# CHALLANGES OF VERTICALLY ALIGNED CARBON NANOTUBES PRODUCTION AND APPLICATION

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## Abstract

Carbon nanotubes (CNTs) have play a dominant role in nanotechnology research for over 20 years due to their exceptional properties. Different solid catalytic substrates can be used to produce vertically aligned carbon nanotubes (VACNTs); however it is important that this structure can be achieved mainly on conductive substrates. It is important that further application of this structure is preferable on conductive substrates. The conditions under which the catalytic layer is prepared and synthesized also have major impact on the structure and properties of the resulting vertically aligned carbon nanotubes. Environmental protection and green chemistry are highly discussed topics nowadays. Therefore, the development of energy-efficient, sustainable technological solutions is also receiving increasing attention in vertically aligned carbon nanotubes research. Thus, the progress in this direction will be briefly review in this work.

## Introduction

Green chemistry and sustainable techniques are focusing on the use of non-hazardous substances, plant extracts as the main precursors, and solvents that are not harmful to the environment. In the field of carbon nanotubes, the vertically aligned carbon nanotubes with their 3 dimensional structure are considered as a seperate branch, first fabricated in 1996 [1] and often referred to in the literature as CNT forests due to their distinctive structure.

The industrial application of VACNTs demands the technical development of large-scale and defect-free production techniques, where the chemical vapor technique has proven to be a promising process for large-scale and high purity production of carbon nanotubes [2]. Methods to fabricate VACNTs are still not at the desired level and further development is needed. This "imperfection" is beneficial for the development of environmentally friendly and sustainable technologies. Currently, only the chemical vapor deposition technique (CVD) and its subtypes are suitable for the production of VACNTs. There are three main directions for the development of environmentally friendly production of carbon nanotube forests. The first one is to replace the carbon sources currently used by using non-toxic, plant-derived or plastic waste, the second is to use equally precise but less energy-consuming methods for the catalyst layer deposition, and finally to improve the technical development of the synthesis method itself [3]. In the literature, there is a growing number of results where VACNTs are produced at lower temperatures of 550 °C, which initially was mainly around 800-900 °C, however, the choice of parameters used in the experiments is of course influenced by a number of factors.

Due to their remarkable physicochemical and mechanical properties VACNTs have extensive potential and application in a broad range of science and technology, emerging nano- and microelectronic devices and industry [4]. These materials can be considered as the elementary unit of molecular electrical circuits and can be used not only as a link between the active molecular elements of a device, but can also serve as a device element themselves [5]. In addition to more environmentally friendly synthesis, environmentally friendly application is also an important goal. VACNTs have several promising applications, such as lightweight and strong composites, supercapacitors, microelectromechanical systems (MEMS), electrodes, batteries *etc.* due to their special electrical properties [3,6,7].

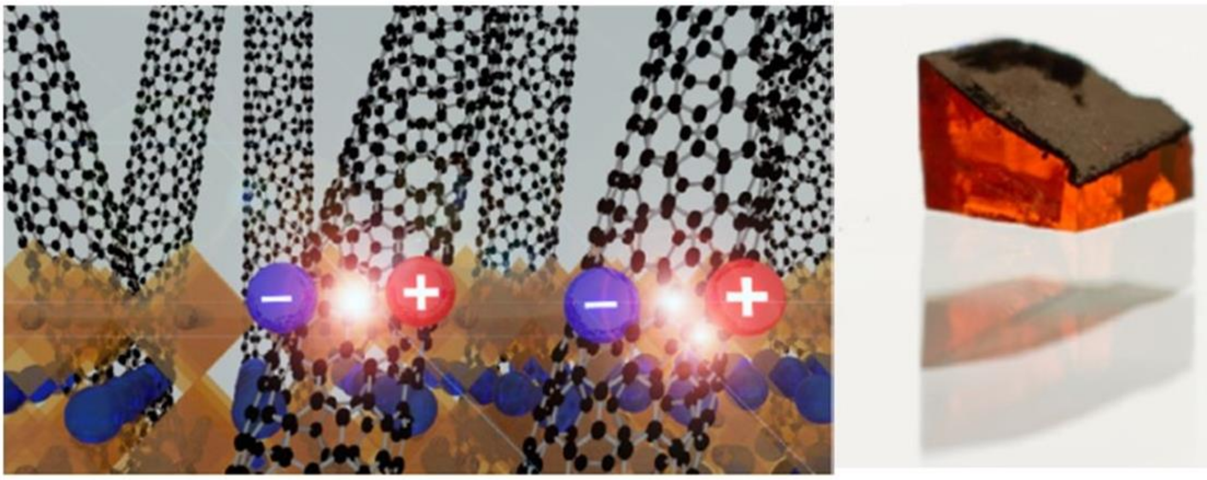

Figure 1. Single crystals of of methylammonium lead bromide ($MAPbBr_3$) grown directly on vertically alligned carbon nanotubes [7]

