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Appendices: Carbon nanotubes

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Appendices: Carbon nanotubes

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Appendix 1. Hybridization of carbon atoms and typical carbon materials

1.1 Introduction

This appendix describes in brief the different types of carbon materials (allotropes) categorized according to the different types of carbon-carbon atom electron bonding (hybridization).

1.2 Carbon atom hybridization

Carbon materials can be bonded in different ways and are often classified by the type of electronic bonding (hybridization) between the carbon atoms. Three types of hybridization occur in solid carbon materials, namely sp^3, sp^2, and mixed sp^2-sp^3. The *s* and *p* refers to the electronic orbitals surrounding the carbon atom.

Classification according to carbon atom hybridization can be used to illustrate the principal atomic structures of the different carbon compounds (allotropes). The type of hybridization is an important parameter controlling e.g, the possible structures, isotropi/anisotropi, hardness, as well as the optical and electronic conducting properties of these carbon materials. A schematic overview of some carbon allotropes is shown in Figure 1.1.

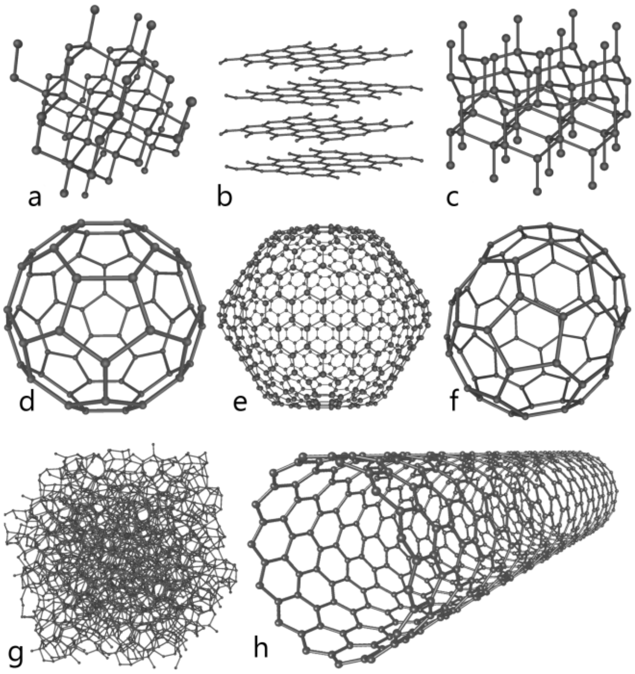


FIGURE 1.1:
EIGHT ALLOTROPES OF CARBON: A) DIAMOND (SP^3), B) GRAPHITE (SP^2), C) LONSDALEITE (SP^3), D) C_{60} (SP^2), E) C_{540} (SP^2), F) C_{70}, (SP^2) G) AMORPHOUS CARBON (SP^{2-3}), AND H) OPEN-ENDED SWCNT (SP^2 WITH SOME SP^3-LIKE PROPERTIES. (HTTP://EN.WIKIPEDIA.ORG/WIKI/ALLOTROPES_OF_CARBON)

1.3 *sp*^{3} hybridized carbon

When carbon is *sp*^{3} hybridized, each carbon atom is bonded by four identical bonds to four carbon atoms arranged in a tetrahedron. The *sp*^{3} materials are isotropic, which implies that they have the same property in along all primary crystallographic axes. Diamond, which naturally may be either cubic (normal) or hexagonal, is an example of a *sp*^{3} hybridized material (Figures 1.1a and c). Diamond is a very hard material and has a high thermal conductivity, but pure diamonds are electrical insulators.

TABLE 1.1:
EXAMPLES OF SP^3 HYBRIDIZED PHASES

Phase	Comment	Use
Diamond (cubic)	-	Gemstone, cutting tools
Lonsdaleite (hexagonal diamond)	-	Gemstone

1.4 *sp*^{2} hybridized carbon

In pure carbon materials with *sp*^{2} hybridized carbon, each atom is bonded to only 3 other atoms in a planar triangular configuration. If the triangle is perfect, the carbon atoms are arranged in a flat hexagonal lattice, also called a graphite or graphene sheet. Imperfect triangles give rise to pentagons or heptagons (or others) and the carbon sheet can no longer maintain being flat. In such defect structures, three of the four bonding electrons of carbon are used for the bonds in the hexagonal lattice and the last electron is delocalized in so-called π-orbitals above and below the sheet. The delocalised electrons can move around on the graphite sheet, which is the reason for its electrical conductivity. The *sp*^{2} carbon materials are anisotropic and hence, do not have similar properties along the different crystallographic orientations.

TABLE 1.2:
EXAMPLES OF SP2 HYBRIDIZED PHASES

Phase	Comment	Use
Graphite	-	Lubricant, steel etc.
Graphene	New isolated material	In development
Fullerenes	-	Lubricant, cosmetics, electronics
Carbon nanotubes	Sometimes listed of a subgroup of fullerenes	See Chapter 3
Glassy carbon	Material with random orientation of graphene	Electrodes
Activated carbon	Very small particles. High surface area.	Absorbent of pollutants and noxious gasses
Carbon Black	Poorly defined structure, Typically planar stacks or multilayer balls	Pigment, printing ink and filler in rubber.
Carbon fibers	Graphite ribbons parallel to the fiber. Has a high tensile strength.	Used in high-strength plastics, e.g. for tennis rackets and aircraft components.

The sp^2 hybridised carbon sheets may be arranged in stacks of sheets, stacks of cones or concentric tube structures (See Figure 1.1). The bonds within a carbon sheet, cone or tube are very strong, but the bonding between the sheets is weak and maintained by Van der Wall forces. The materials are good conductors along the carbon sheets, but poor perpendicular to the sheet structure. CNT as well as graphite, graphene, fullerene, and several other phases belong to this group of materials (Table 1.2). CNT is often considered a subgroup of fullerenes and currently reported as tubular fullerene structures.

Noteworthy, however, the curvature of the tubular and spherical carbon materials makes the sp^2-bonding protrude into the third dimension. Therefore these bend sheet structures achieve some of the characteristics of the sp^3 bonds. Consequently, CNT can exhibit some mechanical and electronic properties in between that of graphite and diamond [2]. Regarding the stacking of graphene sheets, it should be noted that graphite not always occurs in hexagonal arrangement (the so-called α-graphite structure). In nature graphene sheets can also be stacked in rhombohedral form to form the β-graphite structure.

1.5 *sp^3-sp^2* mixed hybridrized carbon

The *sp^3-sp^2* mixed hybridized carbon structures is recognized by the absence of long range order, and are therefore amorphous (Table 1.3). Since this mixed hybridization is completely disordered, these materials are isotropic (See Figure 1.1g). The complete disorder is also the reason why CNT cannot be a *sp^3-sp^2* material despite it also has *sp^3*-like bonds.

TABLE 1.3:
EXAMPLES OF SP2-SP3 HYBRIDIZED PHASES

Phase	**Comment**	**Use**
Amorphous carbon	Term often use generically for sp2 materials	Pigment, rubber, batteries etc.
Carbon nanofoam	Randomly oriented graphitic sheets	Insulation, absorbent, coatings, optics etc.
Soot, coke, coal	Amorphous carbon	Sometimes used as fuel, steel additives etc.

