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Synthesis of Broad Photoluminescence Carbon Nanodots by Femtosecond Laser Ablation in Liquid

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***Abstract*- Carbon nanodots (C-dots) with broad emissions when excitation wavelength changes in a large region are suitable for a broad range of applications, including optical down-conversion devices, bioimaging, and biosensors by selecting different excitation wavelengths without changing their structure. Herein, C-dots exhibiting broad photoluminescence from blue to green regions with strong excitation-dependence have been synthesized via femtosecond laser ablation in ethylenediamine solution. Detailed characterization showed that abundant surface functional groups, such as C-N, C-H, and C-O have been created on the surface of C-dots, which can efficiently introduce new emission centers on the surface site and result in the broad emissions.**

Keywords- laser ablation; carbon nanodots; nanoparticles; photoluminescence materials

I. INTRODUCTION

Carbon nanodots (C-dots), a new class of carbogenic nanomaterial, have attracted rapidly growing interests in recent years due to their unique combination properties of intense photoluminescence (PL), high photostability, high aqueous solubility, low toxicity, and excellent biocompatibility [1]. C-dots are promising substitutes for the present fluorescent nanomaterials for various applications, such as biological imaging [2], drug delivery [3], sensors [4, 5], light-emitting devices [6], and lasers [7]. Typically, C-dots have an sp^2 or amorphous carbon core with size less than 10 nm, and a surface coated with oxygen-, nitrogen-, or sulfur-containing functional groups. To date, C-dots with intense PL can be readily produced on a large scale by many approaches include laser ablation [8, 9], hydrothermal [4, 10, 11], ultrasound [12], and microwave-assisted synthesis [13]. However, the reported C-dots solely exhibit either blue or green emissions with a narrow region of excitation wavelengths. It is ideal that the C-dots can exhibit broad emissions with comparable intensities when excitation wavelength changes in a large region, because this will enable the C-dots to be suitable for various applications by selecting different excitation wavelengths without changing their structure. Herein, we present a simple strategy for preparing C-dots with broad emissions from blue to green regions by femtosecond laser ablation of graphite powders in ethylenediamine (EDA) solution.

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II. EXPERIMENTS

C-dots were synthesized via femtosecond laser ablation of graphite powder in an EDA solution. Typically, 5 mg of graphite powder, with a mean size of 400 nm, was dispersed into 10 ml of EDA via ultrasonication. Next, the femtosecond laser beam (Ti:sapphire femtosecond laser system, central wavelength: 800 nm, pulse duration: 150 fs, and repetition rate: 1 kHz) was focused into the suspension at a laser fluence of 500 J/cm^2 by 100 mm lens for about 30 min. During the laser irradiation, a magnetic stirrer was used to prevent gravitational settling of the suspended powders. After laser irradiation, the solution was centrifuged and the C-dots were obtained from the supernatant.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the C-dots were obtained via JEM-ARM200F transmission electron microscope. The emission spectra measurements were performed on a FLS920 spectrometer (Edinburgh). All wide-field fluorescence images were obtained via an inverted confocal microscope (Nikon C2$^+$) using 60x oil objective (1.49 NA). The C-dots were dispersed on cover slip and excited with 408 and 488 nm laser at laser intensity of ~ 5 mW. PANalytical X-ray diffractometer was employed to measure the X-ray diffraction (XRD) of the sample. Fourier transform infrared (FTIR) spectroscopy was performed on a VERTEX 70 (Bruker) using the KBr pellet method.

III. RESULTS AND DISCUSSION

First, the structure and size distribution of as-prepared C-dots were analyzed by TEM and HRTEM images. Fig. 1 shows a homogeneous distribution of the C-dots with small

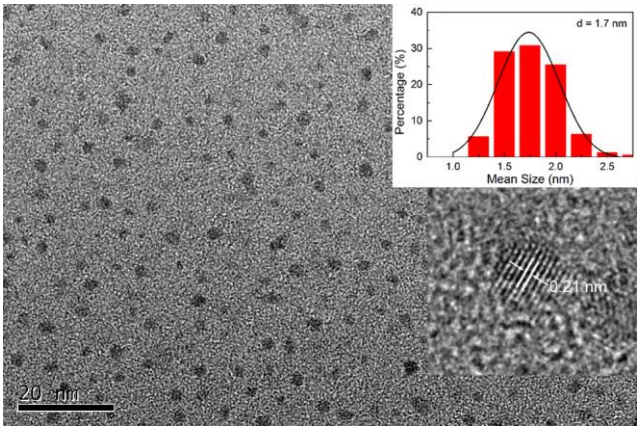

Figure 1. TEM image of the as-prepared C-dots, the insets are the size distribution and HRTEM image of the C-dots.

