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Abstract. Coronene molecules are used as filler for single-walled carbon nanotubes. Variation of the synthesis temperature regimes leads to formation of different types of carbon nanostructures inside the nanotubes. Accurate determination of the structures by optical spectroscopy methods remains an important issue in composite materials. Clear distinction between adsorbed organic molecules on the surface of the tubes and filled structures may be accessed by Raman and photoluminescence spectroscopies. We perform additional heat treatment after the initial synthesis procedure and show the evolution of the optical spectral features corresponding to the filled structures and adsorbed materials on the surface of single-walled carbon nanotubes. © *2015 Society of Photo-Optical Instrumentation Engineers (SPIE)* [DOI: 10.1117/1.JNP.10.012504]

1 Introduction

Single-walled carbon nanotubes (SWCNTs) can be used as a reactor for the synthesis of nanostructured materials.[1] Nanotubes serve as a template and govern the geometry of encapsulated aggregates.[2] Changing the properties of the nanotubes leads to extra control over the inner structures.[3] Despite the fact that inner molecules become concealed by the surface of the nanotubes, Raman spectroscopy and photoluminescence (PL) spectroscopy are convenient tools for their detection and study. For example, encapsulated dye molecules demonstrate significant Raman scattering response and PL light emission.[4,5] Coronene molecules are polycyclic aromatic hydrocarbons which can be used as filler for SWCNTs with diameters starting at around 1.2 nm.[3,6,7] Depending on nanotube diameter, the filling rate, and heat treatment coronene molecules can form stacks inside or can be polymerized into hydrogen-terminated nanoribbons.[6,8] Further energy uploading to the system leads to the formation of double-walled carbon nanotubes. All types of structures demonstrate different PL and Raman responses. The unique feature of a hydrogen-terminated nanoribbon is a large band gap of 2 eV which depends on its width.[9] Therefore, such composite materials can be used as robust PL markers, emitting light in the visible spectral range, while the protecting nanotube shell can emit light only in the near IR spectral range. However, in order to become suitable for applications, such composite materials need to be free of additional side products, such as adsorbed hydrocarbons on the surface of the nanotubes.[10,11] The side products are attached to the external surface of nanotubes via $\pi - \pi$ interaction and are considered to be coronene oligomers, which are formed by the dehydrogenation process.

Optical spectroscopy methods can very efficiently identify the result of the synthesis process.[12] In order to distinguish the response from side products and from structures inside the

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nanotubes, we perform additional heating of materials and follow the changes in the PL and Raman spectra. The combination of both spectroscopy techniques allows unambiguously differentiating responses.

2 Experimental Details

SWCNTs with an average diameter 1.4 ± 0.15 nm have been formed in our laboratory by an electrical arc discharge method using a Ni/Y_2O_3 (1:1 ratio) catalyst in an Ar atmosphere. SWCNTs used in the experiments were deposited on the quartz or Al_2O_3 substrates. Prior to the filling procedure, the nanotube caps were opened by heating in air for 25 min at 450°C. The filling was performed in sealed glass tubes via gas phase technique. SWCNTs in the glass tubes were spatially separated from the coronene powder (Angene). The treatment was performed in an Ar atmosphere at 450°C for 13 h. After synthesis, samples were washed in toluene in order to remove coronene and side products from the surface of the nanotubes. Additional heating was performed for 2 h in an Ar atmosphere in glass tubes without coronene powder. Laser heating was performed in the micro-Raman setup by increasing the laser power up to 1 mW on the sample focused into 5 μm^2.

PL measurements have been performed on the solid samples without the formation of nanotube suspensions. Spectra were recorded with a Horiba Jobin-Yvon NanoLog-4 system supplied with the photomultiplier (R928P) working in a spectral range (180 to 850 nm). A PL excitation in the UV–Vis spectral range was performed with a Xe lamp (250 to 900 nm).

Raman measurements have been performed using a triple monochromator spectrometer Jobin Yvon S3000 in a microconfiguration. The spectral resolution was 1 cm^{-1}. Ar–Kr ion lasers (Stabilite 2018, Spectra-Physics) at 647 nm (1.92 eV), 514.5 nm (2.41 eV), and (Stabilite 2017, Spectra-Physics) at 457.9 nm (2.71 eV) wavelengths were used for excitation. Pristine material and filled nanotubes have been treated the same way prior to the filling procedure.

