

Review

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

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Received: 28 April 2020; Accepted: 16 May 2020; Published: 18 May 2020



**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].

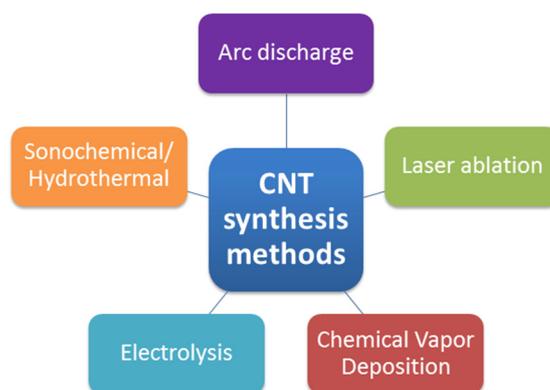
To drive the costs down, one can consider the synthesis of nanomaterials from renewable resources [42–44]. Bio-feedstocks such as biopolymers [45,46] or bio-derived chemical compounds like essential oils [47–49], which are available in high amounts [50–52], have a range of advantages as compared with 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, CO<sub>2</sub> 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 CO<sub>2</sub> 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.

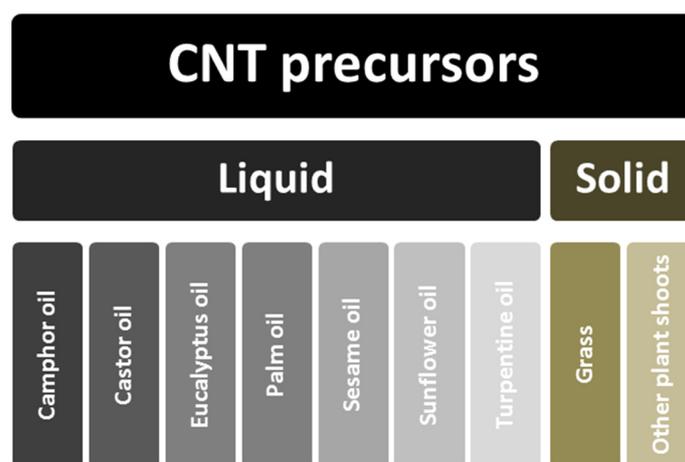


Figure 2. Key renewable bio-precursors for CNT synthesis.

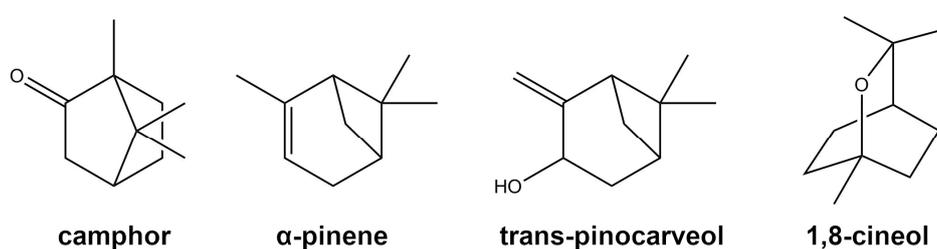
#### 3.1. Liquid Precursors

##### 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%),  $\alpha$ -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

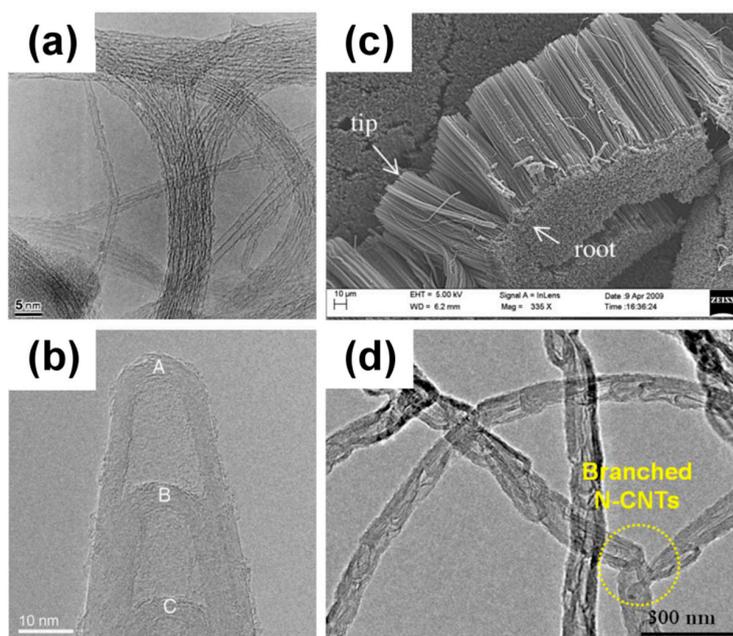
significant content of the N-doping agent (acetonitrile) introduced defects ( $I_D/I_G = 1.02$ ), which in turn enabled splitting of the CNTs. For the bifurcation to take place, thiophene was added to the reaction mixture. Readers are advised to direct attention to this contribution to get a more detailed 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 <sup>1</sup>	MWCNTs	N/A	0.791–0.998	[107]
Camphor	875 °C, ferrocene	MWCNTs and SWCNTs	25–50 (MWCNTs), ~1.2 (SWCNTs)	High purity	[47]
		MWCNTs and SWCNTs	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 <sup>2</sup>	N-MWCNTs and MWCNTs	10–50	0.66–0.98	[112]
	500–1000 °C, Fe-Co on Y-type zeolites	MWCNTs and SWCNTs	5–10 (MWCNTs), 0.8–1.2 (SWCNTs)	High purity (SWCNTs)	[114]
		MWCNTs	~7	N/A	[115]
	650–1100 °C, ferrocene	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]	
850 °C, ferrocene	MWCNTs	~80	N/A	[48]	
Castor oil	850 °C, ferrocene <sup>3</sup>	MWCNTs and N-MWCNTs	20–80	N/A	[119]
	300–400 °C, ferrocene <sup>4</sup>	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]

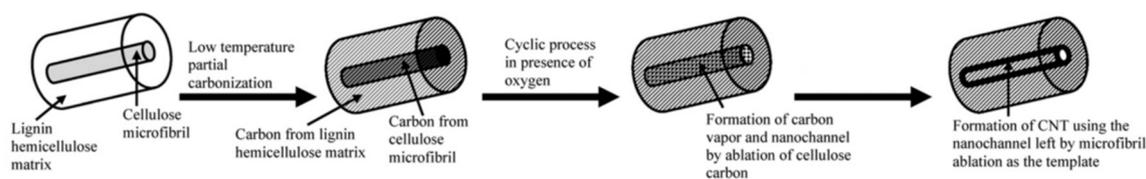
Table 1. Cont.

