Advancements in Biosensor Materials: Synthesis and Applications of Carbon Nanotubes

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This thesis presents the most efficient synthesizing and purification methods for single- and multi-walled carbon nanotubes. The methods are viewed after their suitability for synthesizing or purification of single- or multi-walled carbon nanotubes or both. It is noticed that chemical vapour deposition and arc-evaporation are two of the most effective methods for carbon nanotube synthesis. In terms of purification, it is noticed that multi-step processes of purification are still needed, as not only one method is effective enough to achieve ultra pure carbon nanotubes. The characterization after purification is crucial to find out the properties of carbon nanotubesand their suitability for applications. Carbon nanotubes possess such electrical, mechanical and structural propertis, that they are a great material for biosensor applications, especially for electrochemical biosensors. Their detection capabilities are very effective compared to many other kind of biosensors.

Keywords: single-walled carbon nanotube, multi-walled carbon nanotube, synthesis, purification, characterization, biosensor, electrochemical biosensor

Sisällys

1 Introduction 4

2 Synthesizing of carbon nanotubes 6

2.1 Chemical Vapor Deposition 6

2.2 Arc-evaporation 7

2.2.1 Growth mechanism of multi-walled carbon nanotubes 9

2.2.2 Growth mechanism of single-walled carbon nanotubes 9

2.3 Laser Laser vaporization 10

2.4 Combustion synthesis 12

2.5 Purification of carbon nanotubes 12

2.5.1 Oxidation 14

2.5.2 Solubilization 16

2.5.3 High-temperature annealing 17

3 Characterization techniques of carbon nanotubes 19

3.1 Properties of carbon nanotubes 19

3.2 Raman Spectroscopy 20

3.3 Scanning Electron Microscopy 21

3.4 Transmission Electron Microscopy 21

4 Applications with carbon nanotubes 23

4.1 Operating principle of nanotube based biosensors 23

4.2 Advantages of carbon nanotube based biosensors 24

4.3 Electrochemical biosensors 25

4.3.1 Sensing of cancer 25

4.3.2 Sensing of viruses 26

4.3.3 Sensing of bacteria 26

4.4 Other type of biosensors 27

4.5 Future outlook of carbon nanotube biosensors 27

5 Conclusion 29

References 30

1 Introduction

In modern research carbon nanotubes (CNTs) have caught the interest of many scientists. They were first discovered in the early 1990s and since then, the work targeted into the development of synthesizing and characterization methods as well as the research made to enable their usage in applications has skyrocketed.

Carbon nanotubes are hollow cylindrical tubes, and they can be classified as single- or multiwalled carbon nanotubes by the number of walls a tube consists of. The single wall is a graphene sheet that is bend to a cylindrical form. If the tube is multiwalled the graphene slabs are forming layers over layers in a tube shape. The tubes have a nanometer-scale diameter and a micrometer-scale length. In Figure 1. three different types, single-, double- and multiwalled carbon nanotubes are presented.

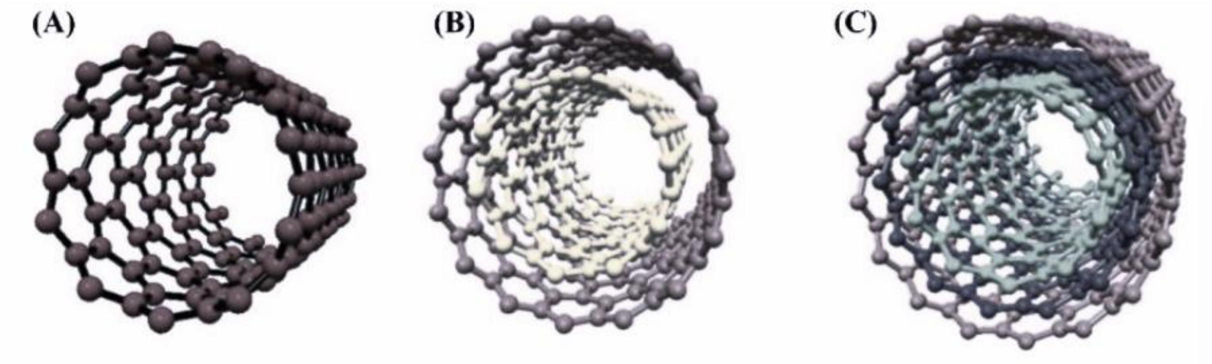

Figure 1. A) Single-walled carbon nanotube B) Double-walled carbon nanotube C) Multi-walled carbon nanotube. The picture is from the work of Ranjbari et al[1].

It was noticed early on that carbon nanotubes have many valuable properties that not many other materials possess simultaneously. Their electrical, mechanical, thermal, and structural properties are known to be at great value in application use. Their strength and stiffness combined with great electrical conductivity and large surface area, makes them durable and effective in the field of biosensors.

There are many ways to synthesize carbon nanotubes, but the most effective ones are chemical vapor deposition and arc-evaporation. These methods along with two more are presented in this thesis. After synthesizing process, the carbon nanotubes cannot be used straight away in applications. Although these methods have been developed a lot during the last few decades, they still cannot produce ultrapure nanotubes. This is why nanotubes must be purified before their usage in applications. The purification is almost every time a multiple-step process as the nanotubes can contain multiple impurities depending on the synthesizing method chosen. In this thesis, all these methods are evaluated in that respect if they are suitable for single- or multiwalled carbon nanotube synthesis or purification. Also, the main advantages and disadvantages are presented for each method.

As there are still uncertainties and disadvantages found in the methods of synthesizing and purification, characterization of the produced carbon nanotubes is crucial. Characterization not only gives us information about the nanotube properties, one can also use it as a mean of optimization when planning the best suited carbon nanotubes for different applications.

Carbon nanotubes are used in many fields of industry, such as microelectronics and biomedical and biological applications. This thesis presents different possibilities for carbon nanotubes as biosensors and sensing biomolecules in human bodies. It also creates an outlook for the future on how carbon nanotube-based biosensors could be developed further.