A Horiba Jobin Yvon T64000 Raman spectrometer operating in double subtractive mode with a charge-coupled device cooled at 140 K for detection was used for Raman measurements with temporal resolution. The spectral resolution for the recorded Stokes side Raman spectra was set to ~2 cm^{-1} (this resolution was achieved by using gratings with 1800 grooves mm^{-1} and 100 mm slits). The microscope system, based on an Olympus BX41 microscope with a 50× objective lens $f = 1.2$ mm with a 0.75 numerical aperture, provides a focal spot diameter of about 2 μm^2 on the sample. Single-mode argon 514.5 nm from a Spectra-Physics Stabilite 2017 Ar$^+$ laser of 0.5 mW on the sample was used as the excitation light source. Each step between the measurements was 30 s.

3 Results and Discussion

The filling process of carbon nanotubes with coronene molecules leads not only to their encapsulation, but also to the formation of coronene oligomers on the outside nanotube surface. A Raman spectroscopy study of coronene oligomers has been previously reported.[13] Oligomers demonstrate a large number of spectral features located within the 350 to 650 cm^{-1} and 1150 to 1550 cm^{-1} spectral regions. Encapsulation of coronene molecules inside the SWCNTs leads to the formation of coronene stacks or graphene nanoribbons depending on the treatment conditions and geometrical parameters of the nanotubes. However, additional spectral features corresponding solely to coronene stacks or graphene nanoribbons located inside nanotubes were not yet detected. The main criterion in the Raman spectrum that proves the successful filling is the shift and the intensity suppression of the radial breathing mode (RBM) position of the host nanotube.[14] Filling of the nanotube interior leads to the changes of nanotube vibrational properties, and thus the shift of the RBM position is observed. At the same time, the filling procedure of nanotubes with coronene molecules usually results in an intensity increase of the spectral features, which correspond to coronene oligomers. We performed the filling procedure of the carbon nanotubes with coronene molecules. The Raman spectra of pristine and filled tubes are presented in Fig. 1.

One can see that RBM positions of filled nanotubes demonstrate a red shift compared to the RBM positions of pristine material. For different excitation energies, the shifts in the RBMs may
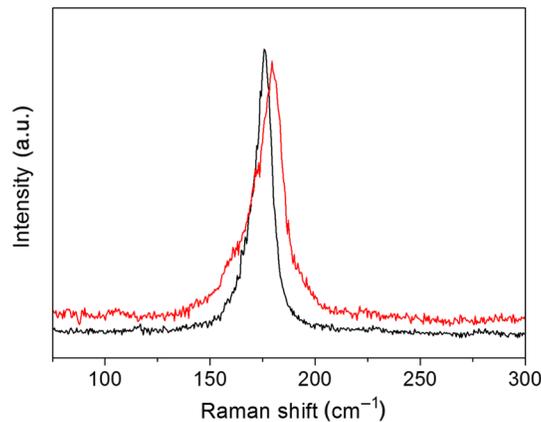
Fig. 1 The Raman spectra of pristine (black) and filled single-walled carbon nanotubes (SWCNTs) (red). Excitation wavelength is 457.9 nm.

reach different values up to 20 cm^{-1}, due to the slightly different filling quality and geometrical superposition of the filler and of the resonantly excited nanotubes. The broader spectral range of the filled nanotubes is presented in Figs. 2 and 3. After the filling procedure, additional spectral components appear in the regions of 350 to 650 cm^{-1} and 1100 to 1650 cm^{-1}. In order to find out the origin of those peaks, we have performed laser heating of the sample. Laser heating affects the Raman spectra of the filled nanotubes (Fig. 2).

