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Oxygen Defects in Single-Wall Carbon Nanotubes for Near-Infrared Light Emitters

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A new peak with an increased intensity was observed in the photoluminescence (PL) spectra of single-walled carbon nanotubes (SWCNTs), exposed to UV irradiation in the presence of sodium hypochlorite. It was concluded on the basis of the spectroscopic data that the new PL peak is associated with oxygen defects in the SWCNT structure. The impact of environmental acidity on the optical properties of oxygen-doped SWCNTs (O-SWNTs) was investigated. An increased sensitivity of the new PL peak to the pH of the medium was observed. It was concluded that the usage of a pH-neutral medium is of crucial importance for the creation of IR light sources based on O-SWNTs.

Keywords: single-walled carbon nanotubes, photoluminescence, localized exciton, acidity, infrared light emitters.

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Introduction

Single-wall carbon nanotubes (SWCNT) — quasi-one-dimensional cylindrical carbon structures demonstrating stable exciton luminescence even at room temperature [1]. The dependence of the wavelength of the emitted light on the chirality of the SWCNT, denoted by the chiral indices (n, m), theoretically allows the use of the SWCNT to create radiation sources with almost any desired wavelength in the range from 800 to 2500nm [2]. However, SWCNTs have a surprisingly low photoluminescence quantum yield for a direct semiconductor, which is only a few percent, which limits the possibilities of using SWCNTs to create radiation sources [1]. There are two main reasons for the low quantum yield of photoluminescence (FL) of SWCNTs: a) free drift of excitons, leading to luminescence quenching at the ends of the CNTs and other centers of FL quenching [3], and b) the presence of a dark exciton state in the energy exciton spectrum of the SWCNT, which has less energy than the light exciton [4].

One of the possible ways to resolve these limitations is to introduce zero-dimensional quantum defects into the structure of the SWCNT due to the covalent attachment of functional groups to their surface [5–8]. The presence of a functional group leads to a distortion of the local potential, in which excitons can have states other than exciton states in the undoped part of the SWCNT [5–38]. Excitons localized in an artificially created defective potential do not drift along the SWCNT and are not subject to scattering at the centers of FL quenching. In addition, the energy gap between light and dark exciton states in the local potential may be smaller than in the non-functional region of the SWCNT [23,32]. Taken together, these factors lead to an increase in the brightness of exciton luminescence of SWCNT, which makes functionalized SWCNTs a promising material for creating IR radiation sources in the near-IR region [15,39,40].

In the context of the creation of IR sources based on SWCNT, an important role is played not only directly by the ability of SWCNT to emit intense light, but also by the sensitivity of the optical properties of SWCNT to the local environment. Indeed, the influence of the local environment on the excitonic luminescence of underformed SWCNTs has been studied in sufficient detail [41–44]. In particular, it was found that the brightness of the photoluminescence of the SWCNT strongly depends on the acidity of the environment [45,46]. The prospects of SWCNT with embedded zero-dimensional quantum defects as a light source in the near IR range makes the question of the sensitivity of zero-dimensional excitons to the local environment, in particular, to the acidity of the medium, relevant.

In this paper, we optimized the method of oxygen doping of the SWCNT, which allowed us to increase the brightness of the FL SWCNT. For the first time, we investigated the effect of medium acidity on the brightness of one-dimensional and zero-dimensional excitons in SWCNT functionalized with oxygen. An increased sensitivity of exciton levels introduced by oxygen doping to local environmental conditions was found in comparison with freely drifting excitons.

Materials and methods

Commercially available SWCNT powder (CoMoCat) was used as the starting material. SWCNT was suspended in a 2% aqueous solution of a surfactant (sodium lauryl sulfate), after which ultrasonic treatment of the suspension was carried out for 4 h. Ultracentrifugation of the suspension at an acceleration of 100000 g for 1 h was carried out to separate the single SWCNTs from the beams. The supernatant was used for further work.

