



Carbon dots originated from methyl red with molecular state and surface state controlled emissions for sensing and imaging



Xiaohua Pan, Yan Zhang, Xiaobo Sun, Wei Pan, Guifeng Yu, Qiangqiang Zhao, Jinping Wang*

College of Chemical and Pharmaceutical Sciences, Qingdao Agricultural University, Qingdao 266109, PR China

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ABSTRACT

In this article, carbon dots (CDs) were synthesized using methyl red (MR) as precursor in the absence and presence of ethanediamine (EDA) by facile hydrothermal pyrolysis, referring to as MR-CDs and MR-EDA-CDs, respectively. MR-CDs synthesized at different temperatures exhibited molecular state controlled photoluminescence (PL) property with the same characteristics (emission position and shape, no contribution from carbon core) as MR, except that their quantum yields (QYs) decreased with the reaction temperature increasing because of the consumption of MR. On the other hand, MR-EDA-CDs were fractionated into four fractions, which individually displayed unique surface state controlled PL property. Moreover, four fractions isolated from MR-EDA-CDs have specific surface groups that can selectively recognize pH, Fe³⁺, Ag⁺ and Hg²⁺, respectively, in aqueous solution, then were developed as the corresponding sensors. In addition, MR-EDA-CDs are potential fluorescent agents with excellent biocompatibility for bioimaging of fungal cells.

1. Introduction

Carbon dots (CDs), a class of newly emerging carbon based nano-materials, have been proven to possess high performances, including intense fluorescence [1], excellent photostability [2], favourable biocompatibility [3,4], low toxicity [5], outstanding water solubility [6], tunable fluorescence emission and excitation [7,8]. Due to their high performances, great potential for applications in wide areas, such as bioimaging [9,10], biosensing [11], medical diagnosis [12], drug delivery [13,14], catalysis [15] and photovoltaic devices [16,17] has attracted much more attention in scientific community. So it is very interesting to pursue more CDs with unique properties via function design so as to meet specific requirements, which need photoluminescence (PL) mechanism to be understood clearly.

CDs are generally believed to be composed of carbon-core and surface domains, which are characterized by graphitic-like sp² carbon structure and abundant functional groups, respectively, and mainly responsible for their PL characteristics [6,18]. However, till now, their PL mechanism is still not very clear [19,20] because different precursors, even the same precursors under different conditions, will result in CDs with their own unique PL properties and ambiguous structures [21]. On the other hand, ideally simplified theoretical models presented in the literatures might ignore some complexity of their real composites [22–24]. Even so, PL mechanism in different manners such as quantum

confinement effect [25], surface states [26], and molecular state [27,28] is well proposed and popularly accepted by scientists. Surface state as PL center is formed by the synergetic hybridization of chemical groups and carbon core, whereas molecule state as PL center is produced solely by an organic fluorophore [29,30].

Functional groups on the surface domain not only result in a series of emissive traps but also impart CDs with specific functions [31]. For example, CDs with surface functional groups as recognition moieties can selectively detect metal ions, such as Hg²⁺ [32], Cu²⁺ [33], Fe³⁺ [34], Pb²⁺ [35], Cr(VI) [36] and Ag⁺ [37], via forming non-fluorescent complexes. Moreover, surface modification is an effective strategy to further functionalize CDs according to the specific requirements in practical applications [9]. Guided by specific recognition molecules immobilized on their surfaces, CDs are endowed with extended functions in bioimaging at high resolution [9,10,38], accurate medical diagnosis and therapy [12,39], and controlled labelling for biological tracing [40]. Obviously, the functions of CDs have close relationship with surface domain.

In this work, methyl red (MR), 2-(4-dimethylaminophenylazo)benzoic acid, was expected to be a precursor for synthesizing CDs with new special functions by a facile hydrothermal pyrolysis method. Ethylenediamine (EDA) was, further, applied as a co-reactant to tune their structures and optical properties. Interestingly, the CDs synthesized with pure MR as precursor at different temperatures (MR-CDs)

* Corresponding author.

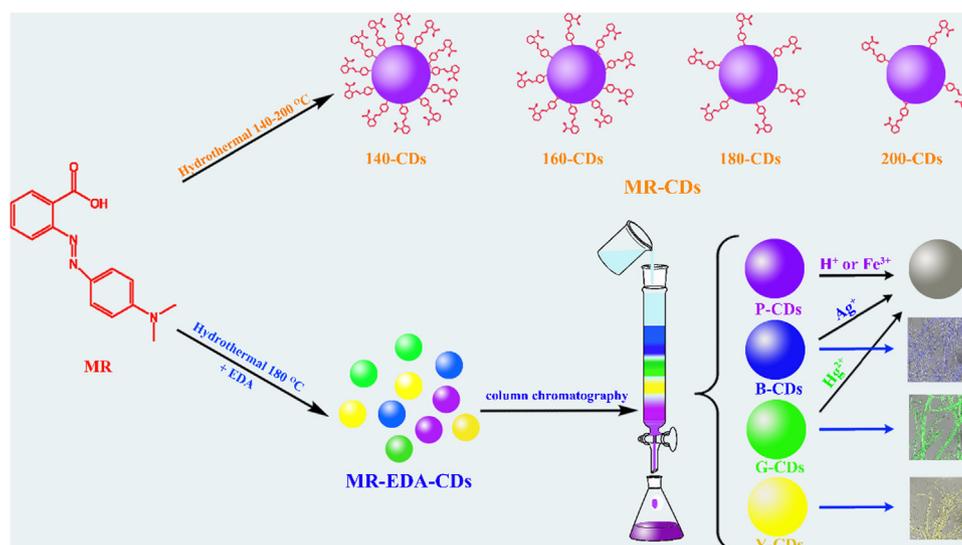
E-mail address: jpwang@qau.edu.cn (J. Wang).

