Synthesis and energy structure of optical transitions of the nitrogen and sulfur co-doped carbon dots

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Abstract. A green and efficient strategy was developed for one-step synthesis of sulfur and nitrogen co-doped carbon dots using urea, thiourea and thioacetamide as nitrogen and sulfur source and citric acid as carbon source. The influence of nitrogen and/or sulfur doping of the carbon dots on their optical transitions is investigated. The as synthesized carbon dots are demonstrated to possess redshifted photoluminescence with relatively high intensity. It is demonstrated that the presence of heteroatoms leads to the red shift of the photoluminescence band and increase of the crystalline phase inherent to amorphous carbon.

1. Introduction

Carbon dots (CDs) are novel fluorophores in the family of carbon nanomaterials – graphene, fullerenes, nanotubes, nanodiamonds, etc. [1] CDs possess unique optical properties, such as tunable photoluminescence, high quantum yield, relatively high photostability. Moreover, the ability of doping CD core and surface by different heteroatoms is a very essential characteristic and may expand the optical transitions range.

Single atom doping can effectively improve the emission properties of CDs. The content of heteroatom in CDs plays an important role in generating high PL quantum yield efficiency, the higher the heteroatom content on CDs, the more surface states get formed on CDs resulting enhancement of optical properties. Nitrogen atoms are well known as dopants of the CDs and introduce additional energy levels into the electronic structure resulting in the CDs emission band shift [2]. Nitrogen and carbon atoms have very close similarity, due to this N-doping is the most widely used way to improve the photoluminescence (PL) properties of CDs. The nitrogen atom changes the inner structure by injecting electrons into CDs, which substantially improve their optical properties. Recently, it was shown [3], that the emission of the N-doped CDs interacting with sulfur compounds is further shifted to the red spectral region. Comparing to the intensively researched N-doped CDs, CDs containing S atoms have been rarely studied. In recent years, S-doped CDs were synthesized from different precursors: sulfuric acid [4], sodium citrate [5], etc. The S-doped CDs possess a relatively high fluorescence QY of ~12% without any surface passivation at the 350 nm excitation. At the same time, efficient routes to enhance the fluorescent properties of CDs remained a challenge. Therefore, combination of heteroatoms has gained much attention in recent years, because it can create a unique electronic structure, due to the interdependent effect between the doped atoms in CDs [6].
Other approach of the heteroatom doping is the implementation of the co-doping multiplex heteroatoms within one precursor molecule. In particular, N and S co-doped CDs have been actively investigated recently and found to be the best combination of heteroatoms to shift PL to the red spectral region [1]. Considering the time-saving process, low toxicity and enhanced fluorescence properties enable the as-prepared CDs further to be used in various applications, such as sensing and photonics field [7]. However, the energy-level structure of doped CDs is still under discussion. In this work we investigate the influence of the heteroatoms on the optical transitions in CDs synthesized from various precursors, containing N and S atoms.

2. Experimental
Chemicals were purchased from Merck and used without additional purification. Poly(p-phenol)-lined stainless steel autoclaves for solvothermal reaction were purchased from Komviks. Raman spectra were obtained by InVia (Renishaw) with 514 nm excitation. Absorption (Abs) spectra were obtained by a spectrophotometer UV-3600 (Shimadzu). Photoluminescence (PL) and PL excitation (PLE) spectra were obtained by spectrofluorometer FP-8200 (Jasco).

3. Results
CDs were synthesized by a modified procedure based on [8]. Urea, thiourea and thioacetamide were used as a heteroatom source. These compounds were mixed with citric acid and dissolved in dimethylformamide (DMF) under solvothermal conditions. The solution was heated in a poly(p-phenol)-lined stainless steel autoclave at 160°C during 6 h, following by cooling down to room temperature. Thus, three samples of CDs, termed as CD-u, CD-tu, and CD-ta, were obtained from urea, thiourea and thioacetamide, respectively. As a reference sample, (termed CD-e), CDs synthesized from citric acid and ethylenediamine by procedure described in [9] was used. For further investigation the synthesized CD solution were diluted to obtain appropriate CD optical density.

![Figure 1(a, b). (a) Photos of the CD-u, CD-ta, and CD-tu under 405 (lower beam) and 532 (upper beam) nm excitation; (b) Typical Raman spectra of CD-e and CD-u.](image)

All CDs synthesized in DMF possess an excitation-dependent emission, as can be seen in the Fig.1a, where the samples demonstrate emission at different wavelengths excited by 450 and 514 nm diode lasers. Typical Raman spectra (Fig.1b) of CD-e and doped CDs possess well known vibrational modes of disordered graphitic materials [10], which are assigned to D band (~1350 cm⁻¹), G band (~1585 cm⁻¹) and amorphous carbon (area of 1480-1530 cm⁻¹). Increased D/G ratio for CD-u, CD-tu, and CD-ta samples suggests that the heteroatom doping can introduce more defects into the graphitic structure of the CD core together with formation of additional surface groups. Therefore, we believe that the defects introduced by implementation of urea, thiourea and thioacetamide instead of ethylenediamine as heteroatoms source influence the CD energy structure and the optical transitions contributing to the PL signal.
FTIR spectra (Fig. 2) contain a set of peaks: 658, 1062, 1091, 1253, 1386, 1498, 1653, 2865, and 2930 cm\(^{-1}\), which are common for all the CD samples. This set is typical for the cyclic organic compounds with amino and hydroxyl groups. In the FTIR spectra of CD-tu and CD-ta the peak at 1718 cm\(^{-1}\), which can be attributed to the \(\text{C}=\text{O}\) vibration in carboxylic group, is more pronounced compared to CD-u sample. Peaks in the area of 1400-1500 cm\(^{-1}\) may be attributed to the stretching of N or S single bonds with C atoms. It also should mentioned, that the FTIR spectra of CD-u and CD-ta possess the peaks at 977 and 2775 cm\(^{-1}\) together with the absence of the peak at 2055 cm\(^{-1}\), compared to CD-tu spectrum. Thus, we can assume that the optical parameters of the CD-u and CD-ta should be similar compared to the CD-tu sample.

The Abs spectra of all samples presented in Fig. 3a possess the band at 350 nm which is typical for the CDs and may be attributed to the n – π transition in the CD core according to Ref. [2]. The position and optical density of low-energy bands attributed to the edge and/or surface states, e.g. originated from the dopants, differ for all samples. For the CD-ta, CD-u, and CD-tu the second Abs band with increased optical density is observed at 440, 455, and 500 nm, respectively. For the CD-u there is an additional wide band at 600 nm. Comparison of the PLE spectra (Fig. 3b) monitored around 540-550 nm shows that the PL signal is determined by the additional energy levels. The PLE spectrum of CD-tu is more structured and contains set of narrow peaks around 450-520 nm, which can be related to the molecular moieties within CD, unlike the CD-e and CD-ta spectra. The PL band (Fig. 3c) of the doped CDs is redshifted compared to the CD-e, which is in accord with Abs and PLE spectra. The largest PL shift is demonstrated by CD-u and CD-ta while excited at 405 and 500 nm, respectively.
In conclusion, we investigated the impact of N- and S-doping of CDs on their photophysical properties. In our study it is shown that the presence of nitrogen or/and sulfur heteroatoms in the CDs leads to the increased volume of amorphous carbon phase and to the appearance of additional energy levels, which in turn results in the red shift of the PL band.

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