

FACILE SYNTHESIS OF CARBON QUANTUM DOTS BY PLASMA-LIQUID INTERACTION METHOD

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Abstract. *Carbon quantum dots (CQDs) are a novel type of fluorescent nano-materials with various unique properties. They are recently attracting enormous interest due to their superiority in water solubility, chemical inertness, low toxicity, ease of functionalization as well as resistance to photo-bleaching and potential applications in biomedical indication, photo-catalysis, energy conversion, optoelectronics, and sensing. In this work, we present a facile and environmentally friendly synthesis of CQDs based on plasma - liquid interaction method. This is a single-step method and does not use toxic chemicals. The size distribution of obtained CQDs is rather uniform at approximately 3 nm. The emission peak of CQDs shifts from 427 nm to 523 nm as the excitation wavelength is varied from 340 nm to 460 nm. The non-equilibrium reactive chemistry of plasma liquid interaction is responsible for acceleration of the CQDs formation process.*

Keywords: carbon quantum dot, plasma device, nano-materials synthesis.

Classification numbers: 52.75.-m; 61.48.De; 62.23.Eg; 81.07.-b.

I. INTRODUCTION

Carbon quantum dots (CQDs) are considered as a less hazardous and greener alternative to the metal-semiconductor quantum dots [1–4] due to their low toxicity and high biocompatibility. A variety of approaches have been used to fabricate luminescent CQDs, although most of them have serious limitations including the need for strong acids, high processing temperatures, and cumbersome multistep procedures.

Carbon quantum dot can be synthesized either by “top-down” or “bottom-up” methods. In “bottom-up” synthetic approach, CQDs are created from small precursors such as carbohydrates, proteins, citrate and many plant extracts under dehydration treatments [5–8]. De and Karak have proposed that those precursors first dehydrated to form larger products and eventually these products forms CQDs under polycondensation and carbonization [9].

Plasma – the fourth state of matter after solid, liquid and gaseous is ionized gas containing free charge carriers (electrons and ion particles). Plasma formed at room temperature and atmospheric pressure is often a random collection of many micrometer-sized plasma channels, so it is often called micro-plasma. Beside free charge carriers, thanks also to other active constituents like free radicals and ultraviolet radiation (UV), micro-plasma has many practical applications, especially in biomedical fields such as sterilizing medical instruments, tissue and cells treatment as well as food preservation.

Currently, manufacturing nanomaterials with micro-plasma is very interesting research field. This new manufacturing method is based on the direct interaction between micro-plasma and precursor solution.

Micro-plasma was generated in argon, helium, or nitrogen flow under the effect of a DC high voltage [4]. There are many advantages that made plasma liquid interaction a promising method to replace traditional ones. Micro-plasma enables fabrication processes and surface techniques directly in this solution [10]. Moreover, this method does not need chemicals to reduce metal ions or dehydrate carbonaceous precursor for nucleation, formation and grown of nanoparticles as in chemical methods [1, 11].

In current attempt, we propose a facile, green and efficient surfactant - free method for synthesis of CQDs. In a synthetic duration of only 15 minutes, the micro-plasma dehydrates Saccharose in a low concentration NaOH solution and allows the formation of electro-statically stable nano-particles without any need of surfactants/stabilizing molecules [3, 4]. This research gives an alternative synthesis method which is more green using less energy and hazardous chemicals. Moreover, the micro-plasma can be easily modified by adding certain reactive gases in order to drive the synthesis pathway for better CQDs products.

II. MATERIALS AND METHODS

The micro-plasma system for CQDs synthesis (Fig. 1) consists of a DC high voltage source, a plasma nozzle, a graphite electrode and a 50 ml glass beaker from Bomex with 20 ml precursor solution. The plasma nozzle is a Teflon housing, its one end is a hollow teflon cylinder with outer diameter of 15 mm and inner diameter of 10 mm covering the plasma electrode and the other end is a 6 mm quick connector. The plasma electrode is a 1.5 mm diameter tungsten rod connected to the negative polarity via a 100 k Ω resistor. The other polarity is grounded and connected to the graphite electrode which is submerged into the precursor solution.

