Supplementary Materials

Carbon Nanotubes as Excellent Adjuvants for Anticancer Therapeutics and Cancer Diagnosis: A Plethora of Laboratory Studies versus Few Clinical Trials

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Tables

The list of references reported in Tables is available under the last Table S3.

Table S1. Structural properties of various modified/activated CNTs vs pristine CNTs (first row).

CNTs	BET (m^2/g)	MIV (cm^3/g)	MEV (cm^3/g)	Characteristics	Refs.
Pristine	150–1587	0.06–0.15	0.85	N.A.P.	[1–6]
HNO_3 modified	157	N.A.	0.37	AT provides O_2 containing -COOH, -OH	[7]
NH_3 modified	195	N.A.	0.42	NH_3 removes -COOH, -OH	[7]
KOH modified	785	0.17	1.04	KOH ⬆ micropores and mesopores ⬆ KOH/CNT ratio, ⬆ PV	[3–6]
Air activated	270	0.06	0.56	⬇ Micropore volume Air removes catalyst metals/AC	[3]
CO_2 activated	420	0.10	0.67	Large micropore volume	[3]
O_3 treated	320	0.12	0.69	Opens end caps Holes in sidewalls OOCA, O_2 containing functional groups	[2]
HY	550	0.18	0.97	⬆ External surface area	[8]

N.A. = Not available; N.A.P. = not applicable; HT = heat treatment; AT = acid treatment; PV = pore volume; AC = amorphous carbon; OOCA = ozonolysis oxidised carbon atoms; ⬆ denotes high, higher, improved, enhanced; ⬇ denotes reduced.

Table S2. Main methods to synthesize carbon nanotubes (CNTs).

Method	Invention paternity/Description	Tube type	Advantages/Disadvantages	Refs
AD	(1991) From procedure to get fullerenes applying a current (110 A) at T >1,700°C CNTs form in the carbon soot of GR electrode	N.R.	⬇Structural defects Macroscopic production	[9–11]
LA	Dr. Richard Smalley *	MWCNTs	N.R.	[12,13]
	Graphite is blasted with a laser			[14]
	Graphite and cobalt/nickel (metal catalyst particles) blasted with a laser	SWCNTs		[15]
CVD	Substrate of nickel, cobalt, iron, or combination catalyst NPs Heating at 700°C under a flux of a “process gas” ** and a “carbon-containing gas” *** to promote CNTs growing	N.R.	⬇ Cost, scaling up Industrial production	[16–21]
	CNTs directly growth on the desired substrate by careful deposition of the catalyst		If present, need to remove the catalyst support via acid treatment, with possible damage to the CNT structure	[16,22]
PECVD	Advanced CVD consisting of plasma generation by applying a strong electric field during CNTs growth	VACNTs	N.R.	[23]
HiPco	Rice University HPCO reacts with FePC, Fe NPs form providing the nucleation surface where CNTs form by the transformation of CO into carbon	SWCNTs	Production from milligrams to grams scale No environmental release of wastes	[12,13]
SGCVD	Kenji Hata, Sumio Iijima at AIST (Japan) Introduction of water into the CVD reactor	VANTAs Forest material	⬆Activity and lifetime of the catalyst ⬆To LA and HiPco by 100 times ⬇ Mass density, >99.98% pure, 2.5 mm height SWNT 10min Easy separation of CNTs from the catalyst >1 mm long VANTAs in several shapes §	[24] [13,25]
PT	Olivier Smiljanic (2000), Institut National de la Recherche Scientifique (INRS), Varennes (Canada) Argon, ethylene and ferrocene into PLASMOTRON, thus developing an intense 'flame' containing CNTs, metallic, carbon NPs and amorphous carbon	SWCNTs	10-fold ⬇consumed energy than in LA or AD.	[13,26]
ITP	Sherbrooke University and the National Research Council of Canada Modified PT procedure TP is generated by HFOCs in a loop and is conserved in flowing inert gas	SWCNTs	CNTs with different diameter distributions	[27]
LEM	Metal ions reduced to metal forms on cathode provide the nucleation surface for CNTs growth which derive from electrolysis of molten carbonates #	MWCNTs	⬆Valued CNTs Strategy for CO_2 capture and conversions	[13,28,29]
NICFE	CNTs form naturally in flames emitted by burning methane, ethylene, benzene		⬆Irregular in dimensions and quality CNT	[30–32]
ACVD	CNTs are synthesized in the gas phase and deposited in the form of randomly oriented networks, ready for many applications including transparent conductors.	SWCNTs TF	Clean defect less SWCNTs with limited yield	[33–35]

