

Facile synthesis of tunable fluorescent carbon dots and their third-order nonlinear optical properties



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ABSTRACT

We report the synthesis and luminescent properties of carbon dots whose peak fluorescence emission are independent of excitation wavelength. Meanwhile, varying the concentrations of carbon dots can achieve a shift in the emission wavelength. Detailed structural characterization and optical properties of carbon dots with different concentrations were studied. Particularly, the blue-shifted excitation-independent emission peaks were observed when the concentration of carbon dots decreased. The decreased fluorescent properties were considered to originate from the surface modification of carbon dots. Additionally, we investigated the third-order nonlinear optical responses of carbon dots with different concentrations by Z-scan technique with single 190 fs laser pulses at 532 nm. It was found that both samples exhibited positive nonlinear refractivity and negative nonlinear absorption coefficient in the fs regime. These tunable optical properties would provide more possibilities for the utility of carbon dots in optical devices.

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1. Introduction

Photoluminescent carbon dots (CDs) have received considerable attention due to their low-toxic, multicolor emission, controlled surface chemistry, good solvent dispersability, excellent photostability as well as superior optical properties [1,2]. Moreover, the surface of CDs can easily be functionalized, doping with nitrogen and sulfur or metal ions may further alter the optical properties of the CDs or even add new functionalities [3–5]. Obtaining tunable fluorescence emission has been recognized as a key requirement for successfully implementing CDs in nearly all practical applications [6,7]. Many studies have reported CDs with tunable photoluminescence (PL) by varying the CDs chemical and physical properties. Jana et al. synthesized highly fluorescent carbon nanoparticles (FCDs) by carbohydrate carbonization method for biological labeling and imaging, which have the particle sizes between 1 and 10 nm and produce tunable emissions such as blue, green, yellow and red [8]. Hu et al. reported the tunable excitation-dependent fluorescence CDs across the entire visible spectrum

excited by white light [9]. Pang et al. prepared a series of CDs exhibiting various colors of excitation-independent fluorescence by varying their degree of surface oxidation and their size [10]. Although many reports have presented excitation-dependent fluorescence emission, typical significant decrease in fluorescence emission intensity [11–13], the excitation-independent fluorescence emission with shifts in the emission wavelength without compromising the peak emission intensity is rarely reported. Nonetheless, the properties of fluorescent CDs remain largely unexplored. So a significant amount of work is still highly needed in this area, including using facile method to achieve tunable PL emission wavelengths of CDs without compromising the peak emission intensity.

In recent years, in addition to the PL and electroluminescent properties of CDs have been thoroughly investigated, the nonlinear optical (NLO) properties of CDs have received some attention. As previous reported, CDs exhibited NLO properties significantly dependent on surface passivation and the nature of the organic moieties [14,15]. B.Bourlinos groups for the first time studied the NLO optical properties of CDs and boron doped CDs under 4 ns and 35 ps, 532 nm and 1064 nm laser excitation conditions by Z-scan technique. They attempted to explore the underlying physical mechanisms between the intrinsic nonlinear absorption and refraction properties of CDs [16–19]. Qiu et al. investigated nonlinear optical response of as-prepared CNDs with

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100 fs laser pulses at 800 nm by open-aperture Z-scan technique, the strong two photon absorption of CDs were observed [20]. At present, the study about NLO optical properties of CDs are still at the early stages of development, much work are highly needed in this area.

In this study, we prepared a series of CDs whose presented tunable excitation-independent fluorescence by simple adjustment of the concentrations. The prepared silane pre-functionalized CDs solution by hot-inject method were diluted by ethanol providing stable, optically transparent dispersions with different colors. The structure of CDs with different concentrations were studied using Fourier transform infrared spectra (FTIR), transmission electron microscope (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). In particular, the blue-shifted excitation-independent emissions peaks from 620 to 530 nm accompanied by remarkable increase in fluorescence emission intensity were observed when the concentration of CDs decreased. The quantum efficiency and the PL decay times of the as-prepared CDs were also varied. Specifically, we revealed that the decreased fluorescent properties of the CDs were considered to originate from the surface modification of CDs. In addition, we investigated the third-order nonlinear optical responses of silane pre-functionalized CDs with different concentrations by Z-scan technique with single 190 fs laser pulses at 532 nm. It was found that both CDs exhibited positive nonlinear refractivity and negative nonlinear absorption coefficient in the fs regime. Both the nonlinear refractivity and negative nonlinear absorption coefficient were decreased when the concentration of CDs decreased.

2. Experimental section

2.1. Materials

Anhydrous citric acid, ethyl alcohol, N-(β -aminoethyl)- γ -aminopropyl methyldimethoxy silane (AEAPMS) and all other chemicals were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). All the chemicals were of analytical grade and were used as received without any further purification.

