

# Single walled carbon nanotube quantification method employing the Raman signal intensity



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## ABSTRACT

A new technique for measuring the number of single walled carbon nanotubes (SWCNTs) and their concentration in a carbon nanotube layer is developed in this work. It is based on the G peak intensity of the Raman spectrum, together with precise mass and optical absorbance measurements. The dependence of the number of the carbon nanotubes on the phonon scattering intensity is observed. This method opens an opportunity for the quantitative mapping of  $sp^2$  carbon atom distribution in the SWCNT layers with a resolution limited by the focused laser spot size.

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## 1. Introduction

Carbon nanotube (CNT) based materials are intensively studied due to a number of novel and unique properties that make them potentially useful in a wide range of applications. CNT layers offer outstanding properties like excellent flexibility, optical transparency, high electrical conductivity, extremely small weight, and low processing costs. Field emission, quantum confined electron devices, passive and active devices and other electronic components are already under development, and results are promising [1–3]. Optical and electrical properties of a CNT layer can be varied with changing the chirality, diameter and length of nanotubes and the CNT network structure.

CNT layers can be employed for transparent electrode fabrication [4,5] fuel and solar cells, supercapacitors, etc. [6,7]. Therefore, a measurement technique for the number of carbon nanotubes in the CNT layer is needed. Various methods are developed for the CNT content measurement as in dispersions as well as at surfaces. These methods are based on optical spectroscopy [8], on direct measurements using thermogravimetry, on weighting after filtration of dispersions [9] and on THz spectroscopy [10,11]. However, direct

weighting is limited by the scale sensitivity (typically 0.1 mg) and it is not applicable for a small area and thin layers.

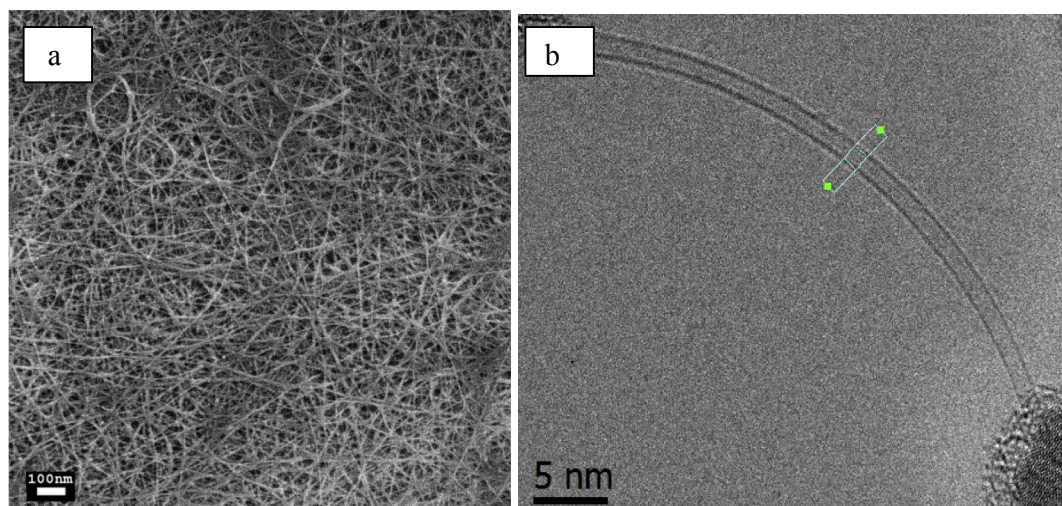
Non-destructive characterization techniques for carbon nanotube content measurements like scanning electron microscopy (SEM), atomic force microscopy (AFM) etc. do not allow to estimate the number of carbon atoms in the layer. Raman spectroscopy is a classical method that can be used for studying the chirality and number of CNT walls. Number of works is devoted to the investigation of bundles of single walled carbon nanotubes (SWCNT) (e.g. Ref. [12]), SWCNTs surrounded by various common wrapping agents, and separated SWCNTs at the single nanotube level [13]. Raman spectra give information about the diameter of a nanotube and its electronic structure [14,15].

Various techniques exist for quantifying the structural defects in the CNTs by the ratio of the intensities of D and G peaks in the Raman spectra. For instance, in Ref. [16] an overview of the original papers is introduced on the measurement of quantitative changes of the D peak after creation of defects in the nanotubes and graphene by ion and electron bombardment. The measurements of the G peak intensity were used for *in situ* control of the CNT forest formation [17,18]. However, the volume fraction of CNTs is often required for, e.g., CNT layer permittivity and electrical conductivity calculation (e.g. Refs. [19,20]).

