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Fabrication of chlorine nitrogen co-doped carbon nanomaterials by an injection catalytic vapor deposition method

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Abstract

The synthesis of both covalently bonded chlorine and nitrogen-doped carbon materials (Cl-N-CNMs) has been little studied. In this paper we report on the investigation of the synthesis of Cl-N-CNMs using a feedstock containing a mixture of dichlorobenzene (DCB), acetylene and acetonitrile over a Fe-Co/CaCO3 catalyst using an injection CVD method at 800 °C. By varying the acetonitrile:DCB concentration ratio (66.7:33.3; 33.3:66.7 and 20:80), the morphology and physicochemical properties of the CNMs was varied. The products contained varying amounts of Cl (0.5%–1.2%) and N (0.88%–1.47%) and the total amount of Cl and N increased with the Cl content in the feed, as determined by XPS. A graphitic N environment dominated in feeds containing 33.3 and 66.7 vol.% DCB, whilst pyrrolic N dominated in feeds containing pure acetonitrile and 80 vol.% DCB. The chlorine in the feed promoted the formation of CNMs with various shapes namely horn-shaped, spaghetti-like, and pencil-like shapes, some with open-ends and others with closed-ends as determined by TEM and SEM studies. Although no direct correlation with the amounts of the reactants used and the morphology of the products was established, trends in the product shapes were noted with highly defected products produced from 66.7 vol.% DCB, and feeds containing 33.3 and 80 vol.% had tubes with similar open-ended horn-shaped morphology and less defects.

1. Introduction

Carbon nanotubes (CNTs) with controlled morphology are well known and the CNT morphology has been shown to impact on the physicochemical properties of the CNTs. Further, foreign atoms (dopants) can be introduced into the CNT structure. The addition of foreign atoms into the CNTs can lead to either functionalization of the CNT walls or substitution of a carbon atom in the CNT wall.

Doping carbon nanomaterials (CNMs) with nitrogen atoms has been shown to enhance the application of the carbons in various fields. These include, their use as polymer fillers in composite materials to enhance their strength or conductivity [1], supports in catalysis [2, 3], adsorbents in water purification [4], adsorbents for CO2 [5], and as storage materials for energy (lithium-ion batteries and supercapacitors) [6]. Indeed, much work has appeared on the use of N-doped carbon nanomaterials (N–CNMs) as electrode materials in supercapacitors [6–11]. Use of N-doped CNMs as supercapacitors has been encouraged by the high surface area, excellent electronic conductivity, high reversibility and eco-friendliness of the doped carbons [12]. The beneficial effect of nitrogen has been related to the specific bond types formed with carbon [13]. The have been reported the magnetic properties of the N-doped CNMs [14].

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Incorporation of halogens and other atoms into the carbon structures have been found to enhance their electrical and thermal conductivity. Decoration of CNT fibers with iodine was found to significantly raise the inter-tube interfacial electrical and thermal transport and thus boosting the overall electrical and thermal transport performance of the fibers [15]. Electrical and thermal properties of CNT films were greatly enhanced after doping them with mild and safe iodonium salts [16]. The interfacial electrical and thermal transport within the inter-tube interface was greatly improved when using carbon nanotubes fibers doped with gold (Au) nanoparticles [17]. Chemical doping of reduced graphene oxide (rGO) sheets with chlorine introduced extra charge carriers into the rGO and these were found to enhance the rGO electrical conductivity [18]. Chlorinated rGO sheets were found to be highly stable in solvents like N,N-dimethylformamide, possibly because of the enhanced repulsive forces between the graphene oxide sheets arising from the absorbed Cl ions [19]. Yeon et al found that etching a polymer SiCN with chlorine resulted in the formation of a carbon material that exhibited meso- and micro-porosity and possessed a high specific surface area of 800–2400 m²·g⁻¹ [20]. Zera et al synthesized a nitrogen-doped carbide derived carbon aerogel with high capacitance by chlorine etching of a SiCN aerogel [13]. In a previous study by our group, the effect of chlorine on the morphology of CNMs prepared by a catalytic pyrolysis of a range of chlorinated organic hydrocarbons using C₂H₃ over an Fe-Co/CaCO₃ catalyst was studied [21]. Here it was shown that the type of chlorinated organic reagent used influenced the morphology of the CNMs [21]. Chlorinated holey double-walled carbon nanotubes (DWCNTs) which showed high repeatable response to humid environment and a good reversible behavior after sensor purging by dry air were synthesized by etching the walls of DWCNTs by hot concentrated sulphuric acid, followed by saturating the edge carbon sites with chlorine via CCl₄ vapor [22].

Interestingly, the role of chlorine (and chloride salts) on the morphology of N-doped CNTs have only been the subject of a few studies. For example, 30% of N-doped horn-like CNTs with dumbbell-shaped open-ends were prepared by reducing pentachloropyridine with metallic sodium in a stainless steel autoclave; the reaction also produced hollow carbon nanospheres [23]. Various N-doped carbon nanostructures including particles, whiskers, square frameworks, lamellar layers, hollow spheres and tubular structures have been synthesized by designed chemical reactions of carbon halides (such as CCl₄, C₂Cl₆) and nitridation reagents such as NaN₃. This reaction occurred in the absence of any templates and catalysts in an autoclave at various temperatures [24]. The rupture of thick CNTs with arms or branches was observed when using a modified pyrolysis CVD method, where sodium chloride was added into a by-product liquid trap [25]. The nitrogen content was increased in N-doped CNTs synthesized using halogenated ferrocenyl catalysts [26]. A fluorine substituted ferrocene catalyst produced a higher nitrogen-doping level in N-CNTs as compared to a chlorine substituted ferrocene catalyst, but the chlorine substituted catalyst also yielded iron-filled N-CNTs [26]. Boron chloride CNTs (BClCNTs), which presented excellent oxygen reduction reactions (ORR) performance, were successively prepared from metal-free substrates via chemical tailoring of two-dimensional boron carbide (B₄C) with Cl₂ [27]. Changes in electronic and magnetic properties of nitrogen doped CNTs were observed after functionalizing them with chlorine in chlorine plasma atmosphere and oxygen. Experimental results and theoretical calculations showed that chlorine bonded compounds (i.e. C-Cl, C-N-Cl) formed on the surface of nitrogenated CNTs [28]. Functionalization of the N doped CNTs with chlorine and oxygen (N-CNTs:Cl and N-CNTs:O), revealed that the density and the length of the nanotubes decreased on chlorination but increased on oxidation whilst the field emission properties were enhanced in N-CNTs:Cl but reduced in N-CNTs:O [29]. From the above reports it can be observed that simple routes to make both N and Cl doped CNTs have only resurfaced recently, from the two reports by Ray et al [28, 29].