2 Synthesizing of carbon nanotubes

This chapter presents few of the most used methods for growing carbon nanotubes. One of these methods is chemical vapor deposition (CVD). With the help of CVD, i.e., chemical gas phase coating, it is possible to grow carbon nanotubes that differ in both their design and operational properties on top of thin films. Other methods discussed are arc- and laser-evaporation, which are efficient ways to produce specifically single-walled nanotubes and combustion synthesis. The chapter also presents a bit information about the purification and large-scale production of carbon nanotubes.

2.1 Chemical Vapor Deposition

Carbon coatings can be produced with the help of CVD, i.e. chemical gas phase coating. CVD has been found to be an effective method, which is why it is widely used to produce carbon nanofibers and carbon nanotubes. CVD is well suited as a coating method for electrically conductive materials. In addition to this, CVD can influence the crystal structure, shape and orientation of the coating when the process parameters are changed.

CVD, i.e. the chemical vapor deposition, is a relatively long-known method. However, it was not until the 1970s that the method had developed so much that it has started to be used more widely and commercially. The process in question starts with the transport of the desired coating material to the reaction chamber and the chemical reactions that take place there. After this, the source material has formed an intermediate. The reaction is achieved by heating the reaction chamber. This can be done, for example, with the help of light or plasma. The intermediates can then be directed to the substrate, where they are absorbed into the heated substrate. A chemical reaction takes place between the substrate and the intermediate molecules, resulting in the formation of a coating. In CVD coating the coating material reacts with the substrate. After this, any excess coating molecules and by-products are finally transported out of the chamber. In Figure 1 the basic operating model of the CVD method is illustrated[2,3].

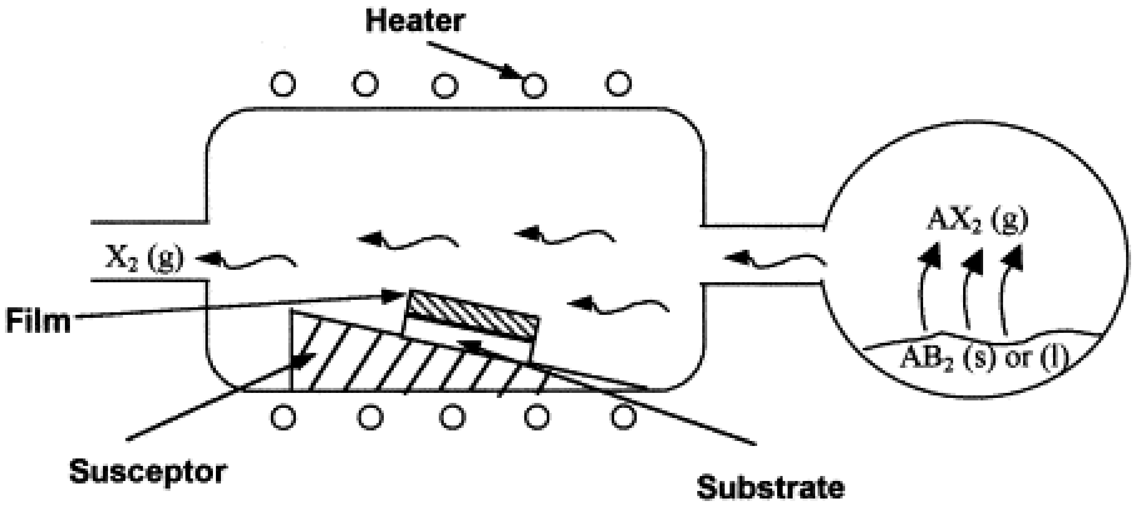

Figure 2. Schematic diagram of the operating principle of chemical vapor deposition.

CVD has several advantages, which is why it is a widely used coating method. It can be used to produce dense and clean coatings. The coating speed of CVD is relatively high and it can be used to coat even complex parts. Very different chemicals can be used as starting materials, so producing different coatings does not become a problem. CVD is also not a hugely expensive method, but one of the cheapest coating methods. The traditional CVD operating model has been refined a lot in the last 40 years, and several different CVD technologies have developed as a result. These include, for example, catalytic CVD or plasma-assisted CVD. By changing the parameters of the CVD process, the final result of the coating can be easily influenced[2].

2.2 Arc-evaporation

Arc-evaporation, also known as arc-discharge method, is a lot used method for the production of both multi- and sigle-walled carbon nanotubes. The device itself functions the same despite synthesizing SWCNTs or MWCNTs. The variating growth mechanisms are making the difference in the amount of walls. The growth can be affected by changing the synthesis conditions, such as the graphite’s features.

This method can be performed in slightly different devices, but the one presented next is one of the most used ones.[4] The schematic diagram is presented in Figure 3 below. The diagram shows that the reaction chamber itself has two graphite electrodes, cathode and anode. The anode usually has a bit smaller diameter. The electrodes are graphite and are connected to a power supply that carries about a 10-35 *V* voltage enabling the current, usually 60-100 *A*, in the synthesis.[5] The current enables the arc discharge plasma to grow. Achieving a stable plasma is the key to successful nanotube growth. The graphite rods are watercooled. In the reaction chamber there is a constant and inert gas flow of helium gas. The chamber is also in vacuum and heated. Temperatures are higher than 4000 °C.[4,5]

The anode is the the source of the carbon and it is consumed during the synthesis. This is why the rods need to be movable. The anode needs to be at the same position compared to the cathode the whole process even though it lessens. The plasma production can not be disturbed by the changes of the anode. The nanotubes are found on the cathode and other carbon products are found on the walls of the reaction chamber.[4] It has been noticed that if the graphite used in the synthesis is pure, the nanotubes tend to have several walls. And if the graphite rod contains some metal catalyst, nanotubes are single-walled. This is the greatest difference between the synthesis of SWCNTs and MWCNTs with arc-evaporation.[5]

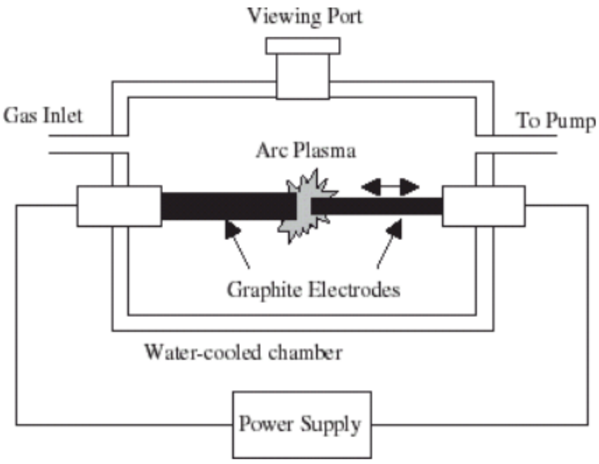

Figure 3. Schematic diagram of the operating principle of arc-evaporation. The picture is from the work of Kingston et al[5].

