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Synthesis of N-doped carbon dots via a microplasma process

Xintong Ma^a, Sirui Li^{a,*}, Volker Hessel^b, Liangliang Lin^c, Stefan Meskers^c, Fausto Gallucci^a

^a Inorganic Membranes and Membrane Reactors, Sustainable Process Engineering, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, De Rondom 70, Eindhoven 5612 AP, the Netherlands

^b School of Chemical Engineering, University of Adelaide, Adelaide 5005, Australia

^c Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, De Rondom 70, Eindhoven 5612 AP, the Netherlands

HIGHLIGHTS

- N-doped CDs with an average size of 5.98 nm were synthesized by microplasma.
- The synthesized N-CDs showed intense blue emission under a UV lamp.
- The quantum yield was up to 9.9% at excitation wavelength of 390 nm.
- Effect of plasma parameters on surface group and PL property of N-CDs was explored.
- Electrode size has an effect on the electron density, resulting a yield up to 0.42%.

GRAPHICAL ABSTRACT

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ABSTRACT

In this study, an effective approach was presented for the synthesis of N-doped carbon dots via a microplasma-assisted process at atmospheric pressure. The effects of operation parameters on the surface groups and photoluminescence (PL) property of carbon dots were studied in detail. Nitrogen element was successfully doped as N–H group and pyrrolic-like structure in the carbon dots. The morphology, structures, chemical compositions and photoluminescence properties of N-doped carbon dots were systematically characterized. The generated chemical species and mechanism were monitored and studied by optical emission spectroscopy. The synthesized particles owned excitation-dependent emission property with a quantum yield up to 9.90%. The plasma treatment time and operating voltage affect the carbonization degree, doping state of nitrogen and particle size, resulting in different PL behaviours. The variation of electrode sizes has slight effects on the yield of N-doped carbon dots from 0.31% to 0.42% owing to the differences in electron density.

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1. Introduction

Carbon quantum dots are a new member of fluorescent carbon nanomaterial with the size below 10 nm (De et al., 2015). In recent

decades, considerable attention has been attracted by carbon quantum dots owing to their unique optical properties, excellent water solubility, low toxicity and good biocompatibility (Gedda et al., 2016). As a result, carbon dots have been applied to various fields including bio-imaging (Yan et al., 2013), photocatalysis (Zhang et al., 2016) and optoelectronics (Li et al., 2012) as replacements of potential toxic metal-contained quantum dots based on

* Corresponding author.

E-mail address: S.Li1@tue.nl (S. Li).

serious safety concern. However, carbon quantum dots have narrow emission wavelengths (<500 nm) within the blue colour range, resulting in the limitation of applications (Huang et al., 2015). As reported in literature, functional groups on the surface of carbon dots are crucial factors to affect the surface level and the level gap (Tuerhong et al., 2017). Nitrogen doping along with sulphur, boron and phosphorous is an effective surface passivation route for carbon dots, it can cause radiation rearrangements and improve the fluorescent properties (Bourlinos et al., 2015) (Parvin and Mandal, 2017). As in the research conducted by Jin et al., the amino groups in the carbon dots result in the red shift of fluorescence (Jin et al., 2013). The band gap shows a decreasing trend with the increase of amino groups. Campos et al. reported the quantum yield of carbon dots was improved from 8% to 11% with nitrogen doping (Campos et al., 2015).

N-doped carbon dots can be synthesized by “bottom-up” polymerization from high carbon/oxygen contained organics with the addition of nitrogen contained chemicals such as ammonia. The synthesis approaches reported so far include microwave method (López et al., 2015), ultrasonic method (Ma et al., 2012), thermal plasma method (Li et al., 2013), hydrothermal method (Campos et al., 2017). López et al. produced the N-doped carbon dots by utilizing microwave method operating at 20 bar and 750 W for 15 min (López et al., 2015). The obtained carbon dots were used as a potential system to quantify heterocyclic aromatic amines, showing the promising prospect in chemical sensing. The N-doped carbon dots with a diameter of 10 nm were prepared by Ma et al. through 300 W ultrasonic treatment for 24 h, presenting effective photodegradation property of MO (Ma et al., 2012). Hydrothermal method is also a popular approach for nanoparticles synthesis. Campos et al. synthesized N-doped carbon dots at 100 °C for 3 h with a quantum yield of 11% (Campos et al., 2017). However, the average diameter is bigger (50 nm) with a wide size distribution (35–65 nm). Overall, most of the reported methods were carried out at high temperature and/or high pressure, which is effective for carbon dots synthesis but also accompanied by problems in the control of synthesis process and product size.