Appendix 2. Overview over commercial carbon nanotubes, types, primary characteristics and venders

2.1 Introduction

In this appendix we list the different commercially available CNT identified in internet searches on suppliers of CNT. The identified commercial CNT were advertized as Single-Walled, Double-Walled, Multi-Walled, as well as Herring-Bone and Cup-Stack CNT, which also forms the basis for the material divisions in the Tables below. The listed CNT are their key physico-chemical characteristics reported by the suppliers. It should be noted that more different commercial CNT may be available, but we assume that the high number of CNT types are sufficient to illustrate the variability in dimensions, types of functionalizations, specific surface area (SSA), as well as their chemical and structural purity (purity).

2.2 Single-walled (SW) CNT

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	Min	Max	(wt%)	
SWNT	Helix	0.5	3.0	1	2	none		300	600	50-70%	Amorphous
SZSS01	AlphaNano	0.5	2.0	1	2	none		400	400	90%	Amorphous carbon
SWNTs 90s 1-2 nm	Cheap Tubes	0.5	2.0	1	2	none		407	407	90%	Additional MWNT content

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	Min	Max	(wt%)	
SWNT 60s 1-2 nm	Cheap Tubes	0.5	2.0	1	2	none		407	407	60%	Additional MWNT content
Short SWNTs 90wt%	Cheap Tubes	0.5	2.0	1	2	none		407	407	90%	Additional MWNT content
SWCNTs	Helix	0.5	40.0	1	1	none		300	600	90%	Amorphous carbon
Low cost SWCNT	Helix	0.5	3.0	1	1	none				50-70%	
SWNT	Helix	0.5	40.0	1	1	none		300	600	90%	Amorphous
BU-202	BuckyUSA	0.5	10.0	1	3	none				90%	
BU-203	BuckyUSA	0.5	5.0	1	3	none				95%	
Short SWCNTs	Chengdu	1.0	3.0	1	2	none				90%	
SISWCNTs	Chengdu	1.0	3.0	1	2	none				60%	
SWCNT-1-S-SL-1	Nanoshel	3.0	8.0	1	2	none		450	550	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
SWCNT-1-S-SL-2	Nanoshel	3.0	8.0	1	2	none		450	550	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
SWCNT-1-S-SL-3	Nanoshel	3.0	8.0	1	2	none		450	550	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
SZS002	AlphaNano	5.0	20.0	1	2	none		400	400	90%	Amorphous carbon
SZS001	AlphaNano	5.0	20.0	1	2	none		400	400	60%	Amorphous carbon
SWNTs 90wt%	Cheap Tubes	5.0	30.0	1	2	none		407	407	90%	Additional MWNT content
SWNTs 60wt%	Cheap Tubes	5.0	30.0	1	2	none		407	407	60%	Additional MWNT content
Short SWNTs 60wt%	Cheap Tubes	5.0	30.0	1	2	none		407	407	60%	Additional MWNT content
ARS001	Arry	5.0	20.0	1	2	none		400	400	60%	Amorphous carbon
ARS002	Arry	5.0	20.0	1	2	none		400	400	90%	Amorphous carbon
ARS001	Arry	5.0	20.0	1	2	none		400	400	60%	Amorphous carbon
NTX8	NanoThinx	5.0	5.0	1	1	none		500	600	60% < x < 65%	Amorphous carbon

Product	**Producer**	**length**		**diameter**		**Functionalization**		**SSA (m^2/g)**		**Purity**	**Primary Impurity**
		min	**max**	**min**	**max**	**Type**	**(wt%)**	**Min**	**Max**	**(wt%)**	
NTX9	NanoThinx	5.0	5.0	1	1	none		900	900	≥85%	Amorphous carbon
SWCNT-2-S-ML-1	Nanoshel	5.0	15.0	1	2	none		450	550	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
SWCNT-2-S-ML-2	Nanoshel	5.0	15.0	1	2	none		450	550	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
SWCNT-2-S-ML-3	Nanoshel	5.0	15.0	1	2	none		450	550	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
MRSW	MerCorp	10.0	50.0	1	1	none					25 wt% metal catalyst particles
SWCNT-3-S-LL-1	Nanoshel	15.0	30.0	1	2	none		450	550	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
SWCNT-3-S-LL-2	Nanoshel	15.0	30.0	1	2	none		450	550	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
SWCNT-3-S-LL-3	Nanoshel	15.0	30.0	1	2	none		450	550	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
NC1000	Nanocyl			2	2	none		1000	1000	70%	Metaloxid
High purity SWCNTs	Chengdu			1	2	none				90%	
SWCNTs	Chengdu			1	2	none				90%	
ISWCNTs	Chengdu			1	2	none				60%	
SWNT	SES Research	1.0	5.0		2	none				90%	Amorphous carbon
SWNT	SES Research	5.0	15.0			none					
MT-SW-HPO-002	CarbonNT&F 21	20.0	20.0	2	2	none		450	450	90%	Amorphous carbon
Short SWNTs 90wt%-OH	Cheap Tubes	0.5	2.0	1	2	OH	3.90	407	407	90%	Additional MWNT content
Short SWCNTs-OH	Chengdu	1.0	3.0	1	2	OH				90%	
SISWCNTs-OH	Chengdu	1.0	3.0	1	2	OH				60%	
ARQS001-OH	Arry	3.0	10.0	1	2	OH	1-5	400	400	90%	Amorphous carbon
OH-SWCNT-1-SO-SL-1	Nanoshel	3.0	8.0	1	2	OH	0,5-3	350	500	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
OH-SWCNT-1-SO-SL-2	Nanoshel	3.0	8.0	1	2	OH	0,5-3	350	500	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon

Product	**Producer**	**length**		**diameter**		**Functionalization**		**SSA (m^2/g)**		**Purity**	**Primary Impurity**
		min	**max**	**min**	**max**	**Type**	**(wt%)**	**Min**	**Max**	**(wt%)**	
OH-SWCNT-1-SO-SL-3	Nanoshel	3.0	8.0	1	2	OH	0,5-3	350	500	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
OH-SWCNT-2-SO-ML-3	Nanoshel	3.0	8.0	1	2	OH	0,5-3	350	500	>80% (carbon nanotubes); >50% (single-walled nanotubes)	
FSQ001	AlphaNano	5.0	20.0	1	2	OH	4.20	400	400	90%	Amorphous carbon
OH-SWNT 90s	Cheap Tubes	5.0	30.0	1	2	OH	3.90	407	407	90%	Additional MWNT content
SWNTs 90wt%-OH	Cheap Tubes	5.0	30.0	1	2	OH	3.90	407	407	90%	Additional MWNT content
OH-SWCNT-2-SO-ML-1	Nanoshel	5.0	15.0	1	2	OH	0,5-3	350	500	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
OH-SWCNT-2-SO-ML-2	Nanoshel	5.0	15.0	1	2	OH	0,5-3	350	500	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
OH-SWCNT-3-SO-LL-1	Nanoshel	15.0	30.0	1	2	OH	0,5-3	350	500	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
OH-SWCNT-3-SO-LL-2	Nanoshel	15.0	30.0	1	2	OH	0,5-3	350	500	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
OH-SWCNT-3-SO-LL-3	Nanoshel	15.0	30.0	1	2	OH	0,5-3	350	500	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
SWCNTs-OH	Chengdu			1	2	OH				90%	
ISWCNTs-OH	Chengdu			1	2	OH				60%	
Short SWNTs 90wt%-COOH	Cheap Tubes	0.5	2.0	1	2	COOH	2.70	407	407	90%	Additional MWNT content
Short SWCNTs-COOH	Chengdu	1.0	3.0	1	2	COOH				90%	
SISWCNTs-COOH	Chengdu	1.0	3.0	1	2	COOH				60%	
ARSS001-COOH	Arry	3.0	10.0	1	2	COOH	1-4	400	400	90%	Amorphous carbon
COOH-SWCNT-1-SC-SL-1	Nanoshel	3.0	8.0	0.7	2	COOH	0,5-3	350	500	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-1-SC-SL-2	Nanoshel	3.0	8.0	0.7	2	COOH	0,5-3	350	500	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-1-SC-SL-3	Nanoshel	3.0	8.0	0.7	2	COOH	0,5-3	350	500	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
FSS001	AlphaNano	5.0	20.0	1	2	COOH	3.10	400	400	90%	Amorphous carbon
COOH-SWNTs 90s	Cheap Tubes	5.0	30.0	1	2	COOH	2.70	407	407	90%	Additional MWNT content