As mentioned before, this method is one of the most used ones. One of the reasons is the possibility to produce both SWCNTs and MWCNTs in a relatively simple way and at a high synthesis rate. The downside then again is the anode consumption. The synthesis requires close monitoring and careful adjusting of the anode graphite rod. In some cases even this unfortunately does not work and the synthesis has to be terminated prematurely[5]. This is still a small disadvantage as the yields are still considered good and reasonable. The yield can also be affected positively with the helium pressure and current. The pressure needs to be 500 *torr* for the best yield. The current needs to be as low as possible for the stable plasma production[4].

2.2.1 Growth mechanism of multi-walled carbon nanotubes

This chapter presents shortly three different growth mechanism models for multi-walled carbon nanotubes produced with arc-evaporation. All three models support the fact that the nanotubes produced wit arc-evaporation are open ended tubes. These models are called vapour, liquid and solid phase growth models[4].

In the vapour phase growth, the arcing results in nanoparticles. As the arcing continues the particles start to form seeds for nanotube growth. After this a stream of carbon ions flow to the cathode, which results to nanotube growth as long as the arcing is continued[4].

In liquid phase growth, it is proposed that the anode is heated due to electron bombardment from the cathode. This causes the graphite to liquefy and carbon droplets end up on the cathode surface which is cooled. When these droplets start to cool in high pressure circumstances the nanotubes start to nucleate and grow[6].

In solid phase growth, the first stage is the vaporization of the graphite with plasma, which condenses on the cathode as fullerenes. As the arcing continues the fullerenes go through high temperatures and result into nanotube seeds. These seeds continue growing until the process is terminated[4,7].

2.2.2 Growth mechanism of single-walled carbon nanotubes

This chapter presents shortly the growth mechanism of the single-walled carbon nanotubes with both methods, arc- and laser vaporization. These two methods have a lot of similar features, so the mechanisms are also assumed similar[4]. These similarities being the vaporization aspect, both methods use doped graphite as carbon source and the reaction chamber conditions are both inert. The SWCNTs produced are also similar as they are both groups of SWCNTs, that contain metal particles and carbon impurities. There is now the first of the two different mechanism models, vapour-liquid-solid and solid-state, presented more detailed, as vapour-liquid-solid model is the most recognized[4].

As shown in the name, vapour-liquid-solid model can be divided into three stages. The first stage is the vaporization of the carbon and metal catalyst particles. In the second stage, these vaporized source materials form a liquid metal nanoparticle supersaturated with carbon. In the final stage when the nanoparticle is transported to the cooler, it starts to condensate. Carbon precipitates out of the solution and forms a seed for nucleation of the SWCNTs. The nanotube itself then starts to grow from the root while the enabling power for the growth comes from the temperature and the carbon concentration[4,8]. The basic growth mechanism of the vapour-liquid-solid model is presented in Figure 4.

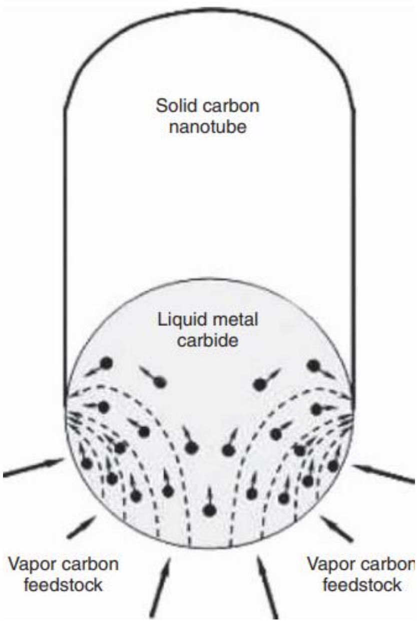

Figure 4. The growth mechanism of vapour-liquid-solid model. The picture is from the book Knovel - Carbon Nanotube Science - Synthesis, Properties and Applications[4].

2.3 Laser Laser vaporization

Laser vaporization is a method for single wall carbon nanotube synthesis. It has a lot of similarities with arc-evaporation method, for example the growth mechanisms barely differ. The growth mechanism of SWCNTs produced with laser vaporization has already been presented in Chapter 2.2.2. Laser vaporization is one of the most used methods alongside chemical vapor deposition and arc-evaporation[9]. And it has been quite some time.

The device itself consists of a laser beam which is focused on a target, the laser beam is usually a few mm diameter[10]. A Nd:YAG laser is one of the most used laser devices[4,9,10]. The most used target material for SWCNT synthesis is graphite. The target is doped with some metal catalyst particles, to enable the synthesis.[4] The laser beam and the target lay in a heated furnace, temperature is about 1200 ℃. There is a constant gas flow in the furnace, the gas needs to be inert, so argon gas is usually used. The laser beam evaporates the graphite and SWCNTs can form. The Ar flow transports the SWCNTs away from the furnace onto a cooler. From where they can be gathered for further processing[4,10]. The operating model of the laser vaporization device is presented in Figure 5.

