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Functionalization of carbon nanotubes with luminescent silicon nanocrystals upon nanosecond laser processing in liquid media

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1. Introduction

Due to unique properties, potential in basic scientific research and technological applications (Xia, 2003, Hu, J. 1999) a discovery of carbon nanotubes (CNTs) (Iijima, 1991) tubular nanostructure has fascinated and activated research in different fields. During recent years nanotubes of many compounds, such as semiconductors, polymers, metals, oxides, sulfides, lipids have been synthesized (Wei et al., 2003; Cao et al., 2003; Mo et al., 2002; Zhang et al., 2002; Nath et al., 2001; Shimizu, 2002**;** Kobayashi et al., 2002**)** and extensively investigated (Schnur, 1993). Particularly utilization of nanotube hollow cylinder that can be easily varied within several nanometer-sized has drawn a lot of attention (Schnur, 1993**;** Tsang, et al., 1994**;** Shimizu, 2002; Kobayashi, 2002). For instance functionalization of human body more compatible lipid nanotubes (LNTs) cavity could be promising for biological applications since the glycolipid nanotubes sugar headgroup have high biocompatibility and specificity to a certain protein (Shimizu, 2002; Kobayashi, 2002).

During last decade especially CNT has proofed to be a nanomaterial with exceptional physical and chemical properties to many chemical reactions (Pham-Huum, 2002). Concave character of inner-mechanically stable CNTs with confined space offer the possibility to generate metal particles with enhanced structural and chemical stability (Ajayan and Iijima, 1993; Ugarte et al., 1996). Additionally to that the CNTs are electrically and thermally conductive, allowing application in electro- and heterogenous catalysis such hybrid nanomaterials (Tessonnier et al., 2005). The prospects application as templates for nano-wires fabrication and one-dimensional nanocomposite materials through the filling has been envisaged (Ajayan and Iijima, 1993; Ugarte et al., 1996; Thamavaranukup et al., 2004; Tsang, 1994; Lago et al., 1995; Yang, 2004).

The key aspect to realize application based on encapsulated nanoparticles in nanotube cavity relays on an insertion of particles selectively (Tessonnier, 2005). Many techniques has been investigated and applied to efficiently encapsulate the metallic or oxide particles within especially the CNTs cavity (Ajayan and Iijima, 1993; Ugarte et al., 1996; Tessonnier et al., 2005; Tsang et al., 1994). One approach is that the CNTs are refluxed in concentrated

containing precursor salts, by which CNTs can be opened and filled by the precursors (Lago et al., 1995) or by impregnation (Pham-Huu et al., 2002). However, due to the high surface tension of semiconductor materials and introduction of semiconductor particles is quite difficult (Svrcek, 2006a). Particularly silicon in the form of quantum dots, i.e., silicon nanocrystals (Si-ncs) in sizes less than 10 nm where the quantum confinement can take place, offer attractive optoelectronic features (Canham, 1990; Kanemitsu, 1995; Wolkin et al., 1998). In fact, due to the maturity of silicon technology and simple Si-nc integration with available technologies, Si-ncs has been widely investigated (Hirsmman et al., 1996; Pavesi et al., 2000; Canham, 1990; Kanemitsu, 1995; Wolkin et al., 1998; Švrček et al., 2004; Švrček et al., 2009a). In addition, since Si-nc have low toxicity and fully compatible with a human body, Si-nc may also be preferable as a fluorescent agent in biological systems when compared to other currently used materials (Švrček et al, 2008b). Fictionalization of the Si-ncs with nanotubes (Švrček, et al, 2006a Švrček, et al, 2006b, Švrček et al., 2008a, Švrček et al, 2008b) might open innovative routes for development new design for advanced hybrid materials.

Silicon nanocrystals dispersed in colloidal sulutions with low surface tension could be a way how to introduce them into the nanotube cavity (Švrček, et al., 2006a). One alternative method that has produce colloidal Si-ncs and at the same time allow nanotube filling is pulsed laser ablation and fragmentation in liquid media (Švrček et al., 2006c; Švrček, et al., 2006d, Švrček, et al., 2008a). The main advantage of the technique is an easy control of the experimental conditions, the ambience and the possibilities of using variety of the solutions (water, ethanol, polymer). Synthesis allows of tuning the surface tension of surfactant-free Si-ncs, permits entering of freshly formed Si-ncs into carbon nanotubes (CNT) cavity (Švrček, et al., 2008a, Švrček, et al., 2008b) and allows unique materials such as inorganic-organic nanocomposite structures fabrication (Švrček 2008b). Due to an interaction of ablated material with surfactant (Mafuné et al., 2003, Mafuné et al., **2000,** Usui et al., 2005) it might results into novel nanotube/nanocrystals nanocomposites with peculiar properties while the Si-ncs properties could be greatly enhanced.

In this chapter we discuss and compare the filling processes of carbon and lipid nanotubes with surfactant-free Si-ncs prepared in colloidal solutions. Influence of colloidal suspension on mechanical and chemical stability of the nanotubes is addressed. Since the small value of zeta potential in water results agglomeration that inhibits the filling process the laser processing in ethanol /polymer prevents Si-ncs agglomeration and favorites encapsulation in CNTs cavity. However, drawback of the LNTs is low mechanical and chemical stability. Weak resistance against the ethanol based solutions do not allow simply cavity filling by capillary forces with Si-ncs dispersed in organic (ethanol, methanol. polymer) based solutions. Furthermore, the CNTs showed also stronger physical properties (e.g. Young`s modulus), mechanical stability that permits the laser processing in silicon technology compatible polymer, which results surface passivation and encapsulation of luminescent Si-ncs at room temperature. One step functionalization CNTs cavity by Si-ncs during the laser processing in liquid protects freshly formed nanocrystals from pollutions, inhibits agglomeration, and induces the cavity entrance. We overview a fabrication method of nanocomposites based on Si-ncs and CNTs/LNTs upon nanosecond laser processing in liquid media. The shock waves generated during Si-ncs formation in liquid media by nanosecond laser processing assure the encapsulation of Si-ncs in CNTs cavities and incorporation within LNTs wall. Involved processes as shock waves generation, consequent filling and wall incorporation are discussed in detail.

2. Experimental details

Since the CNTs with inner diameter about 50 nm were commercially purchased at Pyrograf Products Inc., the LNTs were fabricated by following way. The most common way to form LNTs is to make use of the unsymmetrical monolayer lipid membrane made of heteroditopic I, ω-amphiliphiles having two headgroups differing in size (Shimizu, 2002). The LNTs we prepared from N-(11-cis-octadecenoyl)-β-D-glucopyranosylamine as constructing glycolipid molecule. Particularly 10 mg of lipid powder was dissolved in 1 ml of the ethanol and sonicated for 10 minutes then added 100 ml of de-ionised water. The solution was then heated at 90 ℃ and let it heated for 30 minutes and then naturally cooling down to 25 ℃. As reported elsewhere the glycolipid molecules self-assembled in water have ability to form mono-dispersed and well-defined LNTs at high yields (more than 98 %) determined by chiral molecular packing (Kamiya et al., 2005). In benefit for the filling of the LNT cavity the most of the ends are naturally opened. However, this is not the case of CNTs and an additional thermal treatment is necessary (Švrček, et al, 2006b) to open their ends. For this work the CNTs were opened by thermal annealing at temperature 580 °C in oxygen atmosphere.