Microplasma-assisted nanomaterial synthesis has recently attracted much attention due to its low cost, easy-control operation and high purity of synthesized products (Liang et al., 2010), (Lin et al., 2018b). High energy electrons generated from the non-equilibrium plasma produce active species and give rise to the chemical reactions, accelerating the nanoparticle production at atmospheric pressure and low temperature. Thus, it allows to synthesize the nanoparticles without high pressure or temperature compared with hydrothermal methods. In addition, according to the Paschen's law, the breakdown voltage of discharge for a certain gas is a function of pressure and gap length between two electrodes. It is possible to ignite and sustain microplasma by applying a relatively low voltage. Thus the energy for sustaining microplasma (3–5 W) in this study is much lower than that reported microwave method (750 W) (López et al., 2015) or ultrasonic method (300 W) (Ma et al., 2012). Further, the process and particle size can be controlled by simply varying the residence time and discharge voltage (Saito et al., 2009). In our previous study, a simple and green way was reported for pure carbon dots synthesis by isopropanol dissociation (Ma et al., 2019). However, the yield and quantum yield of pure carbon dots are limited. As reported, nitrogen (or boron, phosphorus) doping is an effective surface passivation route for carbon dots, it can cause radiation rearrangements and improve the fluorescent properties (Parvin and Mandal, 2017). Thus, element doping study of carbon dots is essential to obtain carbon dots with favourable fluorescent performance. There are a few studies for the synthesis of N-doped carbon dots by

microplasma (Wang et al., 2018) (Wang et al., 2015). Wang et al. obtained the N-doped carbon dots with an average diameter of 47.31 nm with folic acid and NaHCO₃ as the reactants (Wang et al., 2018). Wang et al. utilized microplasma as anode and produced N-doped carbon dots with a quantum yield of ~5.1% (Wang et al., 2015). However, the effects of microplasma reaction parameters on the doping states of nitrogen and photoluminescence (PL) behaviour have not been fully studied. The yield study of carbon dots is also limited. Thus, in this study, microplasma was applied as the cathode for the synthesis of N-doped carbon dots. The reaction parameters such as reaction time, operating voltage, electrode size were researched to study the effects of them on the surface groups and PL behaviours of N-doped carbon dots systematically. The production yield and quantum yield of carbon dots were also reported. In addition, there is no addition of metal ions impurity during the synthesis process. The reaction mechanism was explored with optical emission spectrum compared with reported studies.

The main objective of this study is to achieve the doping of nitrogen on carbon dots effectively via a microplasma-assisted process and explore the effects of microplasma reaction parameters on the surface groups and PL properties of carbon dots. The synthesis of N-doped carbon dots was investigated by using microplasma under atmospheric pressure and room temperature. Ar was applied for plasma generation. The functional groups, fluorescent properties and reaction mechanism were studied in detail by characterizations for potential applications.

2. Methodology

2.1. Experimental setup and reactor

N-doped carbon dots were synthesized in the microplasma reactor designed and constructed at TU/e, a schematic of which is represented in Fig. 1. A stainless-steel capillary (I.D. = 0.50 mm, O.D. = 1.6 mm), as a negative electrode, was placed 1 mm above the reactant solution surface. 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 50 kΩ ballast resistor is used to limit the current and provides stability to the discharge. A continuous argon gas stream with a flow rate of 60 sccm was injected through the capillary electrode. The discharge voltage was kept at ~5 kV.

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

2.2. Chemicals

Citric acid (192.1 g/mol, 99.5%) was purchased from VWR and was used as the carbon source in the reaction. Ethylenediamine (60.1 g/mol, 99%) was supplied by Sigma Aldrich and was chosen as the nitrogen source. In the pretests, other nitrogen sources such as ammonia and urea were also tested. But results are not satisfactory due to low yield.

