Synthesis of luminescent carbon quantum dots by microplasma process

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ABSTRACT

Carbon dots have recently emerged and gained much interest as a new class of carbon nanomaterials especially suited for biological applications owing to their characteristic advantages such as non-toxicity, bio-compatibility, and element abundance. In this study, a fast and effective method was developed for the synthesis of fluorescent carbon dots by microplasma technology, at atmospheric pressure, using isopropanol as the only reactant. Characterizations of the synthesized carbon dots including the investigation of their structure, morphology and optical properties were performed. The results show that the carbon dots produced have a narrow size distribution (average diameter of 1.78 nm) and are amorphous and graphitic in nature. The photoluminescent study indicates that the carbon dots present an excitation-dependent emission property with the excitation wavelengths in a range of 310–410 nm. The high density electrons produced by microplasma induce the chemical reactions and accelerate the formation process of functional groups doped carbon dots.

1. Introduction

In recent years, large research efforts have been devoted to the development of advanced carbon nanomaterials such as carbon nanotubes, graphene, fullerenes and carbon dots due to their unique electronic, mechanical, thermal and optical properties [1]. Among them, carbon dots with the diameter below 10 nm are a new member of quantum dots. The luminescent properties of carbon dots allow for their applications in various fields such as bio-imaging/sensing, photocatalysis, analytical chemistry and optoelectronic devices [1–4]. Comparing with commonly used metal-based quantum dots, carbon dots have higher biocompatibility and lower toxicity [5], suggesting they are more suitable for bio-applications.

Generally, carbon dots are mainly synthesized through two pathways: “top down” methods with graphite materials as carbon sources, “bottom up” methods with organic molecules as carbon sources. Thus they are classified into graphene nanodots and carbon nanodots, respectively. The graphene nanodots are synthesized from the “break off” of graphite, carbon nanotubes and other types of carbon materials [6]. On the other hand, carbon nanodots can be obtained by “bottom-up” polymerization mostly from high carbon/oxygen contained organic chemicals such as citric acid, amino acid and D-fructose [7]. The synthesis methods for carbon dots can be categorized in chemical methods (including electrochemical synthesis [8], combustion/hydrothermal synthesis [9,10] and microwave synthesis [11]) and physical methods (including laser [12], thermal plasma synthesis [13]). However, most of the synthesis methods face challenges such as using toxic starting materials, requirement of special reaction conditions, complex separation procedures and low quantum yields. For example, phenylenediamine was used as carbon source to obtain red emitting carbon dots [14]. However, phenylenediamine is a highly toxic organic chemical and the solvothermal synthesis process requires a long reaction time (12 h) to obtain carbon dots. In another research, N-doped graphene quantum dots were synthesized with citric acid and dicyandiamide in 3 h, followed by 48 h dialysis to get rid of unreacted small molecules and solvent [15]. In addition, the majority of carbon dots reported so far have quantum yields lower than 10% [5,16,17].

Besides, most of methods reported above for synthesizing carbon dots require high temperature, which is effective to accelerate chemical reactions but also results in the production of chemical wastes and process control problems during reaction. For example, Shin et al. [18] synthesized carbon dots in a wide size range of diameter (70–150 nm) by hydrothermal method. As reported, particle size is one of crucial factors which significantly influences the carbon dots emission wavelengths, resulting in various fluorescent colors such as blue, green, yellow and red [7]. Thus, further complex separation procedure is needed for non-uniform size distribution carbon dots to control the
luminescent properties.

Non-thermal plasma is a promising technology for material synthesis or pretreatment, which has been widely applied to pretreat the catalysts and synthesize nanomaterials [19–22]. The sizes of nanomaterials synthesized by plasma-liquid interactions are controllable [23–28]. Saito et al. [24] studied the synthesis of Au nanoparticles in a gas-liquid interface glow plasma. The sizes of Au nanoparticles were controllable between 20 nm and 150 nm by varying the discharge time and voltage, which provides more opportunities in applications. The electron temperature in non-thermal plasma reaction significantly exceeds that of heavy particles \( (T_e > T_n) \), promoting the generation of active species and giving rise to the chemical reactions at atmospheric pressure and low temperature. It could be a prospective approach to solve the problem of non-uniform size distribution caused by thermal methods. Huang et al. [5] compared the carbon dots produced by atmospheric pressure helium microplasma with those produced by chemical methods. Their results proved that carbon dots produced by microplasma have smaller size and more uniform size distribution compared to the ones produced by chemical methods. In addition, active radicals like OH, O and H from water molecules can be formed through plasma liquid interaction, which may allow additional surface functionalization of carbon dots without using extra solvents.

