

On the origin of the high capacitance of nitrogen-containing carbon nanotubes in acidic and alkaline electrolytes

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The preparation of nitrogenated carbon nanotubes (N-CNT) using pyridine as a carbon precursor resulted in an eight-times increase in gravimetric capacitance.

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10 On the origin of the high capacitance of nitrogen-
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The synthesis of nitrogenated carbon nanotubes (N-CNTs) with up to 6.1 wt% N, via the use of pyridine as the nitrogen containing carbon precursor, can provide a facile route to significantly enhance the low intrinsic specific capacitance of carbon nanotubes. The nitrogen functionalities determine this, at least, five-fold increase of the specific capacitance.

Carbon nanotubes (CNTs) have long been considered as a suitable material for electrochemical energy storage applications.¹ However, the aggregation problem caused by large van der Waals attractions, coupled with the low specific surface area and low microporosity, reduces the specific capacitance of CNTs significantly, especially when compared with other carbonaceous materials such as activated carbons and graphene. Nevertheless, the synergistic effects between the electroactive polymers such as polyaniline² and pseudo-capacitive metal oxides such as RuO₂, in conjunction with CNTs to enhance the specific capacitance (Cs), are well documented.³

For CNTs, a number of routes for enhancing their Cs have been explored including surface activation, enhancement of surface defect density and heteroatom doping, especially of electron donor groups such as nitrogen.^{4–6} The heteroatom doping of nitrogen significantly alters the microstructure, electrical conductivity, chemical reactivity and electrochemical properties of CNTs including their pseudocapacitance, wherein the electrochemical behaviour

itself is dependent on the dominant nitrogen moiety.^{4–6} In general, the additional electrons provided by nitrogen are expected to produce electron donor regions.⁶ Pyridinic and pyrrole-like functionalities are considered electroactive due to their electron donor character, whereas nitrogen atoms in imides and lactams have been proposed to be electroactive as well owing to their edge locations and the conjugation within their six-membered rings.⁷ While all of these groups have been reported to improve the Cs of carbon materials,⁸ the precise roles of these individual groups are poorly understood.

Here we report the exceptionally high Cs of N-doped CNTs (N-CNTs) synthesized by chemical vapour deposition (CVD) and elucidate the individual roles played by pyrrolic, pyridinic and quaternary nitrogen groups in both acidic and basic electrolytes. The role of structural defects in enhancing the Cs is also analysed *via* comparison with pristine CNTs. Our one-step synthetic route provides a rapid way of enhancing the specific capacitance without the need of introducing conducting polymers or metal oxides.

The synthesis of both CNTs and N-CNTs was conducted using an iron (Fe) catalyst supported on alumina (γ -Al₂O₃), with ethylene and pyridine as the respective carbon feedstock (see ESI†). Thermal gravimetric analysis (TGA) of the products reveals the yield of CNTs and N-CNTs as ~30 wt% and ~10 wt%, respectively, which is consistent with the elemental analysis data (see ESI†). As for producing N-CNTs, this direct CVD approach takes a clear advantage over the mostly used two-step **ones** where CNTs were first synthesized, then they were chemically activated and loaded with nitrogen-rich precursors to generate N-moieties on the material surface.⁹ Moreover, the low-cost, easy-to-use pyridine feedstock, coupled with its structurally high ratio of nitrogen to carbon and hence the potentially highly doped nitrogen in the product, make the direct CVD route more attractive. In the two-step approaches, the surface polymer layer can be electroactive by itself¹⁰ or following a decomposition by heat treatment to produce a nitrogen-rich carbonaceous deposit over the CNTs.^{11,12} However, in the direct CVD synthesis nitrogen will be directly introduced into the carbon lattice and form structurally in-plane nitrogen groups.