2.3. Synthesis process of N-doped carbon dots

The reactant solution was prepared by dissolving 1 g citric acid and 0.6 ml ethylenediamine in 10 ml deionized H₂O. The aqueous solution was fully mixed then transferred into the quartz reactor. The microplasma was applied to treat the solution for 2 h and the transparent solution turned to brown in color after the treatment. The produced solution underwent 24 h dialysis and was filtrated with a 0.2 μm filter membrane to remove unreacted reactants and larger particles. The produced carbon dots solution is directly used for X-ray photoelectron spectroscopy (XPS, film drying), UV-visible absorption and Photoluminescence spectroscopy measurements. Freeze-drying is the last procedure to produce the carbon dots powder for further characterizations such as Transmission electron microscopy (TEM), X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), and Raman analysis.

2.4. Characterization and measurements

The transmission electron microscopy (TEM) measurements were taken on a FEI Tecnai 20 (Sphera) microscopy operating at 200 kV LaB₆ filament for characterization of the morphology of the N-doped carbon dots. The samples were prepared by drop-casting the solution to a carbon-coated copper grid and dried in the oven at 40 °C for 10 min. Chemical elements were analyzed with an X-ray photoelectron spectroscopy (XPS) from Thermo Scientific K-Alpha by depositing the sample on Si substrates. The spectra of samples were recorded by the aluminium anode (Al K_α = 1486.6 eV). The X-ray diffraction patterns (XRD) of the N-doped carbon dots were measured with a Rigaku Miniflex Powder Diffractometer using Cu-K_{α1} radiation with a wavelength of 1.54056 Å. The scans were recorded with a speed of 0.2°/min from 10° to 90°. Functional groups of N-doped carbon dots were studied by using Fourier transform infrared spectroscopy (FTIR) with an Alpha spectrometer. KBr pellet technique was applied for the spectra ranging from 500 to 4000 cm⁻¹. The optical emission spectrum (OES) was recorded by using an HR 2000 + ES spectrometer (Ocean Optics, Inc.), which was used to demonstrate the active species during the reaction. Raman spectrum of the obtained N-doped carbon dots was measured by a Labram confocal Raman microscope (Horiba Jobin-Yvon) with 632-nm laser radiation. Spectral properties of N-doped carbon dots were studied by a UV-vis spectroscopy (UV-2501PC). The photoluminescence measurements were performed with a luminescence spectrometer (Perkin Elmer, Model LS-50B) using excitation wavelengths in the range of 350–430 nm. Quinine sulfate was used as a standard reference for fluorescence measurement, with a relatively constant quantum yield of 54% over the UV absorption region 240–400 nm and photoluminescent emission region (350–600 nm) in the 0.1 M H₂SO₄ solution (Crosby and Demas, 1971). It has been applied in many quantum yield studies of carbon dots (De and Karak, 2013; Huang et al., 2015; Jiang et al., 2014), since the carbon dots also own dominant UV absorption and photoluminescent emission wavelengths in this range. The quantum yield (Φ) of carbon dots was estimated by comparing the absorbance peak values (A) and integrated PL emission areas (I) with quinine sulfate as the standard and calculated according to Eq. (1) (Huang et al., 2015).

$$\Phi = \left[\frac{I(1 - 10^{-A_Q})}{I_Q(1 - 10^{-A})} \right] \left(\frac{n^2}{n_Q^2} \right) \Phi_Q \quad (1)$$

“Q” stands for quinine sulfate. It was dissolved in 0.1 M H₂SO₄ (refractive index $n_Q = 1.33$), and the N doped carbon dots were dissolved in deionized water (refractive index $n = 1.33$).

3. Results and discussion

3.1. Characterization analysis of N-doped carbon dots after 2 h treatment

The dispersed N-doped carbon dots after two-hour plasma treatment (operating at 5 kV) were observed in the TEM images in Fig. 2a–c. Most of the products are particles (Fig. 2a–b) apart from a small number of sheets-like material/dark background in Fig. 2c. It is possible that a few nanosheets were generated with carbon dots. The particle size analysis was done by collecting 100 nanoparticles from scale-based images, measured via Image J software and analyzed via Origin software. The size distribution of N-doped carbon dots is from 3 – 10 nm as shown in Fig. 2d. The average particle size is 5.98 ± 1.37 nm. The XRD pattern of the synthesized particles reveals one diffraction peak centre at around 21° (Fig. 2e), presenting an amorphous structure of the N-doped carbon dots (Lai et al., 2012). In the Raman spectrum shown in Fig. 2f, two peaks are observed between 1000 and 2000 cm⁻¹, which are attributed to the D band (1333 cm⁻¹) and the G band (1580 cm⁻¹). The D band is representative of the vibrations of disordered graphite or glassy carbon, while the G band is related to the in-plane displacement of carbon atoms in a two-dimensional hexagonal lattice. Additionally, the value of I_D/I_G can be used to estimate the degree of graphitization (Li et al., 2014). The intensity of D band is higher than the peak of G band with the I_D/I_G value of 1.39 (see Fig. 2f), implying that more sp³-hybridized carbon was produced and the addition of nitrogen element could disrupt regular graphitic structure (Li et al., 2014) (Zhang et al., 2015).

