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One-dimensional Crystals inside Single-walled Carbon Nanotubes: Growth, Structure and Electronic Properties

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1. Introduction

Single-walled carbon nanotubes (SWNTs) discovered in 1993 are currently among the most exciting and promising nanostructures (Bethune et al., 1993; Iijima & Ichihashi, 1993). They arouse huge interest due to their unique atomic structure, outstanding chemical and electronic properties (thermal and electric conductivity), as well as mechanical characteristics (high values of Young's modulus, tensile and compressive strengths, high cracking resistance etc.). SWNTs possess the maximum geometric anisotropy factors among the nanostructures known so far. The unique properties of carbon nanotubes (CNTs) are governed not only by their unusual tubular structure, but also by the fact that they are virtually devoid of any structural defects (Dresselhaus et al., 1995; Iijima, 1991; Saito et al., 1992). As a result, CNTs are of a great importance for development of nanoelectronics elements (logical gates, memory devices, emitters, and nanowires), nanoelectromechanical systems, nanocomposite fillers (aimed at increasing strength and functionality of bulk materials), probe tips for scanning probe microscopy etc. One of the major areas of SWNTs technological application has been the development of a new generation of field-effect transistors (Tans et al., 1998).

The electronic properties of defect-free SWNTs are extremely sensitive to the nanotube's geometric structure (Avouris et al., 2007; Saito et al., 1992), which depends to a great extent on the chiral vector; this may be regarded both as an advantage and a serious drawback of this material. So far, no efficient methods have been developed for the preparation and isolation of SWNTs with a desired chirality (Hou et al., 2008; Odom et al., 2000). For this reason, many attempts have been undertaken to develop methods that would allow separating the array of SWNTs into semiconducting and metallic nanotubes and/or modify the electronic properties of SWNTs without their separation by chirality (Chaturvedi et al., 2008; Eliseev et al., 2009a; Monthieux et al., 2006).

Modification of nanotubes allows direct adjustment of their electronic properties. One of the simplest ways to controlled modification of the SWNTs is filling of the nanotube channels

with appropriate substances (Brown et al., 2001). Encapsulation of a substance into a nanotube can either lead to a complete amendment of the nanotube's band structure (in case the encapsulated substance interacts intensively with the nanotube walls, e.g. in fluorinated SWNTs), or only to a shift of the electron density within the rigid band structure approximation (Sceats et al., 2006; Sloan et al., 2002a). In the simplest case, if an electron donor with the Fermi level located higher than that of the SWNT is encapsulated into metallic nanotubes, the electron density at the nanotube walls, as well as the nanocomposite conductivity increase, whereas an electron acceptor with the Fermi level located lower than that of the SWNT would cause the nanocomposite transition into the semiconducting state (Chaturvedi et al., 2008; Rahman et al., 2005; Weissmann et al., 2006). Therefore, this approach based on electron transfer upon the introduction of electron-donor or electron-acceptor compounds (metals, semiconductors, dielectrics) into the channels of single-walled nanotubes allows controlling the electronic structure of the SWNTs, as well as creating the p – n-junctions inside a single nanotube if the channels are partially filled (e.g. if a nanotube is half-filled).

The synthesis of filled nanotubes was first reported by Ajayan and Iijima in 1993; they used multi-walled nanotubes as “molecular containers” for lead (Ajayan & Iijima, 1993). These experimental results confirmed the theory-based conclusions on the existence of sufficiently strong capillary forces inside carbon nanotubes, which may retain gases and liquids inside the channels (Pederson & Broughton, 1992). Later on, other researchers developed and employed this approach for filling carbon nanotubes with a variety of metal halides [M^I ($M^I = \text{Li, Na, K, Cs, Rb, Ag}$), M^{II}_2 ($M^{II} = \text{Ca, Cd, Co, Sr, Ba, Fe, Pb, Hg}$), M^{III}_3 ($M^{III} = \text{La, Ce, Pr, Nd, Gd}$), $(\text{Te/Sn})\text{I}_4$, Al_2I_6 , $\text{AgCl}_x\text{Br}_y\text{I}_z$, $M^I\text{Cl}$ ($M^I = \text{Na, Cs, Ti}$), $M^I\text{Cl}_2$ ($M^{II} = \text{Cd, Fe, Co, Pd}$), $M^{III}\text{Cl}_3$ ($M^{III} = \text{La, Nd, Sm, Eu, Gd, Tb}$), $M^{IV}\text{Cl}_4$ ($M^{IV} = \text{Hf, Th, Zr, Pt}$), Al_2Cl_6 , $(\text{Th/V})\text{Cl}_6$], elemental forms (S, Se, Te, I₂, Cs, Re, Bi, Pt, Au, Ru, Fe, Ag), fullerenes (C_{60} , C_{70} , C_{80}), endofullerenes (Gd@C_{82}), a $(\text{KCl})_x(\text{UCl}_4)_y$, oxides (Re_xO_y , V_2O_5 , Sb_2O_3 , CrO_3 , PbO , UO_2 , ZrO_2 , MoO_2 , NiO , CdO , La_2O_3), metals (Pd, Pt, Cu, Ag, Au), hydroxides (KOH, CsOH), and chalcogenides (SnSe , HgTe and $\text{CdBr}_{2-x}\text{Te}_x$) (Chaturvedi et al., 2008; Cohen, 2001; Corio et al., 2004; Eliseev et al., 2009a; Fagan et al., 2005; Govindaraj et al., 2000; Kataura et al., 2002; Monthioux, 2002; Monthioux et al., 2006; Sceats et al., 2006; Sloan et al., 2000a).

At present, several methods are used for filling carbon nanotubes with various substances, which fall into two large groups: filling of nanotubes during their growth (i.e. the *in situ* methods) and encapsulation from the gas or liquid phases into cavities of pre-formed carbon nanotubes (i.e. the *ex situ* methods) (Monthioux et al., 2006).

2. Filling of single-walled carbon nanotubes during their growth (*in situ* methods)

The simplest of all the approaches that have been proposed to date for the nanotubes encapsulation is filling of SWNTs in the course of their catalytic growth (*in situ*). Currently two methods are applied that employ the *in situ* strategy for the encapsulation of inorganic compounds into the nanotubes: catalytic chemical vapour deposition (CCVD) of hydrocarbons and arc-discharge synthesis (Monthioux et al., 2006).

Arc-discharge synthesis of carbon nanotubes filled with various compounds is performed using graphite rods electrodes, a compound-containing anode (usually metals are encapsulated using this approach), and a catalyst. This approach was used to prepare single-walled carbon nanotubes for the first time (Bethune et al., 1993; Iijima & Ichihashi,

1993). To the present day, there has been a number of works on the application of the arc-discharge synthesis for filled multi-walled nanotubes preparation. In most of the cases, a number of substance is incorporated into the NTs in the carbide form (Cr, Mn, Fe, Ni, Pd, Y, Gd, Dy, Yb, La, Ce). The use of elements that do not form carbides or an accurate control of specific synthesis conditions allows encapsulating elemental compounds (Se, Ge, Sb, Cr, Mn, Co, Cu, Re, Au, Sm, Gd, Dy, Yb) (Ajayan & Ebbesen, 1997; Beguin et al., 2006). It was also demonstrated that the presence of sulfur in the graphite anodes in catalytic amounts is of key importance for the formation of filled nanotubes (Demoncey et al., 1998). Most likely it provides liquid phase at the surface of the nanotube channels (i.e. due to the metal-sulfur eutectic), which in its turn ensures encapsulation of the selected substance into the nanotubes' cavities. However, large temperature gradients in the cathode area, which lead to non-uniform nanotubes filling, make control of the filling process impossible. Another disadvantage of this approach is that it does not allow filling of nanotubes with transition metals, since in this case metal-carbon solid solutions and various carbides are formed.

In order to avoid formation of carbide species the catalytic CVD method may be employed. In this case pyrolysis of the carbon source should be accompanied by simultaneous sublimation or decomposition of metal-containing compounds (usually carbonyls or metallocenes) (Monthieux et al., 2006). Most often nanotubes filled with transition metals (Fe, Co, Ni, Cu) used as catalysts for SWNT growth are produced by this technique (Leonhardt et al., 2003). The use of the CCVD method for the preparation of the "ID-crystal@SWNT" nanocomposites is limited due to the need of strict temperature control and restricted number of carbon source - guest precursor combinations. Thus, the CCVD and arc-discharge synthesis are complementary in terms of the initial compounds choice.

The *in situ* approaches do not allow filling of nanotubes with any unstable species and complex chemical compounds (i.e. metal oxides, metal salts), since these methods require maintaining relatively high temperatures and reducing conditions throughout the synthesis. The major disadvantage of the *in situ* strategy for filling of single-walled nanotubes is its low efficiency: the yield of filled SWNTs does not exceed several percent. These drawbacks have facilitated the development of the *ex situ* approaches to filling of SWNTs, which are described below.

3. Filling of pre-synthesized carbon nanotubes (*ex situ* methods)

The filling of pre-synthesized nanotubes (i.e. the *ex situ* method) is considered to be the most universal approach to encapsulated nanotubes preparation. This technique enables filling single-walled nanotubes with virtually any chemical compounds from either gas or liquid phases (depending on the aggregate state of the encapsulated compound at the moment of its contact with the nanotube) (Eliseev et al., 2009a; Monthieux et al., 2006). This approach consists of several steps, the first of them being the opening of the SWNT ends.

3.1 Opening of nanotube ends

In order to fill carbon nanotubes using the *ex situ* methods, first their ends should be opened, which is performed using two main approaches, i.e. thermal treatment of the NTs in an oxidative gaseous medium (either dry air or oxygen) or treatment with liquid oxidation agents, such as concentrated acids (HNO_3 , H_2SO_4 , $\text{HNO}_3\text{-H}_2\text{SO}_4$), hydrogen peroxide, potassium permanganate, osmium tetroxide or HF-BF_3 mixture (Ajayan & Iijima, 1993; Monthieux et al., 2001; Seraphin et al., 1993). Concentrated acids also allow removing

catalytic particles and various contaminants (amorphous carbon, polyaromatic compounds, and graphite particles).

In fact, the oxidation involves both the ends and the walls of carbon nanotubes. For example, treatment of SWNTs with an acid was shown to result in the lateral defects formation (one defect per each 5 nm of the nanotube) (Zhang et al., 2003). Unlike that of multi-walled nanotubes, partial oxidation of single-walled nanotubes leads to formation of “hole” defects, through which substances may penetrate into the tubes both through their ends and walls.

