ORIGINAL PAPER

Nanocarbon Photonics and Optoelectronics

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Optical Properties of Single-Walled Carbon Nanotubes Doped in Acid Medium

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We report a detailed study of changes in optical properties of single-walled carbon nanotubes caused by doping in acid medium and their comparison with those induced by other doping techniques. In this work, a hydrochloric acid was added to the aqueous suspension of nanotubes wrapped with sodium cholate. Additionally to the shift and suppression of several modes in the Raman spectrum and the suppression of the first optical transition in the optical absorption spectrum, we have observed an appearance of a trion band in the photoluminescence spectrum with the energy about 0.2 eV less than the main photoluminescence band.

1. Introduction

Single-walled carbon nanotubes (SWNTs) attracts a huge interest because of their outstanding mechanical, electronic, thermal, and optical properties.[1] Moreover, some of SWNT properties can be tuned by special post-growth procedures, which significantly expand the scope of their possible applications.

Doping of SWNTs by filling of their internal channels with acceptor molecules leads to increasing of their electrical conductivity and optical transparency.[2,3] These phenomena are commonly explained by the downshifting of the Fermi level of nanotubes into the valence band. To describe this process more completely, photoluminescence (PL) spectroscopy should be applied, but commonly used filling technique deals with films or powders of nanotubes, that makes PL studying complicated due to the fast irradiative relaxation of electronic excitations in bundles.[4]

However, doping can also be performed by adding of dopants to the suspension of individual nanotubes.[5] In this work, we studied the SWNTs doped in aqueous suspensions with Raman spectroscopy, optical absorption spectroscopy, and PL spectroscopy.

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DOI: 10.1002/pssb.201700272

2. Materials and Methods

We used commercially available (Sigma–Aldrich) nanotubes synthesized with the CoMoCat method. The powder was dispersed in 2% aqueous solution of sodium cholate in the concentration of 0.05 mg ml^{-1}. The suspension was sonicated with a tip sonicator for 4 h and ultracentifuged at 125 000×g for 1 h. The supernatant was collected and used as the parent material for further investigations. The doping of SWNTs in suspension was performed by adding of different amounts of hydrochloric acid.

The PL spectra were obtained with the Horiba Jobin-Yvon NanoLog-4 spectrometer with the Xe-lamp excitation and the nitrogen-cooled InGaAs detector. The slit bandpass was set to 10 nm, the acquisition time was 60 s. The Raman measurements were done with the LabRAM Evolution spectrometer with the excitation wavelength 633 nm, the power on the sample was 0.5 mW, the acquisition time was 60 s. For the optical absorption measurements, the two-channel UV-vis-NIR Spectrophotometer Perkin Elmer Lambda 950 was used.

3. Results

3.1. PL Measurements

The PL map of the pristine SWNT suspension is shown in **Figure 1**a. The brightest peak with the resonance wavelength of excitation $\lambda_{excit} = 570$ nm and the emission wavelength $\lambda_{emis} = 985$ nm corresponds to the main excitonic peak associated with (6,5) nanotubes.[6] The dim peak with $\lambda_{excit} = 570$ nm and $\lambda_{emis} = 1110$ nm is a phonon side-band associated with (6,5) nanotubes.[7] The peak with $\lambda_{excit} = 585$ nm and $\lambda_{emis} = 875$ nm corresponds to (6,4) nanotubes.

An addition of HCl to the suspension leads to the decrease of the total PL intensity (see Figure 1b) and to the appearance of a new bright peak with $\lambda_{excit} = 570$ and $\lambda_{emis} = 1155$ nm. Taking into account that the central excitation wavelength of this peak equals to that of the main excitonic (6,5) peak, we suppose that the new peak is associated with the (6,5) nanotubes.

Also, one can observe an appearance of another dim peak with $\lambda_{excit} = 585$ nm and $\lambda_{emis} = 1035$ nm, which is almost buried under the sidepiece of the main (6,5) peak, but still can be detected. Analogously, this peak seems to be associated with the (6,4) nanotubes.

