT obtained at 1400 °C shows only a contribution of graphitic nitrogen, while the total nitrogen inclusion percentage is virtually unchanged, which imply the formation of an internal nanotube doped exclusively with graphitic nitrogen.

![HR-TEM and EDX images](image)

**Figure 3.** HR-TEM of a) 1@SWNT and b) N-SWNT@SWNT. Scale bar = 2 nm b) EDX of N-SWNT@SWNT indicating the presence of N. c) XPS of 1@SWNT and N-SWNT@SWNT obtained at different temperatures showing the presence and hybridisation of N atoms.
Table 1. Content and hybridisation of nitrogen in the different nanotubes (%N).

| Sample                        | Total | Inner Tube | Nitrilic[b] | Pyridinic[b] | Graphitic[b] |
|-------------------------------|-------|------------|-------------|--------------|--------------|
| 1@SWNT                       | 10.6% | –          | 8.8%        | 60.6%        | 30.6%        |
| N-SWNT@SWNT (1300 ºC)        | 0.9%  | 2.4%       | 0%          | 16.2%        | 83.8%        |
| N-SWNT@SWNT (1400 ºC)        | 0.8%  | 2.4%       | 0%          | 0%           | 100.0%       |

[a] Estimated assuming an external tube diameter of 1.4 nm, a 100% filling (Table S1). [b] Measured by XPS.

The electrochemical properties of N-SWNT@SWNT were investigated by cyclic voltammetry in a rotating disk electrode (Figures 4a and S5; Table S2). The voltammetric curves in an argon saturated aqueous 0.1 M KOH solution show no redox processes, but in an oxygen saturated solution, the voltammograms reveal a reduction wave characteristic of the oxygen reduction reaction,[2-4, 6-7, 9, 11, 13-14] in which the presence and bonding of nitrogen atoms are directly linked to the electrode potentials.[19-25] The glassy carbon (GC) electrodes containing N-SWNT@SWNT show more anodic potentials at 1 mAcm⁻² than those containing pristine SWNT (0.564 V vs NHE). Furthermore, the potential at 1 mAcm⁻² of the N-SWNT@SWNT (1300 ºC) with 83.8% of graphitic nitrogen (0.580 V vs NHE) is more anodic than that of N-SWNT@SWNT (1400 ºC) with 100.0% of graphitic nitrogen (0.685 V vs NHE). The voltammograms confirm that the presence of graphitic nitrogen shifts the potential to more anodic values and also show that the nitrogen atoms of the internal nanotube are able to modulate the electrochemical properties even if they are encapsulated by the external carbon nanotube.
Figure 4. a) Effect of nitrogen bonding on the electrochemical properties of N-SWNT@SWNT. CVs of a bare GC electrode, SWNT, N-SWNT@SWNT (1300 °C), N-SWNT@SWNT (1400 °C) O₂-saturated 0.1 M KOH aqueous solution (scan rate: 10 mV s⁻¹; rotating rate: 1600 rpm). b) HOMO orbitals of representative N-SWNT@SWNT ((9,0)@(18,0) with 2.3% N) with 0.02 e⁻/Å³ (left) and 0.001 e⁻/Å³ (right) isosurfaces.

To investigate if the internal nitrogen-doped nanotube is able to transduce some of its properties across the external one, computational modelling was performed on semiconducting and metallic DWNT models with different doping degrees in the internal tube (Table S3). First, the extra electron of nitrogen at the doping levels measured yields metallic DWNTs in all cases through a direct electron transfer mechanism (Table S4). In addition, an analysis of the electron distribution indicates that there is a direct charge transfer from the doped internal tube to the external tube and that this transfer increases with N content (Table S4). Secondly, the density of states (DOS) shows very little changes in the states of the external undoped SWNT, in contrast to the electronic structure of the internal nanotubes, which is extensively altered due to the presence of nitrogen (Figures S6 and S7). The analysis of the frontier orbitals shows that there are levels from the internal and external tubes in a similar range of energies and that
the nitrogen atoms area and the external tubes are coupled (Figure S8). This can be seen in the HOMO molecular orbital, showing an enhanced electronic density near the nitrogen atoms in the external tube (Figure 4b). The electronic doping of the external SWNT induced by the internal tube creates potential differences (Table S4), which are consistent with the ones observed by the cyclic voltammetry.

