OPO laser light absorption and evolutionary behaviour of SWCNT thin films

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In this paper we report a systematic study on the properties of irradiated SWCNT films by high power, pulsed visible irradiation of OPO laser in the range from 430 nm to 800 nm. Raman analysis showed that metallic and semiconducting SWCNTs were simultaneously affected by irradiation. It was found that laser irradiation had the most prominent effects on SWCNT films at 430 nm wavelength. To our surprise, semiconducting SWCNTs were more affected by irradiation than metallic and as a result several SWCNTs were isolated partially.

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1. Introduction

Carbon nanotubes have extraordinary characteristics for potential applications in nanoscale electronics and medicine [1]. Single wall carbon nanotubes (SWCNTs) consist of graphene sheet rolled up into seamless cylinder. Depending on chiral indexes nanotubes are either metallic (m-SWCNTs) or semiconducting (s-SWCNTs). It is of great importance to separate these two types of SWCNTs, since current synthesis methods solely product mixture of s-SWCNTs and m-SWCNTs. So far it has been developed several post-synthetic methods to separate metallic and semiconducting nanotubes by selective destruction of one type of nanotubes with hydrogen peroxide [2], electrophoresis and chromatography in agarose gel [3, 4], density gradient centrifugation [5] or by both covalent and non-covalent functionalization [6, 7].

Electromagnetic waves emitted by powerful light source causes free electron movement and heating of the nanotube. Excessive irradiation of SWCNTs by high power light irradiation using laser or lamp results with selective destruction. Several groups have demonstrated that selective oxidation of one type of SWCNTs is caused by resonance with the incident laser energy, and non-resonant nanotubes could not be oxidized neither with higher laser power nor longer exposure time [8, 9]. Laser-based strategy is applied for selective removal of m-SWCNTs from surface deposited SWCNT mixtures [10]. Huang et al. indicated that laser irradiation causes tube type rather than tube diameter oxidation [11]. On the other side, Yudasaka et al. demonstrated preferential oxidation of semiconducting tubes when irradiated at 488 and 514 nm in the presence of H_2O_2 [12]. Conversion of metallic to semiconducting SWCNTs was induced by UV lamp irradiation as a result of diameter dependent photochemical processes [13].

Several authors demonstrated that oxidized SWCNTs show small upshift of RBM peak [14] or no shift of RBM at all [15]. However, theoretical study of Raman spectra of oxidized SWCNTs shows large D band peak upshift and smaller G band peak downshift [16]. Breaking single-walled carbon nanotube bundles by Joule heating results in SWCNT RBM peak downshift without G band splitting [17]. A well-known feature of RBM band is that it reveals two components: one, more intense corresponding to isolated nanotubes, and another, appearing as a shoulder shifted towards higher frequencies associated with the nanotubes in a bundle environment [18]. It was determined that RBM Raman shift of bundled and isolated SWCNTs can be calculated using formulas $\omega=10+(234/d)$ and $\omega=248/d$, respectively, where d is SWCNT diameter [19,20]. For the semiconducting isolated nanotubes, components of the G band are described by sharp Lorentz profiles (full-width at half-maximum (FWHM)≈ 6–15 cm^{-1}). In bundled semiconducting carbon nanotubes, the G band is broader.

The present work investigates the structural evolution of SWCNT thin films upon exposure to OPO laser irradiation in the wavelength region from 430 to 800 nm. The structural changes occurring in the films were analyzed by Raman spectroscopy and atomic force microscopy. It was found that only during laser irradiation at 430 nm semiconducting SWCNTs were more affected than metallic SWCNTs. The photooxidation of SWCNTs was observed dominantly during irradiation at wavelengths above 600 nm.

2. Experimental

An amount of 30 mg of SWCNTs (95% purity, Bucky Corporation, Houston, USA) was dissolved in 100 ml of

0.2 % solution of sodium dodecyl sulphate (SDS) and sonicated (ultrasonic bath power 750 W) for 4 hours. After sonication, SWCNT/SDS solution was centrifuged at 4000 rpm for 1 h to precipitate residual bundles. Thin films of SWCNTs with 2 mm diameters were prepared by vacuum filtration of well-dispersed supernatant on Millipore filters. After thorough washing of residual SDS with 500 ml of distilled water, SWCNT films were dried and transferred onto polished alumina tiles.

