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Microwave-assisted synthesis of luminescent and biocompatible lysine-based carbon quantum dots

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ABSTRACT

Water-soluble carbon quantum dots presenting strong blue photoluminescence with the quantum yield up to 23.3% are simply prepared by microwave treatment of lysine as a building block within 5 min in household microwave oven. The formation of lysine-based carbon quantum dots is estimated to proceed through the microwave induced thermal polyamidation and the subsequent carbonization reaction. More importantly, the control experiments using the other amino acids having linear structures reveals that the branched molecular structure of lysine (AB_2 type polyamidation monomer) is one of prerequisite points to obtain strongly luminescent carbon quantum dots with high mass yield. Lysine-based carbon quantum dots are highly nontoxic and biocompatible, enabling bioimaging of cellular media with high degree of pysiological safety.

Introduction

Recently, intensive research interests have been attempted to develop luminescent carbon quantum dots (CQDs) as the next generation carbon nanomaterials in addition to 0D fullerene, 1D carbon nanotube, and 2D graphene [1]. The promising optoelectrical performance of CQDs enables the replacement of heavy metal-based inorganic quantum dots (QDs) with CQDs in many applications including light-emitting diodes [2], photocatalysis [3], sensing [4], solar energy harvesting [5,6], bioimaging [7,8], and drug-delivery systems [9] due to their excellent biocompatibility, low environmental toxicity, superior photochemical stability, and easy surface functionalization.

Either "top-down" or "bottom-up" approach has been exploited for the synthesis of CQDs until now. However, "bottom-up" approach utilizing the polycondensation or self-assembly of biocompatible small molecules or polymers prevails "top-down" approach employing the chemical or physical breakage of carbon-rich materials in the consideration of environmental and physiological compatibility of prepared CQDs [10]. In "bottom-up" approach, the initiation and progress of CQD formation necessitates the incorporation of harsh reaction conditions such as combustion [11], thermal treatment [12], chemical carbonization [13], and acid/alkali-assisted ultrasonic or oxidation reactions [14].

Very recently, it has been unveiled that the microwave assisted pyrolysis of certain small molecules in aqueous media by household microwave oven successfully facilitates the formation of water-soluble CQDs with high photoluminescence quantum yield (QY) [15]. As the carbon sources, carbohydrates such as glucose have been extensively exploited. Few nm-sized CQDs exhibiting deep ultraviolet (DUV) or blue emission with the QY up to 11% have been prepared by microwave-assisted hydrothermal reaction of glucose within 11 min [16]. Microwave treatment of glucose as the carbon source and polyethylene glycol (PEG) 1500 as

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the co-reactant for 10 min successfully produced 2–4 nm CQDs showing chemiluminescence in strongly alkaline condition [17]. Other carbohydrates (glycerol, glycol, sucrose, etc.) have been also utilized for the preparation of photoluminescent CQDs with the QY up to 9.5% through the microwave treatment in the presence of inorganic ions within a few minutes [18]. Additionally, polymerizable monomers through polycondensation reactions have been incorporated for the preparation of CQDs through the microwave assisted polymerization and pyrolysis. Mostly, polyamidation monomer sets of A_x (A: −COOH, x = 3 in the case of citric acid) and B_y (B: $-NH_2$, y = 2 in the case of urea) type monomers have been utilized for the preparation of CQDs with enhanced fluorescence QY of 14% by the microwave treatment within several minutes through the dual roles of urea as *N*-doping precursors and surface passivation agents [19].

While the "bottom-up" approach based on the above microwave assisted pyrolysis of small molecules is facile, less energy/time consuming, and easily scalable for the preparation of highly fluorescent CQDs, the incorporation of biocompatible and naturally abundant carbon sources is still urgent especially for the bioapplications of CQDs [20,21]. In this study, lysine has been chosen as an alternative biocompatible precursor of CQDs, because lysine is one of naturally abundant amino acids present in high-protein foods such as eggs, meat, soy, beans, etc. [22]. Structurally, lysine is one of AB_2 type monomers which can be polymerized to polylysine through the polyamidation reaction [23]. Because microwave assisted pyrolysis of polymerizable monomers incorporates not only the carbonization and CQD formation process but also the polymerization of monomers, the choice of proper monomers and the control of polymerization during the microwave operation is very critical for the successful formation of highly soluble and strongly photoluminescent CQDs. While A_3 and B_2 monomer sets in previous reports can induce gelation at the early stage of polyamidation reaction [24], AB_2 type monomers such as lysine do not produce gelation along the polycondensation because no intramolecular cyclization is enabled [25]. Additionally, the utilization of AB_2 monomers does not require the optimization of feeding ratio because both A and B functional groups are staying in single molecule, which simplifies the structural characterization of prepared CQDs. For a comparison, A_3 and B_2 type monomer sets require precise control of the feeding ratio between A_3 and B_2 monomers to maximize the fluorescence QY of resulting CQDs.