The reported carbon dots by a simple microplasma-assisted process adopted the reactants such as fructose, citric acid and folic acid [5,29,30]. The synthesis and mechanism study from these reactants have been also explored by using other synthesis methods [31–33]. However, the research of carbon dots synthesized from very small molecule \( (C < 3) \) alcohol are limited particularly in the microplasma-assisted carbon dots synthesis. In this study, IPA, the easiest secondary alcohol for cosmetics and pharmaceutical applications due to its low toxicity of any residues [34,35], was used as a typical small molecule reactant. The mechanism study by OES was added compared with other studies. In addition, there is no addition of acids/ bases or metal ions in this synthesis process. Thus, the production cycle is much shorter without dialysis separation process.

In this study, isopropanol was used as low-toxic carbon source without any acid/alkaline reagents. An Ar microplasma was used for the synthesis of carbon dots at atmospheric pressure. Energetic electrons \( (> 1 \text{ eV}) \) produced in plasma were injected to the reaction volume, initiating and accelerating the synthesis process at the gas-liquid interface. The aim of this research is to demonstrate a simple and green method for characterization of the shape and size of the C-dots. The produced carbon dots have excitation-dependent emission property, which are expected to favor the product application in biological fields after toxicity test in near future.

2. Experimental

2.1. Materials and methods

In this study, all experiments were carried out in an in-house designed plasma reactor as sketched in Fig. 1, which has been successfully used to synthesize yttrium oxides and TiN nanoparticles in previous studies [36,37]. The electrolyte solution was prepared by dissolving 2 ml of isopropanol (60.1 g/mol, VWR) in 8 ml deionized \( \text{H}_2\text{O} \) and filled in the quartz reactor. A stainless-steel capillary (I.D. = 0.51 mm, O.D. = 1.6 mm) was used as a negative electrode and a platinum disk was immersed in the liquid as the ground electrode. Both electrodes were connected to a negatively biased DC power supply (Matsusada Precision, Model AU-10R30) to ignite and sustain the plasma. A continuous argon gas stream at a flow rate of 60 sccm was injected through the capillary electrode which was placed 1 mm above the liquid surface, and the discharge voltage was ~4 kV. The microplasma was applied to treat the solution for 20 min, and the sample solution turned to yellowish in color after the treatment. The solution was filtrated with a 0.2 mM filter membrane and then dried by a vacuum drying machine at room temperature to remove larger particles and unreacted reactants. The carbon dots solution was obtained by dissolving the dried products in deionized water, this solution is used for X-ray photoelectron spectroscopy (XPS, film drying), UV–vis absorption and Photoluminescence spectroscopy (PL) measurements. Freeze-drying is the last procedure to produce the carbon dots powder for further characterizations such as Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction and Raman analysis.

2.2. Characterisation and measurements

The optical emission spectrum was measured by using an HR2000 + ES spectrometer (Ocean Optics, Inc.). The emitted light from the plasma gas-liquid interactions was collected by an optical fiber outside the reactor. The chemical compositions were assessed by using an X-ray photoelectron spectroscopy (XPS) from Thermo Scientific K-Alpha. The sample was prepared by depositing the carbon dots solution on Si substrates and dried at room temperature. The spectra of samples were recorded by an aluminum anode \( (\text{Al } K_{\alpha} = 1486.6 \text{ eV}) \). The Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai 20 (Sphera) microscope operated with a 200 kV LaB6 filament for characterization of the shape and size of the C-dots. The Fourier transform infrared spectroscopy (FTIR) spectra were measured by Alpha spectrometer from Bruker with the KBr pellet technique ranging from 500 to 4000 cm\(^{-1}\). The structure of carbon dots was characterized by a Labram confocal Raman microscope (Horiba Jobin-Yvon) using 632-nm laser as the excitation source. The X-ray diffraction patterns of the synthesized particles were obtained with a Rigaku Miniflex Powder Diffractometer using Cu-K\(\alpha1\) radiation with wavelength of 1.54056 Å. The scans were recorded with a speed of 0.2’/min from 10-90°. The UV–vis absorption spectrum and diffuse-reflectance spectra were recorded on a UV-2501PC. The photoluminescence (PL) measurements were performed on a luminescence spectrometer (Perkin Elmer, Model LS-50B) using excitation wavelengths in the range of 310–410 nm. The quantum yield \( (\Phi) \) of C-dots was estimated by comparing the absorbency peak values \((\text{A})\) and integrated PL emission areas \((I)\) with quinine sulfate (54%) as a reference, as shown in Eq. (1) [5]. “QS” stands for quinine sulphate. It was dissolved in 0.1 M H\(\text{SO}_4\) (refractive index \(n_{\text{QS}} = 1.33\)), and the C-dots were dissolved in deionized
water (refractive index $\eta = 1.33$).