PR = Parameters; Adv = advantages; Disadv = disadvantages; * Rice University; AD = arc discharge; LA = laser ablation; CVD 0 chemical vapor deposition; ⬇ = less, minor, low; ** ammonia, nitrogen, or hydrogen; *** acetylene, ethylene, ethanol, or methane; PECVD = plasma-enhanced chemical vapor deposition; VACNTs = vertically aligned CNTs; HiPco = High-Pressure Carbon Monoxide Process; HPCO = high-pressure carbon monoxide;

FePC = iron pentacarbonyl; SGCVD = super-growth CVD, also known as water-assisted chemical vapor deposition; VANTAs = millimetre-high vertically aligned nanotube arrays; "forests" materials = tubes aligned to the substrate; ACVD = aerosol CVD; TF = thin films; ↑ = enhanced, improved, high, higher, highly, superior; § = sheets and bars, by applying weak compression during the process; PT = plasma torch; PLASMOTRON = microwave plasma torch; LEM = liquid electrolysis method; NICFE = natural, incidental, and controlled flame environments; GR = graphene; HFOCs = high-frequency oscillating currents; TP = thermal plasma; # the reactant is a carbon dioxide greenhouse gas.

Table S3. Most relevant research articles on CNT synthesis from biomass by different methods, operating parameters and main properties.

Feed stock	Method	Support/Catalyst	Operating parameters			CNTs	Properties				Refs
			T (°C)	Time (min)	Carrier gas		SA (m²/g)	D (nm)	*(%)	L (μm)	
Rice straw	P	Al_2O_3/Fe-Ni	830	30	N_2	MWCNT	188	15–40	N.A./N.A.	N.A.	[36]
Olive oil	P	Si wafer/$NiCl_2$	900	60	Ar	SWCNT	N.A.	27–31	N.A./ N.A.	N.A.	[37]
Turpentine oil	P	Zeolite/Fe-Co	850	25	N_2	SWCNT	N.A.	7–20	58/N.A.	N.A.	[38]
Coconut oil	CVD	Fe	850	60	N_2	MWCNT	N.A.	80–100	58/N.A.	3–4	[39]
Sesame oil	P+CVD	FNS/CH_3CN	900	15	Ar	MWCNT	N.A.	30–60	58/N.A.	3–4	[40]
Palm oil	CVD	Silicon/Ferrocene	750	30	Ar	SWCNT MWCNT	N.A.	0.6–1.2	90/N.A.	110	[41]
Plastic waste	P+CVD	Ni	800	30	N_2	MWCNT	N.A.	40–50	N.A./31	N.A.	[42]
Petroleum coke	CVD	Silica/Fe	700	60	He	MWCNT	N.A.	18	N.A./N.A.	N.A.	[43]
Plastic waste	P	Cordierite/*N*-Mg	750	60	N_2	MWCNT	N.A.	30–50	N.A./93	30–50	[44]
NCG	P+CVD	Ni/Al_2O_3	1000	112	N_2	SWCNT	N.A.	10	N.A./82	N.A.	[45]
Ethylene	FC, CVD	Co/Fe, Co/Ni, Ni, Co, Fe	1050	0.17	N_2	SWCNT	N.A.	0.67–2	61–69/ N.A.	N.A.	[46]
Rice straw	T-CVD	Fe, Ni	800	120	N_2	MWCNT	20 (CNT+Fe)35 (CNT+Fe+Ni)	22 (CNT+Fe)66 (CNT+Fe+Ni)	N.A./41–44	N.A.	[47]

*Purity/yield; CH_3CN = acetonitrile; N.A. = information not available; D = Diameter; P = pyrolysis; SA = surface area; T = temperature; NCG = natural condensed gas; floating catalyst; CVD = chemical vapor deposition; T-CVD = thermal CVD; FNS = ferrocene nitrogen source.

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