The SWCNT functionalization technology with oxygen in this paper is based on the method published in [9]. To prepare for functionalization, the resulting SWCNT suspension was diluted with distilled water 10 times to ensure the concentration of surfactant at the level of 0.2%. 50 μl of an aqueous solution of sodium hypochlorite (NaOCl GOST A, diluted in distilled water in 10^5 times) was added to 1 ml of the suspension in a quartz cell. After that, the cuvette was placed in a bactericidal chamber with a 10 W lamp J-10 Ozone (UVL, Russia). The degree of functionalization was regulated by the time of irradiation of the suspension with UV radiation.

The FL spectra were recorded by the InGaAs IR detector when excited by a tunable titanium-sapphire laser with a wavelength of 840 nm. The optical absorption spectra of light are typed on an optical path equal to 5 mm. To register the Raman spectra, the cuvette with suspension was placed at an angle of 10–15% to the horizontal, the focal length was selected so that the laser band was located at a distance of 2–3 mm from the upper face. The Raman spectra were recorded at a wavelength of exciting radiation equal to 532 nm.

Results and discussion

Fig. 1, *a* shows the FL spectra of the initial SWCNT (black line) and O-SWCNT obtained with different duration of the functionalization reaction. As the duration of UV irradiation increases, the suppression of the PL peak with a position of 980 nm corresponding to the radiative recombination of an exciton freely drifting along the one-dimensional SWCNT (1D) is observed. In addition, a new photoluminescent peak of 0D with a wavelength of 1130 nm is observed in doped SWCNTs, the intensity of which increases during the first 25 min of UV irradiation, and then begins to decrease. The spectral position of this peak corresponds to the values previously obtained experimentally and theoretically calculated for the energy of excitons localized in a zero-dimensional defect potential in the vicinity of an oxygen atom covalently attached to the surface of SWCNT-(6,5) [5,36]. Also, a less pronounced spectral feature with a position of 1050 nm is observed in the spectra of doped SWCNT, which corresponds to the radiative recombination of zero-dimensional exciton states in O-SWCNT-(6,4).

