



Fluorination of Carbon Nanotubes – A Review

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ABSTRACT

Carbon nanotubes have become very popular since their discovery at the end of XXth century, due to their unique properties and many potential applications. Depending on the kind of final application, CNTs have to fulfil special requirements, concerning i.e. their purity, specific sizes or properties. Despite of the kind of applied synthesis method, pristine carbon nanotubes are not ready for applications, they have to be first purified and functionalised. For this purpose, the nanostructures have to be subjected to a series of operations aiming to obtain pure carbon nanotubes with specific characteristics. Apart purification, carbon nanotubes can be functionalised and the latter process can occur simultaneously with purification or can be performed as a separate process.

Fluorination is one of the methods enabling an efficient functionalisation of carbon nanotubes.

The paper presents a review of fluorination of carbon nanotubes as well as potential sources of performance improvement of the process.

1. Introduction

The discovery of carbon nanotubes represents a major breakthrough in nanotechnology development [1]. These nanostructures attract attention due to their unique amazing mechanical [2,3], electrical [3–5], thermal [6–8] or adsorption properties [9–11], which can be next translated into many applications in science and technology [12–19].

The most popular methods applied for the synthesis of carbon nanotubes are: arc discharge [20–22], laser ablation [23–25] and chemical vapor deposition [26–30]. The material obtained using these methods is not ready for applications and it should be first treated to remove contaminants (as amorphous carbon or catalysts) and to get desired dimensions or properties [31–37]. A kind and quantity of contaminants depend on the applied CNT synthesis method. The main contaminants can be amorphous carbon, graphene flakes, metallic catalysts and their supports. After purification, CNTs can be functionalised in order to get specific properties required for a given application.

The cycle of life of carbon nanotubes from synthesis to exploitation of CNT containing products (“from cradle to grave”) is shown in Fig. 1. As is the case of other products, the value of the CNTs increases along the chain.

The aim of functionalisation is to adapt CNTs to a planned application, e.g. to cut them to shorter segments, to change the electronic properties or attach some functional groups increasing hydrophilicity or adhesion of tubes to a matrix. The next step after functionalisation can

be then an integration in a matrix, suspension, solution etc., to fabricate an useful product. The product is exploited until the end of its life.

Functionalisation of nanotubes is a very important key element in the value chain. The attachment of various functional groups allows changing their solubility, chemical reactivity and other physico-chemical properties [38]. Functionalisation was also shown to be efficient in breaking the nanotube bundles.

The most common functionalisation types are illustrated below (Fig. 2)

In case of noncovalent functionalisation some species interact with the surface of the nanotube via π - π interactions, or via van der Waals forces. For example, long-chain polymers or polypeptides can wrap carbon nanotubes. In addition, nanotubes can be filled with atoms or molecules of other compounds. The common feature of such a functionalisation is to preserve the original electronic structure of nanotubes.

In turn, covalent functionalisation of CNTs takes place in defects and their sidewalls. An example of the first case can be carboxylic acid groups (or their derivatives), located mainly at the open ends of the nanotubes and the point defects of the sidewalls caused by the oxidation [39]. They combine with carbon by covalent bonds. Modified nanotubes can be better dispersed in polar solvents, such as water, acetone or an alcohol.

Functionalisation of the sidewalls takes place directly on the carbon atoms forming the nanostructures and consists of addition to double bonds, causing a change in the hybridisation of carbon atoms from sp^2

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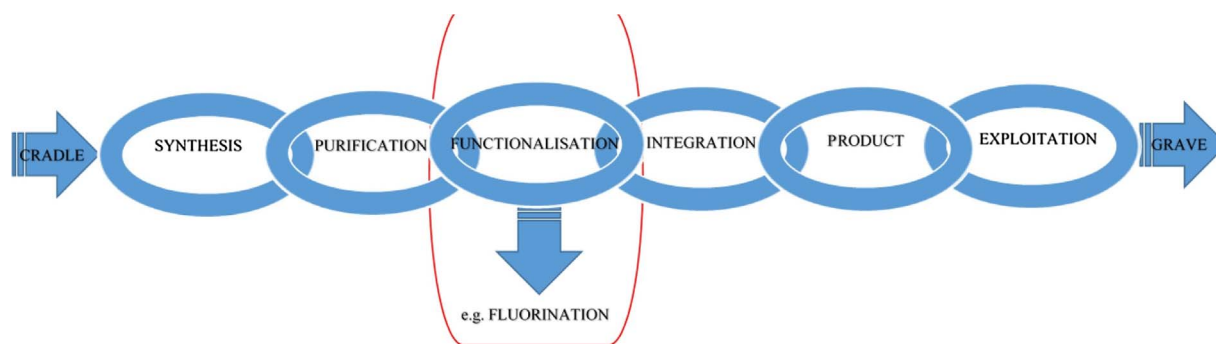


Fig. 1. Value chain of carbon nanotubes.

to sp^3 , which results in a significant change of electronic properties of nanotubes [40].

