

Photoluminescence Study in Solution Driven Carbon Quantum Dot

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Abstract—Luminescent carbon dots (CQDs), due to their interesting and unique features, have recently drawn a lot of attention and have been found to be a prosperous material for numerous applications in bio-imaging, sensing, drug delivery, and optoelectronics owing to their favorable luminescent properties, high chemical stability, low toxicity, biocompatibility, and easy functionalization. In the present work, water-soluble carbon dots (CQDs) were prepared by a simple environmentally friendly bottom-up and wet-chemical method from citric acid and sodium hydroxide. The as synthesized CQDs show excitation-independent bright blue photoluminescence. Only tuning of the intensity of the PL spectra with changing of excitation wavelength has been observed for these CQDs. Moreover the CQDs also exhibit pH dependent fluorescence spectra. The fluorescence lifetime of CQDs fit with two components indicating two different decay pathways. The obtained CQDs could be used as a potential material in different research fields such as sensors, solar cells, catalysis and biomedicine.

1. INTRODUCTION

Optically active nanostructures got major attraction due to their potential applications in optoelectronics, labeling experiments and biomedicine. Discovery of semiconductor quantum dots (QDs) is considered as a major milestone in the matter of developing fluorescent nanomaterials. Usually semiconductor QDs possesses size-tunable and narrow emission spectra, high photostability, and low photo degradation. However, most of the high-performance QDs are comprise of toxic heavy metal elements such as cadmium, which limit their use. Thus, the development of non-toxic or low toxic fluorescent nanomaterials instead of semiconductor QDs is very necessary.

As a green substitute for the toxic transition metal quantum dots, carbon dots (C-QDs), as an emerging type of carbon nanomaterials, have attracted a dramatic interest in recent years for their amazing optical, electronic, and biochemical properties e.g. excellent solubility, easy functionalization, stable photoluminescence (PL), high electrochemical activity, low toxicity, and good biocompatibility. Moreover, C-QDs have found more promising applications in the areas of catalysis, bio-imaging, sensing, drug delivery, and other optoelectronic fields [1-5].

Here, in this manuscript, we report a simple, economical, and one-pot method to synthesize water-soluble fluorescent C-QDs through hydrothermal method using citric acid and sodium hydroxide. As synthesized C-QDs show bright blue luminescence. PL intensity varies with pH variation but unaltered with excitation variation. Photoluminescence life time measurement that gives an insight about the excitonic dynamics, indicate to the two different decay pathways of fluorescent C-QDs. We hope that these fluorescent C-QDs will enable researchers to engineer the chemical and physical properties of graphene for fabrication of opto-electronic devices and fluorescent sensors.

2. EXPERIMENTAL PROCESS

2.1 Synthesis

100 mg citric acid and 60 mg NaOH were dissolved into 40 ml water, and stirred to obtain a clear solution. Then the solution was transferred into a 50 ml Teflon stainless autoclave. The sealed autoclave was heated to 120°C in a vacuum oven and kept for 6 hours. The final product was collected after three time centrifuging at 8000 rpm for 10 min. The synthesis scheme is shown in Scheme 1.



Scheme 1: Synthesis of C-QDs

3. CHARACTERIZATION

To characterize the final product, FTIR spectroscopic measurements are carried out using a Shimadzu IR Affinity-1 spectrometer system. For the TEM study, we used a JEOL-2011 high resolution transmission electron microscope. PL spectra are collected using Shimadzu RF-5301PC

Spectrofluorophotometer. For the time-correlated single-photon counting (TCSPC) measurement, QD solution is excited at 340 nm (by picosecond NanoLED) in Edinburgh luminescence spectrometer (Model No.FLSP-980). Average fluorescence lifetimes (τ) for exponential fitting are calculated from the decay times (τ_i) and the relative amplitudes (a_i), using the following relation

$$\langle \tau \rangle = \frac{\sum_i a_i \tau_i^2}{\sum_i a_i \tau_i}$$

4. RESULT AND DISCUSSION

The functionalities present in C-QDs are further confirmed by the FTIR analysis. Fig. 1a shows the FTIR spectra for C-QDs. The FTIR analysis revealed that there are two main functional groups, -COOH and C-OH, in the surface of the CDs, with the fact: the peak at 3430 cm^{-1} is due to the presence of the -OH group. Asymmetric and symmetric stretching vibration peaks of COO bond at 1628 cm^{-1} and 1400 cm^{-1} and characteristic deformation of C-OH group at 1184 cm^{-1} . Because of the presence of these functional groups, the as-synthesized C-QDs possess good stability in aqueous systems.