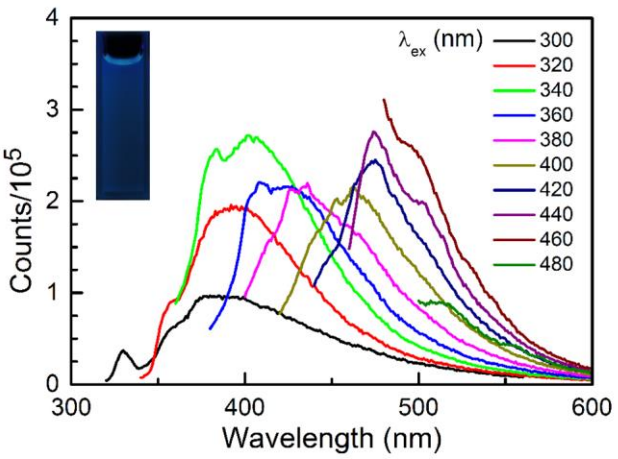

Figure 2. The steady-state PL spectra of the C-dots. The inset is fluorescence image of C-dots solution under 365 nm UV light irradiation.

size distribution, in the range of 1-2.5 nm. The maximum value of the fitted Gaussian peak are 1.7 nm with full width half maximum of 0.7 nm, which further confirms the narrow size distribution of as-prepared C-dots. The HRTEM image of C-dots (insets in Fig. 1) exhibited highly crystalline structures with a lattice spacing of 0.21 nm, which is very close to the (100) in-plane lattice spacing of graphite.

Steady-state fluorescence measurement was conducted for the C-dots dispersed in EDA solution. Unlike many other reported C-dots exhibiting narrow fluorescence emission [14], the C-dots exhibit broad emission spectra with comparable intensities in a broad range of excitation wavelength (Fig. 2). The C-dots show nearly continuously excitation-dependent emission and the emission peak wavelengths ranging from 375 to 525 nm with the excitation ranging from 300 to 480 nm. Due to their unique PL properties, various new applications of C-dots can be anticipated, such as optical down-conversion devices, bioimaging, and biosensors by selecting different working wavelengths.

To shed light on the origin of broad emissions observed at multiple wavelengths in ensemble measurements, fluorescence measurements on isolated single particles of the C-dots were carried out. Fig. 3a and Fig. 3b show representative fluorescence images of C-dots at the same field of view with 408 and 488 nm excitations. The emissions were harvested at blue channel (417-477 nm) and green channel (499-529 nm) for 408 and 488 nm excitations, respectively. The overlaid figure of Fig. 3a and 3b (Fig. 3c) shows complete overlap indicating that single C-dots particle absorbs both wavelengths and possesses multi-color emissions.

The chemical compositions and structures of these C-dots are further investigated using FTIR and XPS analysis. The FTIR spectrum (Fig. 4a) shows that abundant surface functional groups are created on the surface of C-dots, such as N-H bond (3360 cm^{-1}), C-H bond (2920 and 2850 cm^{-1}), CH_2 (1470 cm^{-1}), C=O/O-H bond (1630 cm^{-1}), and C-O bond (1000-1200 cm^{-1}). The XPS survey spectrum (Fig. 4b) shows that carbon (C 1s, 284 eV), nitrogen (N 1s, 400 eV), and oxygen (O 1s, 532 eV) elements were contained in the C-dots. The high-resolution C 1s spectrum (Fig. 4c) reveals the presence of C=C (284.6 eV), C-H (283.5 eV), and C-O/C-N (286.3 eV). The results indicate that during femtosecond laser ablation process, the EDA solution react mightily with graphite and create abundant chemical groups on the surface of C-dots [8].

Although great efforts have been made to investigate the PL mechanisms of C-dots, the origin of their PL remains to be a contentious topic. Recent reports suggested that the PL of C-dots is originated from surface functional groups on its surface [15, 16]. In this mechanism, one kind of surface functional group forms a single surface state energy level and becomes an isolated emission center with specific carrier dynamics on the surface site of C-dots. In this study, the abundant surface functional groups, such as C-N, C-H, and C-O have been created on the surface of C-dots, which can efficiently introduce new emission centers on the surface site and result in the broad emissions.

