

Review

From Bio to Nano: A Review of Sustainable Methods of Synthesis of Carbon Nanotubes

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Abstract: This review summarizes the up-to-date techniques devised to synthesize carbon nanotubes (CNTs) from liquid or solid precursors of sustainable nature. The possibility to replace petroleum-based feeds for renewable resources such as essential oils or plant shoots is critically examined. The analysis shows that the complex nature of such resources requires the optimization of the reaction conditions to obtain products of desired microstructure and chemical composition. However, appropriate tuning of the process parameters enables the synthesis of even high-purity single-walled CNTs with a spectrum of demonstrated high-performance applications at low cost. The sheer number of successful studies completed on this front so far and described herein validate that the development of techniques for the manufacture of such products of high-added value from common precursors is not only possible but, most importantly, promising.

Keywords: bio-feedstock; carbon nanotubes; synthesis

1. Introduction

Ever since they were discovered [1], carbon nanotubes (CNTs) provided evidence that they are one of the most fascinating and promising materials of our times. Due to the leading electrical [2–6], thermal [7–10], mechanical [11–15], and optical [16–21] performance of individual CNTs, they immediately received the focus of numerous scientists. Based on the results of the conducted research, exploitation in many parts of life has been anticipated for them ranging from electronics [22–24], via construction [25–27] to medical diagnostics [28–30]. Their successful implementation, however, requires that the material can be produced at a large scale at a reasonable price. Still, in addition to certain technological constraints [31–34], many nanomaterials do not enter the market primarily because the costs involved in their production are too high [35–37]. As a consequence, the price of the final products becomes too high to bear, so their exploitation is limited to niche applications, for which costs are a secondary issue [38–41].

To drive the costs down, one can consider the synthesis of nanomaterials from renewable resources [42–44]. Bio-feedstocks such as biopolymers [45,46] or bio-derived chemical compounds like essential oils [47–49], which are available in high amounts [50–52], have a range of advantages as compared with synthetic precursors. They are inexpensive, abundant regardless of location (to a large extent), and constantly replenished by nature. Most importantly, because of the high content of carbon, they are valuable as building blocks for nanocarbon synthesis. Since in some cases such carbon reservoirs are even considered as problematic waste [53,54], smart ways how to utilize them should be devised to make the world more sustainable.

In this review, a spectrum of methods of synthesis of CNTs directly from renewable feedstocks is provided. A range of liquid and solid precursors of biological origin such as essential oils or plant shoots are described herein. These techniques, which can easily transform common resources into products of high-added value, are evaluated in detail. The strongest focus is put on the analysis of

the degree of structural perfection of the obtained CNTs. That is because, from the practical point of view, only the material of appropriate quality may give rise to its implementation in high-performance applications. Finally, the contribution is concluded with an overview of the next steps, which should be taken to spread this sustainable concept to deliver some tangible benefits to civilization.

2. CNT Synthesis Methods

After almost 30 years since the influential paper by Iijima [55], which started the CNT boom, an arsenal of techniques for CNT synthesis have been formulated (Figure 1). In brief, CNTs can be obtained by five mainstream methods. In the arc-discharge process, high current is transmitted between two electrodes kept under inert atmosphere [55–58]. This generates a sufficient amount of heat to cause the vaporization of carbon from the anode and its deposition on the cathode. As a consequence, multi-walled CNTs are obtained. It is also possible to synthesize single-walled CNTs instead, but the anode made most commonly of graphite has to be modified. A cavity is drilled in the core, where an appropriate transition metal catalyst such as Fe or Co is placed, which is capable of promoting single-walled CNT synthesis in the gas phase [59,60]. The intermediate double-walled structure can be obtained by arc-discharge under appropriate conditions as well [61]. Furthermore, another popular technique of CNT synthesis involves a high-power laser, which also vaporizes carbon from a graphite target maintained in a high-temperature furnace [62–66]. Bleeding of inert gas enables the collection of the formed CNTs on the colder sides of the reactor. Both of these techniques are of limited use for utilizing a bio-feedstock because a highly-defined CNT precursor is needed to carry out the synthesis. Two more techniques, which are less relevant for the described topic are electrolysis and sonochemical/hydrothermal methods. In the former approach, alkali or alkaline carbonate salt is molten and the electric current is passed through to give CNT material at one of the electrodes [67,68]. In this configuration, CO₂ can also be dissolved to be used as a supplementary CNT building block. Therefore, the approach is, to some extent, green as it is capable of utilizing unwanted CO₂ from the ambient [69–71]. In the latter tactic, ultrasounds or high pressure are utilized to facilitate the synthesis during sonochemical [72] and hydrothermal [73–75] processing of carbon feed, respectively. Finally, beyond doubt, the most popular method of synthesis of CNTs, and simultaneously, the one which can adapt various sorts of bio-feedstocks to the largest extent is the so-called Chemical Vapor Deposition (CVD) [76–78]. In this procedure, a source of carbon is introduced to a high-temperature furnace kept at 700 °C or above wherein a substrate coated with catalyst particles, e.g., Fe or Ni is present. Alternatively, ferrocene or nickelocene can be injected along with the feedstock to form the catalyst particles in situ [79–82]. During the process, carbon-bearing molecules (from bio-feedstock/petroleum) deposit on catalyst clusters made of metal nanoparticles (suspended or immobilized, respectively), where they disintegrate to elemental carbon. Once a steady flow of these building blocks is established, CNTs are assembled in a continuous, but decelerating fashion caused by gradual deactivation of the catalyst [83].

