Supporting Information

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

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Synthesis of the CNTs and N-CNTs

Growths of the CNTs and N-CNTs were carried out by thermal CVD method, with equipments and operations similar to what we have reported elsewhere [1]. In brief, for each growth the catalyst was prepared by a wet chemistry method, i.e., mixing the aqueous solution of iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] with alumina (γ-Al_2O_3) and then drying the samples at 90-100 °C for about 20 hours. The concentration of the solutions may be varied, depending on the growth purpose and catalyst loading. A typical concentration fell in the range 0.1 to 0.5 M, and the catalyst loading 0.6-3.0 wt%. In the CVD process, catalytic Fe nanoparticles formed *in situ* by thermal decomposition of the nitrate precursor. Ethylene (C_2H_4) and pyridine (C_5NH_5) were respectively used as feed gases to grow pure multi-walled CNTs and N-doped CNTs. For growing N-CNTs, the CVD temperature was set at 840 °C, while the undoped ones were made at 800-840 °C. In both cases, Argon (Ar) was used as the buffer gas, and growth operation normally lasted for about 30 min.

Characterization data

(1) Elemental analysis. The C-yield and N-content of the CNTs and N-CNTs were analyzed by using a CE440 Elemental Analyzer. To do this, a weighed (typically 3-6 mg) quantity is first introduced into a furnace where the sample is then combusted in oxygen atmosphere. Sample is placed into a tin container, which gives the advantage of strong exothermic combustion to ensure a complete sample oxidation at approximately 1800°C. Through the combustion process, the elemental carbon and nitrogen in the sample are converted into carbon dioxide (CO_2), nitrogen (N_2) and nitrogen oxides

(NxO). These gases are subsequently passed over copper to remove excess oxygen and reduce the oxides of nitrogen to elemental nitrogen. Helium is used as the carrier gas.

Elemental analysis result of the N-doped samples: the N-CNTs yield was typically 4-9 wt% of the total mass of a given product. For the sample used in this work for electrochemical characterization, the N-CNTs yield was 5.5 wt%. Within the N-CNTs, the N = 6.41 wt%, C = 85.71%, and H = 7.87%. The C/N ratio was thus ~16. Elemental analysis result of pure multi-walled CNTs: the nanotube yield was 30.4 wt% in the whole sample, which means that the alumina support accounted for the rest of 69.6 wt%. Within the CNTs, N = 0.00wt%, C = 99.02 wt%, H = 0.98 wt%.

(2) Raman spectroscopic analysis. Raman examination was performed using a micro-Raman spectrometer with an incident Ar ion laser at $\lambda = 514.5$ nm coupled with the Renishaw software. To avoid possible damage to the samples by the laser, extra care was taken and a minimum laser powder was maintained within a given test. Figure S1 shows Raman spectra of the CNTs and N-CNTs samples, with the data being baseline corrected and normalized to the G peak intensity.

As denoted by the dotted line, the D peak showed an upshift in the peak position due to the addition of N to the carbon lattice, which is consistent with the literature [2,3]. Moreover, an broadening in the FWHM of the D band to 78.32 cm^{-1} was observed as compared to 61.31 cm^{-1} for pristine CNTs, which can be ascribed to the formation of various N moieties and the induced defects [1-3]. Also, the I_D/I_G ratio of the N-CNT samples increased to 0.93 as compared to the pristine CNT samples, which shows a value of 0.82. Zig-zag edge defects are principally related to the D' band [4], which often appears as a shoulder of the G band. Figure S1 clearly show that the G band in N-