From all these considerations, it is motivating to investigate the microwave assisted pyrolysis of AB_2 type monomers such as lysine to produce water soluble, highly fluorescent, and biocompatible CQDs. From the cooperative examination of the microwave assisted pyrolysis of AB type monomers, it is clear that the incorporation of "branching point" in the structure of polymerizable monomers should be inevitable for the successful formation of highly fluorescent CQDs. Lysine-based CQDs showed strong blue emission upon the irradiation of UV (365 nm) light with the fluorescence QY of 23.3% together with excellent in-vitro non-cytotoxicity up to 1 mg/mL, which facilitates the application of lysine-based CQDs for the bioimaging of cellular media.

Experimental

Materials and methods

L-Lysine was purchased from Sigma–Aldrich Corporation. Molecular weight cut-off membrane (MWCO, 3500 Da) was purchased from Spectrum Laboratories, Inc.

Ultraviolet–visible (UV–vis) spectra were obtained with Optizen Alpha UV–vis Smart Spectrometer of Mecasys (South Korea). Photoluminescence (PL) spectra were obtained using a PerkinElmer L550B luminescence spectrometer. Fourier transform infrared (FT-IR) spectra were taken with a Nicolet iS10 FT-IR spectrometer of Thermo Fischer Scientific Inc. Atomic force microscopy (AFM) images were obtained using a Multimode-N3-AM Scanning Probe Microscope of Bruker. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) images were obtained from a Tecnai G2 F20 field emission transmission electron microscope of FEI Corporation. ^{1}H NMR and ^{13}C NMR spectra were obtained using a Bruker Advance 400 MHz spectrometer with deuterium oxide (D_2O) as the solvent. Raman analysis was done with a LabRAM high-resolution UV/vis/NIR dispersive Raman microscope (Horiba John Yvon). X-ray photoelectron spectroscopy (XPS) spectra were obtained by using tetra probe base system (Thermo Fisher Scientific Co.). The multimode microplate reader Filter MaxF3 (Molecular Devices, LLC) was used for MTT assay and quantitative cellular accumulation. Confocal images were obtained An LSM510 confocal laser scan microscope (CLSM) of Carl Zeiss (Germany) at ×10 magnification to take images of stained cells.

Synthesis of lysine-based CQDs

Luminescent and biocompatible lysine-based CQDs was prepared form lysine by one-step microwave pyrolysis method. At first, lysine (1 g) was dissolved in 5 mL of deionized water in

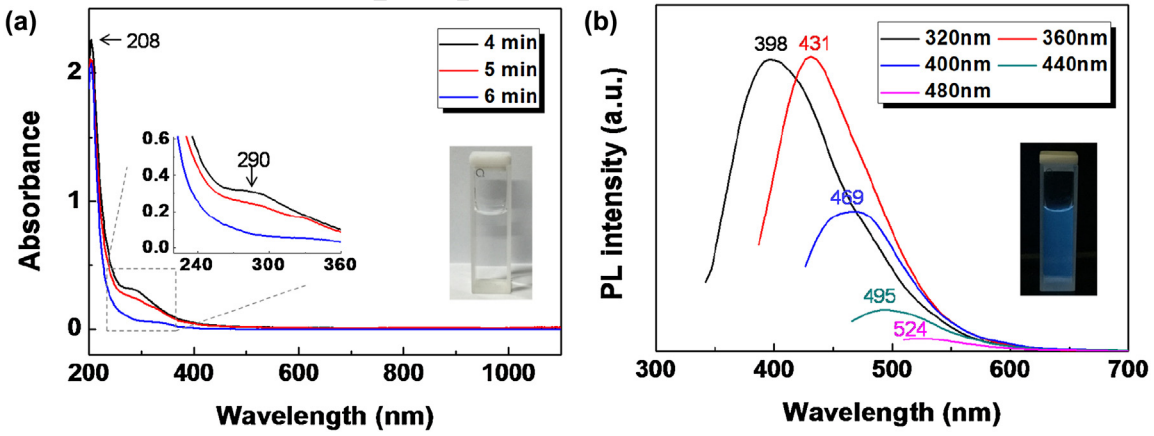

Fig. 1. (a) UV–vis spectra of aqueous solutions of lysine-based CQDs (0.1 mg/mL) with different microwave operation time and (b) PL spectra of lysine-based CQD prepared from 5 min of microwave operation (0.1 mg/mL) upon the different excitation wavelength (the insets are photo images of CQDs under room light and under dark with the 365 nm UV irradiation). (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

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