Single-walled carbon nanotubes can serve as a template for formation of various structures inside. Depending on conditions, the nanotube filling with coronene molecules may lead to creation of coronene stacks, graphene nanoribbons, or inner tubes. In this work, the formation of coronene stacks inside single-walled carbon nanotubes was studied using photoluminescence (PL) spectroscopy. We demonstrate the difference in the excitation PL maps between the spectral features of coronene stacks inside the nanotubes and products formed outside the nanotube interior. The optical investigation was supported by calculations of adsorption energy of coronene molecules inside and outside nanotubes. The theoretical calculations predict the most energetically favorable configurations of coronene molecules with respect to the diameter of the outer nanotubes. Orientation of coronene stacks depends on the nanotube diameter.

1 Introduction

Single-walled carbon nanotubes (SWCNTs) have been demonstrated to serve as the nanoscale reactors [1]. The space inside SWCNTs provides geometrical conditions for formation of one- [2] and zero-dimensional [3] structures. Molecules placed inside SWCNTs are well protected from the external environment and can form inner structures, which are thermodynamically unstable in the absence of encapsulating template. Confinement determines the behavior of molecules encapsulated in SWCNTs. Therefore, the diameter of nanotube not only determines whether the molecule can get inside, but also affects the molecules motion and possibility to form new structures. Various molecules can be inserted into SWCNTs [4–6]. Increase of the system temperature triggers the modifications of internal structures, turning the nanotubes in the nanoreactors [7]. One of the first reactions of such type was the transformation of the filled fullerences into the inner nanotubes [8, 9]. Recently, the polycyclic aromatic hydrocarbon (PAH) molecules were used as precursors for formation of graphene nanoribbons [10] and their further transformation into new nanotubes inside the host tubes [11]. Reaction of polymerization leads to modification of single molecules into a sole spiral nanoribbon. However, the diameter of the outer nanotube plays an important role in such reactions and governs the shape of the interior. For example, a preferential configuration inside the small diameter
nanotubes is an array of the planar coronene molecules \((C_{24}H_{22})\) oriented perpendicular to the nanotube axis, so-called “stacks” [12, 13], instead of the nanoribbons. In such stacks coronene molecules are supported by the outer nanotube and line up due to the \(\pi-\pi\) interaction between each other.

Photoluminescence (PL) spectroscopy is an efficient technique for identification of semiconducting SWCNTs [14, 15], PAH molecules [16] and hydrogen-terminated nanoribbons [17, 18]. It allows accessing the energy band gap of the material and therefore discriminating between the types of structures presented in the sample. SWCNTs emit light in the near IR range, while nanoribbons and PAH molecules exhibit emission usually in a visible spectral range. Despite the fact that the emission of the latter structures can be well resolved, the only complicating fact, which may occur, is the distinction of the spectral features assignment to the structures formed inside or outside nanotubes. For example, during the thermal mediated filling of SWCNTs with coronene molecules some of them can easily attach to the nanotube external surface or form molecular crystals [19].

In this work, we study the filling of SWCNTs with coronene molecules, investigate the PL response of the structures encapsulated in SWCNTs and differentiate it from the spectral features of side products. We present the theoretical calculations of the adsorption energy of coronene molecules placed inside and outside the nanotubes.

2 Experimental procedure SWCNTs with an average diameter 1.3 \(\pm\) 0.2 nm have been synthesized by an aerosol method [20] and tubes with an average diameter 1.4 \(\pm\) 0.15 nm have been formed by an electrical arc-discharge method using Ni/Y_2O_3 (1:1 ratio) catalyst in Ar atmosphere. SWCNTs used in the experiments were either in the form of bucky paper or in the form of film deposited on the quartz substrate. The deposition was performed by a simple dry transfer technique described elsewhere [21]. 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 the sealed glass tubes where nanotubes were spatially separated from coronene powder (Angene). The treatment was performed in Ar atmosphere or in vacuum at 450 °C for 13 h. After the synthesis, samples were washed in toluene in order to remove the coronene and side products from the surface of the nanotubes.