The Si-ncs used for capillary force induced filling were prepared by electrochemical etching of silicon wafer (p-type <100>, resistivity 0.1 ohm·cm, thickness 0.525 mm). Porous silicon wafers were mechanically scratched from the surface and then dispersed in liquid media (Švrček et al., 2006b). The Si-ncs were ultrasonically mixed with methanol and spin on glass (SOG, Filmtronics, Inc. USA). In order to decrease the viscosity of the SOG polymer we added the methanol at ratio methanol:SOG of 2:1 It has to be noted that the homogeneous Si-ncs distribution within the water has been achieved by wetting of the Si-ncs surface by ~20 drops ethanol. Then opened CNTs were directly introduced into solutions (Si-ncs/methanol, Si-ncs/SOG) and kept in an ultrasonic bath for 30 min. In the case of the LNTs prior to introduction in solution, the water from inner cavity has been removed by freeze draying process. Namely, the suspension of nanotubes was freezed with liquid nitrogen becoming completely glassy. Indeed, the water evaporated from solid state was pumped in order to avoid condensation and decomposition of the nanotube tubular structure. It has to be noted, an introduction of LNTs in Si-ncs/ethanol (methanol/SOG polymer) leads to a complete disaggregation of the LNTs structure therefore only capillary induced filling of LNTs of Si-ncs dispersed in water was possible to perform only.

In order to stabilize freshly prepared Si-ncs by laser ablation processing, the experiment was conducted as follows. In 30 ml of de-ionized water, 0.01 mg of CNTs/LNTs was dissolved. At the same time the Si-ncs production and CNT cavity filling were assured in situ in water. Si wafer immersed and fixed on the bottom of a glass vessel in CNTs/water (CNTs/water) suspensions was used as source for Si-ncs. A third harmonic Nd:YAG laser (Spectra Physics LAB-150-30, 355 nm, 30 Hz, 8 ns) was irradiated onto the target immersed in 5 ml of suspension at room temperature for 2 h. The laser beam was focused on the target plate with a beam size of about ~1-1.5 mm in diameter.

For filling CNTs by laser fragmentation processing, the silicon micrograins were prepared by electrochemical etching of silicon wafers. The micrograins were collected by precipitation when Si-ncs were harvested from supernatant parts of solution. Before laser induced fragmentation the porous Si micrograins precipitated on the bottom of vessel had sizes that exceed several micrometers. Precipitated micrograins contain Si-ncs as well and PL at room temperature could be still observed. Those in 30 ml water together with CNTs (0.03 mg)

were homogenously dispersed. We prepared 0.01 wt.% colloidal solutions of Si micrograins in CNT/water solution for the laser fragmentation experiment. Similarly to the capillary induced filling, in order to achieve homogeneous grain distribution within the CNT/water solution, we have wetted the micrograins surface with a few drops of ethanol (20 drops) prior to adding the CNT/water solution (Švrcek, 2008a).

For the laser fragmentation processing in the transparent polymer (Si-59000, Tokyo Ohka Kogyo Co., Ltd.) in 30 ml of polymer solution, 0.01 mg of the CNTs was homogenously dispersed, and 0.01 wt % of Si micrograins was added. It has to be noted that the polymer is a mixture of ethylpolysillicate ($C_2H_5O[SiO(C_2H_5O)_2]_n C_2H_5$), ethanol, and ethylacetate, and homogeneous distribution of micrograins is naturally achieved. To proceed the laser processing filling 5 ml of the solution (micrograins/CNTs/water,micrograins/CNTs/polymer) was placed into a glass container and irradiated by a pulsed Nd:YAG laserat a laser fluence ranging from 0-23.3 mJ/pulse for 2 h at room temperature (Švrcek, 2008a).

The photoluminescence (PL) measurements of colloidal solutions were carried out at room temperature using fluorophotometer (Shimadzu corporation, RF–5300PC) with excitation by Xe lamp at 300 nm. A small droplet of obtained colloidal solution was deposited onto a copper grid with carbon film for high resolution transmission electron (HR-TEM) and scanning electron microscope (SEM) observations. The SEM images were done with a Hitachi SI 4800 microscope with 30 kV acceleration voltage. The HR-TEM studies were performed on a microscope with 200 kV acceleration voltage (JEOL, JEM 2010). An electron diffraction was employed to perform more localized elemental analyses of Si nanoparticles. In order to perform a localized analysis of the providing Si nanoparticles, a convergent incident electron beam was employed in the diffraction measurements convergent beam electron diffraction.

3. Capillary forces filling of nanotube cavities by room temperature luminescent Si-ncs

Theories based on molecular chilarity are commonly applied to describe the LNTs formation (Spector et al., 1996). A chiral interaction is most important factor for formation of nanotubes and cause constituent molecules to pack at a nonzero angle with respect to their nearest neighbor. The chirality of the molecule induces particular orientation to be energetically favorable and results the formation of a cylindrical hollow (Spector et al., 1996). As the LNTs consist of the unsymmetrical monolayer lipid membrane, the geometry of the LNT can be easily tuned and control by determinative way (Yang et al., 2004). The nanotube length can be varied over large range varying from nanometers to hundreds of micrometers due to the changing of the solvent and preparation conditions (Ratna et al., 1992). As also the diameter of the cavity in LNT can be easily controlled than it can be in principle achieve a selection of particle size. Figure 1 shows typical optical image of LNT formed in glycolipid suspension. As dispersed on glass substrate we observe that the nanotubes are well separated and agglomerated structures are rarely observed. The inner and outer diameter vary and giving approximately 40 and 100 nm in average. The lengths of LNTs vary from 2 μm to 40 μm with average size of about 25 μm.
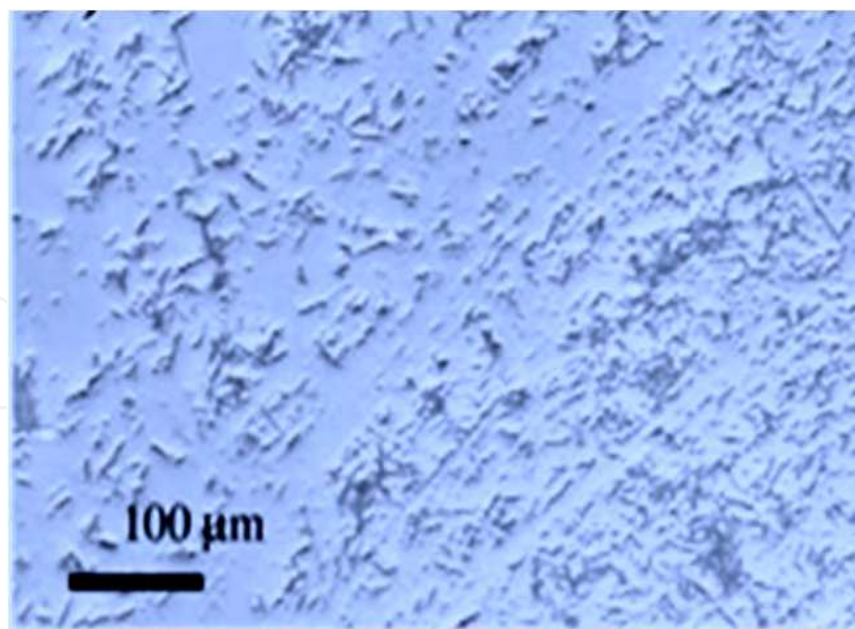
Fig. 1. Optical images of lipid nanotubes (LNTs) formed in glycolipid suspension and dispersed on glass substrate with average length of about 25 μm.

