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Physicochemical properties of nitrogen-doped carbon nanotubes from metallocenes and ferrocenyl imidazolium compounds

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ABSTRACT

Shaped carbon nanomaterials (SCNMs) were synthesized *via* the chemical vapour deposition (CVD) technique by using typical metallocenes (ferrocene, nickelocene, cobaltocene, and ruthenocene), and more interestingly, by use of novel ferrocenyl imidazolium derivatives, containing -Cl (FcImCl), -NO_2 (FcImNO_2) and -CH_3 (FcImCH_3) substituents as catalysts. Acetonitrile was applied both as a carbon and nitrogen source at temperatures 800–900 °C. The SCNMs, namely, carbon nanotubes (CNTs), carbon spheres (CS), carbon fibres (CF) and amorphous carbons (ACs) were obtained in varying ratios depending on the catalyst and carbon sources. The ferrocenyl imidazolium catalysts produced nitrogen-doped CNTs (N-CNTs) with bamboo-like structures. The yields of various reactions were temperature-dependent, with the highest amount of N-CNTs obtained at 850 °C. In all samples, the composition was mainly of CS and N-CNTs except for nickelocene at 800 °C that gave CFs as a “minor” product. Ferrocene and nickelocene in acetonitrile produced well-aligned N-CNTs while cobaltocene and ruthenocene gave ‘spaghetti-like’ structures. In the case of ferrocenyl imidazolium catalyst, a coiled N-CNTs morphology was produced from FcImCl catalyst. Also, higher percentage of N-CNTs with traces of CS were obtained from the FcImCl and FcImCH_3 catalysts in acetonitrile at 850 °C, while higher percentage of CS and AC were obtained for FcImNO_2 catalyst. In all the catalysts, the use of acetonitrile promoted nitrogen-doping (samples with more disordered and with smaller outer-diameters). Thus, this study demonstrates that the synthesis of N-CNTs from nitrogen-containing ferrocenyl imidazolium compounds as catalyst sources, provided higher percentage of N-CNTs which can be suitable for various application.

1. Introduction

Carbon nanotubes (CNTs) have generated profound scientific interest due to their unique structural, chemical and physical properties, such as high thermal [1], electrical conductivities [2], high modulus [3] and low densities [4]. Synthesis methods such as laser ablation [5], arc-discharge [6], pyrolysis [7] and chemical vapour deposition (CVD) [8] have been employed in fine tuning different morphologies of CNTs. CVD method is preferred since it allows; firstly, the use of hydrocarbons in any state (solid, liquid or gas), secondly, relatively a larger scale of CNTs production with various morphologies or forms, and thirdly, a better control of growth parameters compared to laser ablation and arc discharge. In the CVD technique, thermal decomposition of hydrocarbon vapour in the presence of a metal catalyst, is achieved under inert atmosphere. Nano-sized metal nanoparticles such as Fe, Ni and Co are widely used due to their robust bonding to growing CNTs [9]. The choice of a metallic catalyst may affect the morphology and growth mechanism of the CNTs. Other chemical elements such Al, Cu and Zn [10] have been employed to give a pure, multiwalled and well-aligned nanotubes.

Introduction of heteroatoms such as nitrogen, sulphur, phosphorous and boron, into the graphitic carbon of the CNTs alters their physicochemical properties [11]. Nitrogen and boron are the commonly used dopants of CNTs [12]. The introduction of nitrogen atoms in the graphene structure impressively widens the potential applications of CNTs. The modified surface chemistry and bulk properties [13] with different type of nitrogen, such as pyridinic-, pyrrolic- and quaternary-nitrogen atom, favourably impacts on their electronic and conductivities properties which in turn has made them attractive in the field of catalysis [14] and sensing [15]. The nitrogen atom is situated in a five-membered ring in pyrrolic-nitrogen configuration, while nitrogen atoms are usually connected

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within a six-membered ring in the pyridinic-nitrogen configuration [16]. In graphitic-nitrogen configuration, the nitrogen atom replaces the graphitic carbon atom [17]. These configurations have different hybridization of nitrogen atom which in turn influence electrical properties of N-CNTs. These properties could be attributed to the excess nitrogen valence electrons which acts as an extra source of π-electrons in the sp^2 hybridized carbon framework [18] thus, significantly modulating the electrical behaviour of the N-CNTs [19]. However, N-CNTs are mechanically [20] and thermally [21] less stable when compared to their undoped counterparts, due to local strains in the hexagonal carbon structure, leading to structural deformations [22].

Heteroatoms are usually introduced into CNTs *via in situ* or post-synthetic doping [23]. For instance, N-CNTs could be produced by directly incorporating nitrogen atoms into the CNTs backbone during *in situ* doping [24], or *via* the post-synthetic method, which employs the introduction of nitrogen atoms onto the walls of pre-synthesized CNTs [25]. The latter method usually involves the modification of pre-synthesized CNTs by using a precursor, containing the atom of choice [26]. The incorporation of nitrogen either into or onto CNTs significantly change their morphology, thus, indicated by the "bamboo-like" shaped compartments inherent in them [27,28]. However, pristine-CNTs have also been reported to contain "bamboo" compartments because of fluctuations in the carbon concentration on the metal catalyst [29]. In the case of N-CNTs, the bamboo compartments are dependent on the concentration of nitrogen atoms incorporated. The greater the number of bamboo compartments with shorter distance between the compartments, the greater the concentration of nitrogen [30]. N-CNTs are known to have larger inner diameter whilst their outer diameter are small [31]. Other than "bamboo" structure, nitrogen doping have been found to produce coiled or telephone cord-like CNTs [31].