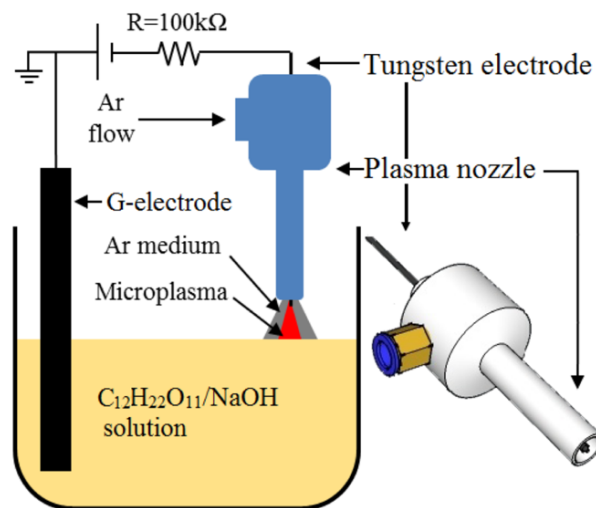


Fig. 1. Schematic setup of micro-plasma system for CQDs synthesis.

Precursor solution used for synthesis of CQDs is 20 ml of 225 g/l $C_{12}H_{22}O_{11}$ and 0.5 g/l NaOH solution which is 100 times less sodium hydroxide needed than in typical chemical method. The processing current was maintained constant (5 mA). The temperature of the 20 ml water solution exposed to the plasma sustained at 5 mA current for 15 minutes was observed to increase from about 30°C to about 40°C.

CQDs containing solution after fabrication does not need any filtration giving a bright luminescent solution under the irritation of 405 nm light (Fig. 4). Their optical densities were measured over the range of 300 - 800 nm in a 1cm long cuvette by a UV-near IR spectrometer V-570 (Jasco). Photoluminescence studies of the colloidal solutions were performed by a spectrofluorimeter Fluoromax-4 (Horiba Jobin-Yvon) using excitation wavelengths with step of 20 nm from 340 to 460 nm. Particle size and uniformity were measured by means of the particle dynamic laser scattering (DLS) measurement and transmission electron microscope (TEM).

III. RESULTS AND DISCUSSION

Under micro-plasma synthesis of 15 minutes duration, without any filtration, the transparent Saccharose solution has turned into light brown (Fig. 2 - left) showing successful dehydration of Saccharose precursor. The obtained solution emits blue light typical for CQDs under the irradiation of 405 nm LED (Fig. 2 - middle).

The DLS result (Fig. 3) shows that about 99% of particles in the synthesized solution have size of about 3 nm. However, there remain a small number of particles with the size larger than 200 nm as can be seen as a prominent peak in the scattering intensity measurement. Since the scattering intensity is proportional to square of particle radius, the number of 200 nm particles estimated from the scattering intensity is only 0.16% that of the 3 nm particles. As the consequence, one cannot see the peak of 200 nm particles in this figure describing size distribution by number. This result is in line with TEM measurement (Fig. 2 - right) where particle size distribution is rather uniform.

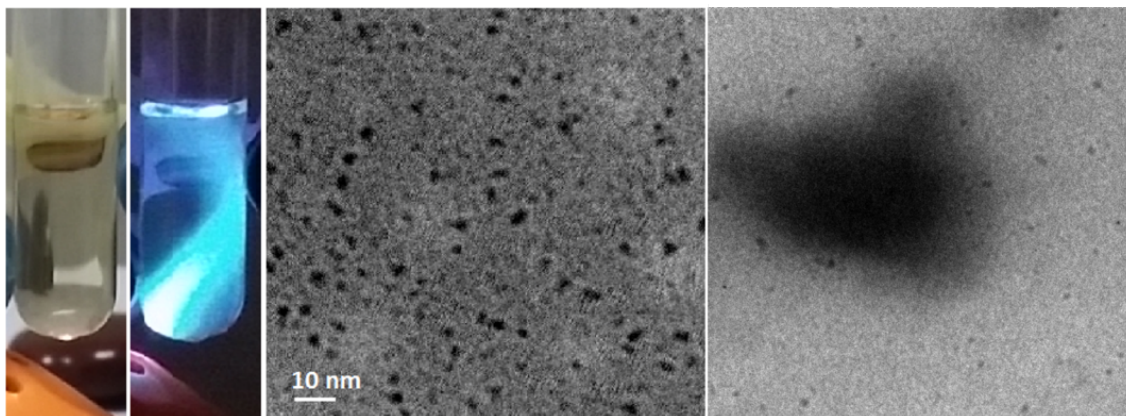


Fig. 2. Solution of luminescence of CQDs produced by micro-plasma method under white light (left) and under irritation of 405 nm light (middle), TEM image of micro-plasma produced CQDs (right).