In this study, the effect of chlorine on the morphology of N-doped CNTs made with 1,2-dichlorobenzene (DCB) using an injection CVD method was investigated. The goal was to evaluate the modification of N-doped CNTs with chlorine. To the best of our knowledge, the role of chlorine on the morphology of N-CNTs using a Co-GO/CaCO₃ catalyst and a simple injection CVD method has not been studied previously. The concentration of chlorine was varied to explore its effect on the morphology of the N-doped CNTs. It was observed that addition of both CH₂CN and DCB (together with C₂H₃) gave products that contained both covalent Cl and N in the new carbons. The results were compared with a previous report that showed that CNTs produced from the pyrolysis of DCB without N showed secondary CNT growth structures [30].

2. Experimental section

2.1. Synthesis of the catalyst [31]

Fe(NO₃)₃ · 9H₂O and Co(NO₃)₂ · 6H₂O were used to prepare the catalyst. Calculated amounts of the Fe and Co nitrates were weighed and mixed in separate beakers. The salts were then dissolved in 30 ml of distilled water to make 0.3 mol l⁻¹ Fe and 0.3 mol l⁻¹ Co precursor solutions. The metal solutions were mixed, transferred to a burette, and added dropwise to a 10 g CaCO₃ support that was placed in a beaker with constant stirring. The
mixture was left stirring for 30 min. The beaker containing the metal-support mixture was then dried in an oven at 120 °C for 12 h. The solid was then cooled to room temperature, ground using a mortar and pestle, and followed by screening through a 150 μm molecular sieve. The catalyst powder was then calcined at 400 °C for 16 h in a static air oven. This catalyst was characterized as reported in an earlier article [31].

2.2. Synthesis of chlorinated CNMs and N-doped CNMs using pure DCB and CH3CN

Synthesis of chlorinated CNMs and N-doped CNMs was carried out at 800 °C in a CVD furnace in the presence of a mixture of N2 and CH2 gases with flow rates of 240 and 90 ml min⁻¹ for N2 and CH2, respectively. Both N2 and CH2 were used as carrier gases with CH2 also as the carbon-containing reactant. The dichlorobenzene (DCB) or acetonitrile (CH3CN) solvent, or solvent mixture (20 ml) was placed into a 20 ml syringe driven by a SAGE syringe pump. After 1 g of the synthesized catalyst was placed in a quartz boat that was then inserted into the middle of the quartz tube reactor (32 cm diam × 1 m length). The quartz tube was then placed inside a furnace with the boat positioned at the center of the furnace at room temperature and then set to start heating. After the temperature of the furnace had reached 800 °C, the solvent was injected at a rate of 0.24 ml min⁻¹ into the quartz tube reactor using a peristaltic pump. The reaction time was 1 h. At the end of the reaction, the furnace was cooled down to room temperature under a N2 atmosphere (40 ml min⁻¹). The formed carbon soot was removed from the tube and weighed. The carbon product produced from CH3CN was purified by reflowing in 30% HNO3 at 110 °C for 4 h. The carbon product produced from DCB was purified using mild conditions (stirring in 30% HNO3 acid at room temperature) since harsher temperatures destroyed the product. Both carbon products were then filtered and washed with distilled water until the pH of the filtrates reached ∼7. The carbon products were then dried in an oven at 120 °C overnight. The schematic representation of the experimental setup is presented in supplementary figure S1 (available online at stacks.iop.org//0/000000/mmmedia).

2.3. Synthesis of chlorinated N-CNMs using DCB/CH3CN mixtures

A similar experiment to that used in section 2.2 was followed, but in this case a 20 ml mixture of CH3CN and DCB of various volume ratios were placed in a 20 ml syringe driven by a SAGE syringe pump. The carbon soot produced was removed from the tube, weighed and some of the product purified by reflowing in 30% HNO3 at 110 °C for 4 h. The carbon product was then filtered and washed with distilled water until the pH of the filtrates reached ∼7. The carbon product was then dried in an oven at 120 °C overnight.

2.4. Characterization of the carbon nanomaterials

The morphology and size distribution of the produced CNMs before and after treatment with HNO3 acid were analyzed by transmission electron microscopy (TEM) using a T12 FEI TECNAI G2 SPIRIT operating at 120 kV. The samples for TEM analysis were prepared by sonication in ethanol and thereafter deposited on a holey carbon coated TEM Cu grid. The morphology and size distribution of the CNMs were also determined by scanning electron microscopy (SEM) using a FEI Nova Nanolab instrument. The powdered samples were placed on a tape that was attached to a stub. The samples were coated with carbon and palladium to prevent them from charging. The graphitic nature of the CNMs was characterized by Raman spectroscopy using a Jobin-Yvon T6400 micro-Raman spectrometer. Excitation was provided by the 532 nm green laser with spectral resolution of 3–5 cm⁻¹. X-ray photoelectron spectroscopy (XPS) analysis was done using an AXIS Ultra DLD with an Al (monochromatic) anode equipped with a charge neutralizer, supplied by Kratos Analytical (UK) at Rhodes University.

3. Results and discussion

The morphology of the CNMs was first evaluated using pure CH3CN and pure DCB (in C2H2/N2), to obtain base-line data for the study.

TEM images of purified CNMs obtained from pure CH3CN revealed the presence of mixtures of CNMs, hollow thin-walled CNTs (figure S1(a)), bamboo compartmented CNTs (supplementary figure S2(a)) and carbon nanospheres (CNs) (figure S1(b)). A rod-shaped carbon nanofiber (CNF) with a cylinder-like tip or base (supplementary figure S2(b) circled part) was also observed from the TEM images.