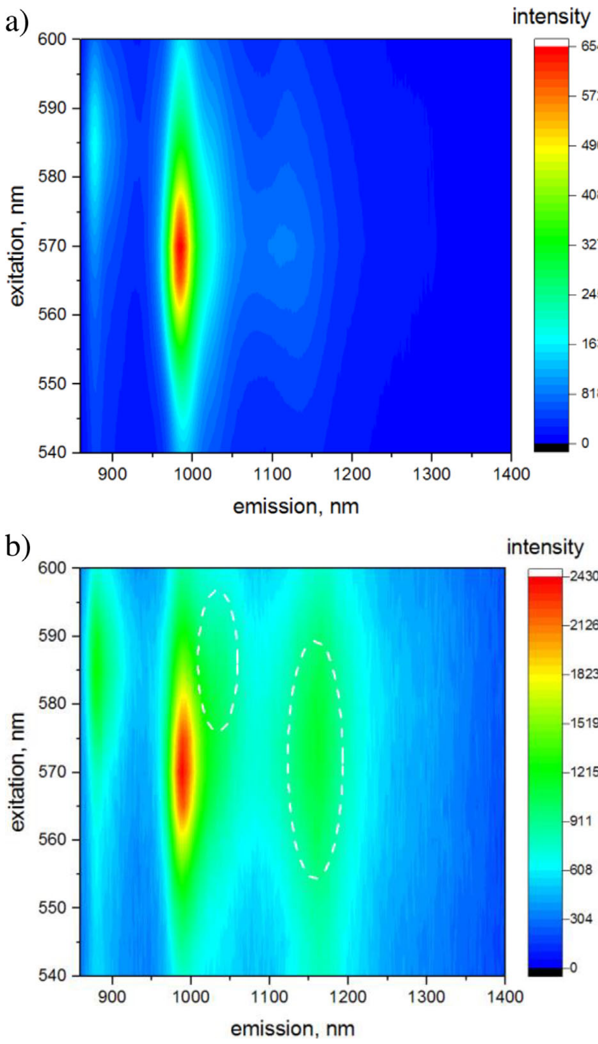

Figure 1. (a) The photoluminescence map of pristine SWNT suspension. (b) Typical photoluminescence map of the suspension of SWNTs after adding of HCl. White ellipses indicate the peaks that appeared due to acid addition.

The dependence of PL spectra on the amount of added hydrochloric acid is shown in **Figure 2**. The concentration of HCl in the suspensions indicated in the top-right corner of the figure.

In Figure 2a, the excitation wavelength set at 570 nm to excite (6,5) nanotubes resonantly. The intensity of the new peak at 1155 nm increases in comparison with the intensity of the main excitonic peak with increasing of HCl concentration. The ratio of these two peaks equals to 0.4 for the lightly doped nanotubes and 0.7 for the heavily doped nanotubes.

In Figure 2b, the excitation wavelength set at 585 nm which matches the resonance condition for (6,4) nanotubes. The new peak at 1035 nm also increases in comparison with the main excitonic peak of (6,4) nanotubes (see Figure 2c) with increasing of HCl concentration.

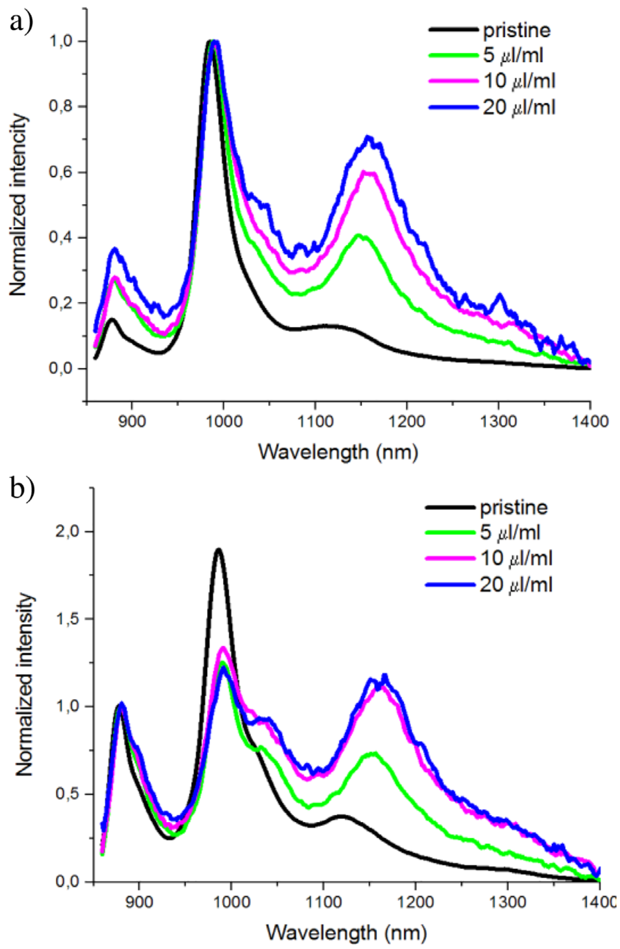

Figure 2. The dependence of photoluminescence spectra of SWNTs suspension on the concentration of HCl. (a) Spectra normalized to the E_{11} exciton band of (6,5) SWNTs under resonance excitation for (6,5) SWNTs (570 nm). (b) Spectra normalized to the E_{11} exciton band of (6,4) SWNTs under resonance excitation for (6,4) SWNTs (585 nm).