$$\Phi = \frac{I(1 - 10^{-4\phi}-\eta)}{4\pi(1 - 10^{-4\phi})} \frac{n^2}{n_{QS}^2} \Phi_{QS}$$  

(1)

3. Results and discussion

3.1. Optical emission spectroscopy study for carbon dots synthesis

Optical emission spectra were measured during the plasma reaction to observe the dissociation of precursor and synthesis of carbon dots, followed by the identification of the excited state of the generated species. Fig. 2 shows the recorded spectra when plasma started to treat the isopropanol solution and the blank water sample. Detailed radiative transition information is summarized in Table 1. The dominant peaks from 690 to 850 nm were resulted from highly excited electronic states of Ar atomic transitions (Ar I) [38]. Apart from the Ar species, prominent emission peaks corresponding to the C2 swan band between 460 and 570 nm and CH modes at 389 nm and 431 nm were observed, which are particularly important for carbon nanomaterial formation and indicating the dissociation of the reactants [21]. According to Wang et al. [39], C2 species in reaction work effectively in nucleating a solid carbon cluster, and CH species form a hydrocarbon layer, promoting the nucleation of carbon nanomaterials. In this research, the reaction is considered to happen in the gas-liquid interface. When plasma was generated in the gas-liquid interface, a high density of electrons was produced and interact with the sample solution, isopropanol was dissociated and produced C2 and CH species, leading to the carbon nucleation and carbon dots formation. Besides, the less intense peaks in 307–310 nm and 656 nm are assigned to OH bands and atomic hydrogen ($H_\alpha$), which were resulted from the dissociation of reactant and water [40]. In the case of blank water sample, OH, $H_\alpha$ and Ar species also appeared in the spectrum, indicating that water was dissociated during plasma treatment. No nitrogen or carbon impurities were indicated during the plasma treatment.

3.2. X-ray photoelectron spectroscopy study for carbon dots elements analysis

The surface composition and elemental analysis of the produced carbon dots were obtained by XPS technique. The XPS results indicate that these carbon dots are composed of atomic C (80.31%) and O (19.68%) in Fig. 3a. The C 1 s spectrum of carbon dots (Fig. 3b) consists of three contributions: 284.5 eV, 286.0 eV and 287.9 eV. The first and main contribution at 284.5 eV can be assigned to the formed graphitic structure carbon. This peak clearly indicates that the prepared carbon dots possess predominantly sp2 carbons, which can be confirmed by Raman spectrum in Fig. 5. The contributions at 286.0 eV and 287.9 eV are

<table>
<thead>
<tr>
<th>Species</th>
<th>System</th>
<th>Transition</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>3064 Å system</td>
<td>A$^2\Sigma^+ \rightarrow X^2\Pi$</td>
<td>308.9 nm</td>
</tr>
<tr>
<td>CH</td>
<td>4300 Å</td>
<td>A$^2\Sigma^+ \rightarrow X^2\Pi$, ground state</td>
<td>432.0 nm</td>
</tr>
<tr>
<td>C2</td>
<td>3900 Å</td>
<td>B$^2\Sigma^+ \rightarrow X^2\Pi$, ground state</td>
<td>389.3 nm</td>
</tr>
<tr>
<td>C2</td>
<td>Swan system</td>
<td>A$^2\Sigma^+ \rightarrow X^2\Pi$, ground state</td>
<td>467.9 nm, 468.5 nm</td>
</tr>
<tr>
<td>H</td>
<td>Balmer series</td>
<td>n $\rightarrow$ 2s,2p</td>
<td>489.6 nm (H$\beta$), 657.2 nm (H$\gamma$)</td>
</tr>
<tr>
<td>Ar</td>
<td>Ar I</td>
<td>4p $\rightarrow$ 4s</td>
<td>696.5 nm (1s$^2$-2p), 706.7 nm (1s$^2$-2p$^2$), 738.4 nm (1s$^2$-2p$^2$), 750.4 nm (1s$^2$-2p$^2$), 763.5 nm (1s$^2$-2p$^2$), 772.4 nm (1s$^2$-2p$^2$), 794.8 nm (1s$^2$-2p$^2$), 826.5 nm (1s$^2$-2p$^2$), 842.5 nm (1s$^2$-2p$^2$)</td>
</tr>
</tbody>
</table>
due to the presence of C–O and C=O groups, respectively [41].