The functional groups of N-doped carbon dots were studied by FTIR spectrum in Fig. 3. The broad peak at 3440 cm⁻¹ and stretching vibration peak at 2960 cm⁻¹ are assigned to O–H and C–H bonds, respectively. The vibrational absorption peak of C=O conjugated with aromatic C=C is found at 1650 cm⁻¹ (Gu et al., n.d.). The bands at 1260 cm⁻¹ and 1563 cm⁻¹ are assigned to vibrations of C–N and N–H bonds, indicating the successful synthesis of N-containing groups (Gu et al., n.d.). The absorptions at 1020–1100 cm⁻¹, 1380 cm⁻¹ prove the existence of C–O–C, C–OH groups in synthesized N-doped carbon dots (Gedda et al., 2016). The existence of carboxylic and hydroxyl groups highly relates to the excellent water solubility of synthesized N-doped carbon dots.

Photoluminescent emission spectra of N-doped carbon dots were measured as a function of excitation wavelengths as shown in Fig. 4a. The emission peaks shift from 450 nm to 479 nm corresponding to excitation wavelengths from 350 nm to 430 nm. This photoluminescence behaviour, excitation-dependent fluorescence emission property, is commonly resulted from the presence of various particle sizes and the distribution of the different surface energy traps (De et al., 2015; Yan et al., 2013). The emission intensities are also different with the variation of excitation wavelengths. Thus, it is important to find the dominant excitation wavelength and emission wavelength with favourable PL behaviour. In our study, the emission shows the highest intensity at 468 nm with an excitation wavelength of 390 nm, which coincides with the maximum excitation spectrum in Fig. 4b. There are three peaks in the excitation spectrum monitored at 468 nm (Fig. 4b), indicating that three types of excitation energy trapping exist on the surface of carbon dots. Further, PL emission spectra, at

Fig. 2. (a)–(c) TEM images, (d) particle size distribution, (e) XRD pattern, (f) Raman spectrum of N-doped carbon dots synthesized by plasma operating at 5 kV after 2 h.

Fig. 3. FTIR spectrum of N-doped carbon dots synthesized by plasma operating at 5 kV after 2 h.

excitation wavelength 390 nm, was explored as a function of carbon dots concentration in water in Fig. S1. The intensity of PL emission peak increases with the increase of carbon dots concentration within the research range. There is a linear relationship between concentration and peak intensity when the concentration is lower than 0.08 mg/ml. The quantum yields of excitation wavelength in a range of 360–390 nm were calculated relative to the quantum yield of quinine sulfate via equation (1). The value is up to 9.90% at the excitation wavelength of 390 nm.

3.2. The effect of reaction time on the surface groups and PL properties of N-doped carbon dots

Fig. 5 reports UV–vis absorption spectra of the sample solution after 1 h, 1.5 h and 2 h plasma treatment. There are three typical

absorption peaks at 250 nm, 280 nm and 340 nm in the spectra, which is in accordance with the result from the excitation spectrum in Fig. 4b. The peaks at 250 nm and 280 nm are ascribed to the π - π^* transition of C=C and n - π^* transition of C=O, which have less effects on fluorescent signal emission of carbon dots (Li et al., 2015). The transition centre around 340 nm is assigned to the trapping of excited carriers by the localized surface states, which may result in strong photoluminescent emission. This is in line with the results achieved by Gu et al. in their study of nitrogen-doped graphene quantum dots (Gu et al., n.d.). Besides, the intensities of peaks increase with the operating treatment time, indicating that the synthesis process continues with the plasma treatment time after 1 h. In addition, the embedded photo in Fig. 5. clearly indicates that the untreated sample solution showed no emission while blue light was observed in the two-hour treated sample solution when they were exposed to a 365 nm UV lamp.