To conclude, we have reported a wall- and hybridisation-selective synthetic methodology to prepare nitrogen-doped double-walled carbon nanotubes (N-SWNT@SWNT). A nitrogen-rich polycyclic aromatic hydrocarbon (1) has been inserted into the cavity of SWNT and then by exposing the samples to an electron beam or to annealing temperatures over 1300 °C, the encapsulated molecules are transformed into a nitrogen-doped carbon nanotube within the SWNT cavity. The transformation can be monitored by Raman spectroscopy and HR-TEM. XPS confirms the inclusion of ~1% of nitrogen in the newly formed carbon nanotube and also illustrate that the hybridisation of the nitrogen atoms can be controlled with the annealing temperature. For instance, thermal annealing at 1400 °C produce double-walled carbon nanotubes with an inner tube doped exclusively with graphitic nitrogen, while annealing at 1300 °C produce double-walled carbon nanotubes with an inner tube doped with both pyridinic and graphitic nitrogen. Electrochemical studies and theoretical calculations confirm that the internal nitrogen-doped nanotube is able transduce some of its properties across the external nanotube. Overall this method enables the synthesis of nitrogen-doped nanocarbons with an unprecedented level of control that allows investigating and harnessing their functional properties.
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Supporting Information

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General Methods

Synthesis: Compound 1 was synthesised according to reported procedures,[1] however additional purification was carried out. Compound 1 was first dissolved in CHCl₃, the solution was passed through an alumina pad and the solvent was evaporated. Then, the compound was reprecipitated from CH₂Cl₂ 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 (10⁻⁶ 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.[2] 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 (2.2x10⁻⁶ 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. EDX spectra were recorded for small bundles of SWNTs (3-10 nanotubes) 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⁻¹. For ease of comparison, all the spectra were normalized to the intensity of the G⁺-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 analyzer. The nitrogen to carbon ratio was calculated via the area analysis of N₁s and C₁s.

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$^{-1}$) and drop cast (50 μL) onto RDE. The ORR performance was tested in O$_2$-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$^{-1}$), $C_0$ and $D_0$ are the bulk concentration and diffusion coefficient of O$_2$ in electrolyte ($C_0$, 8.4 x10$^{-7}$ mol cm$^{-3}$; $D_0$, 2 x 10$^{-5}$ cm$^2$ s$^{-1}$ in 0.1 M KOH), $v$ is the kinematic viscosity of the electrolyte (0.008977 cm$^2$ s$^{-1}$ in 0.1 M KOH), $\omega$ is the angular velocity (rad s$^{-1}$), $j_K$ 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 \textbf{1@SWNT} annealed at different temperatures.
DWNT have been predicted to show an intertube distance slightly superior to the interlayer distance of graphite.[3] 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 ½ 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: O₂-saturated 0.1 M KOH aqueous solution, potential sweep rate: 10 mV s⁻¹).

|               | E (V vs NHE) @ 1 mA cm⁻² | n   | k (cm s⁻¹) |
|---------------|--------------------------|-----|------------|
| SWNT          | 0.564                    | 3.22| 1.8 x 10⁻² |
| N-SWNT@SWNT (1300 °C) | 0.580                   | 2.65| 1.0 x 10⁻¹ |
| N-SWNT@SWNT (1400 °C) | 0.685                   | 3.17| 5.4 x 10⁻² |

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 is 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 (<= 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 DWNT. 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.

![Diagram of molecular orbitals](image)

**Figure S8.** Molecular orbitals (0.005 e⁻ / Å³) 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.
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