doped samples is broader and display some asymmetry, due to the apparition of this D'
contribution.
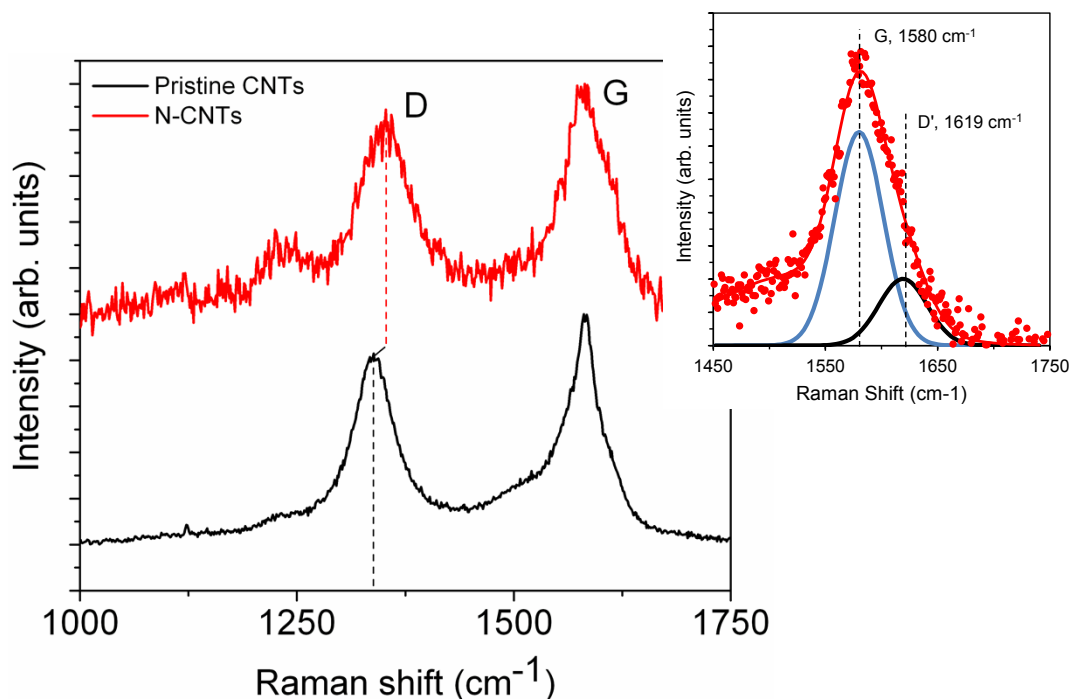
Figure S1. Raman spectra of the CNTs and of N-CNTs show the characteristic D and G
peaks of graphitic structure. Inset includes the deconvolution of the G band.