The morphology of prepared C-QDs was studied by transmission electron microscopy (TEM). From Fig. 1b it can be seen that the C-QDs have a uniform dispersion without any apparent aggregation and the average size of $\sim 5 \text{ nm}$.

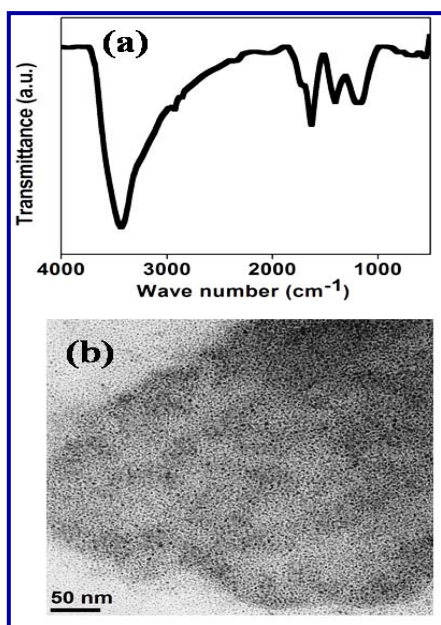


Fig. 1: (a) FTIR and (b) TEM image of CQDs

Fig. 2a shows the PL spectra of C-QDs. The as-synthesized C-QDs exhibit excitation-independent emission behavior. When the CDs are excited at wavelengths from 300 to 440 nm, the corresponding emission peaks remain same at $\sim 443 \text{ nm}$. The strongest PL maximum with PL quantum yield of $\sim 3.21\%$

appears at 440 nm upon 361 nm excitation which is in accordance with the photoluminescence excitation (PLE) spectrum with a strong excitation peak at $\sim 361 \text{ nm}$ (Figure. 2b).

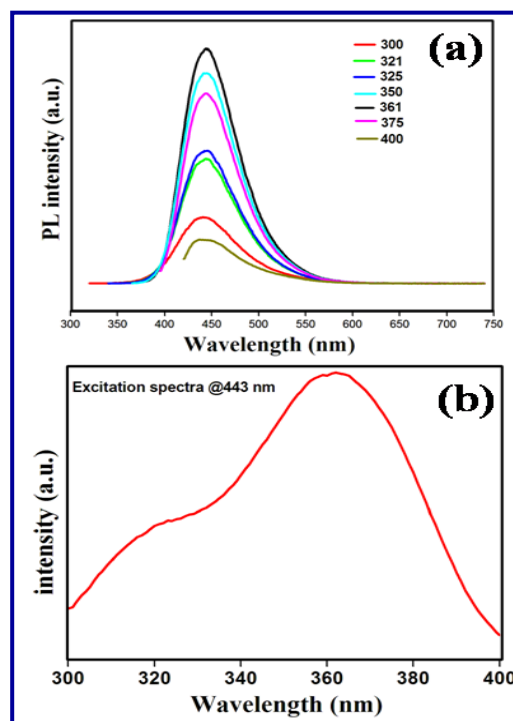


Fig. 2: (a) PL and (b) PLE of CQDs

In addition, the PL intensity of C-QDs enhanced with the decrease in pH (Figure. 3a). These observations indicate that the changes of pH mainly influence the surface of C-QDs. The pH response of fluorescence is related to the passivation of radiative defects embedded in the C-QDs. The protonation and deprotonation of the -OH and -COOH groups due to the changes in pH may cause electrostatic doping/charging to the C-QDs, thereby shifting the Fermi level. With decrease in pH i.e., increase in $[\text{H}^+]$ concentration the -OH, COOH groups are get protonated which destabilizes $n-\pi^*$ state, thus reducing the energy gap between the states and which in turn, decreases the vibronic interaction. This decreases the Franck-Condon factor resulting a decrease in radiation less decay which explains the bright fluorescence intensity of the C-QDs with decrease in pH.