SEM images of the nanomaterials generated from CH3CN revealed that the majority of the CNMs were ‘rod-shaped’ (figure S1(c) and supplementary figure S2(c)). A diameter distribution curve showed that a majority of the rod-shaped CNMs had an average outer diameter of ~53 nm (figure S1(d) and table 1). The rod-shaped CNMs grew from or were attached to some large, agglomerated particles (figure S1(c)). The agglomerates were previously observed in other studies e.g., during pyrolysis of acetonitrile using a Mg-Co-Al layered hydroxide as a catalyst material wherein carbon plate-like particles were observed [32]. The length of the rod-shaped CNMs...
ranged from ∼60 to 160 nm. A few spherical CNMs (supplementary figure S2(d) arrow) and a few long CNTs were also observed from SEM images (supplementary figure S2(d); circled part). No secondary growth of carbon on the rod-like materials was observed when pure acetonitrile was used.

TEM and SEM images of purified CNMs prepared from pure dichlorobenzene (DCB) revealed mixtures of entangled thin- and thick-walled CNTs (figures 2(a)–(c)). The tube tips and bases were not clearly observed from the TEM images due to entanglement and the great length of the tubes. The density and length of the CNTs increased when DCB was used as a carbon source instead of CH$_3$CN. This must be due to the catalyst used or how it was used in this study. Previous studies have shown growth of large density of bamboo-compartmented CNTs, when a mixture of acetonitrile and ferrocene were used as a source nitrogen, carbon and catalyst by an injection-vertical CVD method [33]. Secondary CNF growth was not observed from the TEM images, as were previously observed during pyrolysis of DCB using a bubbling CVD method [21, 30]. A diameter distribution curve revealed that the CNTs had an average outer diameter of ∼45 nm (figure 2(d) and table 1). Growth of a large quantity of highly entangled CNTs in the form of a CNT sponge was also reported in the literature from spray pyrolysis of a mixture of ferrocene and DCB [34].

Figure 1. (a)–(c) TEM and SEM images and (d) diameter distribution curve of purified CNMs generated from pure CH$_3$CN by an injection CVD method (reaction conditions: 0.24 ml min$^{-1}$; 800 °C, 1 h, 240 ml min$^{-1}$ N$_2$, and 90 ml min$^{-1}$ C$_2$H$_2$).

The effect of using DCB/CH$_3$CN solvent mixtures of various ratios on the morphology of N-doped CNMs was also studied by TEM and SEM. The concentrations, based on the volume percent of nitrogen and chlorine sources used were: CH$_3$CN:DCB (66.7:33.3 vol.%); CH$_3$CN:DCB (33.3:66.7 vol.%); CH$_3$CN:DCB (20:80 vol. %). A summary of the results is shown in table 1.

TEM images of purified CNMs obtained from these mixtures revealed the formation of nanomaterials of different morphologies (supplementary figure S3). TEM images of CNTs prepared from solutions containing 33.3 vol.% DCB showed CNTs with open-ends, some with closed-ends (rod-shaped) and other CNFs with 'funnel-shaped' open-ends (supplementary figure S3(a) circled). CNTs obtained from un-purified products had
Table 1. Diameter analysis of CNMs generated from solutions containing various volume ratios of CH$_3$CN:DCB synthesized using an injection CVD method at an injection flow rate of 0.24 ml min$^{-1}$.

| Hydrocarbon source | Molar ratio /vol.% (Mole ratio) | Average outer diameter/nm | Number of structures counted (number of samples analyzed) | Carbon structure                                      |
|-------------------|---------------------------------|---------------------------|-----------------------------------------------------------|-------------------------------------------------------|
| CH$_3$CN          | Pure                            | 53 (Carbon nanorods)      | >200 (in duplicate)                                      | Carbon nanorods (70%), CNTs and bamboo CNTs (15%), CNSs (15%) |
| CH$_3$CN: DCB     | 66.7:33.3 (1:0.25)              | 107 (open-ended CNTs)     | >200 (in duplicate)                                      | Horn- or straw-shaped CNTs (70%), carbon nanorods (20%), CNSs (10%) |
| CH$_3$CN: DCB     | 33.3:66.7 (1:1)                 | 78 (rod-shaped CNMs)      |                                                           |                                                       |
| CH$_3$CN: DCB     | 20:80 (1:2)                     | 157 (open- and closed-ended CNFs and CNTs) | >200 (in duplicate)                                      | Pencil-shaped CNFs (70%) and CNTs (30%)               |
|                   | >200 (in duplicate)             | 95 (straw-shaped CNTs)    |                                                           |                                                       |
|                   |                                 | Straw-shaped CNTs (60%), entangled CNTs (20%), carbon nanorods (10%), CNSs (10%) |                                                          |                                                       |
|                   |                                 | 72 (entangled CNTs)       |                                                           |                                                       |
| DCB               | Pure                            | 45                        | >200 (in duplicate)                                      | Entangled CNTs                                        |
similar shapes and were also open-ended (supplementary figures 4(a) and (b)). Previous studies have shown that acid treatment opens the tube ends [35], but in our study the tube-ends were open even before acid treatment. This could be one of the roles of chlorine; to act as an oxidizing agent leading to opening of the tube ends.

Doubling the DCB concentration in the feed to 66.7 vol.% resulted in formation of CNTs and CNFs with various sizes (supplementary figure S3(b)). A similarity was again observed from CNMs generated from both un-purified (supplementary figures S4(c) and (d)) and purified samples. Rod-shaped CNTs, some with closed-ends and others with open-ends were obtained. Large-sized CNFs with pencil-shapes, some with open-ends and others with closed-ends were also obtained (supplementary figure S3(b) circled parts). A high magnification TEM image of the large, circled tube in supplementary figure S3(b) shows that the materials are fibrous, and a catalyst particle can be seen embedded at the pencil-like tip of the CNF (supplementary figure S3(c)). Previous studies have explained this phenomenon as growth termination of CNT due to the full coverage of the catalyst by the carbon layers [36]. Open-ended CNTs with no catalyst particle at their tip were also observed from the materials obtained at DCB concentrations of 33.3 and 66.7 vol.% (supplementary figures S3(a) and (b) circled). The type of growth termination that took place here can be explained as out-migration of the catalyst from the growing nanotube induced by weakened adhesion strength between catalyst and CNT [36]. Another scenario for growth termination due to Ostwald ripening is observed from the TEM images of the un-purified CNTs generated from feeds containing 33.3 vol.% DCB (supplementary figure S4(b) circled) [36]. A further increase in DCB concentration to 80 vol.% DCB resulted in formation of a large quantity of entangled uniform CNTs (figure S3(d)), which could be attributed to the presence of a large quantity of chlorine in the feed. Enhanced CNT growth, as was observed when pure DCB was used as a feed (figures 2(a)–(c)), was noted.