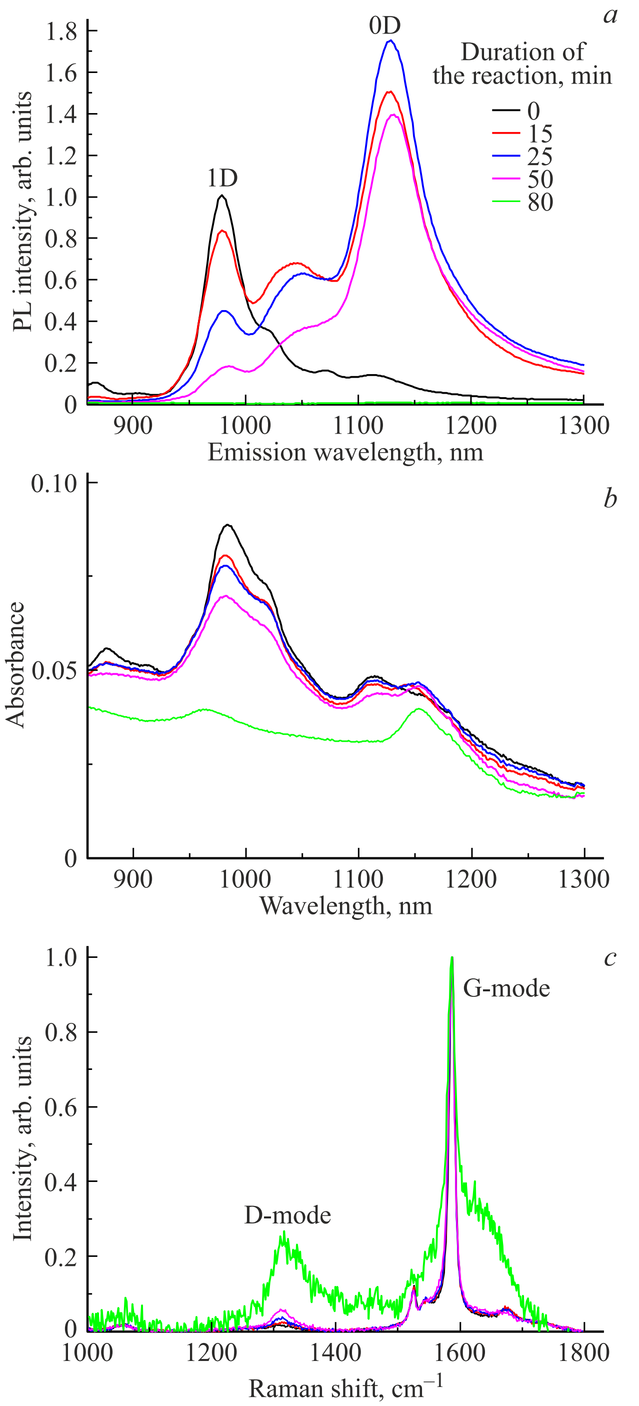

Figure 1. FL (*a*), OPS (*b*), Raman (*c*) SWCNT spectra at different durations of oxygen functionalization reaction.

In the optical absorption spectra of light in the SWCNT, the appearance of a new spectral feature is also observed when doped with oxygen (Fig. 1, *b*), the spectral position of which is close to the position of the peak FL 0D. However, the dependence of the amplitude of the new peak of the OPS on the duration of the reaction does not show an inflection in the region of 25 min, but continues to grow. So, after 80 min of the reaction, a new peak of the OPS is most

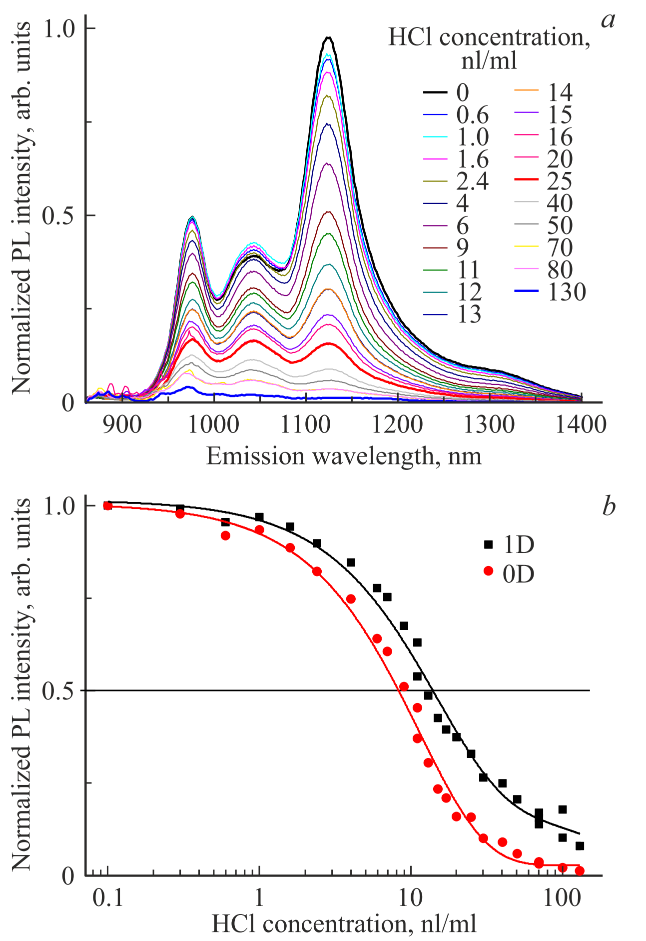

Figure 2. (*a*) FL O-SWCNT spectra before and after the addition of hydrochloric acid in various concentrations to the suspension, (*b*) dependence of the intensity of 1D and 0D FL peaks on the concentration of hydrochloric acid.

clearly expressed in the spectra of the OPS in the region of 1140–1150 nm, while the FL signal of the corresponding sample is indistinguishable from the detector noise (Fig. 1, *a*, green line).

The connection of new spectral features in the FL and OPS spectra with oxygen defects in the SWCNT structure is also confirmed by Raman spectroscopy. Fig. 1, *c* shows the Raman spectra of the suspension of the initial and to varying degrees functionalized SWCNTs. With an increase in the duration of the oxygen functionalization reaction, there is an increase in the defective (D) modes compared to tangential (G) fashion, which indicates an increase in the density of defects on the SWCNT

To study the sensitivity of FL 0D excitons to the acidity of the environment, hydrochloric acid (HCl) was added to the O-SWCNT suspension. Fig. 2, *a* shows the photoluminescence spectra of O-SWCNT suspensions with different concentrations of hydrochloric acid. With an increase in HCl concentration, both 0D and 1D FL peaks are suppressed, but the changes in the long-wavelength part of the spectrum are more pronounced. Indeed, if the 0D peak is about 2 times more intense than the 1D peak before the addition of hydrochloric acid, then at a HCl concentration of 25,nl/ml, these peaks have approximately the same intensity, and at a very high HCl concentration (130,nl/ml), the 0D peak is almost completely suppressed, while 1D the peak is still observed.