PL measurements have been performed on the solid samples, without formation of nanotube suspensions. Spectra were recorded with a Horiba Jobin-Yvon NanoLog-4 system supplied with the InGaAs CCD detector (850–1550 nm) and with the photomultiplier (R928P) working in a spectral range (180–850 nm). A PL excitation in the UV–Vis spectral range was performed with a Xe lamp (250–900 nm). A PL excitation mapping was performed with a 2 nm step in excitation.

2.1 The calculation method details Molecular mechanics (MM) is widely used for the numerical studies of adsorption energies of different molecules on graphite and carbon nanotubes [22–26]. In the present paper, we use MM to characterize the adsorption of coronene molecules on SWCNTs of various diameters. We used common MM+ force field parameter set [27, 28] with a software package HyperChem 8.0 (Hypercube, Inc.) to get the most favorable geometry and to compare the energy of coronene molecule adsorption on the external nanotube surface and inside nanotube.

Since the self-assembly of nanotube and coronene molecules leads to non-chemical bonding between them, the optimization of the adsorption geometry is only governed by the non-bonding forces involving van der-Waals repulsive forces at close range, Lennard-Jones long-range attractive interactions and electrostatic Coulomb forces. The adsorption energy between the coronene molecules and the nanotubes were estimated using Eq. (1):

\[
\Delta E_{\text{ads}} = E_{\text{NT+coronenes}} - (E_{\text{NT}} + E_{\text{coronenes}}),
\]

where \(E_{\text{NT+coronenes}}\) is the energy of the optimized structure of the nanotube and coronene molecules interaction, \(E_{\text{NT}}\) is the energy of the nanotube alone and \(E_{\text{coronenes}}\) is the energy of isolated (gas phase) coronene molecules. Two types of SWCNTs with diameters 1.36 nm (10,10) and 1.49 nm (11,11) were used.

For checking the applicability of MM+ calculations, we have performed a comparative calculation of the adsorption energies of single coronene molecule positioned inside and on the external surface of a small fragment of (11,11) tube using the MM method and the semi-empirical quantum-chemical method P 6 DH2 (Mopac2012) specially modified for the calculations of van-der-Waals interactions and hydrogen bonding [29]. We have found that the data on the adsorption energy were in consistence with the data obtained using the semi-empirical quantum-chemical method P 6 DH2 (Mopac2012), i.e., DH2: \(-43.587\) and \(-32.30\) kcal mol\(^{-1}\), and MM+: \(-43.84\) and \(-32.39\) kcal mol\(^{-1}\), respectively.

3 Results and discussion 3.1 Photoluminescence of coronene stacks We investigate the spectral properties of coronene stacks inside SWCNTs by PL excitation mapping. A high-resolution transmission electron microscope (HRTEM) image of studied material is presented in Fig. 1. Stacking is observed as a common type of encapsulation. Both of the nanotube treatment procedures in Ar atmosphere and in high vacuum for SWCNTs with chosen diameter distribution lead to the same PL properties of materials. In Fig. 2, we show a typical PL map of the sample prepared by annealing treatment at 450 °C in Ar atmosphere followed by washing with toluene. The PL spectrum of coronene stacks inside SWCNTs was previously reported by Okazaki et al. [12]. However, some doubts have been expressed [30], stating that the reported spectral features might correspond to the side products attached to the outer surface of the nanotubes instead of the inner coronene stacks. Nevertheless, both of the works were confirmed by the TEM images of the inner coronene stacks.
In previous works the PL emission spectra of coronene and carbon nanotube materials have been reported only at a few excitation wavelengths. Figure 2 represents the PL excitation map of the annealed sample of SWCNTs filled with coronene molecules. All of the spectral features are located within 475–650 nm emission wavelength range and demonstrate the dependence on the excitation wavelength. In order to avoid complications due to the suspending procedures of carbon nanotubes, which might cause the non-desirable washing out of the studied objects, we have performed all the measurements on the solid samples washed with toluene. We have revealed the difference in the PL spectra of the samples before and after washing with toluene (Fig. 3). Despite the fact that it is hard to completely exclude the influence from the side products, we can follow the decrease of the emission intensity of the spectral components and dominantly of those, located below 480 nm. After the washing procedure, the spectra demonstrate in average three main components located at 498, 537, and 578 nm. These three components, which we refer to the contribution from the structures inside the nanotubes, at some moment after the treatment start, become unaffected by the toluene. One of the possible reasons for such behavior is the carbon nanotube protection of the encapsulated structures. An additional heat treatment of the washed samples, such as a high temperature annealing or a laser beam irradiation, leads to the formation of inner tubes, transforming the SWCNTs with encapsulated coronene stacks into the double-walled carbon nanotubes (DWCNTs). Transformation of the coronene-filled SWCNTs was previously reported [30, 31]. However, prior to the DWCNT, the peapod-like structures start to form [13]. The origin of such reorganization and theoretical investigation will be presented further in the text.

