

CONDENSED MATTER

PARTICULAR SIGNATURE OF ISOLATED
AND BUNDLED CARBON NANOTUBES
IN THEIR RAMAN SPECTRA

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Abstract. The efficiency of different surfactants (anionic, cationic, neutral) as chemical agents favoring in the unbinding of nanotube bundles in isolated entities is investigated by Raman and UV-VIS-NIR spectroscopy. The neutral surfactants Tween 20 – polyoxyethylene sorbitan monolaurate (T-20-PSM) and Tween 80 – polyoxyethylene (80) sorbitan monooleate (T-80-PSM) have been found the most efficient. The isolated single walled carbon nanotubes (SWNTs) nanotubes are appraised at $\lambda_{\text{exc}} = 1064$ nm by two simultaneous modifications of the Raman spectra: i) narrowing of the band associated to the transversal vibration modes, *i.e.*, G band (~ 1592 cm⁻¹); ii) change of shape of the complex band associated to the radial vibration modes (RBM) consequent on the decrease of the intensity of the components associated with the bundled nanotubes. The individualization of nanotubes is evidenced also in the UV-VIS-NIR absorption spectra by the appearance of a fine structure in the wide absorption band (~ 1400 – 1750 nm) that is associated with the transitions E_s^{11} of semiconducting SWNTs. The fine structure grows gradually with the separation degree in isolated nanotubes entities.

Key words: carbon nanotubes, resonant Raman scattering, optical absorption.

1. INTRODUCTION

Carbon Nanotubes (CNT's) are fascinating physical systems, which by the disposing of carbon atoms in different architectures have metallic or semiconducting properties. They are candidates for applications in electronics, photonics, sensors, as well as for the synthesis of hybrid materials with remarkable properties [1, 2].

CNT's are quasi one dimensional structures resulted by wrapping a single, two or more 2D graphene sheets along one axis, named chiral axis. If in the wrapping process a single graphene layer is involved, single walled carbon nanotubes (SWNT)

are formed, and if two or more graphene sheets take part in the wrapping process, then double or multi walled carbon nanotubes (DWNT, MWNT) are generated as concentric cylinders, separated by inner distances of about 7 Å—the distance between 2 graphite layers.

As having diameters from 0.7–0.8 Å to tens and even hundreds of nanometers and length up to millimeters, it is tempting to assimilate them to quantum wires.

Each SWNT is uniquely defined by the chiral vector $\vec{c}_{m,n} = m\vec{a}_1 + n\vec{a}_2$ indicating the rolling direction of the graphene sheet and the dimension of the nanotube unit cell, where \vec{a}_1 and \vec{a}_2 are the unit vectors of the graphene lattice, and we uniquely designate each SWNT by the set (n, m) of his chiral indices.

The mathematic relations establishing between the indices dictates the metallic ($n - m = 3p$) or semiconducting ($n - m \neq 3p$) $p = 1; 2; 3; \dots$ behavior.

The basic properties of nanotube may be changed by chemical functionalization, *i.e.*, attaching various molecular species to its surface. Thus, the carbon nanotube becomes an efficient transporter of chemical information. Evidently, for such a scope the carbon nanotubes are desired to be as isolated entities. Unfortunately, every synthesis method (arc-discharge, CVD, laser ablation) furnish the CNT's as bundles of ten to hundreds units, which are kept together by van der Waals bonds. Association in bundles modifies the electronic and vibrational properties of individual nanotubes.

In the last few years, a particular interest and a sustained effort was paid to develop new procedures of separation of the CNT's in isolated entities. The chemical functionalization accompanied by an intense stirring and ultra-sonication is one of the most used techniques in un-binding the nanotube bundles. In this context, the term of functionalization defines the action by which different molecules – surfactants – wrapping the nanotubes does not change their architecture and prevent re-aggregation. The surfactants which may be used can be of anionic, cationic and neutral type. The same interest has been conferred to the physical methods that permit the evaluation of the separation degree of nanotubes in individual entities too.

