



Luminescence origin of carbon based dots obtained from citric acid and amino group-containing molecules



Qingqing Fang^a, Yongqiang Dong^{a,*}, Yingmei Chen^a, Chun-Hua Lu^a, Yuwu Chi^a, Huang-Hao Yang^a, Ting Yu^{b,**}

^a The Key Laboratory of Analysis and Detection Technology for Food Safety of the MOE and Fujian Province, State Key Laboratory of Photocatalysis on Energy and Environment College of Chemistry, Fuzhou University, Fujian 350108, China

^b Division of Physics and Applied Physics School of Physical and Mathematical Sciences Nanyang Technological University, Singapore 637371, Singapore

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ABSTRACT

Carbon based dots (CDs) have attracted broad attention exhibit due to the unique optical properties. However, the exact origins of their optical properties are still controversial. Citric acid (CA) coupled with some amino group-containing small molecules are believed to be ideal precursors for the synthesis of high luminescent CDs through various thermal treatment processes. Herein, CA coupled with four amino group-containing small molecules are chosen as models to synthesize CDs for a systematical study on the photoluminescence (PL) properties. It is found that the PL properties of CDs are resulted from the synergistic effect of the contained luminescent pyridine-derivatives and the defect states. A reasonable mechanism of PL emission from the CDs has been proposed. The results presented here must be critical for understanding the origins of PL, and also for preparing CDs with strong and wavelength tunable PL emission.

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1. Introduction

Carbon based dots (CDs) are emerging luminescent nanomaterials, usually composed of carbon cores (either graphene nanosheets or carbon nanoparticles) and oxygen-containing functional groups [1–3]. Due to the quantum confinement and edge effect, CDs exhibit unique optical and electro-optical properties, and have accordingly attracted increasing attention [4–6]. Moreover, these CDs usually show none/low toxicity, robust optical/chemical inertness, and are easy to be obtained with low cost. Photoluminescence (PL) is the most important property, based on which CDs have been widely applied in many fields including bioimaging and sensing [3,7,8]. Substantial attention has been paid to the preparation of high photoluminescent CDs. In general, the preparation methods can be classified into “top-down” and “bottom-up” approaches, which refer to cutting big-size carbon sources and carbonizing some special organics into small-size CDs, respectively [6,9]. Although, many “top-down” methods are very facile and suitable for preparing CDs in large-scale, the PL quantum

yields (PLQY) of the obtained CDs are usually low (less than 10%), partially resulted from the surface-passivation [10]. In contrast, the “bottom-up” methods seem to be much more hopeful to synthesize CDs with high PLQY [10]. Various organics, such as some carbohydrate, aromatic organics and vegetations, can be used as the precursors to prepare CDs through different “bottom-up” methods [11–14]. In particular, citric acid (CA) coupled with some amino group-containing small molecules, such as L-cysteine [15], glycine [15], ethanolamine [16], thiourea and ethylenediamine [17,18], are believed to be the most suitable precursors to synthesize high photoluminescent CDs. For example, the CDs synthesized by thermally treating the complex of CA and L-cysteine possess PLQY higher than 70% [15], and the CDs from the complex of CA and ethylenediamine show even higher PLQY, e.g. 80% [17].

Besides preparing various CDs, great efforts have been focused on understanding the PL mechanism of those CDs [19,20]. Although some hypotheses have been proposed to explain the PL behaviors of CDs, such as electronic conjugate structures and emissive traps [2,21–23]. However, it is still unclear why the CDs prepared by “bottom-up” methods, especially those from CA coupled with amino group-containing molecules, exhibit much higher PLQYs than other precursors. Recent results indicated that the extreme high PLQYs of these CDs may be related to some highly luminescent fluorophores [24–30]. Furthermore, it has been proposed that the

* Corresponding author.

** Corresponding author.

E-mail addresses: dongyq@fzu.edu.cn (Y. Dong), yuting@ntu.edu.sg (T. Yu).

CDs should contain multiple PL centers, such as sp^2 -hybridized core, edge states, surface functional groups. In this work, we would further investigate the relationships among the PL properties, the small fluorophore molecules and the surface states of the CDs from CA coupled with amino group-containing molecules.

It has been reported that the CDs from CA coupled with L-cysteine or ethylenediamine have extreme high PLQYs (more than 70%) [15,17], CDs from CA coupled with ethanolamine show relative high PLQY (ca. 50%) [16], and CDs from CA coupled glycine exhibit low PLQY (ca. 17%) [15]. Herein, CA coupled with the four amino group-containing small molecules (L-cysteine, ethanolamine, ethylenediamine and glycine) are chosen as model precursors to synthesize CDs (named CDs1, CDs2, CDs3 and CDs4, correspondingly). Then, the PL behaviors of the four obtained CDs are studied systematically. It is found that these CDs contain abundant high PL conjugating units (mainly some pyridine-derivatives) and a lot of carbon units with defect states (namely the C-related dangling bonds of spin $S = 1/2$). The main emission spectra of the CDs are primarily dependent on the property of the contained conjugating units, while the PLQY of the CDs is affected greatly by both the property of the contained conjugating units and the relative density of defect states. Finally, a reasonable model has been proposed to explain the PL behaviors of these CDs. These results may provide us a new insight into the PL mechanism of the CDs obtained from CA coupled with amino group-containing molecules. More importantly, inspiration may be gained from the results, to prepare high PL CDs with tunable emission spectra.