A comparative study of various methods for the SWNT opening demonstrated that thermal oxidation tends to be a more efficient approach than acidic treatment (Brown et al., 2001). Since products formed during the acidic treatment can react with the carbon atoms of the SWNTs, the use of gaseous oxidants is preferable to avoid contaminations (Monthieux et al., 2001). Oxidation in air for about 30 min at 300-500°C seems to be the optimum choice (Fig.1). For such treatment, the opening of nanotubes is practically complete. In this process the sample loses approximately 40% of its mass (Zhang et al., 2003).

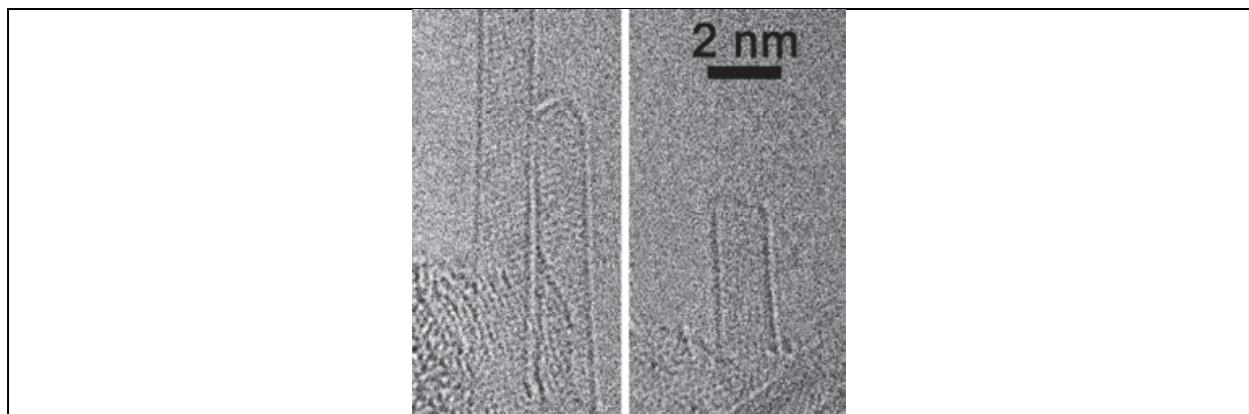


Fig. 1. HRTEM images of closed nanotubes and SWNTs opened by oxidation in air at 500°C

3.2 Filling of single-walled nanotubes from the gas phase

Notwithstanding multiple studies of multi-walled nanotubes filling from the gas phase, the filling of SWNTs remains much less investigated (Chancolon et al., 2006; Eliseev et al., 2009a). As a rule, filling of carbon nanotubes from the gas phase is carried out in vacuum at high temperatures. A sealed tube is heated up to or above the vaporization (or sublimation) temperature of an encapsulated material. In order to synthesize the “1D-crystal@SWNT” nanocomposites, the lowest possible temperatures should be used to avoid (or minimize) deencapsulation. During the NTs annealing, the vapor of the encapsulated compound undergoes capillary condensation and thus penetrates into the nanotube, where it crystallizes during subsequent cooling.

This two-step technique is widely used in order to fill carbon nanotubes with various fullerenes (for instance, C_{60} , Fig. 2), which have high affinities to nanotube surfaces and high vapor pressures (approx. 3×10^{-4} Torr at 500°C) (Pan et al., 2002; Smith & Luzzi, 2000). The fullerenes encapsulation occurs through the ends and wall defects of the SWNTs (Jeong et al., 2003). The encapsulation process depends strongly on the temperature and time of the NT treatment; partial vapor pressure of the introduced compound can also play a certain

role (Smith & Luzzi, 2000). This process is rather time consuming (takes about 2 days), however, it enables homogeneous and complete (virtually 100%) filling of SWNTs.

SWNTs can be successfully encapsulated from the gas phase not only with fullerenes, but also with endofullerenes ($M_x@C_n$) or doped fullerenes (Hirahara et al., 2000; Okazaki et al., 2003). As a rule, endofullerenes are synthesized in advance by the arc-discharge method with some metal added to the graphite anode (Okazaki et al., 2003). Subsequently, a mixture of opened SWNTs and endofullerenes is annealed at 400-500°C in an evacuated tube for several days (Okazaki et al., 2003). This method was used to fill the SWNTs with a variety of fullerenes (C_{60} , C_{70} , C_{80} , C_{84} , C_{78} , C_{90}), doped fullerenes (Cs, K, $FeCl_3$), and endofullerenes ($N@C_{60}$, $La_2@C_{80}$, $Sc_3N@C_{80}$, $Er_xSc_{3-x}N@C_{80}$, $Dy_3N@C_{80}$, $Gd@C_{82}$, $La@C_{82}$, $La_2@C_{82}$, $Dy@C_{82}$, $Sm@C_{82}$, $Sc_2@C_{84}$ @ $Gd_2@C_{92}$) (Monthieux et al., 2006).

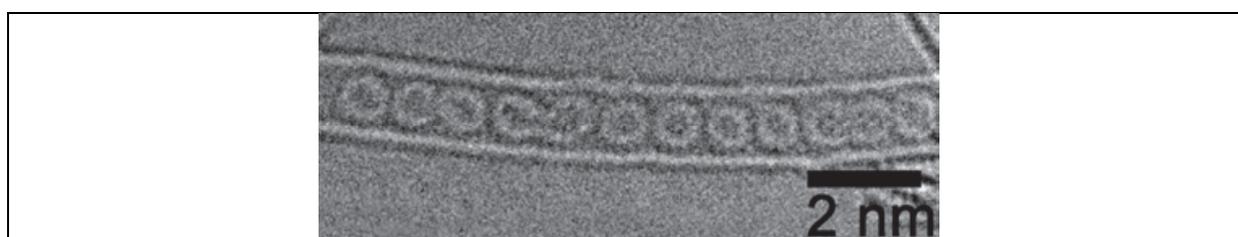


Fig. 2. HRTEM image of an SWNT filled with C_{60} fullerenes from the gas phase

The principle disadvantage of this approach is a limited choice of compounds that can be encapsulated. First, the compound's vaporization (or sublimation) temperature should be below 1000°C to ensure it does not interact with carbon and cause closure of the nanotube ends. Second, the compound (as a rule, a volatile oxide or a salt) should undergo sublimation in molecular form, which substantially limits the number of suitable compounds. Another serious limitation of this method is that the clusters thus formed are usually discrete, and they block the internal tube volume, whereas for practical reasons composites with continuous filling are required.

3.3 Filling of single-walled nanotubes from the liquid phase

Filling of SWNTs from the liquid phase is performed using the so-called capillary method, which involves impregnation of opened nanotubes with solutions or melts of selected compounds (Eliseev et al., 2009a; Monthieux et al., 2006). The use of melts is preferable, since it excludes contamination of composites with the solvent and also eliminates the necessity of filtration, which makes the formed nanocomposite denser. The excess of the encapsulated compound that remains at the SWNT's outer surface can be potentially removed by washing the sample or heating it under dynamic vacuum conditions.

The retraction of liquids into single-walled nanotubes takes place only if a number of conditions is met (Zhang et al., 2003). First, carbon nanotubes must be opened at least from one end. Second, the liquid phase must efficiently wet the SWNT surface, which limits its surface tension to 130-170 mN m⁻¹. This excludes the possibility to fill SWNTs with any melts that have high surface tensions, but, on the other hand, allows employing the majority of organic and inorganic solvents including water ($\gamma = 72$ mN m⁻¹ at 25°C) and benzene ($\gamma = 28.9$ mN m⁻¹). Third, the melting (or decomposition) point of the encapsulated material should be below 1100°C in order to prevent the SWNT closure and destruction during the composite synthesis.

3.3.1 Encapsulation from suspensions or solutions

Filling of nanotubes from solutions was first implemented in 1994 in order to encapsulate NiO and UO_{2+x} nanoparticles into multi-walled carbon nanotubes (Tsang et al., 1994). In the subsequent years, it was applied to fill MWNTs with Ag, Au, Pt, Pd metal particles, etc. (Cohen, 2001; Govindaraj et al., 2000; Satishkumar et al., 1996). In 1998, this approach was employed by a research group from the University of Oxford headed by Sloan to encapsulate single-walled nanotubes with metal Ru nanoparticles (Sloan et al., 1998).

At the moment, aqueous solutions of metal chlorides or nitrates (e.g. RuCl_3 , AgNO_3 , and $\text{Fe}(\text{NO}_3)_2$) are most often employed to encapsulate the SWNTs by the *ex situ* approach from the liquid phase (Chen et al., 1997; Monthieux, 2002; Monthieux et al., 2006) (Fig. 3) Another popular solvent is nitric acid, which is used due to its low surface tension (43 mN m^{-1}), allows avoiding a separate opening procedure (Zhang et al., 2003). As a rule, the second step upon the SWNTs' treatment with a solution is thermal treatment or hydrogenation in an H_2 flow at $150\text{--}450^\circ\text{C}$ for several hours; this leads to the formation of metal or oxide nanoparticles inside the SWNTs.

It is worth noting that filling of SWNTs with inorganic compounds using suspensions or solutions may be employed for a wide variety of substances (e.g. metals, oxides, chlorides, fullerenes and endofullerenes). However, this method has a number of limitations and disadvantages (Zhang et al., 2003). First, due to the procedure's nature the SWNT channels may be contaminated with the solvent, the products of its interaction with the nanotube walls and/or the encapsulated compound. Second, the encapsulated substance is distributed non-uniformly within the CNT channel, and the filling is far from being complete due to the solvent molecules encapsulation into the SWNTs. Indeed, when the solvent is removed and/or gaseous products are formed during the thermal treatment, individual cluster particles with 2 to 100 nm in diameter may be formed with the maximum yield of approximately 25% – 30% (Zhang et al., 2003). It should also be mentioned that nanoparticles formed in such a manner are most often polycrystalline, while from the practical perspective the single-crystalline nanoparticles inside the SWNTs are of major importance.



Fig. 3. HRTEM image of an SWNT filled with Fe nanoparticles introduced from $\text{Fe}(\text{NO}_3)_2$ solution at room temperature with subsequent annealing at 300°C

3.3.2 Encapsulation from melts

Continuous and uniform filling of SWNTs was successfully accomplished by the *ex situ* approach involving filling of nanotubes from melts. This technique provides a 2-3 times larger encapsulation yield as compared to the filling from suspensions and solutions (Eliseev et al., 2009a; Monthieux et al., 2006; Sloan et al., 2002b). The method is based on the melts penetration into the single-walled nanotube channels due to capillary forces.