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 <sup>5</sup>	N-MWCNTs	30–60	1.02–1.26	[133]
Sunflower oil	800–850 °C, ferrocene <sup>3</sup>	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 <sup>6</sup>	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. <sup>1</sup> Camphor was used to convert Fe-filled spherical-like graphene particles to CNTs. <sup>2</sup> Dimethylformamide or octadecylamine were added to cause N-doping of CNTs. <sup>3</sup> Ammonia was added to cause N-doping of CNTs. <sup>4</sup> The process was assisted with microwave radiation. <sup>5</sup> Acetonitrile was added to cause N-doping of CNTs, thiophene was added as a branching agent. <sup>6</sup> 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.

**Author Contributions:** D.J. conceived the article idea, gathered the data, made the analysis, wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** D.J. gratefully acknowledges the financial support of the National Centre for Research and Development, Poland (under the Leader program, Grant agreement LIDER/0001/L-8/16/NCBR/2017).

**Conflicts of Interest:** The author declares no conflict of interest.

## References

1. Monthieux, M.; Kuznetsov, V.L. Who should be given the credit for the discovery of carbon nanotubes? *Carbon* **2006**, *44*, 1621–1623. [[CrossRef](#)]
2. Brady, G.J.; Way, A.J.; Safron, N.S.; Evensen, H.T.; Gopalan, P.; Arnold, M.S. Quasi-ballistic carbon nanotube array transistors with current density exceeding Si and GaAs. *Sci. Adv.* **2016**, *2*, e1601240. [[CrossRef](#)]
3. Muhulet, A.; Miculescu, F.; Voicu, S.I.; Schütt, F.; Thakur, V.K.; Mishra, Y.K. Fundamentals and scopes of doped carbon nanotubes towards energy and biosensing applications. *Mater. Today Energy* **2018**, *9*, 154–186. [[CrossRef](#)]
4. Bandaru, P.R. Electrical Properties and Applications of Carbon Nanotube Structures. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1239–1267. [[CrossRef](#)]
5. Ebbesen, T.W.; Lezec, H.J.; Hiura, H.; Bennett, J.W.; Ghaemi, H.F.; Thio, T. Electrical conductivity of individual carbon nanotubes. *Nature* **1996**, *382*, 54–56. [[CrossRef](#)]
6. Miao, M. Electrical conductivity of pure carbon nanotube yarns. *Carbon* **2011**, *49*, 3755–3761. [[CrossRef](#)]
7. Kumanek, B.; Janas, D. Thermal conductivity of carbon nanotube networks: A review. *J. Mater. Sci.* **2019**, *54*, 7397–7427. [[CrossRef](#)]
8. Lian, F.; Llinas, J.P.; Li, Z.; Estrada, D.; Pop, E. Thermal conductivity of chirality-sorted carbon nanotube networks. *Appl. Phys. Lett.* **2016**, *108*, 103101. [[CrossRef](#)]
9. Che, J.; Çagin, T.; Goddard, W.A. Thermal conductivity of carbon nanotubes. *Nanotechnology* **2000**, *11*, 65–69. [[CrossRef](#)]
10. Martin-Gallego, M.; Verdejo, R.; Khayet, M.; de Zarate, J.M.O.; Essalhi, M.; Lopez-Manchado, M.A. Thermal conductivity of carbon nanotubes and graphene in epoxy nanofluids and nanocomposites. *Nanoscale Res. Lett.* **2011**, *6*, 610. [[CrossRef](#)]
11. Arash, B.; Wang, Q.; Varadan, V.K. Mechanical properties of carbon nanotube/polymer composites. *Sci. Rep.* **2014**, *4*, 6479. [[CrossRef](#)] [[PubMed](#)]
12. Sammalkorpi, M.; Krasheninnikov, A.; Kuronen, A.; Nordlund, K.; Kaski, K. Mechanical properties of carbon nanotubes with vacancies and related defects. *Phys. Rev. B* **2004**, *70*, 245416. [[CrossRef](#)]
13. Kulik, A.J.; Kis, A.; Lukic, B.; Lee, K.; Forró, L. Mechanical Properties of Carbon Nanotubes. In *Fundamentals of Friction and Wear*; Gnecco, E., Meyer, E., Eds.; Springer: Berlin/Heidelberg, Germany, 2007; pp. 583–600. [[CrossRef](#)]
14. Coleman, J.N.; Khan, U.; Blau, W.J.; Gun'ko, Y.K. Small but strong: A review of the mechanical properties of carbon nanotube–polymer composites. *Carbon* **2006**, *44*, 1624–1652. [[CrossRef](#)]
15. Yu, M.-F.; Files, B.S.; Arepalli, S.; Ruoff, R.S. Tensile Loading of Ropes of Single Wall Carbon Nanotubes and their Mechanical Properties. *Phys. Rev. Lett.* **2000**, *84*, 5552–5555. [[CrossRef](#)] [[PubMed](#)]
16. Brozena, A.H.; Kim, M.; Powell, L.R.; Wang, Y. Controlling the optical properties of carbon nanotubes with organic colour-centre quantum defects. *Nat. Rev. Chem.* **2019**, *3*, 375–392. [[CrossRef](#)]
17. He, X.; Htoon, H.; Doorn, S.K.; Pernice, W.H.P.; Pyatkov, F.; Krupke, R.; Jeantet, A.; Chassagneux, Y.; Voisin, C. Carbon nanotubes as emerging quantum-light sources. *Nat. Mater.* **2018**, *17*, 663–670. [[CrossRef](#)]
18. Neelgund, G.M.; Oki, A. Advancement in Photothermal Effect of Carbon Nanotubes by Grafting of Poly(amidoamine) and Deposition of CdS Nanocrystallites. *Ind. Eng. Chem. Res.* **2018**, *57*, 7826–7833. [[CrossRef](#)]