XPS was measured to analyse the surface composition and to identify nitrogen doping in carbon dots after the plasma synthesis process. The spectra of the sample after 1 h, 1.5 h and 2 h treatments were reported to compare the variation of the functional groups. The C 1s spectra in Fig. 6a, c, e consist of three contributions at 284.8 eV, 286.3 eV and 288.0 eV, which are assigned to C–C, C–O/C–N and C=O groups (Campos et al., 2015). The contribution at 284.8 eV is assigned to graphitic structure carbon, indicating that sp^2 carbons are predominant in the synthesized carbon dots with longer plasma treatment time. As for high-resolution N 1s spectrum of Fig. 6b, d, f, it is asymmetric due to the existence of two different peaks at 399.5 eV and 401.2 eV, corresponding to pyrrolic-like N and N–H groups respectively (Zhang et al., 2012; Wang et al., 2019). It can also be confirmed from the FTIR spectra study (Fig. S2). The intensities of N–H and O–H groups decrease when plasma treatment time increases in two hours. Instead, the intensity of C–N increases in the case of longer plasma treatment time. N–H groups exist in the N-doped carbon dots from theoretical and characterization analysis. This implies that the doping mode of N element can be controlled with the

Fig. 4. PL emission spectra (a) and excitation spectra (b) of N-doped carbon dots synthesized by plasma operating at 5 kV after 2 h.

Fig. 5. UV-vis absorption spectra of N-doped carbon dots solution.

variation of plasma treatment time during the plasma-assisted synthesis process.

The tendencies of PL emission spectra of N-doped carbon dots after 1 h, 1.5 h and 2 h plasma treatment (Fig. 7) are almost the same in all cases. The emission peaks shift from 450 nm to 479 nm with the variation of excitation wavelengths from 350 nm to 430 nm. The emission intensities show the highest intensity at 468 nm under the excitation wavelength of 390 nm. However, the intensities of emission peaks with shorter treatment time are higher due to lower carbonization degree and more functional groups, which are important factors for influencing the surface energy levels and level gaps (Tuerhong et al., 2017; Bagheri et al., 2017). The average particle size increases from 3.10 nm after 1 h treatment (Fig. S3) to 5.98 nm after 2 h treatment. However, Sun et al. found the PL properties of N-doped carbon dots are primarily affected by the surface state rather than size differences (Deng et al., 2015). Thus, more functional surface groups such as C—O/C—N, C=O and N—H groups result in the much higher PL emission intensities in the case of the sample with shorter treatment time. The plasma treatment time has evident impacts on the carbonization degree and doping mode of N of carbon dots. When the plasma is applied to treat the reactant solution, the condensation reaction between citric acid and ethylenediamine is

accelerated, which leads to the carbon nucleation. When the plasma treatment time is prolonged, more functional groups are carbonized into carbon core, resulting in the decrease of surface groups such as O—H and N—H and the growth of carbon core (Liu et al., 2019). Thus, the carbonization degree and size of N-doped carbon dots are increased. The doping mode of N transfer from N—H to pyrrolic-like N. Simultaneously, the lessened surface functional groups result in the lower PL intensity in the case of long treatment time.

3.3. The effect of operating voltage on the surface group and PL properties of N-doped carbon dots

The XPS spectra of the samples operating at various voltages (3–5 kV) were reported to compare the variation of the surface functional groups. The concentration of graphitic structure of carbon rises with the increase of operating voltages from 40% to 51%. As for high-resolution N 1s spectrum of Fig. 8, the composition of pyrrolic-like N increases obviously in samples operating at higher voltage, indicating the change of N doping from N—H groups to pyrrolic-like N. This implies that the carbonization degree and doping mode of N element of carbon dots are adjustable with the variation of operating voltages during the plasma-assisted synthesis process. UV-vis absorption spectra of the sample solution operating at 3–5 kV were shown in Fig. S4. Three typical absorption peaks emerged at 250 nm, 280 nm and 340 nm in the spectra, which are ascribed to the π - π^* transition of C=C, n- π^* transition of C=O and trapping of excited carriers by the localized surface states appeared at the same positions with the peaks in Fig. 5. The intensity is higher with the increase of operating voltage. More N-doped dots were produced with the increase of plasma operating voltage.