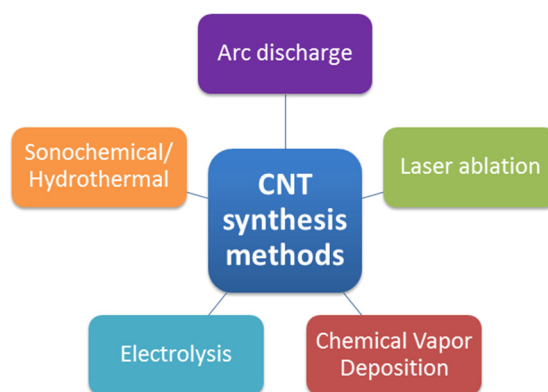


Figure 1. Main bottom-up techniques of CNT synthesis.

An assortment of synthetic feedstocks is used for the process, which involves diverse classes of chemical compounds such as hydrocarbons (both aliphatic [84–87] and aromatic [77,88–90]), alcohols [91–94], ketones [95,96], ethers [97,98], amides [99], etc. These can either be in a gaseous state [86,87] or they are vaporized [91,92,98] before injection to the reactor. What all of them have in common is that they can be decomposed under regular CVD conditions and, most importantly, that they contain carbon. Thus, it is simple to imagine that other carbon-bearing chemical compounds can be used instead. Notable examples of successful implementation of such alternative precursors will be described in detail in the subsequent part of this review.

It is important to note that several top-down approaches and many significant modifications of the concepts described remain at disposal of the nanocarbon community. Readers are advised to seek further information in dedicated reviews published on this topic [83,100–102] to gain more insight into the aspect of CNT synthesis.

3. Bio-Feedstocks for CNT Synthesis

Two classes of CNT precursors are discerned in this review: liquid and solid. Admittedly, the synthesis can also be accomplished from biogas by processing various feedstocks [103,104], but these cases are not considered herein since they are less established. The most popular routes described here involve essential oils harvested from a wide spectrum of sources or they engage certain plant shoots. They are listed in alphabetical order in Figure 2.

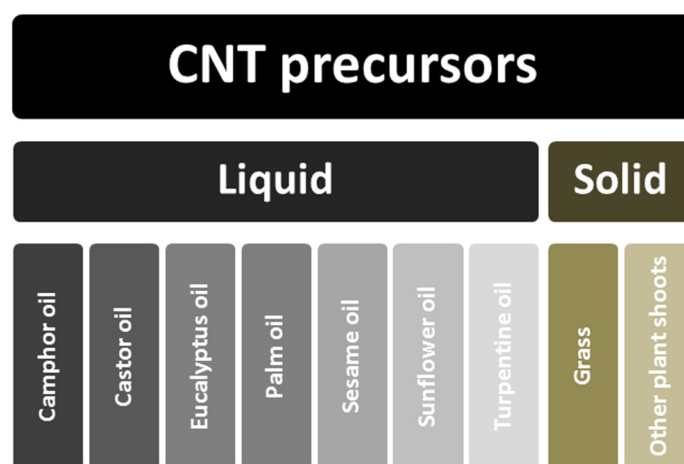


Figure 2. Key renewable bio-precursors for CNT synthesis.