**(3) Examinations by scanning & transmission electron microscopies (SEM &
TEM).** SEM observation was carried out using a JEOL 6340-FESEM system operated
at 5 kV. TEM was performed on a JEOL JEM-3010x operated at 300 kV. TEM samples
were prepared by first dispersing the materials into ethanol or toluene assisted by ultra
sonication. A drop of such prepared solution was cast onto a holey carbon film of a
copper TEM grid for examination. Figures S2 and S3 show SEM and TEM images of
the CNTs and N-CNTs. As calculated from the line profile of the HRTEM image of N-
CNTs, the average lattice spacing upon the introduction of N into carbon lattice is
increased to about 0.35 nm from the 0.335 nm observed in the pristine CNTs.
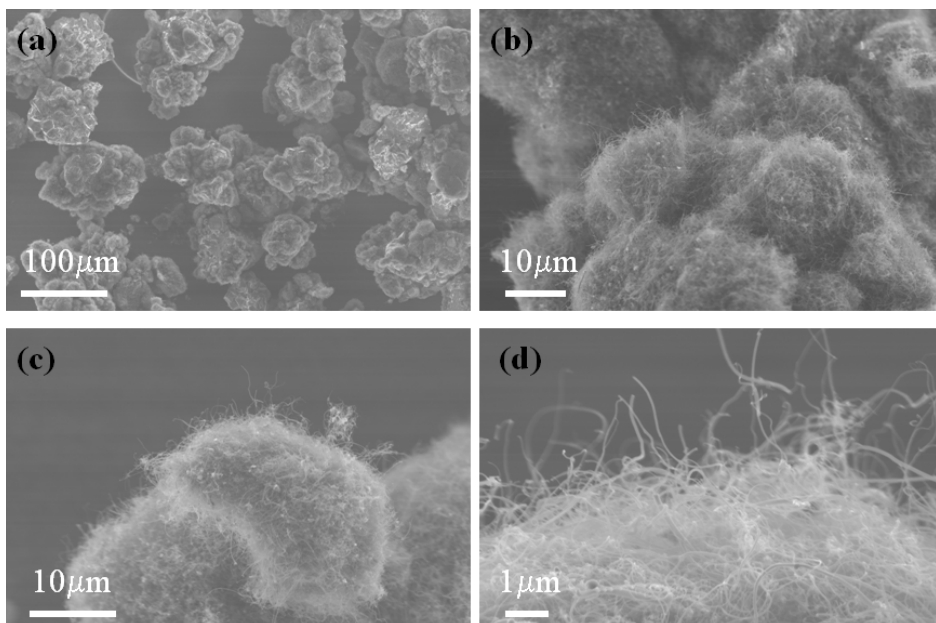
Figure S2. SEM images show N-doped CNTs at different resolutions. From (a) to (d), the magnification increases gradually to show the particle size and morphology.
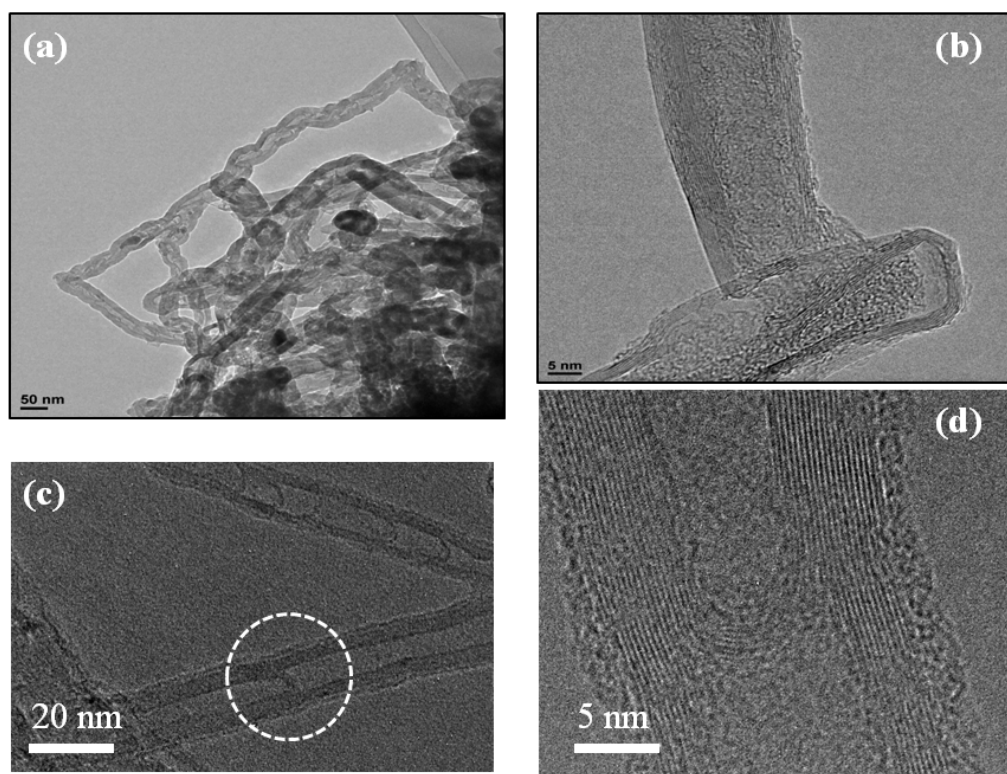
Figure S3. TEM images show the CVD-grown CNTs [(a) and (b)], and N-doped CNTs [(c) and (d)] at different resolutions. Image (d) corresponds to the circled area as shown in (c). The bamboo-like nanostructure is very typical in such N-doped samples.