SEM images were also recorded to obtain more information about the morphology and the dominating carbon nanostructures formed from the different feeds. Images obtained from un-purified samples containing 33.3 vol.% DCB showed the presence of rod-shaped CNMs, covered by droplets of metal catalyst particles (supplementary figures S5(a) and (b)). SEM images of the purified samples revealed that the majority of the
CNMs in this feed contained 'straw-shaped' CNTs of various sizes with open-ends (figures 3(a) and (b)). Diameter distribution curves revealed that the open-ended CNTs had an average outer diameter of \(\sim 107 \pm 44\) nm (supplementary figure S6 and table 1). A measurable quantity of the rod-shaped CNMs was also observed with this feed, with an average diameter distribution of \(\sim 78 \pm 53\) nm (supplementary figures S7(c) and (d)).
The open-ended CNTs were ‘horn-shaped’ (supplementary figure S7(c)) and the rod-shaped CNMs appeared to have increased in length in comparison to those obtained from pure CH₃CN (supplementary figure S2(c)), with the measured lengths of ~350 to 540 nm; this is about three times the value obtained in pure CH₃CN. This suggests that the presence of chlorine enhanced the growth of the CNMs. This must be an effect of the synthesis method and the type of catalyst used because Ray observed a decrease in CNT density and length after chlorination of N-doped CNTs using an inductively plasma-coupled reactor in flowing Cl₂ gas [29]. The diffusion and precipitation of the reactive carbon species was faster when chlorine was added resulting in faster growth rate and increase in nanotubes length and density [29]. A measurable quantity of the carbon nanospheres was also obtained from this feed solution (supplementary figure S7(d)).

SEM images obtained from un-purified samples containing 66.7 vol.% DCB also showed the presence of rod-shaped CNMs, covered by droplets of metal catalyst particles (supplementary figures S5(c) and (d)). SEM images of the purified samples revealed that the majority of the CNMs in this feed were ‘pencil-shaped’ CNFs with most of them showing small un-defined tip-ends (figures 3(c) and (d)). The average outer diameter of the observed CNMs was about 154 nm (supplementary figure S6(b) and table 1). Diameters of the nanotubes were also slightly increased in another study after chlorination of N doped CNTs [29]. Some of the CNFs were very large with ‘pencil-shaped’ morphologies, some had closed-ends whilst others had open-ends (some appear to have broken tips) (supplementary figure S8). An almost full CNM can also be seen in supplementary figure S8(c) and it has both ends narrowed in a form of a ‘pencil’ shape. The increase in the amount of chlorine in the acetonitrile feed resulted in structural changes from the ‘rod-shaped’ CNMs to the ‘pencil-shaped’ CNFs. There was also an increase in the thickness of the CNFs and the increased narrowing of the thick tubes with an increase in the amount of chlorine in the feed (figure 3(c); circled part and supplementary figures S8(b) and (c)). Tube-end narrowing was also observed from the secondary grown CNFs in our previous studies, during pyrolysis of DCB using a bubbling CVD method [21, 30]. CNT tube narrowing at their tips was also observed by other authors and they attributed it to tip growth termination of MWCNTs [37]. The reaction mechanism to form the ‘pencil-shaped’ CNTs is still unknown.

SEM images obtained from solutions containing 80 vol.% DCB concentration revealed a mixture of CNMs. Unpurified samples showed rod-shaped CNMs covered by droplets of metal catalyst particles (supplementary figures S5(e) and (f)). SEM images of the purified samples revealed mixtures of clean CNMs, CNSs (supplementary figure S9(a)), ‘straw-shaped’ open-ended CNTs and entangled CNTs (figures 3(e) and (f), and supplementary figure S9(b)). The ‘straw-shaped’ CNTs dominated with average diameters of about 95 nm (supplementary figure S6(c) and table 1). The average outer diameter of the entangled CNTs was about 72 nm (table 1 and supplementary figure S9(c)). At all concentrations studied, the tube length increased with an increase in the amount of chlorine added to the feed, tube opening was also enhanced in the presence of chlorine.

Raman spectral analysis of the N-doped CNTs before and after addition of chlorine revealed the presence of D, G, G*, 2D and D + G Raman bands (figures 4 and 5). Samples obtained from pure CH₃CN showed the presence of a D’ band that appeared as a shoulder of a G band and indicated the presence of disorder at a lower scale (figure 4). Spectra obtained from solution mixtures prepared by adding 33.3; 66.6 and 80 vol.% DBC into acetonitrile showed overlap between the G and D’ bands, indicating significant structural disorder (figure 5). A high D band intensity was also observed in the chlorinated samples and was attributed to the dominant
sp³–hybridized C–C bonds which may arise from grain boundaries, vacancies, pentagons, heptagons and graphene edges [38]. An amorphous carbon D2 band was observed from the spectra of CNTs generated from feeds containing 33.3 and 66.7 vol.% DCB. The assignment of all the observed Raman bands is given in supplementary table S1.

The intensity ratio of the D and G (I_D/I_G) Raman bands, using a Lorentzian fit, were 0.68, 0.72, 1.8 and 0.63 for purified CNMs generated from solutions containing pure CH₂CN, and 33.3, 66.7 and 80 vol.% DCB in CH₂CN respectively. The degree of disorder increased with an increase in the amount of chlorine in the feed from 33.3 to 66.7 vol.% but decreased for materials prepared from an 80 vol.% DCB feed solution. This shows that the graphitic nature of the carbon materials was affected by the amount of chlorine, and that more than one factor plays a role at low concentration, another at 80% DCB.

