Synthesis of N-doped carbon dots by microplasma process

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Abstract: Carbon dots have gained interests in biological application with their superiorities like non-toxicity and element abundance. In this study, an effective approach was developed for the synthesis of fluorescent carbon dots by microplasma at atmospheric pressure. Nitrogen element successfully was doped in the carbon dots during the synthesis. The synthesized N-doped carbon dots own a tunable excitation-dependent emission property with a quantum yield up to ~10%.

Keywords: Microplasma, Carbon quantum dots, Photoluminescence, Nanoparticle

1. Introduction

Carbon dots with the diameter below 10 nm are a new class of carbon nanomaterial beside carbon nanotubes, graphene, fullerenes. Unlike most of the carbon materials, carbon dots are a new member of quantum dot-like nanomaterials with tunable photoluminescent properties. In addition, they present lower toxicity comparing with metal-based quantum dots [1], exhibiting a great potential in various applications such as bio-imaging, photocatalysis and optoelectronic devices (LEDs) [2-4].

The synthesis of carbon dots can be principally accomplished through either "bottom up" or "top down" methods. "Top down" methods obtain graphene nanodots through the "break off" of graphite or other carbon materials [5]. Carbon dots are synthesized via "bottom up" methods from the polymerization of organic chemicals [6]. Most of synthesis methods for carbon dots require high temperature to initiate chemical reactions. However it also results in the chemical wastes production and size control problems. Non-thermal plasma could be a good choice to solve problem caused by thermal methods. Further, active radicals formed from water dissociation such as OH, H and O are generated during plasma liquid interaction, which may promote surface functionalization of carbon dots without adding extra chemicals.

The majority of carbon dots reported so far have quantum yields lower than 10% [1,7]. In our research before, isopropanol was applied as carbon source to synthesize the carbon dots. Small and uniform size carbon dots with amorphous and graphitic structure in nature were obtained in an optimal reaction time of 20 min. However, the quantum yield of those synthesized carbon dots is only ~1.5%. Thus, in this study, nitrogen element was doped in carbon dots by gas-liquid interface microplasma to improve the fluorescent properties and quantum yield. An Ar microplasma was introduced for initiating and accelerating the synthesis of carbon dots through polymerization reaction at atmospheric pressure. Citric acid and ethanediamine were used as the carbon source and nitrogen source, respectively. Characterizations of Ndoped carbon dots including the structure and optical properties were performed.

2. Experimental setup and measurements



Fig.1. The schematic diagram of the microplasma reactor.

The experiments were carried out in a designed plasma reactor as shown in Fig.1. The reaction solution was prepared by dissolving 1g of citric acid (192.1 g/mol, VWR) and 0.6ml ethane diamine (60.1 g/mol, Sigma Aldrich) in 10 ml deionized H₂O in the quartz reactor. A stainless-steel capillary placed 1 mm above the liquid surface and a platinum disk immersed in the liquid were used as the negative electrode and the ground electrode, respectively. The negative electrode was connected to a negatively biased DC power supply (Matsusada Precision, Model AU-10R30) to ignite and sustain the plasma. Ar gas flowed through the tube at a rate of 60 sccm and the discharge voltage was \sim 5 kV. The microplasma was used to treat the reactant for 2h, and the transparent solution turned to brown in color after the

treatment. The produced solution underwent 24h dialysis and was filtrated with a 0.2 mM filter membrane to remove unreacted reactants and larger particles. This solution is used for X-ray photoelectron spectroscopy (XPS, film drying), UV-visible absorption and Photoluminescence spectroscopy (PL) measurements. Freeze-drying is the last procedure to produce the carbon dots powder for further characterizations such as Fourier transform infrared spectroscopy (FTIR). The quantum yield (Φ) of C-dots was estimated by comparing the absorbency peak values (A) and integrated PL emission areas (I) with quinine sulfate (54%) as a reference, as shown in equation (1) [1]. "QS" stands for quinine sulfate. It was dissolved in 0.1 M H₂SO₄ (refractive index η_{OS} = 1.33), and the C-dots were dissolved in deionized water (refractive index η = 1.33).

$$\Phi = \left[\frac{l\left(1-10^{-A_{QS}}\right)}{l_{QS}\left(1-10^{-A}\right)}\right] \left(\frac{n^2}{n_{QS}^2}\right) \Phi_{QS} \quad (1)$$

