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Removal of Amorphous Carbon and Transition Metal Impurities from Carbon Nanofibers at an Industrial Scale

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Abstract

Carbon nanotubes has been a hot topic in the last 30 years as "the future material of manufacturing and electronic compounds". Besides this, the world is under high distress trying to abate the climatic effects of greenhouse gases such as carbon dioxide. Bergen carbon solutions AS is a startup company developing CNFs from carbon dioxide by molten electrocatalysis to add value to the economy using CO_2 as a resource. However, the applicability of this magnificent material is restricted to the carbonaceous and transition metal impurities in the end product. Such impurities has proved to be a challenge to eliminate ever since tubular nanomaterials were discovered. In spite of this, several methods from scientific literature have been compared and evaluated to propose the most suitable cleansing technique for the company for an efficient and low cost upscaling of their carbon manufacturing. The result of Goaks method are superior to others. However, adapting a multistep method which also applies magnetic separation and Fenton chemistry is also a promising low cost alternative to achieve the highly applicable, ECO-C1 grade purity at a large scale.

1 Introduction

In the global situation there are environmental challenges to face in the coming years. Several studies link the increased atmospheric temperature with rising CO_2 concentrations. With high concern, models confidently predict these effects as irreversible [1]. Among the greenhouse gases, emission of CO_2 is a major contributor. Hence, the utilisation of this gas, and the scale of utilisation, will be important aspects to solve this problem.

Huang assessed several utilizations of CO_2[2]. It may either be used directly in making soft drinks and well as in production of fire extinguishers. Likewise, useful chemicals such as urea and polycarbonates may be synthesized from the global CO_2 abundance. Huang also reviewed the potential of using CO_2 directly as a resource in algae production, which can be utilized in stockfeed, biofuel production, and production of nutrients.

Another solution to this problem will be to utilize the emitted gases as a resource for further production; making carbon nanofiber (CNF) from CO_2 by molten carbonate electrocatalysis[3]. Similarly to Huangs assessment, utilizing CO_2 for nanotube production adds both value and technological advances to society. For instance, the CNFs provide superior material properties, can compete with aluminium and steel in vehicles, jets and bridges due to its lightness and strength[4]. The nanomaterials are also said to be the future of medicine and electric properties[5, 6]. Thus a large scale utilization of the nanotubes may significantly increase the energy efficiency, and a results in a greater good at most aspects of our society. Fortunately, this technology is under establishment in several companies as Bergen Carbon Solutions AS (BCS) trying to abate the atmospheric CO_2 problem, by utilizing the electrocatalysis method. In practice however, achieving a highly

applicable nanomaterial has been a challenging issue the last 30 years, due to impurities in the CNF product. A common method to clean the product at laboratory scale, is by treatment with various concentrations of HCl, sequenced with bath sonication, and drying[7]. This HCl method achieves a carbon yield of 95%, mostly consisting of CNFs [8]. Inversely, the washed product tend to have structural damage, and appearance of amorphous carbon in small fractions affects the materials mechanical properties[4, 5]. Also, the HCl method is unconvincingly ineffective in removing resilient metal particle remains in the CNF product (figure 3).

Such particles have electrocatalytic properties which dominate the inherent properties of nanotubes. For instance Chromium (III) and its oxidized forms are toxic, and may easily form when exposed to natural manganese oxide in the soil [9–11]. In addition to the hazards of impurities, the methods of removing impurities ought to be scalable to industrial levels to match the demand of CNF qualities, lower expenses in production and significantly contribute to reduction of CO_2 emission levels. To reliably achieve applicable nanomaterials, the scope of this thesis will be removal of amorphous carbon and catalyst particles from carbon nanofibers at an industrial scale.

Glossary

as-received The condition of the product when received directly from the manufacturing process or a supplier. . 8, 11, 15–17, 19

carbanogel A material mix of carbonate salt matrix and carbon nanofibers. 12

Acronyms

AD arc discharge evaporation. 6

BCS Bergen Carbon Solutions AS. 1, 4, 7

CF carbon fiber. 6, 8

CFF cross flow filtration. 12, 21

CNF carbon nanofiber. 1, 2, 4, 6, 7

CNT carbon nanotube. 4, 6, 9, 10

CVD chemical vapor deposition. 6

DFT density functional theory. 9

DPP diphenylphosphine. 14

ECD electric current density. 6

GO graphene oxide. 12

HIPco high pressure carbon monoxide. 6

HSE health and security executive. 11

LA laser ablation. 6

MI metal impurity. 14–16

MSEC molten salt electrocatalysis. 4, 6

MWNT Multi walled nanotubes. 4

OA Oleic Acid. 14

PE purification efficiency. 11

SWNT Single walled nanotubes. 4

TBP tributylphosphine. 14

TM transition metals. 9

TOP trioctylphosphine. 14

2 Theory

2.1 Carbon allotropes - Nanotubes and its cousins

Carbon nanotubes are tubular structures of graphene sheets which can be divided into three types, depending on how many layers of tubes are present in the CNT. Single walled nanotubes (SWNT) consist of a single cylindrical graphite sheets with a diameter of 1-2nm [12]. Multi walled nanotubes (MWNT) consist of multiple tubes enclosing each other, with diameters from 5 to 50nm. BCS have only registered MWNTs using their molten salt electrocatalysis (MSEC) method, and may form MWNTs with a nanotube diameter up to 600nm (Appendix). At diameters beyond 100nm, the carbon structure is considered a carbon nanofiber (CNF) (figure 1). In contrary to the MWNTs, the CNFs form a broad variant of structures. In addition to tubular structures, The CNFs may consist of carbon cups stacked in conical layers along the fibre (figure 1)[13]. It is conceived as a herringbone structure when these cups are bottomless. When some of the cups form a bottom, it is named a bamboo structure (figure 2) [14, 15]. The conical layers of CNF makes both inner and outer surface chemically active.
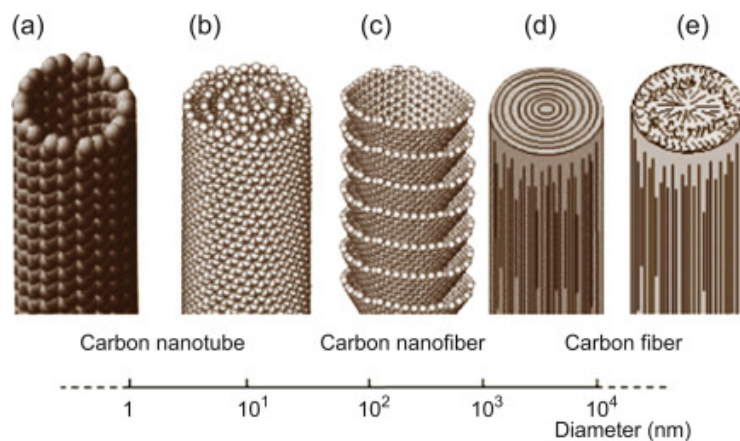

Figure 1: Definitions of various positive-curved carbon structures. Reprinted from Hiremath [13] with permission from Elsevier.