In this work, a new technique for the quantitative measurement of the number of  $sp^2$  carbon atoms as well as the number of

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**Fig. 1.** SEM (a) and TEM (b) images of the SWCNTs. In (b) diameter of a SWCNT is 1.3 nm according to TEM image. (A colour version of this figure can be viewed online.)

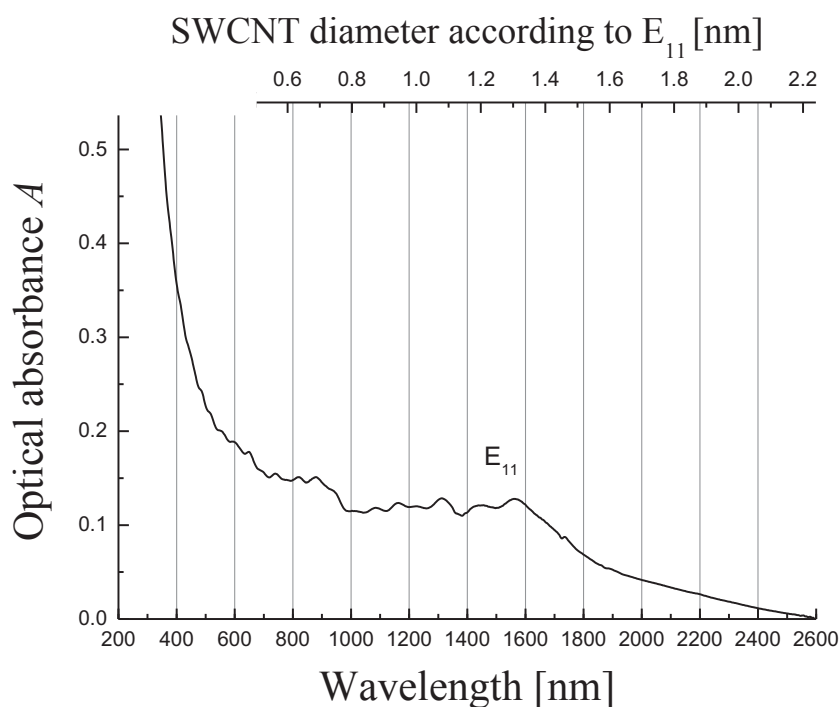
SWCNTs and their volume fraction in the CNT layer is developed. It is based on the measurement of the G mode intensity in the Raman spectrum, precise mass and optical transparency.

## 2. Experimental technique

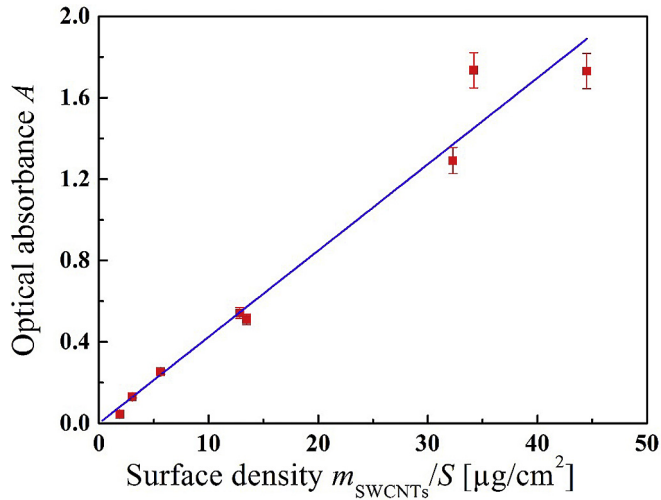
SWCNTs were synthesized by the aerosol chemical vapor deposition method, described in Ref. [21]. The CNT layers with thicknesses of 25–60 nm were transferred from the nitrocellulose filter onto glass with dry transfer.