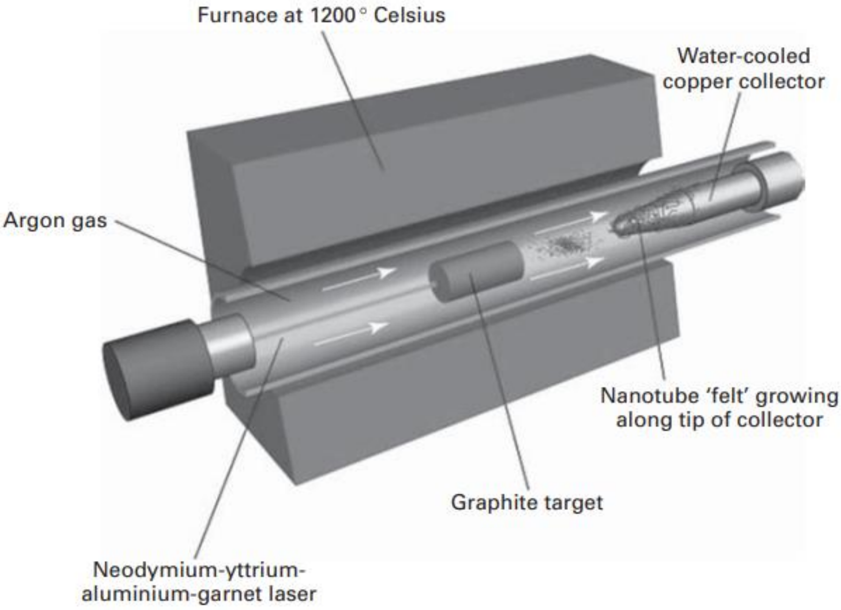

Figure 5.Schematic diagram of the operating principle of laser evaporation. The picture is from the book Knovel - Carbon Nanotube Science - Synthesis, Properties and Applications[4].

This method has a good yield and it is possible to use it for commercial production. Although the lasers are very expensive, which might make it inaccessible in some situations[4]. The advantages that make laser vaporization probably the best method for SWCNT production, in addition to good yield, are the homogeneity of the product and the easily controlled synthesis parameters. By changing the furnace temperature and gas pressure, one can affect the diameter of the SWCNT. Also, by changing the target’s chemical composition, the distribution of the diameter can be affected[11].

2.4 Combustion synthesis

Combustion synthesis is a fairly new method, which uses flames to generate a carbon-rich environment to synthesize carbon nanotubes and other nanostructures. Through combustion synthesis, it is also possible to affect the properties, such as diameter, length and morphology, of the nanotube. Modification of the nanotubes this way is important, so the application possibilities grow. These modifications are done by changing the synthesis parameters, such as flame configuration, fuel type and catalytic materials[12].

The combustion synthesis method consists of a heat source, source of carbon, and a suitable catalytic material. The carbon source is often a hydrocarbon, for example ethyne. The reactive material is often in the gas phase. Those particles nucleate into nanoparticles, which act as inception and enable the carbon nanotubes to grow. The energy for the synthesis is obtained from the heat source.

This method is mostly used to produce multi-walled carbon nanotubes (MWCNT), but it has been noticed that producing single-walled carbon nanotubes (SWCNT) is also possible. On the other hand, it has been noticed that many of the SWCNTs are still somewhat low quality. If these morphological problems could be tackled in the future, this method could be used more to produce SWCNTs. However, one great advantage of this method is, that it is suitable for large-scale production of carbon nanotubes[13]. When the aim is to produce carbon nanotubes for further applications, the method needs to be scalable for high volume production. This method is also very fast, which supports the use of the method for volume production[12].

2.5 Purification of carbon nanotubes

Once carbon nanotubes have been produced, they need to be purified. Purification is just as important part of the process to use the carbon nanotubes in different applications[13]. After variating synthesis methods, the CNTs include different impurities, which interfere with the wanted properties of the nanotubes. Impurities might even make the CNTs inoperable. The most common impurities are different kind of nanoparticles, disordered carbon, and if the nanotube was catalytically produced, then residual catalyst particles and support material[4,13].

Purification as a method simply means that these unwanted impurities are separated from the CNTs, to achieve purified nanotubes, that can be used in applications. Purification methods can be divided into three categories; physical, chemical, and methods that combine both. The purifying method needs to be selected carefully. One needs to take the features of the raw CNTs into consideration as well as the target application. It seems that it still practically impossible to achieve wanted results, i.e. purity, with just one purification method. This is why multi-step methods that combine different advantages are used the most[14].

A futuristic thought has been made in which the purification method could be dissmissed. Some research has been made about the possibilities to produce high-purity carbon nanotubes with the actual synthesis of the carbon nanotube.[15–17] But in fact, not any of the researches mentioned above, were able to produce CNTs without any impurities. The struggle is still too great between controling the synthesis conditions to produce high-purity CNTs and to produce CNTs that have the desired properties, for example diameter and length, at the same time[14]. This is why purification is still a needed method to ensure that high-purity and high-quality CNTs are available for further use in applications.

There are still many barriers to overcome when thinking about the disadvantages of purification. Many of the purification methods are time consuming and costly and are not yet suitable for large-scale production. Some of the methods even ruin parts of the purified sample. Purification methods also do not have very good method assessment. This makes it harder to evaluate which method is the best for each type of CNT, when considering every standard in the process. These being time, costs, purity, CNT quality and yield.

This chapter now further presents a few purification methods. The following text also describes if the methods are suitable for single- or multi-walled carbon nanotubes or for both.

2.5.1 Oxidation

This subchapter introduces three different chemical purifying methods based on oxcidation. All the methods have different advantages and disadvantages. The method should be chosen in a way that considers the features needed in the application.

2.5.1.1 Gas phase oxidation

Gas phase oxidation is one of the first succesful methods for purifying multi-walled carbon nanotubes that were produced non-catalytically[4]. Today this method is used for both SWCNTs and MWCNTs. With this method, it is possible to purify disordered carbon impurities, not metallic residue impurities[14].

This method is based on oxidizing disordered carbons, such as amorphous carbon, fullerenes and carbon nanoparticles. The process is performed in an oxidizing environment with the temperature between 225 ℃ to 760 ℃. There are many possible oxidizing gases, an example of one of the mixture combinations is air, Cl_2, H_2O and HCl[14].

This method is rather simple, but it has its disadvantages. The oxidation selectivity between the CNTs and the impurities is limited. The synthesis conditions must be carefully set up. This condition issue also includes the uneven air exposure, this aspect needs to be carefully controlled also to achieve good results.