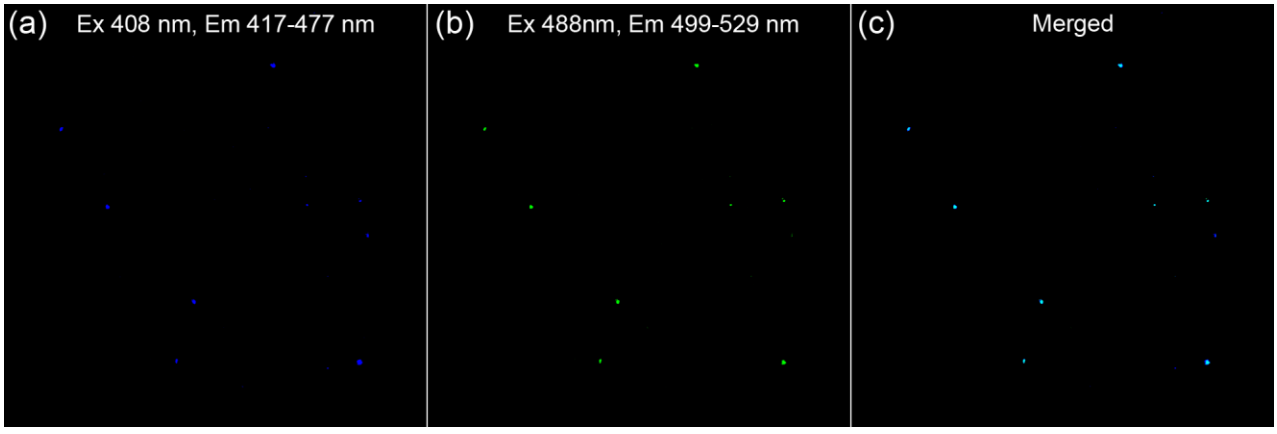

Figure 3. Fluorescence images of the C-dots at the same field of view with (a) 408 and (b) 488 nm exciations. (c) Merged image of both 408 and 488 nm exciations.

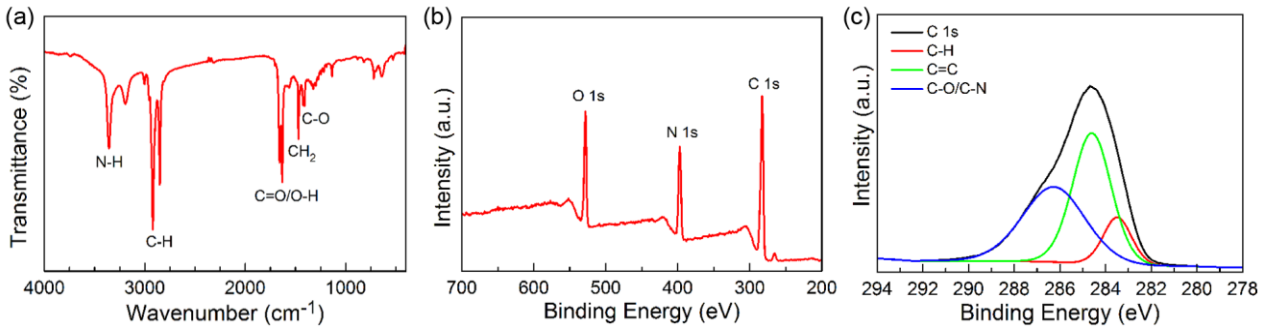

Figure 4. (a) FTIR spectrum, (b) XPS survey spectrum, and (c) high-resolution C 1s spectrum of the C-dots.

IV. Conclusions

C-dots with broad emissions have been synthesized via femtosecond laser ablation in EDA solution. Detailed characterizations showed that abundant surface functional groups, such as C-N, C-H, and C-O have been created on the surface of C-dots, which can efficiently introduce new emission centers on the surface site and result in the broad emissions. Taking advantage of their unique PL properties, the C-dots can be used in various applications, such as optical down-conversion devices, bioimaging, and biosensors by selecting different working wavelengths without changing their structure.

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References

[1] K. Hola, Y. Zhang, Y. Wang, E. P. Giannelis, R. Zboril, and A. L. Rogach, "Carbon dots—Emerging light emitters for bioimaging, cancer therapy and optoelectronics," *Nano Today,* vol. 9, pp. 590-603, 2014.