Ultramicrobalance Mettler Toledo XP2 was used for precise weight measurement with resolution up to 0.1  $\mu\text{g}$ . The nitrocellulose filters with SWCNTs were stored overnight in dry atmosphere

over silicagel for keeping in dry conditions. All measurements were carried out in the dry room with humidity level less than 10%. The weight measurements of 11 mm diameter samples with and without SWCNTs were repeated at least for 5 times. After weight measurements the SWCNTs were transferred to the quartz substrate for the optical transparency measurements. Content of the residual Fe-particles in the SWCNTs was measured with X-ray spectroscopy (EDX) and it was  $54 \pm 3\%$  of the total mass. Fe particles does not affect on the Raman signal in D-G modes range. Therefore, the amount of carbon in the layer is  $n_c = 0.46$ . The residual catalytic Fe nanoparticle concentration in the layer is uniform. Therefore, the value of mass of pure SWCNTs is used in the calculations. The mass of SWCNTs were calculated as  $m_{\text{SWCNTs}} = n_c \cdot m_{(\text{Fe}+\text{SWCNTs})}$ .



**Fig. 2.** Optical absorbance spectrum of a typical SWCNT layer. The average diameter of SWCNTs calculated using Kataura plot [14].



**Fig. 3.** Dependence of optical absorbance  $A$  at 550 nm on the surface density of SWCNTs with Fe particles. (A colour version of this figure can be viewed online.)

The scanning and transmission electron microscopy studies were done with high-resolution scanning electron microscope (SEM) JEOL JSM-7500FA and spherical aberration corrected transmission electron microscope (TEM) JEOL JEM-2200FS at 80 kV. Fig. 1 shows (a) a typical SEM image of the CNT network at the glass substrate and (b) a TEM image of the SWCNTs with diameters of 1.3–2.0 nm. Fig. 2 shows a typical optical absorbance spectrum of a SWCNT layer with transmittance  $T$  of 65%.

The optical absorbance  $A$  of the SWCNT layer was calculated from  $T$  measurements obtained with Perkin Elmer UV-vis-NIR spectrometer in the range of 400–3000 nm wavelengths as a  $A = \log_{10}(100/T)$ . Typical spectrum of a SWCNT layer is shown in Fig. 2.

The 11 mm diameter samples were used for the Raman spectroscopy. The Horiba Jobin-Yvon Labram HR Raman Spectrometer

and He-Ne laser operating at 633 nm wavelength with output power of 30 mW was used. The laser spot was focused with a 50× lens, 2 dB attenuation and numerical aperture 0.75. The diameter of the laser spot was 7.2 μm and the estimated incident power at the sample was 8.5 mW. The signal accumulation time of 10 s was kept constant. The measurement of the Raman signal intensity was repeated for 5 times at different positions. The data difference was negligibly small.

The SWCNT layer thickness measurement method was developed [5], where the SWCNT films were penetrated with epoxy polymer components. The cross-section images of the SWCNTs/epoxy were taken with TEM and analyzed with the Gatan Micrograph software. The obtained [5] dependence of the measured thickness and the optical absorbance at 550 nm is used for calculation of the actual thickness of the SWCNT layers.

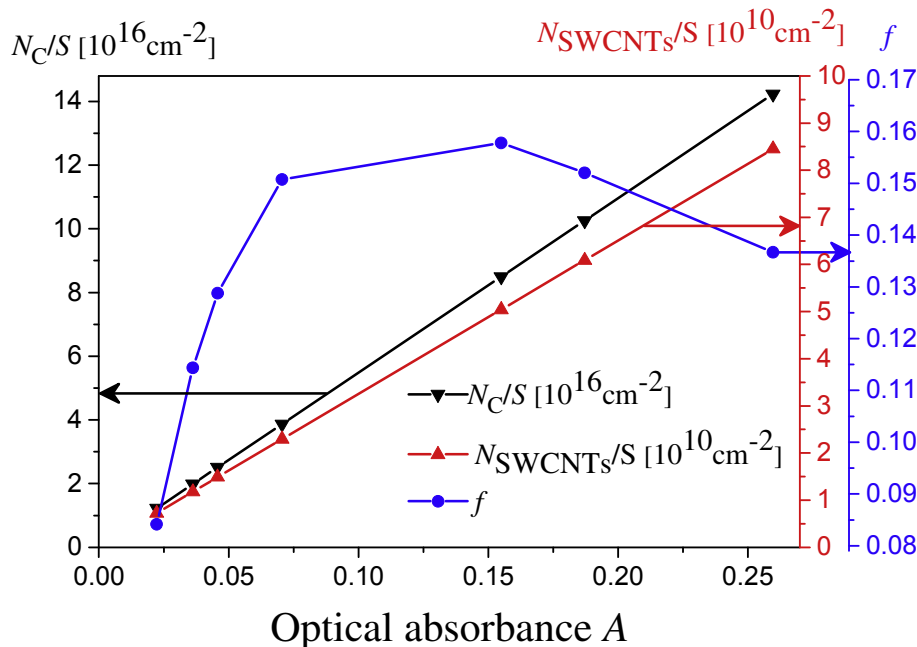
## 2.1. Dependence of optical absorbance on the SWCNT mass