In this work, using different surfactants, we investigate by Raman light scattering and UV-VIS-NIR absorption spectroscopy the efficiency in separation of the SWNTs in isolated units. Taking the Raman spectrum as furnishing the information about the dispersion state of CNT's, we establish that the narrowing of the band G ($\sim 1592 \text{ cm}^{-1}$) that is associated to the transversal vibration modes is one of the most relevant modification found rot the isolated SWNTs .

2. EXPERIMENTAL

All experiments were performed on aqueous solutions with 0.02 %wt SWNTs and 1 %wt of various surfactants: anionic (SDS-Sodium Dodecyl Sulfate,

SDBS-Sodium Dodecyl Benzene Sulfonate 0.3%wt, AOT-bis(2 ethylhexyl) sulfosuccinate), cationic (DTmAB-Dodecyl trimethyl ammonium bromide, TTdAB-Trimethyl(tetra-decyl) ammonium bromide, CTmAB-Cetyltrimethyl ammonium bromide) and neutral (T20-polyoxyethylene (20) sorbitan monolaurate, T80-polyoxyethylene (80) sorbitan monooleate).

The solutions, in form of suspension, were made using commercial SWNT powder, with nanotubes of diameter situated in the 1.2–1.4 nm range. An intense ultrasonication for two hours assured a good homogenization. After another two hours of ultra-centrifugation at 12000 rpm by the decanting of upper part has been obtained a solution containing isolated nanotubes embedded in surfactants micelles. These solutions infused into 0.5 cm × 0.5 cm quartz ampoules were studied by Raman light scattering and UV-VIS-NIR absorption spectroscopy. Surface Enhanced Raman Scattering (SERS) measurements were performed on thin films (ca. 150 nm thickness) layered on rough gold substrates. The Raman spectra were recorded at $\lambda_{\text{exc}} = 1064$ nm with a Bruker RFS1001S Spectrometer. For the nanotubes used, with a diameter situated in the interval 1.2–1.4 nm, the excitation light of 1064 nm ensures the resonant excitation at the E_S^{22} electronic level of semiconducting nanotubes. Absorption UV-VIS-NIR spectroscopy investigations were performed using a Lambda950 Perkin Elmer Absorption Spectrophotometer. Unfortunately, the spectral range 1700–1800 nm where one finds absorption associated to the transition E_S^{11} (being) is strongly disturbed by the presence of the absorption bands of water. So, for the absorption measurements the light water H_2O has been replaced with heavy water D_2O .

3. RESULTS AND DISCUSSION

As it is known, the Raman active vibrations are the symmetric ones. As a starter we focus attention on tangential vibration modes which are associated with the complex G Raman band located in the interval 1550–1600 cm^{-1} . This band discloses six components: $E_2(LO)$, $A_1(TO)$, $E_1(LO)$, $E_1(TO)$, $A_1(LO)$, $E_2(TO)$ [6]. Experimentally, at resonant excitation of semiconducting nanotubes that occur at $\lambda_{\text{exc}} = 1064$ nm only four components with the symmetries:

$$\begin{aligned}\omega_{E_2}^- &\sim 1550 \text{ cm}^{-1}[E_2(E_{2g})], \quad \omega_{E_2}^+ \sim 1602 \text{ cm}^{-1}[E_2(E_{2g})], \\ \omega_G^- &\sim 1571 \text{ cm}^{-1}[A(A_{1g}) + E(E_{1g})],\end{aligned}$$

and $\omega_G^+ \sim 1591 \text{ cm}^{-1}[A(A_{1g}) + E(E_{1g})]$ are observed [6]. Each component fits a Lorentz profile. For the metallic nanotubes the G band profile is modified, a new component with the maximum at $\sim 1540 \text{ cm}^{-1}$ appears at laser excitation energies situated in the interval 1.7–2.2 eV. This wide band, asymmetric towards lower

energies fits a Breit-Wigner-Fano profile which indicates electron-phonon type interaction [6–8].