19. Farrera, C.; Torres Andón, F.; Feliu, N. Carbon Nanotubes as Optical Sensors in Biomedicine. *ACS Nano* **2017**, *11*, 10637–10643. [\[CrossRef\]](#)
20. Lin, M.F.; Shung, K.W.K. Plasmons and optical properties of carbon nanotubes. *Phys. Rev. B* **1994**, *50*, 17744–17747. [\[CrossRef\]](#)
21. Kataura, H.; Kumazawa, Y.; Maniwa, Y.; Umezū, I.; Suzuki, S.; Ohtsuka, Y.; Achiba, Y. Optical properties of single-wall carbon nanotubes. *Synth. Met.* **1999**, *103*, 2555–2558. [\[CrossRef\]](#)
22. Gaviria Rojas, W.A.; Hersam, M.C. Chirality-Enriched Carbon Nanotubes for Next-Generation Computing. *Adv. Mater.* **2020**, *n/a*, 1905654. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Peng, L.-M.; Zhang, Z.; Wang, S. Carbon nanotube electronics: Recent advances. *Mater. Today* **2014**, *17*, 433–442. [\[CrossRef\]](#)
24. Avouris, P.; Appenzeller, J.; Martel, R.; Wind, S.J. Carbon nanotube electronics. *Proc. IEEE* **2003**, *91*, 1772–1784. [\[CrossRef\]](#)
25. Cwirzen, A.; Habermehl-Cwirzen, K.; Penttala, V. Surface decoration of carbon nanotubes and mechanical properties of cement/carbon nanotube composites. *Adv. Cem. Res.* **2008**, *20*, 65–73. [\[CrossRef\]](#)
26. Chen, S.J.; Collins, F.G.; Macleod, A.J.N.; Pan, Z.; Duan, W.H.; Wang, C.M. Carbon nanotube–cement composites: A retrospect. *IES J. Part A Civ. Struct. Eng.* **2011**, *4*, 254–265. [\[CrossRef\]](#)
27. Yu, X.; Kwon, E. A carbon nanotube/cement composite with piezoresistive properties. *Smart Mater. Struct.* **2009**, *18*, 055010. [\[CrossRef\]](#)
28. Simon, J.; Flahaut, E.; Golzio, M. Overview of Carbon Nanotubes for Biomedical Applications. *Materials* **2019**, *12*, 624. [\[CrossRef\]](#)
29. Saliev, T. The advances in biomedical applications of carbon nanotubes. *C—J. Carbon Res.* **2019**, *5*, 29. [\[CrossRef\]](#)
30. Chen, Z.; Zhang, A.; Wang, X.; Zhu, J.; Fan, Y.; Yu, H.; Yang, Z. The advances of carbon nanotubes in cancer diagnostics and therapeutics. *J. Nanomater.* **2017**, *2017*. [\[CrossRef\]](#)
31. Janas, D. Towards monochiral carbon nanotubes: A review of progress in the sorting of single-walled carbon nanotubes. *Mater. Chem. Front.* **2018**, *2*, 36–63. [\[CrossRef\]](#)
32. Tersoff, J. Contact resistance of carbon nanotubes. *Appl. Phys. Lett.* **1999**, *74*, 2122–2124. [\[CrossRef\]](#)
33. Walker, J.S.; Fagan, J.A.; Biacchi, A.J.; Kuehl, V.A.; Searles, T.A.; Hight Walker, A.R.; Rice, W.D. Global Alignment of Solution-Based Single-Wall Carbon Nanotube Films via Machine-Vision Controlled Filtration. *Nano Lett.* **2019**, *19*, 7256–7264. [\[CrossRef\]](#) [\[PubMed\]](#)
34. Komatsu, N.; Nakamura, M.; Ghosh, S.; Kim, D.; Chen, H.; Katagiri, A.; Yomogida, Y.; Gao, W.; Yanagi, K.; Kono, J. Groove-Assisted Global Spontaneous Alignment of Carbon Nanotubes in Vacuum Filtration. *Nano Lett.* **2020**, *20*, 2332–2338. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Cheng, Z.; Al Zaki, A.; Hui, J.Z.; Muzykantov, V.R.; Tsourkas, A. Multifunctional nanoparticles: Cost versus benefit of adding targeting and imaging capabilities. *Science* **2012**, *338*, 903–910. [\[CrossRef\]](#)
36. Zhuo, C.; Levendis, Y.A. Upcycling waste plastics into carbon nanomaterials: A review. *J. Appl. Polym. Sci.* **2014**, *131*. [\[CrossRef\]](#)
37. Charitidis, C.A.; Georgiou, P.; Koklioti, M.A.; Trompeta, A.-F.; Markakis, V. Manufacturing nanomaterials: From research to industry. *Manuf. Rev.* **2014**, *1*, 11. [\[CrossRef\]](#)
38. Chen, Z.-G.; Han, G.; Yang, L.; Cheng, L.; Zou, J. Nanostructured thermoelectric materials: Current research and future challenge. *Prog. Nat. Sci. Mater. Int.* **2012**, *22*, 535–549. [\[CrossRef\]](#)
39. Alvarez, P.J.J.; Chan, C.K.; Elimelech, M.; Halas, N.J.; Villagrán, D. Emerging opportunities for nanotechnology to enhance water security. *Nat. Nanotechnol.* **2018**, *13*, 634–641. [\[CrossRef\]](#)
40. Qu, X.; Alvarez, P.J.J.; Li, Q. Applications of nanotechnology in water and wastewater treatment. *Water Res.* **2013**, *47*, 3931–3946. [\[CrossRef\]](#)
41. Blackburn, J.L.; Ferguson, A.J.; Cho, C.; Grunlan, J.C. Carbon-Nanotube-Based Thermoelectric Materials and Devices. *Adv. Mater.* **2018**, *30*, 1704386. [\[CrossRef\]](#)
42. Baccile, N. Nanomaterials from Renewable Resources. In *Nanomaterials: A Danger or a Promise? A Chemical and Biological Perspective*; Brayner, R., Fiévet, F., Coradin, T., Eds.; Springer: London, UK, 2013; pp. 335–356. [\[CrossRef\]](#)
43. Vivekanandhan, S.; Schreiber, M.; Muthuramkumar, S.; Misra, M.; Mohanty, A.K. Carbon nanotubes from renewable feedstocks: A move toward sustainable nanofabrication. *J. Appl. Polym. Sci.* **2017**, *134*. [\[CrossRef\]](#)

