Understanding the Photoluminescence Mechanism of Carbon Dots

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ABSTRACT

The carbon dots were investigated to reveal their light-emitting mechanism. The fluorescence spectra of carbon dots show typically two different types of photoluminescence: the excitation-independent component in the short wavelength, and the excitation-dependent component in the longer wavelength. The UV-Vis spectrum of carbon dots shows the absorption maximum of 340 nm which should be accredited to the n-π* transition of the carbonyl group in carbon dots. Absolute quantum yields of carbon dots dispersed in Polyvinyl alcohol is around 15% when the excitation wavelength is less than 425 nm, but decreases continuously when the excitation wavelength increases. The decay lifetimes of the carbon dots also show an abrupt change at excitation wavelength 425 nm. Time resolved photoluminescence was implemented from 31K to 291K to study the photoluminescence decay dynamics of carbon dots, resulting in the continuously decreasing of the lifetime as the temperature increases.

Introduction

Fluorescent semiconductor quantum dots have generated broad promising applications including biological labeling and solid-state lighting. Nanometer-size carbon dots which are the counterparts of silicon nanoparticles now light up. They are non-toxic, abundant, stable and bio-compatible. Although the typical photoluminescence quantum efficiency of carbon dots is not high yet, they are non-blinking[1] and have large two-photon absorption cross section[2] which are favorable for one-photon or two-photon bio-imaging.

There are two schools of fabrication methods for carbon dots: top-down, bottom-up. Top-down method starts from bulk carbon, and using laser[2] or electrochemical oxidation[3] to break down the carbon into small pieces which have the size in nanometer scale. Graphene fragment carbon dots exhibit size tunable optical properties[4]. The bottom-up method starts from organic molecules and using chemical reaction, pyrolysis method to fabricate carbon dots, pioneered by Giannelis groups[5]. Following this direction, we can make mass production of carbon dots. Using these carbon dots, we investigate their optical properties and discovered an abrupt change of the photoluminescence lifetime as the excitation wavelength is scanned from UV to visible region. This abrupt change indicates a change of light emission mechanism of the carbon dots.

Experiment

Carbon dot synthesis

The method of synthesis of C dots is adopted from a previously reported method with some modification[6]. In a typical synthesis; a mixture of citric acid or acetylenedicarboxylic acid were mixed with ethanolamine under constant magnetic stirring to get a mole ratio of amine to acid of 3: 1 or 2: 1. After homogeneous mixing the reaction mixture was heated to above 70 °C to get a syrupy suspension which is pyrolyzed directly in a furnace at temperature more than 180 °C. The black product is highly water soluble and is used for different spectroscopic and microscopic analysis.

Electron microscopy

After dialysis, the unreacted precursors were filtered out. The carbon dots exhibit quite uniform size under electron microscope (as shown in Figure 1). No lattice structure was observed from the carbon dots. They are basically amorphous.
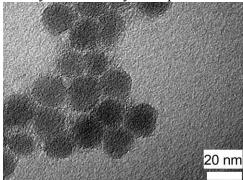

Figure 1. Transmission Electron Microscope (TEM) image of carbon dots.

Optical spectroscopy

The optical absorption spectrum of the carbon nanodots is shown in Figure 2, which shows an absorption maximum at 340nm. According to the previous reports[6], the absorption peak at 340 nm is accredited to the n-π* transition of the carbonyl group. For the shoulder after the absorption peak and the broad tail extending over to the visible spectrum, they could originate from other functionalized surface groups of carbon dots.
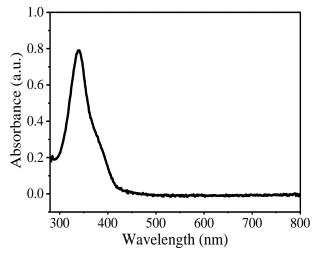
Figure 2. UV-Vis spectrum of carbon nanodots

A remarkable optical property of carbon dots is the excitation-dependent fluorescence, which violates the Kasha-Vavilov rule. In figure 3, the fluorescence spectra of carbon dots show the typical two types of the trending to the excitation process: the excitation-independent component in the excitation wavelength from 275nm to 400nm, and the excitation-dependent component in the excitation wavelength from 425nm to 550nm, which clearly indicates the two different photoluminescence mechanisms. For the independent part, the photoluminescence of carbon dots residents around 450nm. In the previous work[7], the dual emission mechanisms have been attributed to the presence of organic fluorophores for the excitation-independent range and carbogenic cores for the excitation-dependent range.
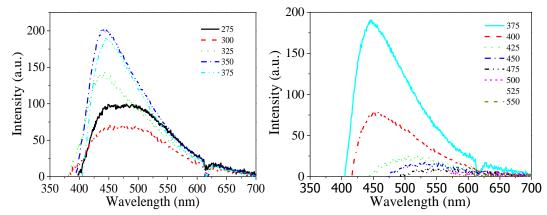

Figure 3. Excitation independent(Left) and dependent(Right)photoluminescence spectra of PVA (Polyvinyl alcohol) dispersions of Carbon nanodots

As shown in figure 4, the quantum yield of carbon dots varies with the excitation wavelength. The quantum yield generally shows two stages with the increasing of excitation wavelength: when excited from 275nm to 400nm, the quantum yield of carbon dots fluctuates between 12.8% and 19.3%; while for the range of 425nm to 550nm, the quantum yield keeps decreasing from 18.8% to 0.34%, which also indicates the existence of two different photoluminescence mechanisms.
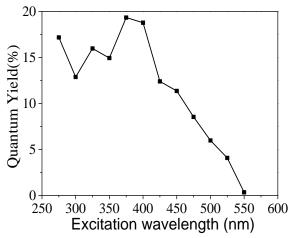
Figure 4. Excitation dependent Photoluminescence Quantum Yield of carbon nanodots

