

Review

Carbon Nanotubes in Electronics: Background and Discussion for Waste-Handling Strategies

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Abstract: Carbon nanotubes (CNTs) are increasingly being used in electronics products. CNTs have unique chemical and nanotoxicological properties, which are potentially dangerous to public health and the environment. This report presents the most recent findings of CNTs' toxicity and discusses aspects related to incineration, recycling and potential remediation strategies including chemical and biological remediation possibilities. Our analysis shows that recycling CNTs may be challenging given their physiochemical properties and that available strategies such as power-gasification methods, biological degradation and chemical degradation may need to be combined with pre-handling routines for hazardous materials. The discussion provides the background knowledge for legislative measures concerning specialized waste handling and recycling procedures/facilities for electronics products containing CNTs.

Keywords: carbon nanotubes; degradation; incineration; biological; chemical; waste handling; methods

1. Introduction

Carbon Nano Tubes (CNTs) are entirely composed of carbon in their original unmodified state. They have diameters in the range of 1–100 nm and length up to a few millimeters. CNTs have unique

physiochemical properties, including semi-conducting and metallic electrical behavior, high mechanical strength and unique chemical and surface properties, as addressed by main contributors to this field [1-7]. Applications for CNTs span wide areas, including microelectronic devices, catalysis, sensors, high-strength composites, and adsorbents [8-15]. In the fields of bionanotechnology, nanoelectronics, and material sciences, CNTs are utilized as damage-sensors, where for instance their electrical properties are used to detect cracks and physical stress in materials [16]. Damage sensors using CNTs could be applied in automotive vehicles and aerospace constructions in the future, increasing the presence of carbon nanotubes in the environment, and thus the need for relevant waste handling policies.

Other recent applications are the use of CNTs as storage structures in lithium batteries; here the CNTs are combined with graphene sheets in order to provide solid energy-storing nano-ensembles [17]. In the future, the use of graphene in LED lights may come to replace indium-tin alloy-based LEDs due to the lower cost of graphene and poor availability of Indium [18]. Given the ongoing search for green energy solutions, as these two examples of consumer electronics shows, the future use of CNTs are likely to grow fast. CNTs are also widely used in nanoarchitectures, for example; in assembly with DNA [19], and for biosensing purposes to detect ultra-low levels of biomolecules in medical and laboratory samples [20]. In addition, CNTs are frequently used as fortifying components in biopolymers and nanocomposites [21].

CNTs are subdivided into two main classes, single walled carbon nano tubes (SWCNT) and multi-walled carbon nano tubes (MWCNT). SWCNTs can be considered as a single sheet of graphene, which is rolled into a cylinder with diameter of 1 nm and length of up to several millimeters. MWCNT consist of two or more such cylinders formed coaxially. MWCNTs can have diameters from 2 to 100 nm and lengths of a few micrometers and be composed of tens of layers [22]. MWCNTs have a stronger physical durability compared with SWCNTs [23].

2. Environmental and Toxicological Aspects of Carbon Nanotubes

Environmental remediation of CNTs is a technological feat that may encounter a series of obstacles. The generation of nanoparticles during the waste handling and processing may present challenges. Reports show that nanoparticles can be deposited at locations very distant from their original source, even as far as the Arctic and remote regions of the Pacific Ocean [24,25]. These environmental pollutants have consequently induced significant problems for organisms and animals in untouched habitats. The majority of these particles derive from naturally oxidized plastic components, traffic exhaust emissions, and leakages from industry and other man-made sources. CNTs are not yet a major constituent of this group of contaminants. However, in the near future, it is likely that CNTs will contribute more to this concern, with a similar impact as we have seen with plastics [26]. In this scenario, CNTs increasingly accumulate in the environment, and due to their small size, become integrated into the nutritional and reproductive environment of humans and animals [27].