44. John, G.; Vemula, P.K. Design and development of soft nanomaterials from biobased amphiphiles. *Soft Matter* **2006**, *2*, 909–914. [[CrossRef](#)]
45. Shaghaleh, H.; Xu, X.; Wang, S. Current progress in production of biopolymeric materials based on cellulose, cellulose nanofibers, and cellulose derivatives. *RSC Adv.* **2018**, *8*, 825–842. [[CrossRef](#)]
46. Boneberg, B.S.; Machado, G.D.; Santos, D.F.; Gomes, F.; Faria, D.J.; Gomes, L.A.; Santos, F.A. Biorefinery of lignocellulosic biopolymers. *Rev. Eletrônica Científica Da UERGS* **2016**, *2*, 79–100. [[CrossRef](#)]
47. Kumar, M.; Ando, Y. Camphor—a botanical precursor producing garden of carbon nanotubes. *Diam. Relat. Mater.* **2003**, *12*, 998–1002. [[CrossRef](#)]
48. Porro, S.; Musso, S.; Giorcelli, M.; Tagliaferro, A.; Dalal, S.H.; Teo, K.B.K.; Jefferson, D.A.; Milne, W.I. Study of CNTs and nanographite grown by thermal CVD using different precursors. *J. Non-Cryst. Solids* **2006**, *352*, 1310–1313. [[CrossRef](#)]
49. Raziah, A.Z.; Junizah, A.R.; Saifuddin, N. Synthesis of carbon nanotubes using natural carbon precursor: Castor oil. *AIP Conf. Proc.* **2012**, *1482*, 564–567. [[CrossRef](#)]
50. Holmgren, J.; Gosling, C.; Couch, K.; Kalnes, T.; Marker, T.; McCall, M.; Marinangeli, R. Refining biofeedstock innovations. *Pet. Technol. Q.* **2007**, *12*, 119.
51. Awasthi, A.; Bhaskar, T. Chapter 11—Combustion of Lignocellulosic Biomass. In *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels (Second Edition)*; Pandey, A., Larroche, C., Dussap, C.-G., Gnansounou, E., Khanal, S.K., Ricke, S., Eds.; Academic Press: Cambridge, MA, USA, 2019; pp. 267–284. [[CrossRef](#)]
52. Ge, X.; Chang, C.; Zhang, L.; Cui, S.; Luo, X.; Hu, S.; Qin, Y.; Li, Y. Chapter Five—Conversion of Lignocellulosic Biomass Into Platform Chemicals for Biobased Polyurethane Application. In *Advances in Bioenergy*; Li, Y., Ge, X., Eds.; Elsevier: Amsterdam, The Netherlands, 2018; Volume 3, pp. 161–213.
53. Abdullah, N.; Sulaiman, F. The oil palm wastes in Malaysia. *Biomass Now-Sustain. Growth Use* **2013**, *1*, 75–93.
54. Dungani, R.; Aditiawati, P.; Aprilia, S.; Yuniarti, K.; Karliati, T.; Suwandhi, I.; Sumardi, I. Biomaterial from Oil Palm Waste: Properties, Characterization and Applications. *Palm Oil* **2018**, *31*. [[CrossRef](#)]
55. Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354*, 56–58. [[CrossRef](#)]
56. Shi, Z.; Lian, Y.; Liao, F.H.; Zhou, X.; Gu, Z.; Zhang, Y.; Iijima, S.; Li, H.; Yue, K.T.; Zhang, S.-L. Large scale synthesis of single-wall carbon nanotubes by arc-discharge method. *J. Phys. Chem. Solids* **2000**, *61*, 1031–1036. [[CrossRef](#)]
57. Huang, L.; Wu, B.; Chen, J.; Xue, Y.; Liu, Y.; Kajiura, H.; Li, Y. Synthesis of single-walled carbon nanotubes by an arc-discharge method using selenium as a promoter. *Carbon* **2011**, *49*, 4792–4800. [[CrossRef](#)]
58. Arora, N.; Sharma, N.N. Arc discharge synthesis of carbon nanotubes: Comprehensive review. *Diam. Relat. Mater.* **2014**, *50*, 135–150. [[CrossRef](#)]
59. Iijima, S.; Ichihashi, T. Single-shell carbon nanotubes of 1-nm diameter. *Nature* **1993**, *363*, 603–605. [[CrossRef](#)]
60. Bethune, D.S.; Kiang, C.H.; de Vries, M.S.; Gorman, G.; Savoy, R.; Vazquez, J.; Beyers, R. Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls. *Nature* **1993**, *363*, 605–607. [[CrossRef](#)]
61. Zhao, J.; Su, Y.; Yang, Z.; Wei, L.; Wang, Y.; Zhang, Y. Arc synthesis of double-walled carbon nanotubes in low pressure air and their superior field emission properties. *Carbon* **2013**, *58*, 92–98. [[CrossRef](#)]
62. Das, R.; Shahnavaz, Z.; Ali, M.E.; Islam, M.M.; Abd Hamid, S.B. Can We Optimize Arc Discharge and Laser Ablation for Well-Controlled Carbon Nanotube Synthesis? *Nanoscale Res. Lett.* **2016**, *11*, 510. [[CrossRef](#)]
63. Arepalli, S. Laser Ablation Process for Single-Walled Carbon Nanotube Production. *J. Nanosci. Nanotechnol.* **2004**, *4*, 317–325. [[CrossRef](#)]
64. Zhang, Y.; Gu, H.; Iijima, S. Single-wall carbon nanotubes synthesized by laser ablation in a nitrogen atmosphere. *Appl. Phys. Lett.* **1998**, *73*, 3827–3829. [[CrossRef](#)]
65. Scott, C.D.; Arepalli, S.; Nikolaev, P.; Smalley, R.E. Growth mechanisms for single-wall carbon nanotubes in a laser-ablation process. *Appl. Phys. A* **2001**, *72*, 573–580. [[CrossRef](#)]
66. Yudasaka, M.; Komatsu, T.; Ichihashi, T.; Iijima, S. Single-wall carbon nanotube formation by laser ablation using double-targets of carbon and metal. *Chem. Phys. Lett.* **1997**, *278*, 102–106. [[CrossRef](#)]
67. Wu, H.; Li, Z.; Ji, D.; Liu, Y.; Li, L.; Yuan, D.; Zhang, Z.; Ren, J.; Lefler, M.; Wang, B.; et al. One-pot synthesis of nanostructured carbon materials from carbon dioxide via electrolysis in molten carbonate salts. *Carbon* **2016**, *106*, 208–217. [[CrossRef](#)]
68. Ren, J.; Li, F.-F.; Lau, J.; González-Urbina, L.; Licht, S. One-Pot Synthesis of Carbon Nanofibers from CO<sub>2</sub>. *Nano Lett.* **2015**, *15*, 6142–6148. [[CrossRef](#)]