The averaged particle size estimation from TEM also give a result of about 3 nm. Unfortunately, the Sacchorose was not completely dehydrated. In the film prepared for TEM measurement, it contains a Saccharose layer covering the CQDs, therefore, it is almost impossible to get the CQDs image of sufficiently good quality.

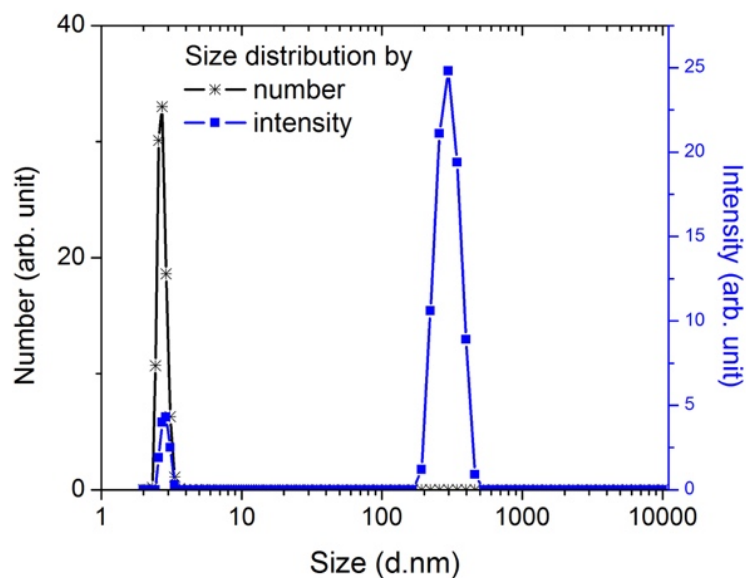


Fig. 3. Dynamic Laser Scattering (DLS) measurement of synthesized CQDs.

The UV-Vis spectra of our sample is typical for CQDs [1, 12, 13] its absorption band mostly locates in the UV region and extends somewhat to the visible range (Fig. 4). Our sample does not

have any absorption shoulders as reported in Ref. [14] which is attributed to the $\pi-\pi^*$ transition of the C=C bonds, the $n-\pi^*$ transition of C=O bonds and/or others.

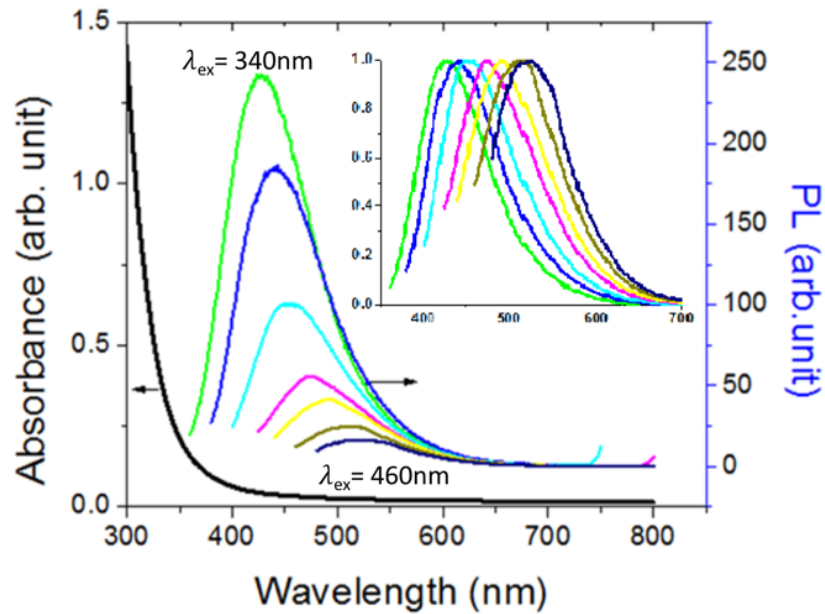


Fig. 4. UV-Vis absorbance (left) and PL (right) spectra of synthesized CQDs. In the inset, the emission spectral intensities are normalized.