As a distinct characteristic of the semiconducting isolated carbon nanotubes the G band narrows and display only two components of frequencies ω_G^+ and ω_G^- [9]. Fig. 1 shows the G band measured into aqueous solution of SWNT in which has been added Tween 80.

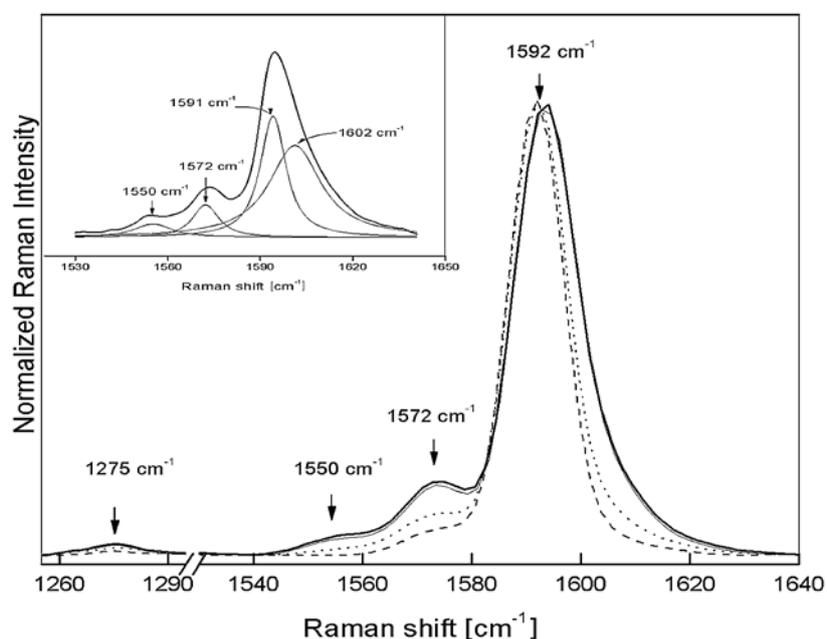


Fig. 1 – The Raman spectrum in the G band region recorded at $\lambda_{\text{exc}} = 1064$ nm on powdered SWNT (thick line), suspension of SWNT in water (thin line), suspension of SWNT in 1%wt Tween 80 solution after ultrasonication (dotted line), and SWNT solubilized in Tween 80 solution and picked-up after centrifugation (dashed line).

The thick line is the Raman spectrum of as prepared nanotubes powder and the thin line is the Raman spectrum when the SWNT were dispersed in water. The two spectra almost coincide, no changes in the G band is observed. The dotted line represents a quite different Raman spectrum obtained on SWNT dispersed in aqueous Tween 80 solution and after two hours of ultrasonication. The same solution and after two hour of centrifugation displays a Raman spectrum illustrated by the dashed line. After ultrasonication and centrifugation, the G band narrows gradually and finally its structure reveals only two components of different intensity, ω_G^- (1572 cm^{-1}) and $\omega_{E_2}^-$ (1550 cm^{-1}). The narrowness of the G band is accompanied by a diminishment of the D band (1275 cm^{-1}) that normally indicates the defect presence in the architecture of CNTs [1]. The decrease of the D band

intensity reveals a new fact, not signaled up to now, that the variations in intensity of the *D* band have to be connected also with the existence of CNTs in bundle structures. The theoretical explanation of *D* band as originating in a double resonant process developed in the isolated nanotube needs to be reviewed because it ignores the bundle structure [13]. The inset of Fig. 1 details the *G* band structure in four Lorentz profiles. When the same solution were used for the preparation of thin films deposited on rough gold substrates, the same data have been obtained by SERS technique too.