As mentioned above, this method can also be used to purify SWCNTs. It is just not as simple as purifying MWCNTs. Oxidation is quite destructive method so when first oxidizing SWCNTs most of the nanotubes were destroyed[18]. This is because of the different curvature compared to MWCNTs and the metal catalyst residues that catalyse the oxidation reaction excessively. Because of the curvature the oxidation gas selection is scarcer for SWCNTs, for not all gases oxidate selectively the impurities. Also the metal particles have to be always removed with acid treatment before oxidation synthesis[14]. In another research that has been made, the SWCNTs were treated first with acid and filtered to remove metal impurities. This was successful, afterwards the SWCNTs were oxidized twice and rinsed wit HCl. This was said produced 99,9 % SWCNTs[19].

2.5.1.2 Liquid phase oxidation

Liquid phase oxidation was developed to tackle the disadvantages of gas phase oxidation. In gas phase oxidation an extra step of acid treatment is always needed. Liquid phase oxidation was developed to increase effectiveness and purify the carbon and the metal impurities both at the same time. This method is used for both SWCNTs and MWCNTs[14].

The basic idea of the method is that oxidative ions and acid ions are mixed in the solution simultaneously. This solves the problem with uneven exposure of the oxidant, unlike in gas phase oxidation. There are many possible reagents, but one example is the combination of H_2O_2 and HCl[20]. This method is effective, simple and can be performed with high yield. The disadvantages, or preferably changes on the sample, on the other hand are considerable. This method causes reaction products on the surface of the nanotubes. It also adds functional groups and might destroy CNT structures[14]. These issues are to take in consideration, when thinking about the further use. When purifying SWCNTs the loss of the sample was much greater than that of MWCNTs. So, this method is preferred for purifying MWCNTs. This method is simple as mentioned and thus can be expanded on a large-scale production synthesis for industrial use[14].

In some applications these alterations mentioned above, can be positive, for example applications in organic solutions, such as biosensors. Carbon nanotubes purified through liquid phase oxidation are modified in different ways after synthesis, and this can be exploited in further use in applications. For example, in one research CNTs were cut in shorter segment during the oxidation synthesis. These shorter CNTs were wanted, for they are more dispersible in water. This feature is desired in the field of biotechnology[21,22].

2.5.1.3 Electrochemical oxidation

Electrochemical oxidation is the third and final oxidation method presented. This method is based on electrocurrent in the solution between anode and cathode. This enables the oxidation process. One research used cyclic voltammetry (CV) in KOH solution to purify SWCNTs. This was successful[23]. This leads to a conclusion that this method works on both SWCNTs and

MWCNTs. Of course, the same issue of metallic impurities remains as in both oxidation methods mentioned before. An acid treatment, in this case, HCl rinsing was necessary[23].

When purifying MWCNTs, the solution can be acidic, and the extra step of acid treatment is not needed. This simplifies the method. This was proved in a research, where vertically aligned MWCNTs were purified in H_2SO_4 acidic solution[24].

Electochemical oxidation is superior to the two other oxidation methods in terms of time and degree of oxidation which can be easily determined. Basic electrochemical method can remove some of the impurities, especially when purifying vertically aligned CNTs. If the degree of impurities is great, the method can be combined with cyclic voltammetry (CV). This enhances the performance and can get rid of more different impurities, such as graphite particles and metal particles on the carbon layers. However, the amount on sample, one can purify with this method is small, which makes this method unsuitable for large-scale production[14].

2.5.2 Solubilization

Solubilization is one of the methods to purify preferably multi-walled carbon nanotubes. This method is used to purify all kind of nanoparticles from the CNTs. This method is a physical method and is based on transforming the nanotube to make it soluble. This is usually made with different kinds of functional groups that are attached to the surface of the CNT[4,14]. In one research it was noticed that by introducing the functional group to the CNT and using water the solution, the carbon nanotubes started to flocculate in the solution, leaving the impurities[25].

Once the nanotubes have been made soluble, it is then also possible to use different purifying methods to purify the sample. These methods being for example filtration and chromatographic methods. After the impurities have been removed the functional groups must also be removed. This can be done for example with heat treatment[14].

Solubilization has been noticed to work on single-walled carbon nanotubes, though is still less used for their purification. One research was made where SWCNTs were mixed in a polymethyl-methacrylate (PMMA) solution with sonication. Afterwards the solution was filtrated twice, and most of the impurities were removed successfully. However, the SWCNTs still contained disordered carbon and the PMMA residues. These impurities have to be removed with other methods, for example heat treatment[26].

This method, as most purification methods, needs to be combined with others. However, this method itself has one great advantage, it being that it does not harm the electronic structure of the carbon nanotube. When talking about using these purified CNTs in biosensor applications, this is a very important feature. In addition making the nanotubes soluble, is an advantage itself, as solubility is an important material's property in therapeutics delivery applications[27]. This method on the reverse is not very effective, as the sample sizes need to be rather small for high-purity results[14].

2.5.3 High-temperature annealing

One of the most effective methods to obtain high-purity metal-free carbon nanotubes is high-temperature annealing. This method is used when the CNTs are produced catalytically, for example via chemical vapor deposition[4]. Single- and multi-walled CNTs produced by this method always contain particles of the metal catalyst or the support material used in the synthesis. Getting these metal particles out of the CNT structure is even more important when the CNTs are further used in biosensor materials.

High-temperature annealing method is based on high temperatures. This method exploits the different physical properties of carbon and metals. The evaporation temperature for these two groups differ a great amount. Carbon structures are known to be stable in vacuum even at 3000 ℃. On the other hand, metals dissolve at significantly lower temperatures at over 1400 ℃. This enables the metal particles to evaporate from the carbon structure before the CNTs will be damaged[14].

This method is rather easy compared to the methods presented above[28]. This is also the reason why chemical vapor deposition is one of the most used synthesis methods. For CVD-produced CNTs are easy to purify with annealing. Another advantage of this method is that it has been noticed to also evolve the structure of the nanotube[28]. Annealing increases also the mechanical strength, thermal stability and electronic transport properties. This method is often used together with other purification methods. This is due to the fact that annealing does not affect disordered carbon. The possible disordered carbons must be removed first and then through annealing, removing the metal particles[14].