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	Max	(wt%)	
SWNTs 90wt%-COOH	Cheap Tubes	5.0	30.0	1	2	COOH	2.70	407	407	90%	Additional MWNT content
COOH-SWCNT-2-SC-ML-1	Nanoshel	5.0	15.0	0.7	2	COOH	0.5-3	350	500	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-2-SC-ML-2	Nanoshel	5.0	15.0	0.7	2	COOH	0.5-3	350	500	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-2-SC-ML-3	Nanoshel	5.0	15.0	0.7	2	COOH	0.5-3	350	500	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-3-SC-LL-1	Nanoshel	15.0	30.0	0.7	2	COOH	0.5-3	350	500	>98% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-3-SC-LL-2	Nanoshel	15.0	30.0	0.7	2	COOH	0.5-3	350	500	>90% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
COOH-SWCNT-3-SC-LL-3	Nanoshel	15.0	30.0	0.7	2	COOH	0.5-3	350	500	>80% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
NC1001	Nanocyl			2	2	COOH	5%	1000	1000	70%	Metaloxid
SWCNTs-COOH	Chengdu			1	2	COOH				90%	
ISWCNTs-COOH	Chengdu			1	2	COOH				60%	

2.3 Double-walled (DW) CNT

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
DWNTs	Cheap Tubes			2	4	none		350	350	60%	Ash
DWCNTs	Helix	0.5	40.0	4	4	none		300	600	90%	Amorphous carbon
DWNT	Helix	0.5	40.0	4	4	none		300	600	90%	Amorphous
Short DWCNTs	Chengdu	0.5	2.0	2	4	none				60%	

NC2100	Nanocyl	1.0	10.0	3.5	3.5	none		500	500	90%	Metaloxid
MRDW	MerCorp	5.0	15.0	3	5	none				35%	Metal particles (Co+Ni+Fe)
ARD001	Arry	5.0	15.0	1	3	none		500	500	80%	Amorphous carbon

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
NC2150	Nanocyl			3.5	3.5	none				90%	Metaloxid
DWCNTs	Chengdu			2	4	none				60%	
DWNT	SES Research	5.0	15.0		5	none				90%	Amorphous carbon
Short DWCNTs-OH	Chengdu	0.5	2.0	2	4	OH				60%	
DWCNTs-OH	Chengdu			2	4	OH				60%	
NC2152	Nanocyl			3.5	3.5	NH2	0.5%			90%	Metaloxid
Short DWCNTs-COOH	Chengdu	0.5	2.0	2	4	COOH				60%	
NC2101	Nanocyl	1.0	10.0	3.5	3.5	COOH	1%	500	500	90%	Metaloxid
NC2151	Nanocyl			3.5	3.5	COOH	3%			90%	Metaloxid
DWCNTs-COOH	Chengdu			2	4	COOH				60%	

2.4 Multi-walled (MW) CNT

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
FMS009	AlphaNano	5.0	20.0	50	80	COOH	0.5-3%	120	120	95%	Amorphous carbon
FMS008	AlphaNano	5.0	20.0	30	50	COOH	0.5-3%	200	200	95%	Amorphous carbon
FMS006	AlphaNano	5.0	20.0	20	30	COOH	0.5-3%	200	200	95%	Amorphous carbon
FMS003	AlphaNano	5.0	30.0	10	20	COOH	0.5-3%	350	350	95%	Amorphous carbon
FMS001	AlphaNano	5.0	20.0	3	10	COOH	0.5-3%	500	500	95%	Amorphous carbon
COOH-MWNTs 50 nm	Cheap Tubes	10.0	20.0	50	50	COOH	0.50%	60	60	95%	Ash
COOH-MWNTs 30-50 nm	Cheap Tubes	10.0	20.0	30	30	COOH	0.70%	60	60	95%	Ash
COOH-MWNTs 20-30 nm	Cheap Tubes	10.0	30.0	20	20	COOH	1.20%	110	110	95%	Ash

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
COOH-MWNTs 10-20 nm	Cheap Tubes	10.0	30.0	10	10	COOH	1.80%	233	233	95%	Ash
COOH-MWNTs 8-15nm	Cheap Tubes	10.0	50.0	8	8	COOH	2.50%	233	233	95%	Ash
COOH-MWNTs-8nm	Cheap Tubes	10.0	30.0		8	COOH	3.80%	500	500	95%	Ash
MWCNTs-COOH	Chengdu				8	COOH				95%	
MWCNTs-COOH	Chengdu			8	15	COOH				95%	
MWCNTs-COOH	Chengdu			20	30	COOH				95%	
MWCNTs-COOH	Chengdu			30	50	COOH				95%	
MWCNTs-COOH	Chengdu			54		COOH				95%	
Short MWCNTs-COOH	Chengdu				8	COOH				95%	
Short MWCNTs-COOH	Chengdu			8	15	COOH				95%	
Short MWCNTs-COOH	Chengdu			20	30	COOH				95%	
Short MWCNTs-COOH	Chengdu			30	50	COOH				95%	
Short MWCNTs-COOH	Chengdu			54		COOH				95%	
Graphitized MWCNTs-COOH	Chengdu				8	COOH				99.90%	
Graphitized MWCNTs-COOH	Chengdu			8	15	COOH				99.90%	
Graphitized MWCNTs-COOH	Chengdu			20	30	COOH				99.90%	
Graphitized MWCNTs-COOH	Chengdu			30	50	COOH				99.90%	
Graphitized MWCNTs-COOH	Chengdu			54		COOH				99.90%	
NC3101	Nanocyl	1.5	1.5	9.5	9.5	COOH	4%			95%	Metaloxid
NC3151	Nanocyl	1.0	1.0	9.5	9.5	COOH	4%			95%	Metaloxid
COOH-MWCNT-1-MC-SL-1	Nanoshel	5.0	15.0	4	12	COOH	1-6wt%	300		>90% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
COOH-MWCNT-1-MC-SL-2	Nanoshel	5.0	15.0	4	12	COOH	1-6wt%	300		>80% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-1-MC-SL-3	Nanoshel	5.0	15.0	4	12	COOH	1-6wt%	300		>70% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-2-MC-ML-1	Nanoshel	15.0	30.0	4	12	COOH	1-6wt%	300		>90% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-2-MC-ML-2	Nanoshel	15.0	30.0	4	12	COOH	1-6wt%	300		>80% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-2-MC-ML-3	Nanoshel	15.0	30.0	4	12	COOH	1-6wt%	300		>90% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-3-MC-LL-1	Nanoshel	15.0	30.0	4	12	COOH	1-6wt%	300		>90% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-3-MC-LL-2	Nanoshel	15.0	30.0	4	12	COOH	1-6wt%	300		>80% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
COOH-MWCNT-3-MC-LL-3	Nanoshel	15.0	30.0	4	12	COOH	1-6wt%	300		>70% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
NC3152	Nanocyl	1.0	1.0	9.5	9.5	NH2	0.5%			95%	Metaloxid
SZSM009	AlphaNano	0.5	2.0	50	80	none		120	120	95%	Amorphous carbon
SZSM008	AlphaNano	0.5	2.0	30	50	none		200	200	95%	Amorphous carbon
SZSM006	AlphaNano	0.5	2.0	20	30	none		200	200	95%	Amorphous carbon
SZSM003	AlphaNano	0.5	2.0	10	20	none		350	350	95%	Amorphous carbon
GYM003	AlphaNano	5.0	10.0	50	100	none		100	100	90%	Ash
SZM009	AlphaNano	5.0	20.0	50	80	none		120	120	95%	Amorphous carbon
LiA-M001	AlphaNano	5.0	20.0	50	80	none		100	100		
GYM002	AlphaNano	5.0	15.0	30	50	none		200	200	90%	Ash
DCM001	AlphaNano	5.0	150.0	30	50	none		250	250	95%	Ash
SZM008	AlphaNano	5.0	20.0	30	50	none		200	200	95%	Amorphous carbon
SZSM001	AlphaNano	0.5	2.0	3	10	none		500	500	95%	Amorphous carbon
SZM006	AlphaNano	5.0	20.0	20	30	none		200	200	95%	Amorphous carbon