Fig. 3 shows the optical absorbance  $A$  measured at 550 nm wavelength vs SWCNT surface density (measured mass  $m_{\text{SWCNTs}}$  (μg) per surface area  $S$  (cm<sup>2</sup>)). The linear approximation of  $A$  and  $m_{\text{SWCNTs}}/S$  results:  $A/(m_{\text{SWCNTs}}/S) = 4.24 \cdot 10^{-2}$ .

The external surface area of an individual SWCNT (without the ends of the surface) is  $2\pi rl$ , where  $r$  is the radius and  $l$  is the length of the nanotube (in our case  $l$  was in the range of 1–10 μm). The square of a single hexagonal unit cell is  $S_{\text{unit cell}} = \frac{3\sqrt{3}}{2}a^2$ , where  $a$  is the distance between neighboring atoms, which is 0.1418 nm [22]. The number of unit cells in an individual nanotube is  $\frac{2\pi rl}{S_{\text{unit cell}}}$ . One unit cell corresponds to two carbon atoms, therefore the number of carbon atoms in an individual nanotube is:

$$N_{\text{atoms}} = \frac{8\pi rl}{3\sqrt{3}a^2}, \quad (1)$$

The total number of the carbon atoms  $N_C$  in a given mass can be calculated as:



**Fig. 4.** Dependencies of the number of carbon atoms  $N_C$ , the number of SWCNTs  $N_{\text{SWCNTs}}$ , normalized to the surface area  $S$ , and volume fraction of nanotubes  $f$  in the layer on the optical absorbance  $A$ . (A colour version of this figure can be viewed online.)

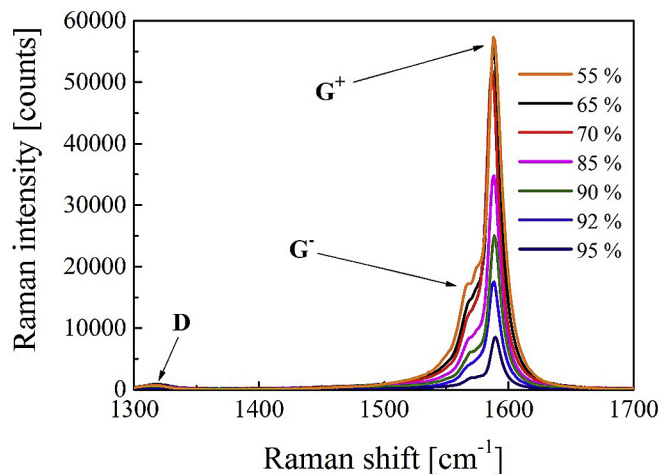


Fig. 5. Raman spectra for SWCNT samples with different optical transparencies (%). (A colour version of this figure can be viewed online.)

The volume fraction of nanotubes in the layer with thickness of  $h$  can be calculated as:

$$f = \frac{V_{\text{SWCNTs}}}{hS} = N_c \frac{3\sqrt{3}a^2r}{8hS}, \quad (5)$$

where  $S$  is the surface area and  $h$  is the thickness of the nanotube layer. Since the thickness of the of SWCNT layer can not be measured precisely, the calculated value of  $f$  can be used only for estimation of the real fraction ratio.

Dependence of optical absorbance on the number of carbon atoms ( $N_c$ ), SWCNTs ( $N_{\text{SWCNTs}}$ ) and volume fraction ( $f$ ) of SWCNTs are presented in Fig. 4. The radius of SWCNTs was taken to be  $r = 0.7$  nm, according to the estimations from TEM [21]. However, the calculation of the volume fraction require a precise knowledge of the height of the SWCNT layer. The height of the layer is somewhat uncertain due to intrinsic randomization of the nanotube and their bundle orientation during aerosol filtration. Fig. 4 shows estimate values of the volume fraction in the SWCNT layer from 0.08 to 0.16.