It has been demonstrated that opened LNTs are able to encapsulate different kind of materials in an efficient manner (Yang et al., 2004). It has been pointed out that in order to insert nanoparticles into LNTs at enough high concentrations the cavity has to be empted. (Yang et al., 2004). Similar approach was also applied here. After freeze dried process the SEM and TEM images showed the empty-tubular structure of LNTs. Homogenous hollow cylinders with completely opened ends were observed in majority of the LNTs (~90 %). We recall that the inner hollow of the lipid nanotube is covered with carbony headgroups while outer surface with sugar head group. Presence of carbony headgroups in principle facilitates introduction of the particles dispersed in aqueous solution into hollow cavity (Yui et al., 2005). Therefore it is expected that hydrophilic surface of the inner cavity and capillary forces are favorable to introduce Si nanoparticles dispersed in aqueous solution
Figure 2 (a) demonstrates typical SEM image freeze-dried lipid nanotubes filled with Si-nc in aqueous solution. Transmision electron microscopy images showed the presence of the nanoparticles in tubular structure. Corresponding EDS analysis (Fig 2 (b)) performed within of the nanotube confirmed an increase of the Si concentration within the LNTs cavity. It has to be noted that only small percentage (~1%) of LNTs was filled. Most of the Si-ncs were agglomerated out of the nanotubes in form of spherical particles Agglomerated Si-ncs spheres exceeded several tenths of nanometers in diameter. Fig 2 (c) shows representative SEM image of such particles. Corresponding EDS analysis taken at the particle confirmed presence of Si (Fig 2 (d)).
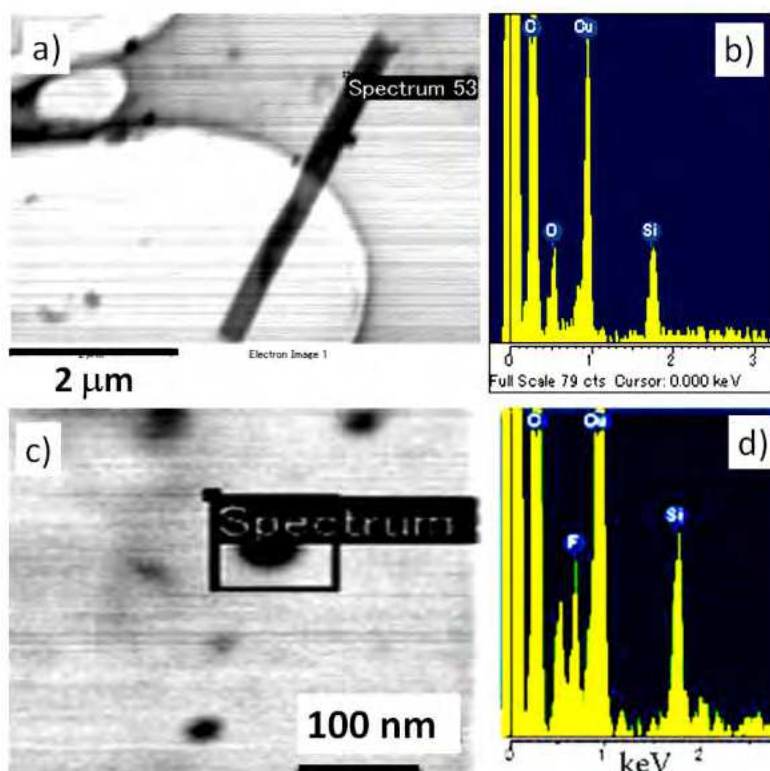
Fig. 2. (a) Freeze-dried lipid nanotubes (LNTs) filled with Si-nc dispersed in aqueous solution. The transmission electron microscopy (TEM) image shows the tubular structure a homogenous hollow cylinder with completely opened end and filled with Si nanoparticles (b) Corresponding EDS taken in the LNTs tubular structure. (c) TEM image of spherical Si particles located outside of LNTs cavity. (d) Corresponding EDS analysis of spherical particle.

The Si-ncs show typical emission at room temperature in spectral range from 500 to 800 nm with maximum around 680 nm. What about the PL properties of the Si-ncs incorporated within LNT tubular structure? Corresponding PL spectra from the solution is shown in Figure 3 (red line). Visible-red PL could be observed in the region where the Si-ncs emission is located only. However, after filling process the colloidal solution showed a decrease in PL intensity. Thus indirectly suggest that some of the Si-ncs could be encapsulated in cavity. It is expected that encapsulation in LNTs cavity, hinders the Si-ncs emission. In order to verify this hypothesis shorter LNTs were prepared with length 3 µm in average. Colloidal solution contained of Si-ncs introduced in shorter LNTs showed stronger PL emission (Fig. 3, blue line). It is probable that as the cavity is shorter also the emission from the Si-ncsLNTs solution could be stronger. Indeed, the longer nanotubes also induce stronger capillary force and Si-ncs introduced deeper within cavity show also weaker emission from Si-ncs. It has to stress that LNTs only did not show up any PL in this region (Fig. 3, open circles).
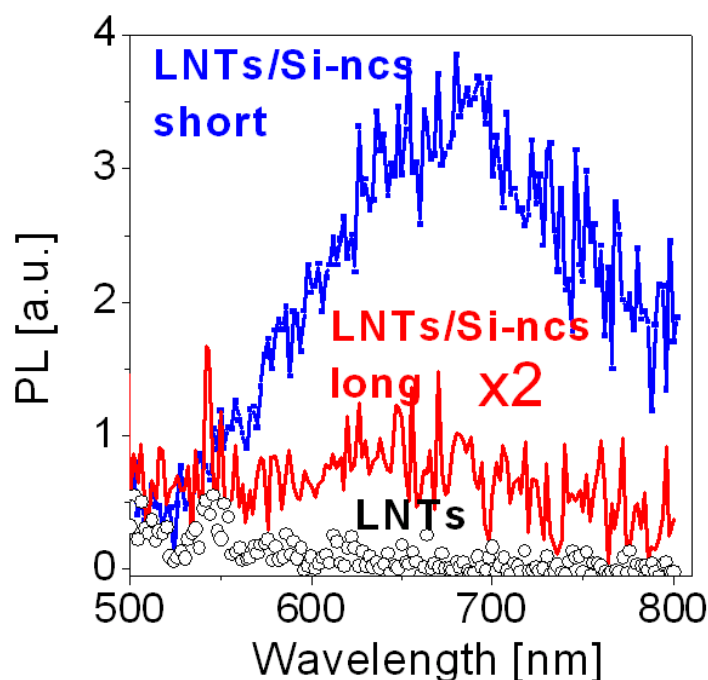
Fig. 3. Photoluminescence (PL) spectra as a function of wavelength for freeze-dried long (red line) and short (blue line) lipid nanotubes (LNTs) filled by silicon nanocrystals (Si-ncs) dispersed in water. The PL spectrum of LNTs only is shown for comparison (open circles).

However, drawback of the Si-ncs dispersed in water is small value of zeta potential, which leads to an agglomeration process (Švrcek, 2009b). As shown in figure 2 (c) agglomerated particles with sizes exceeding of about 50 nm could be find. As the inner diameter of the LNTs is this range than Si-ncs agglomerates cannot in principally enter into LNTs cavity. One possible approach how to increase the zeta potential and allow better Si-ncs dispersion is dispersion in ethanol or methanol. However, in this case the LNTs the tubular structure is destroyed. Figure 4 (a) represents SEM image of freeze-dried lipid nanotubes introduced into Si-nc/ethanol solution. As we can see complete dissociation of lipid tubular structure is experienced.