Spectral components around 350 to 650 cm^{-1} lose their intensity, however, complete removal is usually not possible with applied laser power. Importantly, the RBM red shift of the laser-heated samples is preserved, meaning that tubes remain filled. Laser heating also results in the decrease of the RBM peak intensities (positioned at 190 and 198 cm^{-1}) of the smallest nanotubes. We assume that the origin of the intensity decrease of RBMs is the change of resonant conditions for some of the nanotubes and not the laser destruction of the smallest nanotubes presented in the sample. One can conclude that the origin of the Raman spectral features in the filled samples around 350 to 650 cm^{-1} and several peaks in the 1100 to 1650 cm^{-1} spectral region, with the exception of the D and G bands of SWCNTs, comes from the coronene oligomers, which are formed outside of the nanotubes and remain in the samples even after the toluene treatment. However, longer heat treatment does not result in additional decrease of the peak intensities (Fig. 4). The Raman signal with nondecreasing intensity after the additional laser heating can be attributed to the inner structures. Appearance of such Raman features in the
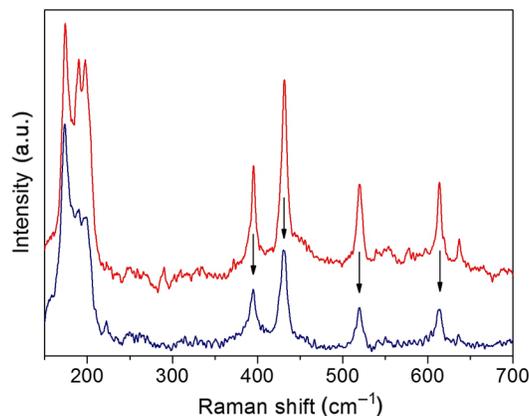

Fig. 2 The Raman spectra of filled SWCNTs (red) and filled SWCNTs after laser heating (blue). The spectra are normalized on the RBM line from the nanotubes positioned at 174 cm^{-1}. Arrows demonstrate the lines, which decrease in intensity after the laser irradiation. Excitation wavelength is 647 nm.
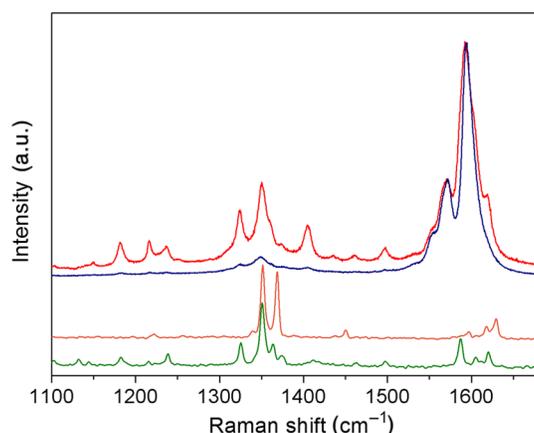
Fig. 3 The Raman spectra of filled SWCNTs (red) and filled SWCNTs after laser heating (blue), coronene (orange), and dicoronylene (olive) powders. Excitation wavelength is 514.5 nm for nanotube samples and 1064 nm for powders. The spectra of filled SWCNTs are normalized on the G band. Laser heating lasted for 50 min. Several spectral components not originating from pristine SWCNTs remain in the spectrum after the treatment.

samples cannot be unambiguous proof for the formation of coronene derivatives, for example, coronene stacks or hydrogen terminated graphene nanoribbons, inside the nanotubes. Study by additional optical methods, such as PL spectroscopy, allows gaining more information on the process taking place during heating.