A significant difference in the sensitivity of 1D and 0D exciton transitions to the acidity of the environment is more clearly shown in Fig. 2, *b*, where the dependence of the intensities of these peaks on the concentration of hydrochloric acid in the suspension is constructed.

The discovered phenomenon of the dependence of the intensity of the FL peaks on the acidity of the medium can be used as the basis for fully optical pH sensors. On the other hand, the data obtained indicate that it is necessary to take into account the high sensitivity of 0D excitons to the acidity of the local environment when creating IR radiation sources based on O-SWCNT.

Conclusion

In this paper, we have optimized the method of functionalization of SWCNT and demonstrated the possibility of increasing the brightness of FL SWCNT due to the introduction of zero-dimensional quantum defects in their structure. For the first time, we found an increased sensitivity of zero-dimensional excitons in the SWCNT to the acidity of the medium, which should be taken into account when creating radiation sources in the near-infrared region. In addition, the effect of the dependence of the ratio of 1D and 0D exciton peaks in the FL spectra of O-SWCNT on the acidity of the medium can be used to create fully optical pH sensors.

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Conflict of interest

The authors declare that they have no conflicts of interest.

References

[1] Y.J. Miyauchi. Mater. Chem. C, **1** (40), 6499 (2013). DOI: 10.1039/c3tc00947e
[2] R.B. Weisman, S.M. Bachilo. Nano Lett., **3** (9), 1235 (2003). DOI: 10.1021/nl034428i
[3] T. Hertel, S. Himmelein, T. Ackermann, D. Stich, J. Crochet. ACS Nano, **4** (12), 7161 (2010). DOI: 10.1021/nn101612b

[4] M.S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio Annu. Rev. Phys. Chem., **58** (1), 719 (2007). DOI: 10.1146/annurev.physchem.58.032806.104628

[5] S. Ghosh, S.M. Bachilo, R.A. Simonette, K.M. Beckingham, R.B. Weisman. Science, **330** (6011), 1656 (2010). DOI: 10.1126/science.1196382

[6] Y. Miyauchi, M. Iwamura, S. Mouri, T. Kawazoe, M. Ohtsu, K. Matsuda. Nat. Photonics, **7** (9), 715 (2013). DOI: 10.1038/nphoton.2013.179

[7] Y. Piao, B. Meany, L.R. Powell, N. Valley, H. Kwon, G.C. Schatz, Y. Wang. Nat. Chem., **5** (10), 840 (2013). DOI: 10.1038/nchem.1711

[8] T. Shiraki, T. Shiraishi, G. Juhász, N. Nakashima. Sci. Rep., **6**, 28393 (2016). DOI: 10.1038/srep28393

[9] C.W. Lin, S.M. Bachilo, Y. Zheng, U. Tsedev, S. Huang, R.B. Weisman, A.M. Belcher. Nat. Commun., **10** (1), (2019). DOI: 10.1038/s41467-019-10917-3

[10] Y. Iizumi, M. Yudasaka, J. Kim, H. Sakakita, T. Takeuchi, T. Okazaki. Sci. Rep., **8** (1), 1 (2018). DOI: 10.1038/s41598-018-24399-8

[11] H. Kwon, M. Kim, B. Meany, Y. Piao, L.R. Powell, Y. Wang. Phys. J. Chem. C, **119** (7), 3733 (2015). DOI: 10.1021/jp509546d

[12] J. Ramirez, M.L. Mayo, S. Kilina, S. Tretiak. Chem. Phys., **413**, 89 (2013). DOI: 10.1016/j.chemphys.2012.10.010