Other set of thin films was deposited by spin coating. An amount of 1 mg of SWCNTs was dispersed in 10 ml of dichlorobenzene by sonication for 4 hours. Colloid was centrifuged at 4000 rpm for 1 hour. Ten microliters of colloid was deposited on freshly cleaved mica substrate with diameter of 9 mm and spin coated at 3000 rpm for 1 minute.

In order to observe evolution of morphology of single SWCNT bundle under irradiation, bundle was deposited by spin coating using SWCNT colloid in dichlorobenzene. One bundle was located on TGX calibration grating (NanoandMore GmbH) made lithographically from silicon near one corner of grating. It was irradiated with laser beam at wavelength of 430 nm by increasing the number of pulses.

An optical parametric oscillator (OPO) wavelength tuneable laser (Continuum, Panther ® EX) was used as the laser source for irradiation of SWCNT films, which provides laser emission ranging from 215 to 2550 nm. Pulsed laser beams with wavelengths in the range from 430 to 800 nm were used for selective removal process. The OPO laser provides laser pulses with pulse duration of 6 ns at a frequency of 3 Hz. The energy of each pulse in the visible range was between 12 and 28 mJ. A lens with 7 cm focal length was used to control the spot size and the laser irradiance fluence on the samples. The power density was estimated to be in the range from 0.64 to 1.5 W/μm^2 for SWCNT films on alumina. For SWCNT films on mica power densities were 21.4 times smaller. TGX grating was irradiated with 4 times smaller power density than film on alumina. All samples were irradiated in air.

Raman spectra of irradiated SWCNT films deposited on alumina were obtained by DXR Raman microscope (Thermo Scientific) using 532 nm excitation line from a diode pumped, solid state laser, with a constant power of 10 mW and spot size of 0.7 μm on the sample. The spectral resolution was 0.5 cm^{-1}. Microstructure and morphological changes of SWCNT films deposited on mica substrate and single SWCNT bundle on TGX grating were recorded by atomic force microscope (Quesant) operating in tapping mode in air at room temperature.

3. Results and discussion

3.1. Raman analysis

In the Fig. 1, RBM evolution band of pristine SWCNTs under laser irradiation with energy of 84 mJ is presented. At each wavelength of OPO laser, different number of pulses was used until energy of 84 mJ was reached. Spectra are displaced vertically for reason of clarity. According to Kataura plot [18], semiconducting and metallic SWCNTs are positioned in the grey and red regions. Further in the text we will refer SWCNT samples irradiated by laser beam at wavelengths of 430, 500, 600, 700 and 800 nm as S430, S500, S600, S700 and S800, respectively.

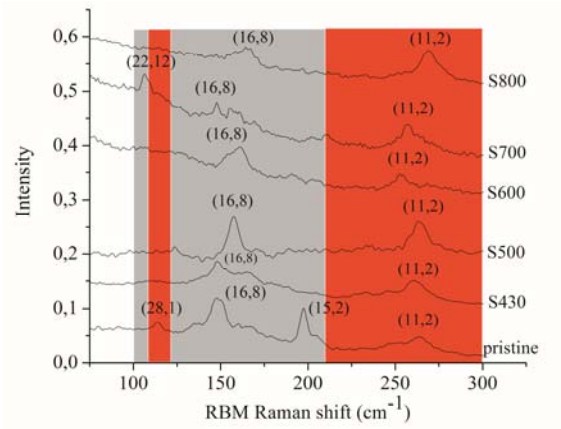

Fig. 1. RBM Raman spectra of pristine SWCNTs and S430, S500, S600, S700 and S800 samples.

Common feature of all RBM spectra of irradiated samples is the absence of metallic SWCNTs (28,1) with diameter of 2.25 nm and semiconducting SWCNTs (15,2) with diameter of 1.25 nm. Peak stem from semiconducting SWCNTs at 150.2 cm^{-1} shifted left in samples S430 and S700 and shifted right in S500, S600 and S800. Peak that corresponds metallic SWCNT (12,0) in pristine SWCNTs at 263.8 cm^{-1} shifted left in samples S430, S600 and S700 and shifted right in sample S800. Sample S700 has peak at 109.2 cm^{-1} that corresponds to semiconducting SWCNTs. Weak peak from semiconducting SWCNTs at 160 cm^{-1} shifted left in sample S500 while it remained position in samples irradiated with larger wavelengths.