3 Characterization techniques of carbon nanotubes

This chapter presents few of the analysing and characterization methods used to study the properties of carbon nanotubes, both single- and multi-walled. The characterization of the nanotube is an important process for applications. As there are still uncertainties and problems with the nanotube synthesis procedures, the closer studying of the resulting nanotubes is very important. This chapter shortly presents the main properties that carbon nanotubes possess and then continues to present few of the most used characterization techniques.

3.1 Properties of carbon nanotubes

Carbon nanotubes have a lot of properties that make them the target of interest around the world. Their electrical, mechanical, thermal, as well as optical and structural properties all have found out to be extraordinary[4,29].

Carbon nanotubes have versatile electronic properties. CNTs can be metallic or semiconductiong depending on their structure. Thus, it is very important to be able to get a clear vision of the structure, as it has the main effect on the electrical conductivity[4]. It was noticed that metallic nanotubes transport electrons ballistically the same as a quantum wire does in nature. This means that scattering does not occur from impurities. If the nanotube is ultrapure, meaning no scattering happens during the transport, CNTs could conduct a very large current without getting hot[4]. This is a very good quality to have in application circuits. This also comes to show how important the purification process of carbon nanotubes is to their functionality.

Carbon nanotubes also possess great mechanical properties. It is known that single-walled CNTs, depending on their structure, can have elastic modulus up to 1000 GPa and tensile strength up to 300 GPa. Multi-walled CNTs have lower values in both, as their elastic modulus comes up to 950 GPa and tensile strength up to 63 GPa[4,29]. For perspective the elastic modulus of SWCNT is five times that of steel, and SWCNT tensile strength 50 times that of steel. This makes nanotubes very strong and and stiff and optimal for application use. The CNTs are very flexible and it has been noticed that once the stress is released upon the tube it can return to its original form[4]. This is a great advantage when thinking about durability of the material in applications.

The thermal conductivity is also large, as it measures up to 200 W/mK. There are many features affecting the conductivity. As diameter, nanotube length, number of walls, chirality differences between graphene sheets all affect thermal energy transportation[29].

Carbon nanotubes are constructed by graphene sheets. This means that all the carbon atoms in the structure are sp^2 hybridized. This enables the nanotube to absorb light in a great variety of wavelength and gives the nanotubes their black colour. Carbon nanotubes can be studied with optical methods. For example, their structures can be studied with fluorescence spectroscopy and Raman spectroscopy[4]. One of their structural properties is also the large surface area and it can be further enlarged through purification[29]. Nanotubes have a low density, as it measures to 1,3-1,5 g/cm^3 for SWCNTs and 1,8-2,0 g/cm^3 for WCNTs[29].

3.2 Raman Spectroscopy

Raman spectroscopy is method that is used a lot to find structural defects in CNTs. Carbon nanotubes tend to have two stornger peaks on their Raman spectrum. First peak is at 1350 cm^{-1}, which is called the D-band. The second peak is at 1580 cm^{-1} and it is called the G-band. The D-band refers to sp^3-hybridized carbon, that should not be a part of the nanotubes graphene layer structure. G-band then again refers to the sp^2-hybridized carbon that are symmetric with each other in the nanotube structure.

If there are many defects in the nanotube structure, it shows proportionally in the intensity of the D-band peak. The amount of the defects can be calculated by the ratio of the intensities of the D- and G-bands. The ratio I_D/I_G describes the level of structural disorder. In a research where scientists used heat treatment as a way to purify these carbon impurities, Raman spectroscopy was used as a characterization method[30]. It has been noticed in several studies that the I_D/I_G ratio for CNTs is usually between 0,27-0,90.[31] In this research, the heat treatment was used to modify the sp^3 carbons to sp^2 carbons. The Raman spectra was measured before and after. Graphitization was noticed to happen through Raman measurements[30].

3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) can be used to study the structure as well as the morphology of the carbon nanotubes on a more general level. SEM is a great tool when information about the structural changes after purification, graphitization (i.e. heat treatment to purify disordered carbon) or functionalization of the nanotubes needs to be evaluated. SEM can be used to gather information about larger groups of CNTs and their alignment and entanglement, as well as their homogeneity and dispersion[29,32]. If the resolution is improved by microscopy analysis SEM can offer more detailed information about a spesific tube itself, features such as length, diameter, curvature and carbon impurities[29].

For example, in a research where scientists wanted to find out, which solution is the best for dispersing multi-walled carbon nanotubes, SEM was used an imaging method[32]. Synthesized MWCNTs were dispersed in three different solutions, methanol, Triton X-100 and an ionic liquid. After that, all three solutions were scanned with SEM. It was noticed that in the ionic liquid the MWCNTs resulted in many individual and homogenously distributed MWCNTs[32]. SEM worked well in this research as they were merely studying a larger group of carbon nanotubes and evaluating their placement compared to each other.

3.4 Transmission Electron Microscopy

Transmission electron microscopy (TEM) can be used for structural characterization of carbon nanotubes with higher magnification than SEM. TEM can detect nanoparticle impurities, defects in the nanotube wall structure and amorphous carbon. It is also possible to measure the length, diameter and number of walls of the tubes[29].

It was noticed that one can investigate the curvature of the nanotubes with TEM. It was discovered that MWCNTs usually are straight in form and SWCNTs are much curvier. This is due to the diameter of the tubes. As the number of walls increases, so does the diameter and the stiffness of the structure. It was also noticed that, although the sample preparation with TEM might be rough, the nanotubes were hardly ever completely fractured[4].

TEM is better for nanoscale characterization than SEM because of its higher magnification. It was noticed that after a heat treatment purification, SEM showed no structural changes. On the other hand, TEM showed that the nanoparticle impurities had dissappeared from the nanotube structure[29]. To conclude, TEM is used to gather information on a one specific tube, and SEM provides information on general CNT bundles.

4 Applications with carbon nanotubes

As stated before in this thesis, carbon nanotubes possess many properties superior to other materials. This is why carbon nanotubes are a real target of interest when it comes to research on modern methods of sensing, imaging and measurements. Carbon nanotubes are used in many fields of industry, such as microelectronics and electronic components, solar cell production, energy storing systems and biomedical and biological research. This chapter now goes on presenting the use of carbon nanotubes specifically in the biosensor field.