3.3. Transmission electron microscopy and X-ray diffraction study for size and morphology

The morphology, size distribution and crystal structure of the carbon dots were confirmed by TEM, selected area electron diffraction (SAED) and XRD. Fig. 4a-b show the TEM images of the produced CDs, which reveal that these spherical nanoparticles were well dispersed and separated from each other. The average diameter of the carbon dots is 1.78 ± 0.47 nm, calculated from collecting and measuring the diameter of 100 particles. SAED in Fig. 4c indicates that the produced carbon dots are amorphous, which is consistent with XRD patterns in Fig. 4d, showing only a broad peak at about 2θ = 21° and no sign of crystalline structure.

3.4. Fourier transform infrared spectroscopy and Raman study for structure of carbon dots

Vibrational spectroscopy data are accessed through FTIR and Raman analysis in Fig. 5 a-5b. The broad and intense peak in Fig. 5a around 3440 cm⁻¹ corresponds to the O–H stretching vibration, followed by C–H stretching vibrations at weak bands of 2922 cm⁻¹ and 2972 cm⁻¹ [16]. The absorption at 1731 cm⁻¹ and 1650 cm⁻¹ are attributed to the generation of C=O and C≡C groups, respectively. Besides, the peaks at 1382 cm⁻¹ and 1050/1278 cm⁻¹ prove the existence of C–OH and C–O–C groups in carbon dots [42]. The Raman spectrum is shown in Fig. 5b, both spectra exhibit two broad features, at 1365 cm⁻¹ and 1590 cm⁻¹, close to the D (disorder) and G (graphite) bands, respectively. D band derives from the vibrations of carbon atoms with dangling bonds in the termination plane of disordered graphite or glassy carbon, while the G band is related to E₀² mode of the graphite and the vibration of sp2-bonded carbon atoms in a two-dimensional hexagonal lattice [43]. The intensity of G band is higher than D band in Fig. 5b, indicating there are principally sp² carbons with some sp³
hybrid carbons in carbon dots. Thus, carbon dots are mainly composed of sp² graphitic carbons with sp³ carbon defects. This is similar with carbon dots synthesized by Mao et al. in report [3]. In conclusion, functional groups such as C=O, C–O and O–H are attached to the graphitic-structure carbon dots during plasma reaction successfully. The existence of carboxyl and hydroxyl groups results in good water solubility of carbon dots. Further, the oxidation state of carbon dots influences the emission properties [7].

3.5. Optical study of carbon dots

Further investigation was carried out to study the photophysical properties of prepared carbon dots. The isopropanol solutions show no emission before and strong blue light emission under the 365 nm UV lamp after reaction. The UV–vis absorption spectrum indicates the extent of reaction (Fig. 6a) from no absorption at 0 min to highest absorption intensity after 20 min reaction, suggesting the optimal reaction time was around 20 min. Lower absorption in spectrum was observed after 20 min, this is possibly caused by the evaporation of isopropanol and aggregation of carbon dots which resulted in the decrease of soluble carbon dots production. Besides, the absorption wavelength of carbon dots is within 450 nm, and the dominating peak is at 252 nm, which is ascribed to the π–π* transition of C=C [44]. PL spectra were measured as a function of the excitation wavelengths as reported in Fig. 6b. The highest intensity PL spectrum was found at 330 nm excitation wavelength. Peak wavelengths are excitation energy dependent, which red shifted from 365 nm to 490 nm with the increase of excitation wavelengths in a range of 310-410 nm. This PL behavior of carbon dots is caused by the presence of different particle sizes and the distribution of the different surface energy traps of the carbon dot as reports [10,45].

