



Supramolecular nanodots derived from citric acid and beta-amines with high quantum yield and sensitive photoluminescence

Xianrui Meng^{a,1}, Yunjing Wang^{a,1}, Xiaohui Liu^a, Mengwei Wang^a, Yanshan Zhan^a, Yingqiu Liu^a, Weiwei Zhu^a, Wenkai Zhang^{a,*}, Lijuan Shi^{b,**}, Xiaomin Fang^{a,***}

^a Institute of Functional Organic Molecular Engineering, Henan Engineering Laboratory of Flame-Retardant and Functional Materials, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, PR China

^b Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, PR China

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ABSTRACT

Herein, we reported the characterization of a highly fluorescent and sensitive amorphous nanodots synthesized by hydrothermal treatment of citric acid in the presence of various β -amines below 200 °C. Five-membered ring fused 2-pyridone compounds are effectively produced in the condensation reaction, and serve as the main building blocks to self-assemble into supramolecular nanodots under hydrogen bonding. The 2-pyridone compounds are not the sole blue species, but effectively enhance the photoluminescence quantum yield of citric acid derived nanodots. Compared with the excitation-independent emission in dilute solution, the dense nanodots exhibit red-shifted, suppressed and unexpected excitation-dependent emission. Moreover, the supramolecular nanodots have high sensitivity in various ambient conditions, such as pH, solvent polarity and metal ions.

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1. Introduction

Photoluminescent carbon dots (CDs) are increasingly being explored as novel fluorescent nanomaterials due to their strong fluorescence, low cytotoxicity, excellent water solubility and stable photoluminescence, which make them great promising materials for applications in optoelectronic and energy devices, photocatalyst, sensor, and bioimaging [1–8]. Various approaches have been developed to fabricate CDs including “top-down” and “bottom-up” methods. The “top-down” methods refer to carving bulk carbon materials into nanoparticles by using physical or chemical approaches, such as acid oxidation, electrochemical, and hydrothermal. Compared with “top-down” routes, the “bottom-up” routes have obvious advantages in adjusting the composition and physical properties of CDs by the careful selection of diversified organic precursors and carbonization conditions via thermal

pyrolysis or carbonization. In the recent years, citric acid (CA) has become one of the most frequently used bioproducts for the synthesis of CDs through bottom-up carbonization routes due to the direct process involved and high fluorescence quantum yields (QYs). Many CDs have been prepared from CA and amines via heating, hydrothermal methods or microwave assisted methods [9–18]. However, because of the complex constituent of the synthesized CDs and consequently their undetermined chemical structures, there are ongoing debates over the origins of their fluorescence [9,19–22]. Therefore, identifying the compositions and determining the related chemical structures are essential for resolving the fluorescence origins of citric acid derived carbon dots (CACDs). Lately, the possible origin of their luminescent properties has been revealed by isolation and identification of luminescent species from the CACDs. Detailed analyses confirmed the chemical structure as citric-acid derived organic molecules or fluorophores [11,21,23–25]. Yang's group [26] and Kasprzyk's group [27] have reported a series of five ring fused 2-pyridone based fluorophores from condensation of CA and specific amines.

However, the photoluminescence (PL) intensity and quantum yields of CACDs are diminished greatly as the pyrolysis of the CA-amine complex proceeds to the high temperature, because the strongly intense molecular fluorophore is gradually consumed as

* Corresponding author.

** Corresponding author.

*** Corresponding author.

E-mail addresses: zhangwenkai@henu.edu.cn (W. Zhang), shilijuan@tyut.edu.cn (L. Shi), xmfang@henu.edu.cn (X. Fang).

¹ These authors contributed equally to this work.

the building block of the much less photoluminescent carbogenic core [11,13,28,29]. Therefore, low temperature (mainly below 200 °C) during pyrolysis seems to be the key to preserve the fluorescence. Zhang et al. suggested that an intermediate form of self-assembled organic dots between carbon dots and fluorophores is dominant in the CACDs that are prepared through the condensation of CA and amines at low reaction temperatures [24]. Chan's group disclosed CA-derived nanodots exist as supramolecular clusters with their individual monomer units linked together through noncovalent bonding forces [30]. Recently, we performed a study of the formation mechanism of nanodots prepared from CA-amine system and demonstrated the self-assembly behaviors in the complex system [31]. It was found that a number of CA and a single diethylenetriamine (DETA) combined together via hydrogen bonding to fabricate self-assembled constructions, that was, DETA@5CA. Then the dimeric and trimeric fluorophores coupled with DETA@5CA led to “dots” topologies in the CNDs solution. However, this area is still in its infancy and faces several key challenges. First, more synthetic approaches should be developed to shed light on the role of 2-pyridone compounds in the fluorescence of CACDs. Second, the chemical structure and intermolecular force corresponding to these amorphous/molecular “dots” is difficult to be characterized, and the effect of self-assembly on PL of CACDs remains to be further investigated.