In order to perform not only local heating within the micron area size, we have used conventional heating in an Ar atmosphere. Prior to heating treatment, the samples were purified. PL spectroscopy was used to study the differences between the samples after the additional heating procedure (Figs. 5 and 6). During the additional heating in the sealed tubes without the presence of coronene powder, molecules which previously settled on the outer surface of the nanotubes, sublimate and change their final position in the sealed tube during the cooling stage. The process of molecules sublimation from the outside surface leads to a partial decrease of the side product PL response. In Fig. 5, we demonstrate the changes in the PL spectra after the additional heating. We follow the changes of the peak centered at 660 nm coming from the coronene oligomer.[7] In order to see the real intensity change of the peak for the filled and additionally heat-treated samples, we have normalized the spectra on the reference peak, which comes from the Al_2O_3 substrate. It can be clearly seen that the peak intensity can be significantly reduced during the heating process. The result of the heating is similar to the laser heating process monitored via
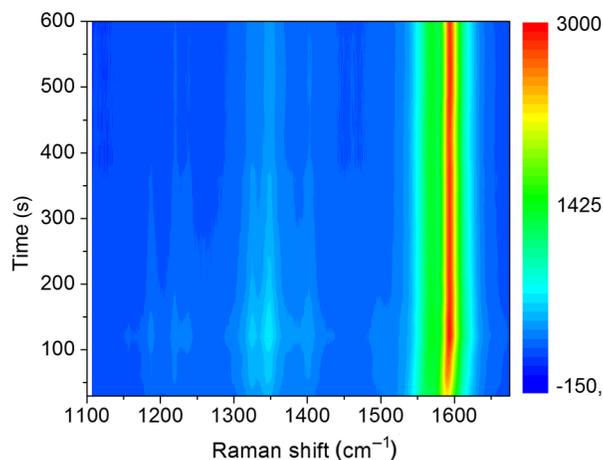

Fig. 4 The Raman spectra counterplot of filled SWCNTs depending on the laser heating time. Drastic changes in the spectra appear in the first seconds of the treatment. Excitation wavelength is 514.5 nm.
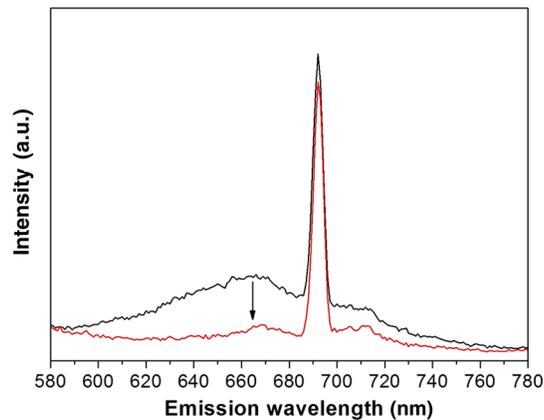
Fig. 5 The photoluminescence (PL) emission spectra of filled SWCNTs (black) and filled nano-tubes after the conventional heating (red). The PL emission peak centered at 660 nm is significantly suppressed. The spectra are normalized on the reference peak, which originates from the Al_2O_3 substrate.
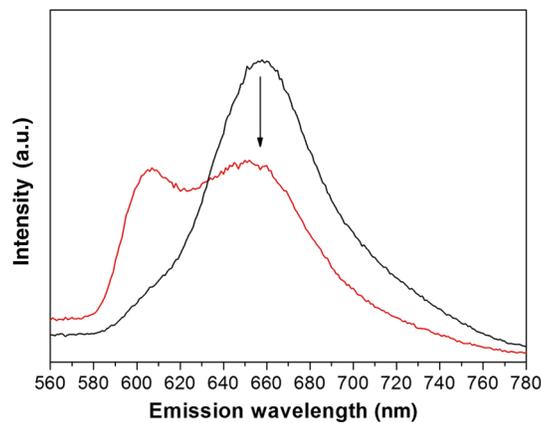

Fig. 6 The PL emission spectra of filled SWCNTs (black) and filled nanotubes after the conventional heating (red). The PL emission peak centered at 660 nm is suppressed, while the peak at 608 nm appears after the polymerization process. Samples were mounted on the quartz substrate.

the Raman scattering. Additional heating leads to purification of samples because coronene oligomers settled on the surface of carbon nanotubes can be partially removed. In addition to purification of samples, heating can lead to the transformations of the filler inside nanotubes. In Fig. 6, the PL decrease of the peak centered at 660 nm is accompanied with the increase of the peak centered at 608 nm. In this set of experiments, we use quartz instead of the Al_2O_3 substrate. Two peaks demonstrate opposite intensity changes during the heating process. The origin of the new peak appearing at 608 nm is the result of the polymerization inside the nanotube. Previously filled coronene molecules arrange into stacks[6,7] and further transform into a more complicated structure, which later forms the hydrogen-terminated graphene nanoribbon.[3] With PL spectroscopy, we detect not only the decrease of the signal intensity from the surface contamination, but also follow the transformations taking place inside the nanotubes.