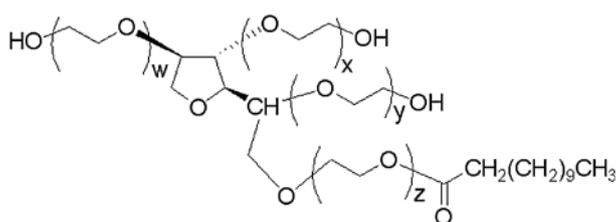
Hereinafter, we consider that a good estimation of the surfactants efficiency in the action of decomposition of the bundles in isolate nanotubes, can be achieved by the ratios $R_2 = I_1/I_2$ and $R_3 = I_1/I_3$, where I_1 , I_2 and I_3 are the Raman intensities of the modes of frequency ω_G^+ , ω_G^- and $\omega_{E_2^-}$, respectively.

Table 1 summarizes the above data where by distinct columns are presented the $R_{2,3}$ ratios for SWNT dispersed in various surfactants. The rows named U and C present the values of the $R_{2,3}$ ratios after ultrasonication and centrifugation respectively. Table 1 concludes that the neutral surfactants Tween 20 and Tween 80 are the most efficient in separation of SWNTs in individual entities.

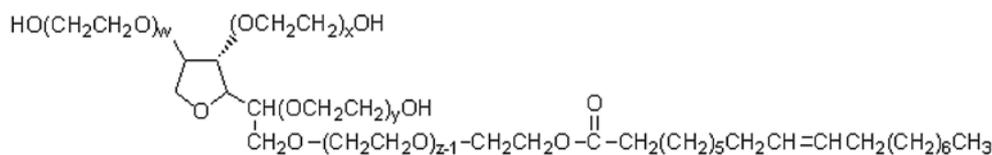
Table 1

$R_2 = I_1/I_2$ and $R_3 = I_1/I_3$ ratios associated to different degrees of isolation of SWNT, depending on each surfactant nature

	Powder		In water		SDS		DTmAB		SDBS		CTmAB		TTdAB		AOT		Tw20		Tw80	
	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3	R_2	R_3
U	3.8	8.9	5.3	15	9	37	9.2	35	9.4	31	11	32	9	28	9	33	7.5	22	8.3	27
C					11	63	11	42	11	37	14	35	11	40	11	50	12	49	12	85



Tween 20



Tween 80

This conclusion is supported also by the variation of the Raman spectrum associated with the radial vibration modes (RBM) that is located in the low frequency region at 100–300 cm^{-1} . The peak position of this band relates the nanotube diameter according with the formula [10]:

$$\omega [\text{cm}^{-1}] = 223.75/d [\text{nm}]. \quad (1)$$

This band is not a simple one, two components: one associated with the isolated nanotubes and another with the bundled nanotubes are found. The latter is shifted with $\Delta\omega = 14 \text{ cm}^{-1}$ towards higher energies as a result of the interaction between nanotubes inside the bundles [11, 12].

Fig. 2 displays the Raman spectra recorded on as prepared SWNT powder (thick line), SWNTs as suspension in water (thin line), SWNTs dispersed in Tween 80 aqueous solution and ultrasonicated for two hours (dotted line) and the same solution after 2 hours of centrifugation (dashed line).

