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Efficient synthesis of highly fluorescent carbon dots by microreactor method and their application in Fe^{3+} ion detection

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ABSTRACT

Rapidly obtaining strong photoluminescence (PL) of carbon dots with high stability is crucial in all practical applications of carbon dots, such as cell imaging and biological detection. In this study, we proposed a rapid, continuous carbon dots synthesis technique by using a microreactor method. By taking advantage of the microreactor, we were able to rapidly synthesized CDs at a large scale in less than 5 min, and a high quantum yield of 60.1% was achieved. This method is faster and more efficient than most of the previously reported methods. To explore the relationship between the microreactor structure and CDs PL properties, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) were carried out. The results show the surface functional groups and element contents influence the PL emission. Subsequent ion detection experiments indicated that CDs are very suitable for use as nanoprobes for Fe^{3+} ion detection, and the lowest detection limit for Fe^{3+} is 0.239 μM, which is superior to many other research studies. This rapid and simple synthesis method will not only aid the development of the quantum dots industrialization but also provide a powerful and portable tool for the rapid and continuous online synthesis of quantum dots supporting their application in cell imaging and safety detection.

1. Introduction

Carbon dots (CDs) are a new class of carbon nanomaterials that are regarded as a type of quantum dot with sizes below 10 nm. CDs have received steadily growing interest as a result of their peculiar and fascinating properties, such as excellent optical properties, low toxicity, good biocompatibility and robust chemical inertness [1–4]. The outstanding properties of carbon dots distinguish them from traditional fluorescent materials and make them promising candidates to replace heavy metal-based semiconductor quantum dots for numerous exciting applications, such as sensors [5], bioimaging [6], lasers [7], LEDs [8], photocatalysis [9], and photovoltaic devices [10]. Spurred by the special properties of CDs, various studies have been carried out on facile synthesis approaches and photoluminescence (PL) mechanisms. Since CDs originated from the production of carbon nanotubes by electrophoresis in 2004 [11], a broad series of methods for obtaining CDs have been developed, including pyrolysis [12], laser ablation [13], electrochemical oxidation [14], acidic oxidation [15], hydrothermal treatment [16], microwave or ultrasonic passivation [17] and plasma treatment [18]. Although remarkable successes have been achieved, the properties of these as-produced CDs, in terms of quantum yield (QY) and productivity, greatly limiting industrial applications such as in the development of photoelectric conversion devices. Beside, current synthetic methods are mainly deficient in accurately controlling the reaction conditions and continuous preparation as well as in obtaining high QYs. Therefore, it is necessary to develop a method for rapid and large scale production as well as in obtaining high QYs.

Ion pollution has become a worldwide issue due to the severe risks in organisms and environment. Up to now, a number of highly sensitive and selective methods for sensing ion or biology detection have been developed, based on quantum dots, fluorochrome, polymer materials and so on [19–23]. However, these methods generally suffer from several limitations, such as high cost, complicated operation procedures and time-consuming sample post-treatment, which greatly limit their practical application of the methods for rapid on-site analysis. Currently, the fluorescent methods have been widely employed to detect

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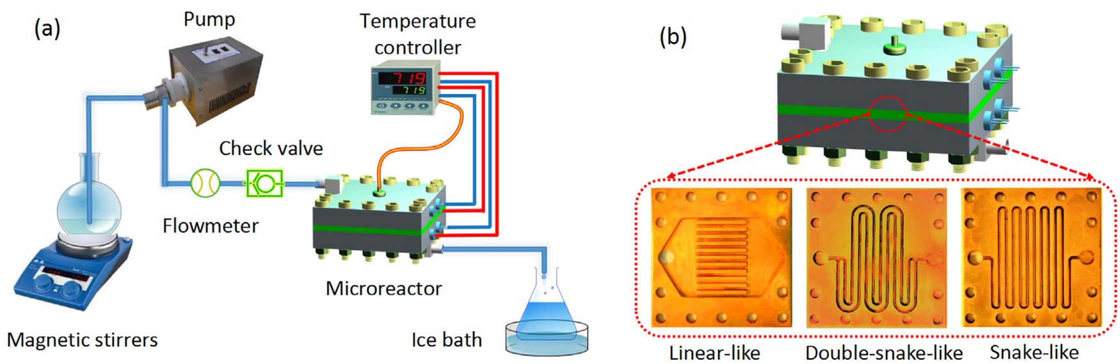

Fig. 1. (a) Diagram for the synthesis of CDs by Microreactor system. (b) Detail view of three different channels (Liaear-like, Double-snake-like, Snake-like) embed in microreactor.

targets in recent years because of their simplicity, cost-effectiveness, easy operation. The CDs has been used for ion detection due to its particular chemical and optical properties. It is well known that, a high QY is the essential factor for ion detection. However, it is still hard to rapid and efficient synthesis of CDs with high QY. In addition, it is urgent to prepare CDs online for ion detection in order to ensure measurement precision due to it is difficult to synthesize CDs using common methods outdoors or in remote areas. Therefore, it is essential to develop a powerful and portable tool for the rapid and continuous online synthesis of CDs.