Product	**Producer**	**length**		**diameter**		**Functionalization**		**SSA (m^2/g)**		**Purity**	**Primary Impurity**
		min	**max**	**min**	**max**	**Type**	**(wt%)**	**min**	**max**	**(wt%)**	
GYM001	AlphaNano	5.0	20.0	10	30	none		300	300	90%	Ash
SZM003	AlphaNano	5.0	30.0	10	20	none		350	350	95%	Amorphous carbon
SZM002	AlphaNano	5.0	30.0	8	15	none		350	350	95%	Amorphous carbon
SZM001	AlphaNano	5.0	20.0	3	10	none		500	500	95%	Amorphous carbon
C150P	Bautybes	1.0	1.0	13	13	none				95%	
C150HP	Bautybes	1.0	1.0	13	13	none				99%	
C70P	Baytubes	1.0	1.0	13	13	none				95%	
BU-200	BuckyUSA	1.0	10.0	5	15	none				95%	
BU-201	BuckyUSA	1.0	5.0	5	15	none				98%	
	CarbonNT&F 21	1.0	2.0	60	100	none		40	300		
	CarbonNT&F 21	1.0	2.0	40	60	none		40	300		
	CarbonNT&F 21	1.0	2.0	20	40	none		40	300		
MT-MW-060-100	CarbonNT&F 21	5.0	15.0	60	100	none		40	300	95%	Amorphous carbon
	CarbonNT&F 21	1.0	2.0	10	20	none		40	300		
	CarbonNT&F 21	1.0	2.0	10	30	none		40	300		
MT-MW-040-060	CarbonNT&F 21	5.0	15.0	40	60	none		40	300	95%	Amorphous carbon
MT-MW-020-040	CarbonNT&F 21	5.0	15.0	20	40	none		40	300	95%	Amorphous carbon
MT-MW-ALO-010	CarbonNT&F 21	5.0	15.0	10	10	none		40	300	95%	Amorphous carbon
MT-MW-010-020	CarbonNT&F 21	5.0	15.0	10	20	none		40	300	95%	Amorphous carbon
Mt-MW-010-020	CarbonNT&F 21	5.0	15.0	10	30	none		40	300	95%	Amorphous carbon
MT-MW-000-010	CarbonNT&F 21	5.0	15.0	10	10	none		40	300	95%	Amorphous carbon

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
MWNTs 30-50 nm	Cheap Tubes	0.5	2.0	30	50	none		60	60	95%	Ash
MWNTs 20-30 nm	Cheap Tubes	0.5	2.0	20	30	none		110	110	95%	Ash
MWNTs 10-20 nm	Cheap Tubes	0.5	2.0	10	20	none		233	233	95%	Ash
MWNTs 8-15 nm	Cheap Tubes	0.5	2.0	8	15	none		233	233	95%	Ash
MWNTs 50-80 nm	Cheap Tubes	10.0	20.0	50	80	none		60	60	95%	Ash
MWNTs 8 nm	Cheap Tubes	0.5	2.0		8	none		500	500	95%	Ash
MWCNTs	Chengdu				8	none				95%	
MWCNTs	Chengdu			8	15	none				95%	
MWCNTs	Chengdu			20	30	none				95%	
MWCNTs	Chengdu			30	50	none				95%	
MWCNTs	Chengdu			54		none				95%	
Short MWCNTs	Chengdu				8	none				95%	
Short MWCNTs	Chengdu			8	15	none				95%	
Short MWCNTs	Chengdu			20	30	none				95%	
Short MWCNTs	Chengdu			30	50	none				95%	
Short MWCNTs	Chengdu			54		none				95%	
Graphitized MWCNTs	Chengdu				8	none				99.90%	
Graphitized MWCNTs	Chengdu			8	15	none				99.90%	
Graphitized MWCNTs	Chengdu			20	30	none				99.90%	
Graphitized MWCNTs	Chengdu			30	50	none				99.90%	
Graphitized MWCNTs	Chengdu			54		none				99.90%	

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
Ni coated MWCNTs	Chengdu				8	none				98%	
Ni coated MWCNTs	Chengdu			8	15	none				98%	
Ni coated MWCNTs	Chengdu			20	30	none				98%	
Ni coated MWCNTs	Chengdu			30	50	none				98%	
Ni coated MWCNTs	Chengdu			54		none				98%	
MWNT - small diameter	Helix	0.5	40.0		10	none		40	300	95%	Amorphous
MWNT - small diameter	Helix	0.5	40.0	10	20	none		40	300	95%	Amorphous
MWNT - standard	Helix	0.5	40.0	10	30	none		40	300	95%	Amorphous
MWNT - standard	Helix	0.5	40.0	20	40	none		40	300	95%	Amorphous
MWNT - standard	Helix	0.5	40.0	40	60	none		40	300	95%	Amorphous
MWNT - standard	Helix	0.5	40.0	60	100	none		40	300	95%	Amorphous
MWCNTs	Helix	1.0	2.0		10	none		40	300	95%	Amorphous carbon
MWCNTs	Helix	1.0	2.0	10	20	none		40	300	95%	Amorphous carbon
MWCNTs	Helix	1.0	2.0	10	30	none		40	300	95%	Amorphous carbon
MWCNTs	Helix	1.0	2.0	20	40	none		40	300	95%	Amorphous carbon
MWCNTs	Helix	1.0	2.0	40	60	none		40	300	95%	Amorphous carbon
MWCNTs	Helix	1.0	2.0	60	100	none		40	300	95%	Amorphous carbon
MWNT - short	Helix	1.0	2.0	10	20	none		40	300	95%	Amorphous
MWNT - short	Helix	1.0	2.0	10	30	none		40	300	95%	Amorphous
MWNT - short	Helix	1.0	2.0	20	40	none		40	300	95%	Amorphous
MWNT - short	Helix	1.0	2.0	40	60	none		40	300	95%	Amorphous