**Experimental**

During the syntheses of VACNTs, substrates are used to provide a base for growing CNT forests. On this substrate, a catalyst layer is formed by a thin layer building method, on which the growth of carbon nanotubes is achieved. Many materials can be used as substrates, depending on the purpose of use, but mainly metals (aluminium, copper, stainless steal, titanium), silicon and glass with or without transparent conductive oxide layers are used during the synthesis. Also there is a wide variaty of thin layer coating methods such as atomic layer deposition (ALD), dip coating, magnetron sputtering (MS), pulsed layer deposition (PLD), spin coating, spray coating, to build the catalyst layer on the surface of the substrate. These methods are suitable to control the parameters of catalyst layers, but there are large differences in their material, energy and cost requirements which vary significantly. Transition metals (Fe, Co, Ni, Mo *etc.*) and their alloys are mostly used as catalysts for the synthesis of CNT forests, which ensure the growth of carbon nanotubes and determine their yield and structure. During the CVD synthesis, first inert gas flows in the system, followed by hydrogen gas to create a reductive environment and then the carbon source is introduced, which decomposes into its components under the effect of both the presence of catalyst and high temperature and carbon is deposited on the catalyst particles, which initiate the growth of carbon nanotubes. Water vapor is also a common component in the synthesis process, which ensures that amorphous carbon is oxidized from the surface of the catalyst particles, thus regenerating the catalyst and improves the quality of CNTs, contributing to the height of VACNTs.

**Results and discussion**

In this section, the circumstances of the synthesis of VACNTs and the materials will be briefly described, as well as the efforts to make them environmentally friendly. Unfotrunately, it is a clear issue in the literature that the structure and the properties of VACNTs are affected by multiple factors during their fabrication, which is why VACNTs are underperfomed in large-scale, industrial production compared to carbon fibers and CNTs.

As it was described before in the experimental section, a thin catalyst layer is formed on the surface of the substrate, the CNT forests are grown on the surface at high temperature (600-1200 °C) *via* CVD technique.

During the synthesis inert gas is needed to provide inert environment, uniform gas flow rate in the system and to remove by-products from the system. Noble gases (Ar, He) and nitrogen gas have been used as inert gas during VACNT synthesis. The great advantage of nitrogen over noble gases is that it can be produced relatively cheaply and with simple industrial technology, yet it is chemically stable under extreme conditions of synthesis and can create a pseudo-inert environment.

The synthesis of VACNTs also requires reducing gas, in order to activate the catalyst particles on the substrate surface and to influence the catalyst particles diameter, as it is known that the catalyst distributions influence the height and structure of VACNTs. $H_2$ and $NH_3$ gases are mainly used as reducing agents, where $H_2$ favours uniform catalyst nanoparticles distributions and $NH_3$ forms mainly large clusters [8].

The range of carbon sources, which are suitable to produce carbon nanotubes, is reasonably wide. At the beginning only gaseous phase materials, mainly short-chain hydrocarbons (ethylene, methane, acetylene, natural gas, *etc.*), later organic solvents (ethanol, tholuol, acetone, cyclohexane, diethyl ether *etc.*) were used as well [9] and it was observed that small amount of oxygen-containing carbon compounds resulted low height VACNTs, on the otherhand selectivity is lower, amorphous carbon and carbon fibers were present as well. Nowadays many experiments can be found about CNTs and VACNTs where green resources such as biomass and plant extracts, $CO_2$ and plastic waste [10][11] [12] are used as carbon source.

Water vapor plays an important role in the synthesis of VACNT, extending the activity and lifetime of the catalyst particles by removing the amorphous carbon deposited on their surface, and improves the height, the quality and the structure of carbon nanotubes [13]. However, it is also important to consider the flow rate of water vapor, because if there is too much in the system, it will oxidize the outer walls of the carbon nanotubes as well, which will degrade the otherwise good conductive properties.

## Conclusion

In summary, there is still a lot of development and work to be done before VACNTs can be manufactured industrially, but current awareness and ongoing research are working to make this process as environmentally friendly and sustainable as possible. Many researchers expect to be able to produce VACNTs and other carbon nanomaterials by using $CO_2$, the greenhouse gas with the highest concentration, and from the large amount of plastic waste around us in the near future. However, there are still many obstacles to overcome and resolve.

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