69. Novoselova, I.A.; Oliinyk, N.F.; Volkov, S.V.; Konchits, A.A.; Yanchuk, I.B.; Yefanov, V.S.; Kolesnik, S.P.; Karpets, M.V. Electrolytic synthesis of carbon nanotubes from carbon dioxide in molten salts and their characterization. *Phys. E Low-Dimens. Syst. Nanostruct.* **2008**, *40*, 2231–2237. [[CrossRef](#)]
70. Hu, L.; Song, Y.; Ge, J.; Zhu, J.; Han, Z.; Jiao, S. Electrochemical deposition of carbon nanotubes from CO<sub>2</sub> in CaCl<sub>2</sub>–NaCl-based melts. *J. Mater. Chem. A* **2017**, *5*, 6219–6225. [[CrossRef](#)]
71. Johnson, M.; Ren, J.; Lefler, M.; Licht, G.; Vicini, J.; Liu, X.; Licht, S. Carbon nanotube wools made directly from CO<sub>2</sub> by molten electrolysis: Value driven pathways to carbon dioxide greenhouse gas mitigation. *Mater. Today Energy* **2017**, *5*, 230–236. [[CrossRef](#)]
72. Raja, M.; Ryu, S.H. Synthesis of Carbon Nanotube Through Sonochemical Process Under Ambient Conditions. *J. Nanosci. Nanotechnol.* **2009**, *9*, 5940–5945. [[CrossRef](#)]
73. Gogotsi, Y.; Libera, J.A.; Yoshimura, M. Hydrothermal synthesis of multiwall carbon nanotubes. *J. Mater. Res.* **2011**, *15*, 2591–2594. [[CrossRef](#)]
74. Dai, K.; Zhang, X.; Fan, K.; Peng, T.; Wei, B. Hydrothermal synthesis of single-walled carbon nanotube–TiO<sub>2</sub> hybrid and its photocatalytic activity. *Appl. Surf. Sci.* **2013**, *270*, 238–244. [[CrossRef](#)]
75. Kumar, D.; Singh, K.; Verma, V.; Bhatti, H.S. Low-temperature hydrothermal synthesis and functionalization of multiwalled carbon nanotubes. *Indian J. Phys.* **2016**, *90*, 139–148. [[CrossRef](#)]
76. Kumar, M.; Ando, Y. Chemical Vapor Deposition of Carbon Nanotubes: A Review on Growth Mechanism and Mass Production. *J. Nanosci. Nanotechnol.* **2010**, *10*, 3739–3758. [[CrossRef](#)] [[PubMed](#)]
77. Öncel, Ç.; Yürüm, Y. Carbon Nanotube Synthesis via the Catalytic CVD Method: A Review on the Effect of Reaction Parameters. *Fuller. Nanotub. Carbon Nanostruct.* **2006**, *14*, 17–37. [[CrossRef](#)]
78. Sinnott, S.B.; Andrews, R.; Qian, D.; Rao, A.M.; Mao, Z.; Dickey, E.C.; Derbyshire, F. Model of carbon nanotube growth through chemical vapor deposition. *Chem. Phys. Lett.* **1999**, *315*, 25–30. [[CrossRef](#)]
79. Lim, Y.D.; Avramchuck, A.V.; Grapov, D.; Tan, C.W.; Tay, B.K.; Aditya, S.; Labunov, V. Enhanced Carbon Nanotubes Growth Using Nickel/Ferrocene-Hybridized Catalyst. *ACS Omega* **2017**, *2*, 6063–6071. [[CrossRef](#)] [[PubMed](#)]
80. Igbokwe, E.C.; Daramola, M.O.; Iyuke, S.E. Production of carbon nanotube yarns via floating catalyst chemical vapor deposition: Effect of synthesis temperature on electrical conductivity. *Results Phys.* **2019**, *15*, 102705. [[CrossRef](#)]
81. Zhang, J.; Tu, R.; Goto, T. Preparation of carbon nanotube by rotary CVD on Ni nano-particle precipitated cBN using nickelocene as a precursor. *Mater. Lett.* **2011**, *65*, 367–370. [[CrossRef](#)]
82. Weissker, U.; Hampel, S.; Leonhardt, A.; Büchner, B. Carbon nanotubes filled with ferromagnetic materials. *Materials* **2010**, *3*, 4387–4427. [[CrossRef](#)]
83. Janas, D.; Koziol, K.K. Carbon nanotube fibers and films: Synthesis, applications and perspectives of the direct-spinning method. *Nanoscale* **2016**, *8*, 19475–19490. [[CrossRef](#)]
84. Hussein, M.Z.; Zakarya, S.A.; Sarijo, S.H.; Zainal, Z. Parameter optimisation of carbon nanotubes synthesis via hexane decomposition over minerals generated from Anadara granosa shells as the catalyst support. *J. Nanomater.* **2012**, *2012*, 525616. [[CrossRef](#)]
85. Ibrahim, R.; Hussein, M.Z.; Yusof, N.A.; Abu Bakar, F. Carbon Nanotube-Quicklime Nanocomposites Prepared Using a Nickel Catalyst Supported on Calcium Oxide Derived from Carbonate Stones. *Nanomaterials* **2019**, *9*, 1239. [[CrossRef](#)] [[PubMed](#)]
86. Zhang, Q.; Liu, Y.; Hu, L.; Qian, W.-Z.; Luo, G.-H.; Wei, F. Synthesis of thin-walled carbon nanotubes from methane by changing the Ni/Mo ratio in a Ni/Mo/MgO catalyst. *New Carbon Mater.* **2008**, *23*, 319–325. [[CrossRef](#)]
87. Ramírez Rodríguez, F.; López, B.L.; Giraldo, L.F. Single Wall Carbon Nanotubes Synthesis through Methane Chemical Vapor Deposition over MCM-41–Co Catalysts: Variables Optimization. *C—J. Carbon Res.* **2018**, *4*, 37. [[CrossRef](#)]
88. Roy, S.; David-Pur, M.; Hanein, Y. Carbon nanotube growth inhibition in floating catalyst based chemical vapor deposition and its application in flexible circuit fabrication. *Carbon* **2017**, *116*, 40–49. [[CrossRef](#)]
89. Manawi, Y.M.; Ihsanullah; Samara, A.; Al-Ansari, T.; Atieh, M.A. A Review of Carbon Nanomaterials' Synthesis via the Chemical Vapor Deposition (CVD) Method. *Materials* **2018**, *11*, 822. [[CrossRef](#)]
90. Yahyazadeh, A.; Khoshandam, B. Carbon nanotube synthesis via the catalytic chemical vapor deposition of methane in the presence of iron, molybdenum, and iron–molybdenum alloy thin layer catalysts. *Results Phys.* **2017**, *7*, 3826–3837. [[CrossRef](#)]