Both CNTs and CNFs share the same types of hexagonal carbon pattern with graphene, which is known for its pure sp^2-hybridization. Diversely, depending on the degree of tube curvature, the hydridization of bonds will increase by ϵ in $sp^{2+\epsilon}$, which also increases the tubes' reactivity[16, 17]. Thus, it is expected a higher reactivity from small outer-diameter structures as SWNTs than from CNFs. VSEPR theory affirms that the most stable sp^2 hybridization of carbon is planar, and that pyramidalization of sp^2 hybridization to $sp^{2+\epsilon}$ implies a more comprehensive interaction with certain foreign atoms. This would suggest higher reactivity at the inner-diameter of bottomless CNF cups. An intrinsic effect of CNFs being larger than nanotubes, makes the material easier to disperse in liquids (table 1) [13]. Amorphous carbon is defined "as sp, sp^2 and sp^3 hybridizations coexisting together in various combinations" [18].
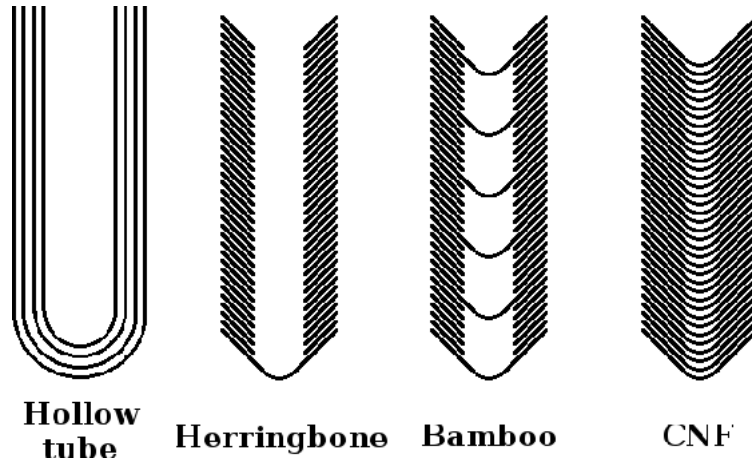
Figure 2: Variants of CNF. Reprinted from Puscas[15] with permission from Semantic scholar.

Table 1: Comparison between physical parameters of CNFs and CNTs. Reprinted from Hiremath[13] with permission from Elsevier.

Property	CNFs	CNTs
Diameter (nm)	50–200	1–50
Length (μm)	50–100	1–100
Aspect ratio	250–2000	100–10,000
Density (g/cm^3)	2	1.75
Thermal conductivity (W/mK)	1950	3000–6000
Resistivity (Ω cm)	$1*10^4$	$1*10^4$ to $2*10^3$
Strength GPa	2.92	10–60
Modulus GPa	240	1000

2.2 Carbon nanomaterials - How are they made?

CNFs were first produced in an effort to achieve a cheaper alternative to carbon fiber (CF) in composites. In the 1980s, Hyperion made entangled CNFs by the chemical vapor deposition (CVD) method [13]. This involved an arbitrary decomposition of a hydrocarbon gas or solvent on an catalyst nanoparticle in an inert environment. In 1991, the first discovery of "helical microtubules of graphitic carbon" was made by Iijima by an arc discharge evaporation (AD) method [19]. AD applies a low-voltage, high current power supply onto close, but nontouching graphite electrodes in an inert environment (He, Ar) to form the tubes [13]. As the nanotubes incredible properties were revealed (table 1), research started to revolve around cheap production of the nanotubes. Today, the CVD method is the most common method of producing CNTs[20]. Several other methods to form CNTs such as laser ablation (LA), and high pressure carbon monoxide (HIPco) have been developed. Laser ablation involves vaporization of graphite using a laser in an inert gas environment at reduced pressures[6]. In this method, CNTs are collected from cooled copper plate which was exposed by graphitic gas. HIPco applies preheated CO to $1000°C$ at 30 atm such that the Ni-carbonyl precursor decomposes into nucleation sites when exposed to the CO. This initiates CNT growth at Ni-particles[21].

BCS manufactures their CNFs with molten salt electrocatalysis (MSEC), a recent method developed from Ren in 2015 [3]. The principle of BCSs' manufacturing method of CNFs are equivalent with the common CNTs manufacturing methods; to destabilize a carbon compound until it decomposes and the carbon deposits on a catalytic surface to form a continuous carbon structure. As details in their production is confidential, we will consider the papers which has inspired BCS' approach [3, 4, 7, 8, 22, 23]. The electrolytic system consists of a zinc-coated steel cathode, a Nickel crucible anode and a Li_2CO_3 molten salt electrolyte. with added Fe, Ni, Cu and particles as nucleation sites. Starting the electrolysis at 723 °C, the zinc-coating initiates the nucleations of solid carbon from liquid Li_2CO_3 to the steel cathode(equation 1). The dissolved Li_2O easily dissolve CO_2 from the atmosphere to regenerate the former carbonates(equation 2). Bubbling pure CO_2 in the system will result in direct utilization of CO_2 to form solid CNFs at the cathode surface(equation 3). The cathode is cooled and uncoiled to extract the grown carbon structure. The raw CNF is rinsed with HCl and filtrated to remove remainders of electrolyte and catalysts particles to form the promising product shown in figure 3A. The characteristic structure is achieved when gradually increasing current density, starting at low values for the added metals to form nucleation sites at the cathode, and growth starts at higher electric current density (ECD). Ren uses solar energy to perform the electrolysis, while BCS uses hydropower to sustainably manufacture the nanofibers [3].

