Some possible rules governing the syntheses and characteristics of nanotubes, particularly carbon nanotubes

CrossMark

S. Noor Mohammad

Sciencotech, 780 Girard St. NW, Washington, DC 20001, USA

ARTICLE INFO

ABSTRACT

Universally true rules constitute the very foundation of modern science and engineering. They are, in fact, the backbones of modern science and engineering. Nanotubes are promising materials, and nanotube science and engineering do not yet, to our knowledge, have these rules. Attempts have been made to explore if nanotube syntheses and characteristics follow any rule. Simple theoretical calculations were performed. Results of these calculations suggest that there may indeed be well-defined rules for nanotubes. The theoretical predictions are widely supported by available experiments. They indicate that the proposed rules may have broad appeal. They may have implication on exploring mechanisms most useful for growths of vertically aligned nanotubes of narrow chirality distributions.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Nanotubes, particularly carbon nanotubes, are promising materials [1–3]. They are less understood than, for example, thin film semiconductors. It is therefore important that the basic science of nanotube materials, their syntheses, and their characteristics be explored and established, if possible, in the form of rules. The proposed rules should however have wide acceptability and solid foundation. They must be supported by experiments. Nanotubes may, in general, be called X_mY_n nanotubes (X and Y are nanotube components, X may be metal, but Y non-metal). Thus, $X \equiv C$, $Y \equiv 0$, $m = 1$, and $n = 0$ for carbon nanotubes (CNTs); $X \equiv B$, $Y \equiv N$, $m = n = 1$ for BN nanotubes, and $X \equiv Si$, $Y \equiv 0$, $m = 1$, and $n = 0$ for Si nanotubes. There may be single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs), few-walled carbon nanotubes (FWCNTs), and multiwalled carbon nanotubes (MWCNTs). The nanotube source species may, in general be called the R_S species. So, $R_S \equiv X = C$ for carbon nanotube growth, and $R_S \equiv X = B$ and $R_S \equiv Y = N$ for BN nanotube growth. The nanotubes may be grown with or without

the assistance of foreign element catalytic agent (FECA). Nanotubes grow on the surface of nanoparticle, suppose, of atoms Ω and diameter D_{nano}; it may be a FECANO (e.g., FECA nanoparticle) or a SUBSANO (e.g., substrate nanoparticle). A FECANO is a small (suppose, $D_{nano} \approx 1–10$ nm) metal, oxide, semiconductor, ceramic, or polymer formed on a substrate. But a SUBSANO is a tiny grain, island, pocket, or patch (suppose, $D_{nano} \approx 1–5$ nm) created on a substrate. The growth may take place at a temperature T lower or higher than, or equal to the FECA/X eutectic temperature T_E.

2. Rule 1

The precursors of the R_S species, that land or are created on the nanoparticle surface, undergo dissociation releasing the R_S species on this surface. These R_S species may, for example, be sp^2 C atoms for CNT growth, and B and N atoms (or BN molecules) for BN nanotube growth. How does catalytic decomposition of the precursor take place on the nanoparticle surface? To answer this question, we argue that it is caused by high-energy sites (HETs) generated on the

nanoparticle surface with or without the assistance of an external agent. The HETs serve to lower the activation energy needed for the dissociation of the precursor. The top atomic layer(s) of the nanoparticle at the growth temperature is relatively loosely bound to the nanoparticle bulk and becomes anharmonic due to charge transfer. As stated earlier, the atoms of the top atomic layer(s) of the nanoparticle may be called the Ω atoms. These atoms are relatively loosely bound to the atoms of the nanoparticle bulk, which lie underneath the top atomic layer(s) of the nanoparticle and yield the crystalline structure of the nanoparticle. The nanoparticle surface thus formed becomes disturbed, disordered, amorphous-like giving rise to HETs. Alternatively, one or more of the chemical compounds placed or formed on nanoparticle surface for nanotube growth may have amorphous intermediate(s) during structural transformation(s), and this intermediate(s) serves as HET. The HETs are the sites of unsaturated accumulated charges, bonded oxygen atoms, bonded hydroxygenated radicals, and/or dangling bonds. Good examples of HETs are SiO_x and ZrO_x ($1 \leqslant \times \leqslant 2$) in SiO_2 and ZrO_2 nanoparticles, respectively. The surface, for example, of FECANO $\equiv$ Ni, may be converted to the Ni-bound carbidic carbon. The latter is highly reactive intermediate different from Ni_3C. This was noted by Hofmann et al. [4], who recorded time-resolved evolution of C 1s core level during Ni exposure to C_2H_2. They found chemical shift in the 1s binding energy from ~282.6 eV to ~283.2 eV, and finally to ~284.5 eV. It must have happened at the peripheral surface, as the core of the FECANO $\equiv$ Ni was found to remain crystalline during the continuous exothermic C_2H_2 dissociation. Note that the shift in C 1s binding energy ~282.6 eV corresponds to C chemisorbed on the FECA surface [5], C 1s binding energy ~283.2 eV to the chemisorbed C eventually transitioned to carbidic (endothermic) carbon [6], and C 1s binding energy ~284.5 eV to sp^2 bonded carbon [7] generated under the influence of HETs of the carbidic carbon. Esconjauregui et al. [8] observed Ni_3C during postgrowth characterization, instead of Ni-bound carbidic carbon, plausibly because the Ni-bound carbidic carbon was converted to Ni_3C during cooling after growth. We emphasize again that HETs are probably the key entities that lower the activation energy for the dissociation of the precursor needed for the release of the R_S species. It appears to be true as Neubauer et al. [9], found carbidic carbon, rather than Ni_3C, to be the single remaining species on the FECA surface upon decomposition of C_2H_2 and C_2H_4 on FECANO $\equiv$ Ni. Our observations made above points to the possibility of a rule, called Rule 1:

For nanotube growth, the precursor of the R_S species must dissociate on the nanoparticle (FECANO and SUBSANO) surface releasing the R_S species on this nanoparticle surface. For this, the precursor should be unstable under the influence of HETs. If the HETs do not already exist in the precursor, they would be created by (1) the surface disorder of the nanoparticle (FECANO or SUBSANO) itself with or without the assistance of external agent, or (2) the chemical conversion of some chemical compound(s) placed on this nanoparticle surface.

Liu et al. [10] observed that the catalyst-free CNT growth could be carried out only if the SiO_2 nanoparticle had SiO_x ($1 \leqslant X \leqslant 2$) intermediate(s) on its surface. Ma et al. [11] found that the formation of an amorphous intermediate product (e.g., B–N–O cluster) promoted reactions leading to the release of the R_S species for BN nanotube growth. Tang et al. [12] employed SiO precursor, which unlike Si and SiO_2, is quite unstable, and hence underwent dissociation (e.g., $2SiO \rightarrow Si + SiO_2$) yielding $R_S \equiv C$ for Si nanotube growth. Hash and Meyyappan [13] noted that, if plasma is used during growth, atomic and radical moieties are also generated in the gas phase which adsorb and react at the catalyst surface resulting in excited species such as HETs.

3. Rule 2

How do nanoparticles otherwise mediate nanotube growth? To address this problem, we noted that there can be two pathways for diffusion, namely volume (bulk) diffusion and surface diffusion, of the R_S species released on the nanoparticle surface. The volume (bulk) diffusion of the R_S species through the nanoparticle bulk (called VD1 process) may be given by $D_V = D_{V0} \exp(-E_{AV}/k_B T)$, where k_B is the Boltzmann constant and T is the temperature. If r_0 is the interatomic distance, and v_0 is the frequency of thermal vibrations, the surface diffusion of the R_S species through a nanoparticle (called the SD1 process) surface may, on the other hand, be given by $D_S = r_0^2 v_0 \exp(-E_{AS}/k_B T)$. The surface diffusion of the R_S species through a nanoparticle may also be given by $D_S = D_{S0} \exp(-E_{AS}/k_B T)$. Experimental data [14–23] for the volume diffusion and surface diffusion of some R_S species through several nanoparticles are listed in Table 1. The characteristic time τ required, for example, for the $R_S \equiv C$ species to migrate [24] via volume diffusion ($\lambda = 2$ nm) through the bulk, and via surface diffusion ($\lambda = 3.1$ nm) from the central core to the peripheral surface of a nickel particle, suppose,

Table 1 – Pre-exponential diffusivities (D_{V0} and D_{S0}), activation energies (E_{AV} and E_{AS}), and other parameters used for the calculations of bulk diffusions and surface diffusions of the R_S species through some selected nanoparticles (Ni, Fe, and Si); the nanoparticle is abbreviated by NP.

NP, R_S	Volume diffusion			Surface diffusion				
	D_{V0} (cm^2/s)	E_{AV} (eV)	Ref	r_0 (nm)	v_0 (Hz)	D_{S0} (cm^2/s)	E_{AS} (eV)	Ref
NP $\equiv$ Ni, $R_S \equiv$ C	2.48187	1.74	[14]	0.249	3×10^{13}	–	0.20–40	[15]
NP $\equiv$ Fe, $R_S \equiv$ C	7.9×10^{-3}	0.79	[16]	0.290	3×10^{13}	–	0.35	[17]
NP $\equiv$ Ni, $R_S \equiv$ C	6.7124×10^{-2}	1.50	[18]	–	–	2.83×10^{-5}	0.30	[19]
NP $\equiv$ Si, $R_S \equiv$ Ge	7.55×10^3	5.08	[20]	–	–	3.0×10^{-4}	0.96	[21]
NP $\equiv$ Si, $R_S \equiv$ B	2.20×10^{-2}	2.5	[22]	–	–	1.1×10^{-3}	0.66	[23]
NP $\equiv$ Si, $R_S \equiv$ N	2.70×10^3	2.9	[22]	–	–	–	–	–