In order to rapid and efficient synthesize CDs, we draw our attention to microreactors. Recently, microreactors have increasingly attracted our attention due to their advantages, including their quick heat and mass transfer properties, high speed mixing, controllable feed rates and high reproducibility [24–26]. Moreover, microreactors can provide better choices than conventional reactors for the synthesis of products that require anaerobic anhydrous environments that avoid the degradation of certain sensitive compounds. These remarkable properties have allowed their broad application in organic synthesis, nanoparticle synthesis, and medicine production [27–29]. Currently, microreactors have been regarded as a preferred method for the synthesis of high quality metal-oxides and semiconductor quantum dots [30–32]. Moreover, microreactor can not only be conveniently joined with temperature control systems or heating equipment but can also attach to analytical instruments. This enables carrying out reactions under more precisely controlled conditions than those of macroreactors. These are very important for some applications, especially in bioanalysis and safety detection.

Among reports on the use of microreactors for the synthesis of quantum dots, most of the microreactors productivity are inefficient and hardly obtain high QY. In addition, there have been few reports on the preparation of CDs using microreactors, especially less focus on the effect of microreactor structure on heat transfer. Lu et al. [33] used a microreactor with a certain length of teflon capillary tubing in oil bath to screen more than hundred of reaction conditions and investigated the relationship between different developmental stages of the CDs and their PL properties, while the QY of as-prepared CDs not more than 37%. Meanwhile, they haven't considered the effect of the inner microreactor structure on productivity and QY of CDs. Therefore, it is necessary to further explore high QY and more efficient synthesis method.

Herein, we proposed a rapid, continuous synthesized CDs method using microreactors with high efficiency. By taking advantage of the microreactor, we can rapidly synthesized CDs at a large scale in less than 5 min. Moreover, using microreactor methods, quantum yields of 60.1% and stable CDs were obtained, which is faster and more efficient than most of the previously reported methods. The relationship between the microreactor structure and the CD PL properties was also investigated, indicating inner structures have a great effect on quantum yields due to heat transfer significantly influences the synthetic process. The as-prepared CDs were used to detect Fe^{3+} ions, and the lowest detection limit (LOD) was 0.239 μM, which is superior to many other research studies. This rapid and simple synthesis method will not only aid the development of quantum dot industrialization but also provide a powerful and portable tool for the rapid and continuous online synthesis of CDs applications in bioanalysis and safety detection.

2. Materials and methods

2.1. Materials

For synthesis of carbon dots (CDs), citric acid anhydrous ($C_6H_8O_7$, ≥ 99.5%), ethylenediamine ($C_2H_8N_2$, ≥ 99.5%), and ethanol absolute (C_2H_6O, 99.5%) purchased from Aladdin have been used without further purification. Distilled water (18 MΩ) was used for all experiments.

2.2. Synthesis of CDs by microreactor method

A series of CDs was successfully synthesized by three different microreactors, as shown in Fig. 1. Typically, anhydrous citric acid and ethylene-diamine were used as precursors with deionized water as a solvent. A colourless transparent solution was prepared by dissolving anhydrous citric acid (2.25 g) in 60 ml of deionized water, followed by a few minutes of continuous stirring at room temperature. Then, additive concentrations (volumes of ethylenediamine ranging from 0.5 ml to 6.0 ml) were slowly dropped into the citric acid solution with vigorous stirring to achieve a homogeneous dispersion. Before the mixtures were injected into the microreactor, the microreactor was preheated to the rated temperature. Subsequently, distilled water was injected to clear impurities and check for gas leakages in the system. After that, when the rated temperature was achieved, the mixtures were injected by a magnetic pump with a flowmeter through a PTFE tube (inner diameter: d = 2 mm) and stainless steel tube into the linear-like microreactor. The microreactor temperatures between 80 °C and 160 °C (real temperature) were precisely controlled by a digital temperature controller. Importantly, to ensure that the flow rates (ranging from 16 ml/min to 160 ml/min) stabilized, a check valve was placed between the flowmeter and microreactor to prevent any solution and vapor from reverse flowing when the microreactor was operating at high temperatures. The samples were collected by a flask and soaked in ice water. A UV analyser with an emission maximum at 365 nm was placed on the bottom of the collection to observe the samples online. Similar procedures were also carried out for the snake-like and double-snake-like microreactors depending on the variation of the reaction temperature, additive concentration and flow rate.

2.3. Metal ion detection

For the detection of metal ions, various metal ion solutions,