$$Li_2CO_{3(molten)} \longrightarrow C_{(CNF)} + Li_2O_{(dissolved)} + O_2(g) \tag{1}$$

$$CO_2(g) + Li_2O_{(dissolved)} \rightleftharpoons Li_2CO_{3(molten)} \tag{2}$$

$$CO_2(g) \longrightarrow C_{(CNF)} + O_2(g) \tag{3}$$
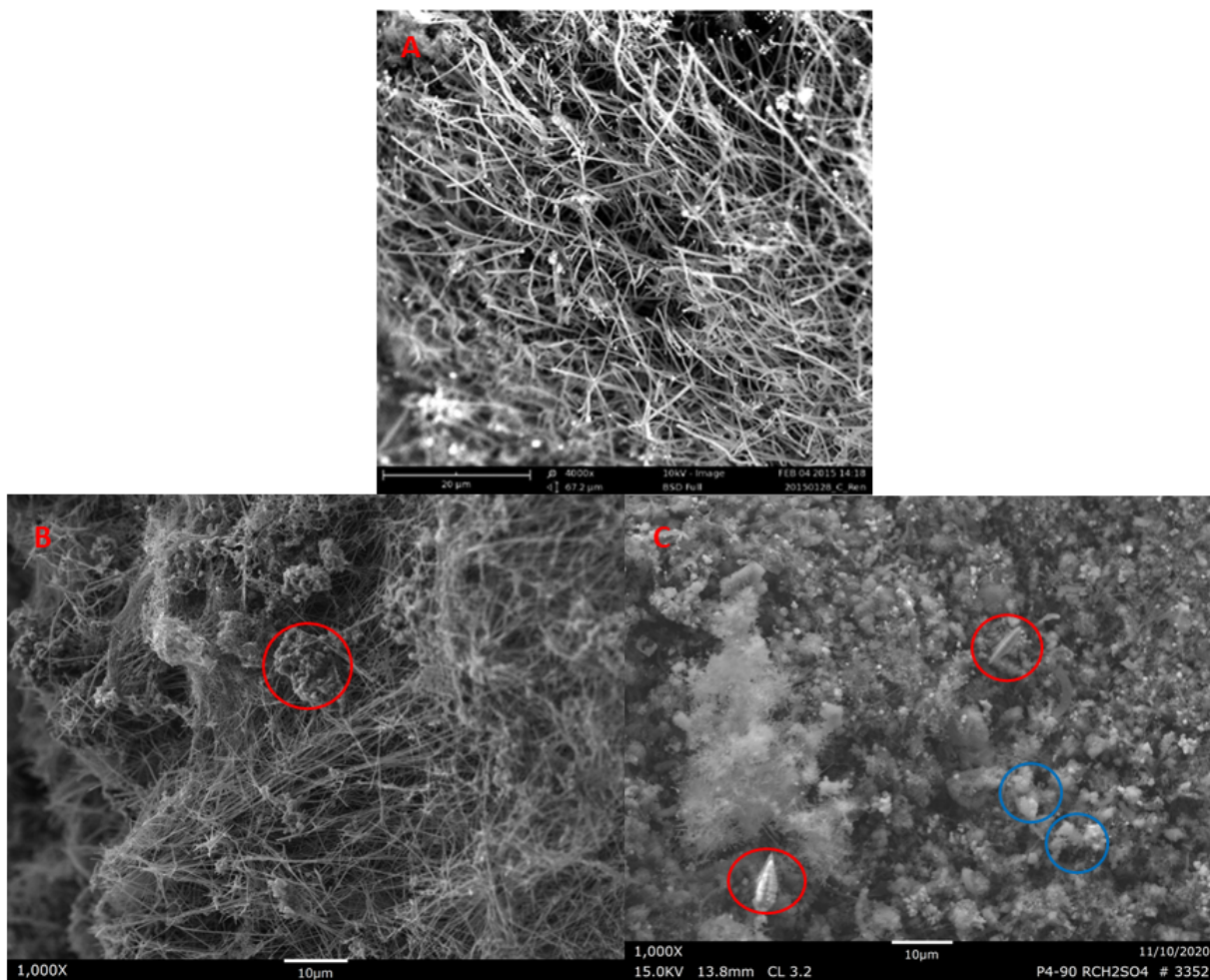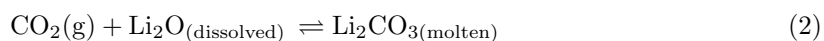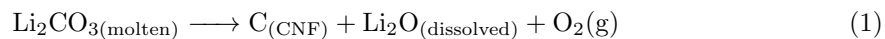

Figure 3: Comparison between the pure product and the contaminated products from SEM prior to washing. A: CNF with few to no impurities [3]. B: CNF containing amorphous carbon impurities encircled in red. C: Chromium NPs encircled in red and iron oxide/ other metal oxides encircled in blue. Figure B and C is borrowed from BCS. Figure A is reprinted from Ren [3] with permission from ACS.

2.3 Application of CNTs and CNFs

The application of the CNTs and CNFs are vast [6, 14]. The combination of high surface to mass ratios and high electric conductivity makes nanomaterials good candidates as supercapacitors. Niu and Ma demonstrated that MWNTs used in cells with 38% H_2SO_4 could produce power densities up to 8000W/kg[24, 25]. Pant utilized CNFs as a framework to form CNF/TMO composite supercapacitors [26]. Such super-capacitors are essential for further development of electric cars, as current lithium batteries lose its effect over time due to reactivity, while intercalation of nanotubes in lithium batteries stabilize them. Even damaging the nanostructures is suggested by Meunier to increase battery storage capacity[27].

CNFs and CNTs both have excellent mechanical properties, and can be used as a filler integral in carbon fiber (CF), epoxy or other polymeric materials [18]. For instance, adding only 1,5wt% SWNT to a nylon mixture, increased tensile strength and modulus by 66% and 174%[13]. Also, the tensile strength of SWNT was achieved to be about 200 times larger steel of the same dimension. As seen in table 1, the mechanical properties are lower for CNFs, however they are cheaper and more applicable for use in composite materials[13].

2.4 Impurities - Occurrence and species

In this project, impurities are defined as any unwanted species or structures in the product. Although, this report will only consider amorphous carbon and catalyst particles, while other expected impurities will be considered as preparation processes. As-received CNFs will include remnants from manufacturing which may vary from each batch[3, 28, 29]. BCS has also observed metallic chromium colloidal particles in their sample, which they suspect have leached out from the nickel electrode. Carbonate salts and TMs may also be encapsulated inside the nanotube, or in layers of carbonaceous shells, as first discovered by Pumera[29–31]. These shells are often found in products other manufacturing methods (AD, HIPco and CVD)[30]. During purification, harsh treatment may also induce tube damage, defects and functional groups on the product. The correlation between atomic metal occurrence and concentration was studied in the range between 0.04 and 0.5 wt% with Pd (table 2)[32].
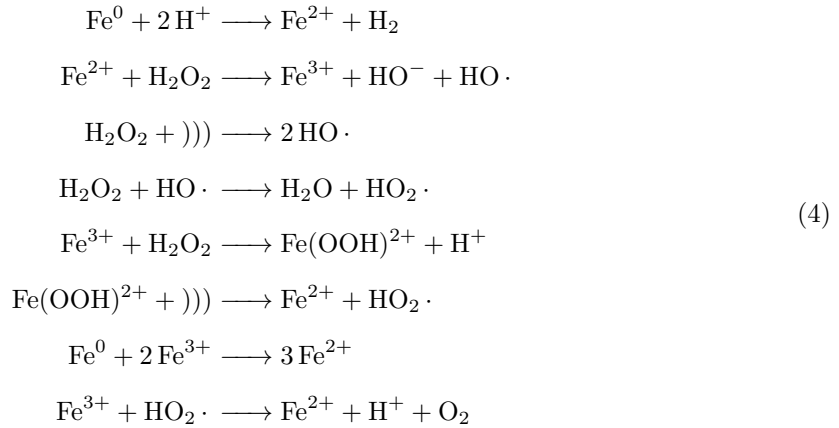
Table 2: Occurence of Pd atom deposition at different concentrations[32].