Figure 5. (a), (b) Lower and higher wavelength deconvoluted Raman spectroscopy curves of purified CNTs generated from pure DCB using an injection CVD method (injection rate = 0.24 ml min⁻¹).

Large ID/IG values were obtained for the purified CNTs which decreased in a consistent manner with DCB feed content (I_D/I_G = 16, 9.3 and 3.7 for 33.3, 66.7 and 80 vol.% DCB). These values are related to the sp³ content (16), a mixture of vacancy-like and hoping defects (9.3) and boundary-like (3.7) defects, respectively [41–43].

Raman bands obtained from CNMs generated from pure DCB also showed a highly intense D band that indicates the existence of disorder (figure 6). A large I_D/I_G value of 1.5 also suggested that the materials had disordered carbon. The most plausible explanation is that the presence of chlorine created disorder due to functionalization of the outer wall of the graphene sheet, but the phenomena depends on the amount of chlorine in the feed.

Second order bands were also observed from purified CNMs generated from solutions containing 33.3 and 80 vol.% DCB. A G” band at ~2400 and a 2D band split into two bands (figures 6(b) and (e)) were also noted. A defect induced G” band was very weak in both samples. A weak 2D band for CNMs generated from feeds containing 33.3 vol.% DCB was very intense for CNMs generated from feeds containing 80 vol.% DCB CNMs. The data suggest that the latter materials were highly graphitic, which is in agreement with the I_D/I_G ratio.

Another weak defect induced band (D + G band) at ~2900 cm⁻¹ was observed from purified CNMs generated from solutions containing 80 vol.% DCB (figure 6(e)).

The degree of disorder was also related to the concentration of DCB in the feed and was found to increase tremendously with an increase in DCB concentration from 33.3 (I_D/I_G = 0.72) to 66.7 (I_D/I_G = 1.8) vol.%, but decreased when the DCB concentration was increased further to 80 vol.% (I_D/I_G = 0.63) (figure 7(a)). Among all studied products, chlorinated nitrogen doped CNTs generated in feeds containing 66.7 vol.% DCB had the largest amount of defects that are conducive to electrocatalytic processes [44]. This data agrees with the TEM analysis where CNMs of various shapes, and sizes were obtained from feeds containing 66.7 vol.% DCB due to increased disorders in the CNMs. The data also agrees with the results obtained by Kou et al for their BGCNTs.
where the degree of defects was highest in feeds containing 6.6% Cl (studied feeds were 3.3, 6.6 and 9.9 Cl ratios) [27]. To further explain the formation of highly graphitic materials for acetonitrile feeds that contained a large concentration of chlorine, we compared the wavelength of the D and G peaks. The D and G bands blue shifted after addition of 80 vol.% DCB as compared to those obtained in feeds containing 33.3 vol.% DCB (figure 7(b)). According to literature the blue shift is due to decreased doping of an atom in quantity, which in our case will be decreased doping of nitrogen [27]. The data is consistent with our earlier conclusions that at high DCB concentrations of 80 vol.% most of the chlorine enters the reactor as Cl₂ molecules which act as purifying agents. However, the D and G bands red shifted for feeds containing 66.7 vol.% DCB, which suggests p-type doping and increased doping, this suggests doping or functionalization of material with both chlorine and nitrogen.

XPS data were collected on all the samples generated from CH₃CN, DCB and CH₃CN:DCB with various ratios (supplementary figures S10 and S11). All spectra revealed peaks for C, O, N and Cl. The spectra for the Cl-containing samples are shown in figure 8. The Cl spectra contained two peaks that are associated with the Cl2p₃/₂ and Cl2p₁/₂ binding energies, due to the spin–orbit splitting of the Cl2p core level (0.5 ratio and 1.6 eV separation) [45–47]. The two peaks centred at 200.1 eV and 201.7 eV are associated with covalent C–Cl (and/or

Figure 6. (a)–(e) Lower and higher wavelength deconvoluted Raman spectroscopy curves of purified CNMs generated from various vol.% of CH₃CN:DCB solutions using an injection CVD method (injection rate = 0.24 ml min⁻¹).
Figure 7. (a) Amount of defects created ($I_{D}/I_{G}$ peak ratio) as a function of the amount of DCB added to the CH$_3$CN feed. (b) Comparison of wavelength of D and G Raman bands of purified chlorinated nitrogen doped CNTs generated at various volume ratios of CH$_3$CN and DCB.

Figure 8. Cl 2p XPS spectra of purified CNTs generated from (a) 66.7:33.3, (b) 33.3:66.7, (c) 20:80 vol.% of CH$_3$CN:DCB and (d) pure DCB synthesized by an injection CVD method at a flow rate of 0.24 ml min$^{-1}$. 

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Cl–C=O bonds [45–47], while the two peaks at lower energies (199.6 eV and 198.1 eV) are associated with ionic Cl. It is thus clear that the synthesis method produced covalent C-Cl bonds in all cases. The total amount of Cl present in the samples and the distribution of covalent and ionic chlorine on the CNMs are shown in table 2 and in supplementary table S2. The total amount of chlorine in the samples increased with an increase in the amount of DCB in the CH$_3$CN feeds. The C1s XPS data also confirmed the functionalization of carbon with chlorine as evidenced by the presence of C-Cl peak at ~287 to 289 eV (supplementary figure S12).

The data shows that C-Cl bonds were formed on the CNT surface. The bonds could be formed by attack of Cl radicals or by attack from Cl$_2$ [48]. The C-Cl bonds are expected to be formed by reaction of carbon defects or dangling bonds with chlorine to form covalent bonds with the carbon.

The presence of the ionic chlorine could be due to incomplete removal of the catalyst during acid treatment which resulted in formation of metal chlorides due to the reaction of the Cl with the Fe/Co. The percentage of metal residues present in the purified samples after TGA analysis are presented in supplementary table S3. The residual mass left after purification was 0, 5.0, 7.0 and 1.8 for pure DCB, 33.3, 66.7 and 80 vol.% DCB respectively (supplementary table S3) which paralleled the ionic chloride content. Also a shift to higher to higher temperatures for the first peak due to oxidation of CNTs was observed for materials generated from feeds containing 80 vol.% DCB which suggest removal of amorphous carbon and metal content (supplementary table S3). The data agrees with the low I$_D$/I$_C$ value obtained from Raman spectroscopy.