The encapsulation procedure is usually performed under vacuum conditions at temperatures 10-100°C higher than the melting point of the guest material, which is followed by the slow cooling of the system in order to allow crystallization of the encapsulated particles. As a rule, metal halides as well as substances with low melting points are encapsulated using this approach, since they meet all the requirements to the introduced materials, i.e. low surface tension (<170 mN m⁻¹) and melting point (<1100 °C) (see Table 1) (Brown et al., 2003).

For the first time, Ajayan and Iijima (1993) employed the *ex situ* introduction of melts into the NT channels to fill multi-walled carbon nanotubes with the PbO particles (Ajayan & Iijima, 1993). The encapsulation yield was 90%, which is approximately twice the filling yield achieved by other methods (Ajayan & Iijima, 1993). Later Ajayan demonstrated that this approach can be successfully used to fill the SWNTs without performing preliminary opening of the nanotube ends (Xu et al., 2000).

The *ex situ* introduction of inorganic substances from melts was used to fill the SWNTs with nanoparticles of various metal halides [M^I (M^I = Li, Na, K, Cs, Rb, Ag), M^{II}I₂ (M^{II} = Ca, Cd, Co, Sr, Ba, Fe, Pb, Hg), M^{III}I₃ (M^{III} = La, Ce, Pr, Nd, Gd), (Te/Sn)I₄, Al₂I₆, AgCl_xBr_yI_z, M^ICl (M^I = Na, Cs, Ti), M^{II}Cl₂ (M^{II} = Cd, Fe, Co, Pd), M^{III}Cl₃ (M^{III} = La, Nd, Sm, Eu, Gd, Tb), M^{IV}Cl₄ (M^{IV} = Hf, Th, Zr, Pt), Al₂Cl₆, (Th/V)Cl₆], elemental forms (S, Se, Te, I₂, Cs, Re, Bi, Pt, Au, Ru, Fe, Ag), fullerenes (C₆₀, C₇₀, C₈₀), endofullerenes (Gd@C₈₂), a (KCl)_x(UCl₄)_y mixture, oxides (Re_xO_y, V₂O₅, Sb₂O₃, CrO₃, PbO, UO₂), hydroxides (KOH, CsOH), and chalcogenides (SnSe, HgTe and CdBr_{2-x}Te_x) (Brown et al., 2003; Carter et al., 2006; Dujardin et al., 1994; Eliseev et al., 2009a; Flahaut et al., 2006a; Monthioux et al., 2006; Sloan et al., 1999).

Table 1 lists the surface tension and the melting points of a number of substances encapsulated into the SWNTs, as well as the filling temperatures and yields (Brown et al., 2003; Eliseev et al., 2009a; Monthioux et al., 2006; Xu et al., 2000). According to the TEM data, the SWNT channels filling yield for encapsulation with inorganic compounds was 50% to 90%.

In most cases, the encapsulated nanoparticles were found in the form of one-dimensional nanocrystals within the SWNT. Based on the analysis of the TEM micrographs (Fig. 4 a,c), structural models of the one-dimensional nanocrystals may be proposed (Fig. 4 b,d) (Sloan et al., 2000b; Sloan et al., 2002a).

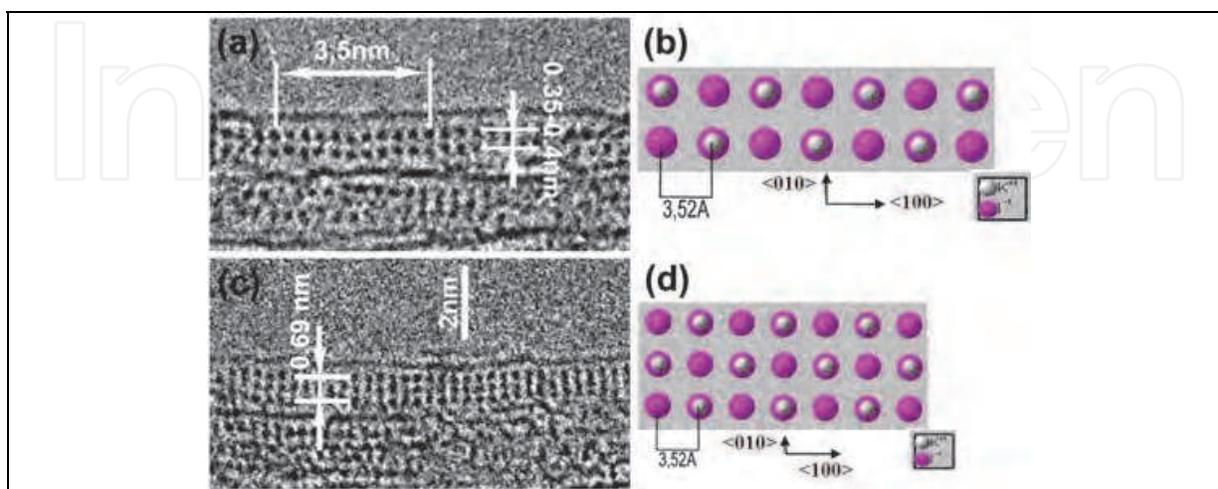


Fig. 4. HRTEM images of the KI nanocrystals inside the SWNT channel (a,c) and atomic models of the 1D crystals (b,d)

Material	γ (mN · m ⁻¹)	T_{melt} , °C	T_{int} , °C	Loading factor (%)	Material	γ (mN · m ⁻¹)	T_{melt} , °C	T_{int} , °C	Filling yield (%)
AgCl	113-173	560	560-660	40-50	K	117	336		
AgBr	151	432	532-590	40-50	KCl	93	771	870	
AgBr _{0.2} Cl _{0.8}	173	410	510	40-50	(KCl) _x (UCl ₄) _y	44-65	335, 562	435, 662	< 10
AgI	171	455	555	80-90	KI	70	681	781	60-80
Al	860	660	-		LaCl ₃	109	860	910	20-40
BaI ₂	130	740	840	< 10	LiI	94	449	549	20-30
Bi ₂ O ₃	200	825			NaI	81	661	761	10-20
CaI ₂	83	784	884	< 10	NdCl ₃	102	784	834	20-40
Cs	67	29			Pb	470	327	-	
CsI	69	627	727	30-40	PbO	132	886		80-90
CuCl	-	430	530	30-50	Re ₂ O ₃	32	220	250	50-60
CuBr	-	492	590	60-80	Rb	77	39		
CuI	-	606	705	>90	RbI	70	647	747	60-70
EuCl ₃	-	850	860	20-40	S	61	115	165	20-30
FeCl ₂	-	674	774		Se	97	221	320	20-40
FeBr ₂	-	684	784		Te	190	450	520	20-40
FeI ₂	-	587	687	50-60	SnTe	-	807	907	60-70
CoBr ₂	-	678	778		TbCl ₃	-	588	638	20-40
Ga	710	30	-		SmCl ₃	-	686	706	20-40
GdCl ₃	92	609	659	20-40	UCl ₄	27	590	690	< 10
Hg	490	-38	-		V ₂ O ₅	80	690		
HF	117				YbCl ₃	-	854	904	20-40
HNO ₃	43				ZrCl ₄	1.3	437	487	50-70

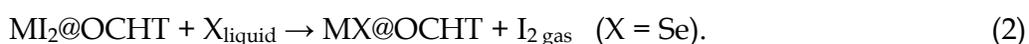
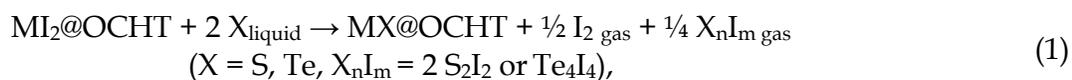
Table 1. Surface tension values and melting points of encapsulated materials, synthesis temperatures of the "1D-crystal@SWNT" nanocomposites (encapsulation from melt) and encapsulation yields

The *ex situ* encapsulation from melt has a number of advantages in comparison with other filling techniques. Among them are the possibility to use a wide range of substances to fill the SWNTs, the simplicity of approach's, the composites uniformity, high loading factor (up to 90%), and high crystallinity of the synthesized nanoparticles. Another benefit is the absence of any solvent and/or by-products (oxides, carbides) contamination in the "1D-crystal@SWNT" systems. This makes the *ex situ* filling of single-walled nanotubes from melt the most efficient approach for the "1D-crystal@SWNT" systems synthesis that has been developed so far.

3.3.3 Direct synthesis within the SWNTs

Notwithstanding its efficiency, the encapsulation from melts has a number of limitations. This approach cannot be employed for compounds with surface tension values exceeding 170 mN m^{-1} and melting points above 1100°C . This essentially limits the possibilities to directly introduce many metals (due to high γ values of their melts) and covalent compounds (e.g. metal oxides or chalcogenides) into the SWNT channels. On the other hand, encapsulation of metallic nanoparticles into semiconducting SWNTs or semiconductor crystals into metallic tubes is expected to result in the most significant changes in the electronic structures of the single-walled nanotubes (Eliseev et al., 2009b; Kramberger et al., 2009a; Shiozawa et al., 2009a). Moreover, low-dimensional broadband $A^{II}B^{VI}$ and $A^{IV}B^{VI}$ semiconductors with an exciton diameter of several nanometers (e.g. exciton diameter of CdS is 4.8 nm) are of interest both for the quantum-size effects studies and possible application in light emitters, sensors, solar cells etc. (Cao et al., 2004).

Although direct filling of nanotubes with semiconducting materials having high melting points failed, such materials can be synthesized directly in the internal channels of the SWNTs (Eliseev et al., 2009b). First, the nanotube channels are filled with molten metal iodides (ZnI_2 , CdI_2 , PbI_2) using the capillary approach at temperatures exceeding the substances' melting points by 100°C ($T_{\text{melt}} = 446, 388$ and 412°C , respectively). The obtained MI_2 @SWNT composites undergo sulfidation, selenation or telluration when treated with molten chalcogens:



Slow cooling of the chalcogenides synthesized in the SWNT channels results in their crystallization in the form of one-dimensional crystals. It is assumed that the chalcogen atoms are transported into the single-walled nanotubes filled with the iodides (MI_2), and the I_2 and X_nI_m gaseous molecules formed in the reactions (1) and (2) are removed through defects in the SWNT walls (Eliseev et al., 2009b). This suggestion is in line with the observed destruction of one-dimensional crystals in the SWNT channels upon the system's irradiation with high-energy electrons, that leads to escape of the encapsulated compounds through the defects in the nanotube walls and their subsequent decomposition on the NT's external surfaces (Hutchison et al., 2008).