wt%	deposition
< 0.04	deeply intercalated atoms
0.04 − 0.2	singular atoms on CNF surface
> 0.1	metal clusters

2.5 Fenton chemistry

Fenton processes are based on the production of higly reactive OH-radicals under acidic conditions when H_2O_2 is exposed to ferrous ions (Fe^{2+}) [33]. The process is commonly used in industrial wastewater treatment, reducing toxicity. An advanced Fenton chemistry process includes decomposing zerovalent iron with the generated Fe^{3+} ions aswell (equation set 4). Similar advanced Fenton processes has also been performed with other metals when at a low oxidation state, and sonication increases the effect of the reaction marked as "))))" (equation set 4) [34].

$$Fe^0 + 2\,H^+ \longrightarrow Fe^{2+} + H_2$$
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO\cdot$$
$$H_2O_2 +))) \longrightarrow 2\,HO\cdot$$
$$H_2O_2 + HO\cdot \longrightarrow H_2O + HO_2\cdot$$
$$Fe^{3+} + H_2O_2 \longrightarrow Fe(OOH)^{2+} + H^+ \tag{4}$$
$$Fe(OOH)^{2+} +))) \longrightarrow Fe^{2+} + HO_2\cdot$$
$$Fe^0 + 2\,Fe^{3+} \longrightarrow 3\,Fe^{2+}$$
$$Fe^{3+} + HO_2\cdot \longrightarrow Fe^{2+} + H^+ + O_2$$

2.6 Transition metals and their interaction with carbon

Transition elements originate from the incomplete d-subshells in neutral atoms or ions [35]. The excellent catalytic properties of transition metals (TM) stem from low ionization energies, and that the TMs can exist in several oxidation states. The interaction between TMs and carbon was distinguished in four categories by Haddon [36–39]; physisorption, ionic chemisorption, covalent chemisorption with preserved carbon structure and covalent chemisorption with change in carbon structure. Examples on the interactions are given in table 3. The fourth variant may be destructive, forming sp^2 carbon into sp^3 formation, or constructive, filling holes in the CNTs as an extrinsic defect. Defects tend to increase metal adhesion [40], while adsorbed atoms stabilises in CNF vacancies. This promotes defect sites to be preferable nucleation sites for metals, while studies also show high reactivity for the CNT ends[41, 42]. For CNFs, this will imply high reactivity along the conical ends, widespread on along the surface. Other studies predict that single atom Fe would be stable on defect free graphene, while Cr and Ni having low enough diffusion barriers to form into aggregates on the surface, as observed for BCS (figure 3C) [43].

Chromium provide several anomalous properties in the periodic table. Its electron configuration possess 6 valence orbitals and 6 valence electrons, with only a singular 4s electron ($3\,d^5s^1$) [44]. From density functional theory (DFT) studies, it was concluded that Ni and Fe strongly chemisorb to a graphene surface, and that chemisorption was most stable at the hollow site (figure 4)[45].

Table 3: Transition metal interactions and examples[36–39]

Number	Interaction	Example
1	Physisorption (van der Waals)	Au on Graphite
2	Ionic chemisorption	Li on graphite
3	Covalent, no carbon deformation	(η6-C6H6)2M complexes
4	Covalent, carbon deformation	TMs at defect locations, carbide formation

While for chromium, this was unfavourable as chromium had unfavourable electric potential energies due to repulsion from the $5s^1$-electron. Hence, any adsorption had to occur physically at the carbon ring bridges and top sites (figure 4)[46]. However, as studies proved that Au and Pt atoms chemisorbed to CNT vacancies and edges, it is expected that any TM will chemisorb correspondingly[47].
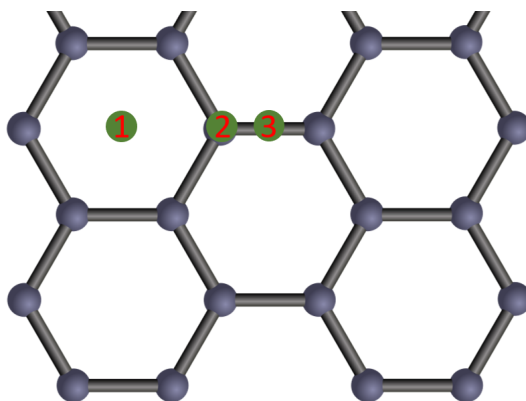

Figure 4: Adsorption sites on graphene. 1: Hollow site 2: Top site 3: Bridge. Structure is drawn in Inkscape.

2.7   Effects of impurities in the nanofiber product

Pure CNTs are considered harmless to humans with no paramagnetic properties[48]. Contrarily, metal NPs will exceed any other TM atom signal by several orders of magnitude [49]. Also, Compton discovered that metallic impurities can completely dominate electrochemical properties in nanotube structures, even at impurities as low as 1.0wt%[18]. Smith and Banks confirmed that only 99.99% pure CNTs have insignificant catalytic effects [41, 50]. This correlates which studies that proved excellent biocompabities of nanotubes with metal content less than 20ppm [51]. This dominating effect of impurities explains why nanomaterials must be close to metal free to apply in electric and medical applications. For material applications, the tolerancies are less strict (around 1000 ppm)[18], but the mechanical properties of nanotubes drastically change with large amounts of amorphous carbon and TMs. Kim registered this difference as he reported a 2 and 3-fold improvement in tensile strength and electric properties when comparing the mechanical

properties of as-received nanotubes and purified nanotubes[52].

2.8   Criteria for industrial validity

For the purification method to be viable at an industrial scale, it must be scalable. The principle of scalability resembles the ability for the process to grow and adapt to changing needs and demands by clients [53]. Thus, the method ought to evenly purify the nanotubes such that the local impurities in larger batches are predictable. BCS have also defined certain criteria for the validity of the purification method. They classify their products in three grades. ECO-C1, ECO-C2 and ECO-C3 (Appendix). These product ought to have impurities less than 1,5%, 5% and 7% after TGA. Regarding type of impurity, it is desirable for a method which gives consistent results. Hence, it would be highly practical method which could remove most transition metals, anywhere and any particle size. Correspondingly, the cost will also be a priority for a startup to have a competetive advantage in the market. Also, net CO_2 emission ought to be zero or a negative value to remain true to their sustainable branding. If hazardous chemicals are utilized, there will also be a health and security executive (HSE) concern during manufacturing.