The effect of reaction conditions including precursor concentrations (1–2 ml) and operating voltages (3–4 kV) on PL properties were also explored in study. All the experiments were kept running for 20 min. The purified carbon dots were dissolved in water and adjusted to the same concentration (0.1 mg/ml) in all cases. The PL spectra were present in Fig. 7. The intensity and tendency of the PL spectra are different in the case of various precursor concentrations in Fig.7a-7c. The intensity of emission peaks at 310 nm and 330 nm excitation wavelengths are similar in the case of 1 ml isopropanol. However, there is only one highest emission spectrum appearing at 330 nm excitation wavelength in the case of 2 ml isopropanol. This behavior could be explained by the domain size distribution and carbonization degree analyzed from the difference of carbon dots surface composition [7,46]. The dominant size distribution with 1 ml isopropanol is between 1.0–2.0 nm (%85%). But main size distribution with 2 ml isopropanol is narrower between 1.5 nm–2.0 nm (%50%). The average size (1.78 nm) of 2 ml isopropanol is bigger than the size (1.55 nm) with 1 ml isopropanol (as in Fig.S1). The size difference may lead to the shift of maximum emission wavelength [7]. In addition, the surface content of carbon in carbon dots made with 2 ml isopropanol is narrower between 1.5 nm–2.0 nm (%50%). The average size (1.78 nm) of 2 ml isopropanol is 80.31%, which is higher than 73.79% with 1 ml isopropanol (as in Fig.S5). The graphitic structure carbon is also higher with 2 ml isopropanol (69.17%) in the carbon spectrum of XPS. Thus, the reaction with lower concentration of isopropanol in this research range could lead to less intense dissociation reaction under plasma treatment, which results in the low carbonization degree and the difference in PL emission intensity. The difference of emission spectra in the case of various operating voltages can be also explained in the size distribution in the same way. The average size of carbon dots with 3 kV is smaller (1.51 nm) (as in Fig.S1). Since there is no obvious difference in the composition and PL emission intensity of carbon dots between the samples treated by plasma operating at 3 kV and 4 kV. The effect of voltage on PL emission of carbon dots are considered to principally influence the intensity of dissociation reaction, which leads to the variety of size distribution and PL emission. It is obvious that both of precursor concentration and operating voltage are able to affect the formation and optical properties of carbon dots in this research range.
Quantum yield of the produced carbon dots with 2 ml isopropanol is around 1.5% based on the calculation with the reference solution quinine sulfate as Table 2. As reported, most of reported carbon dots show low quantum yields within 10% and limited blue/green emitting, resulting in the difficulties and restrictions in application. However, this problem can be hopefully improved by doping various elements (N, B, P) and altering the specific carbon sources [7].

4. Conclusion

A simple, effective and green way was developed for producing carbon dots by microplasma process without involving highly toxic chemicals and complex purification processes. During the microplasma reaction, energetic electrons generated by plasma dissociated the isopropanol and achieved the carbonization of reactant without using conventional heating methods. Precursor concentrations and operating voltages during plasma treatment are able to affect the composition and size distribution of carbon dots resulting in the difference of PL emission. In addition, gas-liquid interface microplasma produced carbon dots possess different functional groups such as C=O, C–O, OH, which could result in good water solubility of carbon dots and may lead to the intense blue emissions in the range of 365–490 nm. This method may be extended to the synthesis of photoluminescent carbon dots with different compositions through variation of the carbon precursors, such as N-, B- and P- doped reactants, which could improve the quantum yields of carbon dots and expand controlled emission wavelength ranges to red fluorescence. Carbon dots synthesized by non-thermal plasma have great potentials in a number of applications such as sensing, LED devices and bimodal biological imaging in near future.

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Fig. 7. (a) PL spectra of reactant with 1 ml isopropanol sample treated by plasma operating at 4 kV (b) PL spectra of reactant with 2 ml isopropanol treated by plasma operating at 3 kV (c) PL spectra of reactant with 2 ml isopropanol treated by plasma operating at 4 kV.

Table 2

Quantum yield of carbon dots.

<table>
<thead>
<tr>
<th>Excitation wavelength</th>
<th>I</th>
<th>I₀₀₀</th>
<th>A₀₀₀</th>
<th>λ</th>
<th>QY %</th>
</tr>
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<tbody>
<tr>
<td>350</td>
<td>1962.917</td>
<td>78047.04</td>
<td>0.05402</td>
<td>0.04906</td>
<td>1.5</td>
</tr>
<tr>
<td>360</td>
<td>1559.859</td>
<td>63894.69</td>
<td>0.04301</td>
<td>0.03963</td>
<td>1.4</td>
</tr>
<tr>
<td>370</td>
<td>1238.211</td>
<td>37303.71</td>
<td>0.02693</td>
<td>0.03421</td>
<td>1.4</td>
</tr>
<tr>
<td>380</td>
<td>927.635</td>
<td>15357.77</td>
<td>0.0139</td>
<td>0.02931</td>
<td>1.6</td>
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<tr>
<td>390</td>
<td>584.5303</td>
<td>4424.035</td>
<td>0.0039</td>
<td>0.02452</td>
<td>1.2</td>
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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cep.2019.04.017.

References