The approach based on chemical reactions within the SWNT channels was successfully employed to synthesize the 1D crystals of semiconducting $A^{II}B^{VI}$ and $A^{IV}B^{VI}$ compounds ($A = \text{Zn, Cd, Pb}$; $B = \text{S, Se, Te}$) (Fig. 5) with high melting points (up to 1750°C) and the band gaps of 0.3 to 3.7 eV (Eliseev et al., 2009b).

4. Structures and properties of the "1D-crystal@SWNT" nanocomposites

The "1D-crystal@SWNT" nanostructures arouse huge interest for theoretical studies and possible applications. Since this research area has been under development only for the past 10 years, the information on the properties of the "1D-crystal@SWNT" composites is rather scarce (Eliseev et al., 2009a; Monthieux et al., 2006). The same is true for the simulation of structures and electronic properties of encapsulated carbon nanotubes (Kramberger et al., 2009a; Shiozawa et al., 2009a). The experimental studies focus mainly on the possibility to alter the SWNTs band gaps by filling them with electron-donor or electron-acceptor

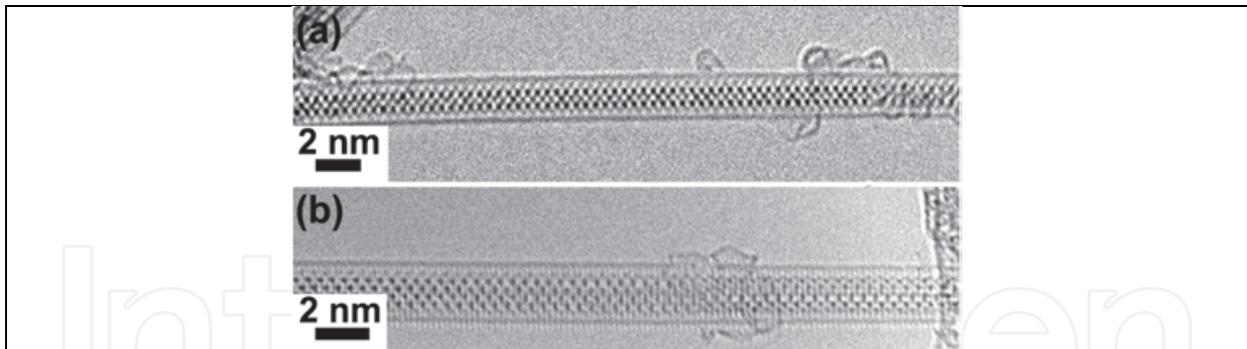


Fig. 5. HRTEM image of the $\text{PbTe}_x\text{I}_{2-2x}@SWNT$ composite (two types of the observed projections)

compounds or changes in the atomic and electronic structure of the encapsulated compounds due to forced structural deformations of the materials inside the single-walled nanotubes (Shiozawa et al., 2008).

The “1D-crystal@SWNT” nanocomposite structures are most efficiently studied by high resolution transmission electron microscopy. Since a “1D-crystal@SWNT” nanocomposite is a single-walled carbon nanotube with a 1D-crystal inside, the HRTEM images display either crystallographically ordered atomic arrangements or columns of several atoms (see fig. 3). Historically, HRTEM was first implemented to study the “1D-KI@SWNT” nanocomposites (Meyer et al., 2000; Sloan et al., 2000b). In these systems one-dimensional KI crystals with 2×2 or 3×3 atoms in diameter were observed depending on the tube diameter. Peapods can also be considered as the “1D-crystal@SWNT” nanocomposites (Smith et al., 1998).

It stands to mention that in the SWNTs of various diameters the encapsulated compounds (for instance, KI, PbI_2 , CuI, HgTe) can form structures that differ by the number of atoms in the nanotube cross section or by symmetry (Carter et al., 2006; Flahaut et al., 2006a; Kataura et al., 2002; Kiselev et al., 2008). The structure of such nanocrystals differs substantially from the bulk substances both with regards to their symmetry, bond lengths, and bond angles. The distortion of geometric parameters is obviously caused by the steric limitations of the one-dimensional nanocrystals within the nanotube walls, as well as by the adjustment of nanoparticle structures to the internal diameter of the SWNTs channel (Eliseev et al., 2009a; Kataura et al., 2002). For some systems the spatial confinement of an intercalated substance by the channel walls leads to the formation of a 1D-crystal with a structure that is not typical for the 3D-crystals of the same compound. For instance, 3D-AgBr is cubic, while the 1D-crystals formed within the SWNTs have a hexagonal structure that is absent from the Equilibrium phase diagram related to bulk state. In certain situations entirely new structures with unusual properties (including a five-fold symmetry) can be formed ((Ebbesen, 1996; Kirkland et al., 2005; Mittal et al., 2001; Sloan et al., 2002c).

In fact, such deviations pertain to the choice in the nanocrystal’s crystallographic orientation with respect to the nanotube axis (different crystallographic directions of the bulk substance can coincide with the long axis of a one-dimensional nanocrystal), reduction of the coordination number for atoms within the encapsulated inorganic substance, the difference between the crystal lattice parameters for the one-dimensional crystal and those for the bulk material, as well as the formation of nanocrystals with a crystal lattice that is not typical for the bulk materials (Eliseev et al., 2009a; Kataura et al., 2002; Monthieux et al., 2006).

The crystallographic orientation of the nanocrystals relative to the nanotube axis changes due to the demand to preserve the stoichiometry of the encapsulated compound to the highest possible extent, whereas the reduction of the coordination number and the change in the nanocrystal's lattice parameters along the radial direction are apparently explained by the spatial limitations of the nanocrystal within the SWNT walls (Mittal et al., 2001). The nanocrystal's lattice parameters along the nanotube axis are less distorted, since the nanocrystal experiences virtually no steric limitations along this direction. Nevertheless, a number of studies indicate the extension/compression of the 1D crystal lattice along the SWNT axis. In particular, this effect was observed for the KI, CuI, Ag, Sb₂O₃, KI nanocrystals and the (C₆₀)_n fullerene chains (Friedrichs et al., 2002; Meyer et al., 2000; Sloan et al., 2002b). The observed lattice distortion can be as high as 14%. The compression (or stretching) of the lattice parameter along the nanotube axis is likely to be caused by the stretching (or contraction) of the unit cell within the SWNT channel in the radial direction; the cell volume remains unchanged.

Analysis of possible one-dimensional crystal configurations formed within single walled carbon nanotubes indicates that the structure of a crystal is mostly governed by the SWNT diameter (Table 2). To the moment a number of crystal geometries unusual for bulk case have been reported in the SWNT channels. As most of these crystals are not easily described in terms of traditional space groups, here we would utilize the following notation:

1. One-dimensional unit cell is further denoted as (A_xB_y)_n/L, where *n* corresponds to a number of molecular formula units, and *L* to the number of layers in the unit cell.
2. To describe the lattice of a one-dimensional crystal, additional symmetry notation is involved based on Bravais lattices with a rotation axis C_n (or an inverse rotation axis S_n) aligned along the tube using a P letter for primitive, an C for base-centered and an F for face-centered structures. In several cases the structures could be described as a dense packing.
3. When the anion/cation diameter ratio for the 1D crystal is substantial, there is a number of vacant cationic positions in the structure, and cations can easily migrate inside of the channel. In this case the cationic positions cannot be easily determined and symmetry notation is applicable only to anion sublattice. Nevertheless, few detailed studies performed with microscopy image simulation allow distinguishing between different cationic forms of one-dimensional crystals (fig. 6).
4. For a number of crystals the formation of helix structures can be observed. The most common examples include I₂@SWNT, RbI@SWNT and H₂O@SWNT (Chen et al., 2009; Fan et al., 2000; Kirkland et al., 2005; Liu & Wang, 2005). For these crystals we use the 1/N(A_xB_y)_n/L notation, where N is a number of unit cells per period of rotation, i.e. N = $\phi/360$ with ϕ - rotation angle (distortion) for a single unit cell.

The most interesting structural changes are observed for low-diameter SWNTs, where the lattice constant is comparable to the nanotube diameter. Moreover, the structural deviations are more frequently observed for crystals with complex (non-primitive) structures in the bulk. Obviously, the packing rules for non-interacting atoms within SWNT channel should comply with simple geometric considerations (Table 3). These kinds of structures are typical for inert metals crystallized within the SWNT. However, due to a lack of informative HRTEM studies only few examples can be found in the literature (Govindaraj et al., 2000; Jeong et al., 2003).