The aim of covalent CNT functionalisation is to permanently join the molecules of other substances to the surface of the nanotubes. Applying smart modification makes possible to obtain carbon nanotubes of required physico-chemical properties, such as mechanical resistance, solubility or electric conductivity, adjusting material for a particular application [41–43].

CNTs with small diameter have a higher chemical reactivity (and they are more prone to functionalisation) than nanotubes with larger diameter. This is related to pyramidisation of carbon atoms, and the off-center arrangement of π orbital between adjacent carbon atoms in the nanotube structure [44].

2. Fluorination of various carbon materials

Process of fluorination of carbon materials depends on characteristics of the starting material and of the fluorinating agent. There are several methods for the fluorination of carbon materials. In majority of cases a direct fluorination is used, nevertheless in numerous studies different other fluorinated compounds have been also applied.

The process of functionalisation, including the choice of carbon materials and fluorinating reagent, is schematically illustrated in Fig. 3.

The high reactivity, oxidising properties and the highest electronegativity of fluorine, offer the ability to create very strong bonds with

majority of other elements. Therefore, fluorine compounds provide a unique tool to modify the surface properties of materials [45,46].

Zhang et al. [47], studied the effect of fluorination on curvature on C-F bonding. The authors investigated various fluorinated carbons, as fullerenes C(60) and single, double and multi-walled carbon nanotubes. To reflect an ideal planar or spherical geometry, graphite fluorides and highly fluorinated fullerenes were taken, respectively. According to the authors' opinion, the curvature resulted in a weakening of the C-F bonding covalence.

2.1. Fluorination of graphite or graphitised carbon

Process of fluorination of carbon materials as well as chemical composition and structure of obtained product depends on characteristics of the starting material. First of all, the degree of graphitisation and dimensions of the particles should be taken into account.

There are several methods for the fluorination of polymer and carbon materials. In majority of cases a direct fluorination is used, which involves treating with gaseous fluorine (pure or in a mixture with an inert gas) of materials [48–52]. In this case, hydrogen atoms are substituted with fluorine atoms and the double bonds between carbon atoms are saturated with fluorine. Numerous studies were devoted mainly to fluorinated graphite or graphitised carbon and specific applications of fluorinated compounds [53–65].

Both ionic and covalent bonds are created between C and F atoms. If

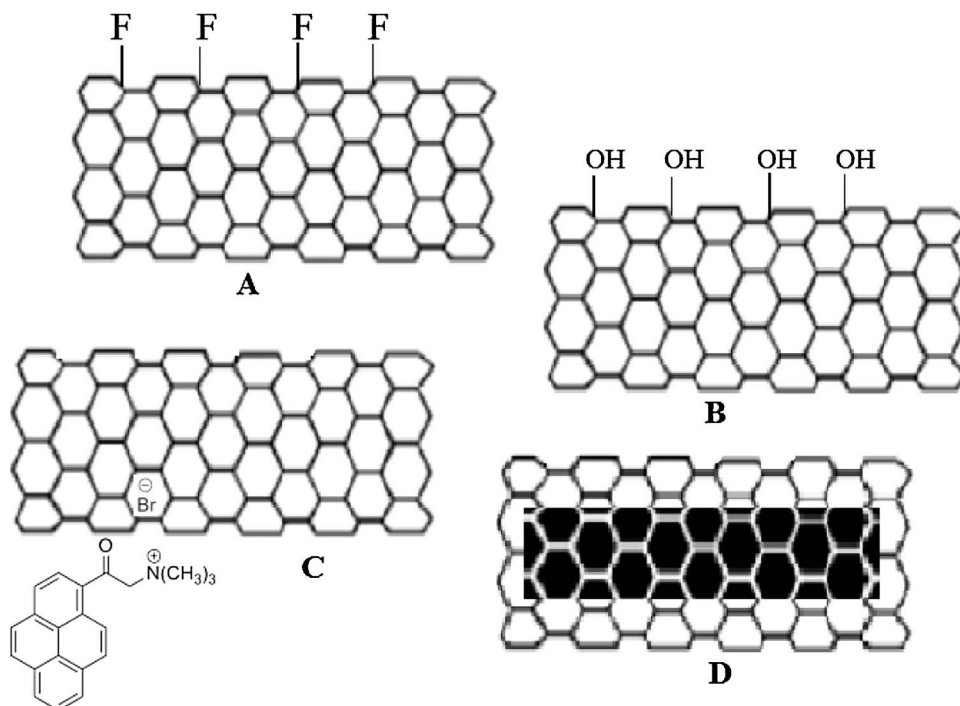


Fig. 2. Types of functionalisation of carbon nanotubes: A - covalent functionalisation, B - defect-group functionalisation, C - noncovalent functionalisation, D - endohedral functionalisation.

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