3.1. Liquid Precursors

3.1.1. Camphor Oil and Camphor

Camphor oil can be obtained from many sources such as *Cinnamomum camphora* (evergreen tree found in Asia) and *Dryobalanops aromatic* (a large emergent tree found in Sumatra and Borneo) among other related trees in the laurel family [105]. Contributions by Yousefi [105] and Salifairus [106] indicated that CNTs can be synthesized readily from camphor oil in the presence of ferrocene. The former group showed that such reactions' conditions give material, with some degree of vertical alignment. Interestingly, when Salifairus and co-workers carried out a similar synthesis above 800 °C with an additional source of catalyst (aluminum isopropoxide), single-walled CNTs were also detected by Raman spectroscopy based on the appearance of Radial-Breathing Modes (RBM). The positions of these features correspond to the 0.63–1.14 nm diameter range. Unfortunately, these findings were not supported by TEM micrographs, which would give definite proof if indeed this material was formed. Furthermore, Shamsudin et al. reported a composition of camphor oil, which show how complex is the chemical composition of such precursor [107]. Almost 30 chemical compounds of the

rather sophisticated structure were detected. The major ones (with amounts exceeding 10%) were: eucalyptol (35.21%), α -pinene (15.43%) and camphor (10.01%). Thus, understanding the course of the synthesis of nanostructures from such resources is not trivial. What is more, in the same study, Fe-filled spherical-like graphene particles were converted to CNTs of a notable aspect ratio. Although in this case, such template was used for the synthesis, the results are nevertheless interesting since conversion of spherical particles to an anisotropic material is always challenging from the thermodynamics point of view.

Instead of camphor oil, camphor itself (Figure 3) can be employed as a CNT precursor as well. It is solid with a relatively low boiling point of 209 °C, so it can be introduced to a reactor with ease by a carrier gas upon heating. To make the comparison simpler, the results of the camphor-based synthesis of CNTs are presented here rather than in Section 3.2 devoted to solids, where exclusively plant shoot-based precursors are described.

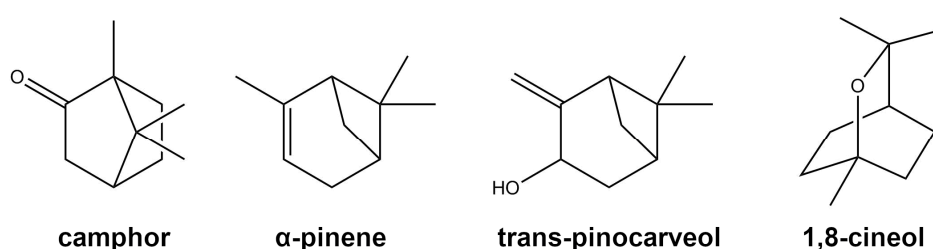


Figure 3. A selection of bicyclic compounds detected in bio-feedstocks used for CNT synthesis.