(4) Thermal gravimetric analysis (TGA). The CNTs and N-CNTs samples were thermally treated up to 900 ºC (heating rate: 20 ºC/min) under oxidizing atmosphere (100 mL/min, high purity synthetic air) in a thermal balance (SDT Q-600, TA instruments). Samples were dried in the thermal balance chamber at 120ºC for 2 hours before running the experiments. The obtained TGA curves are shown in Figure S4. Those unreacted samples recovered at the end of the runs are the catalyst support, whereas the total weight lost was accounted to the combustion of the carbonaceous fraction of the sample, i.e. the carbon nanotubes. The nanotube yields obtained by this method are consistent with those obtained by elemental analysis technique mentioned above.
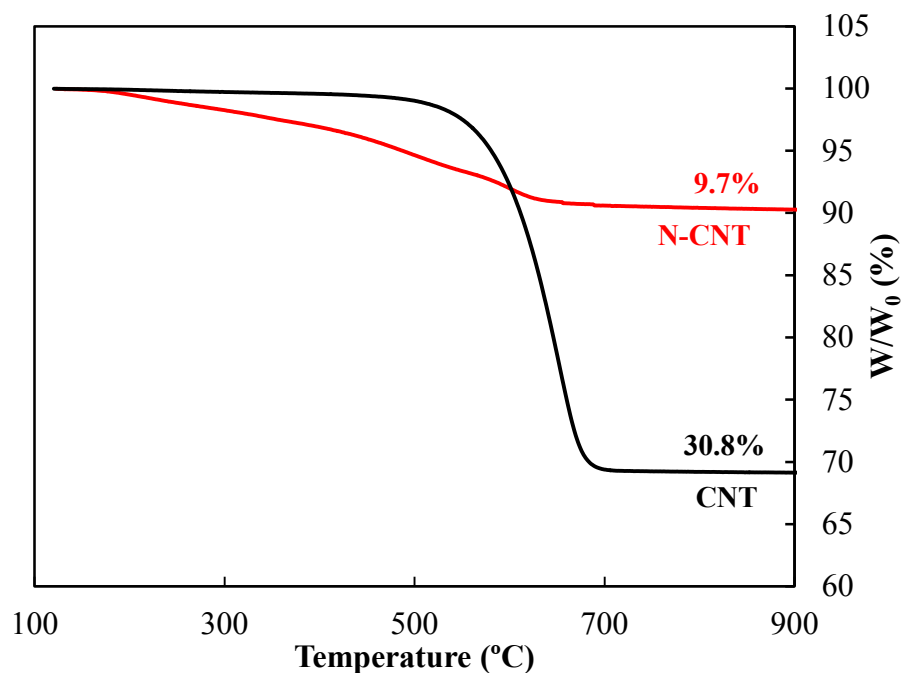

Figure S4. TGA profiles were obtained in air for the samples of CNTs (black line) and N-CNTs (red line).

(5) Electrochemical analysis. The CNT and N-CNT samples were first suspended in N, N-dimethylformamide (1 mg·ml^{-1}) and then deposited on polished glassy carbon electrodes (10 µl) to act as working electrodes. The three electrode configuration was completed by a further reversible hydrogen electrode (RHE) and a platinum wire, being used as reference and counter electrodes, respectively.Cyclic voltammetry was carried out at scan rates between 5-100 mV/s in both electrolytes. Alumina is electrochemically inactive, it is an electrical insulator and therefore cannot contribute to the capacitance obtained by CV. As for the iron nanoparticles, they can be easily detected in the CV through the Fe^{2+}/Fe^{3+} redox pair at 0.8V vs RHE in sulfuric acid. The lack of oxidation/reduction peaks in this region on the cyclic voltammograms confirms the absence of any contribution from the catalyst to the overall capacitance of the electrode.