Contrary to that the CNTs are chemically stable and easily resist many common organic solutions. As results a filling by capillary forces with Si-ncs dispersed in methanol/ethanol can be achieved (Švrcek et al., 2006a). The typical transmission electron microscopy images showed the tubular structure and hollow cylinder of CNTs. Most of the CNTs (~90%) used in this work had two completely opened ends with inner diameter about 50 nm in average. Figure 4 shows a plan-view HRTEM image of an open CNT filled with a Si-nc/dispersed in methanol. Contrasted darker areas are observed in the cavity of the CNT. The location of those Si-ncs inside the CNT channel was examined by tilting the sample along the tube axis (Švrcek et al., 2006a). When the electron beam was focussed on the walls of the starting nanotubes the interplanar distance characteristic of graphite (0.337 nm) and contrasted Si-ncs were evaluated (Švrcek et al., 2006a). Parallel stripes corresponding to atomic columns with an interplanar distance 0.198 nm (inset Fig. 4(b)). This is an agreement with the

expected interplanar distance of 0.192 nm in the <220> orientation of silicon. It is worth noting that the HR-TEM image of the Si-ncs was not straightforward due to the very low contrast between the Si-ncs and the grapheme shells. Those were further confirmed by selected area electron diffraction technique (Švrcek et al., 2006a, Švrcek et al., 2006d). The selected area electron diffraction pattern showed Si crystal structure close to a <111> and the JEMS simulation clearly witnesses the presence of Si-ncs with planes with <220>, <422>, <440> orientations (Švrcek et al., 2006d).
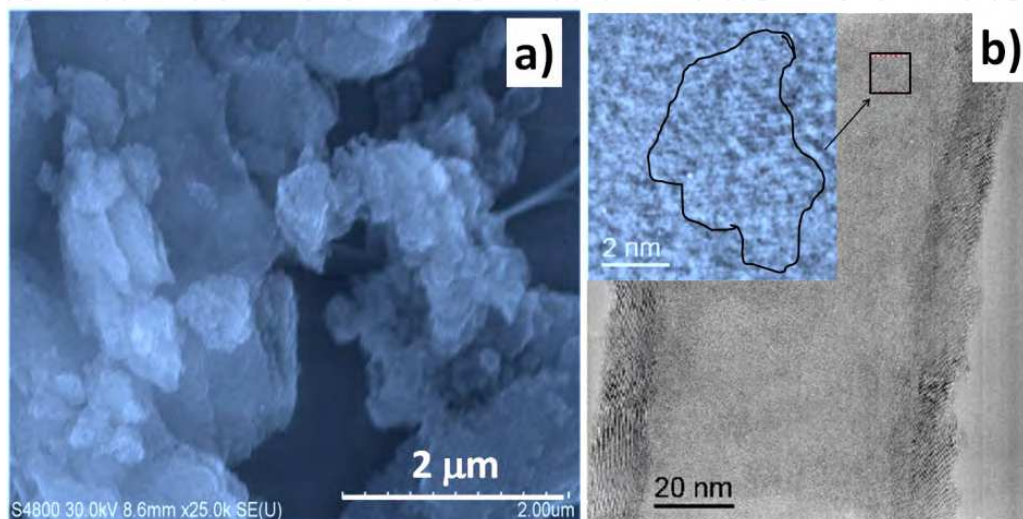
Fig. 4. (a) SEM images of freeze-dried lipid nanotubes (LNTs) introduced into Si-ncs/ethanol solution. Due to the presence of ethanol complete dissociation of LNTs is observed. (b) A plan-view HRTEM image of an open CNT filled with a Si-ncs dispersed in methanol. In set detailed HR-TEM image of the hollow part of the tube with contrasted Si-ncs inside.

One approach that we applied is first the formation of the Si-ncs directly in water by laser ablation (Svrcek et al., 2006c) and then introduction the freeze-drayed LNTs. Induced capillary then can accomplish filling LNT tubular structure. Figure 5 shows SEM images of LNTs in Si-ncs aqueous solution prepared by laser ablation. The SEM image shows the tubular structure a homogenous hollow cylinder of LNT with opened end and inner diameter about 40 nm. However due to the spherical agglomeration of the Si-ncs particles (Svrcek et al., 2009b) a simple dissolution did not allow efficient filling of LNT cavity. Most of the agglomerated Si-ncs nanoparticles with diameter that exceeds the inner diameter of the nanotube (~ 40 nm) remain located out of the cavity (Fig.5, indicated by arrows). It has to be noticed that some parts of the LNT contained darker areas containing smaller sized Si-ncs.

CNT surface can be wetted and filled if the substance having low surface tensions. Similar to the case of LNTs it is expected (M. R. Pederson and J. Q. Broughton, 1992) that liquid solution having a surface tension below < 200 mN/m allows to enter dispersed Si-ncs into the hollow cavity of the CNTs through the capillarity (Durjardin, et al., 1994; Švrcek et al., 2006a). This happened after the surface tension of Si-ncs dispersed in methanol/ethanol dropped and then filling of Si-ncs dispersed in liquids into the channel of the nanotubes occurred.
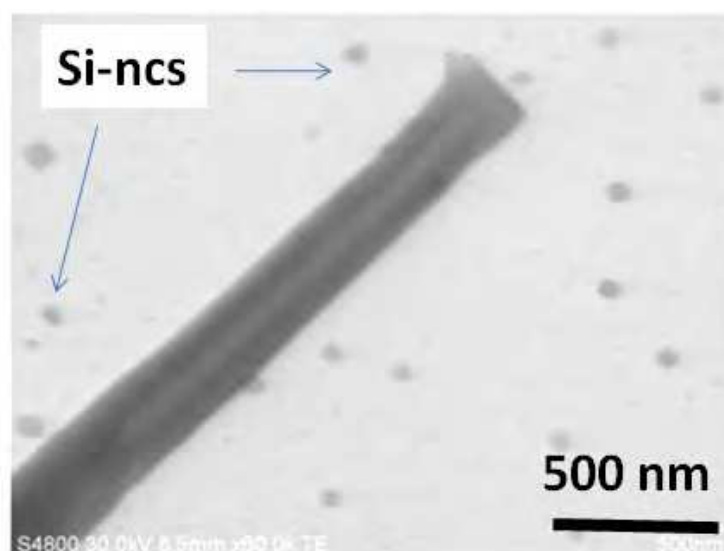
Fig. 5. SEM transmission electron microscopy image of freezed-dried lipid nanotube (LNT) dissolved with Si-nc aqueous solution prepared by laser ablation in water. The image showed the tubular structure a homogenous hollow cylinder with opened end. The presence of Si-ncs spherical clusters outside of LNTs are indicated by arrows.

4. Filling nanotubes through the laser processing in liquid media

4.1. Filling carbon nanotubes during nanosecond laser induced fragmentation of silicon micrograins

It is observed that the rates of filling of CNTs and LNTs by Si-ncs through the capillary forces are quite low. Thus is due to the many factors that act at the same time (i.e. agglomeration of Si-ncs). Recently, some alternative possibilities by nanosecond laser processing in liquid media were shown (Švrceka, 2008a). Namely when Si-ncs micrograins are dispersed in liquid media and the nanosecond laser fragmentation occur generated shock waves - which propagate through the liquid – allow filling nanotube cavity. Shock wave can have enough energy to introduce newly generated Si-ncs particles within carbon nanotubes cavities (Švrcek, 2008a). However, in our experience a weak mechanical strengthens of LNTs leads to dissociation and braking of the LNT tubular structure when nanosecond laser irradiation is applied.

This is not case of mechanically stronger CNTs. In present experiment - in order to exclude the filling CNTs by capillary forces - prior irradiation by ns laser we dispersed CNTs in water and then mixed with wetted Si-ncs micrograins. Figures (2a-b) show photos of the vessels with colloidal suspensions before laser irradiation and after irradiation at fluence 23.3 mJ/pulse. SEM and TEM analysis showed that the micrograins with sizes of several micrometers do not enter into cavity without fragmentation process. Our experiments also showed that at higher laser fluences (>20 mJ/pulse) along with the presence of CNTs, the yellow color of the suspension disappeared. As the irradiation is continuing conducted the solution becomes more transparent (Figure 6 (b)).