2. Experimental

2.1. Materials

Citric acid (99.9%), L-cysteine (97.0%), glycine (99.0%), ethanolamine (99.0%), ethylenediamine (99.0%), citrazinic acid (97.0%) and quinine sulfate ($\geq 98.0\%$) were purchased from Sigma-Aldrich and used as received.

2.2. Preparation of CDs and control-CDs (C-CDs)

Four kinds of CDs were synthesized by thermal treating the mixture of citric acid and amino group-containing molecules. In typical preparation procedures, 1 mM CA monohydrate (2.10 g) and 0.5 mM amino group-containing molecule (0.605 g L-cysteine, 0.30 mL ethanolamine, 0.33 mL ethylenediamine or 0.375 g glycine) were dissolved in 3 mL water and heated at 70 °C for 24 h. Subsequently, the mixtures were heated hydrothermally in a Teflon-equipped stainless-steel autoclave at 220 °C for 3 h. Finally, all the four as-obtained materials were separated into two fractions (>1 kDa and <1 kDa) by dialyzing against deionized water through a dialysis bag (retained molecular weight: 1 kDa) for a week. The fractions of >1 kDa labeled as CDs1, CDs2, CDs3 and CDs4, respectively. The fractions of <1 kDa were collected and labeled as F1, F2, F3, F4, respectively. For the synthesis of C-CDs, CA only was used as the precursor, using the same method described above.

2.3. Instrumentation

The transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded on a HRTEM JEOL 2100 system operating at 200 kV. Fourier transform infrared (FTIR) spectra were obtained on a FTIR spectrophotometer (Thermo Nicolet 360). UV/Vis spectra were obtained by a UV/Vis spectrophotometer (Lambda 750). All PL spectra were obtained by a spectrophotometer (F 4600). Electrochemiluminescence (ECL) measurements are carried out by an ECL & EC multi-functional

detection system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China) equipped with three electrodes system (a Pt wire working electrode with area of 0.31 cm², a Pt wire counter electrode and an Ag/AgCl reference electrode). Elemental analysis was performed on an organic elemental analyser (VarioMICRO). Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker A-300-EPR X-band spectrometer. Mass spectra of the organics in the four filtrates are measured using an Exactive Plus mass spectrometer. The PL decays were recorded a Fluorescence Steady State and TCSPC Fluorescence Lifetime Spectro-Fluorimeter (FLS920, Edinburgh Instruments, UK). X-ray powder diffraction (XRD) pattern was obtained from a Rigaku D/max-3C (Japan) using Cu K α radiation. Single-crystal structure analysis: Crystals were collected on a RIGAKU/SATURN 724 CCD diffractometer equipped with a fine focus, 2.0 kW sealed tube X-ray source (MoK α radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Raman spectra were measured using a Renishaw 1000 microspectrometer (excitation wavelength of 632.8 nm). The CD samples for the Raman investigation were mixed with CuSO₄ to quench the PL signal. X-ray photoelectron spectroscopy (XPS) spectra of CDs were measured using an ESCALAB 250 XPS system having an Al K source.

3. Results and discussion

3.1. Structural characterization of CDs

During the dialysis processes, both of the inside and outside solutions were collected. The amount variations of the luminophores inside and outside of the bags against dialysis time were monitored by measuring the PL intensity. It can be seen that the PL intensities of the four kinds of CDs decrease sharply in the two days, decrease slowly in the subsequent three days, then have nearly no decrease in the last two days (Fig. S1). Contrarily, the PL intensities of the four filtrates increase dramatically in the first two days, and increase slowly in the following three days, then have nearly no increase in the last two days. The results indicate that the dialysis is completed within one week.

The TEM images (Fig. 1) reveal that the lateral size of the obtained four CDs is 4–8 nm. The HRTEM images indicate that all the CDs are crystalline with lattice spacing of about 0.24 nm, which corresponds to the in-plane lattice spacing of graphite (100). The morphologies of all the CDs have no obvious difference from that of C-CDs from the hydrothermal treatment of CA only (Fig. S2). The Raman spectra (Fig. S3) of all the four CDs show the characteristic “disorder” D and crystalline G bands at around 1385 and 1580 cm⁻¹, respectively. The FTIR spectra of CDs (Fig. S4) exhibit the absorption peaks of C=C groups at around 1650 cm⁻¹, the peaks of C=O group at around 1710 cm⁻¹, the peaks of COO⁻ groups at 1550 and 1420 cm⁻¹, and the peaks of C–O, C–N and/or C–S groups at around 1185 cm⁻¹. The XPS spectra (Fig. S5) further confirm the results from the FTIR. Furthermore, the high resolution XPS spectra of N1s indicate that the nitrogen atoms in the CDs are presented mainly in the form of pyridinic type. The results indicate that all the four CDs have similar structural characterizations of most commonly reported CDs, namely a carbon core of graphite nature and a surface with functional groups [3]. The XRD patterns of the four CDs show a broad peak centered at around 21.0° (Fig. S6), which is smaller than that of graphite. It suggests that the interlayer distances of the CDs are larger than that of graphite due to the presence of the functional groups.

3.2. Optical characterization of CDs

As shown in Fig. 2a–d, all the four obtained CDs present strong PL activities, i.e. they show bright blue emission under the

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