91. Maruyama, T.; Kondo, H.; Ghosh, R.; Kozawa, A.; Naritsuka, S.; Iizumi, Y.; Okazaki, T.; Iijima, S. Single-walled carbon nanotube synthesis using Pt catalysts under low ethanol pressure via cold-wall chemical vapor deposition in high vacuum. *Carbon* **2016**, *96*, 6–13. [[CrossRef](#)]
92. Li, Y.-L.; Zhang, L.-H.; Zhong, X.-H.; Windle, A.H. Synthesis of high purity single-walled carbon nanotubes from ethanol by catalytic gas flow CVD reactions. *Nanotechnology* **2007**, *18*, 225604. [[CrossRef](#)]
93. Bystrzejewski, M.; Huczko, A.; Byszewski, P.; Domańska, M.; Rümmele, M.H.; Gemming, T.; Lange, H. Systematic Studies on Carbon Nanotubes Synthesis from Aliphatic Alcohols by the CVD Floating Catalyst Method. *Fuller. Nanotub. Carbon Nanostruct.* **2009**, *17*, 298–307. [[CrossRef](#)]
94. Ordoñez-Casanova, E.G.; Román-Aguirre, M.; Aguilar-Elguezabal, A.; Espinosa-Magaña, F. Synthesis of carbon nanotubes of few walls using aliphatic alcohols as a carbon source. *Materials* **2013**, *6*, 2534–2542. [[CrossRef](#)]
95. Gomez, J.A.; Marquez, A.; Pérez, A.; Duarte-Moller, A. Simple method to synthesize functionalized carbon nanotubes employing cobalt nitrate and acetone by using spray pyrolysis deposition technique. *Adv. Mater. Sci. Eng.* **2012**, *2012*, 258673. [[CrossRef](#)]
96. Melezhik, A.V.; Smykov, M.A.; Filatova, E.Y.; Shuklinov, A.V.; Stolyarov, R.A.; Larionova, I.S.; Tkachov, A.G. Synthesis of carbon nanotubes from acetone. *Theor. Found. Chem. Eng.* **2013**, *47*, 435–443. [[CrossRef](#)]
97. Luo, T.; Liu, J.; Chen, L.; Zeng, S.; Qian, Y. Synthesis of helically coiled carbon nanotubes by reducing ethyl ether with metallic zinc. *Carbon* **2005**, *43*, 755–759. [[CrossRef](#)]
98. Hou, B.; Xiang, R.; Inoue, T.; Einarsson, E.; Chiashi, S.; Shiomi, J.; Miyoshi, A.; Maruyama, S. Decomposition of ethanol and dimethyl ether during chemical vapor deposition synthesis of single-walled carbon nanotubes. *Jpn. J. Appl. Phys.* **2011**, *50*, 065101.
99. Tang, C.; Bando, Y.; Golberg, D.; Xu, F. Structure and nitrogen incorporation of carbon nanotubes synthesized by catalytic pyrolysis of dimethylformamide. *Carbon* **2004**, *42*, 2625–2633. [[CrossRef](#)]
100. Prasek, J.; Drbohlavova, J.; Chomoucka, J.; Hubalek, J.; Jasek, O.; Adam, V.; Kizek, R. Methods for carbon nanotubes synthesis—Review. *J. Mater. Chem.* **2011**, *21*, 15872–15884. [[CrossRef](#)]
101. Rahman, G.; Najaf, Z.; Mehmood, A.; Bilal, S.; Mian, S.A.; Ali, G. An overview of the recent progress in the synthesis and applications of carbon nanotubes. *C—J. Carbon Res.* **2019**, *5*, 3. [[CrossRef](#)]
102. Carole, E.B.; Cedric, B. Carbon Nanotube Synthesis: A Review. *Int. J. Chem. React. Eng.* **2005**, *3*. [[CrossRef](#)]
103. Zhang, B.; Piao, G.; Zhang, J.; Bu, C.; Xie, H.; Wu, B.; Kobayashi, N. Synthesis of carbon nanotubes from conventional biomass-based gasification gas. *Fuel Process. Technol.* **2018**, *180*, 105–113. [[CrossRef](#)]
104. Januszewicz, K.; Klugmann-Radziemska, E. Synthesis of reduced graphene oxide nanosheets using nanofibers from methane and biogas thermal decomposition with various catalysts. *Chem. Pap.* **2018**, *72*, 1991–1999. [[CrossRef](#)]
105. TermehYousefi, A.; Bagheri, S.; Shinji, K.; Rouhi, J.; Rusop Mahmood, M.; Ikeda, S. Fast synthesis of multilayer carbon nanotubes from camphor oil as an energy storage material. *BioMed Res. Int.* **2014**, *2014*. [[CrossRef](#)] [[PubMed](#)]
106. Salifairus, M.; Rusop, M. Synthesis of carbon nanotubes by chemical vapour deposition of camphor oil over ferrocene and aluminum isopropoxide catalyst. *Adv. Mater. Res.* **2013**, *667*, 213–217. [[CrossRef](#)]
107. Shamsudin, M.S.; Mohammad, M.; Zobir, S.A.M.; Asli, N.A.; Bakar, S.A.; Abdullah, S.; Yahya, S.Y.S.; Mahmood, M.R. Synthesis and nucleation-growth mechanism of almost catalyst-free carbon nanotubes grown from Fe-filled sphere-like graphene-shell surface. *J. Nanostruct. Chem.* **2013**, *3*, 13. [[CrossRef](#)]
108. Kumar, M.; Ando, Y. Single-wall and multi-wall carbon nanotubes from camphor—A botanical hydrocarbon. *Diam. Relat. Mater.* **2003**, *12*, 1845–1850. [[CrossRef](#)]
109. Mukhopadhyay, K.; Krishna, K.M.; Sharon, M. Fullerenes from camphor: A natural source. *Phys. Rev. Lett.* **1994**, *72*, 3182–3185. [[CrossRef](#)]
110. Kumar, M.; Ando, Y. A simple method of producing aligned carbon nanotubes from an unconventional precursor—Camphor. *Chem. Phys. Lett.* **2003**, *374*, 521–526. [[CrossRef](#)]
111. Kumar, M.; Kakamu, K.; Okazaki, T.; Ando, Y. Field emission from camphor—Pyrolyzed carbon nanotubes. *Chem. Phys. Lett.* **2004**, *385*, 161–165. [[CrossRef](#)]
112. Ghosh, K.; Kumar, M.; Maruyama, T.; Ando, Y. Micro-structural, electron-spectroscopic and field-emission studies of carbon nitride nanotubes grown from cage-like and linear carbon sources. *Carbon* **2009**, *47*, 1565–1575. [[CrossRef](#)]