Contrary to CNTs absorption only the Si micrograins have a quite significant absorption cross-section at 355 nm wavelength (Švrcek, 2008a) at which the irradiation is conducted. Therefore the majority of the laser energy goes into Si-ncs grain and mostly the grain fragmentation occurs. Corresponding PL spectra of aqueous colloidal CNTs/micrograins

solutions fragmented by different laser fluences are depicted in Fig. 6 (c). Similarly to the capillary induced filling, as the laser irradiation power increase, a decrease in PL emission is recorded. At increased irradiation intensity the rate of introduction of Si-ncs in the CNTs cavity is enhanced. Generated reflux increased the Si-ncs concentration within the cavity, which results the PL emission decreases. It has to be noted that the CNTs only dispersed in water did not show any PL in this spectral region at room temperature.
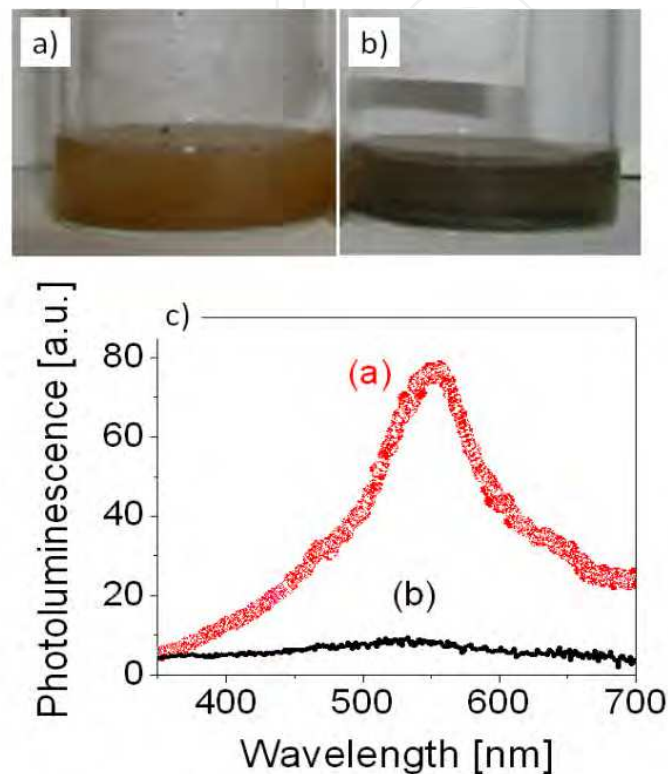
Fig. 6. (a) Photos of 0.01% silicon micrgrains in 5 ml CNT/water solution in glass vessel before and (b) after nanosecond laser induced fragmentation at laser fluence of 23.3 mJ/pulse. (c) Corresponding photoluminescence spectra of aqueous colloidal CNTs/micrograins solutions before (red symbols) and after fragmentation (black line) at laser fluence of 23.3 mJ/pulse are shown.

The question arises how the laser beam interact with the CNTs present in solution during the irradiation and induced filling process. If no ablation is performed the surface of nanotubes is flat and the cavity is mostly empty (Fig 7 a, b). However, when the irradiation is applied even at low laser fluence on the CNT surface are attached same particles or CNT surface is occasionally damaged. Figure 7 c-d show the SEM and corresponding TEM image of nanotube when the solution was irradiated at 5 mJ/pulse. As the power irradiation is increased surface of CNTs is more damaged and also larger amount of nanotubes is found to be broken. At the same time in the cavity higher concentration of silicon particles can be seen. As the fluence is increased smaller particles in diameter could be find in CNTs cavity. Figure 7 (e, f) shows CNT image when the laser fragmentation process was conducted at 23.3 mJ/pulse. Detailed HR-TEM analysis showed that the smaller sized Si-ncs with diameter less then CNTs diameter were localized within the cavity. A detailed HR-TEM

analysis has confirmed that the crystalline nanoparticles with quantum confinement size effect are introduced into CNT cavities (Švrcek, 2008a). Results further showed presence of Si-ncs with an interplanar distance of 0.315 nm corresponding to a diamond lattice with different plane orientation (Švrcek, 2008a).
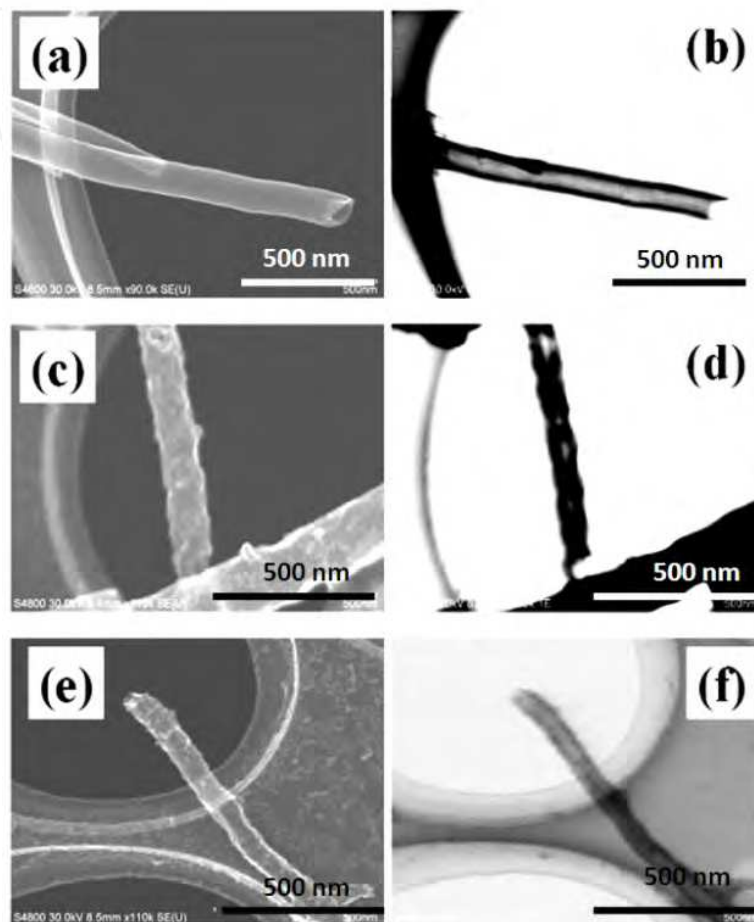

Fig. 7. SEM images of fragmented silicon grains with presence of CNTs a) just dispersed and c) and e) after irradiation at laser fluence at 5 mJ/pulse and 23.3 mJ/pulse respectively. Corresponding TEM images (b, d, f) are shown for comparison to visualize the nanotube cavity, indeed.

An introduction of the Si-nc into silicon technology compatible SOG-transparent polymer allows the stabilization and enhanced of the Si-ncs luminescence properties (Švrcek et al., 2004, Švrcek et al 2008c). Since the CNTs resist ethanol based polymer and mechanical strength also stronger nanocomposites based on Si-ncs/SOG could be envisaged. Furthermore, incorporated Si-ncs within the cavity with efficiently stabilized surface by polymer could be 1D luminescent composite. Dissolution of Si-ncs in liquid SOG modifies the surface tension of the Si-ncs which promotes the filling of CNTs. In addition, compared to water, the SOG polymer is an efficient liquid medium for micrograin fragmentation (Švrcek et al., 2006d). Because of the more efficient fragmentation in SOG solution one can