Camphor was one of the earliest described bio-feedstocks for CNT synthesis [47,108] building on the successful transformation of camphor to fullerenes reported before [109]. Kumar and Ando described that a mixture of multi- and single-walled CNTs can be obtained from camphor by CVD [47]. Optimization of the reaction conditions can be used to produce some single-walled CNTs of an average diameter of 1.2 nm [108]. Another benefit of using camphor as compared with traditional CNT precursors is that its bicyclic structure makes it less thermally stable. Hence, an order of magnitude lower amount of catalyst is required to drive the process [110]. This, in turn, causes the product to be of high purity. Defect-induced D-band was virtually non-existent (as gauged by micro-Raman spectroscopy), which indicates the absence of amorphous carbon or CNT defects. Since any means to alleviate or avoid the post-synthetic purification of the material are welcome (as they can affect the nature of the processed material), camphor-based CNT synthesis appears attractive. Over the next years, these two scientists deepened understanding of CNT synthesis from camphor and indicated the application potential of the product. They showed that vertically-aligned forest obtained this way can be a promising material for field emission purposes [111]. The material had even better field emission properties when octylamine or dimethylformamide was employed during the synthesis, which caused N-doping of the material [112]. The inclusion of nitrogen-rich species for the synthesis has a documented ability to increase the alignment of CNT forests [113]. Anisotropy of such networks is one of the key required attributes for field emission. Finally, the mentioned researchers employed catalytic systems based on Fe-Co immobilized on zeolites to control the diameter distribution of the manufactured CNTs [114]. Multi-walled CNTs of uniform diameter distribution centered at 10 nm were obtained in high yields having significantly reduced content of the residual catalyst between 600 and 700 °C. Interestingly, when the temperature was increased to 850–900 °C, as much as 30% of single-walled CNTs was formed in the obtained soot. They had a rather narrow diameter range of 0.86–1.23 nm (Figure 4a). The contributions of other authors also disclosed interesting insight. Firstly, it was possible to optimize the conditions of the synthesis so that CNTs are obtained preferentially on the silicon substrate in the form of aligned arrays whereas adulterants are deposited mostly on the quartz tube wall inside the furnace [115]. Secondly, CNT materials produced from camphor also showed modest mechanical properties and high hydrophobicity [116], which could be significantly

reduced upon employing a spectrum of oxidation methods [117]. Lastly, when ferrocene catalyst was substituted for Co or Co/Fe thin films, the product besides the CNTs contained many coiled carbon nanofibers (CNFs), a blend of which showed appreciable field emission performance [118].

3.1.2. Castor Oil

Castor oil obtained from castor beans is a popular triglyceride used in numerous formulations for cosmetics, paints, perfumes, etc. Awasthi and co-workers showed that it can also be employed for the synthesis of CNTs [119]. Multi-walled CNTs of diameters between 20 and 60 nm were produced from this precursor. When ammonia was added to the feed, bamboo-shaped N-MWCNTs with a notably straight structure were obtained. Finally, Raziah et al. made a successful attempt of synthesis of MWCNTs also of the bamboo morphology from castor oil at a reduced temperature of 300–400 °C (Figure 4b). To facilitate the transformation, the reaction was conducted under the influence of microwaves, which promoted the process [49].

3.1.3. Eucalyptus Oil

Y-zeolites as the catalyst substrate provided an excellent platform for CNT synthesis when eucalyptus oil was employed as the carbon source [120]. In this case, the material of predominantly single-walled CNT nature was obtained. The CNT had high purity and their diameter distribution spanned from 0.79 to 1.71 nm as probed by Raman spectroscopy. Since eucalyptus oil is comprised of many bicyclic chemical compounds (Figure 3, excluding camphor) [121], which resemble camphor, the product is characterized by a low degree of contamination due to the reasons already described above for camphor. Besides that, zeolites make suitable special constraint to the synthesis process, so that the process yields predominantly single-walled CNTs [122,123]. When the synthesis was conducted in the absence of these spatial limitations, multi-walled CNTs were obtained from eucalyptus oil [124]. A relatively high amount of defects and other carbonaceous species in that material can be justified by a surplus of catalyst used for the process (as compared with other works), which promotes side reactions giving other forms of carbon [113].

3.1.4. Palm Oil

Palm oil is derived from several oil palms, which have been cultivated for this purpose for thousands of years [125]. Its high abundance and replenishable nature make it an attractive feedstock for a wide range of processes. Suriani and co-workers were probably the first to report the successful synthesis of CNTs from such a source [126]. A mixture of vertically-aligned single- and multi-walled CNTs of average purity were obtained ($I_D/I_G = 0.52$, Figure 4c). The concept was later reproduced by others [127–130]. In one of these works, two types of catalytic systems based on Fe or Co were compared [128]. The material produced on the surface of the former metal was slightly purer, but both CNT fractions showed, in fact, a high level of adulteration. A similar outcome was obtained by Kudin et al., who also did not succeed in optimizing the conditions to get materials free from defects or unwanted species [129]. Finally, Robaiah and colleagues also produced CNTs of low crystallinity from this source [130]. Based on the reports of these efforts, it can be concluded that palm oil is not a good carbon reservoir for CNT synthesis. This most probably results from the incompatibility of the decomposition pathways of the chemicals from the feedstock. Palm oil seems to contain molecules, for which the reaction conditions favor transformation of feed into non-CNT species.