Analysis of the N XPS data for pure CH$_3$CN and mixtures containing 33.3, 66.7 and 80 vol.% DCB, respectively gave N incorporation amounts as 1.31, 1.57, 0.88 and 1.47 at.% (table 3). For all samples, the N 1s peak was deconvoluted into four peaks at 399.3, 401, 402.7 and 405.8 eV attributed to pyrrolic (N$_{pyr}$), quaternary (N$_{Q}$), oxidized (N$_{ox}$) and molecular (N$_{mol}$) nitrogen respectively (figure 9). C1s spectra was also deconvoluted and it confirmed the presence of C-N groups (supplementary figure S13).

An additional peak appearing at 397.6 eV assigned to pyridinic nitrogen (N$_{P}$) appeared in the N 1s spectra of CNTs generated from feeds containing 33.3 vol.% DCB (figure 9). In our earlier studies chlorine was found to introduce on-site defects on the walls of the CNTs [30], and the presence of these defects can possibly provide an easy route for nitrogen to be added onto the walls of the CNTs substituting some of the carbon atoms.

A pyridic nitrogen peak was only observed in feeds that contained DCB and can be ascribed to chlorine induced edge defects (figure 9). A decrease in the pyrrolic and molecular nitrogen peak ratios was observed after addition of 33.3 and 66.7 vol.% DCB, which suggests rearrangement of the carbon and nitrogen atoms within the carbon lattice, which is enhanced in the presence of chlorine (figure 10). A quaternary or graphitic nitrogen peak concentration increased tremendously (twice the amount obtained in pure CH$_3$CN) after addition of 33.3 vol.% DCB suggesting increased substitution of carbon atoms with nitrogen into the CNT walls (table 2, figures 9 and 10). The concentration of the quaternary N peak after addition of 66.7 vol.% DCB decreased and was the same intensity as of that obtained in pure CH$_3$CN (table 3, figures 9 and 10). This could be due to competition between chloride functionalization of carbon and nitrogen doping, which was affirmed by Raman data where a high I$_D$/I$_C$ of ~1.8 and p-type bonding was obtained from feeds containing 66.7 vol.% DCB as compared to I$_D$/I$_C$ values of 0.63 and 0.72 obtained from feeds containing pure acetonitrile and 33.3 vol.% DCB. An increase in the concentration of quaternary N (twice the amount obtained in pure CH$_3$CN) was also observed from feeds containing 80 vol.% DCB (table 3, figures 9 and 10). Pyrrolic N also increased greatly in feeds containing 80 vol.%, authors have suggested that pyrrolic N arises due to N substitution in a Stone-Wales defect [49, 50] or due to asymmetric local bonding [51]. Highly defected CNMs contained lower amounts of graphitic nitrogen incorporated into the CNTs (figure 10).

| Table 2. Total chlorine content and amounts of ionic and covalent Cl present in each feed solution. |
|---------------------------------------------------------------|
| CH$_3$CN:DCB vol ratio (Cl peak ratio) | Total Cl | Ionic Cl | Covalent Cl |
|----------------------------------------|----------|----------|------------|
| 66/33 (0.32 ratio)                     | 0.55     | 0.13     | 0.42       |
| 33/66 (0.56 ratio)                     | 0.66     | 0.25     | 0.41       |
| 20/80                                 | 1.20     | 0.05     | 1.15       |
| Pure DCB                             | 0.50     | 0.0      | 0.50       |

3.1. Conclusion

The synthesis of chlorine-functionalized nitrogen-doped and un-doped CNMs using an injection CVD method and a Fe-Co/CaCO$_3$ catalyst was successful. DCB was found to be a good chlorine source and that impacted on the nitrogen doping into the CNTs. Chlorine influenced the morphology, length, and outer diameters of the N-doped CNMs, and enhanced their growth. A limited quantity of short rod-shaped CNMs were obtained when
Table 3. Nitrogen content and type of the N-species incorporated in the chlorinated N-doped CNTs grown at various volume ratios of CH$_3$CN:DCB solution.

| Sample                     | Pyridinic N (%) | Pyrrolic N (%) | Graphitic N (%) | N oxides (%) | Molecular N (%) | Total N (%) |
|----------------------------|-----------------|----------------|-----------------|--------------|-----------------|-------------|
| CH$_3$CN                   | —               | 0.42           | 0.31            | 0.026        | 0.55            | 1.31        |
| CH$_3$CN:DCB (66.7:33.3 vol.%) | 0.11           | 0.13           | 0.97            | 0.023        | 0.33            | 1.57        |
| CH$_3$CN:DCB (33.3:66.7 vol.%) | 0.12           | 0.074          | 0.30            | 0.097        | 0.30            | 0.88        |
| CH$_3$CN:DCB (20:80 vol.%)  | —               | 0.63           | 0.61            | —            | 0.23            | 1.47        |
pure CH$_3$CN was used as a feed solution, whilst highly entangled CNTs were obtained when pure DCB was used as a feed. Variation of the amount of DCB in the CH$_3$CN feed led to horn-, straw-, spaghetti-like and pencil-shaped open-ended and closed-ended N-doped CNTs and CNFs. Various scenarios of for the growth termination of CNTs were observed i.e., (i) growth termination of CNTs due to full coverage of catalyst by carbon

**Figure 9.** N 1s XPS spectra of purified CNTs generated from (a) pure CH$_3$CN, (b) 66.7:33.3, (c) 33.3:66.7 and (d) 20:80 vol.% of CH$_3$CN:DCB synthesized by an injection CVD at a flow rate of 0.24 ml min$^{-1}$.