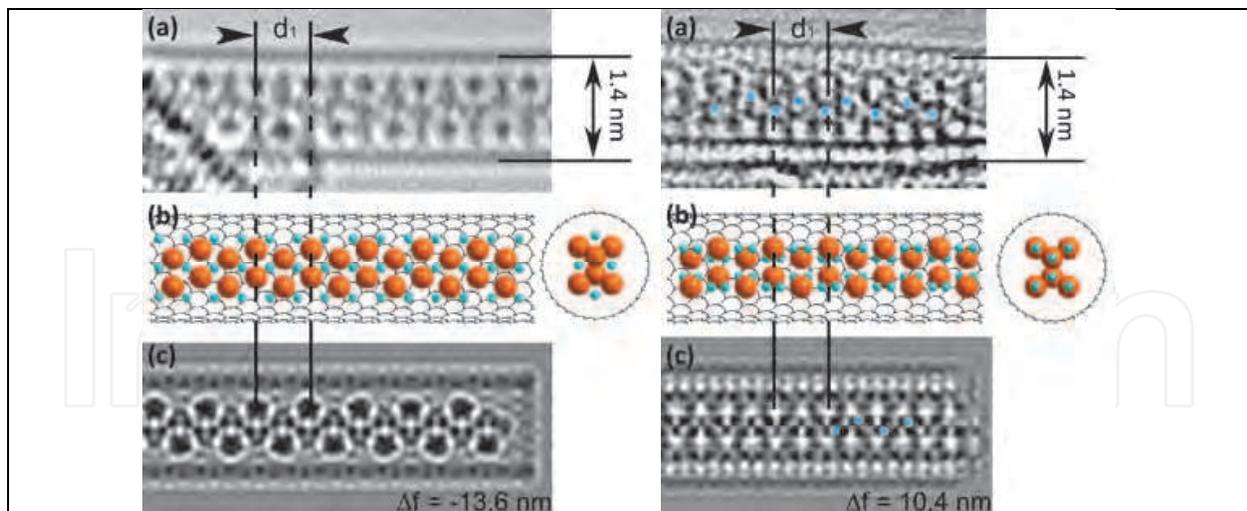


Fig. 6. HRTEM images (a, d) structural models (b, e) and TEM image simulation results (c, f) for two types of the CuI one-dimensional nanocrystal within a 1.4 nm SWNT channel. Copper atoms are located in the tetrahedral (a-c) and octahedral (d-f) sites of a two-layer hcp $(\text{CuI})_6/2$ structure

Another simple case is ionic crystals, such as alkali metal halides, for example, KI. All the projections for KI crystal resolve in a simple cubic lattice with a (001) axis aligned along the tube channel. This structural motif is least subject to confinement by a nanotube: for low-diameter (below 1.5 nm) tubes $(\text{MX})_4/2$ crystals with a face centered cubic structure (a 2×2 crystal) are formed within the channel, $(\text{MX})_9/2$ fcc (a 3×3 crystal) is typical for tube diameters of 1.5 - 1.7 nm, while for greater diameters lattices of bulk NaCl type are formed. In this case the major structural changes are the variation of the interatomic distances and the cell volume expansion. It is worth noting that CsI intercalated into SWNTs also has a NaCl-type structure, despite the fact that the bulk substance has a bcc structure.

Most of less-ionic crystals having dense packing of anions in their bulk structures (2- or 3-layer hexagonal lattices) tend to form a two-layer hexagonal packing within the tube. This case is characteristic for copper and silver halides, which have been recently studied in detail (Eliseev et al., 2010; Eliseev et al., 2011). Crystals with covalent bonding tend to preserve some structural fragments in one-dimensional crystals. Atomic coordination numbers can play a certain role in defining the crystallographic orientation of the nanocrystals relative to the nanotube axis (Kiselev et al., 2008).

The degree of crystallinity and the structure of the one-dimensional nanocrystals within the nanotube channel depend strongly on the ratio between the structural parameters of the encapsulated compound and the internal diameter of the SWNT channel. For example, for the CuHal@SWNT and AgHal@SWNT (Hal = Cl, Br, I) systems the degree of crystallinity for nanoparticles incorporated into the SWNT channels increases when passing from the metal chlorides to iodides, which is presumably caused by the increase in the halogen ion radius when passing from Cl to I [$r(\text{Cl}^-) = 1.67$, $r(\text{Br}^-) = 1.82$, $r(\text{I}^-) = 2.06 \text{ \AA}$], which causes the increase in the M-Hal bond lengths in this series (Eliseev et al., 2010; Eliseev et al., 2011). As a result, in the CuCl@SWNT composite the CuCl single crystal does not completely fill the nanotube's channel, which results in substantial mobility of the Cu and Cl atoms; this, in its turn, leads to a decrease in the degree of crystallinity. At the same time, in the CuI@SWNT composite the size of the CuI crystal fits well the diameter of the tube, which results in the enhanced degree of crystallinity.

Compound	d ₁ nano-tube, nm	Type of packing	Cell formulae	Crystal symmetry	d ₂ crystal	Expansion		d ₂ /(d ₁ - d ₀₀₁ graphite)
						across tube axis	along tube axis	
KI	1,4		(MI) ₄ /2 Helix 1/20	P $\bar{4}$	1,06	+14%	+14%	0,995
RbI	1,4				1,00	+6,4%	-1,8%	0,957
CsI	1,4				1,11	+7,1%	+2,9%	1,042
LiI	1,6		(MI) ₉ /2	F4 (fcc)	1,13	+25%	+25%	0,893
KI	1,6				1,31	+7,4%	+4,9%	1,036
CsI	1,6				1,37	+9,3%	+2,3%	0,988
NaI	2,5		(NaI) ₃₆ /2	P $\bar{4}$	2,00	+4%	+4,7%	0,924
AgBr	1,4		(MHal) ₆ /2	P $\bar{2}mm$	0,98	-2%	+4,9%	0,920
AgI	1,4				1,11	-4,5%	-0,7%	1,042
CuBr	1,4				1,00	0,0%	+2,1%	0,957
CuI	1,4				1,06	-2,8%	+2,3%	0,995
BaI ₂	1,4			P2	1,21	-	-	1,136
PbI ₂	1,6				1,43	-	-	1,130
HgTe	1,36		(HgTe) ₄ /2	P $\bar{4}$	0,99	-	-	0,966
SnSe	1,4		(MChal) ₄ /2	P $\bar{4}$	0,91	-	-	0,854
SnTe	1,35				0,84	+10,3%	-16,7%	0,828
SnTe	1,35		(SnTe) ₅ /2	C4	1,08	+4,8%	-7,0%	1,064
CdS	1,4		(CdS) ₆ /2	P $\bar{6}$	0,86	+6,4%	+9,5%	0,832

Table 2. Structural parameters of the "1D-crystal@SWNT" nanocomposites resolved by HRTEM

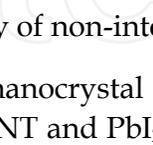
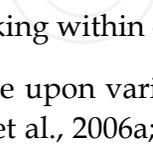
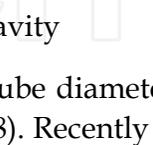
D/d		D/d		D/d	
1,00 - 2,00		2,15 - 2,41		2,70 - 3,00	
2,00 - 2,15		2,41 - 2,70		3,00 - 3,30	

Table 3. Geometry of non-interacting atomic packing within one-dimensional cavity

Apparently, the nanocrystal structure can change upon variation of the nanotube diameter (e.g. for CuI@SWNT and PbI₂@SWNT) (Flahaut et al., 2006a; Kiselev et al., 2008). Recently it has been experimentally determined that copper and silver bromides (MHal)₆/2 can change their symmetry from $P2mm$ in the (19,0) and (18,0) SWNTs to $P2m$ in the (17,0) SWNTs due to contraction of the <111> and extension of the <112> axis (Kiselev et al., 2011).

In summary, the total confinement effect should be considered with relation to the nanocrystal size/SWNT diameter ratio. According to the available data, the following cases of one-dimensional nanocrystal/SWNT size misfit should be considered:

1. $d_{\text{cryst}} / (d_{\text{SWNT}} - d_{\text{graphite}(00l)}) < 0,8$
The crystals are highly unstable and tend to undergo phase transformations that yield more stable configuration. These structures could be observed as intermediates during deintercalation caused by electron beam irradiation (Hutchison et al., 2008).
2. $0,9 < d_{\text{cryst}} / (d_{\text{SWNT}} - d_{\text{graphite}(00l)}) < 1$
This is the most common case. The crystal lattice is slightly expanded to fit the SWNT channel diameter well. Usually it is associated with a reduction of the lattice parameter along the tube channel at constant unit cell volume. Twisting of the lattice can appear in case of significant host-guest interaction. In a number of cases the lattice can both expand along and across the tube, thus providing an evidence for a strong crystal-SWNT interaction.
3. $d_{\text{cryst}} / (d_{\text{SWNT}} - d_{\text{graphite}(00l)}) \sim 1$
If the nanotube diameter fits the nanocrystal size well, the crystal is stable even under electron beam irradiation (Hutchison et al., 2008). Slight variation of the crystal cell parameters can occur while the cell volume remains constant.
4. $1 < d_{\text{cryst}} / (d_{\text{SWNT}} - d_{\text{graphite}(00l)}) < 1,1$
A slight confinement for cubic and hexagonal phases is observed in this case. One-dimensional crystal parameter can be reduced up to 10% in the cross-section accompanied by distortion of the crystal lattice and increase of the lattice parameter along the SWNT. In this case some deformation of the SWNT can occur. For layered structures the crystal can be stable even for higher ratios due to possible SWNT deformation, as it was observed for PbI₂@SWNT (Flahaut et al., 2006b). Slight deformation of the tube can also be observed for more symmetric crystals (Sloan et al., 2002a). For chiral tubes some twisting of the crystal within the channel is expected.
5. $1,2 < d_{\text{cryst}} / (d_{\text{SWNT}} - d_{\text{graphite}(00l)})$
The crystals are highly unstable and tend to undergo phase transformation yielding a more stable configuration. These structures can be observed as intermediates during deintercalation caused by electron beam irradiation (Hutchison et al., 2008).

Most structures of one-dimensional nanocrystals within the SWNTs were shown to be metastable (Eliseev et al., 2009a). This was demonstrated for metal halides nanoparticles (i.e. AgBr, AgI, CoCl₂) formed within the SWNTs. After removal of the carbon nanotube shell, these particles lose their nanowire morphology (Bendall et al., 2006). Dynamic behavior was reported for the ZrCl₄, Re_xO_y, and CuI nanoparticles within the SWNT channels upon electron beam irradiation (Brown et al., 2001; Costa et al., 2005; Kiselev et al., 2008). The ZrCl₄ nanoparticles form clusters, the Re_xO_y particles evenly rotate inside the single-walled nanotubes, while one-dimensional CuI crystals deencapsulate onto the nanotube surface and decompose yielding metallic copper. Live HRTEM study of the 1D-CuI@SWNT nanocomposite brought two phenomena to light: (1) the CuI crystal rotation and oscillation within the nanotube channel and (2) its emergence from the nanotube through macro-defects (Hutchison et al., 2008). In a series of images (some shown in Fig. 7) a small fragment of the CuI 1D-crystal (about 5.1 nm long) within the nanotube moved and rotated. By the end of the scanning process, the crystal was destroyed. The reason for the crystal movement and escape was charge generation at the SWNT walls in concert with the OH⁻ generation; these particles interact with the SWNT walls, thus producing defects. The observed effects enabled to propose a technique for controllable nanocrystal deencapsulation. In case of its application for partial crystal removal the method provides a p-n-junction within a single SWNT.