3.1.5. Sesame Oil

Sesame is considered to be the oldest oilseed crop known to mankind [131]. Kumar showed that it can be used as a precursor of multi-walled CNTs [132]. In a subsequent study by the same group, aligned and stacked N-MWCNTs were produced by spray pyrolysis carried out periodically. Three-layered structures of bamboo morphology were formed this way at the decelerating growth rate. A peculiar observation was made that the produced CNTs are branched (Figure 4d) [133]. The

significant content of the N-doping agent (acetonitrile) introduced defects ($I_D/I_G = 1.02$), which in turn enabled splitting of the CNTs. For the bifurcation to take place, thiophene was added to the reaction mixture. Readers are advised to direct attention to this contribution to get a more detailed description of the mechanism of the process.

3.1.6. Sunflower Oil

Another essential oil with notable global production is sunflower oil, which also served as a CNT precursor already [134]. The inclusion of ammonia into the feed enabled the synthesis of bamboo-shaped multi-walled CNTs. The quality of the obtained material was once more inferior and resembled that obtained from sesame or palm oil ($I_D/I_G \sim 1.00$), which strongly suggests that these precursors are not ideal for CNT synthesis. Unfortunately, there are no other reports of using sunflower oil for this purpose to validate this reasoning.

3.1.7. Turpentine Oil

A useful building block can be obtained by distillation of resins from pine trees found in Asia, Europe, and the USA. Turpentine oil, commonly used nowadays for organic synthesis, can also be employed for CNT manufacture using similar principles. Afre et al. were the first to show that such an opportunity is possible [135]. Vertically-aligned arrays of multi-walled CNTs were manufactured from this source. Although the product showed reasonable alignment of the constituting CNTs, the CNTs themselves were quite defected. What is more, the substrate was also found important. The obtained CNTs were of better quality when synthesized on quartz rather than on silicon. In the following work, the authors decided to probe the effect of temperature on the microstructure and chemical composition of the material [136]. As the temperature of the process was raised, the diameter of the CNTs increased along with the degree of structural perfection, judging on the provided I_D/I_G ratios. The yield of the synthesis, on the other hand, peaked at 700 °C. Below this temperature, the catalyst had a low activity whereas in high-temperature regime, the side-reactions were favored, which decreased the selectivity of the process towards CNT production.

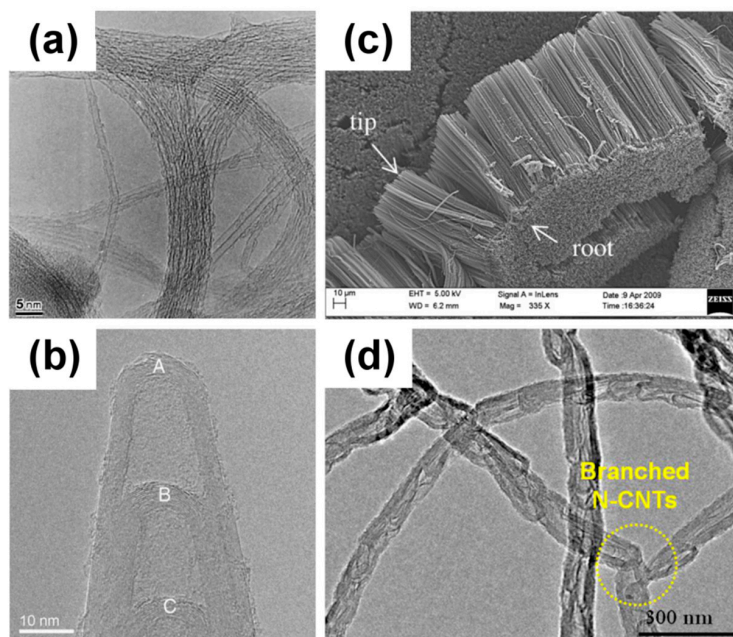


Figure 4. Examples of CNT materials obtained from bio-feedstocks in the form of (a) single-walled CNTs adapted from [114] with permission, (b) bamboo N-doped multi-walled CNTs adapted from [112] with permission, (c) aligned array of multi-walled CNTs adapted from [126] with permission, (d) branched bamboo N-doped multi-walled CNTs adapted from [133] with permission.