apply lower irradiation intensities and avoid CNT damage. However at higher fluencies the damage of the CNTs was observed (Fig. 8). After performing of the laser processing for 2 h, it is observed that nanotubes cavities are almost fully filled with Si-ncs/polymer composite. Similar to defragmentation and filling in water, it is observed by naked eye, that the solution loses yellowish color when the fragmentation occurred (>4 mJ/pulse). SEM together with EDS analysis showed an excess and increase of silicon content. In addition to elemental analysis, the corresponding electron diffraction pattern in HR-TEM analysis the tube showed the presence of Si-ncs with crystal structure of Si cubic phase (Svrcek, 2008b). Silicon diffraction rings could be assigned to the lattice planes <111>, <220>, and <311>. Importantly corresponding PL spectrum of solidified of a polymer/micrograin/CNT composite showed shift of the PL spectra as a function applied laser fluence. This is similar to the as fragmented Si micrograins in polymer and is due to formation of smaller sized Si-ncs (Švrcek et al., 2006d). It has to be stressed that filling LNTs with Si-ncs/SOG polymer nanocomposites is impossible due to the methanol based polymer solution which dissolve the LNTs tubular structure.
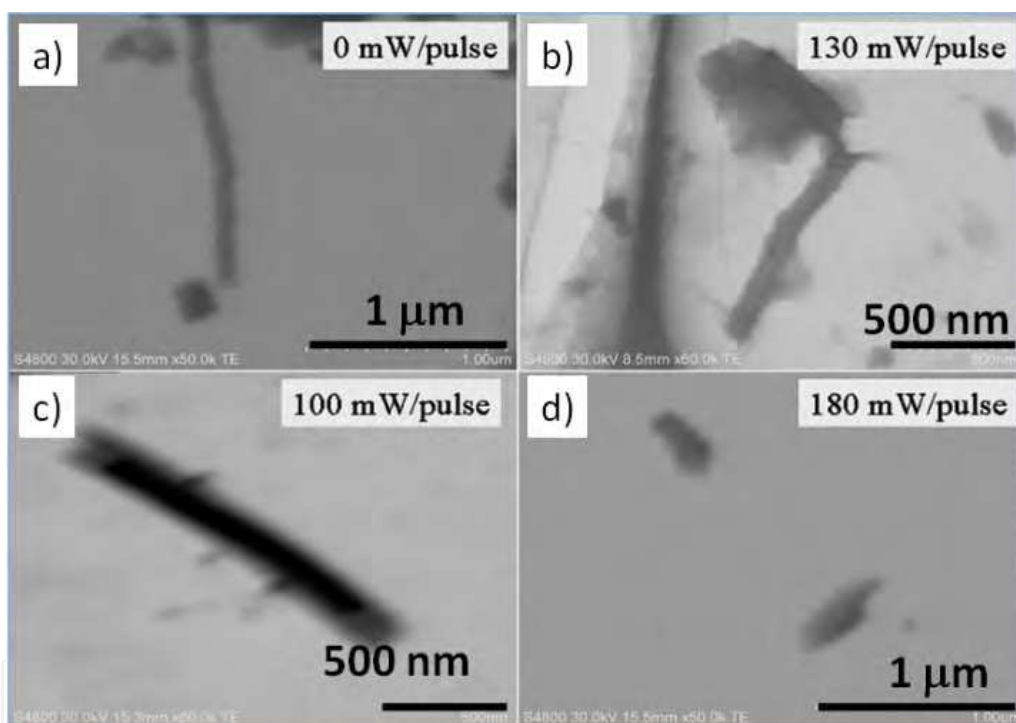

Fig. 8. (a) SEM images of Si-ncs micrograins dispersed in SOG and fragmented jointly with presence of carbon nanotubes (CNTs) at different laser fluencies ranging from 0-180 mW/pulse. With increased the laser fluence irradiation also destruction of some CNTs is observed.

4.1 Filling lipid nanotubes with freshly prepared Si-ncs by laser ablation in water

LNTs mechanical fragility and sensitivity to organic solutions do not allow applied the laser fragmentation process in organic based liquid where the filling is more efficient. Some alternative approaches that allow direct fabrication of Si-ncs in water could be applied. For instance, one approach that we explored is to fabricate Si-ncs directly by ns laser ablation

when the silicon target is immersed in N-(11-cis-octadecenoyl)-β-D-glucopyranosylamine
suspension. Then increase the temperature higher than 80 °C. As it is well known the
glycolipid molecules in suspension around 100 °C exist as vesicle structure. These structures
loose fluidity of the alkyl chains and transit to metastable helical phase via unstable lamellar
structure, and finally form LNT with temperature decrease (Kamiya et al., 2005). However
in our experience during the cooling down step and formation of nanotubes the Si-ncs are
mostly incorporated within the lipid nanotube wall. The good dispersibility and glycolipid
molecules modified Si-ncs is most likely favorable for chiral molecular packing and
incorporation within the wall. However, issues whether some Si-ncs get incorporated inner
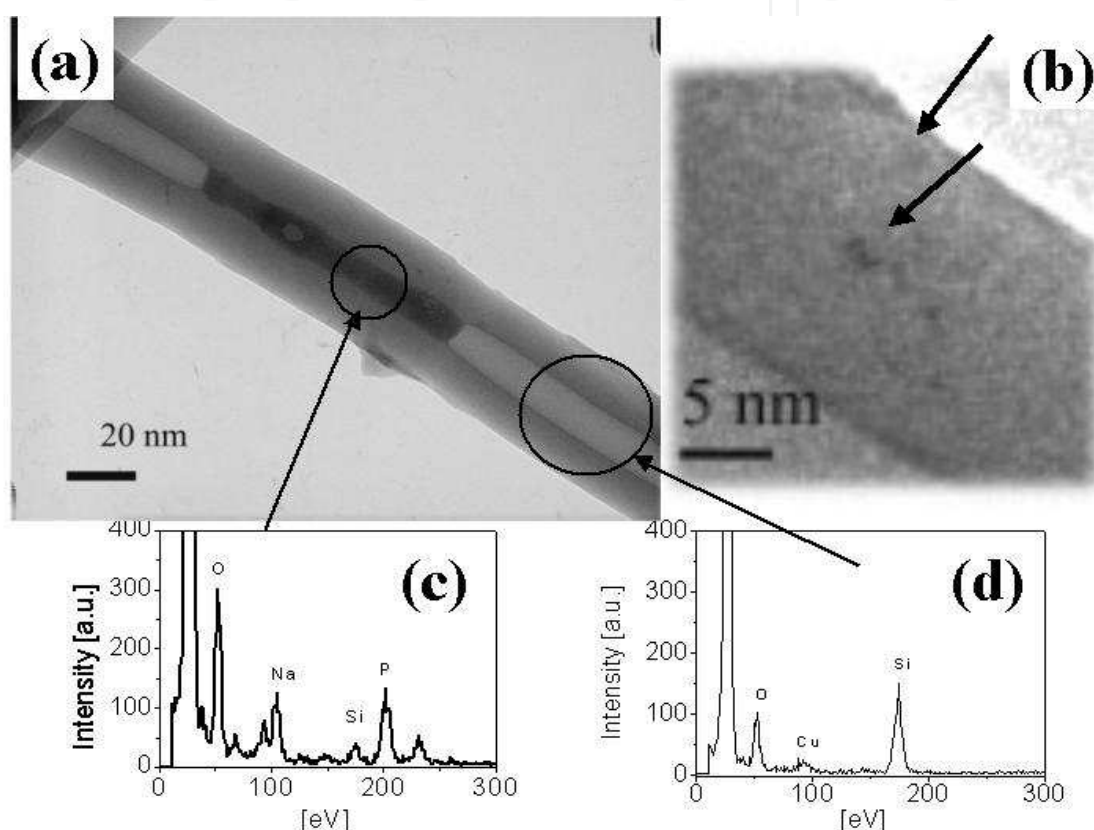wall has to be investigated in detail in near future.

Fig. 9. (a) HR-TEM image of lipid nanotube (LNT) filled with fresh Si-ncs prepared by laser
ablation of silicon target immersed in LNTs aqueous solution. (b) Corresponding detailed
HR-TEM image of LNT wall. Dark spots indicated by arrows present presence of Si-ncs
within the LNT wall. Images (c, d) represent corresponding EDS analysis.