## 2.2. Raman spectra measurements

The CNTs have the G peak in the Raman spectrum at  $1580 \text{ cm}^{-1}$ , also called the “Graphitic peak”, ( $\text{sp}^2$ ). The G peak consists of two main peaks: the high intensity  $G^+$  peak and the low intensity  $G^-$  peak. For metallic SWCNTs there is only one wide  $G^+$  peak, associated with a transverse optical mode [23]. Also, there is the D peak, located at  $1320 \text{ cm}^{-1}$ , which is due to distortion of the two dimensional graphene structure. The intensity ratio of G/D is widely used to estimate the quality of SWCNTs. For the investigated samples this ratio appeared to be up to 100. Both high value of G/D ratio in the Raman spectra and TEM observations allow to suppose that all carbon in the investigated samples are incorporated with the SWCNT cell structure. The intensity of the G and D peaks vs Raman shift of SWCNT samples with different transparencies is presented in Fig. 5. It should be noted that the measurements of G peak intensity provide high sensitivity, the  $G^-$  peak intensity is more

$$N_c = \frac{m_{\text{SWCNTs}}}{M_c} \times N_A, \quad (2)$$

where  $m_{\text{SWCNTs}}$  is the mass of carbon atoms,  $M_c$  is the molar mass of carbon atom (12.011 g/mol), and  $N_A$  is the Avogadro constant ( $6.022 \times 10^{23} \text{ mol}^{-1}$ ). Then the number of carbon nanotubes is:

$$N_{\text{SWCNTs}} = \frac{N_c}{N_{\text{atoms}}}. \quad (3)$$

An individual tube occupies a volume of  $V_{\text{SWCNT}} = \pi r^2 l$ . Therefore, the total volume  $V_{\text{SWCNTs}}$  occupied with nanotubes in the layer is:

$$V_{\text{SWCNTs}} = N_{\text{SWCNTs}} V_{\text{SWCNT}} = \frac{N_c}{N_{\text{atoms}}} \pi r^2 l. \quad (4)$$

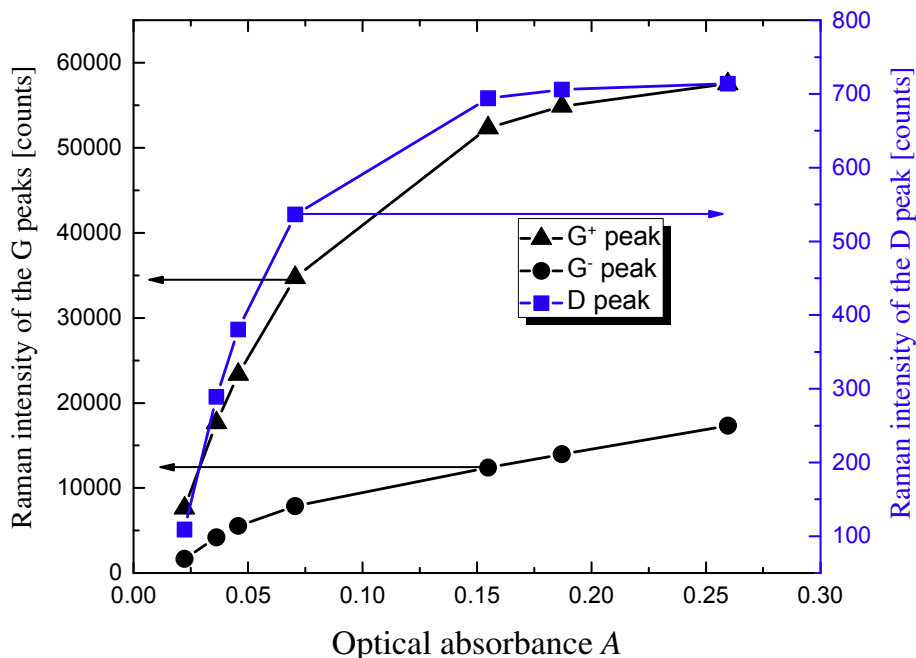
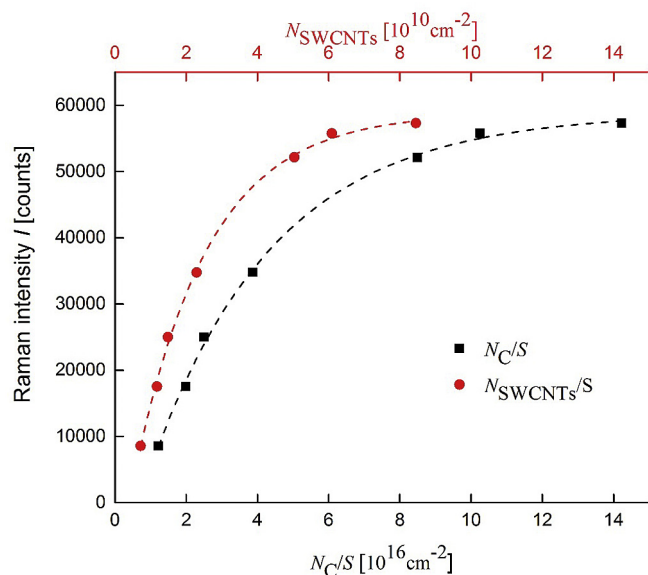