3   Results

Carbon nanomaterial purification has been thoroughly studies for SWNTs, Graphene and MWNTs manufactured from CVD, LA and HIPco methods. Contrarily, there were few to no studies which specifically conducted purification experiments on CNFs from MSEC. In spite of this, the encountered methods deal with similar impurities as what is experienced in Bergen. Hou summarized and compared several purification principles for CNTs such as gas/liquid oxidation/reduction , and concluded that combination of chemical and physical methods are most suitable for CNT purification [5]. Vejpravova reviews the common strategy of removal of magnetic impurities in the literature [54]. This is a three-step strategy : 1. opening carbonaceous shells, 2. dissolving/separating/removing TM catalysts and 3. high temperature annealing or chemical treatment to remove/restructure the carbonaceous shells and amorphous carbon. Several of the results base their purification on this strategy [8, 55–59]. Kiscinski thoroughly reviewed the challenges of removing the transition metals in carbon materials and the most promising TM-removal methods since 2020[18]. Table 4 summarizes the results from the purification methods mentioned in this text below. Table 5 is an overview on the manufacturing data from the mentioned methods. Table 6 projects the methods by their calculated purification efficiency (PE).

3.1 Preparation - Removal of molten salts

Ever since Ren developed the molten electrolysis method in 2015, a crucial improvement in the production process has recently been developed. The conventional purification method with HCl to purify the CNF, emits CO_2 in reaction with remains of carbonate salt (equation 5) [29]. To reduce chemical waste, CO_2-emission and use of thermal energy, Wang deleveloped a High temperature press filtration method to recycle molten salt residues from carbanogel in a MSEC process.

$$Li_2CO_3\,(s) + HCl(aq) \longrightarrow 2\,LiCl\,(aq) + CO_2(g) + H_2O\,(l) \tag{5}$$
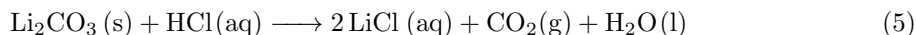
Wang conducted the filtration replicating a previous molten electrolysis process [60]. The electrolyte composition did consist of 80% Li_2CO_3 and 20% Na_2CO_3, using brass and inconel 718 sheets as cathode and anode. Running electrolysis at $0.2 A/cm^3$ did result in CNT products with 100nm average diameter, 30-100nm long and 5% amorphous carbon. Effect of mesh material, filter pore size, pressure time and temperature were also studied. The ambient condition was to use a Commercial Monel screen filter with mesh size 200x200 (hole diameter $86 \mu m$) at 750°Cat 7000kg force for 30 minutes to remove 95% of electrolyte from a 535g carbanogel sample. Heating the sample for 1 hour resulted in removal of amorphous carbon. The extracted electrolyte can then be reused and the CNT can be further treated to remove catalyst particles. At this time, this techonology is uncontested, and it is highly advised to implement this in molten electrolysis manufacturing before ever considering further purification of a raw CNF product. For BCS dimension, this may also require lower pressures. As removal of carbonate salts is crucial, the complete removal of salt impurities can be ensured with cross flow filtration (CFF) or dialysis. Bhunia, Tölle and Abdel Mogataly recently developed fast, scalable and sustainable ways to desalinate GO, and a similar technique should be applicable to purification of easily dispersable CNFs [61–64]. Organic solvents may be used to separate other carbon species such as fullerenes and graphene flakes [65].

3.2 Purification methods - Removal of amorphous carbon and catalyst particles.

Several methods applied a multistep approach to reliably remove impurities. Cabana used an argon and steam mixture to remove transition metal impurities. [56]. MWNTS were exposed by this gas At 900°Cfor 1 to 15 hours. The sample was subsequently washed with 6M HCl, filtrated through a polycarbonate membrane and then washed with distilled water. SQUID results show a non oxidizing way to receive an iron content of 0.0022 wt% when the process is run for 1.5 hours. Cabana also discovered that the distribution of nanotube lengths correlated with treatment time. At 15 hours, most of the tubes had roughly the same length. Metal impurities was only registered to 0.01wt%. Kim proposed a multistep purification of SWNTs from a induction thermal plasma process [65]. Kim utilized air oxidation, HNO_3 oxidation, centrifugation and vacuum filtration

through a μm pore size polycarbonate membrane. Results show a total yield at 15-20% and remaining metal content at 7%. Wu proposed purification for the arc discharge method to achieve 99wt% purity SWNTs, with magnetic impurities as low as 0.2wt% [8]. Amorphous carbon was registered to burn off at 400°C, and SWNTs burned at 520°Cby TGA. Xu proposed a multistep method for which a raw HIPco product was oxidised in air and metal catalysts were deactivated by a fluoride reactant and then removed by HCl. After hexane extraction, Xu achieved a high yield and purity of 68% and 98% [59]. CO_2 development was detected at 175 and 325°C, suggesting removal of carbonaceous impurities. Similarly, Mercier proposed a method implementing chlorine gas to deactive catalyst particles at 1000°C. [57]. Goak attemped a more advanced halogenous method, high temperature, multistep gas oxidation with chloroform, H_2O and ethanol gas. He achieved nanotube samples only containing 12ppm metal impurities [66]. Chlorine content in sample was registered to only 0.02 at%, however, surface roughness increased.

Wang purified tubes with a liquid oxidation approach, using H_2O_2 and HCl [67] at SWNTs. He achieved purity rates of 96wt% with high yield when pH values were adjusted. Carbonaceous shells with metal catalysts were efficiently decomposed. Another purification method was invented by Abbas, whom used a liquid separation method [68]. Using alcohol and H_2O_2 to separate particles in a separation funnel, resulting in removing most of the catalyst particles in several steps. The purification began with dispersing MWNTS in methanol and was mixed for 2 hours, distilled and filtrated with distilled water, and then dried at 90°C. Results show impurities less than 0.6wt%, with a nanotube loss less than 5%.

Bass developed a method which reversibly electrodeposited NPs onto an electrode surface to separate mixed particles [69]. Electropurification includes three steps; electrophoretic migration to the electrode surface, aggregation at electrode surface and redispersion in a new solvent. By adding several ligands to the NPs, Extraction efficiency of metal particles reached as high as 98%.

Romanov used joule heating as a rapid and efficient physical purification method. Temperature was increased locally in the TM NPs at 1600°Cin vacuum for 2 minutes to achieve nanotubes with purity of 99wt% [70].

Ghosh purified SWNT by coating the tubes in surfactant before separating the NPs by their magnetic properties[71]. According to Ghosh' results, magnet separation proved to be as effective as ultra high centrifugation in separating metal particles from CNTs. Pacakova proved that repeating magnetic separation proved to separate more magnetic NPs for a HIPco raw product[72]. Subsequently, Gurova assembled a method by dispersing tubes in an aqueous surfactant solution, and the magnetic particles were separated by magnets. By subsequently washing with HCl, Gurova achieved a purification of 99 wt% and a yield by 75%, with some carbonaceous shells remaining[73].