113. Boncel, S.; Pattinson, S.W.; Geiser, V.; Shaffer, M.S.; Koziol, K.K. En route to controlled catalytic CVD synthesis of densely packed and vertically aligned nitrogen-doped carbon nanotube arrays. *Beilstein J. Nanotechnol.* **2014**, *5*, 219–233. [[CrossRef](#)]
114. Kumar, M.; Ando, Y. Controlling the diameter distribution of carbon nanotubes grown from camphor on a zeolite support. *Carbon* **2005**, *43*, 533–540. [[CrossRef](#)]
115. Musso, S.; Fanchini, G.; Tagliaferro, A. Growth of vertically aligned carbon nanotubes by CVD by evaporation of carbon precursors. *Diam. Relat. Mater.* **2005**, *14*, 784–789. [[CrossRef](#)]
116. Musso, S.; Porro, S.; Giorcelli, M.; Chiodoni, A.; Ricciardi, C.; Tagliaferro, A. Macroscopic growth of carbon nanotube mats and their mechanical properties. *Carbon* **2007**, *45*, 1133–1136. [[CrossRef](#)]
117. Pavese, M.; Musso, S.; Bianco, S.; Giorcelli, M.; Pugno, N. An analysis of carbon nanotube structure wettability before and after oxidation treatment. *J. Phys. Condens. Matter* **2008**, *20*, 474206. [[CrossRef](#)]
118. Somani, S.P.; Somani, P.R.; Tanemura, M.; Lau, S.P.; Umeno, M. Carbon nanofibers and multiwalled carbon nanotubes from camphor and their field electron emission. *Curr. Appl. Phys.* **2009**, *9*, 144–150. [[CrossRef](#)]
119. Awasthi, K.; Kumar, R.; Raghubanshi, H.; Awasthi, S.; Pandey, R.; Singh, D.; Yadav, T.; Srivastava, O. Synthesis of nano-carbon (nanotubes, nanofibres, graphene) materials. *Bull. Mater. Sci.* **2011**, *34*, 607. [[CrossRef](#)]
120. Ghosh, P.; Afre, R.A.; Soga, T.; Jimbo, T. A simple method of producing single-walled carbon nanotubes from a natural precursor: Eucalyptus oil. *Mater. Lett.* **2007**, *61*, 3768–3770. [[CrossRef](#)]
121. Sebei, K.; Sakouhi, F.; Herchi, W.; Khouja, M.L.; Boukhchina, S. Chemical composition and antibacterial activities of seven Eucalyptus species essential oils leaves. *Biol Res.* **2015**, *48*, 7. [[CrossRef](#)]
122. Okamoto, A.; Shinohara, H. Control of diameter distribution of single-walled carbon nanotubes using the zeolite-CCVD method at atmospheric pressure. *Carbon* **2005**, *43*, 431–436. [[CrossRef](#)]
123. Zhao, W.; Basnet, B.; Kim, I.J. Carbon nanotube formation using zeolite template and applications. *J. Adv. Ceram.* **2012**, *1*, 179–193. [[CrossRef](#)]
124. Ghosh, P.; Soga, T.; Tanemura, M.; Zamri, M.; Jimbo, T.; Katoh, R.; Sumiyama, K. Vertically aligned carbon nanotubes from natural precursors by spray pyrolysis method and their field electron emission properties. *Appl. Phys. A* **2009**, *94*, 51–56. [[CrossRef](#)]
125. Henson, I.E. 1—A Brief History of the Oil Palm. In *Palm Oil*; Lai, O.-M., Tan, C.-P., Akoh, C.C., Eds.; AOCS Press: Urbana, IL, USA, 2012; pp. 1–29. [[CrossRef](#)]
126. Suriani, A.B.; Azira, A.A.; Nik, S.F.; Md Nor, R.; Rusop, M. Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor. *Mater. Lett.* **2009**, *63*, 2704–2706. [[CrossRef](#)]
127. Maryam, M.; Suriani, A.; Shamsudin, M.; Rusop Mahmood, M. Synthesis of Carbon Nanotubes from Palm Oil Precursor by Aerosol-Assisted Catalytic CVD method. *Appl. Mech. Mater.* **2012**, 229–231, 247–251. [[CrossRef](#)]
128. Suriani, A.B.; Asli, N.A.; Salina, M.; Mamat, M.H.; Aziz, A.A.; Falina, A.N.; Maryam, M.; Shamsudin, M.S.; Md Nor, R.; Abdullah, S.; et al. Effect of Iron and Cobalt Catalysts on The Growth of Carbon Nanotubes from Palm Oil Precursor. *IOP Conf. Ser. Mater. Sci. Eng.* **2013**, *46*, 012014. [[CrossRef](#)]
129. Kudin, T.I.T.; Zainal, N.F.A.; Ali, A.M.M.; Abdullah, S.; Rusop, M.; Sulaiman, M.A.; Yahya, M.Z.A. Electrochemical performance of anode material from palm oils derived carbon nanotubes for lithium ion batteries. *Mater. Res. Innov.* **2009**, *13*, 269–271. [[CrossRef](#)]
130. Robaiah, M.; Rusop, M.; Abdullah, S.; Khusaimi, Z.; Azhan, H.; Fadzlinaatul, M.Y.; Salifairus, M.J.; Asli, N.A. Synthesis of carbon nanotubes from palm oil on stacking and non-stacking substrate by thermal-CVD method. *AIP Conf. Proc.* **2018**, 1963, 020027. [[CrossRef](#)]
131. Ram, R.; Catlin, D.; Romero, J.; Cowley, C. Sesame: New approaches for crop improvement. In *Advances New Crop*; Timber Press: Portland, OR, USA, 1990; pp. 225–228.
132. Kumar, R.; Singh, R.K.; Kumar, P.; Dubey, P.K.; Tiwari, R.S.; Srivastava, O.N. Clean and Efficient Synthesis of Graphene Nanosheets and Rectangular Aligned-Carbon Nanotubes Bundles Using Green Botanical Hydrocarbon Precursor: Sesame Oil. *Sci. Adv. Mater.* **2014**, *6*, 76–83. [[CrossRef](#)]
133. Kumar, R.; Singh, R.K.; Tiwari, R.S. Growth analysis and high-yield synthesis of aligned-stacked branched nitrogen-doped carbon nanotubes using sesame oil as a natural botanical hydrocarbon precursor. *Mater. Des.* **2016**, *94*, 166–175. [[CrossRef](#)]
134. Kumar, R.; Yadav, R.M.; Awasthi, K.; Tiwari, R.S.; Srivastava, O.N. Effect of nitrogen variation on the synthesis of vertically aligned bamboo-shaped C–N nanotubes using sunflower oil. *Int. J. Nanosci.* **2011**, *10*, 809–813. [[CrossRef](#)]