[13] N.F. Hartmann, S.E. Yalcin, L. Adamska, E.H. Hároz, X. Ma, S. Tretiak, H. Htoon, S.K. Doorn. Nanoscale, **7** (48), 20521 (2015). DOI: 10.1039/c5nr06343d

[14] S. Kilina, J. Ramirez, S. Tretiak. Nano Lett., **12** (5), 2306 (2012). DOI: 10.1021/nl300165w

[15] A.H. Brozena, M. Kim, L.R. Powell, Y.H. Wang. Nat. Rev. Chem., **3** (6), 375 (2019). DOI: 10.1038/s41570-019-0103-5

[16] B.J. Gifford, S. Kilina, H. Htoon, S.K. Doorn, S. Tretiak. Acc. Chem. Res., **53** (9), 1791 (2020). DOI: 10.1021/acs.accounts.0c00210

[17] H. Kwon, M. Kim, B. Meany, Y. Piao, L.R. Powell, Y. Wang. J. Phys. Chem. C, **119** (7), 3733 (2015). DOI: 10.1021/jp509546d

[18] X. He, L. Sun, B.J. Gifford, S. Tretiak, A. Piryatinski, X. Li, H. Htoon, S.K. Doorn. Nanoscale, **11** (18), 9125 (2019). DOI: 10.1039/c9nr02175b

[19] S. Settele, F.J. Berger, S. Lindenthal, S. Zhao, A. Ali, E. Yumin, N.F. Zorn, A. Asyuda, M. Zharnikov, A. Högele, J. Zaumseil. Nat. Commun., (2021), 1 (2021). DOI: 10.1038/s41467-021-22307-9

[20] A.H. Brozena, J.D. Leeds, Y. Zhang, J.T. Fourkas, Y. Wang. ACS Nano, **8** (5), 4239 (2014). DOI: 10.1021/nn500894p

[21] T. Shiraki, Y. Miyauchi, K. Matsuda, N. Nakashima. Acc. Chem. Res., **53** (9), 1846 (2020). DOI: 10.1021/acs.accounts.0c00294

[22] B.J. Gifford, X. He, M. Kim, H. Kwon, A. Saha, A.E. Sifain, Y. Wang, H. Htoon, S. Kilina, S.K. Doorn, S. Tretiak. Chem. Mater., **31** (17), 6950 (2019). DOI: 10.1021/acs.chemmater.9b01438

[23] Y. Kim, K.A. Velizhanin, X. He, I. Sarpkaya, Y. Yomogida, T. Tanaka, H. Kataura, S.K. Doorn, H. Htoon. J. Phys. Chem. Lett., **10** (6), 1423 (2019). DOI: 10.1021/acs.jpclett.8b03732

[24] H. Onitsuka, T. Fujigaya, N. Nakashima, T. Shiraki. Chem. — A Eur. J., **24** (37), 9393 (2018). DOI: 10.1002/chem.201800904

[25] M. Nutz, J. Zhang, M. Kim, H. Kwon, X. Wu, Y. Wang, A. HÖgele. Nano Lett., **19** (10), 7078 (2019). DOI: 10.1021/acs.nanolett.9b02553

[26] X. He, N.F. Hartmann, X. Ma, Y. Kim, R. Ihly, J.L. Blackburn, W. Gao, J. Kono, Y. Yomogida, A. Hirano, T. Tanaka, H. Kataura, H. Htoon, S.K. Doorn. Nat. Photonics, **11** (9), 577 (2017). DOI: 10.1038/nphoton.2017.119

[27] A. Saha, B.J. Gifford, X. He, G. Ao, M. Zheng, H. Kataura, H. Htoon, S. Kilina, S. Tretiak, S.K. Doorn. Nat. Chem., **10**, 1089 (2018). DOI: 10.1038/s41557-018-0126-4

[28] X. Ma, N.F. Hartmann, J.K.S. Baldwin, S.K. Doorn, H. Htoon. Nat. Nanotechnol., **10** (8), 671 (2015). DOI: 10.1038/nnano.2015.136

[29] M.E. Sykes, M. Kim, X. Wu, G.P. Wiederrecht, L. Peng, Y.H. Wang, D.J. Gosztola, X. Ma. ACS Nano, **13** (11), 13264 (2019). DOI: 10.1021/acsnano.9b06279