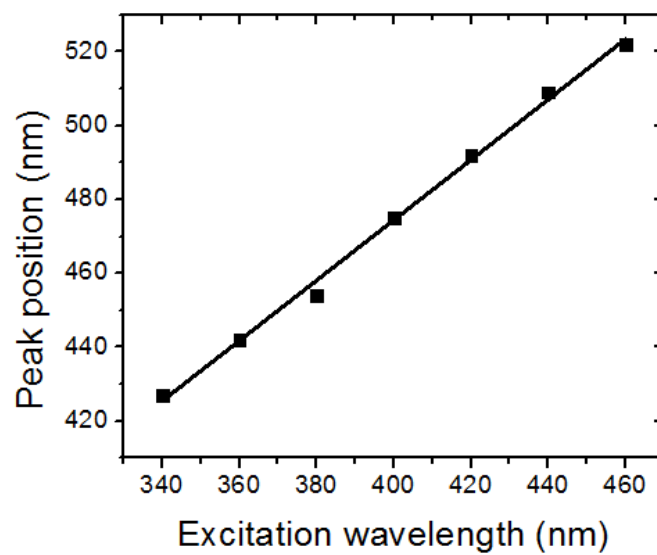


Fig. 5. Relationship between excitation and emission wavelength of PL spectra.

The emission peak of CQDs shifts from 427 nm to about 523 nm as the excitation wavelength was varied from 340 nm to 460 nm. This result is in a good agreement with the measurement as reported in Ref. [15], however, our CQDs show a better linear dependence between excitation wavelength and peak emission wavelength of PL spectra (Fig. 5).

IV. CONCLUSION

We have successfully synthesized carbon quantum dots by electrochemical method making atmospheric pressure micro-plasma in interact with Saccharose solution. Synthesized CQDs are rather uniform with mainly spherical morphology and diameter of about 3 nm. Our synthesis method has several advantages compared to chemical methods such as high purity, fast fabrication, easy production on a large scale. This method is efficient to fabricate CQDs for further research and practical applications.

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REFERENCES

- [1] H. Li, Z. Kang, Y. Liu and S.-T. Lee, *Journal of materials chemistry* **22** (2012) 24230.
- [2] S. N. Baker and G. A. Baker, *Angew. Chem. Int. Ed.* **49** (2010) 6726.
- [3] X. Xu, R. Ray, Y. Gu, H. J. Ploehn, L. Gearheart, K. Raker and W. A. Scrivens, *J. Am. Chem. Soc.* **126** (2004) 12736.
- [4] D. Mariotti and R. M. Sankaran, *J. Phys. D: Appl. Phys.* **43** (2010) 323001.
- [5] H. Peng and J. Travas-Sejdic, *Chem. Mater.* **21** (2009) 5563.
- [6] H. Zhu, X. Wang, Y. Li, Z. Wang, F. Yang and X. Yang, *Chem. Commun.* **34** (2009) 5118.
- [7] A. Mewada, S. Pandey, S. Shinde, N. Mishra, G. Oza, M. Thakur, M. Sharon and M. Sharon, *Mater. Sci. Engineer.: C* **33** (2013) 2914.
- [8] G. Oza, K. Oza, S. Pandey, S. Shinde, A. Mewada, M. Thakur, M. Sharon and M. Sharon, *J. Fluoresc.* **25** (2015) 9.
- [9] B. De and N. Karak, *RSC Adv.* **3** (2013) 8286.
- [10] R. A. Sperling, P. R. Gil, F. Zhang, M. Zanella and W. J. Parak, *Chem. Soc. Rev.* **37** (2008) 1896.
- [11] H. Li, Y. Zhang, L. Wang, J. Tian and X. Sun, *Chem. Commun.* **47** (2011) 961.
- [12] Q. Wang, H. Zheng, Y. Long, L. Zhang, M. Gao and W. Bai, *Carbon* **49** (2011) 3134.
- [13] B. Chen, F. Li, S. Li, W. Weng, H. Guo, T. Guo, X. Zhang, Y. Chen, T. Huang, X. Hong, S. You, Y. Lin, K. Zeng and S. Chen, *Nanoscale* **5** (2013) 1967.
- [14] F. Li, C. Liu, J. Yang, Z. Wang, W. Liu and F. Tian, *RSC Adv.* **4** (2014) 3201.
- [15] X. Li, H. Wang, Y. Shimizu, A. Pyatenko, K. Kawaguchi and N. Koshizaki, *Chem. Commun.* **47** (2010) 932.