CNTs, which have many physical characteristics similar to plastics, represent a group of solid and ultra-stable nanoparticles with strong adsorptive properties, binding various molecules and biomolecules efficiently. CNTs have also been shown to interfere with living organisms, to pose health risks and cause genotoxicity, mortality and cellular damage as aerosol or hydrosol particles [28-38]. At the critical end of the spectrum, recent aquatic studies on CNTs show induced

organ pathology disturbance of respiratory function in rainbow trout, as well as causing terminal effects on mono-cellular aquatic organisms [34,36]. Furthermore, severe damage to mice has been shown [5,31-33,35,37-39], where more violent reactions than asbestos and carbon black were observed [38].

CNTs do not easily degrade. This is a key problem for end-of-life treatment. As such, CNTs constitute similar problematics as asbestos [40,41]. However, attempts at degradation of CNTs by horseradish peroxidase combined with peroxide have been made [42]. Although relevant, these chemical/biochemical conditions do not reflect natural conditions found in the environment. The resistance to degradation is a key issue, which must be taken into consideration when developing strategies for future waste handling on materials containing CNTs. For this reason, life cycle assessment (LCA) studies and remedies for waste handling of CNTs are increasingly being sought. European legislative authorities are increasingly focusing on products containing carbon nano materials, utilizing environmental studies as basis for developing new regulations [43,44].

In light of the emergence of this grave problem, there is an urgent need for a complete human and ecotoxicological assessment of CNTs. Multitudes of different chemical variants derived from pristine CNTs are being synthesized and increasingly phased into society through new consumer products. These compounds will end up as a serious waste problem [8-15].

3. CNTs in the Environment

The magnitude of the presence of CNTs in the environment is not well known. However, in 2009, it was estimated an average concentration from anthropogenic sources of 0.003–0.02 ng/kg soil [45]. In addition to this modeled concentration, an unknown amount of naturally occurring CNTs and fullerenes are found in glaciers, volcano ash and soil [46]. Even though the estimated amount of CNTs in circulation does not appear to present any ecotoxicological threat to the environment, this is strongly contrasted by findings in aquatic species [34,36].

The prevalence of CNTs in the environment is increasing due to the rapid pace of CNTs being introduced into consumer products, also made possible by the lowering of the cost for producing these materials [45,47,48]. In 2008, it was estimated that a yearly global production of CNTs of 350 tons, of which 50% was assumed to be incorporated into consumer electronics and 50% into plastic products [47]. It can be presumed that the CNTs not being land-filled are being taken to incineration plants, where partial and full incineration of CNTs occurs. In these plants, there is a risk of CNTs being released to air and soil, as a result of their incomplete incineration.

The yearly deposition of CNTs in the environment was in 2008 assumed to be more than 150 tons, and rapidly increasing [39,47,49]. With this basis, there is an evident need for CNT recycling strategies to be developed. However, the impact of CNTs for human health must also be assessed in this context.

4. Recycling Aspects and Strategies for CNTs

An important aspect of CNTs is their “super-aerosol” property in their pre-fabricated state, making them behave as nanoparticles that easily stick to surfaces, very unlike the behavior of carbon black. This is due to the different electrostatic properties of these two types of nanoparticles [49,50]. Carbon

black subdivides into more or less round particles while CNTs aggregate into rope-like fibers, with similarities to asbestos [39-41,49]. CNTs are increasingly being used in vehicles [50], consumer products [51] and microelectronics [17,18]. During their life time, the general wear and tear during eventual waste handling of the products may release CNT as rod-like nanoparticles [39-41,49]. Even though the amount of CNTs, in the form of particles emitted into the environment, is not known, a precautionary approach should be applied to avoid releases during the waste handling.

Impurities from the CNT production process may pose an additional danger. The metals nickel, yttrium, cobalt and copper are toxic, and may be released during the waste treatment. Metals can be found at significant percentages in CNTs, adding up quickly to several hundred tonnes being released each year [39,47].