Human body consist of countless number of different biomolecules. The variation in the concentration of a biomolecule can usually interpreted as a change in one's health status. The early information of these variations is crucial in the medical field for an early diagnosis. Body's own biomolecules are not the only target of sensing. Differentiating levels of metabolites are important to keep track on. In addition, biosensors can be used to check the amount of drug molecules in the body. This is good way to inspect the therapeutic effects in the body and optimize drug use for treatment[33].

4.1 Operating principle of nanotube based biosensors

There are different classes of biosensors in means of their technical features. The most used type is the electrochemical biosensor, as it is superior in size, cost response, sensitivity, and measuring range[34]. The other type of biosensors can be optical, semiconductor, calorimetric and others, which includes all the biosensor that cannot be included in the classes mentioned previously. The electrochemical biosensors can be used to detect for example cancer, glucose levels, bacteria and ensuring food safety as well as monitoring the environment[1].

The sensing procedure is similar in all the sensor, though the technique behind it variates. This principle is portrayed in Figure 6. The sensing starts with a bioreceptor, that is usually a molecule, which detects and reacts a certain way with the analyte. Analyte is the biomolecule to be identified or investigated more closely. A bioreceptor is a kind of a probe and it is usually an antibody, enzyme, aptamer, a cell, or a nanoparticle. The bioreceptor converts the analyte biochemically. This reaction causes a chemical response or a physical phenomenon in the body which the transducer detects and further transforms into a readable signal. The transducer is used together with a reference device to compare the changed circumstances to the so-called level zero where the detected analyte is not present. Next, the sensing process belongs to the electronics part, which includes an amplifier and a processor. This is where amplifier amplifies the signal from the transducer and convert it into a form that can be displayed for example as a data curve on a computer monitor.

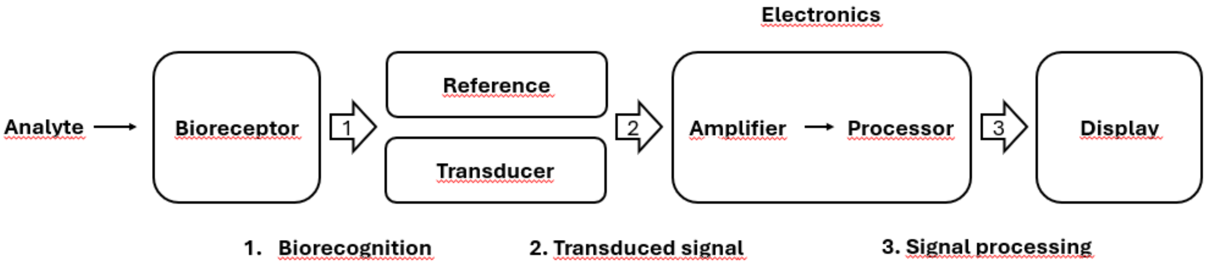

Figure 6. A schematic figure of the operating principle of a carbon nanotube-based biosensor.

The functionality of the biosensor depends a lot on the bioreceptor chosen and the transducer. The transducer defines the class of the biosensor. For example, electrochemical biosensors can measure different variables. These biosensors could then be amperometric, potentiometric, voltammetric, conductometric or impedometric[1].

4.2 Advantages of carbon nanotube based biosensors

Before the advancements in the medical field, in the means of biosensors, the process of sensing and detection was slow and costly. The biomolecule research demands laboratory testing, such as the comparison between normal and infected organisms and extraction of all the proteins, antibodies and genes from the blood. The standardization of previous studies was challenging and research demands a lot of working hours. Nowadays, carbon nanotube biosensors offer both invasive and noninvasive as well as a more united way for detection of biomolecules and metabolites. The process is easier, it is faster, less costly, more sensitive and more effective[33].

In Chapter 3.1, there are some properties described that create advantage for carbon nanotubes compared to other materials. These properties are the reason carbon nanotubes are so much used in the medical field. One of the most important properties, when thinking about biosensor use and electrochemical use in precise, is the electrical conductivity. It enables the manufacturing of CNT-modified electrodes and thus faster electron transfer which provides even more sensitive detection levels[33]. Another major advantage is the large surface area the carbon nanotube has due to its structure. This enables the catalytic modification of the biosensor which enables a faster process[33]. This also enables improvements in the target analyte identification and so reduces the detection sensitivity threshold.[1] Carbon nanotubes are also used a lot in composite materials in applications[4]. As they might not fill all the expectations demanded of a biosensor alone. This creates even more versatile usage possibilities for carbon nanotube applications.

4.3 Electrochemical biosensors

Electrochemical sensors are used a lot and in a variety of ways for different detection purposes. This chapter now reviews closer the usage of electrochemical biosensors in cancer, virus and bacterial detection.

4.3.1 Sensing of cancer

Cancer has become most fatalities causing decease in the world during the last few decades. Cancer treatment is difficult and not always successful, which makes the early on detection of cancer cells in the human body even more crucial. Electrochemical biosensors could be the answer to this need[1].

Researchers have combined carbon nanotubes with DNA and have found that to be an effective way to detect cancer cells but also many other biomolecules. DNA has natural stability in biological environment and the capability to recognize different organism through their molecule and DNA structure[1,35]. DNA recognizes other structures, as in complimentary DNA sequences, through hybridization. The DNA used in the sensor is usually aptamer-length and it is called the probe. The probe is designed, so that it can recognize specific sequences. The probes are usually produced either chemically or by molecular biology, as in reverse-transcription of messenger RNA[35].

To achieve a working DNA biosensor, the DNA aptamer must be immobilized to the carbon nanotube transducer. This offers good support for the hybridization process[35]. DNA sequence is rather easy to immobilize to the CNT surface, as special modification is not needed. Immobilization happens through van der Waals interaction[1].

4.3.2 Sensing of viruses

DNA-based biosensors are used also for the detection of viruses. When targeting viruses, the detection technique with DNA-based biosensors is the same as presented in Chapter 6.3.1. For example, in one research the scientists developed a an electrochemical DNA biosensor based on a carbon nanotube/aerogel film[36]. The biosensor was label-free so it could detect the virus, or its proteins without the need of altering it beforehand. Researchers used the sensor to detect COVID-19. The usage of the CNT/aerogel film enlarged the electrode area to capture more viruses through hybridization. This technique was noticed also to be more selective due to this. The DNA was conjugated with sulphur and iron particles. This conjugation method has become popular, as it enhances the properties, such as electroconductivity and larger surface area, of the biosensors[36].