Product	**Producer**	**length**		**diameter**		**Functionalization**		**SSA (m^2/g)**		**Purity**	**Primary Impurity**
		min	**max**	**min**	**max**	**Type**	**(wt%)**	**min**	**max**	**(wt%)**	
MWNT - short	Helix	1.0	2.0	60	100	none		40	300	95%	Amorphous
MRCSD	MerCorp	5.0	9.0	110	170	none				>90%	
MRMW	MerCorp	1.0	5.0	6	20	none					
MRGC	MerCorp	1.0	5.0	6	20	none					
MRCMW	MerCorp	30.0	30.0	25	45	none				>90%	Fe
XNRI MWNT-7	Mitsui			40	90	none		26		>99.5% (carbon)	
NC3100	Nanocyl	1.5	1.5	9.5	9.5	none				95%	Metaloxid
NC3150	Nanocyl	1.0	1.0	9.5	9.5	none				95%	Metaloxid
NC7000	Nanocyl	1.5	1.5	9.5	9.5	none		275	275	90%	Alumina
MWCNT	NanoLab	5.0	20.0	10	30	none				>85%	
MWCNT-1-M-SL-1	Nanoshel	3.0	10.0	4	12	none		50	350	>90% (carbon nanotubes); >70% (multi-walled nanotubes)	Amorphous carbon
MWCNT-1-M-SL-2	Nanoshel	3.0	10.0	4	12	none		50	350	>80% (carbon nanotubes); >65% (multi-walled nanotubes)	Amorphous carbon
MWCNT-1-M-SL-3	Nanoshel	3.0	10.0	4	12	none		50	350	>65% (carbon nanotubes); >50% (multi-walled nanotubes)	Amorphous carbon
MWCNT-2-M-ML-1	Nanoshel	5.0	15.0	4	12	none		50	350	>90% (carbon nanotubes); >70% (multi-walled nanotubes)	
MWCNT-2-M-ML-2	Nanoshel	5.0	15.0	4	12	none		50	350	>80% (carbon nanotubes); >65% (multi-walled nanotubes)	Amorphous carbon
MWCNT-2-M-ML-3	Nanoshel	5.0	15.0	4	12	none		50	350	>70% (carbon nanotubes); >50% (multi-walled nanotubes)	Amorphous carbon
MWCNT-3-M-LL-1	Nanoshel	15.0	30.0	4	12	none		50	350	>90vol% (carbon nanotubes); >70vol% (multi-walled nanotubes)	Amorphous carbon
MWCNT-3-M-LL-2	Nanoshel	15.0	30.0	4	12	none		50	350	>80vol% (carbon nanotubes); >65vol% (multi-walled nanotubes)	Amorphous carbon
MWCNT-3-M-LL-3	Nanoshel	15.0	30.0	4	12	none		50	350	>70vol% (carbon nanotubes); >50vol% (multi-walled nanotubes)	Amorphous carbon
NTX3	NanoThinx	10.0	10.0	25	40	none		200	250	≤98.5%	Amorphous carbon
NTX1	NanoThinx	10.0	10.0	15	35	none		200	250	97%	Amorphous carbon

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
NTX2	NanoThinx	10.0	10.0	15	35	none		200	250	≥95%	Amorphous carbon
NTC4 (thin MWNT)	NanoThinx	10.0	10.0	6	10	none		300	300	>90%	Amorphous carbon
MWNT	SES Research	1.0	2.0		10	none				95%	Amorphous carbon
MWNT	SES Research	1.0	2.0	10	30	none				95%	Amorphous carbon
MWNT	SES Research	1.0	2.0	40	60	none				95%	Amorphous carbon
MWNT	SES Research	1.0	2.0	60	100	none				95%	Amorphous carbon
VGCF	Showa Denko	10.0	20.0	150	150	none		13			
MWNTs	Sun Nano China			10	30	none				90%	
FMQ009	AlphaNano	5.0	20.0	50	80	OH	1-7%	120	120	95%	Amorphous carbon
FMQ008	AlphaNano	5.0	20.0	30	50	OH	1-7%	200	200	95%	Amorphous carbon
FMQ006	AlphaNano	5.0	20.0	20	30	OH	1-7%	200	200	95%	Amorphous carbon
FMQ003	AlphaNano	5.0	30.0	10	20	OH	1-7%	350	350	95%	Amorphous carbon
FMQ001	AlphaNano	5.0	20.0	3	10	OH	1-7%	500	500	95%	Amorphous carbon
OH-MWNTs 50 nm	Cheap Tubes	10.0	20.0	50	80	OH	0.70%	60	60	95%	Ash
OH-MWNTs 30-50 nm	Cheap Tubes	10.0	20.0	30	50	OH	1.00%	60	60	95%	Ash
OH-MWNTs 20-30 nm	Cheap Tubes	10.0	30.0	20	30	OH	1.60%	110	110	95%	Ash
OH-MWNTs 10-20 nm	Cheap Tubes	10.0	30.0	10	20	OH	2.00%	233	233	95%	Ash
OH-MWNTs 8-15 nm	Cheap Tubes	10.0	50.0	8	15	OH	3.70%	233	233	95%	Ash
OH-MWNTs 8 nm	Cheap Tubes	10.0	30.0		8	OH	5.50%	500	500	95%	Ash
MWCNTs-OH	Chengdu				8	OH				95%	
MWCNTs-OH	Chengdu			8	15	OH				95%	

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
MWCNTs-OH	Chengdu			20	30	OH				95%	
MWCNTs-OH	Chengdu			30	50	OH				95%	
MWCNTs-OH	Chengdu			54		OH				95%	
Short MWCNTs-OH	Chengdu				8	OH				95%	
Short MWCNTs-OH	Chengdu			8	15	OH				95%	
Short MWCNTs-OH	Chengdu			20	30	OH				95%	
Short MWCNTs-OH	Chengdu			30	50	OH				95%	
Short MWCNTs-OH	Chengdu			54		OH				95%	
Graphitized MWCNTs-OH	Chengdu				8	OH				99.90%	
Graphitized MWCNTs-OH	Chengdu			8	15	OH				99.90%	
Graphitized MWCNTs-OH	Chengdu			20	30	OH				99.90%	
Graphitized MWCNTs-OH	Chengdu			30	50	OH				99.90%	
Graphitized MWCNTs-OH	Chengdu			54		OH				99.90%	
OH-MWCNT-1-MO-SL-1	Nanoshel	3.0	10.0	4	12	OH	1-6wt%	300		>90% (carbon nanotubes); >70% (single-walled nanotubes)	Amorphous carbon
OH-MWCNT-1-MO-SL-2	Nanoshel	3.0	10.0	4	12	OH	1-6wt%	300		>80% (carbon nanotubes); >65% (single-walled nanotubes)	Amorphous carbon
OH-MWCNT-1-MO-SL-3	Nanoshel	3.0	10.0	4	12	OH	1-6wt%	300		>70% (carbon nanotubes); >50% (single-walled nanotubes)	Amorphous carbon
MT-MW-000-010	CarbonNT&F 21	1.0	2.0								
MWCNTs	Helix	0.5	40.0	10	20						
MWCNTs	Helix	0.5	40.0	10	30						
MWCNTs	Helix	0.5	40.0	20	40						
MWCNTs	Helix	0.5	40.0	40	60						