5. Aspects for Incineration Processes

Incineration of carbon nanoproducts, as a strategy for their waste handling, may also present important dangers. CNTs are highly thermo-stable. Conventional incineration temperatures of 800–900 °C may not be sufficient to obtain complete combustion of CNTs into biodegradable carbon products. Even though Sobek and Bucheli [52] claim that CNTs breaks down at temperatures above 500 °C, parts of their molecular structure is intact at temperatures above 1300 °C [53]. This is supported by information that CNTs remain structurally stable at 950 °C (*Personal communication, Johan Liu, Chalmers University of Technology, Sweden*), and that CNTs are reported to be partly resistant to conventional incineration [54]. Consequently, there is a need to investigate efficient incineration methods for CNTs, as well as land-filling of the incineration ash. These aspects are relevant with polycyclic aromatic hydrocarbons (PAHs) and their biopersistent properties. PAHs are not fully oxidized during combustion, leading to deposition on soil and vegetation, accumulating in sediments and living organisms [55], so that the formation of PAHs from the combustion of CNTs will be thus an expected scenario, with different ratios of heavy and middle weight PAHs than from natural sources such as forest fires and volcanic eruptions.

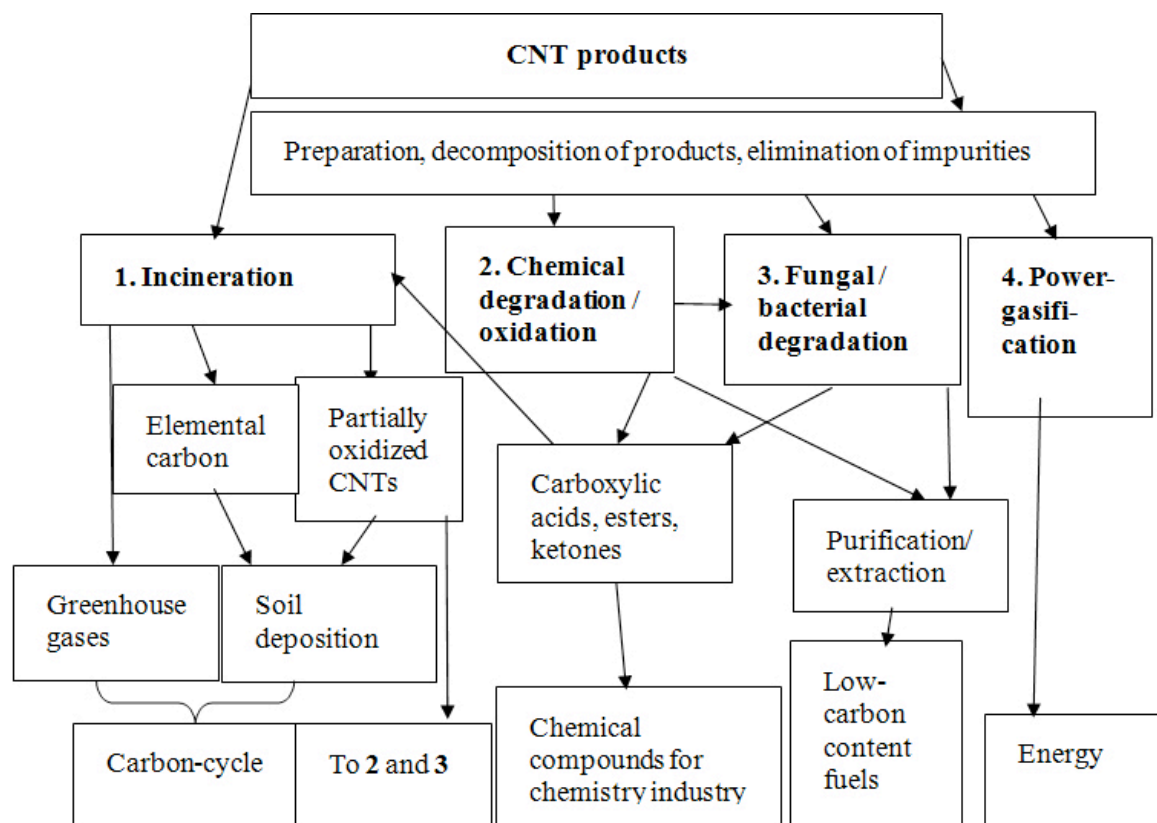
During incineration, PAHs are normally retained in the gas filters. However, a key problem may be the presence of semi-combusted CNTs in the bottom ash and filter ash with the potential for release into the environment from the subsequent final land-filling of the ash.