3. Results and discussion

XPS was measured to analyse the surface composition and to identify the doping of nitrogen in carbon dots. The XPS results indicate that these carbon dots are composed of atomic C (51.81%), O (36.08%) and N (12.11%), as in Fig.2. The C 1s spectrum in Fig.2a consists of three contributions at 284.8 eV, 286.3eV and 288.0 eV, which are assigned to C-C, C-O/C-N and C=O groups [8]. The main contribution at 284.8 eV is assigned to graphitic structure carbon, indicating that the synthesized carbon dots possess predominantly sp² carbons. As for high resolution N 1s spectrum of Fig.2b, it is asymmetric due to the existence of two peaks at 399.5 eV and 401.2 eV, assigning to pyrrolic–like N and N-H groups, respectively [9].



Fig. 2. XPS spectrum of carbon dots: (a) C 1s spectrum (b) N 1s spectrum.

The reactant solution show no emission before plasma treatment and intense blue light emission after plasma treatment under the 365 nm UV lamp in Fig.3. The optical property of N-doped carbon dots is inspected using UV-vis spectroscopy. Two absorption peaks appear at 280nm and 340nm in Fig.3, which is ascribed to the π - π * and n- π electronic transition in carbon dots surface.



Fig. 3. UV absorption spectra of N-doped carbon dots solution.

Photoluminescent spectra were measured as a function of excitation wavelengths as shown in Fig.4. With the excitation wavelength increasing from 350nm to 430 nm, the emission peak shift from 455nm to 482nm. The highest intensity of photoluminescent spectrum was found under 390 nm excitation wavelength. This photoluminescent behaviour of N-doped carbon dots is common, which resulted from the presence of various particle sizes and the distribution of the different surface energy traps of Ndoped carbon dots as reported [10]. Further, quantum yield of carbon dots was calculated based on equation (1). The highest quantum yield 10% was obtained at the excitation wavelength of 390 nm, indicating the highest fluorescence property.



Fig. 4. The emission spectra as a function of excitation wavelengths.

FTIR spectrum of product also confirms the nitrogen doping of carbon dots in Fig.5. The bands at 801 cm⁻¹, 1260 cm⁻¹ and 1563 cm⁻¹ are assigned to vibrations of N-H, C-N and N-H bonds [11]. The broad peak at 3440 cm⁻¹ and stretching vibration peak at 2960 cm⁻¹ stand for O-H and C-H bonds, respectively. Besides, the absorption at

1020/1100 cm⁻¹, 1380 cm⁻¹ and 1650 cm⁻¹ prove the existence of C-O-C, C-OH and C=C/C=O groups in synthesized N-doped carbon dots [12], which could result in good water solubility and influencing emission properties of carbon dots.



Fig. 5. FTIR spectrum of carbon dots.

Optical emission spectrum was measured during the plasma reaction to observe the generated species of reactant in order to explore the mechanism of reaction in Fig.6. The dominant peaks from 690-850 nm were derived from highly excited electronic states of Ar atomic transition [13]. The less intense peaks in 307-310 nm and 656 nm are assigned to OH bands and atomic hydrogen (H_a), which were from the dissociation of reactant and water. There are no obvious carbon species existing in the spectrum, suggesting that the reaction mainly happened in the liquid phase. When plasma was generated in the gas-liquid interface, high energetic electrons interacted with the reactant solution, initiating and accelerating the polymerization of reactants.



Fig. 6. Optical emission spectrum during plasma reaction.

4.Conclusion

We have successfully synthesized the N-doped carbon dots by microplasma at atmospheric pressure. During the

plasma reaction, a high density of electrons generated from plasma promotes the polymerization process of reactants and the synthesis of N-doped carbon dots. Pyrrolic–like N and amino groups were attached in carbon dots along with other functional groups such as C-O, C=O, OH. It was proved N-doped carbon dots owns the tunable excitation-dependent emission properties. The highest quantum yield of N-doped carbon dots is ~10%, presenting intense blue emissions under a 365nm UV lamp. This method may also extend to the synthesis of carbon dots doped with other elements, demonstrating the great potentials in applications such as sensing, photocatalysis and bio-imaging.

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5.References

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