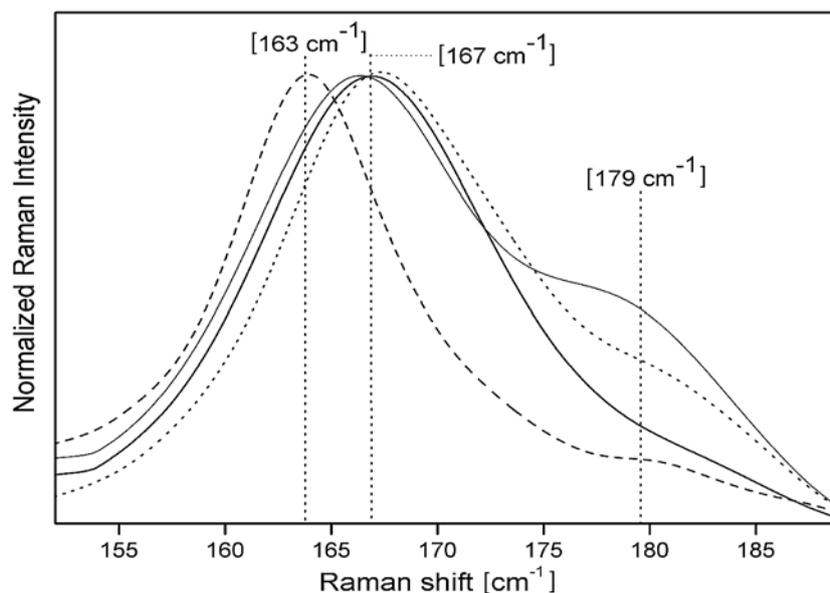


Fig. 2 – The RBM region of the Raman spectrum recorded at $\lambda_{\text{exc}} = 1064 \text{ nm}$ on powdered SWNT (thick line), suspension of SWNT in water (thin line), suspension of SWNT in 1 %wt Tween 80 solution after ultrasonication (dotted line), and SWNT solubilized in Tween 80 solution and picked-up after centrifugation (dashed line).

In Fig. 2 the thin line reveals an interesting fact; an increase of the intensity of radial Raman components associated with the bundle structure. Comparing with the spectrum recorded on as prepared sample (Fig. 2 thick line) this indicates a stronger inter-tube interaction when the dispersing medium is only the water. Taking this spectrum as reference one observe that in the Tween 80 aqueous

solution the radial Raman components associated with the bundle structure decreases in two steps, after ultrasonication (dotted line) and after centrifugation (dashed line). In accordance with the expectations this result proves that the Tween 80 surfactant is an efficient agent of un-binding (of) the nanotube bundles in individual SWNTs.

The absorption spectrum of SWNTs, of mean diameter situated in the interval 1.2–1.4 nm, display three bands at 1750 nm (0.7 eV), 970 nm (1.28 eV) and 680 nm (1.82 eV) which are associate with the transition in the excited states E_S^{11} and E_S^{22} of semiconducting nanotubes and E_M^{11} state of metallic tubes, respectively, [1]. Actually these wide bands represent a convoluted sum, favored of the bundle structure, over many narrow bands that are associated to each carbon nanotube of diameter situate in the 1.2–1.4 nm range. In this case, an un-binding process of the bundles in isolated tubes must be observed as a fine structure in constitution of the wide absorption bands. Among these, the most sensitive to an un-binding process are the absorption bands of the semiconducting nanotubes. In this case, the band at 1750 nm (0.7 eV) that involves a resonant transition at the E_S^{11} state is most convenient to be investigated.

Indeed, the presents the absorption spectrum recorded on SWNTs powder (inset) and an ultrasonicated for two hours of Tween-80 aqueous (D_2O) solution containing 0.02%wt suspension of SWNTs (curve a), a subsequent centrifugation

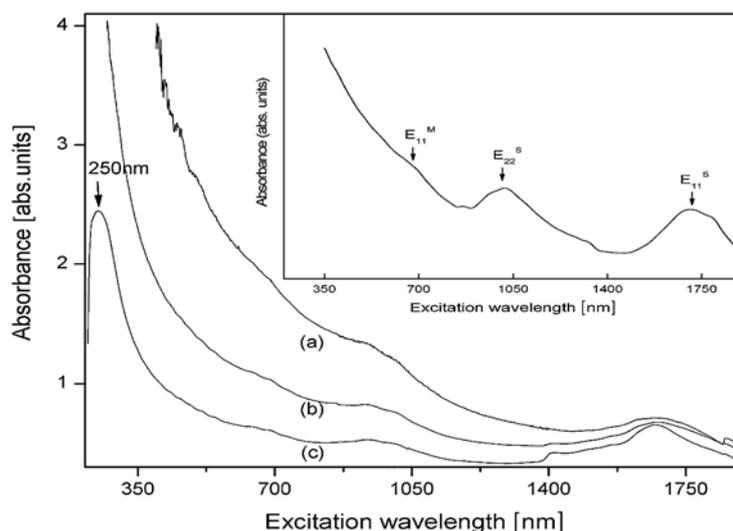


Fig. 3 – Absorption spectrum recorded on SWNT powder (inset), the absorption spectrum of SWNT suspension in 1%wt Tw80 solution after two hour ultrasonication (curve a), SWNT solubilized in Tween 80 solution and picked-up after one hour centrifugation (curve b) and SWNT solubilized in Tween 80 solution and picked-up after a two hour centrifugation (curve c).