Next, we prepared Si-ncs in aqueous solution by laser ablation with presence of LNTs. In
order to achieve same structure of nanotubes we have removed the water from inner cavity
by freeze draying step and then introduced them again in the water. The LNTs aqueous
solution was putted in the glass vessel where on the bottom crystalline silicon wafer was
glued. After laser ablation process some of the nanotubes were damaged however some of
the nanotubes were in good shape without any significant damage. It is also observed that
the presence of the LNTs in solution during ablation process inhibits Si-ncs spherical
agglomeration. It is observed that same parts of the LNT contains dark areas and are
possibly filled with freshly formed Si-ncs. Figure 9 (a) represents a typical HR-TEM image of

LNT after laser ablation processing with inner diameter of ~15 nm. Detailed EDS analysis showed that in this parts an increase concentration of Si is recorded (Fig. 9 (c)). However the Si-ncs were not only present in the cavity but some of them were located within the LNTs wall as well (Fig. 9 (b)). Freshly formed Si-ncs has enough energy to enter within the LNT wall when ejected from target during laser ablation process. On the other hand freshly formed Si-ncs modified with glycolipid molecules in glycolipid suspension create also reflux, which results not only introduction of Si-ncs within the wall but also within the hollow cavity.

Figure 10 presents normalized room temperature PL spectra of LNTs/Si-ncs colloidal solution (solid red symbols) and Si-ncs prepared by laser ablation in water (open blue symbols). The PL spectra of LNTs only dispersed in aqueous solution is shown for comparison and do not show PL in this part of the spectra. The PL spectra of LNTs/Si-ncs solution show clear contribution from Si-ncs. The presence of Si-ncs enhances emission band with maximum located at 420 nm. Interestingly, the PL of the LNTs/Si-ncs was visibly stronger than from Si-ncs only. This can be attributed multiple factors. Firstly, as HR-TEM images indicate low filling rate of Si-ncs low within LNTs cavity and the large number of small Si-ncs embedded in LNTs wall that facilitates the PL emission. Secondly, glycolipid molecule modified the surface of Si-ncs particles prepared in presence of LNTs. During the direct processing in LNTs solution freshly formed Si-ns surface is covered by thin layer of lipid that act as surfactant and prevent agglomeration (Mafuné et al., 2003). Then an increased PL emission also results from well separated and lipid passivated Si-ncs that prevent re-absorption and enhances PL at room temperature.
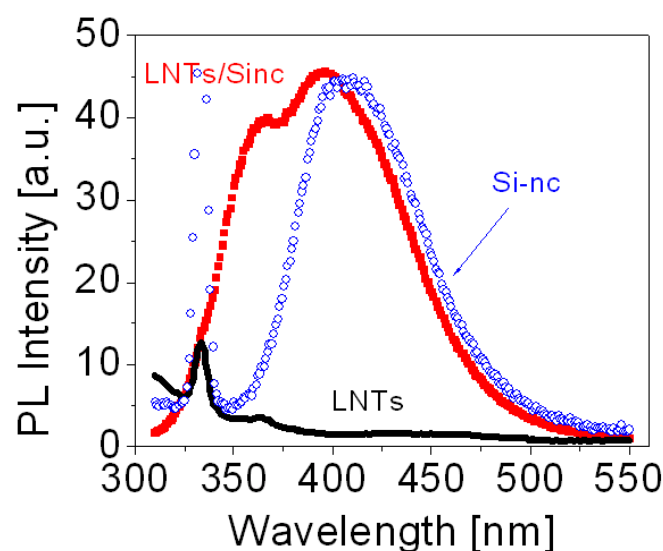

Fig. 10. Normalized room temperature photoluminecence (PL) spectra of LNTs/Si-ncs colloidal solution (full red symbols) and Si-ncs prepared by laser ablation in water only (open blue symbols). The PL spectrum of LNTs is shown for comparison (black line).

One can speculate that contrary to mechanically more stable CNTs, advantage of using laser ablation in LNTs aqueous suspension could be useful for fabrication of nanotubes composites through a simple one-step process. The modification of Si-ncs surfaces with

glycolipid molecule within the lipid nanotube wall might then find important implication for luminescent glycolipid composites design. Luminescent Si-ncs particles modified with glycolipid molecules during ablation, which interact with intermediate structures of LNT such as vesicle, helical, and lamellar phases could be designed.

4.3. Filling CNTs by freshly Si-ncs prepared by laser ablation in SOG-polymer and water

Contrary to LNTs, the reflux generated during ablation process in organic based polymer or water lead to introduction of freshly produced nanocrystals in the mechanically and chemically more stable CNT cavity (Svrcek, 2008a). As mentioned above, the most important feature of the Si-ncs is the PL emission at room temperature. The silicon dioxide-based transparent polymer is proven to be an efficient liquid medium for laser processing and suitable for stabilization of Si-ncs PL emission properties (Svrcek et al., 2004). After laser processing it is observed that most of carbon nanotubes cavities are almost fully filled with luminescent Si-ncs/polymer composite (Svrcek, 2008a). Compared to the pure polymer, elemental analysis confirmed the excess of the silicon content in the CNT cavity laser processing occurred. It is observed that the ns laser processing in polymer media aside from the generation and introduction of Si-ncs in the CNT's cavity also leads at the same time to stabilization of Si-ncs PL emission at room temperature (Svrcek, 2008a).
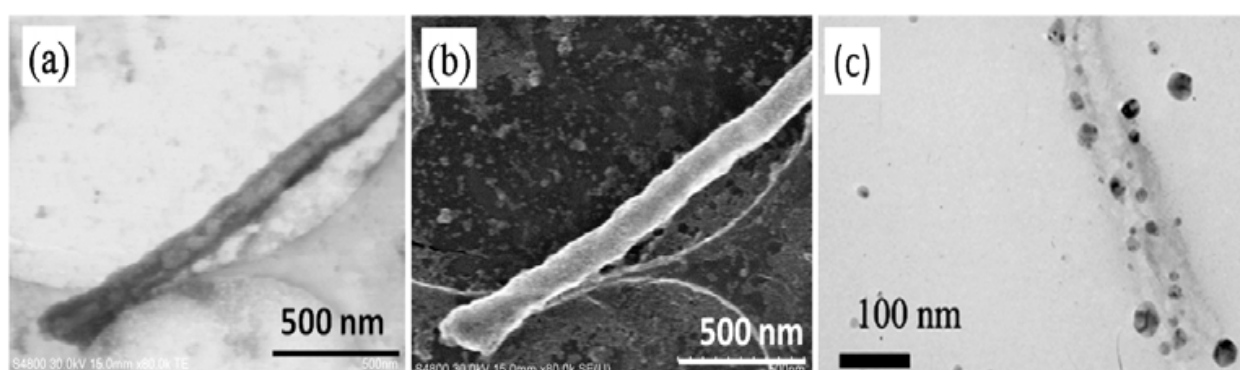

Fig. 11. (a) SEM and (b) corresponding TEM images of Si-ncs/CNT structure prepared by nanosecond laser ablation of immersed silicon wafer in a CNT/water suspension at laser fluence of 1.1 mJ/pulse. (c) Detailed HR-TEM image of CNT filled with spherically agglomerated Si-ncs particles.

On the other hand an unique wetting phenomenon for Si-ncs obtained by laser ablation of crystalline silicon target in water decrease surface tension and allow filling CNTs cavity (Svrcek, 2008a, Svrcek et al., 2009b). Figure 11 (a) and (b) shows SEM and corresponding TEM images of CNT with Si-ncs prepared in water at the laser fluence of 1.1 mJ/pulse. Contrary to the Si-ncs/LNTs the Si-ncs in CNTs/water suspension form spherically aggregated particles. As result most of them remain out of the cavity. However, some Si-ncs enter within the cavity. Detailed HR-TEM analysis was performed to confirm the presence of Si-ncs within the cavity. Figure 11 (c) shows a HR-TEM image of a filled CNT with an inner diameter of 50 nm. It is observed that spherical Si-ncs agglomerates with diameter around 25 nm are in the CNT cavity. Naturally within the cavity Si-ncs get stabilized into spherical particles, which diameter is considerably smaller as for those agglomerated out of the cavity. The Si-ncs agglomerates are found in the entire nanotube cavity far from the

opened ends. Energy dispersive X-ray analysis systematically showed excess of silicon content within CNTs cavity. Corresponding electron diffraction pattern taken in the CNT cavity showed discrete spots on the circles indicate the presence of crystalline silicon in cubic phase (Svrcek, 2008a).

