Carbon 112 (2017) 131–141

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Rational design of high quality citric acid-derived carbon dots by selecting efficient chemical structure motifs

Fang Gao, Shiyao Ma, Jun Li, Kang Dai, Xincai Xiao, Dan Zhao*, Weifan Gong

School of Pharmaceutical Sciences, South-central University for Nationalities, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form
5 October 2016
Accepted 29 October 2016
Available online 1 November 2016

ABSTRACT

A green pyrolysis approach to prepare ultra-small nitrogen and sulfur-co-doped carbon dots (N,S-C-dots, QY reaches 55.7%) with precursors citric acid (CA) as carbon source and N-acetyl-L-cysteine as N and S dopant has been explored. The optical properties and the origin of photoluminescence (PL) have been investigated at length. The mixed excitation independence character ($200 \leq \lambda_{ex} \leq 380$ nm) and the excitation dependence feature ($\lambda_{ex} > 380$ nm) along with the biexponential behavior of lifetime of prepared C-dots all indicate the existence of two different emissive sites: the surface state caused by the introducing of N and S on C-dots surfaces and the molecular state induced by the fluorophores covalently bonded onto C-dots surfaces. More importantly, for the first time, through comprehensively comparing the PL performances of various types of N,S-C-dots, N-C-dots and S-C-dots synthesized under same condition, we report the efficient chemical structure motif of reactant, which could form small fluorophore molecules with high PL during the synthesis and thus exhibits favorable impact on PL performances of resulting C-dots. Detailed structural and property studies suggest that the chemical structure motif of reactant (−HN−C−C−SH) determines the optical properties of CA-derived C-dots, which would be valuable in selecting efficient reactants for preparing highly fluorescent CA-derived C-dots.

1. Introduction

Fluorescent carbon dots (C-dots), as a new type of ultra-small photoluminescent (PL) nanomaterial (<10 nm), have drawn tremendous attention due to their outstanding optical properties, customizable surface functionalization, excellent biocompatibility, robust chemical inertness, superior resistance to photobleaching, simple and inexpensive preparation, abundance of raw material in nature, etc [1]. After their serendipitous discovery dating back to 2004 [2], C-dots have exhibited great potential as a substitute for toxic metal-based quantum dots (QDs), and as promising candidate for applications of broad ranges, such as drug delivery [3], medical diagnosis [4], two-photon fluorescence imaging [5], fluorescent ink [6], detection of metal ions [7] and catalysis [8].

In the past decade, a number of approaches, with a large variety of techniques and starting materials utilized, have been developed to prepare satisfactory fluorescent C-dots. In general, these synthetic methods can be divided into two types: top-down approaches and bottom-up approaches. The top-down approaches include arc discharge [2], laser ablation [9], chemical oxidation in strong acid [10], or electrochemical synthesis [8], which smash a range of carbon allotropes, such as carbon nanotubes, nanodiamonds or graphite into the products with characteristics of fluorescent nanoparticles. By contrast, in bottom-up approaches, the C-dots are formed from molecular precursors with different chemical functionalities, and the majority of these synthetic routes involve high temperature pyrolysis, by employing mircrowaves [11] solvothermal technique [12], or simple thermal combustion of the organic precursor molecules [13]. Compared to top-down methods, the bottom-up procedures usually require no further surface passivation and allow easy introduction of heteroatoms into C-dots, which could significantly affect the properties of the resulting C-dots.

However, there have long been two issues restricting the development of bottom-up approaches. One is that though a plethora of methods for generating carbon based nanoparticles were reported, the efficient preparation route for high PL and QYs (quantum yields) C-dots were seldom seen in literature [12,14]. The second is that it is difficult to capture the whole picture of the PL mechanism due to the PL mechanism and the structure of prepared

---

* Corresponding author.
E-mail address: wqzhdpai@163.com (D. Zhao).

http://dx.doi.org/10.1016/j.carbon.2016.10.089
0008-6223/

C-dots vary along with the diverse synthesis processes and the types of precursor materials [15], thereby making the rational design of high-quality C-dots under the theoretical guidance still challenging. The easy synthesis method that can produce C-dots with high QYs would be the breakthrough to offer a better opportunity to study its PL mechanism and synthesis pathway [16], which is conducive to propelling the theoretical research, and meets the needs of practical application.

Since previous studies have suggested the doping of nitrogen element into C-dots could dramatically enhance its initial optical properties [12,14], top priority should be given to the controlled synthesis of doped C-dots from selected nitrogen-containing molecular precursors [12,14,17–21]. Generally, the preparation of doped C-dots involves the combination of two types of molecular precursor materials, in which one provides the major carbon framework and another introduces other elements into the structure. In this regards, the most prominent combination has been citric acid (CA) as carbon source, while nitrogen containing molecules as the dopants [12,14,17–20]. For example, Zhu et al. produced high-quality N-C-dots by hydrothermal treatment of CA and ethylenediamine (EDA) [12]. Dong et al. prepared N,S-C-dots with strong blue luminescence by thermal treatment of CA and L-cysteine (L-Cys) [14]. Besides, CA-derived N,B-C-dots [22] and N,P-C-dots [23] were also prepared, while N,S-C-dots were specially studied here due to their attractive QYs and easy synthesis route [14,17–19].