The photoluminescence lifetime of the carbon-dots dispersed in PVA changes depending on the excitation wavelength (Figure 5). It clearly indicates two different stages of the photoluminescence Lifetime with excitation wavelength where the 1st stage is around 6ns with excitation wavelength from 275nm to 400nm and the lifetime of 2nd stage is ~1ns after a sudden rising to 9.5ns. the intrinsic photoluminescence lifetime was calculated and reveals the two stages trending. For the photoluminescence excitation-independent part, the intrinsic photoluminescence lifetime shows a continuous declining trend from 55ns to 30ns. However, after the sudden rising of 78ns, the intrinsic photoluminescence lifetime falls to 9ns with a growing trend from 9ns to 28ns. Recently, the exciton lifetime of partially reduced graphene oxide(GO) was demonstrated to be dependent on the reduction time where the larger size sp^2 domain will be formed with longer reaction time[8]. The increase of the intrinsic photoluminescence lifetime with the emission wavelength may originate from the larger size sp2 domain in the carbogenic core which also cause the red-shifting of the photoluminescence spectra and the decreasing of the photoluminescence intensity due to their energy gaps.
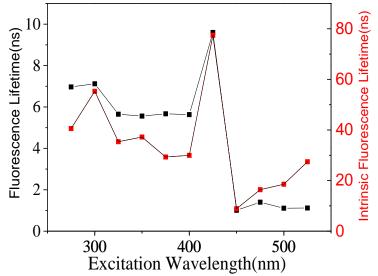

Figure 5. Excitation dependent photoluminescence Lifetime of PVA (Polyvinyl alcohol) dispersions of Carbon nanodots.

The temperature-dependent Time-Resolved Photoluminescence Lifetime(TRPL) shows the faster decay curves with the increasing of the temperature from 31K to 291K (Figure 6-(a)), which means the more contribution from the nonradiative decay process of carbogenic core of carbon dots. In figure 6-(b), the average carrier lifetime calculated from the temperature-dependent TRPL measurements features a continuously decreasing trend from 4.2ns to 2.9ns when increasing the temperature. From the temperature-dependent decay curves of figure 6, the photoluminescence relaxation dynamics of carbon dots reveals multiexponential from low temperature to room temperature, which is quite different with the conventional semiconductor QD that usually shows the mono-exponential decay trace at low temperature.[9]
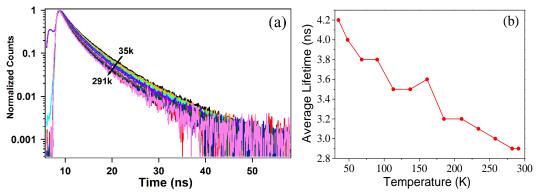

Figure 6. (a)Temperature-Dependent TRPL for the carbon dot sample from 35 K to 291K. (b)Estimations of average carrier lifetime from bi-exponential fits for the data.

The XPS measurements was carried out to confirm the presence of amide groups. In figure 7, the characteristic peaks of carbonyl group, amide nitrogen and carbonyl oxygen were located at 288.2ev, 400ev and 532.1ev, respectively.
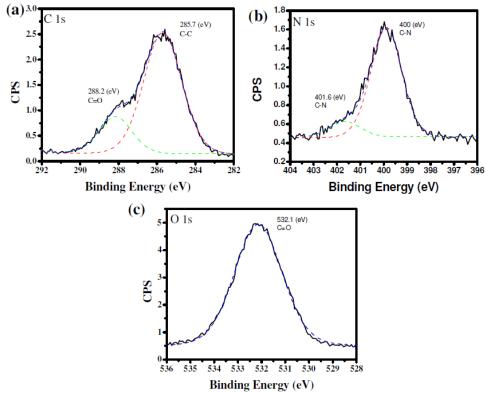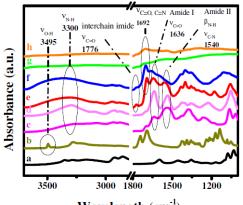
Figure 7. XPS spectra of carbon dots (a) C 1s, (b) N 1s and (c) O 1s. Full and dashed lines represent the data recorded and the fitted curves.[7]

Meanwhile, the FTIR spectrum of carbon dots was also collected and support the existence of amide functional groups (figure 8) with their vibrational fingerprints centered at 1550 cm^{-1} of N-H in-plane bending, 1636 cm^{-1} of C=O stretching of the amide bond, and 3300 cm^{-1} of N-H stretching.

Figure 8. FTIR spectra of (a) ethanolamine, (b) citric acid, (c) CNP180, (d) PL-CNP180, (e) CNP230, (f) CNP300, (g) CNP400 and (h) ox-CNP400. Peaks that correspond to functional groups mentioned in the text are noted and identified. (The abbreviations used are: CNP, Carbon nanodot; ν, stretching; β, in plane bending.)[7]

Discussion

The abrupt change of the photoluminescence lifetime at excitation wavelength of 425 nm is a strong indication that there are two different emission mechanisms. This is consistent with the result of excitation-wavelength dependent photoluminescence spectra. The low-temperature experiments show that the photoluminescence lifetime increases as the temperature decrease. This may indicate there are phonon-assisted exciton decays. Further experiments including temperature dependent photoluminescence spectroscopy will be carried out to obtain a better picture of the light-emitting mechanism of the carbon dots.

Conclusion

The photoluminescence studies including spectra, quantum yield and lifetime reveal the light-emitting mechanism of carbon dots. They are important to further our understanding of the carbon dots and to provide the knowledge for their future applications.

Acknowledgements

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