Organometallic precursors, such as, ferrocene and its nitrogen-containing derivatives have been employed both as catalyst and carbon or nitrogen source for the synthesis of CNTs, N-CNTs and other shaped carbon nanomaterials (SCNMs) [32,33]. Jang and co-workers [34] reported the synthesis of N-doped CNTs with CVD by using ferrocene as a precursor at different ratio of NH_3/acetylene carbon or nitrogen source. A decrease in the length of bamboo compartment with increased nitrogen concentration was observed leading to the deterioration of the crystalline graphene sheets [35]. Also, the bamboo compartment separation was reported to increase with an increase in the synthetic temperature [34,36]. Similarly, researchers have reported the use of iron pentacarbonyl and ferrocene, together with their derivatives, as catalysts and carbon source for the synthesis of CNTs [37,38].

Investigation of synthesis parameters, such as, growth temperature, gas flow rate, catalyst injection rate and catalyst concentration have been extensively explored when ferrocene is used as a precursor [39]. Varying different parameters, such as temperature, nitrogen or carbon source controls the physicochemical properties of N-CNTs [40]. Other metallocenes, as catalysts, have also proved to be promising candidates for the synthesis of CNTs and N-CNTs [39]. However, very few reports exist on the application of other metallocenes, such as, cobaltocene, nickelocene and ruthenocene in the synthesis of SCNMs; particularly, N-CNTs.

In most cases, nitrogen-containing ferrocenyl derivatives catalysts for N-CNTs synthesis improves the chemical and physical properties compared to when ferrocene is dissolved in nitrogen-containing solvents such as aniline and acetonitrile, among others [41]. An alternative approach to improve the properties and nitrogen content in N-CNTs is the use of halogens [42] in conjunction with nitrogen-containing functional groups on the ferrocenyl moiety [43]. In the case of halogen, e.g. Cl is a potential good oxidizing agent that could induce defects in CNTs during the nucleation; these defect sites can easily accept nitrogen species resulting in higher nitrogen-doping levels [44,45]. Hence, halogens such as chlorine should work well with nitrogen-containing functional groups on the ferrocenyl derivatives. The use of neutral substituents (such as $-CH_3$) could be used to study the effect of heteroatoms on the physicochemical properties of N-CNTs. However, there are limited reports on the use of functional groups (i.e $-NO_2$, $-CH_3$, and -Cl), especially, when used conjointly with ferrocenyl imidazolium compounds synthesized herein to modulate nitrogen-content in N-CNTs.

In this work, three new ferrocenyl imidazolium derivatives, 1-ferrocenylmethyl (2-chloroimidazole) (1), 1-ferrocenylmethyl (2-nitroimidazole) (2), and 1-ferrocenylmethyl(2-methylimidazole) (3) were synthesized and characterized. The X-ray crystallographic structure of the 1-ferrocenylmethyl(2-nitroimidazole) catalyst is reported for the first time. The use of metallocenes (i.e. ferrocene, cobaltocene, nickelocene, ruthenocene) and three new ferrocenyl imidazolium compounds as catalysts for synthesis of SCNMs (such as N-CNTs, carbon spheres (CS) and carbon nanofibres (CFs) was investigated. Reactions with metallocenes (especially ferrocene) were performed to provide reference data from which the effect of the substituted imidazolium ferrocenyl compounds would be deduced. We also report the effect of functional groups (i.e $-NO_2$, $-CH_3$, and -Cl) in ferrocenyl imidazolium catalysts on the yields, morphology, diameter, and nitrogen content of N-CNTs. The effect of nitrogen doping on the thermal stabilities and the crystallinity of N-CNTs were also explored.

2. Experimental

2.1. Materials

Ferrocene (≥97%), nickelocene (≥97%), cobaltocene (≥97%), ruthenocene (≥97%) ferrocenemethanol (98%) and ferrocene-carboxaldehyde (98%) were obtained from Sigma Aldrich Ltd. 2-nitro-1H-imidazole (≥98.1%), 2-chloro-1H-imidazole (≥98.2%) and 2-methyl-1H-imidazole (>98%) were supplied by DLD Scientific. Sodium hydroxide (≥97%) was supplied by Associated Chemical Enterprises (Pty) Ltd, South Africa. Acetonitrile (HPLC grade, 99.9%), $NaBH_4$ (95%) and ethanol (98%) were purchased from Merck. Nitric acid (55%) and sulphuric acid (98%) were purchased from Saarchem, South Africa. 10% Hydrogen in argon (purchased from AFROX gases, South Africa) was used as a carrier gas for the synthesis of SCNMs.

2.2. Characterization

The obtained substituted ferrocenyl imidazolium compounds were spotted on a thin layer chromatographic plates (POLYGRAM SIL N-HR/UV_{254}) with different solvent mixture as eluents. The retardation factors of all compounds in different solvent were also recorded. All ferrocenyl imidazolium compounds were purified with 0.0062–0.2000 mm silica gel in column chromatography using different solvent polarities. FTIR spectra were performed on PerkinElmer Universal 100 FTIR spectrometer equipped with an ATR accessory. The melting points of the compounds were determined by using a SMP3 Bibby Stuart Scientific apparatus. ^1H and ^{13}C NMR analysis were performed on a 400 MHz Bruker Ultrashield spectrometer after the compounds have been dissolved in deuterated chloroform. Mass spectra of the synthesized compounds were obtained from an Agilent 1100 series, ion-trap mass spectrometer. N-CNTs were synthesized in a quartz tube reactor (0.85 m length and 0.027 m inner diameter) placed in Elite Thermal muffle furnace (Model No. TSH12/50/610). The syringe injection rate was