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
MWCNTs	Helix	0.5	40.0	60	100						
MWNT	SES Research	5.0	15.0								

2.5 Heering-Bone (HB) CNT

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
MT-DW-HPO-005	CarbonNT&F 21	5.0	15.0	10	20	none		40	300	95%	Amorphous carbon

2.6 Cup-Stack (CS) CNT

Product	Producer	length		diameter		Functionalization		SSA (m^2/g)		Purity	Primary Impurity
		min	max	min	max	Type	(wt%)	min	max	(wt%)	
AR10 24PS	GSI Creos	5	5	80	100	none		50	50		

Appendix 3. Proposal for a physico-chemical categorization system for CNT

3.1 Introduction

Today the manufactors' description of CNT products is usually limited to the type of CNT based on general side-wall topology; i.e. their number of tube walls (single walled (SWCNT), double walled (DWCNT), and multi-walled (MWCNT)) or the special type in the case of deviation from "simple" straight sidewall CNT (e.g., Herring-Bone (HB), and Cup-stack (CS) CNT). As discussed in Chapter 2 of the report and appendix 2 herein, information on general impurity levels of other carbon compounds and catalyst materials, which may be non-specific, may also be available (Appendix 2). Even for SWCNT, where it is possible to give a more precise and technologically relevant description based on chirality, such information is rarely given. Some distributers, however, do give information on the conductivity of specific CNT products. Similar can occur regarding exchange on the information about their tensile strength?

Considering the reported variability in CNT structures and purities given in Chapter 2 and Appendix 2, a more precise classification of CNT would be highly beneficial for quick evaluation of the suitability of specific CNT nanomaterials. It is evident that such a categorization would require a substantial improvement of the amount and quality of the physico-chemical data given on the nanomaterials today.

3.2 CNT categorization for proper communication

It is evident that, at least industrial grade CNT may be very complex containing tubes with different numbers of tube walls, different lengths and diameters and different configurations of the carbon atoms. Other carbon allotropes and residuals of catalyst material will typically also occur. Therefore, a commercial CNT product can rarely be assumed to consist of one or just two different distinct types of CNT. A specific dedicated purification processes is required, if high-quality pure CNT materials are needed.

A proper categorization and product naming could therefore be highly beneficial to enable a quick and simple way of reporting and understanding the CNT materials and evaluate their specific potential use in the application intended. The CNT categorization should be generic and relevant for both chemistry and engineering as well as for hazard assessment and regulatory purposes. The regulatory categorization will require inclusion of specific properties, which can indicate if there are potential risks to human and environmental health. These end-points, however, still needs to be fully identified (see Chapter 7 the main report).

For categorization of CNT nanomaterials, it is important to note that most CNT nanomaterials do not consist of one phase. As shown in Chapter 2 in the main report, they do not have a fixed molecular size such as the spherical fullerenes and they may contain both carbonaceous and catalyst impurities of different kinds. Current CNT grouping simply use the CNT structure and their functionalization, where functionalized types by some are considered "meta-nanotubes", i.e. the pristine CNT is a substrate, structural skeleton or host for a new compound.

The proposed categorization system is based on the general sidewall topology, a mineral-like structural and impurity chemical formula, and a descriptive indicator of post-production treatment and carbon tube characteristics (Fig. 3.1).

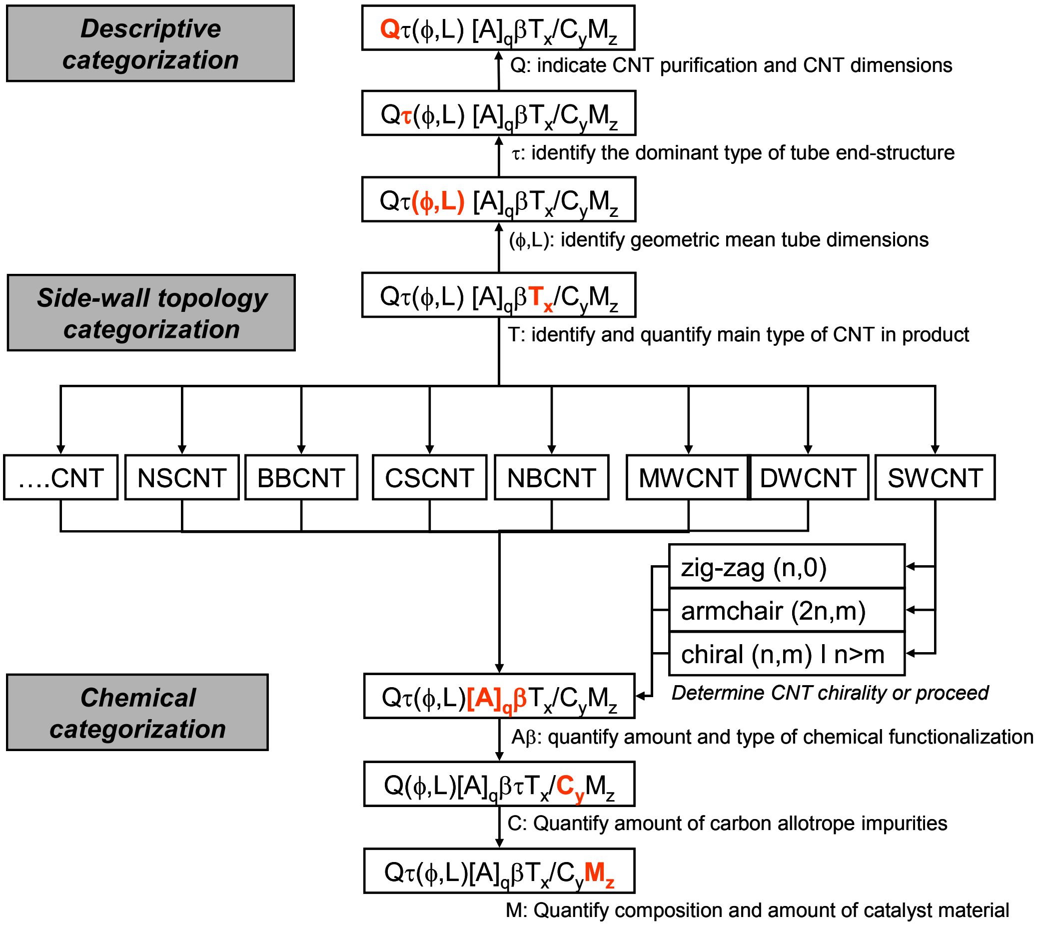


FIGURE 3.1:
SUGGESTED CNT CATEGORIZATION NAMING SCHEME FOLLOWING THE CRITERIA LISTED IN SECTION 2.7.

The CNT nanomaterial can then be described using the following formula:

$Q\tau(\Phi;L)[A_q]\beta T_x/C_yM_z$, where

- A: functionalization/coating of compound [A] in q weight fraction
- β: type of functionalization divided into adsorbed (•), endohedral (@) atoms, molecules and compounds, and functionalizations with a covalent bond (written in continuation)
- T: type of CNT (SW, DW, MW....) in x weight fraction of the sample and chirality for SWCNT.
- /: Associated y and z weight fractions of carbonaceous (C) and specific catalyst (M) impurities, respectively.
- Q: Labeling of post-production treatment as an indicator of the quality of the CNT nanomaterial product: Industrial grade (I), Milled/Grinded (M), Purified in acid (P), Annealed/Oxidized (A), Size-fractioned/filtered (S) etc.
- (Φ;L) geometric mean CNT diameter (Φ) and length (L).
- τ: type of tube ends denoted o, c, m for open-ended tubes, close-ended tubes, and close-ended by catalyst material, respectively.