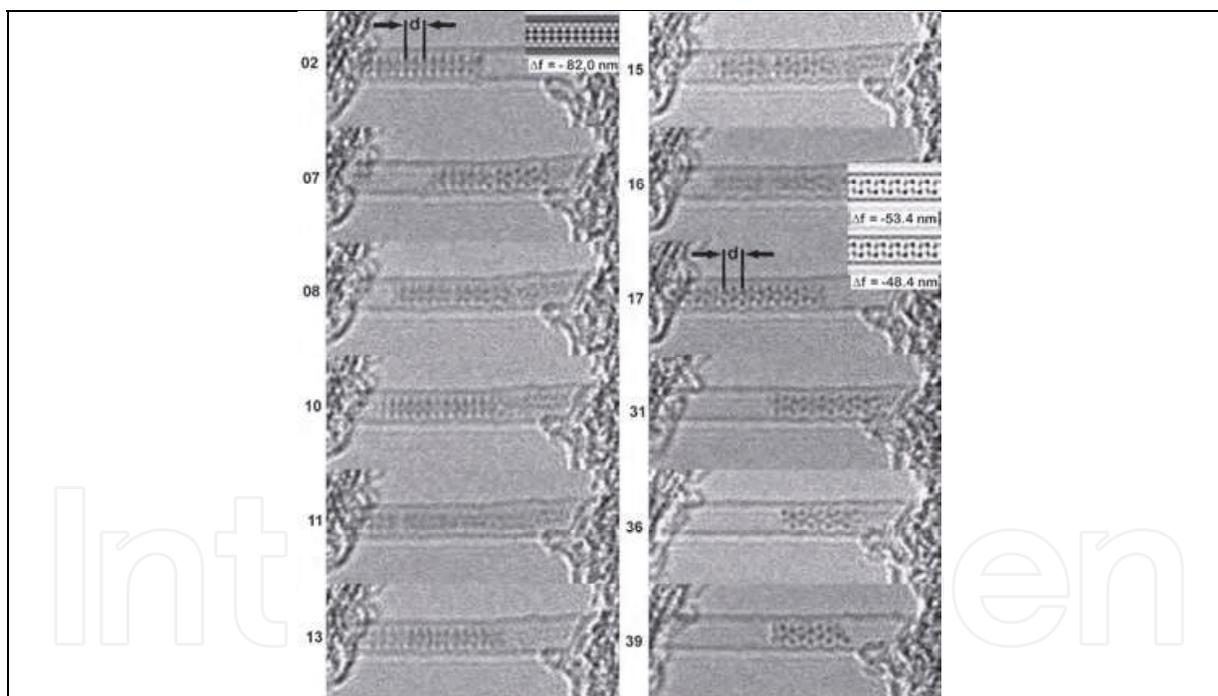


Fig. 7. Oscillation and rotation of the 1D-CuI nanocrystal within the SWNTs

5. Electronic structure of the "1D-crystal@SWNT" composites

For the 1D crystal encapsulated into a nanotube, the interaction between the 1D crystal and the template may play a crucial role and therefore can govern the structure and electronic properties of such a system. The 1D crystal - SWNT interaction may include the formation of local chemical bonds, a template-induced distortion of the crystal structure and the bond geometry, as well as non-local effects (i.e. charge transfer etc). If there are no local chemical

bonds formed between the 1D-crystal and the nanotube, the charge transfer can be described within the rigid bands model, which considers the interaction in terms of a “doping” effect with the corresponding increase (*n*-doping) or decrease (*p*-doping) of the SWNT’s Fermi level. Tuning of the doping level modifies a number of crucial fundamental properties, e.g. allowed optical transitions, the phonon spectrum, the bulk conductance, the internal charge neutrality level, and the collective free charge carrier response. To a first approximation, the charge transfer may be predicted using a difference in the work function between the SWNTs and the crystal and the equilibrium distance from the outer atoms of 1D crystal to the SWNT, as it has been recently demonstrated for graphene (Khomyakov et al., 2009). There are two weak points for such a prediction. First, the 1D crystal WF apparently differs from that for the bulk material, however, it may be obtained from the quantum chemical modeling relatively easily. Second, the 1D crystal geometry can undergo changes once embedded into the SWNT. It should be noted that the exact *ab initio* modeling of the 1D crystal@SWNT nanocomposites is complicated by the period uncertainty, thus a fragment consisting of a very large number of atoms must be retranslated. The doping level can be determined experimentally by direct WF measurements, optical absorption spectroscopy, XPS/UPS, Raman (including electrochemical charging behavior) or XANES spectroscopy, EELS, as well as theoretically by *ab initio* quantum chemical calculations.

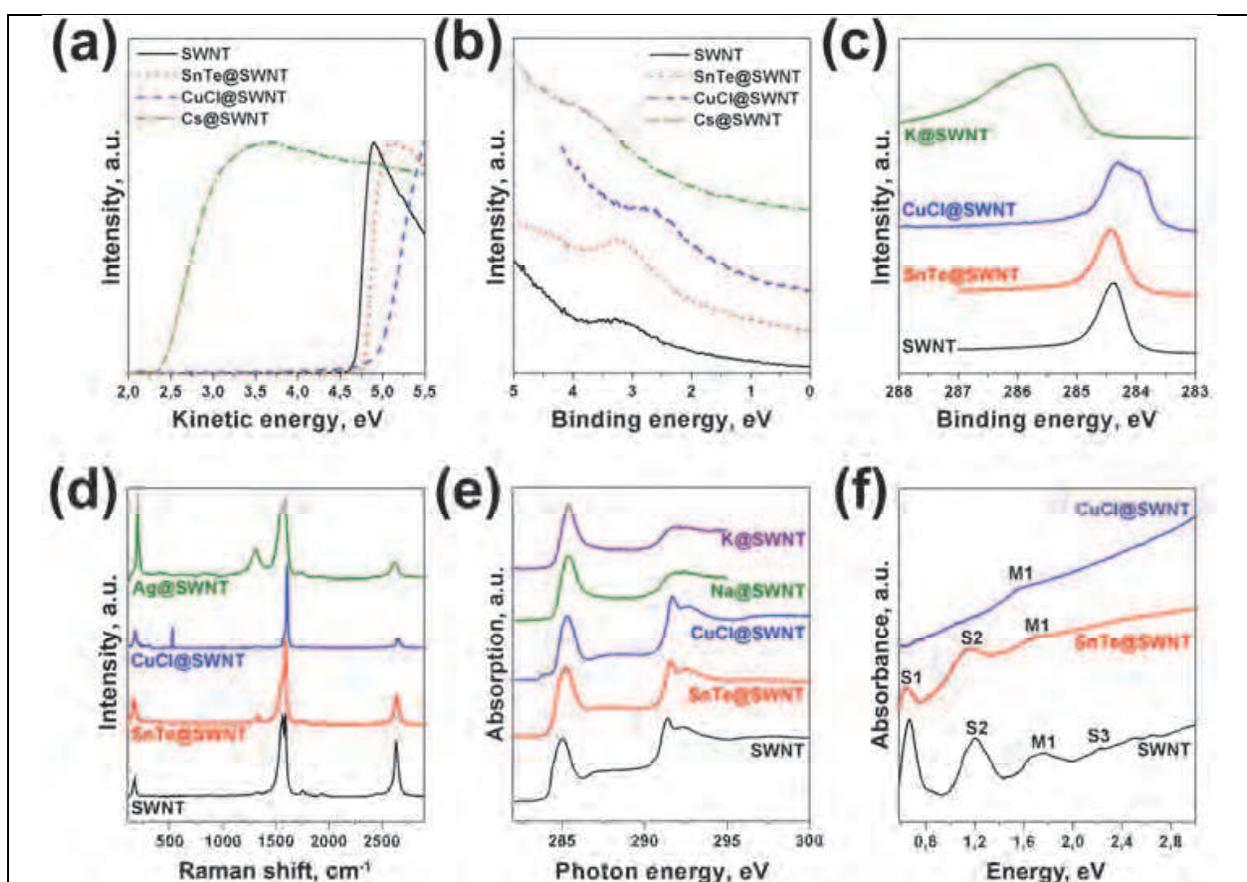


Fig. 8. Secondary electrons cutoff spectra (a), valence band spectra (b), C 1s photoemission spectra (c), Raman spectroscopy data (d), C 1s X-ray absorption spectra (e), optical absorption data (f) for pure SWNTs and SWNTs intercalated by different compounds (Corio et al., 2004; Eliseev et al., 2011; Kramberger et al., 2009b; Liu et al., 2003; Suzuki et al., 2000; Yashina et al., 2011)

Quasi-free-standing 1D crystals within the SWNTs

Free-standing one-dimensional crystals with 3-5 atoms in diameter currently attract attention due to their unique properties, in particular, size-dependent quantum effects like van Hove singularities etc. Better understanding of the 1D crystal physics can be achieved through development of inert substrates or templates that allow minimizing the crystal-template/substrate interaction. Single-walled carbon nanotubes have been considered as a promising template for growing 1D-crystals due to their chemical inertness towards most inorganic substances, as well as their well-studied electronic properties.