for one hour (curve b) and two hours (curve c). Fig. 3 shows clearly a gradual modification of the absorption spectra, the fine structure that appears in the interval of 1400–1750 nm proves an un-binding process of bundles in isolated nanotubes. Fig. 4 adduces more details. Same as the Raman scattering, testing by absorption spectroscopy all surfactants mentioned above, one found that the neutral compounds Tween-20 – polyoxyethylene sorbitan monolaurate and Tween-80 – polyoxyethylene (80) sorbitan monooleate are the most efficient.

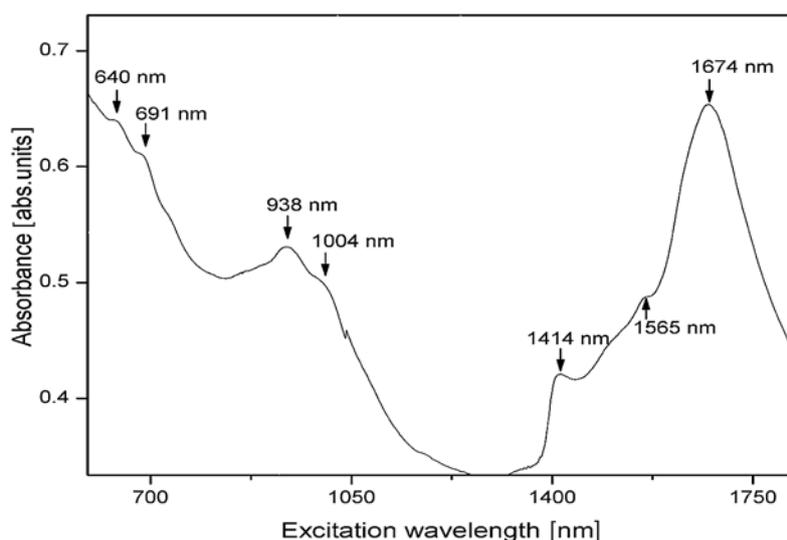


Fig. 4 – SWNT solubilized in Tween 80 solution and picked-up after a two hour centrifugation.

4. CONCLUSIONS

Resonant Raman scattering and UV-VIS-NIR absorption measurements were performed on single walled carbon nanotubes dispersed in surfactant solutions. We used anionic (anionic: SDS-Sodium Dodecyl Sulfate, SDBS-Sodium Dodecyl Benzene Sulfonate 0.3%wt, AOT- bis(2 ethylhexyl) sulfosuccinate), cationic (DTmAB-Dodecyl trimethyl ammonium bromide, TTdAB-Trimethyl(tetra-decyl) ammonium bromide, CTmAB-Cetyltrimethyl ammonium bromide) and neutral (Tween20-polyoxyethylene (20) sorbitan monolaurate, Tween80-polyoxyethylene (80) sorbitan monooleate) surfactants. The most efficient in the dispersing of the nanotube bundles in isolated entities have been found the neutral surfactants Tween 20 and Tween 80. The existence of SWNTs as isolated entities is attested by a modification of the Raman spectrum, more precise a narrowing of the G band and a change of the shape of the band associated with the radial vibration modes. In the later case, the contribution of the bundled tubes, pointed by up-shifted shoulder

of the radial Raman band, decreases until its disappearance. The conclusions that the neutral surfactants Tween 20 and Tween 80 are the most efficient is confirmed by UV-VIS-NIR absorption measurements.

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