Furthermore, when the same bimetallic Fe-Co catalyst was employed under optimized conditions, preferential synthesis of single-walled CNTs from turpentine oil was found possible [137]. The authors observed that single-walled CNTs can be obtained at 850 °C and under the right flow rate of turpentine oil precursor into the reactor (0.1 g/min). Slower injection resulted in the production of multi-walled CNTs. Too fast introduction of precursor, on the other hand, increased the abundance of amorphous carbon. Moreover, CNTs synthesized from turpentine oil also proved to be able to assume the N-doped architecture upon the introduction of a nitrogen atom precursor into the feed [138]. The addition of 4-tert-butylpyridine increased the alignment of CNTs and transformed it into a bamboo form. Unfortunately, the obtained product had a high level of structural disorder—the I_D/I_G ratio was close to unity. Lastly, most of the CNTs obtained from turpentine oil demonstrated medium [139] to low [138] purity. We can hypothesize that the chemical composition of this feedstock is unsuitable or requires an appropriate catalytic system to produce high-quality CNTs. As demonstrated by Ghosh and colleagues [137], this is indeed possible when the parameters are tuned to yield single-walled CNTs. When a bimetallic catalyst composed of Fe and Co was employed, CNTs of such sort and high purity were obtained.

All the results described above are summarized in Table 1, which summarizes the effect of reaction conditions on the type and purity of the obtained CNT materials.

Table 1. Comparison of CNTs obtained from various bio-feedstocks using CVD.

Precursor	Conditions <i>T, cat.</i>	Product	Diameter [nm]	Quality I_D/I_G	Ref.
Camphor oil	750–850 °C, ferrocene	MWCNTs	30–75	0.89	[105]
	700–900 °C, ferrocene and aluminum isopropoxide	MWCNTs and SWCNTs	N/A	~0.90	[106]
	875 °C, ferrocene ¹	MWCNTs	N/A	0.791–0.998	[107]
Camphor	875 °C, ferrocene	MWCNTs and SWCNTs	25–50 (MWCNTs), ~1.2 (SWCNTs)	High purity	[47]
			10–50 (MWCNTs), ~1.2 (SWCNTs)	0.50	[108]
	800–1050 °C, ferrocene	MWCNTs and SWCNTs	20–40	N/A	[110]
	900 °C, ferrocene	MWCNTs	N/A	N/A	[111]
	850 °C, ferrocene	MWCNTs	N/A	N/A	[111]
	800 °C, ferrocene ²	N-MWCNTs and MWCNTs	10–50	0.66–0.98	[112]
	500–1000 °C, Fe-Co on Y-type zeolites		5–10 (MWCNTs), 0.8–1.2 (SWCNTs)	High purity (SWCNTs)	[114]
		MWCNTs and SWCNTs	~7	N/A	[115]
		MWCNTs	10–100	N/A	[116]
	850 °C, ferrocene	MWCNTs	30–80	N/A	[117]
	700–800 °C, Co and Fe-Co films	MWCNTs and CNF	35–150	~0.80–1.00	[118]
Castor oil	850 °C, ferrocene	MWCNTs	~80	N/A	[48]
	850 °C, ferrocene ³	MWCNTs and N-MWCNTs	20–80	N/A	[119]
	300–400 °C, ferrocene ⁴	MWCNTs	7–50	N/A	[49]
Eucalyptus oil	850 °C, Fe-Co on Y-type zeolites	SWCNTs	0.71–1.71	High purity	[120]
	700 °C, ferrocene	MWCNTs	15–25	~1.0	[124]
Palm oil	750 °C, ferrocene	MWCNTs and SWCNTs	0.6–1.2 (SWCNTs)	0.52	[126]
	700 °C, ferrocene	MWCNTs	~30	0.73	[127]
	750 °C, Fe and Co films	MWCNTs	~30 (Fe cat.), ~90 (Co cat.)	0.65–0.78	[128]
	700 °C, Ni and Co	MWCNTs	~20	N/A	[129]
	750–950 °C, ferrocene	MWCNTs	20–70	0.89–0.95	[130]

Table 1. Cont.