In this work, we described the structure and photoluminescence properties of the supramolecular nanodots that are formed by hydrothermal treatment of CA in the presence of various β -amines below 200 °C. Five-membered ring fused 2-pyridone compounds are effectively produced in the condensation reaction, and serve as the main building blocks to self-assemble to supramolecular nanodots under noncovalent bonding. In dilute solution, the 2-pyridone fluorophores are identified as the PL origin of nanodots, exhibiting high quantum yield and excitation-independent emission. While the concentrated nanodot solution gives red-shifted, suppressed and unexpected excitation-dependent PL. It was also found that CACDs have high sensitivity in various ambient conditions, such as pH, organic solvent and metal ions. In the present systems, molecular fluorophores bonded with supra-molecules are important PL and morphological origin, which is very different with previous sp²-carbon networks and surface defects.

2. Experimental section

2.1. Chemicals

Citric acid (CA), ethylenediamine (EDA), 1,2-propylenediamine (AP), diethylenetriamine (DETA), triethylenetriamine (TETA), tetraethylenepentamine (TEPA) and dimethylvinylendiamine (DMEDA) were purchased from Sigma-Aldrich. Ethanol and acetone were purchased from the Sinopharm Chemical Reagent Co., Ltd. The other reagents were analytical-grade.

2.2. Preparation of supramolecular nanodots

Nanodots were synthesized by a hydrothermal treatment of citric acid and various β -amines according to previous reports [15,16]. In a typical procedure, 0.42 g (2 mmol) of citric acid and 0.44 g (6 mmol) of 1,2-propylenediamine (AP) were dissolved into 15 mL water, and stirred to form a clear solution. The mixed solution was transferred to a 30 ml Teflon-equipped stainless-steel autoclave, and then heated to 180 °C and kept for additional 4 h. After that, the solution naturally cooled to room temperature. Next it was dried by rotary evaporation under reduced pressure, and then yellow viscous oil was obtained. Then the oil was rinsed with acetone, followed by supersonic expansion and centrifugation at

10,000 rpm for 0.5 h. The precipitated material at the bottom of the centrifuge was vacuum dried at 65 °C and the brown powder was denoted as Dots-AP. Similarly, Dots-EDA, Dots-DETA, Dots-TETA, Dots-TEPA and Dots-DMEDA were prepared by using ethylenediamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA) and N,N'-dimethylethylenediamine (DMEDA) as β -amines, respectively.

2.3. Characterization

The atomic force microscope (AFM) images were measured with Dimension Icon (Bruker Instruments Inc.) on new cleaved mica surface in tapping mode in air. High resolution microscopy measurements were performed using a JEM1200EX transmission electron microscopy (TEM) with an operating voltage of 120 kV. X-ray photoelectron spectra (XPS) was performed on a Thermo Fisher Scientific ESCALAB 250XI photoelectron spectrometer with Al K α ($h\nu = 1486.6$ eV) as the X-ray source. Fourier transform infrared spectroscopy (FT-IR) characterization was carried out on a Bruker Vertex 70 FTIR spectrometer. UV–vis absorption spectra were recorded with a Hitachi U4100 Spectrometer. A high-resolution electrospray ionization-mass spectrometry (ESI-MS) was performed on a Solarix XR FTICR (Fourier transform ion cyclotron resonance) mass spectrometer equipped with a 7.0 T magnet (Bruker Daltonics, Billerica, MA, USA). The PL spectra were recorded by a Hitachi F-7000 spectrophotometer, and the relative quantum yield (QY) of the CDs were measured via the slope method by using quinine sulfate (in 0.5 M H₂SO₄, $\Phi = 0.54$) as a reference. For details in the mathematic calculation of quantum yields, please refer to the Supporting Information. The time-resolved PL spectra were performed with F980 spectrometer (Edinburgh Instruments, UK), equipped with a single photon photomultiplier detector (S900-R). The pulse width, wavelength, and repetition rate were chosen as 40 ps, 360 nm, and 5 MHz, respectively.

3. Results and discussion

3.1. Morphological and chemical structure of nanodots

The synthetic approach for supramolecular nanodots follows the hydrothermal treatment of citric acid in the presence of β -amines, including EDA, AP, DETA, TETA, TEPA and DMEDA. In this process, hydrothermal temperature is the key to preserve the fluorescence intensity of nanodots, because molecular fluorophores have been suggested to be dominant in the nanodots at low hydrothermal temperatures (mainly below 200 °C). Further carbonization occurs at higher temperatures, leading to the production of “carbon” rather than molecular nanodots. As shown in Fig. 1, a group of “dots” are detectable from atomic force microscope (AFM) image, giving the evaluated height of 0.8–1.5 nm for all nanodots. In addition to “dots”, a wide range of morphologies can be also found in the products, such as worms (Fig. S1). Due to the little mass-thickness contrast of supra-molecular assemblies, almost none of carbogenic domains can be found in the TEM images (Fig. S2).

The element analysis (Table S1) and XPS (Fig. S3, Table S2) were performed to determine the chemical composition of nanodots. The high resolution N1s spectrum of the nanodots can be fitted into two broad peaks, where the peaks near 399 and 401 eV are likely to correspond to the pyridinic N and amide N respectively (Table S3), indicating the possible existence of pyridone compounds. Compared with the primary amine, the secondary amine is unlikely to form pyridone compounds, revealed by the low content of N atoms and the lack of pyridinic N in Dots-DMEDA. The C1s spectra can be fitted into 3 Gaussian peaks at 284.5, 286.1 and 288.6 eV

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