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† Electronic supplementary information (ESI) available: Synthesis of CNTs and N-CNTs, elemental analysis, Raman spectroscopy, SEM and TEM images, thermal gravimetric analysis, CVs recorded at different sweep rates. See DOI: 10.1039/c4cc04876h

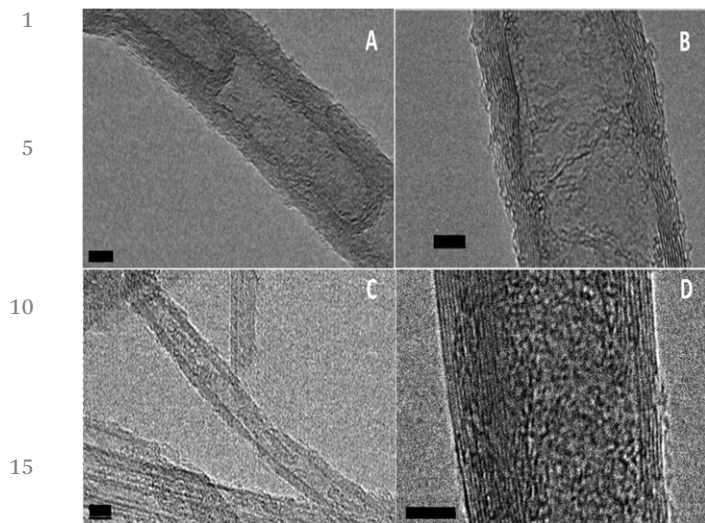


Fig. 1 TEM images of (A, B) N-CNTs, and (C, D) CNTs produced by the direct CVD technique (bar length: 5 nm).

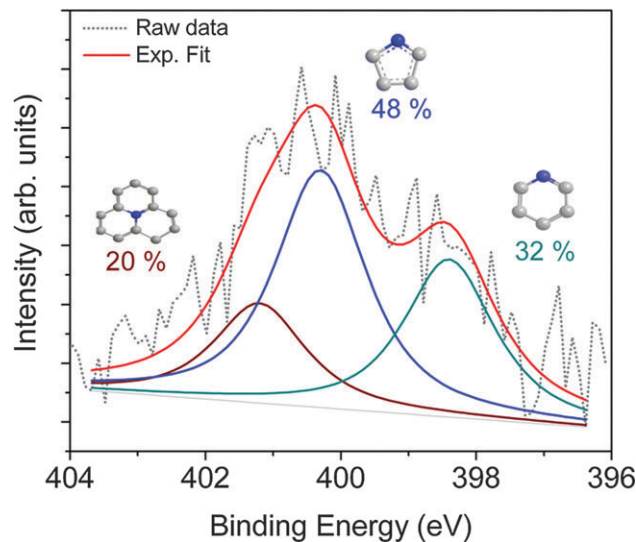


Fig. 2 N 1s core level XPS spectrum of the N-CNTs.

Transmission electron microscopy (TEM) analysis revealed the microstructure of both pristine and N-doped carbon nanotubes produced by the direct CVD method. Both samples displayed external diameters of 20–35 nm with typical 10–12 graphene layers (Fig. 1, and also ESI[†]). In N-CNTs, the positive curvature induced by the formation of possible N-containing pyrrolic structures resulted in faster tubular closure and the formation of multi-shell bamboo-like tubular structures.¹³ The length, size and structure of these N-CNTs are highly mediated by N incorporation into the graphitic lattice. Additionally, nitrogen can adopt either the sp^2 bonding mode (pyridinic/pyrrole functionalities) or form three C–N bonds (quaternary nitrogen). While the former functionalities are accompanied by a C atom vacancy,¹⁴ the enhanced electron transport properties could be produced by positively charged, highly coordinated nitrogen¹⁵ such as quaternary nitrogen. The incorporation of nitrogen into carbon nanostructures introduces pentagonal defects in the hexagonal structure of graphene sheets, creating structural distortion and bending, leading to the graphene sheets with high curvatures, cross-linked and defective.¹⁶ This increase in the defects was further confirmed by Raman analysis (see ESI[†] Fig. S1).

Elemental analysis by CHN analysis and X-ray photoelectron spectroscopy revealed nitrogen content of 6.4 wt% and 6.1 wt%, respectively, with the oxygen content of N-CNTs less than 1 wt%. The core-level N 1s XPS spectra were deconvoluted into three different peaks, centred at binding energies of 398.4 eV, 400.3 eV and 401.2 eV, respectively. They have been, respectively, assigned to pyridinic (N-6), pyrrolic (N-5) and quaternary nitrogen (N-Q).¹⁷ Due to the low oxygen content, the presence of pyridonic groups (usually found at 400.5 eV¹⁷) would be very low, and hence the peak at 400.3 eV is assigned to pyrrolic species. The N-5 groups show the maximum contribution (48%), with the contributions from N-6 and N-Q groups being 32% and 20%, respectively (Fig. 2).