[2] K. Jiang, S. Sun, L. Zhang, Y. Lu, A. Wu, C. Cai, *et al.*, "Red, Green, and Blue Luminescence by Carbon Dots: Full-Color Emission Tuning and Multicolor Cellular Imaging," *Angew. Chem. Int. Ed.,* vol. 54, pp. 5360-5363, 2015.

[3] J. Tang, B. Kong, H. Wu, M. Xu, Y. Wang, Y. Wang, *et al.*, "Carbon nanodots featuring efficient FRET for real-time monitoring of drug delivery and two-photon imaging," *Adv. Mater.,* vol. 25, pp. 6569-6574, 2013.

[4] J. Wang, F. Peng, Y. Lu, Y. Zhong, S. Wang, M. Xu, *et al.*, "Large-Scale Green Synthesis of Fluorescent Carbon Nanodots and Their Use in Optics Applications," *Adv. Opt. Mater.,* vol. 3, pp. 103-111, 2015.

[5] V. Nguyen, L. Yan, J. Si, and X. Hou, "Femtosecond laser-assisted synthesis of highly photoluminescent carbon nanodots for Fe^3+ detection with high sensitivity and selectivity," *Opt. Mater. Express,* vol. 6, pp. 312, 2016.

[6] W. Kwon, S. Do, J. Lee, S. Hwang, J. K. Kim, and S.-W. Rhee, "Freestanding Luminescent Films of Nitrogen-Rich Carbon Nanodots toward Large-Scale Phosphor-Based White-Light-Emitting Devices," *Chem. Mater.,* vol. 25, pp. 1893-1899, 2013.

[7] W. F. Zhang, H. Zhu, S. F. Yu, and H. Y. Yang, "Observation of lasing emission from carbon nanodots in organic solvents," *Adv. Mater.,* vol. 24, pp. 2263-2267, 2012.

[8] V. Nguyen, L. Yan, J. Si, and X. Hou, "Femtosecond laser-induced size reduction of carbon nanodots in solution: Effect of laser fluence, spot size, and irradiation time," *J. Appl. Phys.,* vol. 117, pp. 084304, 2015.

[9] D. Tan, S. Zhou, B. Xu, P. Chen, Y. Shimotsuma, K. Miura, *et al.*, "Simple synthesis of ultra-small nanodiamonds with tunable size and photoluminescence," *Carbon,* vol. 62, pp. 374-381, 2013.

[10] S. Zhu, Q. Meng, L. Wang, J. Zhang, Y. Song, H. Jin, *et al.*, "Highly photoluminescent carbon dots for multicolor patterning, sensors, and bioimaging," *Angew. Chem. Int. Ed.,* vol. 52, pp. 3953-3957, 2013.

[11] Z. L. Wu, M. X. Gao, T. T. Wang, X. Y. Wan, L. L. Zheng, and C. Z. Huang, "A general quantitative pH sensor developed with dicyandiamide N-doped high quantum yield graphene quantum dots," *Nanoscale,* vol. 6, pp. 3868, 2014.

[12] H. Li, X. He, Y. Liu, H. Huang, S. Lian, S.-T. Lee, *et al.*, "One-step ultrasonic synthesis of water-soluble carbon nanoparticles with excellent photoluminescent properties," *Carbon,* vol. 49, pp. 605-609, 2011.

[13] L. Tang, R. Ji, X. Cao, J. Lin, H. Jiang, X. Li, *et al.*, "Deep ultraviolet photoluminescence of water-soluble self-passivated graphene quantum dots," *Acs Nano,* vol. 6, pp. 5102-5110, 2012.

[14] H. Ding, S.-B. Yu, J.-S. Wei, and H.-M. Xiong, "Full-Color Light-Emitting Carbon Dots with a Surface-State-Controlled Luminescence Mechanism," *Acs Nano,* vol. 10, pp. 484-491, 2016.

[15] L. Wang, S. J. Zhu, H. Y. Wang, S. N. Qu, Y. L. Zhang, J. H. Zhang, *et al.*, "Common origin of green luminescence in carbon nanodots and graphene quantum dots," *Acs Nano,* vol. 8, pp. 2541-2547, 2014.

[16] V. Nguyen, J. Si, L. Yan, and X. Hou, "Electron–hole recombination dynamics in carbon nanodots," *Carbon,* vol. 95, pp. 659-663, 2015.