Materials Chemistry and Physics 199 (2017) 435–453

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Some perspectives on nitrogen-doped carbon nanotube synthesis from acetonitrile and *N,N′*-dimethylformamide mixtures

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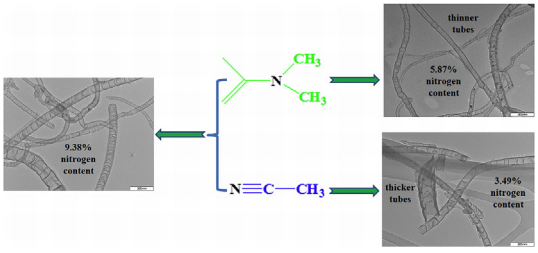
HIGHLIGHTS

- Sp^3:*sp* reagent ratios were varied in N-doped carbon nanotubes (N-CNTs) synthesises.
- Varying sp^3:*sp* nitrogen sources ratio tailored N-CNT physicochemical properties.
- The sp^3:*sp* ratio of 1:3 had highest N-doping content of 9.38%.
- The major nitrogen moieties in the N-CNTs was pyrrolic.
- Highest yield of N-CNTs was obtained at 900 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 April 2017
Received in revised form
8 July 2017
Accepted 11 July 2017
Available online 12 July 2017

Keywords:
Nitrogen-doping
Carbon nanotubes
Nitrogen sources
N,N′-dimethyl formamide
Acetonitrile

ABSTRACT

This work reports on the influence of the ratio of sp^3 (*N,N′*-dimethylformamide, DMF) to *sp* (acetonitrile) hybridised nitrogen within the carbon source used in the synthesis of nitrogen-doped carbon nanotubes (N-CNTs) by means of the floating catalyst chemical vapour deposition method. The physicochemical properties of the N-CNTs were investigated by means of scanning and transmission electron microscopies, textural characteristics, powder X-ray diffraction, X-ray photoelectron spectroscopy, thermal gravimetric analysis and elemental analysis. When the two nitrogen sources were compared before mixing, it was found that sp^3 hybridised nitrogen in DMF was a more effective source for the incorporation of nitrogen atoms (5.87%) than *sp* hybridised nitrogen in acetonitrile (3.49%). The number of walls within the N-CNT synthesised from the sp^3 nitrogen source was tailored by changing the synthesis temperature. Overall, a 1:3 sp^3:*sp* ratio produced N-CNTs with the highest nitrogen content of 9.38% and a general abundance of pyrrolic nitrogen moieties within the samples. The best synthesis temperature in terms of nitrogen content and largest composition of N-CNTs with least residual iron was found to be 900 °C. Varying ratio of sp^3:*sp* hybridised nitrogen is suitable for tailoring the physicochemical properties of N-CNTs towards preferred applications.

1. Introduction

Carbon nanotubes (CNTs) can be synthesised by chemical vapour deposition method in scalable quantities [1,2]. CNTs are

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http://dx.doi.org/10.1016/j.matchemphys.2017.07.044
0254-0584/

formed when both the carbon source and the catalysts are passed through a hot region of a suitable vessel in a temperature controlled furnace. Nitrogen-doped carbon nanotubes (N-CNTs) can be synthesised by either post or in situ doping [3]. In the in situ synthesis of N-CNTs, the nitrogen source can either be part of the carbon source [3] or the catalyst [4]. As an example of the latter, Keru et al. [5], synthesised N-CNTs using (4-phenyl)ferrocene that acted as both catalyst and nitrogen source [1]. On the other hand, Yadav et al., synthesised N-CNTs using acetonitrile, *N,N′*-dimethylformamide (DMF), triethylamine, and hexamethylenetetramine as nitrogen sources [6].

Nitrogen gas is a suitable post-synthesis chemical vapour deposition N-doping strategy but studies have shown that there is little incorporation of nitrogen in the graphitic frameworks [7–9]. NH_3 has been widely used in the preparation of N-CNTs [10] and is popularly reported in post-synthesis N-doping [11,12]. The final amount and functionalities of N-doping are of paramount importance for practical application in different fields [12]. Hence, different precursors and tuning strategies need to be explored to achieve better control of the above-mentioned attributes. The different approaches to N-CNTs production have resulted in differences in both nitrogen species and effects on carrier concentration with distinctive allied electronic structures, amongst other physicochemical properties [4,11]. Additionally, NH_3 mainly produces graphitic N-CNTs [12], whereas the current study is one of the approaches sought to produce higher composition of other nitrogen moieties, such as pyridinic and pyrrolic, using less toxic nitrogen sources, that also act as carbon sources, at relatively lower temperatures. Furthermore, according to theoretical studies [10], NH_3 doping effectiveness in the in-situ synthesis of N-CNTs is subject to 1) the pre-existing defects; 2) the ability to trap the $-NH_2$, $-NH$, $-N$ active species, from NH_3 thermal decomposition, at appropriate locations; and 3) their associated dehydrogenation. This has been proved difficult to control and achieve. Hence, the current report utilises a different doping strategy in which different active species are involved as building blocks of the graphitic framework. Where NH_3 has been used in in-situ growth of N-CNTs, some of the common adversities have been poor uniformity and widely varied nitrogen content of lower levels. Zhu et al. [13] attributed these observations to the low NH_3 flow rate requirement in similar approaches.