**Figure 10.** XPS data analysis of N-doped CNT and chlorinated N-doped CNTs as a function of DCB vol.% showing the relative abundance of different types of nitrogen as a function of chlorine content (Np, black; Npyr, red; NQ, blue; Nox, purple; Nmo, green).
layers, (ii) due to out-migration of the catalyst from the growing CNT induced by Ostwald ripening and weakened adhesion strength between the catalysts and the CNT. Defects associated with sp³ hybridization, and a combination of vacancy-like, hopping defects and boundary like defects were obtained from Raman analysis of materials generated from feed solutions containing 33.3, 66.7 and 80 vol.% DCB, respectively. Graphitic nitrogen species dominated from the XPS data of CNMs generated from feeds containing 33.3 and 80 vol.% DCB, which correlates with the Raman data where low I_D/I_G values below 1 were obtained. The highest amount of chlorine that is covalently bonded to carbon was observed in acetonitrile feeds that contained the largest amount of DCB. It appears that the presence of nitrogen created defects in the graphene sheet due to nitrogen doping, while chlorine created disorder due to functionalization of the outer wall of the graphene sheet. Chlorine also acted as a purifying agent for nitrogen feeds that contained the largest amount of chlorine.

This work has shown that it is possible to modify the morphology of N-doped CNMs by adding chlorine to the N source. The open-ended CNTs generated from chlorine-nitrogen feed mixtures could potentially be applied in field emission devices, as supercapacitor electrodes, for an electrochemical storage of energy, and as electro catalyst for oxygen reduction reactions.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

[1] Vanyorek L, Sikora E, Balogh T, Román K, Marossy K, Pekker P, Szabó T J, Viskolczi B and Fiser B 2020 Nanotubes as polymer composite reinforcing additive materials—a comparative study Arabian J. Chem. 13 3775–82
[2] Shi X, Yu H, Gao S, Li X, Fang H, Li R, Li Y, Zhang L, Liang X and Yuan Y 2017 Synergistic effect of nitrogen-doped carbon-nanotube-supported Cu–Fe catalyst for the synthesis of higher alcohols from syngas Fuel 210 241–8
[3] Mabena L P, Ray S S, Mhlanga S D and Coville N J 2011 Nitrogen-doped carbon nanotubes as a metal catalyst support Appl. Nanosci. 1 67–77
[4] Wang L, Zhu D, Chen J, Chen Y and Chen W 2017 Enhanced adsorption of aromatic chemicals on boron and nitrogen co-doped single-walled carbon nanotubes Environ. Sci. Nano. 4 538–64
[5] Babu D J, Bruns M, Schneider R, Gerthsen D and Schneider J J 2017 Understanding the influence of N-doping on the CO₂ adsorption characteristics in carbon nanomaterials J. Phys. Chem., C 121 616–26
[6] Guenon D and Moon J H 2015 Nitrogen-doped carbon nanotube spherical particles for supercapacitor applications: emulsion-assisted compact packing and capacitance enhancement ACS Appl. Mater. Interfaces 7 20083–8
[7] Chen L-P, Zhang X-., Liang H-W, Kong M, Guan Q-F, Chen P, Wu Z-Y and Yu S-H 2012 Synthesis of nitrogen-doped porous carbon nanofibers as an efficient electrode material for supercapacitors ACS Nano 6 7092–102
[8] Hou J, Cao C, Iredes F and Ma X 2015 Hierarchical porous nitrogen-doped carbon nanosheets derived from silk for ultrahigh-capacity battery anodes and supercapacitors ACS Nano 9 2556–64
[9] Shin W H, Jeong H M, Kim B G, Kang J K and Choi J W 2012 Nitrogen-doped multiwall carbon nanotubes for lithium storage with extremely high capacity Nano Lett. 12 2283–8
[10] Xu B, Hou S, Cao G, Wu F and Yanga Y 2012 Sustainable nitrogen-doped porous carbon with high surface areas prepared from gelatin for supercapacitors J. Mater. Chem. 22 19088–93
[11] Zheng Y, Xu J, Zhang Y, Yang X, Zhang Y and Shang Y 2018 Nitrogen-doped carbon nanotube supported double-shelled hollow composites for asymmetric supercapacitors New J. Chem. 42 150–60
[12] Inagaki M, Komho H and Tanaike O 2010 Carbon materials for electrochemical capacitors J. Power Sources 195 7880–903
[13] Zera E, Nickel W, Hao G P, Van Zetti L, Kaskel S and Soraru G D 2016 Nitrogen doped carbide derived carbon aerogels by chlorination etching of a SiCN aerogel J. Mater. Chem. A 4 4525–33
[14] Mhlanga S D, Nxumalo E N, Coville N J and Srinivasu V V 2011 Nitrogen doping of CVD multiwalled carbon nanotubes: observation of a large g-factor shift Mater. Chem. Phys. 130 1182–6
Ghosh S, Ganesan K, Polaki S R, Ravindran T R, Krishna N G, Kamruddin M and Tyagi A K 2014 Evolution and defect analysis of carbon nanotubes by absorption spectroscopy and Raman microscopy. Carbon 74 854–864.

Gui X, Wei J, Wang K, Cao A, Zhu H, Jia Y, Shu Q and Wu D 2010 Carbon nanotube sponges: a facile approach to prepare carbon nanotube sponges. Carbon 48 1418–1423.

Hachimi A, Merzougui B, Hakeem A, Laoui T, Swain G M, Chang Q, Shao M and Atieh M A 2015 Synthesis of nitrogen-doped carbon nanotubes using in situ reduction of nitrogen-doped carbon nanotubes. J. Phys. Chem. C 119 23830–23836.

Kakaei K, Hamidi M and Husseindoost S 2016 Chlorine-doped reduced graphene oxide nanosheets as an efficient and stable electrode for supercapacitor in acidic medium. J. Colloid Interface Sci. 479 121–125.

Kim J Y, Lee W H, Suk I W, Potts J R, Chou H, Kholomanov I V, Piner R D, Lee J, Akinwande D and Ruoff R S 2013 Chlorination of graphite oxide enhances the dielectric constant of reduced graphene oxide/polymer composites. Adv. Mater. 25 2308–13.

Yeom S H, Reddington P and Gogotsi Y 2010 Carbide-derived carbons with hierarchical porosity from a preceramic polymer. Carbon 48 201–207.

Mhlanga S D, Mondal K C, Carter R, Witcomb M J and Coville N J 2009 The effect of synthesis parameters on the catalytic synthesis of carbon nanotubes by chemical vapor deposition. Carbon 37 39–46.