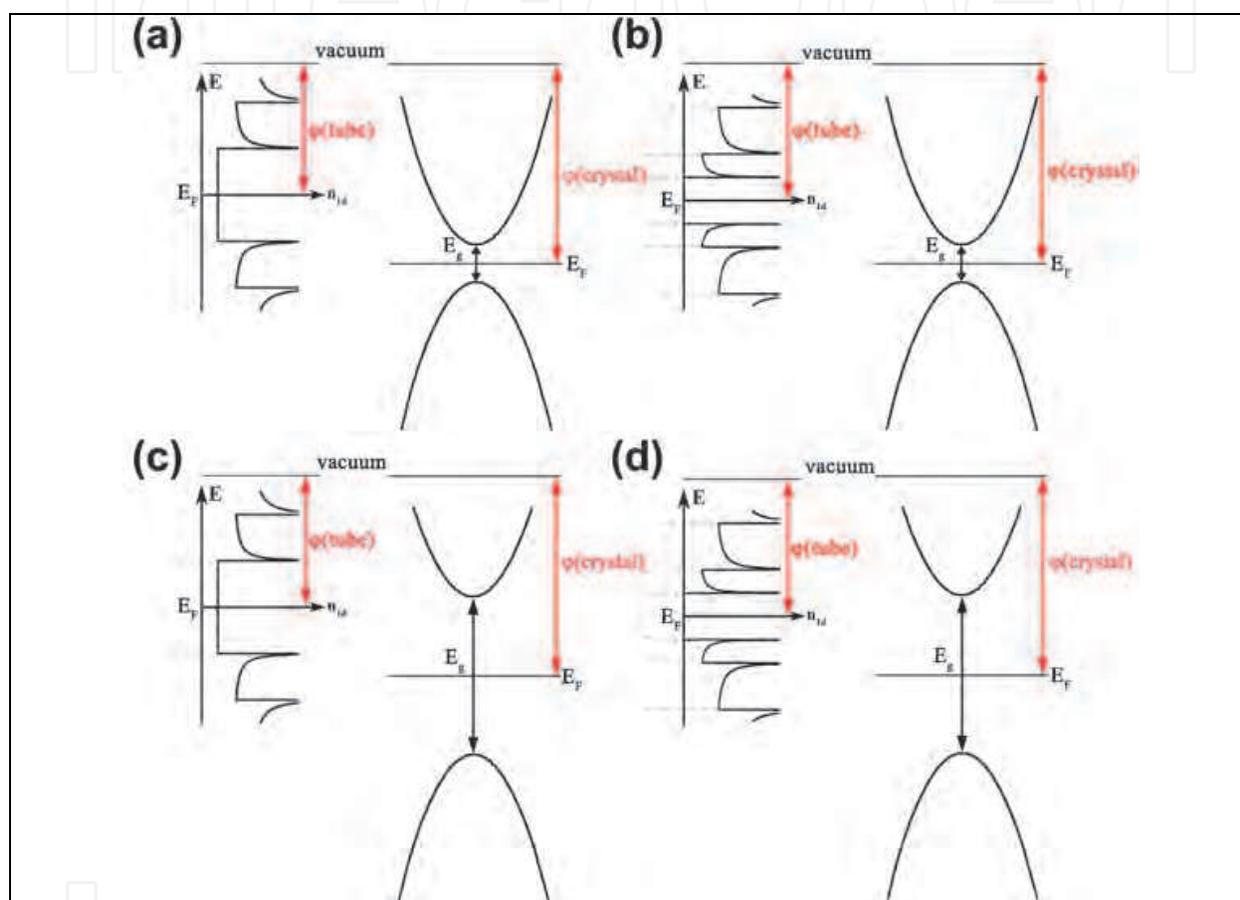


Fig. 9. Semiconductor/SWNT DOS scheme, illustrating possible charge transfer between the guest compounds and the SWNTs: (a) narrow gap semiconductor/metallic SWNT, (b) narrow gap semiconductor/semiconducting SWNT, (c) wide gap semiconductor/metallic SWNT, (d) wide gap semiconductor/semiconducting SWNT

For the quasi-free-standing 1D crystals obtained in such a manner, the Fermi-level shift is absent if the work function of the 1D crystal is nearly the same as that of the SWNT (within the range of ± 0.3 eV). This condition may be met for narrow gap semiconductors. Among them, tin telluride (SnTe), an A^4B^6 semiconductor, was used as a model case for studying the 1D-crystal formation effect (Yashina et al., 2011) (Fig. 8). The C 1s photoemission spectra and Raman spectroscopy data indicate that there are minor differences between the carbon binding energies and the C-C bond vibrations for pristine nanotubes and the nanocomposite (Fig. 8c, d). Both optical absorption and the C 1s X-ray absorption spectra obtained for SnTe@SWNT (shown in Fig. 8e and f) proved that the valence band structure of the

composite does not essentially change due to the SnTe intercalation. Only minor influence of the intercalated crystal on the metallic SWNTs was detected by Raman spectroscopy resulted in a slight increase of WF of the metallic nanotubes (Fig. 8a and b). DFT modeling of this system also confirmed a very small (but non-zero) interaction between the $(\text{SnTe})_{5/2}$ one-dimensional crystal and the nanotube with a diameter of 1.34 nm (Yashina et al., 2011). This suggests that the SnTe@SWNT nanocomposite is a well-suited model system to study the physics of quasi-free-standing 1D-crystals. One may expect similar behavior for other cubic narrow-gap semiconductors, i.e. PbTe, PbSe, and PbS.

The possibility of charge transfer between the encapsulated compound and the SWNT walls generally depends on the filler's band structure (fig. 9). If the guest compound is not chemically bonded to the nanotube, it is possible to adjust the electron density at the SWNT walls by encapsulating narrow gap semiconductors with a desired energy position of the conduction band. To estimate the electron transfer efficiency, one can use the work function and the band gap values for the guest material taking into account the density of states at the bottom of the semiconductor conduction band and the nanotube walls (fig. 10). Contrary, encapsulation of noninteracting wide gap semiconductors with work functions similar to those of SWNT will not result in any charge transfer, thus giving quasi-free-standing 1D crystals within the SWNT channel.

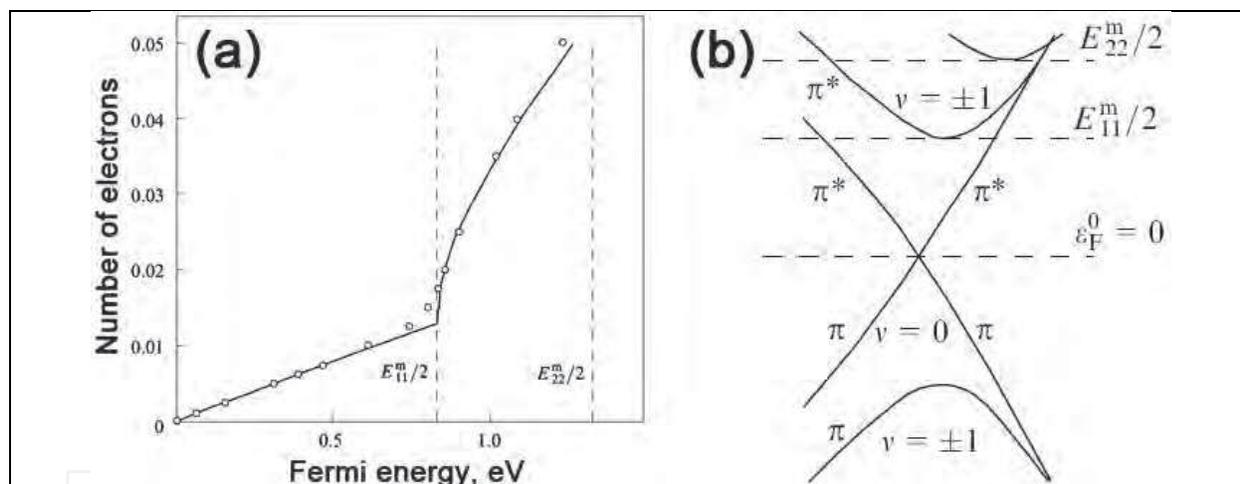


Fig. 10. (a) Charge per carbon atom versus the Fermi energy shift plot for (9,9) SWNT, (b) (9,9) SWNT electronic structure near K-point

Acceptor doping of SWNT

Acceptor doping of the SWNTs can be performed by filling nanotubes with a number of inorganic substances, i.e. Se, Te (Chernysheva et al., 2008), FeCl_3 (De Blauwe et al., 2009; Liu et al., 2004a), FeCl_2 , FeBr_2 , FeI_2 (Kharlamova et al., 2009), AgCl , AgBr , AgI (Eliseev et al., 2010), CuCl , CuBr , CuI (Eliseev et al., 2011), CoBr_2 (Kharlamova et al., 2010) etc. Acceptor doping causes a corresponding shift of the C 1s line towards lower BEs in XPS, the upshift of the G-mode in the Raman spectra and the appearance of a new empty state in the NEXAFS C 1s spectra (Fig. 8). Similar to the donor doping (see below), the S1 peak in the optical absorption spectrum disappears, so that the Fermi level shifts into the valence band, as evidenced by the disappearance of optical transitions and the emergence of an additional pre-peak in the C 1s core-level excitations.

A new approach to detail studies of the doping effect is Raman spectroscopy applied at electrochemical charging. A good illustration of this technique is the CuI@SWNT nanocomposite studies (Eliseev et al., 2011). Raman spectroscopy maps obtained for the CuX@SWNT composites under electrochemical charging illustrate a shift of the Kohn anomaly positions to more negative potentials (fig. 11). For CuCl@SWNT, it moves to $V_{\text{bias}} = -1.1$ V as compared to $V_{\text{bias}} = -0.4$ V for raw SWNTs. Since the position of the Kohn anomaly corresponds to the equivalent electron density and the Fermi level position in both the pristine SWNTs and the nanocomposite, the relative bias shifts of the Kohn anomaly can be used as an evaluation tool for the Fermi level position changes. This assumption allows direct determination of the Fermi level downshift in the composites, which equals -0.7 eV for CuCl@SWNT. This means that the first Van Hove singularities of SWNTs are emptied due to the acceptor effect of copper halide, which is in good agreement with the optical absorbance spectroscopy results. The mechanism proposed for the acceptor behavior of copper halides involves a formation of a new level, which takes place due to the Cu-SWNT interaction (as observed by XAS), and binding of SWNT conduction π -electrons with copper $3d$ electrons at these localized states. This leads to the corresponding Fermi level downshift for the SWNTs. Besides, the dependence charge transfer efficiency on the nanotubes chirality was also reported (Eliseev et al., 2011). The behavior and the mechanism are applicable to most of acceptor dopants.