[30] H. Kwon, A. Furmanchuk, M. Kim, B. Meany, Y. Guo, G.C. Schatz, Y. Wang. J. Am. Chem. Soc., **138** (21), 6878 (2016). DOI: 10.1021/jacs.6b03618

[31] X. He, K.A. Velizhanin, G. Bullard, Y. Bai, J.-H. Olivier, N.F. Hartmann, B.J. Gifford, S. Kilina, S. Tretiak, H. Htoon, M.J. Therien, S.K. Doorn. ACS Nano, (July), acsnano.8b02909 (2018). DOI: 10.1021/acsnano.8b02909

[32] N.F. Hartmann, K.A. Velizhanin, E.H. Haroz, M. Kim, X. Ma, Y. Wang, H. Htoon, S.K. Doorn. ACS Nano, **10** (9), 8355 (2016). DOI: 10.1021/acsnano.6b02986

[33] M. Iwamura et al. ACS Nano, **8** (11), 11254 (2014). DOI: 10.1021/nn503803b

[34] T. Shiraishi, G. Juhász, T. Shiraki, N. Akizuki, Y. Miyauchi, K. Matsuda, N. Nakashima. J. Phys. Chem. C, **120** (29), 15632 (2016). DOI: 10.1021/acs.jpcc.5b07841

[35] X. Ma, J.K.S. Baldwin, N.F. Hartmann, S.K. Doorn, H. Htoon. Adv. Funct. Mater., **25** (39), 6157 (2015). DOI: 10.1002/adfm.201502580

[36] X. Ma, L. Adamska, H. Yamaguchi, S.E. Yalcin, S. Tretiak, S.K. Doorn, H. Htoon. Nat. Nanotechnol., **7** (July), 1 (2015). DOI: 10.1038/nnano.2011.227

[37] C.F. Chiu, W.A. Saidi, V.E. Kagan, A. Star. J. Am. Chem. Soc., **139** (13), 4859 (2017). DOI: 10.1021/jacs.7b00390

[38] N. Akizuki, S. Aota, S. Mouri, K. Matsuda, Y. Miyauchi. Nat. Commun., **6**, 1 (2015). DOI: 10.1038/ncomms9920

[39] J. Zaumseil. Adv. Opt. Mater., **10** (2), (2022). DOI: 10.1002/adom.202101576

[40] X. He, H. Htoon, S.K. Doorn, W.H.P. Pernice, F. Pyatkov, R. Krupke, A. Jeantet, Y. Chassagneux, C. Voisin. Nat. Mater., **17** (8), 663 (2018). DOI: 10.1038/s41563-018-0109-2

[41] C. Fantini, A. Jorio, M. Souza, M.S. Strano, M.S. Dresselhaus, M.A. Pimenta. Phys. Rev. Lett., **93** (14), 1 (2004). DOI: 10.1103/PhysRevLett.93.147406

[42] F. Wang, M.Y. Sfeir, L. Huang, X.M.H. Huang, Y. Wu, J. Kim, J. Hone, S. O'Brien, L.E. Brus, T.F. Heinz. Phys. Rev. Lett., **96** (16), 1 (2006). DOI: 10.1103/PhysRevLett.96.167401

[43] J.G. Duque, M. Pasquali, L. Cognet, B. Lounis. ACS Nano, **3** (8), 2153 (2009). DOI: 10.1021/nn9003956

[44] Y. Miyauchi, R. Saito, K. Sato, Y. Ohno, S. Iwasaki, T. Mizutani, J. Jiang, S. Maruyama. Chem. Phys. Lett., **442** (4–6), 394 (2007). DOI: 10.1016/j.cplett.2007.06.018

[45] T. Koyama, S. Shimizu, Y. Miyata, H. Shinohara, A. Nakamura. Phys. Rev. B — Condens. Matter Mater. Phys., **87** (16), 165430 (2013). DOI: 10.1103/PhysRevB.87.165430

[46] T. Eremin, E. Obraztsova. Phys. Status Solidi Basic Res., **255** (1), 1700272 (2017). DOI: 10.1002/pssb.201700272