On the basis of DOS spectrum [20] low chiral semiconducting SWCNT (15,2) absorbs light at wavelengths of 426 and 503 nm. In the samples S430 and S500 at this position we failed to detect any signal, but in samples S600, S700 and S800 we detect certain amount of signal slightly shifted to higher frequency. These SWCNTs are either completely removed in S430 and S500 or photooxidized in S600, S700 and S800.

Metallic SWCNT (28,1) has DOS spectrum that intensively absorbs wavelengths 428, 500 and 692 nm. In the sample S700 we detected peak in the semiconducting region that is 3.8 cm^{-1} shifted left from peak of metallic SWCNT (28,1) in the pristine sample. It is established that metallic nanotubes can transform in the semiconducting under powerful UV radiation [21]. Therefore metallic bundled SWCNT (28,1) is transformed into the semiconducting isolated tube (22,12).

Metallic SWCNT (12,0) also debundled under irradiation of 430, 600 and 700 nm but it kept electronic type. Under irradiation with 800 nm SWCNT (12,0) photooxidized. Semiconducting SWCNT with 1.66 nm diameter debundled in the course of irradiation with 430 and 700 nm laser wavelengths, but photooxidized in the samples S500, S600 and S800.

RBM analysis reveals that metallic SWCNTs can be removed, transformed into semiconducting SWCNTs, debundled or photooxidized. On the other hand, response

of semiconducting SWCNTs to OPO laser irradiation is either debundlation or photooxidation.

G band analysis of semiconducting SWCNTs involves the fitting procedure by four Lorentzians with peak positions at 1553(E_{2g}), 1569(A_{1g}+E_{1g}), 1592(A_{1g}+E_{1g}) and 1607(E_{2g}) cm^{-1} [22]. Metallic SWCNTs have G band structure that can be fitted by one Lorenzian with peak position at 1580 cm^{-1} and asymmetric Lorentzian (Breit Wigner Fano line) with peak position in the range from 1520 to 1560 cm^{-1}.

Results indicate that sample S430 has no semiconducting Raman modes at 1592 and 1607 cm^{-1}. Since mode at 1592 cm^{-1} depicts low chiral SWCNTs such as (15,2) we can conclude that this result is in accordance with RBM analysis. Value of I_D/I_G is 2.3 times smaller than adequate value for pristine SWCNTs. In the sample S430 semiconducting SWCNTs are removed significantly (Fig. 2). Since FWHM of BWF line is 13.7 cm^{-1}, metallic SWCNTs are well isolated. Only in this sample one of the G band components has FWHM below 15 cm^{-1} and satisfied criteria for SWCNT isolation.

According to Kataura plot visible radiation at wavelengths of 430, 500, 600, 700 and 800 nm will resonantly excite 5,2,2,5 and 0 metallic SWCNTs and 10,3,5,2 and 0 semiconducting SWCNTs, respectively.

Therefore, visible radiation at wavelengths of 430 nm and 700 nm interacts with 15 and 7 types of SWCNTs, respectively. Under assumption that only metallic SWCNTs interact with visible photons due to the large number of highly mobile electrons, effects of radiation on Raman spectra of S430 and S700 should be similar. Since there is a huge difference in Raman spectra of S430 and S700, it is apparent that semiconducting SWCNTs also intensively absorb laser beam, heat up and oxidize.

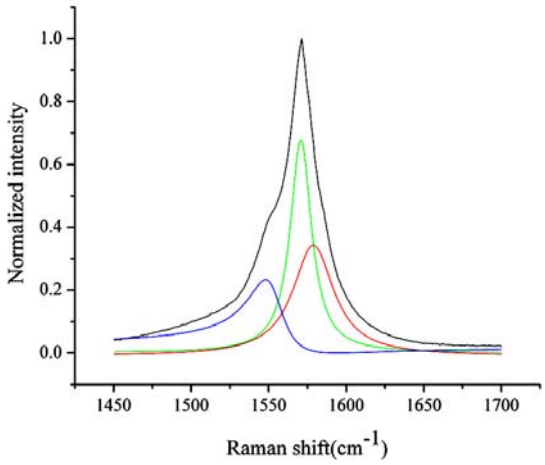

Fig. 2. G band of sample S430 irradiated with 84mJ and fitted with two Lorentzians (green and red curves) and BWF line (blue curve).