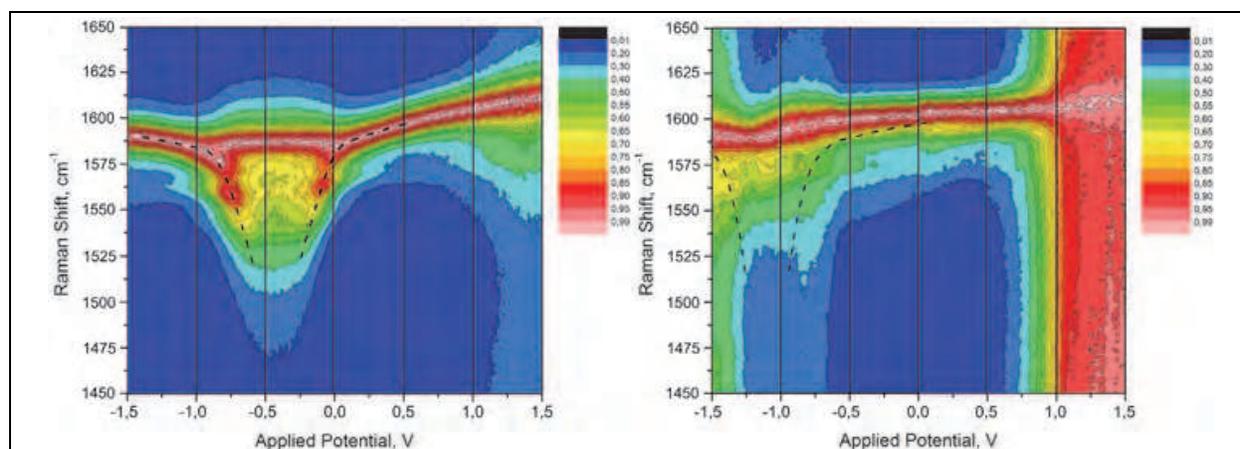


Fig. 11. G-region Raman scattering maps for charged pristine SWNTs (a) and CuCl@SWNT (b) nanocomposites illustrating the Kohn anomaly shift upon intercalation of the CuX compounds. The maps were normalised to the maximum scattering intensity in the 1450-1650 cm^{-1} region to improve the data presentation. Dashed lines indicate the softening phonon branches just for illustration purposes

Donor doping and acceptor-to-donor doping transformation

Donor doping of SWNTs is performed by their filling with certain metals or metallorganic compounds (Kramberger et al., 2009a; Kramberger et al., 2009b). Most opportunities to tune the electronic properties of SWNTs are provided by alkali metals doping. In a series of publications (Kramberger et al., 2009a; Kramberger et al., 2009b), the donor effect of the metal intercalated from the vapor phase was reported. Gradual potassium intercalation was achieved by vacuum metal deposition on the SNWT bundles; this opens a way to tickle the delicate balance of the internal charge transfer and the local WF (Kramberger et al., 2009a).

However, it should be noted that in this case the filling of the SWNT cavity probably takes place concurrently with the intertube space filling within the bundle. To overcome this problem, an elegant approach was proposed, which includes filling of the SWNTs from the vapor phase with large metalloorganic compounds like FeCp₂ (Shiozawa et al., 2008) and CeCp₂ (Shiozawa et al., 2009b) with their subsequent transformation upon heating. For example, annealing in vacuum converts the encapsulated cerocene into the nano-structured cerium within the nanotubes; at the same time, the cyclopentadiene rings form an internal wall of the nanotube, thus it becomes double-walled. As a consequence of the increased electron doping of the outer tubes by the encapsulated cerium chains, the Fermi level upshift is observed (Shiozawa et al., 2009b).

Another approach was implemented for rare-earth nanowires within the SWNTs (Ayala et al., 2011). Quantum ErCl₃ nanowires templated inside carbon nanotubes tailored under high temperature and vacuum, were studied within a combined XAS and resonant photoemission approach. It was shown that the wire formation occurs spontaneously inside the tubes at thermal heating. The salt filling undergoes a chemical transformation upon high temperature heating in vacuum, which leads to the formation of elemental Er nanowires inside the SWNTs. The XAS and the XPS core level spectroscopy data for the filler and the SWNT, as well as from RES-PES across the 4*d* and 3*d* edges indicate that both the bonding environment and the hybridization change upon thermal annealing. During the annealing of the SWNTs doped with ErCl₃, which initially illustrates an acceptor behavior, it transforms into an n-doped SWNT due to conversion to metallic Er.

P-n junctions

Local variation of the WF allows development of nanoelectronics elements, i.e. transistors, due to the possibility to create a p-n junction within an individual nanotube by acceptor and donor filling of its different parts. The example was demonstrated in (Kato et al., 2009) where ultimate one-dimensional heterojunctions of electron donor and acceptor materials were realized within the inner hollow space of a SWNT. The heterojunction structures of Cs/I and Cs/C₆₀ inside the SWNTs yield the air-stable rectifying performance. Clear tunneling currents through the p-n junction barrier were detected only for Cs/I@SWNTs, which is explained by the difference in the depletion layer structures. Based on potential calculations, symmetrical and asymmetrical depletion layers were found to be formed in Cs/I@SWNTs and Cs/C₆₀@SWNTs, respectively. Low temperature measurements also supply evidence of asymmetric depletion layer formation in Cs/C₆₀@SWNTs.

Local interactions between the 1D crystal and the SWNT

Due to the SWNTs inertness, the formation of strong chemical bonds with the 1D crystal is hardly possible. Nevertheless, relatively weak local interactions may be observed rather frequently. This was already demonstrated for a number of metal crystals like Ba (Liu et al., 2004b) and Ag (Borowiak-Palen et al., 2006) intercalated into the SWNT bundles. In these cases, new energy levels were observed in the C 1s NEXAFS spectra at photon energies corresponding to the lower π -resonance for Ba or between the π - and σ -resonances for Ag. In case of Ba, at lower doping pure ionic charge transfer from Ba to the nanotubes occurs similar to the alkali-metal-doped SWNTs. However, at high doping levels a simple rigid band filling of the SWNT's conduction band is not applicable anymore, and one has to take into account hybridization between the Ba and the C states within the intercalation compound. This is in contrast to alkali-metal-intercalated nanotubes where a purely ionic charge transfer is observed. At high Ba content the covalent interaction results in a greater

lattice expansion than expected for Ba^{2+} . The suppression of the π -plasmon and a splitting of the π^* -states lead to the appearance of an additional peak in the C 1s spectra. Regarding the charge carrier plasmon, for fully doped samples the plasmon energy is approximately two times higher than for the alkali-metal-doped SWNTs, although the dc limit of the optical conductivity is of the same order.

The local interactions issue can be clarified through detailed structural study of the local atomic geometry using EXAFS (Eliseev et al., 2011). CuX nanocrystals were found to bond to the nanotube walls with a length of 2 Å; and copper to carbon coordination increased in the sequence $CuI@SWNT \rightarrow CuBr@SWNT \rightarrow CuCl@SWNT$. In $CuCl@SWNT$, copper is “bonded” to four carbon atoms and only one Cl atom. These interactions are clearly indicated by XPS, NEXAFS, HERFD XAS, XES, EXAFS, optical absorption and Raman spectroscopy data (Eliseev et al., 2011; Generalov et al., 2010).

Thus encapsulation of electron donor or acceptor compounds into SWNT channels results in the changes in the electronic structure due to both charge transfer between SWNT wall and the guest compound and the chemical interaction between the filler and the carbon nanotubes. This interaction is realized through hybridisation of the $2p_z$ π -orbitals of carbon with p - or d -orbitals of filler, forming new localised states. The absolute energy positions of these states remain virtually the same for different fillers, but the total charge transfer increases with an increase of the electron affinity of the intercalated compound.

6. Conclusions

By intercalating inorganic compounds into single-walled carbon nanotubes, the electronic properties of SWNTs can be directly modified. Namely, the filling of nanotubes with electron donors (such as metals or metalorganic compounds) can lead to the electronic conductivity of the “1D-crystal@SWNT” composite, which is caused by an increase in the electron density on the nanotube walls within the rigid band structure approximation. Alternatively, intercalation of SWNTs with electron acceptors leads to an electron density transfer from the SWNT walls to the one-dimensional crystal, which results in the system transition into a semiconducting state. To control the charge transfer efficiency upon encapsulation, one should consider the work functions and the band gap values for the guest material taking into account the density of state at the bottom of the semiconductor conduction band and the nanotube walls. Moreover, one should always take into account possible chemical interaction between the filler and the carbon nanotubes. This interaction is realized through hybridisation of the $2p_z$ π -orbitals of carbon with p - or d -orbitals of filler, forming new localised states. Depletion of electrons from the SWNT walls to these localised states will result in decrease of electron density on the conjugated π -orbitals of graphene layer and the corresponding Fermi level downshift. Encapsulation of noninteracting wide gap semiconductors with work functions similar to those of the SWNT will not result in any charge transfer, thus yielding quasi-free-standing 1D crystals within SWNT channel.

This approach enables control of the SWNTs’ electronic structures and development of ground-breaking nanosystems such as quantum threads, single nanotubes with a $p - n$ -transition, and nanocables (for conductor intercalation into semiconducting nanotubes) (Zhao & Xie, 2003; Zhou et al., 2006). In this context, nanocomposites based on single-walled nanotubes are considered to be extremely promising for nanoelectronics applications, especially for creating the $p - n$ -junctions inside a single nanotube.

In one of the recent studies a possibility to develop efficient electrodes for symmetric supercondensers based on the CrO_3 @SWNT composites was demonstrated; high charging rates can be achieved for such electrodes due to reactions between the CrO_x nanocrystals and the electrolyte (Lota et al., 2007). Nanotubes filled with the electron donor compound nanocrystals display low photoelectric work functions, which may be used to manufacture field effect emitters for modern electroluminescent tubes and X-ray minitubes. The above-described experiments are just the very first examples of how the unique properties of the intercalated SWNTs can be used, and the actual applicability of such nanocomposites should be assessed in more detail. The fundamental and practical advancement in this sphere requires further development of the intercalation techniques for various compounds, as well as of the analytical methods and theoretical approaches for studying such nanocomposites.

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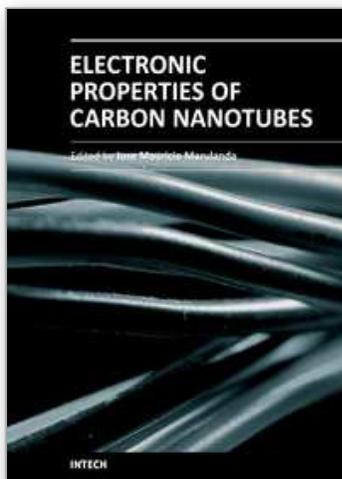
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Carbon nanotubes (CNTs), discovered in 1991, have been a subject of intensive research for a wide range of applications. These one-dimensional (1D) graphene sheets rolled into a tubular form have been the target of many researchers around the world. This book concentrates on the semiconductor physics of carbon nanotubes, it brings unique insight into the phenomena encountered in the electronic structure when operating with carbon nanotubes. This book also presents to reader useful information on the fabrication and applications of these outstanding materials. The main objective of this book is to give in-depth understanding of the physics and electronic structure of carbon nanotubes. Readers of this book should have a strong background on physical electronics and semiconductor device physics. This book first discusses fabrication techniques followed by an analysis on the physical properties of carbon nanotubes, including density of states and electronic structures. Ultimately, the book pursues a significant amount of work in the industry applications of carbon nanotubes.

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