4.4. Induced nanotubes filling by nanosecond laser processing in liquid media

Several concurrent processes that act simultaneously are responsible for the formation of Si-ncs by nanosecond laser processing in liquid media. Particularly, superheating occurs and material ejection arises from mechanical rupture of silicon wafer or micrograins homogenously dispersed in nanotube contain liquid media (Svrcek et al., 2006d). Ejected Si-ncs particles randomly move within the liquid medium. A random walk of a particle motion in a colloid is due to the nanosecond pulsed laser irradiation (ablation) and Brownian motion. At first approximation a displacement for Brownian motion derive as follow (Watkins, 1990; Bakefi and Barret, 1987).

$$m\frac{dv}{dt} = \alpha v + F(t)$$

(1)

where m is the mass of the particle, v its speed, and α is the coefficient.

When the grains are fragmented, silicon target ablated or nanotube interact with pulsed laser beam the shock wave in liquid media is formed and even enhanced. As shock wave moves away a sufficiently large distance from the point of explosion it expands in the water/SOG solution and propagate mainly in the volume liquid (Svrcek et al., 2006d, Svrcek et al., 2006e), In the medium with nonlinearities as the colloids are these shock waves can develop after propagation over a characteristic distance (L) (Svrcek et al., 2006d). The L linearly depends on density and homogeneity of liquid media. Due to an increased density the ns laser fragmentation process in SOG polymer is more efficient than in water. The shock waves in colloid with higher concentration can propagate farther from the point of explosion and are stronger for filling CNTs. In case of laser processing immediately after the laser strike the target.grain a dense cloud of Si-ncs are spread within liquid medium (Svrcek et al., 2008c; Svrcek et al., 2009b]. An equation that describes well the release of energy *(E)* in explosions through Bukinghams pi theorem (Bukingham, 1915)

$$R^5 \propto \frac{Et^2}{\rho},$$

(2)

where the R is the shock wave radius, t is the time and ρ is liquid medium density.

When we consider an isotropic wave propagating outward from a central point then a harmonic spherical pressure wave (i.e., having angular symmetry) is given by

$$p = \frac{A}{r}\cos(\omega t - kr + \theta)$$

(3)

where ω is the angular frequency, k is the wavenumber and θ is the phase. Then the radial displacement $s(r,t)$ can be given via

$$\frac{\partial^2 s}{\partial t^2} = -\frac{1}{\rho}\frac{\partial p}{\partial r} \tag{4}$$

The flux *(S)* of a spherical wave can be written by following expression

$$S = Z\left(\frac{\partial \varphi}{\partial t}\right)^2 = Z\frac{c^2\omega^2}{r^2}\cos^2(\omega t - kr + \phi) \tag{5}$$

where Z represents the wave impedance.

The propagation of a shock wave induced by a strong point explosion in a liquid media can be qualitatively evaluates as follow. The stage the wave motion at which the wave has moved away from the source of the explosion through distance comparable to scale height *h* is schematically sketched in Fig.12. We shall assume that we are dealing with a wave with the pressure behind the front much greater than the pressure ahead of the front (Zeldovich and Raizer, 2001). If *R* is the distance of the upper point of the shock wave to the explosion center, then the volume of the cavity is proportional to *R³* and the pressure can be express as follow *p~E/R³* (Svrcek, 2008). The time (t₁) required by the wave to move upward to infinity is

$$t_1 = \int_0^\infty \frac{dR}{v} \sim \frac{\rho_E^{1/2}}{E^{1/2}}\int_0^\infty E^{3/2}.\exp\left(-\frac{R}{2h}\right)dR \tag{6}$$

The physical reason for the acceleration of the shock wave is that the energy is located at the point of the explosion. The energy has the tendency to flow from the bottom and this can also accelerate the shock wave upward. This estimate appears to be for a high energy (Svrcek, 2008). As can be seen from v-~$(p/\rho)^{1/2}$, the wave velocity first decreases as the wave moves away from the point of explosion and has minimum at *R=3h*. The time required by the wave to move to infinity is found equal to

$$t_1 = const\left(\frac{h^5}{\rho_E E}\right)^{1/2} \tag{7}$$

The time for the wave to move from the point of the explosion to the point *R=3h* is much smaller than *t₁*. Thus a shock wave produced by a strong explosion moves downward from the point of explosion through distance of about *4h* (Svrcek, 2008). When the shock wave moves away a sufficiently large distance from the point of explosion after the shock wave emerges. The formation of these shocks during ns laser irradiation is important as they propagate through the liquid media and may cause consequently filling of CNTs nanotubes. However, in case of mechanically less strong LNTs Si-ncs most likely directly enter mainly within the soft wall where get stabilized and further cannot fill the hollow cavity.
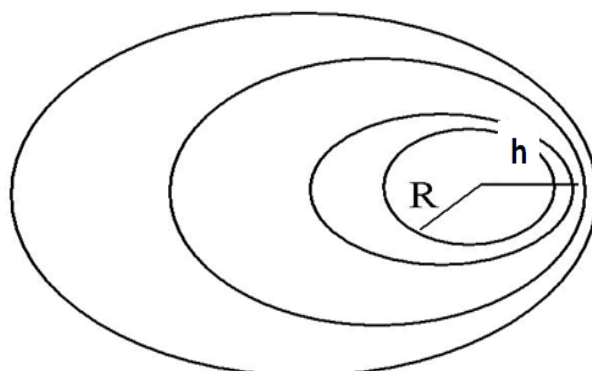
Fig. 12. Sketch of the shock front wave at successive instants.

5. Conclusions

Scalable and low cost approaches of introducing the silicon nanocrystals (Si-ncs) within carbon nanotubes (CNTs) and lipid nanotubes (LNTs) were discussed. We have shown that after opening CNTs ends and freeze-draying of the LTNs it has been possible to introduce Si-ncs inside the empted cavity of both type of nanotubes. It is demonstrated that the capillary force is strong enough to fill surfactant free Si-ncs inside nanotubes far from their opened ends. Filling of Si-ncs dispersed in ethanol and methanol polymer based solutions is possible in the case of chemically more sensitive CNTs. In the case of LNTs presence of organic solvent destroy tubular structure of the LNTs and filling cannot be achieved.

Furthermore we have demonstrated that CNTs due stronger mechanical properties compared to LNTs allow filling through the laser processing in liquid media. We argue that the nanosecond pulsed-laser processing by ablation and fragmentation in liquid medium (water, SOG) would be a reasonable solution to encapsulate Si-ncs within a CNT cavity. The generated shock waves during laser processing protect freshly formed nanocrystals and induce the entrance of freshly prepared Si-ncs into CNT opened end cavities. In the case of the soft LNTs structure the luminescent Si-ncs are mostly incorporated within the wall. It has to be noted that during the direct processing in LNTs solution freshly formed Si-ns surface is covered by thin layer of lipid that acts as surfactant, prevents agglomeration and increases PL emission from Si-ncs.

The results might have important implications to further extend the usability of Si-ncs as zero dimensional systems in colloidal solution. It is expect that those relatively simple and cheap approaches will be useful in a wide variety of applications. In case of LNTs, the direct modification of freshly formed Si-ncs surfaces with glycolipid molecule within the wall might find an important implication for luminescent glycolipid composites design. Next, direct preparation of luminescent Si-ncs in spin on glass polymer and consequent encapsulation in CNTs cavity might serves as template to align 1D Si-ncs/SOG nanocomposites. Stabilized Si-ncs in 1D alignment could be than beneficial to the stimulated emission processes, i.e. optical gain. We believe that such introduced luminescent Si-ncs nanoparticles within nanotubes will offer an attractive route for the design of a new generation of single nanoparticle-based nanodevices for biology and optoelectronics.

Acknowledgement

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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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