Precursor	Conditions <i>T, cat.</i>	Product	Diameter [nm]	Quality I_D/I_G	Ref.
Sesame oil	800 °C, ferrocene	MWCNTs	N/A	N/A	[132]
	900 °C, ferrocene ⁵	N-MWCNTs	30–60	1.02–1.26	[133]
Sunflower oil	800–850 °C, ferrocene ³	N-MWCNTs	20–40	~1.00	[134]
Turpentine oil	700 °C, ferrocene	MWCNTs	50–100	~0.50–1.00	[135]
	500–900 °C, Fe-Co	MWCNTs	N/A	~0.30–1.10	[136]
	800–850 °C, Fe-Co	MWCNTs and SWCNTs	0.8–1.5 (SWCNTs)	High purity (SWCNTs)	[137]
	700 °C, ferrocene ⁶	N-MWCNTs	7–30	~1.10	[138]
	700–900 °C, ferrocene	MWCNTs	15–45	0.245	[139]

N/A: Data was not available or the I_D/I_G ratio/diameter were difficult to determine from the data. ¹ Camphor was used to convert Fe-filled spherical-like graphene particles to CNTs. ² Dimethylformamide or octadecylamine were added to cause N-doping of CNTs. ³ Ammonia was added to cause N-doping of CNTs. ⁴ The process was assisted with microwave radiation. ⁵ Acetonitrile was added to cause N-doping of CNTs, thiophene was added as a branching agent. ⁶ 4-tert-butylpyridine was added to cause N-doping of CNTs.

3.2. Solid Precursors

Alternatively, CNTs can be obtained directly by thermal pyrolysis of biomass such as grass or leaves. Perhaps the first to report the former opportunity was Kang et al., who showed that appropriate processing of grass in the presence of oxygen transforms it to multi-walled CNTs [140]. Grass has a large content of vascular bundles composed of cellulose, hemicellulose, and lignin, which, as other polymers, can be dehydrated to give elemental carbon [141]. In such an approach, initially, the grass is dried, crumbled, and heated at about 250 °C in the air to disintegrate unwanted proteins and greases. Then, after washing the substrate from these residues, the CNT precursor is transferred to a closed container filled with a suitable amount of oxygen, which is subjected to cyclic heating to 600 °C for short periods of time, between which the depleted oxygen is replenished. After ca. 50 cycles, multi-walled CNTs are produced. The authors justify the successful synthesis by the presence of tubular carbohydrate structures in the parent material, which structurally resemble CNTs. As the polymer dehydration proceeds, vascular bundles contract about three times in diameter to give multi-walled CNTs of 30 to 50 nm diameter distribution. An appropriate amount of oxygen is deemed necessary to hamper many possible side-reactions, which could predominantly lead to char and tars rather than the desired nanostructure. Subsequent research by Goodell and co-workers confirm that the precursor structure is a key factor for the synthesis of CNTs [142,143]. In their work, multi-walled CNTs of 10 to 20 nm diameter were obtained from dehydration of cellulose microfibrils present in wood fiber after similar cyclic oxidation. Subsequently, they also validated the importance of the aforementioned pretreatment step at low temperature [144]. The results of the experiments showed that exposure of the raw material first to 240 °C increases the yield of the transformation and the microstructure of the obtained product by initial dehydration of cellulose and stabilization of lignin. Then, the dehydration leading to CNTs proceeds in a templated way to a larger extent. The mechanism, which summarizes the described findings is given in Figure 5.

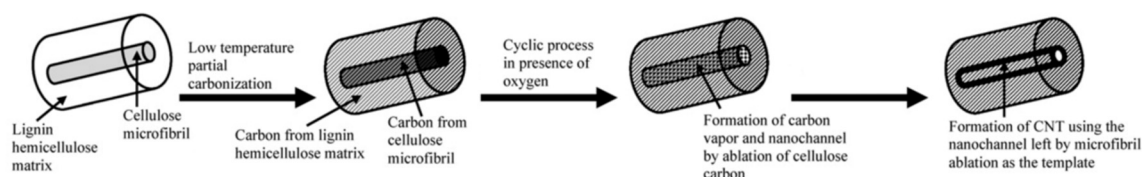


Figure 5. Mechanism of CNT synthesis directly from cellulose microfibrils adapted from [144] with permission.