Fig. 3b shows the CIE 1931 chromaticity diagram for C-QDs. The CIE chromaticity coordinate calculated from the PL spectrum is (0.154, 0.101) which means that C-QDs can be used as a promising material in blue-light-emitting optoelectronics.

To obtain insight into the excitonic dynamics, we have measured the fluorescence lifetimes of C-QDs. The average lifetime together with the component decay times obtained from the fitted decay curves (Fig. 4), are summarized in Table 1.

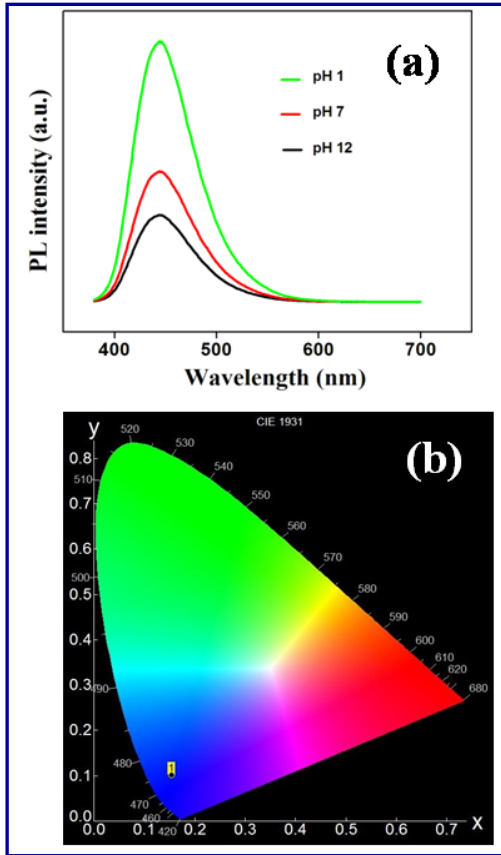


Fig. 3: (a) PL with pH variation and (b) CIE index of CQDs

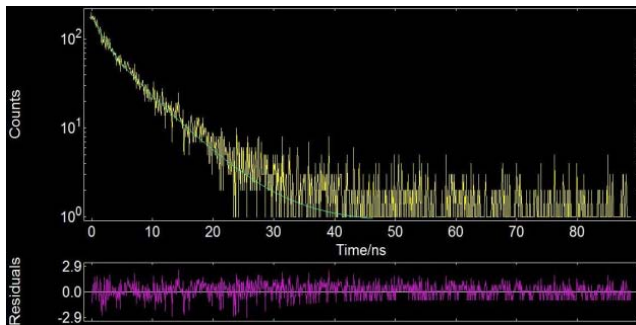


Fig. 4: Decay curves of CQDs

Average fluorescence lifetime $\langle \tau \rangle$ for exponential fitting is calculated from the decay times τ_i and the relative amplitudes a_i using the following relation:

$$\langle \tau \rangle = \frac{\sum_i^n \alpha_i \tau_i^2}{\sum_i^n \alpha_i \tau_i}$$

Table 1: Lifetime Values of CQDs

System	τ_1 (ns)	a_1	τ_2 (ns)	a_2	$\langle \tau \rangle$ (ns)
C-QD	1.81	19.22	6.59	80.78	6.297

5. CONCLUSION

In summary, C-QD material is successfully synthesized using simple hydrothermal technique from citric acid. As synthesized C-QDs show excellent excitation independent bright blue PL spectra. Its PL intensity is also changed with pH. We believe this study will emerge an effective impact in optoelectronic applications in near future.

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