Influence of heteroatoms on optical properties and photoluminescence kinetics of carbon dots

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Abstract. Carbon dots have attracted much attention due to the ease of synthetic methods and their stable photoluminescence with relatively high quantum yield. By the doping of carbon dot by heteroatoms the optical transitions can be tuned in a wide spectral range. In this work, the impact of heteroatoms on the optical properties of carbon dots has been investigated: the appearance of the luminescent states attributed to the CD surface states and the dependence of the photoluminescence lifetime versus emission wavelength have been revealed.

1. Introduction
Carbon dots (CDs) are novel class of fluorophores which possess unique properties such as tunable photoluminescence, high quantum yield, relatively high photostability and possibility of room-temperature phosphorescence realization. Moreover, another significant characteristic of CDs is an ability of doping their core and surface by a variety of heteroatoms, which allows the altering their optical transitions in a wide range. In recent studies, influence of doping by nitrogen, sulfur and phosphorus on optical properties of CDs is widely investigated [1-3]. However, it is under discussion how the doping changes not only CDs' energy structure, but also the kinetics of creation and relaxation of charge carriers. Understanding this mechanism that originates in CDs will help to predict and control their properties by the heteroatom doping. In this work we will discuss the impact of sulfur compounds on CDs' optical properties with focus on photoluminescence kinetics.

2. Experimental
2.1. Synthesis of CDs
The CDs were synthesized based on a solvothermal procedure described in [4]. Under solvothermal conditions, the nitrogen or/and sulfur compound were mixed with citric acid and then dissolved in dimethylformamide. Then the solution was to a Teflon lined autoclave and heated at 160°C for 6 hours. After the reaction, autoclave was cooled to a room temperature. Urea, thiourea and thioacetamide were
used as a heteroatom source; the synthesized CDs were designated hereafter as CD-u, CD-tu, and CD-ta, respectively. For further investigation the synthesized product was diluted to obtain appropriate optical density of the CD solution.

2.2. Experimental setup
Absorption (Abs) and photoluminescence (PL) spectra were obtained by a spectrophotometer UV-3600 (Shimadzu) and fluorescence spectrophotometer FP-8200 (Jasco), respectively. PL decay measurements were carried out by MicroTime 100 (PicoQuant) with excitation wavelength of 405 nm in spectral range of 430-780 nm. For the spectral selection the interferential filters with full width at half maximum (FWHM) of 10 nm were used.

3. Results
The Abs spectra of the samples presented in Fig. 1a possess the band at 350 nm which is typical for the CDs and attributed to the n - π transition in the CD core. The position of low-energy band attributed to the surface states, e.g. originated from the dopants, is redshifted in the set CD-ta, CD-tu, and CD-u. The PL spectra of CDs presented in Fig. 1b follow the Abs spectra trend: the PL band is centered at 470, 485, and 495 nm of the CD-ta, CD-tu, and CD-u, respectively. The PL decay of the CDs (Fig. 1c) in the wide spectral range can be approximated by multi-exponential function with average PL lifetime of 9.4, 10.1, and 11.0 ns for CD-ta, CD-tu, and CD-u, respectively.

![Figure 1](image.png)

Figure 1. Abs (a), PL (b) spectra (excitation wavelength of 405 nm), and PL decay curves (c) of CD-ta (blue), CD-tu (green), and CD-u (orange).

To understand the process of radiative relaxation of charge carriers in the synthesized CDs the spectrally resolved PL decay measurements were carried out. Average PL lifetimes vs PL spectra of the CDs are presented in Fig. 2.
Figure 2. Average PL lifetime (squares) vs Abs (grey dashed line) and PL (grey solid line) spectra of CD-ta (a), CD-tu (b), and CD-u (c).

The PL lifetime measured in narrow spectral range within CDs’ PL band depends on the emission wavelength, which confirms that the PL signal originates from the CDs instead of molecular fluorophores. At the same time, the PL lifetime behavior is complicated and varies for the synthesized CD set. For the CD-ta (Fig.2a) the PL lifetime decreases with the increase of the emission wavelength, which may be attributed to the influence of trap-states to the radiative relaxation process. For the CD-tu (Fig.2b) the PL lifetime reflects both Abs and PL bands shape with its prolonged value in the low-energy spectral region. For the CD-u (Fig.2c) the increase of the PL lifetime with the emission wavelength is observed, which is presumably due to the nonradiative energy transfer of the photoexcitation within the CD. These results indicate the complexity of the energy structure and, in particular, of the carrier relaxation processes in the investigated CDs.

In conclusion, it is shown that the presence of heteroatoms in the CDs may result in the altering of their optical properties: appearance of the luminescent states with lower energies, and complicated dependence of the PL lifetime vs emission wavelength. The revealing of the physical mechanism of the observed optical properties requires further investigation in the light of the CD’ utilization in the wide field of photonics, sensing, and bio applications.

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