4 Conclusions

We performed heating by laser irradiation and by oven in an Ar atmosphere of SWCNTs filled with coronene molecules. Raman and PL spectroscopies allow detecting the response not only from the structures located outside the nanotubes, but also from the filler. With both heating techniques, it is possible to partially remove coronene oligomer structures from the outside

surface of carbon nanotubes. Raman lines in the spectral regions 350 to 650 cm^{-1} and 1100 to 1650 cm^{-1}, with the exception of the D and G bands of SWCNTs, originate dominantly from coronene oligomers on the outside surface of carbon nanotubes. However, long-time laser treatment gives reasons to consider that the inner structures can also contribute to the abovementioned spectral components. Filled carbon nanotubes demonstrate significant shifts in the RBM peak positions.

PL study shows that coronene oligomers on the outer surface of carbon nanotubes can mostly be removed from the sample. The above discussed PL component corresponding to coronene oligomers is the peak centered at 660 nm. Together with the removal of side products, additional heating can result in polymerization of previously encapsulated coronene molecules inside carbon nanotubes. We were able to follow the intensity increase of the new peak appeared around 608 nm and compare the behavior with the PL response from coronene oligomers on the outer surface of carbon nanotubes. The intensity dynamics of two PL peaks is opposite during the heating process. Simultaneously with evaporation of side products from the outer surface of carbon nanotubes, filled molecules polymerize and form new one-dimensional structures with their own unique PL response.

Acknowledgments

References

1. A. N. Khlobystov, "Carbon nanotubes: from nano test tube to nano-reactor," *ACS Nano* **5**(12), 9306–9312 (2011).
2. A. I. Chernov and E. D. Obraztsova, "Geometry sorted single-walled carbon nanotubes as a reactor for controllable filling," *J. Nanoelectron. Optoelectron.* **8**, 75–78 (2013).
3. A. I. Chernov et al., "Optical properties of graphene nanoribbons encapsulated in single-walled carbon nanotubes," *ACS Nano* **7**(7), 6346–6353 (2013).
4. E. Gaufrès et al., "Giant Raman scattering from J-aggregated dyes inside carbon nanotubes for multispectral imaging," *Nat. Photonics* **8**, 72–78 (2014).
5. M. A. Loi et al., "Encapsulation of conjugated oligomers in single-walled carbon nanotubes: towards nanohybrids for photonic devices," *Adv. Mater.* **22**(14), 1635–1639 (2010).
6. I. V. Anoshkin et al., "Coronene encapsulation in single-walled carbon nanotubes: stacked columns, peapods, and nanoribbons," *ChemPhysChem* **15**, 1660–1665 (2014).
7. A. I. Chernov et al., "Single-walled carbon nanotubes as a template for coronene stacks," *Phys. Status Solidi B* **251**(12), 2372–2377 (2014).
8. A. V. Talyzin et al., "Synthesis of graphene nanoribbons encapsulated in single-walled carbon nanotubes," *Nano Lett.* **11**(10), 4352–4356 (2011).
9. X. Zhu and H. Su, "Scaling of excitons in graphene nanoribbons with armchair shaped edges," *J. Phys. Chem. A* **115**, 11998–12003 (2011).
10. H. J. Lempka, S. Obenland, and W. Schmidt, "The molecular structure of Boente's 'dicoronylene,' as deduced from PE and UV spectroscopy," *Chem. Phys.* **96**, 349–360 (1985).
11. B. Botka et al., "Interactions and chemical transformations of coronene inside and outside carbon nanotubes," *Small* **10**(7), 1369–1378 (2014).
12. M. He et al., "Low temperature growth of SWNTs on a nickel catalyst by thermal chemical vapor deposition," *Nano Res.* **4**(4), 334–342 (2011).
13. M. Fujihara et al., "Dimerization-initiated preferential formation of coronene-based graphene nanoribbons in carbon nanotubes," *J. Phys. Chem. C* **116**, 15141–15145 (2012).
14. P. V. Fedotov et al., "Optical study of nanotube and coronene composites," *J. Nanoelectron. Optoelectron.* **8**, 16–22 (2013).

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