Doping CNTs with nitrogen creates nitrogen rich centres such as pyridinic moieties that improve electrical properties (charge storage and oxygen reduction reactions, being two examples of those), and alters other physicochemical properties in devices that include fuel cells, organic solar cells and electrochemical capacitors [4,5,14–16]. The addition of a lone pair of electrons to the delocalised *pi* system enhances electronic properties [17,18]. Additionally, N ions in the N-CNTs create channels for electron transport [19]. The possibility of nitrogen inclusion in the graphitic network is due to the similar bond lengths of 1.38 Å and 1.34 Å for C═C and C═N, respectively. The shorter C═N bond length of N-CNTs, relative to the C═C in pristine-CNTs, introduces defects in the carbon framework. Hence, N-CNTs typically display bamboo compartments by virtue of strain from the presence of nitrogen. This is explained theoretically through the mechanism that suggests the introduction of defects and pentagon rings in the graphitic network [1,20], culminating in the formation of a positive curvature of the tube layers. Typically, nitrogen can be incorporated into the graphitic structure of N-CNTs as either pyridinic, pyloric, nitrogen oxide, cross-linked sp^3, nitrile or quaternary [16,18,21–23].

Growth-limiting reactions are subject to composition of reagents in the hot zone of the furnace, amongst other factors [24]. Understanding of the N-doping process is key for better control of N-CNT properties [16]. Hence, nitrogen-doping is still a research focus towards better understanding of N-CNTs. This includes the study of the influence of numerous parameters such as effect of nitrogen source [17,20], synthesis temperature, reaction time, gas flow [15] and different catalysts. For example, Kim et al. [16], recently reported on the influence of dopant amount in nitrogen content and doping type. Also, Ombaka et al. [4], reported on the enhancement of nitrogen content of N-CNTs through the use of various oxygen containing moieties.

This study builds upon these earlier findings and explores the use of ferrocenecarboxaldehyde (Fc), an oxygen-containing organometallic compound, as the catalyst. The chemical nature of reactants controls species of products [25]. Additionally, small molecules have been reported to be suitable sources of carbon in synthesis of CNTs. Therefore DMF and acetonitrile were chosen in this work. The use of DMF in the synthesis of N-CNTs has been done before, though not common. For instance Tang et al. [17], achieved a nitrogen doping level of 20 at.% using Fe_2O_3/AlO_3 catalyst and ammonia in an aerosol assisted CVD method. The current work investigates influence of mixing ratios of reagents different from previously reported works. Furthermore, it specifically investigates the effect of mixing sp^3-hybridised nitrogen in DMF and *sp*-hybridised nitrogen in acetonitrile and the physicochemical properties of the ultimate products. Additionally, DMF and acetonitrile were compared as both carbon and nitrogen sources in the synthesis of N-CNTs.

2. Experimental

The materials were synthesised with chemicals given in the subsequent sections and characterized as elaborated in the following subsections.

2.1. Chemical reagents

Acetonitrile (99.9%) was purchased from Merck, Germany while *N,N′*-dimethylformamide (DMF) (99.8%) and ferrocene carboxaldehyde (98%) were procured from Sigma Aldrich.

2.2. Synthesis of N-CNTs

Synthesis of two series of N-CNTs at 900 °C was carried out by mixing DMF and acetonitrile, as both carbon and nitrogen sources, by means of the floating catalyst CVD method. The series was synthesised by firstly, varying the ratio of DMF (x) to a fixed mass of acetonitrile, which was generally referred to as DxA1 whilst the reverse was D1Ax. The DxA1 samples were named D0A1, D1A1, D2A1, D3A1, D4A1 and D5A1 for DMF:acetonitrile ratio of 0:1, 1:1, 2:1, 3:1, 4:1 and 5:1, respectively. D1Ax samples, with reverse ratios, were similarly named as D1A0, D1A1, D1A2, D1A3, D1A4 and D1A5, referring to DMF:acetonitrile ratio of 1:0, 1:1, 1:2, 1:3, 1:4 and 1:5. A similar notation based on the mol fractions of DMF and acetonitrile in the reagents is also presented in Table S1 (supplementary information) for reference, otherwise the notation based on the mass ratios was used. Secondly, the influence of temperature on the products was also investigated by using the ratios that gave the highest level of nitrogen-doping, as determined by elemental analysis.

In general, the synthesis procedure used a quartz tube with length and inner diameter of 0.85 m and 0.027 m, respectively. The quartz tube was placed inside a tube furnace (model TSH12/50/610, Elite Thermal Systems Ltd) equipped with a main zone temperature controller (Eurotherm 2416). The purging and reducing gas used was 10% hydrogen in argon (v/v) at a flow rate of 100 mL min^{-1}.