The capacitance values were calculated in the interval 0-1.0 V of the 10th cycle according to the formula, $C_s = [(Q_a + |Q_c|)/(2m\Delta V)]$, where C_s is the specific capacitance (in F g^{-1}), Q_a and Q_c are the anodic and cathodic charges in coulombs, ΔV is the voltage window (in volts), and m is the weight of the sample (in grams).

Figure S5 and S6 demonstrate that CNT and N-CNT samples keep all their distinctive features even at the highest rate tested. Capacitance was determined from the area enclosed by the CV and the scan rate used in each experiment, revealing full capacitance retention in all the tested electrolyte and samples.
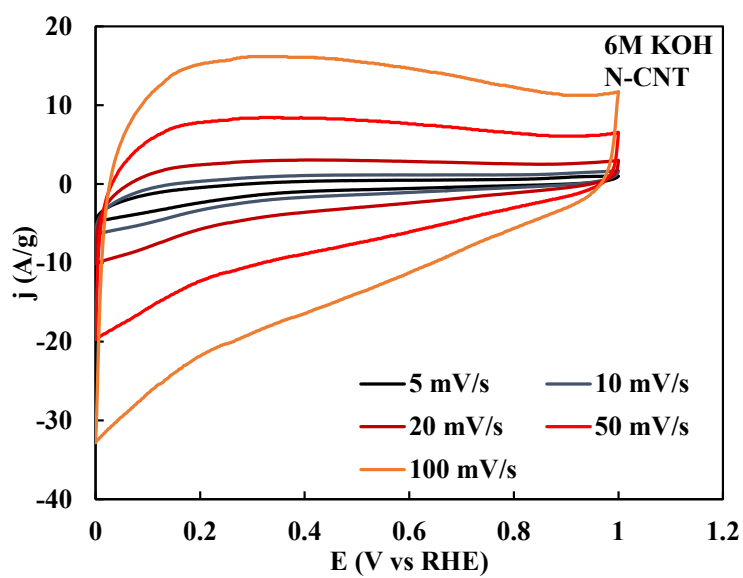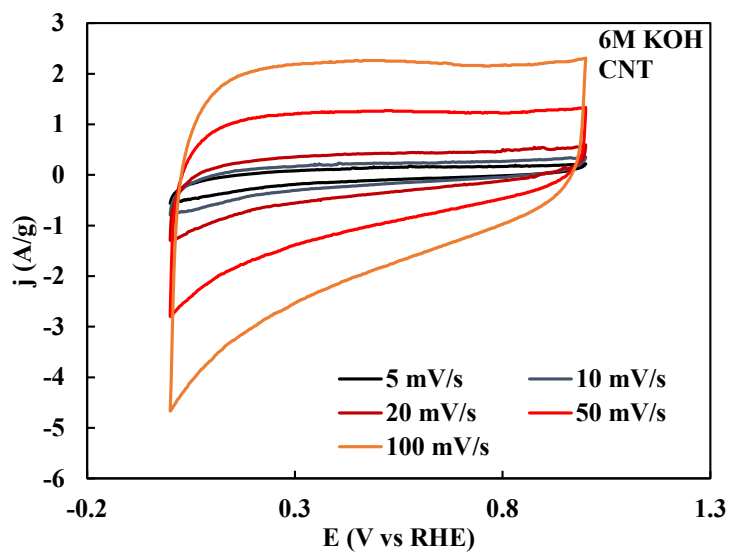
Figure S5. Steady state cyclic voltammetry at different scan rates in 6M KOH for CNTs (upper part) and N-CNTs (lower part).
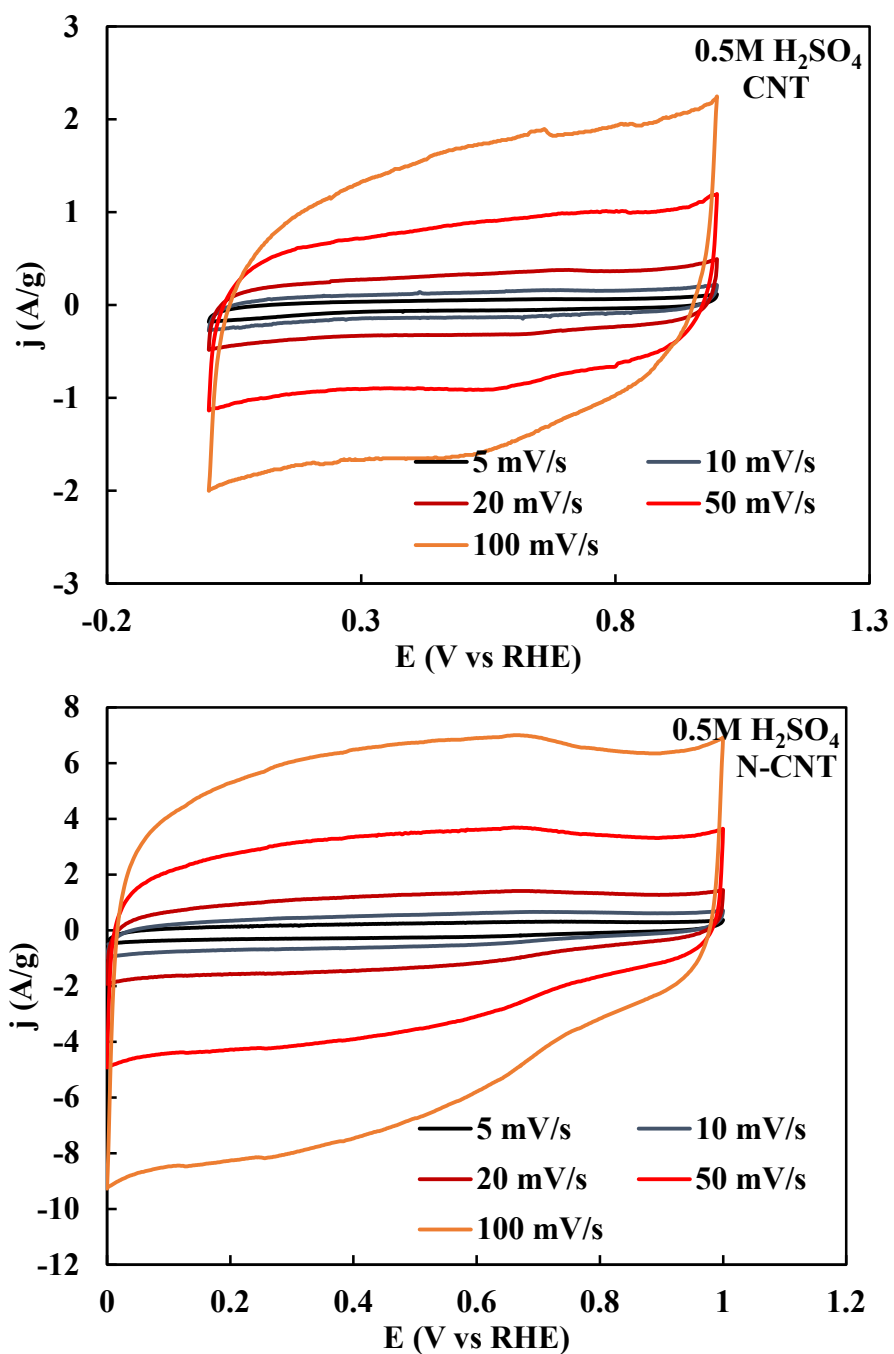
Figure S6. Steady state cyclic voltammetry at different scan rates in 0.5M H$_2$SO$_4$ for CNTs (upper part) and N-CNTs (lower part).

References:

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