The origins of PL from these CA-derived C-dots have not hitherto been fully understood, regardless of several principles have been raised to explain their PL emission origins. For example, Dong et al. argued that the PL emission of N,S-C-dots mainly result from the newly formed surface state (N-state), while sulfur atoms plays a cooperative role by comparing the PL performances of O-C-dots, N-C-dots and N,S-C-dots [14]. Kwon et al. chemically modified the surface of N-C-dots with a series of para-substituted anilines, which featured the same amine head group but had different functional groups including $-OCH_3$, $-SCH_3$ and $-N(CH_3)_2$ to control their PL [24]. Their results proved that there existed at least two competitive PL centers, while surface functional groups determine the wavelength of PL. Zhu et al. [12] and Krysmann et al. [25] have compared PL features of CA-derived C-dots synthesized at different temperatures with EDA or ethanolamine (EA) as N-precursor. They proposed that molecular fluorophores predominate in the PL at low temperatures (<180 °C), while the carbogenic core starts forming at higher temperatures, which plays an ever greater role in contributing to the PL of C-dots as synthesis temperature increases. Zhai et al. demonstrated that the N-doping and amine passivation contribute to the fluorescence enhancement through comparing the PL performances of various types of N-C-dots fabricated by the microwave pyrolysis of CA and various amine molecules, including EDA, diethylamine (DEA), triethylamine (TEA) and 1,4-butanediamine (BDA) [26]. In their study, the PL QY and lifetime increase with increasing N content. Wang et al. synthesized a series of N-C-dots through condensation carbonization of CA and linear polyethylenic amine (PEA) analogues with increased amount of nitrogen and chain length of the precursors. While the longer chain of the PEA molecule gives better photo-stability, but lower PL QYs. They speculated that the PL emission of high QY C-dots origins not only from the sp^2/sp^3 carbon core and surface passivation of C-dots, but also possibly from the molecular fluorophores integrated in the C-dots, and the cyclic imines that enhanced the conjugated π-domains in the carbon core have favorable impact on PL QY [20].

Therefore, the type of doping elements, the functional groups of reactants, reaction temperature, the contents of nitrogen, and the chain length of precursors all affect the optical property and PL mechanism of prepared C-dots. It is worth noting that several groups have reported the findings of fluorescent synthetic intermediate during the formation of CA derived C-dots, and the small fluorophore molecule that bonded onto the surface of C-dots after carbonization was a major source of C-dots' fluorescence [15,27,28]. Besides, the raw materials utilized in bottom-up synthesis with CA as the carbon source are mostly small molecule compounds, whose structures' impacts upon the optical quality of prepared products haven't been sufficiently studied. Thus, a comprehensive comparison among the impacts of different structure motifs on the fluorescent synthetic intermediate, the formation pathway and the PL mechanism of CA-derived C-dots will be valuable aids in guiding the rational design of highly fluorescent CA-derived C-dots from the theoretical perspective [15].

Herein, we reported the preparation of N,S-C-dots with thiol N-acetyl-L-cysteine (L-NAC) as the N and S dopant. L-NAC works as an ideal raw material since it contains both N and S elements, possesses excellent water-solubility and biocompatibility, and is inexpensive and inodorous. Through preciously controlling the experimental parameters, the N,S-C-dots with a high QY of 55.7% was obtained. The morphology and structure have been carefully characterized, and the PL mechanism has been systematically studied. Besides, through fully investigating the relationship between the chemical structures of reactants and the PL performances of prepared C-dots by comparing various types of N,S-C-dots, N-C-dots and S-C-dots synthesized under same condition, the possible formation pathway of CA-derived C-dots was proposed. Additionally, a chemical structure motif ($-HN-C-C-SH$) was proposed to be an important factor in enhancing the optical properties of C-dots, which provides the theoretical guidance for the rational design of highly fluorescent CA-derived C-dots.

2. Experimental procedures

2.1. Chemicals

L-NAC (99%), and DL-Homocysteine (DL-Hcy) (95.0%) were obtained from Aladdin Chemistry Co., Ltd. Cysteamine (β-CA) (≥95.0%) was purchased from Shanghai yuanye Bio-Technology Co., Ltd. Glutathione (Reduced) (GSH) (98.0%), L-Methionine (L-Met) (98.0%), L-Lysine (L-Lys) (99.0%), L-Isoleucine (L-Iso) (≥99%), L-Glutamic acid (L-Glu) (≥99%), L-Histidine (L-His) (≥99%), L-Arginine (L-Arg) (≥98%), and L-Cys (>99.9%) were purchased from Sigma. CA monohydrate (≥99.5%), D-Cys (>98.5%), urea (≥99.0%), ammonium chloride (NH_4Cl) (≥99.5%), 3-mercaptopropionic acid (3-MPA) (98%), sublimed sulfur (S) (≥99.5%), thioacetamide (TAA) (≥99.0%), sodium thiosulfate pentahydrate ($Na_2S_2O_3$) (≥99.0%), hexamethylene, trichloromethane, ethyl acetate, tetrahydrofuran, acetone, ethanol, methyl alcohol, acetonitrile and trifluoroacetic acid (TFA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Methyl alcohol for high performance liquid chromatography (HPLC) was purchased from Tedia Company. All chemicals used were of analytical grade or of the highest purity available. All solutions were prepared using Milli-Q water (Millipore) as the solvent.

2.2. Preparation of C-dots

The N,S-C-dots were prepared through a thermal treatment with CA as the carbon source and materials contained both nitrogen and sulfur, such as L-NAC, L-Cys, D-Cys, L-Met, DL-Hcy, GSH, β-CA, and TAA as nitrogen and sulfur precursors. In a typical preparation procedure, CA monohydrate (0.1051 g, 0.5 mmol) and L-NAC (0.0653 g, 0.4 mmol) were dissolved in water (4 mL), followed by evaporation at 70 °C for 12 h. Subsequently, the resulted colorless solid products were heated in a Teflon-equipped stainless-steel