Fig. 3 shows the cyclic voltammograms (CVs) (0–1 V vs. RHE) recorded for CNTs and N-CNTs in alkaline (6 M KOH) media at a scan rate of 50 $mV s^{-1}$ (ESI[†] Fig. S6 includes the CV in 1 M H_2SO_4). The characterization was done in a 3-electrode cell (see ESI[†] for

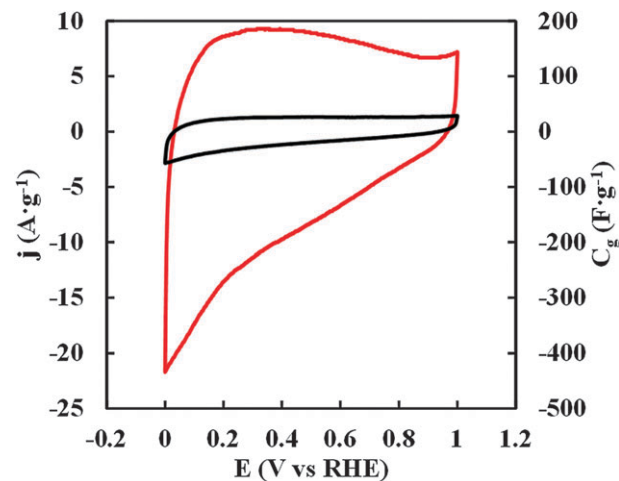


Fig. 3 Steady-state cyclic voltammograms of N-CNT (red line) and CNT (black line) electrodes in 6 M KOH solutions at 25 °C temperature. $\nu = 50 mV s^{-1}$. Detailed CVs measured at different scan rates can be found in the ESI[†].

experimental details). The CV in acidic media exhibits a quasi-rectangular-like shape for both the electrodes, while in alkaline medium the N-CNT sample shows an asymmetric-like shape. The shape observed for CNTs in both acidic and basic electrolytes indicates the absence of pseudocapacitive contribution. The slope observed in the negative sweep for N-CNTs has been attributed to the pseudocapacitive contribution of the nitrogen moieties.⁸

For CNT electrodes, the specific capacitances are 14 $F g^{-1}$ in acid medium and 21 $F g^{-1}$ in alkaline medium, respectively. These C_s values are in good agreement with the data for pristine MWCNTs.¹⁸ However, for the N-CNT electrodes, the C_s values are much higher at 67 and 160 $F g^{-1}$ in acid and alkaline medium, respectively. This huge increment observed with the N-CNTs is similar to values reported for low-porosity melamine-based nanocarbons.¹⁹ Our literature search seems to suggest that there is a lack of data for the capacitance values of N-containing CNTs prepared by a similar CVD

1 process. However, the data obtained in this work can be compared
to the highest values obtained from the 3-D graphene–CNT network
doped with nitrogen,²⁰ and the N-doped carbon nanotubes pro-
duced by carbonization of a melamine shell over a CNT core.⁹
5 However, these values are lower than those of 300 F g⁻¹ reported *via*
the carbonization of polypyrrole over KOH-activated CNTs.^{10,11}

To elucidate how this huge enhancement of specific capacitance
occurs with N-CNTs in comparison with CNTs, we investigated the
contribution of each of the nitrogen moieties and the surface
defects. The difference in the capacitances could arise from either
10 (i) the ion accessibility to the nanotube surface, (ii) structural
differences or (iii) pseudocapacitance and/or enhanced electron
transport in N-CNTs. As for the ion accessibility to the nanotube
surface, it is known that the N doping can enhance the hydrophili-
15 city and improve the wettability of the CNT electrodes by reducing
their entanglement level, since it weakens the van der Waals forces,
therefore disrupting the π - π interactions and leading to weaker
interactions between nanotubes.¹⁴ Even so, the measured surface
areal capacitance for N-CNTs is more than 75 $\mu\text{F cm}^{-2}$ (calculated
20 from the estimated surface area obtained from the tube diameters),
which is far over the expected 10–20 $\mu\text{F cm}^{-2}$ traditionally assigned
to graphite-like surfaces. Thus, the capacitance enhancement in
N-CNTs cannot be attributed to better ionic accessibility alone.