Another research presented an carbon nanotube field-effect transistor based biosensor for another way of detecting COVID-19 and its surface protein[37]. The researchers developed an electrochemical immunosensor that used the antibody of COVID-19 surface protein S1 as the probe. They deposited single-walled carbon nanotubes on SiO_2 film and immobilized the antibodies to that surface. The SWCNTs were deposited between two electrodes, source and drain. The detection was based on the current changes between these two electrodes. The current was to change depending on the binding of the antigen to the probe. The accuracy was found to be great. These sensors are also easy to be manufactured and their detection time is fast, which makes them good for mass-level use in Pandemic situations[37].

4.3.3 Sensing of bacteria

Escherichia coli is still one one most fatal and illnesses causing bacteria in the world[38]. It is very important for food safety to be able to detect *E.coli* in the sample fast and easy to prevent foodborn illnesses. The researchers developed an electrochemical biosensor that used a bacteriophage as a probe and the electrochemical detecting itself was conducted by single-walled carbon nanotube-modified electrode. The bacteriophage recognizes specific strains of the bacterial genome. The phage then starts to replicate in the bacterial cell and as a result of that, triggers cell lysis and release of an endogenous bacterial enzyme. That bacterial enzyme is the target of the electrochemical detection. The single-walled carbon nanotubes are used in this case to enhance the electroconductivity of the electrode and to amplify the signals gathered from the sample[38].

4.4 Other type of biosensors

As noted before there are many different kinds of electrochemical biosensors in use nowadays. They possess a lot of properties concerning shorter detection time, better precision, lower costs and easier manufacturing. Despite electrochemical biosensor superiority there are other types of biosensors in use. One of these types is optical biosensor. Another is field-effect transistor biosensor. Sensors can also combine different aspects of multiple sensors. As was presented in Chapter 4.3.2 concerning the electrochemical field-effect transistor biosensor.

Optical biosensors can be used to detect for example cancer. In one research, chemiluminescence was used to detect 5-hmC-sDNA that can cause tumor genesis[39]. The probe in this biosensor was the antibody of 5-hmC-sDNA doped with Ru(bpy)2(dcbpy)NHS to start the chemiluminescence in the target. The amplifier was a composite with multi-walled carbon nanotubes with poly-(dimethyl diallyl ammonium chloride). This composite was used to get a stronger signal and to get a larger surface area in the biosensor[39].Field-effect transistor (FET) is also showing great potential as a label-free detection method. The FET is commonly used to amplify the weak signal. In one research, the FET biosensor SiO_2 substrate was coated with suspended carbon nanotubes to get a stronger sensing performance. The suspended nanotubes made a layer between the substrate and the nanotube that had the DNA strains, thus the probe, attached to it. The extra layer was noticed to lower the limit of detection[40].

4.5 Future outlook of carbon nanotube biosensors

Although carbon nanotube-based biosensors hold a lot of potential, there are still obstacles to be addressed. A careful investigation of the carbon nanotube is necessary. The evaluation of its length and diameter, its mechanical properties, lifetime estimation, and durability as well as toxicity must always be performed. The target of detection must also always be evaluated. The needs always depend on whether the biosensor is invasive or non-invasive. Another important thing to consider is the immobilization of the bioreceptor. The bioreceptor must be perfectly intact with the CNT in order to achieve a fully functional biosensor[1].

One of the sensor types researchers find great potential is in wearable sensors. Wearable sensors could be invasive and non-invasive. Wearable sensors could offer a long-term and real-time detection of different chemical and physical signals in human body. Only the problem of biocompatibility still exists. The CNTs must be nontoxic for the human body, so they must be functionalized, as in their surface modified as needed to fit to biological surroundings, properly. Biotoxicity varies depending on the tissue where the sensor detects and the form of the sensor itself. These are some of the questions that still need to be answered concerning wearable carbon nanotube biosensors[41].

Another type of biosensor that is considered very potential in the future is a fluorescent carbon nanotube biosensor. They also are able to perform long-term detection on different chemical and physical signals in the human body. However, the impurities CNTs still might have cause a problem for the usage of these type of biosensors. Also, the different chiralities of the nanotubes pose a threat. Usually, it is the most simple and effective way to use a mixture of different CNTs in applications. These different CNTs might have different properties, for example chirality. Different chirality causes different emission wavelengths, which distorts the output of the sensors. Despite these disadvantages, both, wearable and fluorescent, biosensors are important vessels for personalized medicine and health status monitoring. These sensors offer a great step forward for diagnosis making, integrated model of treatment and a possibility for expanding medical applications[41].

5 Conclusion

Carbon nanotubes have many properties that make them valuable in biomedical applications. Especially their electronic and mechanical properties make them of great value. Their strongness combined with structural features make them very suitable especially for electrochemical sensing and biosensors.

As interest in carbon nanotubes has risen, so has the interest in developing the synthesizing and purification methods of CNTs. Carbon nanotubes can be synthesized in various techniques, but it has been noticed that chemical vapor deposition and arc-evaporation are the best methods. They are both effective, relatively non-costly and fast. They can both produce both single- and multi-walled carbon nanotubes. Also, purification of the nanotubes still holds a very important part in the nanotube synthesizing process. No synthesizing method has yet to be able to produce ultrapure carbon nanotubes ready for application use. Nanotubes still contain significant impurities and this is why multiple-step process of purification is conducted on the CNTs after synthetization.

The disadvantages of carbon nanotubes that need to be taken in to account when considering their usage in biosensors. Biotoxicity and impurities make the use of CNTs more difficult in biosensors. This is why it is really important to investigate all the features CNTs might possess. Different characterization techniques can help solve these problems. If scientist get a more thorough picture of what are the exact requirements CNTs must fill, so that they can be used in applications, the manufacturing of biosensors could take a leap towards future developments. Although there are obstacles concerning CNT usage in biosensors, the properties and features of carbon nanotubes are unique, thus making them one of the best material options for modern biomedical applications.

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