Consequently, $[\mathrm{A_q}]\beta\mathrm{T_x}/\mathrm{C_y}\mathrm{Z_z}$ describes the CNT sidewall topology and chemical composition and $\mathrm{Q}\tau(\Phi;\mathrm{L})$ is a physical quality descriptor. Hence, using the reporting strategy a:

$$\mathrm{P}o(1.2\mathrm{nm};1\mu\mathrm{m})\mathrm{COOH}_{0.03}\mathrm{SWCNT}_{0.92}/\mathrm{C}_{0.01}\mathrm{Fe}_{0.03}\mathrm{Co}_{0.01}$$

describes a purified open-ended single-walled COOH-functionalized SWCNT with a mean tube diameter of 1.2 nm and a length of 1 µm, with impurities of 1 wt% of other carbon materials as well as 3 wt% Fe and 1 wt% Co catalyst material. If the SWCNT also had been size-fractioned, the descriptive categorization would have been PS*o*(1.2nm;1µm).

3.2.1 Topological categorization

Tube sidewall structure (T)
The categorization starts by determination of the type (T) of CNT based on the side-wall tubular structure. It is denoted T, used as the short form for TCNT in the formula. CNT are already grouped based on their sidewall structure and it is one of the most basic characteristics, which enables some general assumptions about the CNT properties. So far the grouping has been based on the number of tube walls, but also tubular morphology. I.e. they may be SWCNT, DWCNT, MWCNT etc. Special for SWCNT, the chirality may be determined (Fig. 2-3), which gives immediate information about the electronic properties of the specific CNT type.

There is general consensus about the naming of the “straight” single-, double-, and multi-walled CNT, but the nomenclature appears still to be open in the characterization of “unusual” tube structures such as cup-stacked and bamboo CNT as well as mixed morphologies. For full categorization of CNT types, it will be useful to agree on an extended list of abbreviations to officially include:

- Nanoscrolls (suggested abbreviation: NSCNT)
- Cup-Stacked CNT (suggested abbreviation: CSCNT)
- Bamboo CNT (suggested abbreviation: BBCNT; where subdivision into normal and inverse BBCNT might be considered)
- Branched Y-shaped CNT (suggested abbreviation: Y(SW,DW,MW)CNT)
- Branched T-shaped CNT (suggested abbreviation: T(SW,DW,MW)CNT)
- Helical MWCNT (suggested abbreviation: H(MW)CNT)
- Nanobuds (suggested abbreviation: NBCNT).

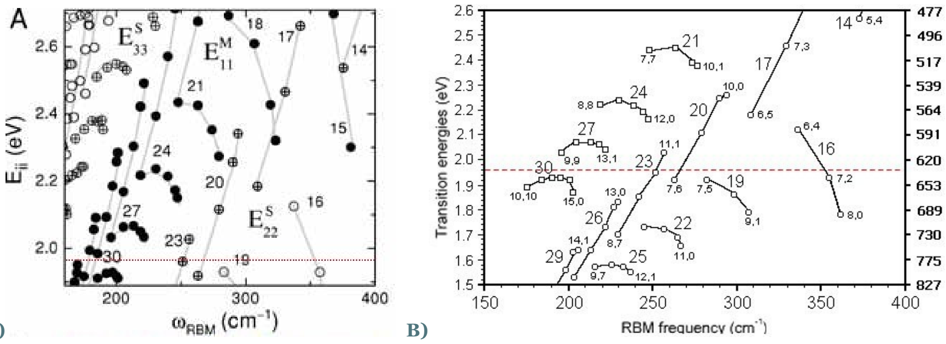
…

Tube structure and side-wall morphology can be determined using e.g., scanning or transmission electron microscopy, atomic force microscopy. The number of tube walls can be determined by transmission electron microscopy. Possibly, spectral analysis of data from high-resolution thermogravimetry can be applied to quantify the amount of single- double- and multi-walled CNT as well as impurity contents in unknown samples.

The chirality of SWCNT can be classified as arm-chair (n,0), zigzag (2n,m), and chiral (n,m), where n always is larger than m (see section 2.2). The specific chirality groups the SWCNT into conducting and metallic types. Specific identification of the chiral number gives all information about the CNT type and its principle diameter (Figure 2-4).

The chirality (CNT type) and carbon impurity contents may be determined by RAMAN (e.g., or Near Infrared (NIR) spectroscopy. Chirality can also be determined by high-resolution STM (Scanning-Tunneling Microscopy), but this is a highly advanced technique. However, it is important to understand that even using RAMAN spectroscopy, identification of different CNTs requires the use of many different laser wave-lengths. This can be illustrated by a so-called Kataura plot, which shows the position of radial breathing mode (RBM) signals as function of laser energy or wavelength (Fig. 2-9).

As an example we assume analyzing a SWCNT sample with a HeNe laser, which has the wavelength 633 nm corresponding to an energy of 1.96 eV (shown by the red dotted line). When using a HeNe-laser the RBM-lines from only the specific tubes that are activated at this line wavelength will be amplified and seen – in this case only 3 tubes will be seen. In order to see other tubes and make a complete sample analysis, lasers with several other wavelengths must be used. Therefore, proper determination of chiralities in SWCNT may require extensive analysis and might not be mandatory for reporting. In any case, a typical notation for chirality would be e.g., (9,0)SWCNT.



A)

B)

FIGURE 3-9
A) A KATAURA PLOT WHERE EACH MARK CORRESPONDS TO THE RBM RESPONSE OF A SPECIFIC CNT.
B) ENLARGEMENT OF FIGURE 2-9A WITH FEWER TUBES ARE INCLUDED. HERE IT IS POSSIBLE TO SE THE NUMBERS OF THE TUBES: THE “ROLL-UP” VECTOR IS IN SMALL FONT AND THE CAPITAL NUMBERS ARE THE FAMILY (ENERGY IS SHOWN ON THE LEFT AXIS, THE CORRESPONDING WAVELENGTH ON THE RIGHT). THE RED DOTTED LINE SHOWS THE WAVELENGTH OF A HENE LASER. E=HC/λ, H (PLANCKS CONSTANT)=4.135 X 10-15 EV/SEC AND C (SPEED OF LIGHT) = 3 X 108 M/S, CORRESPONDING TO λ = 1240.5 EV·NM/E. ωRBM = FREQUENCY OF THE RBM.

3.2.2 Chemical categorization

Chemical CNT (T_x) purity and carbon impurity (C_y) concentrations

Quantification of CNT purity is one of the key parameters enabling evaluation of the immediate quality of the nanomaterial. Here we discriminate between the concentration of the CNT, and other carbon allotrope impurities. One problem we are facing is the presence of other types of CNTs in the same material. This could be handled by quantification of the different types and reporting it as e.g, $(SW_{0.20}DW_{0.10}MW_{0.70})CNT_{0.90}/C_{0.03}Fe_{0.07}$ to describe a MWCNT with 30 wt% single- and double-walled CNT. 2 wt% other carbon allotropes and 7 wt% Fe. Another issue is heterogeneous CNT with elemental substitutions of mainly He and B in the graphene sheet. This type of structural impurity can traditionally described as $(C_{1\text{-}s}R_s)NT$, where R is the substituting element and s and 1-s denotes the molar fractions of the constituting C and B. From the previous example, the CNT could be $(SW_{0.20}DW_{0.10}MW_{0.70})[(C_{0.90}B_{0.10})NT_{0.90}]/C_{0.03}Fe_{0.07}$ if B replaced 10% of the C in the CNT alone.