Here, we demonstrate that the slight change in the diameter distribution of host SWCNTs leads to the change of the coronene stacks spectral features (Fig. 4a and b). We detect the intensity redistribution and the emission peak positions changes. Going into more details of the measured PL spectra, three components behave differently depending on the excitation wavelength, type of the host nanotube diameter and slight changes of the synthesis parameters. The component at 498 nm emission wavelengths is not changing its peak position, although the intensity can be significantly decreased. The minimal emission intensity was detected for the 410 nm excitation wavelength and 20 °C increased treatment temperature (Fig. 4d). A relative intensity of the peak in comparison with the intensity of two others inversely depends on the treatment temperature. The spectral component positioned at 537 nm only slightly changes its position when the synthesis temperature is changed and it is demonstrated to be dependent on the excitation wavelength. The longest-wavelength spectral component of the triplet strongly depends on the
experimental parameters and the excitation wavelength. The maximal shift of the peak position is 7 nm. In our experiment, the PL emission spectra of the identically prepared samples of the filled coronene stacks inside carbon nanotubes with an average diameter 1.3 nm, 1.3 ± 0.2 nm (Fig. 4a) and an average diameter 1.4 ± 0.15 nm (Fig. 4b) demonstrate the different spectral positions of two components, while the one at 498 nm stays unchanged. The peak positions shifts may reach up to 8 nm. However, the overall type of the spectral band is similar for both diameter distributions of nanotubes. The change of intensity and positions of the spectral components can be explained by the fact that coronene molecules inside the nanotubes have different organization. Recently, Anoshkin et al. [13] demonstrated the dependence between the stack axis angle and the host SWCNT diameter. The nanotube diameter value determines the configuration of encapsulated molecules. Important to mention, that in our study three peak type of the emission spectrum is typical only for the coronene–nanotubes systems formed in the narrow diameter SWCNTs, which are close to the filling limit with coronene molecules [12, 17]. In case of larger diameter nanotubes, the formation of coronene stacks becomes not favorable and gives a way to the formation of other forms of encapsulated structures [18, 11, 13], which exhibit completely different PL emission [18].

### 3.2 Molecular models

The models of tubes with ten inserted coronene molecules are presented in Fig. 5. It was found that the adsorption of coronene molecules inside tubes is more energetically favorable than the adsorption of molecules on the external surface of tubes (for the (10,10) tube: 47.35–32.24 kcal mol⁻¹; for the (11,11) tube: 44.86–33.01 kcal mol⁻¹, respectively; data were normalized per one coronene molecule). A significant deformation of the tube with a smaller diameter after the coronene adsorption was observed. The angle between the nanotube axis and the plane of the coronene molecules depends on the nanotube diameter.

We have also analyzed a possibility of the formation of DWCNT using a thermal decomposition of pre-adsorbed coronene molecules inside the SWCNT. Thus, we compare the volume of forming internal nanotube with the volume of pre-adsorbed coronene molecules. The thermal decomposition of coronene molecules even in the case when they completely occupy the internal channel of the nanotubes cannot provide the formation of prolonged ideal double-walled nanotube because of the lack of carbon atom required per the unit length of internal nanotube. One also must remember that the hydrogen atoms filled a significant part of the nanotube internal space after adsorption of coronene molecules. We can propose the formation of defective prolonged internal nanotube or the formation of short closed nanotubes separated from each other (see Fig. 6). The formation of peapod-type structures was recently reported [13].