Other oxidizing agents can also drive the transformation. In a recent study by Ma and colleagues, hydrolysis, and oxidation of grass worked as well, when it was put in contact with $H_2O_2/HNO_3/H_2SO_4$

mixture at 300 °C [145]. Interestingly, such a solvothermal approach gave predominantly graphene and carbon nanospheres when the temperature was increased to 400 °C and 500 °C, respectively. As the temperature is increased from ambient conditions, the CNTs are first unzipped to give graphene, which then undergoes restructuring to carbon nanospheres to minimize the surface energy by assuming a spherical shape.

Other plant shoots have also been documented as a viable source of carbon for CNT synthesis. The pioneering work came from Qu and co-workers who synthesized CNTs from fallen leaves of poplar [146]. Similarly to grass, such material also had to be pretreated. It was crumbled, dried, and heated at 250 °C in the air before carrying out the synthesis at 500 °C for a short time. The transformation was also conducted in the presence of oxygen and cycled multiple times to yield multi-walled CNTs of ca. 80 nm in diameter. Inclusion of catalyst was not required, as the leaves of poplar contained multiple heavy metal species such as Cu with a documented ability to facilitate CNT synthesis [147]. This concept was then extended by the same group when they engaged shoots of hyperaccumulator plants as feedstock for CNT synthesis. *Brassica juncea* L. [148] and *Sedum alfredii* H. [148,149] collected around copper or copper-zinc mines gave multi-walled CNTs of about 80 nm diameters as well, thanks to sufficient amount of catalyst available in the shoots. However, the inner diameter of CNTs synthesized from these sources was different—60 nm and 20 nm, respectively. The difference can be ascribed to the different morphology of the vascular bundles in these two plant shoot types. Moreover, one could also expect a different ratio of cellulose, hemicellulose, and lignin. Both of these factors make an impact on the microstructure and chemical composition of the obtained materials. Despite the indisputably lower quality of the synthesized CNTs (as compared with the material obtained from synthetic precursors), these proof of concept studies are very valuable because they validated that the direct synthesis of nanostructured carbon from such bio-feedstocks is possible.

4. Conclusions and Future Outlook

In summary, state-of-the-art of production methods of CNTs from several renewable resources was described. Camphor, castor, eucalyptus, palm, sesame, sunflower, and turpentine oils all proved to be a suitable reservoir of carbon, which after appropriate thermal treatment can give single- and multi-walled CNTs. Analogous processing of solid resources such as camphor, grass, and other plant shoots also resulted in the formation of nanocarbon material. This justifies that such alternative feedstocks have an application potential to replace petroleum-based sources, which are expensive, limited in amount and constrained to certain geographical locations. Using bio-feedstocks as described above can not only solve these problems but also align the civilization more with the philosophy of circular economy to eventually make the world more sustainable

Perhaps one of the most important findings of the reviewed studies is that the resources, which are rich in bicyclic compounds offer the product of the highest purity. This results from the fact that the thermal stability of such chemical compounds is much lower than that of other CNT precursors. As a consequence, it is possible to minimize the amount of employed catalysts for the process, the high content of which usually promotes the formation of carbonaceous contamination and the introduction of defects to the CNT structure. Furthermore, catalyst engineering such as immobilization of active metal species on zeolites or formation of bimetallic systems promoted synthesis of single-walled CNTs, which generally have a much higher implementation potential than multi-walled CNTs already present on the market in thousands of tonnes.

The published findings are very encouraging, but further research is required to reach the appropriate technology readiness level for commercial implementation. Beyond doubt, more insight is needed to understand the behavior of the catalyst and the mechanism of how bicyclic chemical compounds decompose as compared to typical simple precursors. For the former issue, only a small number of catalyst formulations (mostly ferrocene) and substrates have been evaluated. It would be helpful to conduct more experiments using recently discovered catalytic combinations (e.g., tungsten carbides), which may either be more efficient or even offer some chiral selectivity for bio-feedstock

transformations. For the latter factor, on the other hand, a more thorough understanding of how individual bicyclic species contribute to the CNT synthesis should be investigated. Essential oils commonly contain a large number of such chemical species types, so it would be important to find out which structures exactly are most appropriate for CNT synthesis. This, in turn, would be key for the determination of the best essential oil sort for CNT production at large scale and reduced cost.

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