2.2. Preparation of tunable luminescent CDs

The CDs were prepared by modifying a previous reported method.²¹ Briefly, 20 mL AEAPMS were placed into a three-necked flask and were degassed with nitrogen for 10 min. When the temperature reached 200 °C, 1.5 g citric acid dissolved uniformly with 4 mL ethanol was quickly injected into the solution with vigorous stirring. The mixture was kept at the temperature for 1 min, during which the solution changed from a colorless liquid to yellow and then finally dark brown clustered solid, indicating the formation of SiCDs (CDs). Subsequently, the CDs solution was cooled to room temperature and diluted to different concentrations with ethanol. Finally, the different concentrations of CDs solution were obtained (original concentration C), which were labeled as C, 1/2C, 1/5C, 1/10C, 1/20C respectively for convenience.

2.3. Characterization

Fluorescence spectra and PL QYs were recorded with a Horiba Jobin Yvon Fluoromax-4P spectrophotometer equipped with absolute QY measurement apparatus. For the UV/vis absorption, the UV-2600 spectrometer was used at room temperature. Time-resolved PL lifetime measurements were carried out using a time-correlated single-photon counting (TCSPC) lifetime spectroscopy system with a picosecond-pulsed diode laser (EPL-460 nm) as the single wavelength excitation light source. The TEM and high-

resolution TEM (HRTEM) measurements were carried out with a FEI Tecnai F20 performing with an acceleration voltage of 200 kV. In obtaining the Fourier transform infrared (FTIR) spectra, the sample was grounded with KBr power and was measured using Bruke Equinox 55 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) was carried out using an Axi Ultra DLD spectrometer with monochrome Al K α as the excitation source. The XRD patterns were obtained using an X-ray diffract meter (Bruker D8 Advance) in the 2θ range of 10–80° using Cu K α radiation with wavelength λ of 1.5406 Å. Temperature dependent emission spectra were measured with a Horiba Jobin–Yvon Fluorolog-3 FL3-211 spectrometer equipped with a 450W xenon lamp as the excitation source. The optical absorption was obtained by a Perkin Elmer Lambda 750 UV–vis Spectrometer. All the measurements were carried out at room temperature.

3. Results and discussion

The blue-Green, green, yellow-green, yellow, orange CDs with emissions at 530 nm, 550 nm, 575 nm, 605 nm, 620 nm respectively could be obtained by varying the concentrations from C to 1/20C, and were labeled as BG-CDs, G-CDs, YG-CDs, Y-CDs, O-CDs respectively for convenience. The relevant parameters for the various samples with different concentrations were summarized in Table S1 and are discussed in next section.

3.1. Characterization of CDs

The surface groups were identified by FTIR and XPS. Fig. 1 shows the variation of surface groups of a series of CDs. With varying the concentrations of CDs, no new IR peak appears, but the relative intensities of different peaks changed obviously. Typical signals for —NH_2 groups at 3450 cm^{-1} and the C=O vibration at 1654 cm^{-1} . In addition, CH_2 bending (1450 cm^{-1}), Si–O–Si stretching (1070–1098 cm^{-1}), and Si– CH_2 stretching (790 cm^{-1}) bands appeared in all spectra. Remarkably, the peak intensity of the Si–O–Si stretching group increased with the decrease of concentration of CDs, which was due to further modification. The chemical composition of CDs was further analyzed by a series of XPS analyses. The full XPS spectrum revealed that CDs is mainly composed of carbon, oxygen, silicon, and nitrogen in descending order of content (Fig. 2c). The C1s XPS spectra of CDs in Fig. 2d showed that the following contribution can be assigned: C=C (284.3 eV), C–O (285.7 eV) and Si– CH_2 (282 eV), which was well-consistent with FTIR spectra. Fig. S1 shows the XRD patterns of the CDs with

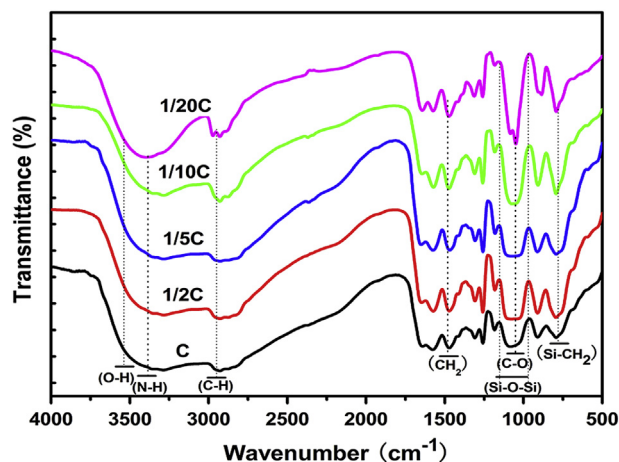


Fig. 1. FTIR spectra of CDs with different concentrations.

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