

OVERVIEW OF SINGLE WALLED CARBON NANOTUBES & TOXICITY PROFILE

Vijayalakshmi V¹, PriyaAshrit², BinduSadanandan³

¹Department of Biotechnology, M S Ramaiah Institute of Technology, MSR Nagar, MSRIT Post, Mathikere, Bangalore-560054

²Department of Biotechnology, M S Ramaiah Institute of Technology, MSR Nagar, MSRIT Post, Mathikere, Bangalore-560054

³Department of Biotechnology, M S Ramaiah Institute of Technology, MSR Nagar, MSRIT Post, Mathikere, Bangalore-560054

Abstract

Carbon nanotubes (CNTs) have attracted the fancy of many scientists in the recent decade. They are produced on a large scale due to their demand of being strong and light weight. Single Walled Carbon Nanotubes (SWCNTs) are an important class of CNTs. SWCNTs structurally resemble graphite sheets which are rolled up with usually one end capped. The major strengths of SWCNTs are small size, larger length, high permeability, tensile strength, electrical & mechanical properties. Major methods of synthesis of SWCNTs are arc discharge, laser ablation and chemical vapor deposition (CVD). SWCNTs have potential applications in many fields such as medicine, industry, research, and computers. However, there are many studies that implicate the toxicity of SWCNT. To evaluate the toxicity of SWCNTs they have been studied both in vitro and in vivo. Toxicity of SWCNTs can be reduced by functionalization of the SWCNTs. In this review we mainly provide an overview of CNTs especially SWCNT & its toxicity.

Keywords: Carbon Nanotubes, Single Walled Carbon Nanotubes, Toxicity, Synthesis

1. INTRODUCTION

1.1 Carbon Nanotubes (CNTs)

Various sized particles surround us on an everyday basis, the tiniest of the particles which is visible to the naked eye to the ones which are not visible. Many of such particles are the ones which causes various diseases when entered into the body. Some of them are removed by the defence system in our bodies while the others go past these defences and enter the body causing discomfort & diseases (Buzea *et al.*, 2007).

Nanomaterials have been used extensively in the recent era in research, medicine & industries (Bang *et al.*, 2011; Hardas *et al.*, 2012; Yang *et al.*, 2010). Nanomaterials such as Nanotubes, Nanoparticles, Nanocomposites are the next generation materials used for the manufacture of faster computers, drug discover and sensitive sensors (Asmatulu, 2011).

Carbon Nanotubes (CNTs) have been used from the past decades & also is emerging as an important class of nanomaterials (Bang *et al.*, 2011; Ravichandran *et al.*, 2010). Carbon nanotubes were discovered and first characterized in 1991 by Iijima from NEC laboratories, Japan (Iijima, 1991). CNTs have gained tremendous attention as promising nanomaterials, owing to their distinct characteristics such as small size, strength, conductivity, high surface area, possibility of conjugation with therapeutics including small molecules & biologics (Wong *et al.*, 2013; Bang *et al.*,

2011). However, CNTs are considered toxic for the environmental as well as human health (Bang *et al.*, 2011).

The conductivity of CNT is determined by its chirality, tube diameter & number of graphene walls. The graphene sheet of carbon atoms are arranged in 3 different chirality: armchair, chiral & zigzag (Bareket-Keren & Hanein, 2013). Nanotubes of the type $(n,0)$ $\theta=0^\circ$ are called zigzag tubes. Nanotubes of the type (n,n) $\theta=30^\circ$ are called armchair tubes. Both zigzag and armchair nanotubes are achiral tubes, in contrast with general $(n,m\neq 0)$ chiral tubes (Charlier *et al.*, 2007; Dai H, 2002).

1.2 Types of Carbon Nanotubes

CNTs come in two different forms, Single Walled Carbon Nanotubes (SWCNTs) & Multi Walled Carbon Nanotubes (MWCNTs) (Bang *et al.*, 2011; Sargent *et al.*, 2014; Berhanu *et al.*, 2009). SWCNTs are simple with diameter ranging from 0.4 to 2.5nm and length up to few millimetres. MWCNTs are a set of coaxially organized SWCNTs with 2-100nm diameter and length varying up to several hundred micrometres (Bareket-Keren & Hanein, 2013).