Table 4: Overview on key information from purification results from the reported purification methods in the literature.

Reference	purification method	yield	CNT damage	purity TGA wt%	process time	chemicals	Steps	Impurity removed
Wang[29]	HPTF	N/A	none	94.7%	2h	mesh screens	4	Na_2CO_3, Li_2CO_3, catalyst
Cabana[56]	Steam-HCl-filtration	N/A	none	98.11-99.58	1.5-16h	Ar, HCl	3	Fe, Al_2O_3
Mercier[57]	oxide gas	10 %	none	99.3	26h	O_2, HCl	3	Fe, Ni
	oxide gas	79.80 %	none	94.7	26h	O_2, HCl	3	Fe, Ni
	chlorine gas	75.20 %	none	97.8	5h	Cl2, HCl	2	Fe, Ni
	chlorine gas	84 %	none	96	5h	Cl2, HCl	2	Fe, Ni
Wang[67]	Liquid oxidation	75 %	little	95	7h	H_2O_2, HCl	2	Fe
Romanov[70]	vacuum joule heating	100 %	insignificant	99	2min	none	1	TMs
Gurova[73]	dispersion, magnetic separation	74-77	none	99-99.8	9.5h	varies, 2	3	Fe
Xu[59]	multistep oxidation,C2H2F4	68 %	little	98	38.5h	$C_2H_2F_4$, N_2,O_2, HCl, Hexane	5	Fe
	multistep gas oxidation SF6	62 %	little	98	38.5h	SF_6,N_2,O_2, HCl, Hexane	5	Fe
Kim[65]	multistep	20%	little/partial	93	19h	HNO_3, HCl, H_2O_2	5	Ni, Co, Y_2O_3
Wu[8]	multistep	56 %	little?	99	25h	HNO_3, HCl, H_2O_2	7	Fe, Co, Ni
Goak[66]	halogen heating	100%	none	MI 12ppm	30min	ETOH,$CHCL_3$, N_2, NaOH	2	Al, Mg, Co, Fe
Abbas[68]	oxidation and liquid separation	95 %	n/a	99.3	10h	EtOH, H_2O_2,	7	Mo, Co
Bass[69]	reversible electrodeposition	N/A	N/A	90-98*	40min	OA or TOP or TBP or DPP, Hexane, Acetone	3	CdTe, PbSe, CdSe, CdS

Table 5: Key manufacturing data from the reported purification methods.

Reference	CNT type (As-received wt%)	CNT diameter (nm)	catalyst size(nm)	production type
Wang [29]	MWNT (10wt%)	100	N/A	MSEC
Cabana[56]	MWNT (98wt%)	10-12,10	N/A	CVD, CoMoCAT
Mercier[57]	SWNT (83.6 wt%)	1.15-1.55	N/A	AD
	SWNT (91.1 wt%)	1.15-1.55		AD
	SWNT (91.1 wt%)	1.15-1.55		AD
	SWNT (68 wt%)	0.7-1.3		HIPco
Wang [67]	SWNT (65wt%)	2-7	2.0-7.0	HiPco
Romanov[70]	SWNT (83wt%)	2.2	1.0-25.0	CVD
Gurova[73]	SWNT (93wt%)	100-200	20	N/A
Xu[59]	SWNT (70wt%)	1.0-7.0	3	HIPco
	SWNT (70wt%)	1.0-7.0	3	HIPco
Kim[65]	SWNT (83.8 wt%)	15	2.0-20.0	induction thermal plasma
Wu[8]	SWNT (10wt%)	1.4	5-100	AD
Goak[66]	MWNT (MI 5.133ppm)	8.7		CVD
Abbas[68]	MWNT (96.6wt%)	35-90	N/A	CVD
Bass[69]	N/A	N/A	5.0-50.0	N/A

Table 6: Purification data with calculated purification efficiencies. PE is calculated by percentage of as-received weight removed divided by total impurity wt% in as-received sample. As-received wt% is how much how the product before purification that is carbon nanotubes. "TGA wt%" is the remains of the purified nanotubes in wt% after the nanotubes are combusted.

Reference	purification method	As-received wt%	TGA wt%	PE at best (%)
Wang [29]	HPTF	10wt%	94.7%	95 %
Cabana[56]	Steam-HCl-filtration	97.16wt%	98.11-99.48	85 %
Mercier[57]	oxide gas	83.6 wt%	99.3	96 %
	oxide gas	91.1 wt%	94.7	40 %
	chlorine gas	91.1 wt%	97.8	75 %
	chlorine gas	68 wt%	96	87 %
Wang[67]	Liquid oxidation	65wt%	95	85 %
Romanov[70]	vacuum joule heating	83wt%	99	96 %
Gurova[73]	dispersion magnetic separation	93wt%	99-99.8	97 %
Xu[59]	multistep halogen oxidation,C2H2F4	70wt%	98	93 %
	multistep halogen oxidation SF6	70wt%	98	93 %
Kim[65]	chemical multistep	83.8 wt%	93	43 %
Wu[8]	multistep	10wt%	99	95 %
Abbas[68]	oxidation and liquid separation	96.6wt%	99.3	20 %
Bass[69]	reversible electrodeposition	N/A	N/A	98 %
Goak[66]	halogen heating and reduction	MI 5.133ppm	MI 12ppm	99.8%

4 Discussion

4.1 Expert opinions on the problem

Kiscinski also reviews the disagreement on the origin of catalytic effects in impure nanotubes[18]. Regarding toxicity, evidence suggests that both single atom particles and oxygen functional groups have both catalytic effect, and at some point it is hard to determine which impurity contributes most to the material toxicity. Thus is it hard to also determine the toxicity of TMs if functional groups are not being taken account for, making toxicity studies of nanotubes irreproducible. Nevertheless, it is a shared opinion between the three great review writers; analysis of CNTs and impurities ought to be standardized [5, 18, 54]. If metals were present at any stage in manufacturing, its exact value should always be reported. In addition, functional group analysis should also be implemented to achieve a true image on the nanomaterials applicability.

Instead of directly pursuing the profit, Kiscinski believes that purification of traditional carbons

(graphite) to a nuclear grade should be further investigated before considering further development of CNT purification. Moreover, Kiscinski believes that TMs do not prevent the nanotubes application, however their presence and effects must always be taken account for. He also agrees with Vejpravova that the correct manufacturing is bottom-up to achieve atomic presision pure nanotubes, although this quality is for now restricted to laboratory scale research[54].

