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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.

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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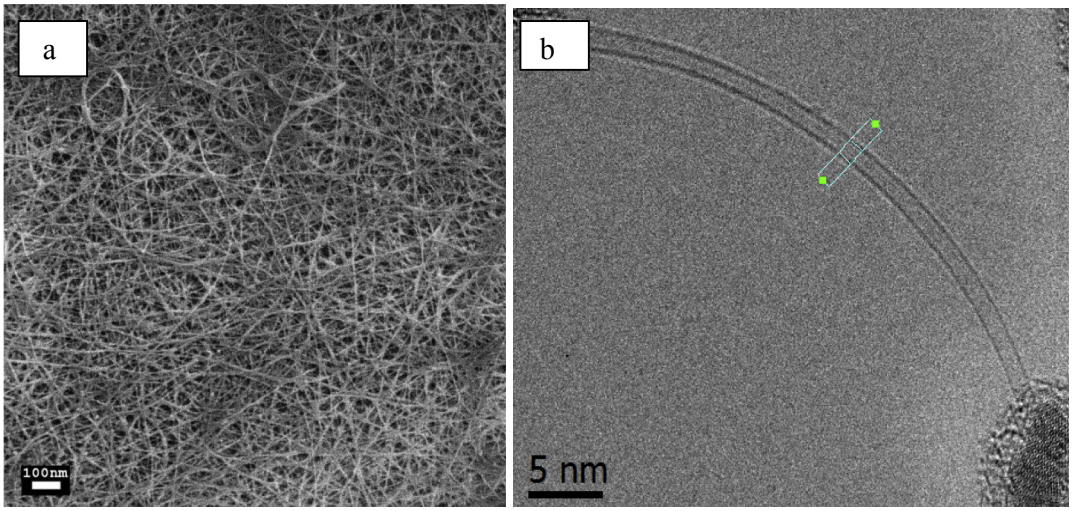

Fig. 1. SEM (a) and TEM (b) images of the SWCNTs. In (b) diameter of a SWCNT is 1.3 nm according to TEM image. (A colour version of this figure can be viewed online.)

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 μg. 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 ± 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 $m_{SWCNTs} = n_C \cdot m_{(Fe+SWCNTs)}$.

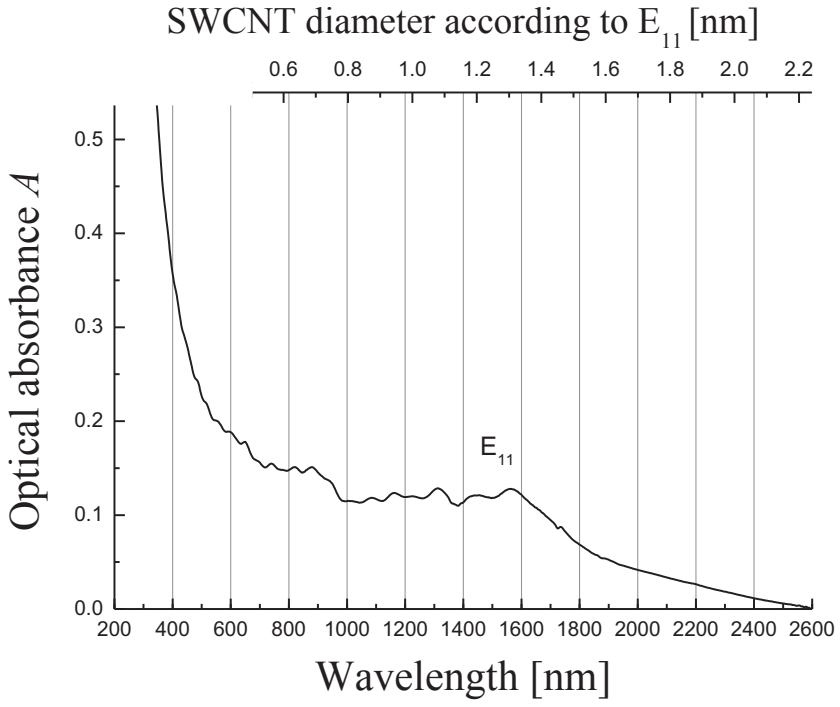

Fig. 2. Optical absorbance spectrum of a typical SWCNT layer. The average diameter of SWCNTs calculated using Kataura plot [14].