1.3 Synthesis of Single Walled Carbon Nanotubes

Single walled carbon nanotubes can be synthesized by many methods (Dhai, 2001). Arc-discharge, laser ablation involve carbon vaporization at high temperatures and employs solid state carbon precursors. CVD utilizes hydrocarbon gases as sources for carbon atoms (Dai, 2002).

SWNTs were produced from a low cost catalytic decomposition of hydrocarbons using an improved floating catalyst method, which yielded SWCNTs of larger diameters and are self-organized into ropes. The addition of thiophene was found to be effective in promoting the growth of SWNTs (Cheng *et al.*, 1998). SWCNTs were synthesised by CVD method in which water enhanced the activity and lifetime of catalyst (Hata *et al.*, 2004).

There is also studied which have used alcohol as a carbon source to synthesize SWCNTs by chemical vapour deposition method at low temperatures (Maruyama *et al.*, 2002).

SWCNTs can also be produced by zipping effect of liquids to draw tubes together. This helps in fabricate the solids in numerous shapes and structures by retaining the individual property (Futaba *et al.*, 2006).

1.4 Applications of Single Walled Carbon Nanotubes

SWCNTs are been widely used many fields such as industry, medicine, research, computer, aerospace and biomedical (Onget *et al.*, 2016).

SWCNTs are well suited for neuronal electrical interfacing owing to their large surface area, electrical & mechanical properties and their support as an excellent neuronal adhesion (Bareket-Keren&Hanein, 2013).

SWCNTs have been used in the protein studies especially enzyme activities to study the loss of structure and catalytic activity. Some of the enzymes such as horse radish peroxidase, chicken egg white lysosome on SWCNTs retain their structure & activity even under denaturing conditions (Saptarshiet *et al.*, 2013).

SWCNT has covered through many other applications such as *in vivo* delivery of drugs, proteins, peptides and nucleic acids, *in vivo* tumour imaging and tumour targeting of SWCNTs as an anti-neoplastic treatment (Schipperet *et al.*, 2008).

Highly purified SWCNT can exhibit good antimicrobial activity (Kang *et al.*, 2007).

Some of the limitations of SWCNTs are nanotube cost, processing and assembly difficulties and polydispersity in nanotube type (Baughman *et al.*, 2002).

1.5 Toxicity of Single Walled Carbon Nanotubes

Cytotoxicity studies revealed that toxicity of SWCNTs *in vitro* and *in vivo* is more when compared to MWCNTs and other forms of CNTs. Cytotoxicity of SWCNTs may be due to their geometry and surface chemistries (Poma& Di Giorgio, 2008).

CNTs having high length and diameter gives them an appearance as a fibre, hence, they are compared to asbestos

(Berhanuet *et al.*, 2009). CNTs such as SWCNTs may cause asbestos like pathology in lung & mesothelium. CNTs in the form of long chains have greater propensity to inflammation & fibrosis than long chained asbestos (Donaldson *et al.*, 2010).

Nanoparticle aerosol exposure is increasing in the modern society due to the advancement of nanotechnology (LeBlanc *et al.*, 2010). Studies conducted till date have shown that SWCNTs do not show any carcinogenic activity, however, toxicity studies of these materials are less and they have a potential to produce Reaction Oxygen Species (ROS) (Tsuda, 2010). Toxicity & carcinogenicity of Carbon Nanotubes are of a concern, despite their desired structure, since they are very stable and lead to continuous inflammation when deposited in tissues (Totsuka *et al.*, 2009).

2. IN VITRO TOXICITY

There are studies which reveal that SWCNTs cause acute pulmonary inflammation & chronic fibrosis (Lam *et al.*, 2004; Warheitet *et al.*, 2004). Pulmonary deposition of SWCNTs results in the release of inflammatory mediators activated blood cells & Thrombogenic proteins which may induce endothelial dysfunction (Erdelyet *et al.*, 2008).