3.2 Atomic force microscopy analysis

In order to investigate physical changes in carbon nanotubes after OPO laser irradiation, atomic force microscopy analysis was performed on SWCNT thin films deposited on mica. Deposited films were irradiated at wavelength of 430 nm. This wavelength was chosen since Raman analysis of S430 indicated the presence of isolated SWCNTs.

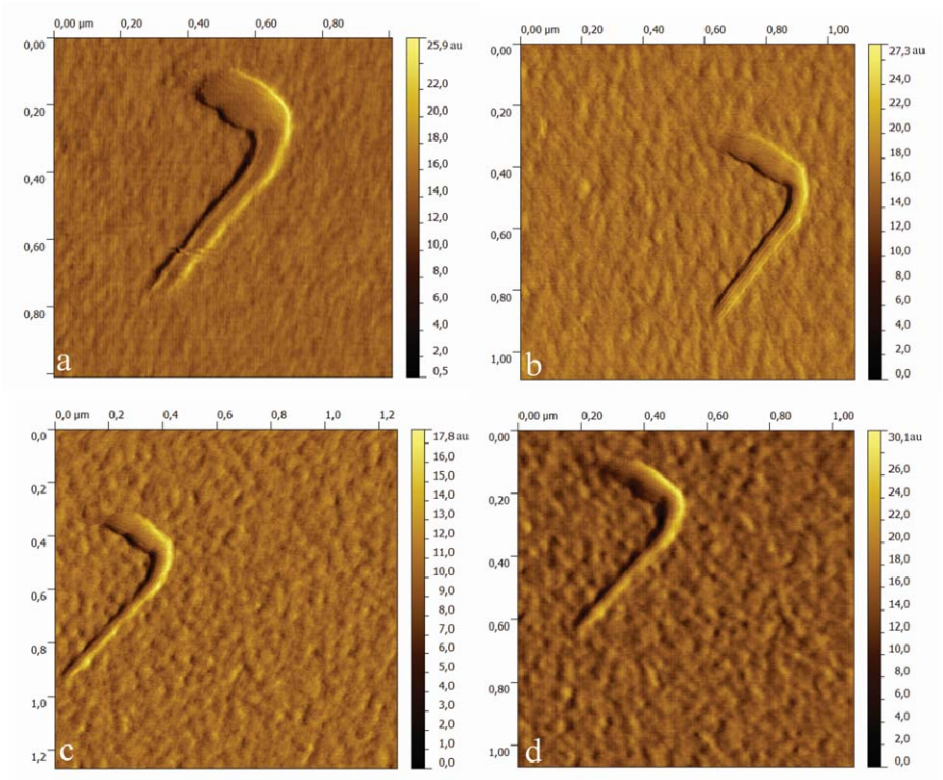

Fig. 3. AFM images of SWCNT bundle deposited on AFM calibration grating TGX01 and irradiated with 0(a),3(b),6(c)and 12(d) pulses at 430nm, respectively. Energy per pulse is 28mJ.

In Fig. 3, irradiated SWCNT bundle with different number of laser pulses at wavelength of 430 nm is presented. SWCNT bundle was deposited on AFM calibration grating TGX01 in the vicinity of one corner and its position on pattern was always determined apparently. In this way we were always sure that we recorded the same SWCNT bundle. By applying surface analysis in Quesant SPM software the variations in carbon nanotube dimensions after each laser irradiation were determined. The average diameter of lower part of SWCNT bundle before laser irradiation was 69 nm (Fig. 3a). After irradiation with 3 pulses, the average diameter of SWCNT bundle was 56 nm (Fig. 3b). By laser irradiation with 6 and 12 pulses the average diameters were reduced on 49.5 nm and 35.5 nm, respectively (Figs. 3c and 3d). The average diameter of SWCNT bundle was decreased almost 50 % after irradiation with 12 pulses. Further laser irradiation with 24 pulses caused very small reduction of carbon nanotube bundle diameter or length changes.