Maboya W K, Coville N J and Mhlanga S D 2016 The synthesis of carbon nanomaterials using chlorinated hydrocarbons over a Fe-Co/CaCO3 catalyst. S. Afr. J. Chem. 69 15–26.

Bulusheva L G, Sysoev V I, Lobiat E V, Fedoseeva Y V, Makarova A A, Dubois M, Flahaut E and Okotrub A V 2013 Chlorinated holey double-walled carbon nanotubes for relative humidity sensor. Carbon 64 413–20.

Wu X, Tao Y, Mao C, Wen J and Zhe X 2007 Synthesis of nitrogen-doped horn-shaped carbon nanotubes by reduction of pentachlorophenol with metallic sodium. Carbon 45 2253–9.

Wu C G, Yin P, Li T, Yang Q and Xie Y 2005 Synthesis of nitrogen-doped carbon nanostructures by the reactions of small molecule carbon halides with sodium azide. J. Phys. Chem. B 109 2597–604.

Garcia-Betancourt M L, Vega-Cantu Y I, Vega-Diaz SM, Morelos-Gomez A, Terrones M and Muñoz-Sandoval E 2015 Magnetic and electrical properties of nitrogen-doped multwall carbon nanotubes fabricated by a modified chemical vapor deposition method. J. Nanomater. 2015 587416.

Ombaka L M, Ngungu P G, Omondi B, McGettrick J D, Davies M L and Nyamori V O 2016 A facile approach towards increasing the nitrogen-content in nitrogen-doped carbon nanotubes by halogenated catalysts. J. Solid State Chem. 235 202–11.

Kou Z, Guo B, He D, Zhang J and Mu S 2018 Transforming two-dimensional boron carbide into boron and chlorine dual-doped carbon nanotubes by chlorination for efficient oxygen reduction. ACS Energy Lett. 3 184–90.

Ray S C, Pao C W, Tsai H M, Chiu J W and Pong W F 2007 Electronic structures and bonding properties of chlorine-treated carbon nanomaterials using chloride/iodine co-doped carbon nanotubes. Appl. Surf. Sci. 253 5472–6.

Hachimi A, Merzougui B, Hakeem A, Laoui T, Swain G M, Chang Q, Shao M and Atieh M A 2015 Synthesis of nitrogen-doped carbon nanotubes using injection-vertical chemical vapor deposition: effects of synthesis parameters on the nitrogen content. J. Nanomater. 2015 4537525.

Gu X, Wei J, Wang K, Cao A, Zhu H, Jia Y, Shu Q and Wu D 2010 Carbon nanotube sponges. Adv. Mater. 22 617–21.

Ye X R, Chen L H, Wang C, Aubuchon J F, Chen J C, Gapiñ A I, Talbot J B and Jin S 2006 Electrochemical modification of vertically aligned carbon nanotube arrays. J. Phys. Chem. B 110 12938–42.

Huang X, Farra R, Schlögl R and Willinger M–G 2019 Growth and termination dynamics of multilayered carbon nanotubes at near ambient pressure: an in situ transmission electron microscopy study. Nano Lett. 19 5380–7.

Fajardo–Díaz J L, López–Urias F and Muñoz–Sandoval E 2020 Chloride functionalized carbon nanotube sponge: high charge capacity and high magnetic saturation. Carbon 164 324–36.

Ghoshr S, Ganesan K, Polaki S R, Ravindran T R, Krishna N G, Kamrudin M and Tyagi A K 2014 Evolution and defect analysis of vertical graphene nanosheets. J. Raman Spectrosc. 45 642–9.

Pelech I, Pelech R, Narkiewicz U, Moszynski D, Jezdezezewska A and Witkowski B 2013 Chlorination of carbon nanotubes obtained on the different metal catalysts. J. Nanomater. 2015 836281.

Sahin H and Ciraci S 2012 Chlorine adsorption on graphene: chlorographene. J. Phys. Chem. C 116 24075–83.

Eckmann A, Fellen A, Mishchenko A, Brittell N, Krupke R, Novoselov K S and Casiraghi C 2012 Probing the nature of defects in sp2 carbon by Raman spectoscopy. Nano Lett. 12 3925–30.

Venezuela P, Lazzari M and Mauri F 2011 Theory of double–resonant Raman spectra in graphene: intensity and the shape of defect-induced and two–photon bands. Phys. Rev. B 84 035433.

Cuesta A, Dhamelincourt P, Laureyns J, Martinez–Alonso A and Tascon J M D 1994 Raman microprobe studies on carbon materials. Carbon 32 1523–32.

Yang J, Sun H, Liang H, Ji H, Song I, Gao C and Xu H A 2016 Highly efficient metal–free oxygen reduction electrocatalyst assembled from carbon nanotubes and graphene. Adv. Mater. 28 4606–13.

Gu J, Hu M J, Guo Q Q, Ding Z F, Sun X L and Yang J 2014 High-yield synthesis of graphene quantum dots with strong green photoluminescence. RSC Adv. 4 50141–4.

Wu Y, Lin X, Shen X, Sun X, Wang Z and Kim J K 2015 Exceptional dielectric properties of chlorine-doped graphene oxide/poly (vinylidene) fluoride. Carbon 89 102–12.

Graspmann R, Abraham J, Venclová A, Seyller T, Hennrich F, Kappes M M, Hirsch A and Ley L 2003 Doping of single-walled carbon nanotube bundles by Bronsted acids. Phys. Chem. Chem. Phys. 5 5472–6.

Yang M, Zhou L, Wang J, Liu Z and Liu Z 2012 Evolutionary chlorination of graphene: from charge-transfer to covalent bonding and nonbonding. J. Phys. Chem. C 116 844–50.

Gong K, Du F, Xia Z, Durstock M and Dai L 2009 Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction. Science 323 760–4.

Shan B and Cho K 2010 Oxygen dissociation on nitrogen-doped single wall nanotube: a first-principles study. Chem. Phys. Lett. 492 131–6.
[51] Arenal R, March K, Ewels C P, Rocquefelte X, Loiseau M and Stéphan O 2014 Atomic configuration of nitrogen-doped single-walled carbon nanotubes *Nano Lett.* 14 5509–16