It is also known that the structural defects in the form of edge
25 sites can be generated in N-CNTs *via* the presence of in-layer
pyridine groups.²¹ Since the double-layer capacitance of edge sites
is reported to be an order of magnitude higher than that of the basal
plane,²² one of the contributors towards the higher capacitance of
the N-CNT sample is its higher edge site to basal plane ratio, as
30 observed in the higher Raman D/G ratio. By an estimation, we
considered that each pyridine group (as measured by XPS) can
induce the formation of two C vacancies; then one can expect an
additional 4% of edge sites in N-CNTs which could be responsible
for a maximum of one-fold increase in the capacitance, which is
35 clearly lower than the observed 5 to 7-fold increase. It could be
argued that the structural defects could bring the internal area of
the nanotubular structure more exposed to the electrolyte, like for
chemically activated CNTs,²³ increasing the available surface area of
the tubes. However, this **one fold** increase ascribed to the formation
40 of **higher edge** sites and enhanced surface area is again not enough
to explain the huge increase in the specific capacitance.

In addition to the above effects, we believe that the N-Q func-
tional groups play a role in enhancing the capacitance. Zhu *et al.*²⁴
45 have suggested that the N-Q functionalities could be more positively
charged when used as anode materials in supercapacitors, attract-
ing the negatively-charged ions more, thereby increasing the
capacitance. Seredych *et al.* have proposed that N-Q functionalities
enhance electron transport through the graphene layers.⁸ We
50 believe that a combination of these mechanisms could partially
explain the 5-fold increment observed in acidic media, but cannot
justify the very different behaviour observed in the basic media.
While, the anion size is smaller for KOH than for the H₂SO₄
electrolyte, this difference in the ionic size is not enough to explain
55 such a huge increment in double layer formation by enhanced ion
adsorption by N-Q presence when moving from an acid to basic
electrolyte. Therefore, it is proposed that the N-5 and N-6

functionalities can also contribute to the capacitance through
pseudocapacitance, and this contribution would be different with
different electrolytes. In this regard, Moreno-Castilla *et al.*²⁵ have
observed a good correlation between interfacial capacitance and
pyrrolic and pyridinic nitrogen functionalities under acidic condi-
5 tions. Thus, part of the observed capacitance enhancement of
N-doped CNTs in both acidic and basic electrolytes can be attrib-
uted to the pseudocapacitance arising from the N-5 and N-6
moieties. Considering that pyrrole moieties are within the nanocaps
of the bamboo-like structure of CNTs,¹¹ and are therefore inacces-
10 sible by ions, and that Q-N does not contribute, the amount of
pyridinic functionalities can be estimated to be 2.0 wt% (from XPS
analyses). Assuming a one electron transfer process, the contribu-
tion of pyridinic functionalities to the capacitance is of the order of
135 F g⁻¹. This value is in good agreement with the capacitance
15 measured under alkaline conditions (160 F g⁻¹), which suggests
that most of the pyridinic functionalities are accessible to the
electrolyte due to their location in the outer layers of the N-CNTs.
The lower capacitance values for N-6 moieties in an acid electrolyte
can be due to their protonation under such conditions. The
20 additional electron that may donate the N-6 moieties and the redox
processes should be impeded in this medium, producing a decrease
in capacitance.

An efficient one-step procedure for obtaining N-containing CNTs
has been developed and their electrochemical capacitance mea-
25 sured against pristine CNTs. For N-CNTs, a detailed assessment of
various nitrogen moieties and surface defects allowed us to hypothe-
size the origin of the enhancement of specific capacitance, the effect
of which is mainly resulting from the contribution of pseudocapa-
citanace of redox reactions by N-6 groups, especially in basic media.
30 On the other hand, the higher level of structural disorder and the
presence of N-Q groups further enhance the formation of the
electrical double layer and its interaction with the anions in the
electrolyte, contributing to the high capacitance. A combination of
these factors provides a huge capacitance of 160 F g⁻¹ in 6 M KOH,
35 enabling the possible use of these materials as flexible electrodes in
micro capacitor devices.

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