### 3.3 A comparison between stacks and coronene wires

As it was previously mentioned, the synthesis technique used for formation of coronene stacks inside SWCNTs may also lead to formation of side products. The influence of the treatment temperature on the types of the grown structures has been discussed in detail in the paper of Talyzin et al. [32]. It is very important to clearly distinguish the spectroscopic response from the inner
structures and from the side products, which may be formed outside nanotubes. A PL study of the materials synthesized at different temperatures shows that PL mapping may be a convenient tool to detect the change of the spectral features corresponding to various materials. We have performed the same synthesis procedure as in the case of coronene stacks inside SWCNTs, but without the nanotubes. As the result, when no nanotubes are presented during the synthesis, we have obtained the yellow color coronene narrow wires around 1 cm long. The PL excitation map of such wires is presented in Fig. 7. Two main differences can be easily noticed when we compare the PL map of coronene wires and coronene stacks inside SWCNTs (Fig. 2). For the coronene wires, a larger number of spectral features are presented and the excitation range is much broader (up to 575 nm). Despite the fact that three spectral components, which we previously discussed for encapsulated molecules, are presented in the map, their spectral positions are shifted. The peaks positioned at 537 and 578 nm in Fig. 2 are shifted to 529 and 568 nm, respectively. The best similarities in the peak positions are found for coronene stacks formed inside the nanotubes with an average diameter 1.3 ± 0.2 nm (Fig. 4a), with the main difference in a smaller range of excitation wavelengths. In the solid coronene, the molecules are positioned in the adjacent stacks and are nearly perpendicular to each other. The plane of coronene molecules is inclined at approximately 45° to the crystal axis [19]. Such crystal structure gives the origin for a larger number of emission peaks in comparison to the PL spectra of coronene stacks inside SWCNTs.

The increase of the treatment temperature in the experiment leads to the formation of additional side products. For example, when the temperature is raised up to 530 °C without the presence of nanotubes, we obtain the red color material. Previously, such material was determined as a dicoronylene crystal [32, 33]. In contrast to the previously reported PL emission spectra of dicoronylene at room temperature [16], for the red color material, obtained in our process in Ar atmosphere, we get only one broad peak positioned around 661 nm (Fig. 8). According to the PL excitation mapping, the spectral features are not resonant and molecules emit light while excited in a wide spectral region. The shape and position of the PL emission peak of the red-colored material look the most similar to the quaterrylene [16], although the peak position is 10 nm shifted. In Fig. 3e, we show the PL response of the encapsulated SWCNTs. Such spectral line shape was reported to be a signature of dicoronylene [16, 31]. In contrast to the aforementioned works, we demonstrate, that changing the diameter of the host nanotubes and treatment temperature modifies the intensity distribution between the triplet peaks and drastically changes the spectral line shape, together with the spectral peak positions. In Fig. 8, we demonstrate the difference in PL emission spectra between the molecular coronene crystal, red color dicoronylene crystal and coronene stacks inside SWCNTs.

Figure 6 Size comparison of a closed nanotube model containing 240 carbon atoms (black) and a set of closely packed ten coronene molecules (red) also containing 240 carbon atoms inside the (11,11) nanotube. One can see that the closed nanotube has a smaller molecular volume than a set of ten coronene molecules.

Figure 7 The PLE contour plot of the molecular coronene crystal formed without the presence of nanotubes.

Figure 8 The photoluminescence emission spectra of the solid coronene wires (black), solid dicoronylene (blue) and coronene stacks inside SWCNTs (red color dashed line) measured at a 410 nm excitation wavelength.
4 Conclusions In this contribution, we show the importance of the PL excitation mapping in a wide spectral range in order to clearly detect the difference between the spectral features of the coronene stacks inside the nanotubes and products, which can be formed outside the nanotube interior. The coronene and dicoronylene crystals formed outside the nanotubes and coronene stacks inside SWCNTs possess their own intrinsic resonant and non-resonant spectral features. We demonstrate the PL response of the coronene stacks inside different diameter SWCNTs formed at various treatment temperatures. Theoretically estimated adsorption energies of coronene molecules inside and outside the nanotubes predict the most favorable nanotube parameters for the formation of coronene stacks. It was found that adsorption of coronene molecules inside the tubes is more energetically favorable than the adsorption of the molecules on the tube external surface. Orientation of coronene stacks depends on the nanotube diameter. An extensive interest in the area of utilization of carbon nanotubes as the reactors for transformation of filled PAH molecules requires an efficient tool for the control of synthesized materials. We demonstrate that PL spectroscopy can serve as such tool and provide the basis for further study of the peculiar properties of novel materials.

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