Most scientists agree that the largest obstacle for commercialization of carbon nanomaterial is the impurities [74]. Toxicologists seem only associate TM impurities with problems. Diversely, the electrochemists states that the only differences of dopants and impurities is language and intention[75]. Pumera insists that should focus on the benefits of impurities, as all discoveries within the field of electrocatalysis has involved catalytic properties from doping. Conjointly, L.Wang satirically investigated if any crap (bird dropping) put into graphene will increase its electrocatalytic effect, which actually was the case for certain reactions[76]. This experiment primarily projected the meaninglessness of pursuing dopants electrocatalytic effects in the field, and more importantly, affirming that impurities and dopants are the same thing. L.Wangs paper became one of the most read in 2020, and it led to many reactions[76]. It made Schaak to reflect upon the general statement "what does it take to push a field forward? What is the Guano-doped result in other fields?" [77]. For materialtechnology, trying to develop better methods to remove impurities may be just as meaningless. I believe it might be better to move on and see the opportunities these impurities achieve rather than the opposite.

Its apparent that graphitic structures bind to most substances and that impurities are inevitable, and that transition metals are catalytic intrinsically. Maybe changing catalyst type will solve the problem? Recent studies are showcasing the opportunity to use natural materials such as garnet ($A_3B_2Si_3O_{12}$), quartz (SiO_4), or zeolite (aluminosilicate) as a substitute to TMs as catalysts [78]. Kumar recently showcased this in his review how to efficiently utilize natural materials as catalyst and how to separate them from the product(figure 5)[78]. Using catalysts containing an insignificant amount of TMs will avoid the problem of electric and catalytic effects in the product to begin with, and we may finally introduce carbon nanotubes into medicine and nanoelectronics.

4.2 Inconsistencies in papers

Evaluating which purification method is most suitable for BCS unfolds as a challenging task when the results in the literature are inconsistent. To begin with, most of the scalable methods have mostly been conducted with SWNTs. As observed in 5, whether its type, initial purity, tube diameter or catalyst size, there is at least one parameter between the conducted purification experiments that differ. For instance, Cabana reported "ultrapure steam purification with metal content below 0.01wt%"[56]. Would it not be cheating to conclude this when the purity of the MWNTS was 98% as-received? There is also inconsistencies in reporting yields. Mercier reports only purification yield or PE%, while Kim reports yield only as a difference in weight before and
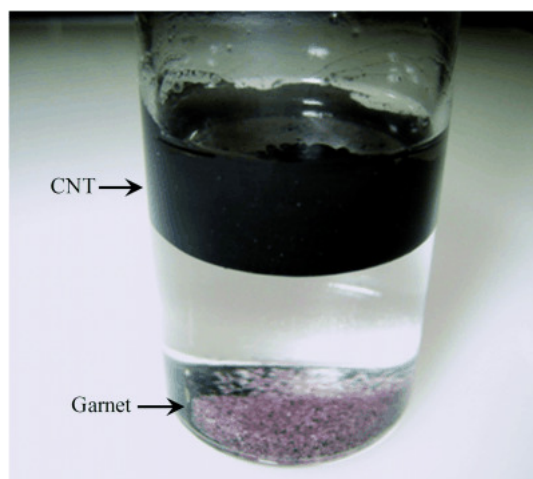
Figure 5: Separation of garnet sand from CNTs. Reprinted from Endo[79] with permission from Chemistry Europe.

after the purification[57, 65]. For purification purposes, the only yields of interest is carbon product yield, and purification yield. Besides, critical information such as type of impurity, tube diameter and catalyst size lack in some papers. This is crucial for comparing a physical and a chemical method. As the interaction between a single tubular structure with a TM vary with diameter, and regarding that the material is heterogenous, it is no wonder that results are inconsistent, when distribution of tubular width is not considered in most of the literature. To reliably clean, high yield heterogenous systems, we need to always take the such distributions into account. For instance, the promising results of Abbas are incomparable to the other results due to no data on the TM impurities. Another example is Wang's method, only reporting particle size of catalyst [67, 68]. To properly compare results of different methods requires this information. Such parameters should be reported regardless of relevancy of the papers, as it is relevant to solving the common problem the papers are trying to solve.

Although many conditions differ to BCS' manufacturing condition, Kiscinski also states that "MWNT purification is easier and more effective than SWNT"[18], which makes sense considering that most impurities are on the surface (table 2). Thus, acknowledging that CNFs carbons have a more planar hybridization than any of the materials in the literature(4)(Appendix). We ought to expect higher yields and purification efficiencies for chemical methods on CNF than on CNTs. However, we must also consider that the variance in diameter for BCS' CNFs is high[80]. A difference in 400nm for the outer surface diameter changes the ϵ value significantly, and it would be expected higher inconsistencies in purification for BCS. This includes inconsistencies in carbonaceous shells, expecting variable shell purification efficiency of TM impurities aswell.

4.3 Comparing methods

Considering the arguments above, it is sufficient to compare the presented scalable methods represented in table 4, 5 and 6.

Inconsistency seems to be the main issue at hand for BCS. However, methods using easily adjustable parameters may be practical to apply. For instance, strength of magnetic field, electric parameters and concentration mixture may be program controlled with respect to the distribution of nanotubes in a batch. Xu agrees upon that such a gradient of optimal conditions is how you achieve higher yields for SWNT manufacturing [59]. Goak, Romanov, Bass and Gurova utilized systems where such parameters can easily be adjusted. Multistep methods such as Wu, Xu, and Kims approach seem to take into consideration of all possible impurities to remove, despite that some steps may not be useful for all scenarios. However the guaranteed consistency of a multistep method counterbalances its possible setback of labor intensity.

At lab-scale, chemical treatment to remove large chromium NPs, has not proven effective for BCS. Although BCS' HCl purification proved ineffective, both Goak and Wang has improved chemical purification by considering the Fenton chemistry (equation set 4). Wang included H_2O_2 in the liquid oxidation process, which dissolves into $OH \cdot$ radicals when near the metal surface. Wang also states that there is potential for higher yields and purity by tuning parameters as pH, temperature and Fe^{2+} and H_2O_2 concentration, and the suboptimal carbon yield (56%) is due to the as-received SWNT contained 5-10wt% fullerene, which he states can be increased to 75% for other methods [67]. Xu and Kim also recognized that carbon yield was affected due to acid-decomposition of fullerenes generated from manufacturing [59]. The use of organic solvents may also explain how Abbas achieved such high carbon yields [68]. All proposed methods have at some point applied HCl washing in their procedure, and these results of these may improve by implementing parts of Wangs technique to the process.