Electronic structure of selected bundle is such that semiconducting SWCNTs were on the circumference of bundle. They are easily removed. If the interior of bundle is rich with semiconducting SWCNTs, bundle explosion due to rapid CO_2 formation might appear that will result with debundlation and isolation of SWCNTs. Such example is shown in Fig. 4 where two SWCNT bundles irradiated by 430 nm with 62 pulses are presented. As can be seen from this figure isolated SWCNTs emerge from nanotube bundle–Fig. 4a. From surface profile analysis diameters of these isolated carbon nanotube are 1.32 nm, 1.950 nm and 2.734 nm, respectively. The diameters of isolated SWCNTs from Fig. 4b are 5.395 nm and 5.897 nm, respectively.

This is not a common feature for all SWCNT bundles imaged. Only few bundles showed this pattern.

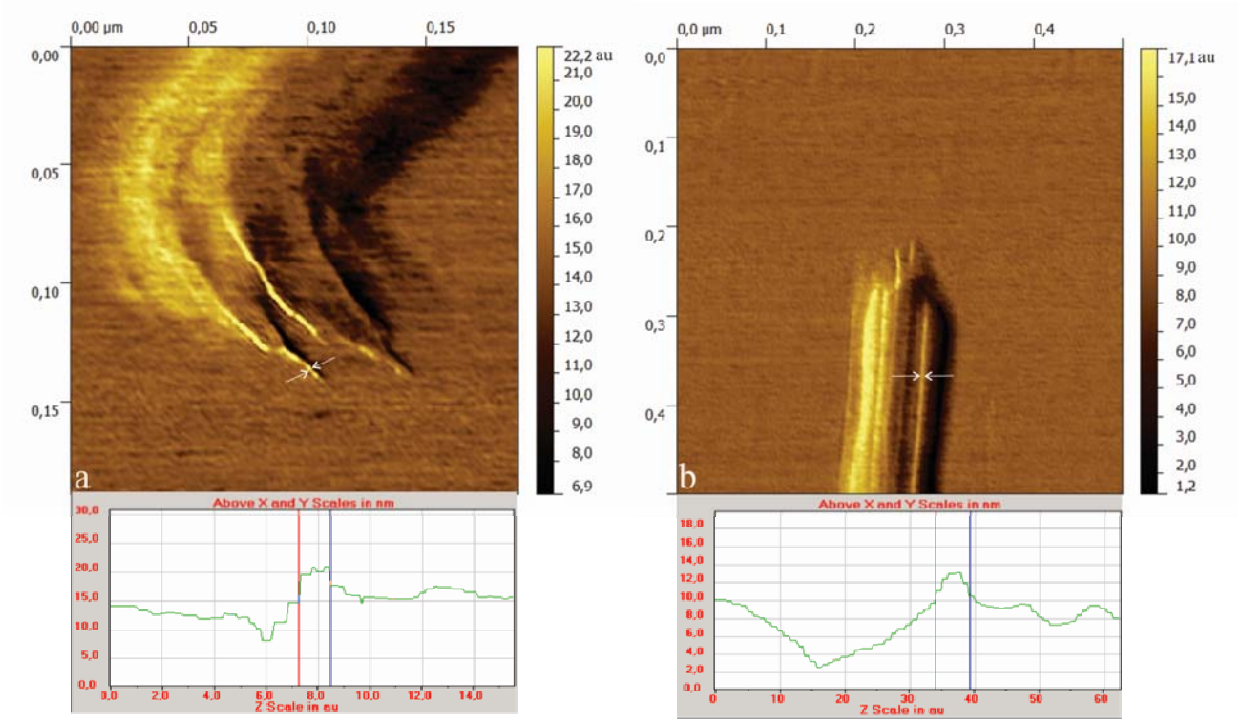

Fig. 4. AFM images of SWCNT bundles irradiated by OPO laser at wavelength of 430 nm with energy 1736mJ.

Obviously, debundlation of SWCNTs depends on the content and distribution of semiconducting and metallic SWCNTs in the bundle. Upper segments of isolated SWCNTs in Fig. 4a are coated with diffuse film unlike straight isolated thicker SWCNTs in Fig. 4b where we cannot detect such coating.

4. Conclusion

In this paper, we report a systematic study concerned the influence of OPO laser irradiation on the structure of SWCNTs. SWCNT thin films were irradiated by high power, pulsed visible irradiation of OPO laser. It was found that both metallic and semiconducting SWCNTs were affected by irradiation. At wavelength of 430 nm, semiconducting SWCNTs were more affected by irradiation than metallic and as a result several SWCNTs were partially isolated. At higher wavelengths, majority of SWCNTs is photooxidized.

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