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Scheme 1. Schematic illustrations of MR-CDs and MR-EDA-CDs synthesis and multi functions of MR-EDA-CDs.

exhibited molecular state controlled emission. Whereas, the CDs prepared by MR in the presence of EDA (MR-EDA-CDs) could be fractionated into four fractions, which individually emitted unique surface state controlled photoluminescence. Moreover, different surface functional groups imparted MR-EDA-CDs with multi functions, such as pH, Fe^{3+} , Ag^+ and Hg^{2+} sensing, and bioimaging of fungal cells (see Scheme 1).

2. Experimental

2.1. Reagents

AgNO_3 ($\geq 99.8\%$), CaCl_2 ($\geq 99.0\%$), NiCl_2 ($\geq 98.0\%$), CoCl_2 ($\geq 99.0\%$), CdCl_2 ($\geq 98.0\%$), CuCl_2 ($\geq 99.0\%$), $\text{Fe}(\text{NO}_3)_3$ ($\geq 98.5\%$), $\text{Hg}(\text{Ac})_2$ ($\geq 98.0\%$), MgCl_2 ($\geq 99.0\%$), MnSO_4 ($\geq 99.0\%$), $\text{Pb}(\text{NO}_3)_2$ ($\geq 99.0\%$), AlCl_3 ($\geq 99.0\%$), BaCl_2 ($\geq 99.0\%$), CrCl_3 ($\geq 99.0\%$), NaCl ($\geq 99.5\%$), LiNO_3 ($\geq 99.5\%$), KCl ($\geq 99.5\%$), NaOH ($\geq 96.0\%$) and $\text{Zn}(\text{NO}_3)_2$ ($\geq 99.0\%$) were purchased from Damao Chemical Corp (Tianjin, China). MR ($\geq 99.0\%$), EDA ($\geq 99.0\%$), NaH_2PO_4 ($\geq 99.0\%$), Na_2HPO_4 ($\geq 99.0\%$) and HCl (36–38%) were obtained from Aladin Ltd. (Shanghai, China). All chemicals used in this work are analytical reagents without any further purification. The ultrapure water used throughout all the experiments was purified through Water Purifier Nanopure water system (18.3 M Ω cm). The lake water samples were collected from Hongzi lake of Qingdao Agricultural University (located at 36.3°N and 120.4°E, water temperature of 19 °C). And the lake water were pretreated by qualitative filter paper and 0.45 μm filter membrane to remove the solid suspensions and other impurities. Tap water and lake water were used as the real samples. Generally, tap water contains a lot of cations and anions [41]. Besides cations and anions, there are many organic matters present in lake water [42].

2.2. Characterization

The morphology and the size of CDs were analyzed using the transmission electron microscopy (TEM, Hitachi H-7000, operated at 80 kV). PL spectra were performed by a fluorescence spectrometer F-2500 (Hitachi, Japan). The X-ray diffraction (XRD) of CDs were collected using a D8 ADVANCE X-ray diffractometer (Bruker AXS, German) with Cu-K α radiation (40 kV, 40 mA, $\lambda = 1.5418 \text{ \AA}$) at a scanning rate of 1° min $^{-1}$ in the range from 5° to 80°. The Fourier transform infrared spectroscopy (FTIR) spectrum of CDs were recorded using a FT-IR200 spectrometer (Thermo, America) with KBr pellets

technique, over the range 400–4000 cm^{-1} . The hydrodynamic sizes of CDs were measured via dynamic light scattering (DLS) using a Zetasizer Nano ZS90 (Malvern Instruments Ltd., Worcestershire, UK) with standard parameters at 25 °C. The quantum yields (QYs) of the prepared CDs were determined using quinine sulfate in 0.1 M H_2SO_4 (literature QY: 54.6%) as the standard sample by comparing the integrated PL intensities (excitation at optimum wavelength) and absorbance values at corresponding wavelength of the CDs aqueous solutions with those of quinine sulfate [43].

2.3. Synthesis and purification of MR-CDs

MR-CDs were prepared through dissolving 0.2 g MR into 25 mL ultrapure water. Subsequently, MR solution was heated hydrothermally in a Teflon-equipped stainless steel autoclave at 140, 160, 180 °C for 5 h and 200 °C for 3 h. After naturally cooling down to room temperature, the deep red products were neutralized with 1 M NaOH solution. All the obtained materials were filtered through a 0.45 μm filter membrane to remove large particles. The solution was dialyzed against ultrapure water through a dialysis membrane (MWCO 500) for 2 days and concentrated by means of rotary evaporation at 60 °C. Finally, the solid CDs were obtained by freeze drying under vacuum at -50 °C for 48 h.

2.4. Synthesis of MR-EDA-CDs

MR-EDA-CDs were prepared through hydrothermal treatment of the mixture of MR and EDA. 0.2 g of MR and 1 mL of EDA were dissolved in 25 mL ultrapure water. Subsequently, the mixture solution was heated hydrothermally in a Teflon-equipped stainless steel autoclave at 180 °C for 5 h. Then the orange red products were neutralized with 1 M HCl solution. Finally, all the obtained materials were filtered through a 0.45 μm filter membrane to remove large particles. The solution was concentrated by means of rotary evaporation at 60 °C.

2.5. Separation and purification of MR-EDA-CDs

The components of MR-EDA-CDs were separated by column chromatography on a Sephadex G-25 gel filtration column using ultrapure water as eluent. MR-EDA-CDs aqueous solution was added to the gel column, and then eluted with ultrapure water. UV light at the wavelength of 365 nm was used to monitor the fractions eluted from the column. All solutions were concentrated by means of rotary evaporation at 60 °C. Finally, MR-EDA-CDs were obtained by freeze drying

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