135. Afre, R.A.; Soga, T.; Jimbo, T.; Kumar, M.; Ando, Y.; Sharon, M. Growth of vertically aligned carbon nanotubes on silicon and quartz substrate by spray pyrolysis of a natural precursor: Turpentine oil. *Chem. Phys. Lett.* **2005**, *414*, 6–10. [[CrossRef](#)]
136. Afre, R.A.; Soga, T.; Jimbo, T.; Kumar, M.; Ando, Y.; Sharon, M.; Somani, P.R.; Umeno, M. Carbon nanotubes by spray pyrolysis of turpentine oil at different temperatures and their studies. *Microporous Mesoporous Mater.* **2006**, *96*, 184–190. [[CrossRef](#)]
137. Ghosh, P.; Soga, T.; Afre, R.A.; Jimbo, T. Simplified synthesis of single-walled carbon nanotubes from a botanical hydrocarbon: Turpentine oil. *J. Alloy. Compd.* **2008**, *462*, 289–293. [[CrossRef](#)]
138. Ghosh, P.; Soga, T.; Ghosh, K.; Afre, R.A.; Jimbo, T.; Ando, Y. Vertically aligned N-doped carbon nanotubes by spray pyrolysis of turpentine oil and pyridine derivative with dissolved ferrocene. *J. Non-Cryst. Solids* **2008**, *354*, 4101–4106. [[CrossRef](#)]
139. Awasthi, K.; Kumar, R.; Tiwari, R.S.; Srivastava, O.N. Large scale synthesis of bundles of aligned carbon nanotubes using a natural precursor: Turpentine oil. *J. Exp. Nanosci.* **2010**, *5*, 498–508. [[CrossRef](#)]
140. Kang, Z.; Wang, E.; Mao, B.; Su, Z.; Chen, L.; Xu, L. Obtaining carbon nanotubes from grass. *Nanotechnology* **2005**, *16*, 1192–1195. [[CrossRef](#)]
141. Cho, W.S.; Hamada, E.; Kondo, Y.; Takayanagi, K. Synthesis of carbon nanotubes from bulk polymer. *Appl. Phys. Lett.* **1996**, *69*, 278–279. [[CrossRef](#)]
142. Goodell, B.; Xie, X.; Qian, Y.; Daniel, G.; Peterson, M.; Jellison, J. Carbon Nanotubes Produced from Natural Cellulosic Materials. *J. Nanosci. Nanotechnol.* **2008**, *8*, 2472–2474. [[CrossRef](#)]
143. Xie, X.; Goodell, B.; Daniel, G.; Qian, Y.; Jellison, J.; Peterson, M. Carbonization of wood and nanostructures formed from the cell wall. *Int. Biodeterior. Biodegrad.* **2009**, *63*, 933–935. [[CrossRef](#)]
144. Xie, X.; Goodell, B.; Qian, Y.; Daniel, G.; Zhang, D.; Nagle, D.C.; Peterson, M.L.; Jellison, J. A method for producing carbon nanotubes directly from plant materials. *For. Prod. J.* **2009**, *59*, 26.
145. Ma, Y.; Lu, N.; Lu, Y.; Guan, J.-N.; Qu, J.; Liu, H.-Y.; Cong, Q.; Yuan, X. Comparative Study of Carbon Materials Synthesized “Greenly” for 2-CP Removal. *Sci. Rep.* **2016**, *6*, 29167. [[CrossRef](#)]
146. Qu, J.; Cong, Q.; Luo, C.; Yuan, X. Adsorption and photocatalytic degradation of bisphenol A by low-cost carbon nanotubes synthesized using fallen leaves of poplar. *RSC Adv.* **2013**, *3*, 961–965. [[CrossRef](#)]
147. Rümmele, M.H.; Bachmatiuk, A.; Börrnert, F.; Schäffel, F.; Ibrahim, I.; Cendrowski, K.; Simha-Martynkova, G.; Plachá, D.; Borowiak-Palen, E.; Cuniberti, G.; et al. Synthesis of carbon nanotubes with and without catalyst particles. *Nanoscale Res. Lett.* **2011**, *6*, 303. [[CrossRef](#)]
148. Qu, J.; Luo, C.; Cong, Q.; Yuan, X. Carbon nanotubes and Cu–Zn nanoparticles synthesis using hyperaccumulator plants. *Environ. Chem. Lett.* **2012**, *10*, 153–158. [[CrossRef](#)]
149. Liu, H.; Ren, M.; Qu, J.; Feng, Y.; Song, X.; Zhang, Q.; Cong, Q.; Yuan, X. A cost-effective method for recycling carbon and metals in plants: Synthesizing nanomaterials. *Environ. Sci. Nano* **2017**, *4*, 461–469. [[CrossRef](#)]