In vitro studies were conducted to study the effect of SWCNTs on human macrophage like cells. It was observed that macrophage was uptaken by SWCNT to form nanoparticle-loaded macrophages (Poma& Di Giorgio, 2008).

There is also a possibility of translocation of carbon nanotubes such as SWCNTs when used in lower diameters. (Pacurariet *et al.*, 2008) Wang *et al.*, 2004 revealed the presence of functionalized SWCNT I₁₂₅ in stomach, kidneys and bone. There are also studies showing the difference in biokinetics between modified and unmodified SWCNTs. Modified SWCNTs were found to be in the blood and tissues whereas, unmodified SWCNTs were found only in liver after 24h. (Elgrabliet *et al.*, 2008)

SWCNTs when fused with plasma membrane have showed cell damage through lipid peroxidation and oxidative stress (Manna & Ramesh, 2005; Poma& Di Giorgio, 2008).

In a study by Davoren *et al.*, 2007, with human lung cell line A549, it was observed that SWCNT showed very low acute toxicity and also alamar blue (AB) assay was found to be the most sensitive and reproducible assay among the different cytotoxicity assays.

Exposure of SWCNT on the skin causes dermal toxicity. A study showed that topical exposure to un-purified SWCNT, induced free radical generation, oxidative stress, and inflammation (Murray *et al.*, 2009). *In vitro* studies on the human dermal fibroblasts (HDF) showed that as the sidewall functionalization increases the toxicity to SWCNT decreases (Sayes *et al.*, 2006).

Studies by Manna *et al.*, 2005 showed that SWCNTs induced toxicity in HaCaT cells. Reaction Oxygen Species (ROS) was also measured for a dose dependant treatment. ROS production of SWCNT increased as the dose increased in HaCaT cells.

3. IN VIVO TOXICITY

In a study by Poland *et al.*, 2008, showed carbon nanotubes when introduced in the abdominal cavity of mice it showed asbestos like pathogenicity (Stimers, 2008).

SWCNT induced dose-dependent epithelioid granulomas. It was studied that with higher dose of SWCNT toxicity increased causing death of the mice. Peribronchial inflammation and necrosis was observed in lungs of some animals that had extended into the alveolar septa. This is a serious occupational health hazard in chronic inhalation exposure (Lam *et al.*, 2004).

SWCNT not only affects the human but also the aquatic life. Toxicity studies have been done on rainbow trout. SWCNTs are basically respiratory toxicant in trout and showed no variations in the oxidative stress and osmoregulatory disturbances, but cellular pathologies raise concerns about cell cycle defects & neurotoxicity (Smith *et al.*, 2007).

Toxicity of SWCNTs was observed within 10 to 15 days of exposure to the mice. But functionalization has reduced the toxicity of SWCNTs to a greater extent. Schipper *et al.*, 2008 have studied the functionalized SWCNTs toxicity in the bloodstream of injected mice. They revealed that there was no sign of toxicity even until 4 months of exposure, only changes which was seen was age related. Yang *et al.*, 2008 also proved very low toxicity of SWCNTs on the mice when accumulated for longer duration of time. Very slight inflammation of organs was observed with no apoptosis.

4. CONCLUSION

CNTs are an important class of nanomaterials having wide properties and used in wide range of applications. CNTs can be basically grouped into SWCNTs and MWCNTs based on their conductivity. There are three basic methods of synthesis of SWCNTs viz. arc discharge, laser ablation and chemical vapor deposition (CVD). CVD is the most accepted and used method. Researchers are trying to improvise on this method so as to produce large quantities of SWCNT with lesser diameter and larger length. With the widespread applications of SWCNTs there is a need for its production on a large scale. It has however been proven *in vitro* and *in vivo* that SWCNTs are toxic especially to humans. There are also studies which prove that the toxicity of SWCNTs is dose dependant. Hence SWCNTs are functionalized to reduce their toxicity. Though SWCNTs are being used commercially for many applications, the upcoming scope is in the areas of drug delivery and in antimicrobial therapy.

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