It is thus an open question if conventional incineration strategies are effective enough for bringing carbon nanotubes back to their native carbonic state.

6. Options for Recycling CNTs

Establishing a proper recycling and waste handling strategy is dependent on that alternative ways from the existing ways of waste-handling are being explored for CNTs. An overview of the discussed options is shown in Figure 1.

Figure 1. Handling and recycling strategies for electronics containing CNTs. Alternative routes for handling discarded CNT-containing products, with focus on breaking down CNTs.



Before the degradation processes are considered, the disassembly of CNT-containing consumer products requires manual force. Such a process requires masks, goggles and protective wear due to the potential risk of CNT materials releasing nanoparticles during the process.

The next step is the removal of metal, with particular focus on the heavy metals [56]. As an end stage of the process, chemical degradation and microbiological degradation are options. An optimal dispersion of CNTs into a solution is necessary, and this can be conducted through sonication of the granulated material containing CNTs. Studies have shown that CNTs are more uniformly dispersed in solutions using sonic dispersion rather than stirring in the dust-state [57,58]. Following sonication, ozonation can be used to convert CNT products into smaller compounds, similar to what is seen with large oxidized PAHs [59]. However, this depends ultimately on what condition the CNT is in, e.g., intact, dust-like particles or partly degraded.

For further decomposition of the oxidized fragments, the method of applying Fenton's reagent reaction and sono-chemical degradation can be used [60]. This has been shown to degrade PAHs under catalyzed conditions using transition state metals, such as nickel or chrome [61]. These methods are applicable if CNTs are sufficiently dispersed in aqueous solutions first, which may be a challenge, particularly when treating CNTs in automobiles and microelectronics.

A second set of chemical conversion alternatives is the use of strong oxidizers, such as permanganates. The disadvantage of this method lies in the emissions generated. Biological methods

are more environmentally friendly methods and can, with basis in studies on microbial and fungal degradation of PAHs, be considered instead [61,62,64,66]. Such methods have limitations for larger PAHs (more than 7 benzene rings), which CNTs supersede in size. A biological degradation preceded by chemical decomposition may, for that reason, be required, and would involve CNTs being pre-ozonated, as has been done for PAHs [59]. Fungal / bacterial degradation of large and medium size PAHs have been published [61-65], in particular using the fungi *Phanerochaete* [64]. These methods can therefore be combined with the chemical treatment mentioned, precessed by decomposition of CNTs into smaller fragments first. Direct bacterial/fungal degradation of CNTs, without pre-oxidation or chemical treatment, has not been shown [63]. However, taking into account recent findings on the degradation of multi-walled carbon nanotubes, using horseradish peroxidase in combination with hydrogen peroxide [66], a combination of bacterially produced peroxidase in combination with peroxide, may represent a viable biochemical method.

A different option is the use of power-gasification methods, which are increasingly being studied for potential use in waste treatment. However, still in their infancy, such methods are debated because of the environmental challenges they need to overcome. Waste products, such as discarded coal, are used for the generation of energy, but this emits greenhouse gases. Discarded CNTs may be considered handled by such methods as well, as investigated by Koukoulas *et al.* [65]. However, very few projects world-wide include handling of waste coal and biomass for co-gasification, but they may however be included in future alternatives, with CO₂ capture, if sufficiently management of greenhouse emissions occurs.

An important aspect of recycling is thus related to the emissions being released. Life cycle assessments are necessary to provide the basis for any recycling strategy of CNTs [67].

7. Conclusions

The knowledge of future carbon nanotube recycling and waste treatment is important to develop in context of the rapid increase in use of CNTs in consumer products [39,47]. This is due to their toxic properties, and lowering of costs leading to their higher application and consumption. The dangers from the increased presence of CNTs in society is aggravated by the potential implication of the practice of converting polyethylene-based used plastics into CNTs [68]. Although plastics are often considered as the modern age's peril, a replacement by carbon nanotubes may encounter several obstacles, as here described. Through this paper, it is hoped that this discussion on the impacts and handling of these technologies will stimulate the discovery of viable solutions to the emerging problem of CNT waste remediation.

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