3.2. Raman Measurements

Changes in the Raman spectra of SWNTs induced by adding of acid to the SWNT suspensions are shown in **Figure 3**.

Although used excitation wavelength (633 nm) is not resonant neither for (6,5) or (6,4) nanotubes and obtained results mainly correspond to SWNTs with other chiralities, some important features should be taken into account.

Firstly, a weak shift and a strong suppression of radial breathing modes (Figure 3a) were observed. Such effects were also reported for gate-doped SWNTs[8] and SWNTs filled with acceptors[9] and are due to depletion of the first Van-hove singularity of the valence band.

Secondly, the acidification of the suspension induces a strong upshift and a moderate suppression of D- and 2D modes, which was also observed for SWNTs doped by filling with acceptors.[9]

Regarding the G-mode region, it is widely known,[10] that the doping of single-walled carbon nanotubes leads to a strong upshift and a moderate suppression of G-mode. However, no

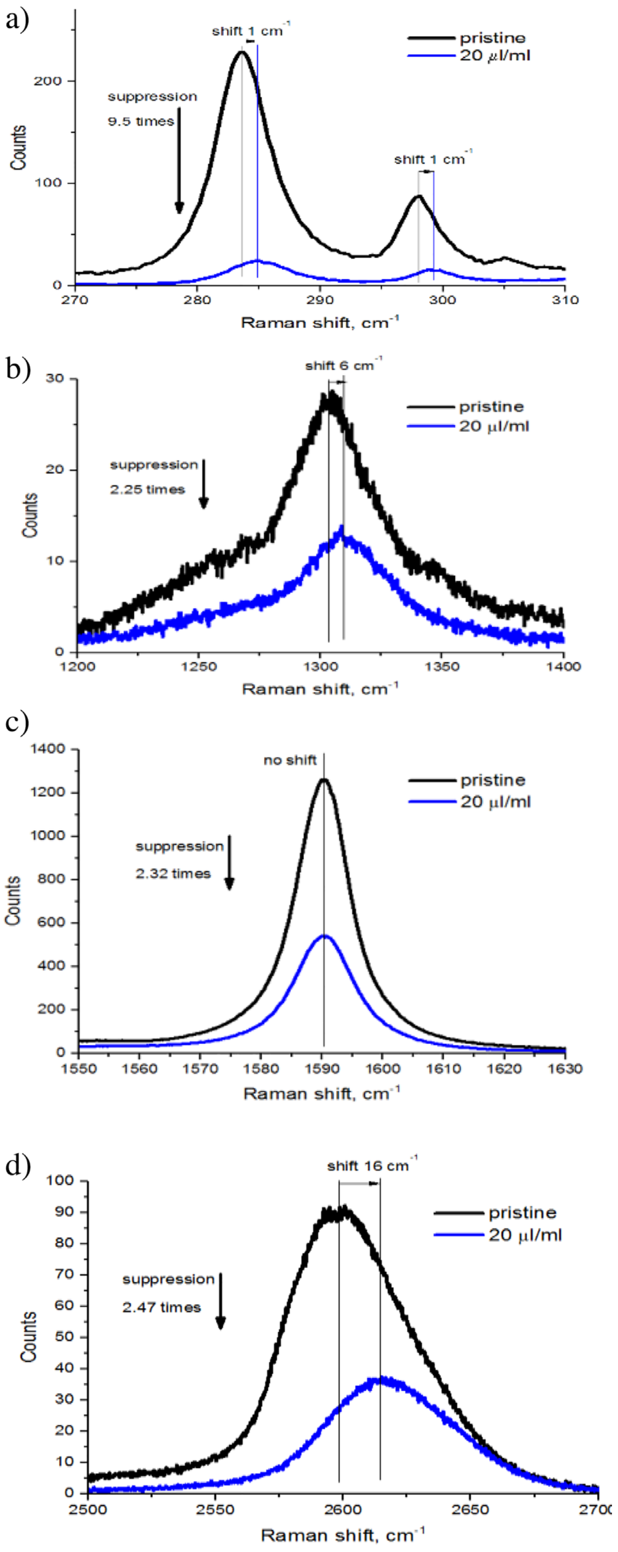

Figure 3. Changes in Raman spectra of SWNTs due to adding of HCl to suspension. (a) RBM frequency region, (b) D-mode frequency region, (c) G-mode frequency region, (d) 2D-mode frequency region.

upshift of the G mode was observed in this work after adding of HCl to the suspension, although, the suppression of G-mode is seen.

It is revealed, that acidification does not change the defectiveness of nanotubes, since the intensity of "defective" D-mode in the Raman spectrum does not increase with increasing of HCl concentration, even in comparison with the G-mode. Thus, the new peaks in the PL spectra can not be attributed to acid-induced defect levels of carbon nanotubes.