Fig. 6. Dependencies of the  $G^+$ ,  $G^-$  and the D peak intensities on the optical absorbance of the SWCNT layer. (A colour version of this figure can be viewed online.)





**Fig. 7.** Dependencies of the number of carbon atoms in the SWCNT layer, normalized to the surface area  $N_C/S$  (black) and the number of SWCNTs in the layer, normalized to the surface area  $N_{\text{SWCNTs}}/S$  (red) on the Raman intensity  $I$ . (A colour version of this figure can be viewed online.)

than 60000 counts and the background level is less than 1000 counts.

Fig. 5 shows the Raman spectra for SWCNT samples with a different optical transparencies. The dependence of intensities of the G peak and the D peaks on the optical absorbance (see Fig. 6) can be expressed as:

$$I/I_G^+, G^-, D = \exp(x \cdot A), \quad (6)$$

where the coefficients are the following:  $I_G^+ = 58784$ ,  $x_G^+ = -15.67$ ;  $I_G^- = 20507$ ,  $x_G^- = -6.62$ ; and  $I_D = 715$ ,  $x_D = -25.25$ .

The Raman intensities of the  $G^+$  peak vs. both the number of carbon atoms  $N_C/S$  and the number of SWCNTs  $N_{\text{SWCNTs}}/S$ , normalized to the surface area  $S$ , are shown in Fig. 7. The Raman intensity dependences appear to be exponentials and can be expressed as:

$$\frac{I}{I_0} = \exp\left(x \frac{N_C}{S}\right), \quad \frac{I}{I_0} = \exp\left(x \frac{N_{\text{SWCNTs}}}{S}\right) \quad (7)$$

where the coefficients are the following  $I_0 = 5.89 \cdot 10^4$ ,  $x = -7.14 \cdot 10^4$ , and  $S$  is the surface area.

For not-high quality nanotubes the defects or nontubular carbon forms will increase disordered (D) mode of the Raman signal. As can be concluded from Fig. 6, intensity of the D peak depend on the layer thickness the same way as G peak and should depend also on the SWCNT quality.

The dependence of the optical absorbance of the G-peak intensity in the Raman signal and the concentration of SWCNTs in the layer can be found from the results shown in Figs. 4, 6 and 7. The Raman spectroscopy gives an opportunity of a fast nondestructive quantitative estimation of the SWCNT content in the layer with a high resolution, limited by the laser footprint.

The observed dependencies are in an agreement with an expression given in Refs. [24,25]:  $I/I_0 = \exp(-E_{\text{ph}}/kT)$ , where  $E_{\text{ph}}$  is the phonon energy,  $k$  is the Boltzmann constant and  $T$  is the temperature.

### 3. Conclusions

The concentration measurements of the carbon nanotubes in a layer or in polymer/colloidal systems transparent for the wavelengths in the range of 633–740 nm is reported. The measurement technique is based on the Raman spectroscopy, optical spectroscopy and precise mass measurements. Exponential dependence of the concentration of  $\text{sp}^2$  carbon atoms/nanotubes on the G peak intensity of the Raman signal is obtained. That means that the number of the  $\text{sp}^2$  carbon atoms and nanotubes are proportional to the Raman signal intensity. The total mass and carbon content measurement allows to estimate the number of carbon atoms in the layer but it has accuracy and sensitivity limitations. This method opens an opportunity of the quantity mapping of  $\text{sp}^2$  carbon atom distribution in the SWCNT layers with a resolution limited the focused laser spot size.

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