The purified N-doped carbon dots were dissolved in water and adjusted to the same concentration (0.05 mg/ml) for PL measurement in all the cases. The PL spectra were discussed in Fig. 9. The intensity and emission wavelength of PL spectra in various cases have no obvious change, indicating that the surface groups do not play a decisive role in this case. However, the intensity tendency of PL emission peaks shifts from short wavelength to long wavelength. This could be explained by the size differences leading by the variation of operating voltages. The average particle sizes increase from 3.41 nm operating at 3 kV to 5.98 nm operating at 5 kV (Fig. S3). Higher plasma voltage leads to an expansion of discharge volume and more energetic electrons generation (Lin and Wang, 2015). It leads to more intense condensation reaction between reactants and accelerates carbon nucleation and growth,

Fig. 6. XPS spectra comparison of N-doped carbon dots synthesized by plasma operating at 5 kV after 1 h (a, b), 1.5 h (c, d), after 2 h (e, f).

Fig. 7. The emission spectra N-doped carbon dots by plasma operating at 5 kV after 1 h (a), 1.5 h (b), and 2 h (c) plasma treatment.

Fig. 8. XPS spectra comparison of N-doped carbon dots after 2 h plasma treatment operating at 3 kV (a, b), 4 kV (c, d), 5 kV (e, f).

Fig. 9. PL spectra comparison of N-doped carbon dots after 2 h plasma treatment operating at 3 kV (a), 4 kV (b), 5 kV (c).

resulting in larger particle generation and more carbon dots produced. It coincides with other reports (Lin et al., 2018a; Ma et al., 2019). Thus, the effect of plasma operating voltage is considered to principally influence the intensity of the condensation reaction between reactants, resulting in the changes in particles sizes and PL emission tendency.

3.4. The effect of electrode sizes on the N-doped carbon dots

The particles synthesized with different electrode sizes (0.25 mm/0.50 mm) were studied in this section. Tests were all operated at 5 kV for 2 h. Surface groups (Fig. S5) and PL spectra (Fig. S6) of synthesized carbon dots have no significant differences in two cases. However, the concentration of N-doped carbon dots solution synthesized with 0.25 mm electrode is higher than that with 0.50 mm electrode in the sample photo of Fig. S7. The yield of carbon dots was calculated based on the mass of produced carbon dots and the average yield of carbon dots (0.42%) synthesized with 0.25 mm electrode is slightly higher than that with 0.50 mm electrode (0.31%). Notably, the yield of carbon dots is generally low (~0.1%) based on the reports (He et al., 2018; Ma et al., 2019). The yield in this study is already three times higher. If relatively growth rate was considered, the yield increased by 35% from 0.31% to 0.42% when the electrode size decreased by 50% from 0.50 mm to 0.25 mm. Thus, the yield difference resulting from the electrode size variation is reasonable. This reason could be explained by the difference in electron density owing to the various electrode sizes. As reported in similar studies (Jögi et al., 2014; Wu et al., 2019), the current density and electron density increase as the tube diameter of microplasma decreases. The electron densities were estimated in both cases as Eq. (2) (Lu et al., 2013). n_e stands for electron density, j is the current density, E is the electric field, μ_e is the electron mobility and e is the elementary charge constant. The electron

mobility μ_e is $4.3 \times 10^2 \text{ cm}^2/(\text{V} \cdot \text{s})$ for argon at atmospheric pressure (Lu et al., 2013). The density with 0.25 mm electrode, $9.24 \times 10^{18} \text{ m}^{-3}$, is higher than that with 0.5 mm electrode $2.34 \times 10^{18} \text{ m}^{-3}$. These numbers are within the reported estimated electron density range ($10^{15} \text{ m}^{-3} - 10^{20} \text{ m}^{-3}$) of microplasma (Lu et al., 2013) and in consistence with the conclusion from the similar study (Jögi et al., 2014; Wu et al., 2019). When the electrode size decreases 50%, the electron density is ~ 3 times higher than before based on the calculation in Eq. (2), thereby leading to a 35% increase of the yield. It can be proved that electron density is higher in the case of smaller size electrode in this study, resulting in a higher yield of particles production.