Comparing the methods by purification efficiency projects Bass, Goak, Romanov and Gurova to be most efficient in removing the impurities regardless of as-received purity (table 6). The purification efficiency of Xu and Wu's multistep methods show about the same efficiency. The most inefficient purification methods are Kims multistep, Abbas liquid separation and Merciers oxide method. Although Abbas efficiency seems disappointing, it might be due to not considering optimal conditions for the Fenton chemistry to occur by the H_2O_2 formation. Comparing this method to Wangs results, we observe that Abbas have high yields, but low efficiency, while Wang has lower yield but promising efficiency. In contrary to BCS, Abbas lack the prominent pH value to achieve efficient purification, while BCS lack the Fenton reagent for more high-impact purification. Wu and Kim also applied the Fenton reagent and HCl as chemical purification steps, however in seperate steps. Consequently, they did not achieve to efficiently remove carbon shells. The multistep methods were also dependent of high temperature annealing to remove amorphous carbon, which also exposed the product to oxidation at SWNT defects sites [65]. The most straightforward,facile

method to obtain high yield, near metal free CNTs is by exposing the impurities to very high temperatures, either by locally heating up NPs or heating up the entire product [70, 81, 82]. The trend of all these methods show high yield and high purity. Though high temperature annealing is scalable, it is very costly to invest in. Regarding the fact that BCS aims for ton-scale production, heating a ton scale oven 2000°Cwould be unaffordable at this stage for their company. The concern regarding costly ovens also includes Mercier, Goak and Cabana who applies heat around 900°C, and Wu's multistep method is applying 1200°C. Xu and Wu applied lower temperature oxidations at 350 and 500°Cand still achieve promising purification of amorphous carbon. Investing in such ton scale ovens could be more viable choice for BCS.

Although scalability may not be an option for most ovens, Romanovs method stand out by being thousandfold faster than most of the other methods. A solution could therefore be to purify thousands of small fractions of a large batch, may compensate for the lack of scalability. This will require automation to avoid labor intensity. Still, we must acknowledge that Romanovs experiment was conducted with SWNTs, and that TM diffusion through CNFs may be more demanding [18]. Romanovs method did only report removal of metallic impurities, and is also dependent on chemical methods to remove the carbonaceous shells.

One method have considered applying all the mentioned principles above, which also explains the excellent results. Goak applies high temperature to achieve high diffusion rates. Chloroform and ethanol decomposes into Cl and OH radicals and HCl to efficiently remove TMs with carbon shells, similar to Wang[66]. However, the TMs conform to metal halides similar to Xu and Merciers halogen gas approach. Ethanol -modified MWNTs works as a protective layers in the purification process. In addition, Goak states that the ethanol gas in milder a milder reagent than steam as less OH radicals were formed, which was the main reagent in Cabanas method. The post treatment was with a liquid ethanol and water separation process which reduced the amount of other impurities similar to Abbas separation principle. The only concern of the method is regard to some surface modification of alkyl groups.

Kiscinski also recommended using the TMs magnetic properties when dealing with large oxidation-resistant NPs [18]. As BCS has hundredfold larger chromium particles in their sample than usual, it is expected highly effective results applying Gurovas methods for this special case. Moreover, the higher inherent physical ability for CNFs to disperse in water, may ease the dispersing process. In comparison of Bass' results, this method guarantee effective and scalable purification. Yet, having some setbacks with particles in shells [73],Applying methods from the other proposed methods may solve this.

Similar to Romanovs method, Bass' fast and highly efficient method of extracting NPs could also be viable to remove metal NP impurities. In contrast to the other methods, Bass' methods selectively collect and separate particles using electrodes. Bass claims the method to be scalable, which may be true if heterogeniety is accounted for. Still, this fast and efficient wildcard may be

worth an attempt, or atleast be an asset to the nanotechnologists' toolbelt for future NP separation problems.

5   Conclusion

As raw product from manufacturing tends to be heterogenous and inconsistent, proceeds also to which purification method is most applicable. For an upscaling of this technology, It is advisable to have a wide toolbox of purification methods available to reliably confront further challenges regarding purification in nanoscale. An established purification report protocol is required to consistently compare results in this field. According to literature, it is recommended using halogen oxidation and high temperature annealing for common industrial scale manufacturing of SWNTs. Multistep methods seem to be consistent as they take into account every scenario of impurity, despite that most of the process may not be nescessary for every case. Methods which can be easily adjusted over time with controllable treatments might be the right approach to highly heterogenous systems. Goaks method show superior results in efficiently removing amorphous carbon and TMs to achieve a high yield, medical grade purity MWNT. For BCS' case, the main challenge revolves in consistency and cost, and not in fragility as concerned with SWNTs. Pretreatment methods such as High pressure temperature filtration and CFF is highly recommended before considering to remove amorphous carbon and TMs. Besides Goaks method, adapting Wu or Xu's approach by also including the Fenton process should reliably achieve ECO-C1 grade purity at a cheaper alternative to Goaks setup. Gurovas magnetic separation is the preferred method to remove the giant chromium particles.

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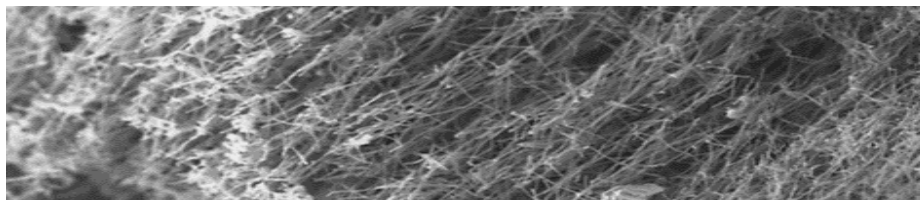(82) Andrews, R.; Jacques, D.; Qian, D.; Dickey, E. C. *Carbon* **2001**, *39*, 1681–1687.

Appendix
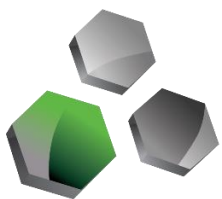
Product Data Sheet

Bergen Carbon Solutions AS

CNF grades at BCS	ECO-C1	ECO-C2	ECO-C3
Linear formula	C	C	C
Molecular weight (g/mol)	12.01	12.01	12.01
Apperance	Powder	Powder	Powder
Color	Black	Black	Black
Carbon content (± %)	80-95	80-95	80-90
CNF content (± %)	80	70	50-55
Ash (± %)	1.5	5	7
Length (± μ)	5-150	5-100	5-100
Thickness (± nm)	200-600	200-600	200-600
Melting point (^{0}C) *	N/A	N/A	N/A
Tap density (kg/m^3) *	N/A	N/A	N/A
Bulk density (kg/m^3) *	N/A	N/A	N/A
Specific surface area *	N/A	N/A	N/A
Solubility in water *	N/A	N/A	N/A
Electrical conductivity *	N/A	N/A	N/A

*Bergen Carbon Solutions AS is producing three grades of carbon nano fibers and is currently testing its carbon nano fibers for detailed analysis of product and data for these theoretical properties will be added as soon as Bergen Carbon Solutions AS got the result from research institutes. In a mean while there is some data available from research articles on these properties that can be provided on demand.