Quantification of the amount of CNT and types of CNT as well as other carbon allotropes in a sample may require a combination of thermogravimetric analysis Raman spectroscopy and electron microscopy. As mentioned, high-resolution thermogravimetry may be used to quantify the amount of single- double- and multi-walled CNT as well as amorphous carbon and non-combustable elemental impurity contents. However, there appears to be some variation in combustion temperature depending on metal impurities in the sample as well. Therefore the types and impurity contents should be described and quantified using different methods.

Quantification of the elemental impurity by substitution requires in situ analysis by e.g, energy dispersive spectrometry (EDS) and electron energy loss spectroscopy (EELS) in TEM combined with bulk analysis (see below).

Functionalization (Aβ)
The role of functionalization on CNT properties and behavior is dramatic. It may change the solubility in water completely in addition to altering the physico-chemical properties. Especially defect and covalent functionalization will affect chemical reactivity (see section 2.6).

In this categorization it is proposed to discriminate between

- non-covalent functionalization (adsorbed or doped) atoms, molecules, and compounds ($[A_q]\cdot$SWCNT)
- covalent functionalization chemically bonded atoms, molecules, and compounds.
- sidewall ($[A_q]$SWCNT)
- endohedral ($[A_q]$@SWCNT)

Different methods may be used to characterize the functionalization depending on the type. These methods may include High-Performance Liquid Chromatography with or without Mass Spectrometer (HPLC/HPLC-MS), Matrix-Assisted Laser Desorption Time-of-Flight (MALDI-TOF), Gas Chromatographic Mass Spectrometry (GC-MS), and Fourier-Transformed Infrared (FTIR) spectroscopy. In situ electron microcopy and other microscopy techniques should be employed to verify the bulk analysis. Thermogravimetric analysis is excellent to quantify the total mass of the non-combustible residue and facilitate subsequent elemental analysis. For functionalization by inorganic materials, bulk analysis listed in the section on elemental impurity concentrations may be used.

3.2.3 Elemental impurity concentrations (M_z)

The typical use of catalysts for the production of CNT materials results in some percentage of inorganic elements in crude CNT. These catalyst impurities may not be completely extracted during purification processes if such procedures are applied (Tables 2-4 to 2-7). The elemental impurities are often transition heavy metals, which may play a role on the technical application and the potential toxicity (see chapter 4 and 5). Other impurities may be Al_2O_3, SiO_x, and silicate minerals. Therefore, inorganic impurities may alter the quality, the chemical reactivity or usability of the actual CNT nanomaterial product.

Elemental impurities can be determined after acid digestion using Inductive Couple Plasma Mass Spectrometry (ICP-MS) or Optical Emission Spectrometry (ICP-OES) and Atomic Absorption Spectrometry (AAS) or un-extracted using e.g., X-ray Fluorescence analysis (XRF). The amount of different metals is given as mass-fractions of the bulk sample.

3.2.4 Descriptive categorization (should also include morphology)

The descriptive categorization is used to give immediate first tier indication of the quality of the CNT in the product. This is done by noting type based on post-production treatment and tube dimensions, which also indicate the potential chemical reactivity of the CNT.

Type of post-production treatment (Q)
The type of post-production treatment was selected to be the primary indicator of CNT quality. One might also have selected the production method as an indicator of quality, but the production methods develop quickly and there may be large differences in the metal impurity content and tube quality using even the same production method (Section 2.4; Table 2-4). Instead, it was found that the post-treatment procedures were highly important for the final quality and chemical reactivity of the CNT nanomaterials.

The Q labeling is suggested to be:

I: Industrial grade, which is a harvested raw untreated as-produced CNT material.

M: Mechanically treated, which is CNT that has been e.g., milled and grinded to purify or homogenize the tube lengths.
P: Chemically purified, which are CNT that has been subjected to acid treatment that normally increases defect concentrations and lowers the concentration of inorganic impurities.
A: Annealed/Oxidized, which are CNT that has been graphitized or structurally improved by high-temperature recrystallization.
S: Size-fractioned/filtered,

Dimensions (Φ;L)

The tube dimensions diameter (Φ) and length (L) can be used to indicate the use and some of the properties of the CNT. The diameter notion can indicate whether the CNT is a small-diameter and high-reactive (or strain-defect rich) or large-diameter and low-reactive (low strain-defect) material. The lengths indicate whether the material generally is mostly suitable for use in electronic, composites or other applications.

The dimension of the CNT is also are of high importance. The tube diameter is generally related to the number of tube walls and its properties. We found above that the there is higher strain low-diameter tubes and therefore a possibility for higher number of sidewall DB- and SW-type defects, which again will lead to higher adsorption potency and chemical reactivity. One may consider both outer and inner diameter, but usually only the outer diameter is reported. The length of the tubes is also important and is especially important for its potential use as. Length is needed to calculate the aspect ratio.

Tube dimensions can be determined directly using e.g., scanning or transmission electron microscopy, atomic force microscopy. Alternative methods include scanning tunneling microscopy and in some cases indirect spectroscopic methods.

Type of tube ends (τ)

The type of tube ends, both determines the potential accessibility to internal surface area in the tubular structure and the inherent defect types present at the tube extremities. Open-ended tubes have a much greater surface area than close-ended tubes. Hence, information on tube ends enables immediate evaluation of adsorption and storage capacity, chemical reactivity, and possibilities for functionalization.

The type of tube-ends can be determined using e.g., scanning or transmission electron microscopy or atomic force microscopy.

The specific surface area (SSA) can also be used to indicate whether the tube is open- or close-ended, because SSA determines the total accessible surface (both outer and inner) of a dry powder material. SSA is usually determined with the so-called BET (Brünauer-Emmet-Teller) nitrogen adsorption method. Wetting with other gases, such as Kr and H, is also possible. However, the SSA can be modified by sample preparation methods such as functionalization, granulation or aggregation. Tube length and presence of impurities will also change the measured SSA. Yet SSA is still a very useful parameter for characterization of the material, but has not been included in the current categorization, because electron microscopy analysis gives higher confidence in the tube-end categorization.

It is proposed to categorize after:

- *o*: for open-ended tubes,
- *c*: close-ended tubes,
- *m*: close-ended by catalyst material

3.3 Concluding remarks

The proposed categorization system is intended to give immediate and structured description of the complex CNT materials. The categorization is developed based on material characteristics and chemistry, which is of interest from technological point of view, but also from their toxicological properties. Yet, at this point it is still unclear, which specific properties should be known for satisfactory identification and categorization of the CNT type in aspects of human and environmental health. It is anticipated that the technologically interesting physico-chemical properties also has importance for their hazard. Certainly, the CNT nanomaterial morphology should also be considered to assess potential for exposure as well as their behavior in environmental and biological systems.

Appendices: Carbon nanotubes

This report contains appendices for the environmental project No. 1805: Carbon Nanotubes.

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