$$n_e = j/(E\mu_e e) \quad (2)$$

3.5. Mechanism analysis

The optical emission spectrum was recorded to observe the excited state of generated chemical species and to further analyse the reaction mechanism. The prominent peaks in Fig. 10 are assigned to highly excited electronic states of Ar atomic transitions (Ar I) between 690 and 850 nm (Crintea et al., 2009). Apart from the Ar species, peaks at 307–310 nm, 656 nm and 777.2 nm indicate OH bands, atomic hydrogen (H_α) and O I bands, which correspond to the dissociation of H_2O in the sample solution (Lee et al., 2013). A very weak hydrogen (H_β) peak appears at 486.1 nm (Jamróz et al., 2012). Detailed radiative transition information is summarized in Table 1. There are no typical peaks of carbon species (C_2) appearing between 460 and 570 nm (Kumar et al., 2013), suggesting that the dominant mechanism for N-doped carbon dots synthesis is not derived from the hydrocarbon dissociation as previous study (Ma et al., 2019). In this research, blank tests were done without plasma treatment. No particles were generated in the reactant solution after 1 h or 2 h. Thus, microplasma is required for the N-doped carbon dots synthesis in this research, which is considered to accelerate the condensation reaction between citric acid and ethylenediamine. Then polymer-like materials were generated and further carbonized to final N-doped carbon dots (Wang et al., 2015). When plasma was ignited, electrons with high density were produced and interact with the surface of the sample solution, initiating and accelerating the condensation reaction between citric acid and ethylenediamine, towards the formation of N-doped carbon dots.

4. Conclusions

An effective approach for the synthesis of fluorescent N-doped carbon dots via a microplasma-assisted technique at atmospheric pressure was presented in the study. Energetic electrons generated by plasma initiate the condensation of reactants and accelerate the production of N-doped carbon dots without any heating process as used in the conventional method. Nitrogen element was successfully doped in the carbon dots in the forms of N–H groups and

Fig. 10. OES spectrum during the N-doped carbon dots synthesis process.

Table 1
Summary of emission lines from spectra.

Species	System	Transition	Wavelength
OH	3064 Å system	$A^2\Sigma^+ \rightarrow X^2\Pi$	308.9 nm
H	Balmer series	$n \rightarrow 2s, 2p$	489.6 nm (H_β), 657.2 nm (H_α)
O		$3p^5P \rightarrow 3s^5S$	777.2 nm
Ar	Ar I	$4p \rightarrow 4s$	696.5 nm ($1s^5-2p^2$), 706.7 nm ($1s^5-2p^3$) 738.4 nm ($1s^4-2p^3$), 750.4 nm ($1s^5-2p^1$) 763.5 nm ($1s^5-2p^6$), 772.4 nm ($1s^3-2p^2$) 794.8 nm ($1s^3-2p^4$), 826.5 nm ($1s^2-2p^2$) 842.5 nm ($1s^4-2p^8$)

pyrrolic-like N, which was examined by XPS analysis. Functional groups like C=O, C–O, N–H, C–N were attached in synthesized carbon dots, leading to intense blue emission under a UV lamp and a quantum yield up to 9.90%. Plasma treatment time has an obvious effect on carbonization degree and surface groups of N-doped carbon dots. Longer plasma treatment time leads to higher carbonization degree and larger particle generation. The lessened surface groups could be the dominant reason for the decrease of PL emission intensity. Operating voltages, related to discharge volume and the number of energetic electrons, can influence the intensity of condensation reaction between reactants. Higher operating voltage promotes carbon nucleation and growth, resulting in larger particle generation and the differences of PL emission tendencies. The sizes of the electrode in this study do not have obvious effects on the structure of synthesized carbon dots. However, it has an impact on the electron density. Electron density is higher in the case of smaller size electrode in this study, resulting in a higher yield of particles production. The maximum yield of N-doped carbon dots is 0.42% operating at 5 kV after 2 h plasma treatment in the case of smaller size electrode. The presented microplasma technique can be potentially applied to the synthesis of controllable N or other elements such as B, P doped carbon dots.

CRedit authorship contribution statement

Xintong Ma: Conceptualization, Methodology, Software, Data curation, Writing - original draft. **Sirui Li:** Conceptualization, Methodology, Visualization, Writing - review & editing, Supervision. **Volker Hessel:** Resources, Supervision. **Liangliang Lin:** Resources. **Stefan Meskers:** Resources, Writing - review & editing. **Fausto Gallucci:** Writing - review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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