3.3. Optical Absorption Measurements

The most notable changes in the optical absorption spectra due to the acidification are a strong suppression of the first optical transition and a weak suppression of the second optical transition. Such phenomena are also widely detected for doped nanotubes[3,11] and are explained by depletion of Van-Hove singularities.

The spectrum of optical absorption of ensemble of SWNTs includes a number of overlapping peaks, making their identification complicated. Nevertheless, one can observe a hint on the appearance of a new absorption peak at 1160 nm induced by the acidification. Taking into account the difference between positions of E_{11}-exciton absorption peak (990 nm, Figure 1) and the E_{11}-exciton emission peak (985 nm, **Figure 4**), we tend to assume that the new absorption peak at 1160 nm in Figure 4 and the emission peak at 1155 nm in Figure 1 have the same physical origin and correspond to the same energy level.

4. Discussion

The similarities have been observed of spectroscopic changes caused by acidification, filling with acceptors, and gate-doping. This confirms, that HCl really dopes nanotubes. But behavior of G-mode in case of HCl treatment is curious, making this topic interesting for further investigations.

An appearance of new peaks in PL spectra and, apparently, in optical absorption spectra are caused by impact of HCl on the

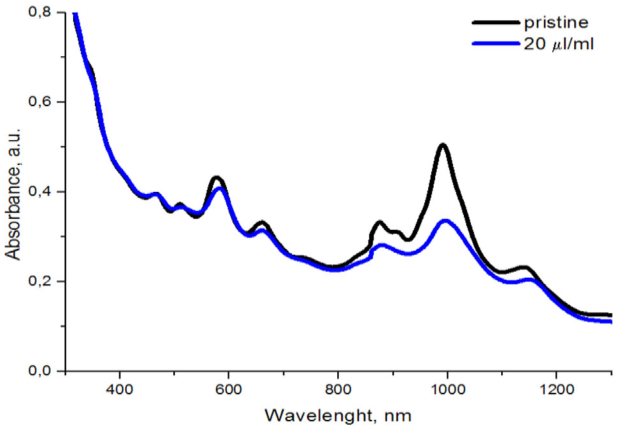

Figure 4. Changes in optical absorption spectrum of SWNT due to adding of HCl to suspension.

Table 1. Energy separation of trion and bright exciton energy levels.

	Experiment (this work)	Experiment[12]	Theory[5]
(6,5)	185 meV	190 meV	201 meV
(6,4)	222 meV	220 meV	232 meV

nanotubes. We demonstrated that these new peaks do not correspond to any new acid-induced defect energy levels. Instead, we assume, that the new peaks correspond to trion levels in carbon nanotubes doped by HCl in suspension.[5,12] Trion is a quasi-particle consisting of two holes and one electron. Introduction of acceptors into nanotubes leads to p-type doping, and to excess of holes.

Comparison of theoretical calculations with the measured energy difference between the trion level and the bright exciton level for (6,4) and (6,5) nanotubes confirms such assumption (see **Table 1**). Experimental values obtained in work [12] are also shown.

The mismatch between the theoretical and experimental values (about 5–7%) can be caused by the influence of surfactants on the peaks positions[6] and the partial overlapping of the trion peaks with the phonon side-band peak and the main excitonic peaks. Moreover, in this work, due to the low quantum yield, we were obligated to use quite wide slits in the PL measurements, missing resolution. Due to this an accurate estimation of peak position is complicated.

The total PL brightness depends not only on purely physical reasons, but also on the aggregation processes,[13] since acids impact the effectiveness of surfactant micelle formation.[14]

According to literature,[5,12,15] the acid treatment doping occurs due to interaction of H^+ ions with the walls of carbon nanotubes. However, it is rarely mentioned why the acid residue does not neutralize the influence of H^+ ions. We suppose that Cl^- ions in the suspension do not cancel the impact of H^+ ions on the properties of SWNTs, because sodium cholate molecules, which surround the nanotubes in the suspension, do not allow the big Cl^- ions to achieve nanotube, but miss small H^+ ions. Moreover, sodium cholate is a polar molecule with a positively tail directed outward the nanotube, which creates an additional hurdle for the negative Cl^- ions.

5. Conclusions

Acidification of SWNT suspension leads to doping of nanotubes. The corresponding spectroscopic fingerprints are appearance of trion peaks in PL spectra, shift and suppression of Raman modes, and suppression of the band corresponding to the first optical transition in optical absorption spectra.

Acknowledgement

The work was supported by project 15-12-30041 of Russian Science Foundation.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

carbon nanotubes, doping, photoluminescence, trions

Received: June 4, 2017
Revised: July 31, 2017

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