Emission from Trions in Carbon Quantum Dots

Yanling Hao,‡‡ Zhindong Gan, ‡ Xiaobin Zhu, ‡ Tinghui Li,§ Xinglong Wu,*‡∥ and Paul K. Chu⊥

‡‡Key Laboratory of Modern Acoustics, MOE, Institute of Acoustics and Collaborative Innovation Center of Advanced Microstructures, National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, P. R. China
‡Department of Physics, XingYi Normal University for Nationalities, Xingyi, Guizhou 562400, P. R. China
§College of Electronic Engineering, Guangxi Normal University, Guilin 541004, P. R. China
∥Department of Physics, NingBo University, NingBo 315001, P. R. China
⊥Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

ABSTRACT: The photoluminescence (PL) spectra acquired from 1 to 6 nm large carbon quantum dots (CQDs) prepared by refluxing activated carbon in HNO₃ show blue emission independent of the excitation wavelength as well as long-wavelength emission depending on the excitation wavelength. The dependence of the two emissions on pH is investigated, and the experimental results show that the peak position of the long-wavelength emission does not change with pH; however, the blue emission becomes more asymmetrical, and obvious shoulder peaks emerge as the pH increases. A model based on defect-bound trions in the CQDs is proposed to explain the shoulder peaks in the blue emission at high pH, and the calculated results agree well with experimental data concerning the integral intensity ratio of the trion to exciton emissions versus pH. Our experimental and theoretical results demonstrate for the first time emission from trions in CQDs.

INTRODUCTION

pH is an important parameter in many environmental, industrial, and biomedical applications.1−3 Precise measurement of the pH and local fluctuation, especially intracellular pH, is thus essential, and many types of nano pH sensors based on fluorescent proteins, polymers, and quantum dots have been designed to detect intracellular pH.4,5 Carbon quantum dots (CQDs) have recently been used to monitor the intracellular pH because of their superior properties such as small size, water solubility, good biocompatibility, and optical stability.1,2 However, development of CQDs as pH sensors is still in the infancy stage primarily because the fluorescent mechanism of CQDs at different pH is not well understood. In fact, the photoluminescence (PL) response of CQDs to pH tends to vary. Some researchers have reported that different pH leads to different PL intensity,6−8 but others have indicated that not only the intensity but also the emission wavelength shift with changing pH.9,10 On the basis of the theory that PL from CQDs originates from the oxygen-related surface state, it has been suggested that the variation of the PL intensity may be due to the protonation and deprotonation of surface oxygen-containing groups which may cause electrostatic doping/charging of the CQDs, thereby shifting the Fermi level.8,11,12 However, based on our knowledge, the change in the emission wavelength of CQDs with pH has not been explained. It has been shown that blue light emission from CQDs is influenced more by pH than green emission,10,13,14 and we have determined the origins of blue and long-wavelength (LW) emissions from CQDs and graphene oxide (GO). The blue emission arises from the carbon vacancy defect state, and LW emission originates from the CQD size or the sp² cluster size effect.15−17 The fluorescent response to pH may help explain the nature of the PL from CQDs. In this work, CQDs with sizes of 1−6 nm are prepared by refluxing wood-based activated carbon in HNO₃. The PL spectra of the CQDs show obvious excitation wavelength independent blue emission and excitation wavelength dependent LW emission. In addition, the response of the blue and LW PL spectra to pH is markedly different. The blue emission becomes more asymmetrical, and obvious shoulder peaks appear at high pH; however, the LW emission is hardly affected by pH except the PL intensity. A model based on defect-bound trions is proposed to explain the multipeak structure of the blue emission, and the calculated PL intensity ratio of trions to excitons is in good agreement with experimental results. In addition, based on the evolution of surface charges, the variation of the PL intensity with pH is elucidated.

EXPERIMENTAL SECTION

Sample Preparation. CQDs were synthesized by a top-down approach according to the reported method.10,13 An amount of 1 g of activated carbon powder (200 mesh) was...
dispersed into 100 mL of 1 mol L\(^{-1}\) HNO\(_3\) and sonicated for 1 h. The mixture was refluxed for 12 h at 120 °C. After cooling to room temperature naturally, the suspension was neutralized with Na\(_2\)CO\(_3\) and centrifuged at 10,000 rpm/min for 15 min. The supernatant was dialyzed in a dialysis bag with a molecular weight cutoff of 3500 Da for 3 days to remove inorganic salt. The pH of the CQD solution was varied from 2 to 13 by adding HCl and NaOH. The added HCl or NaOH only accounted for 1/10,000 of the initial volume so that the concentration of the CQDs remained the same.

**Characterization.** The morphology and dimensions of the CQDs were determined on a JEOL JEM-2100F transmission electron microscope (TEM). The PL and PL excitation (PLE) spectra were acquired on an Edinburgh FLS-920 fluorescence spectrometer. The lifetime was measured by time-correlated single-photon counting (TCSPC) excited by the 375 nm picosecond pulsed laser. Fourier transform infrared spectroscopy (FT-IR) was performed on the Nicolet Nexus 870 spectrometer.

**RESULTS AND DISCUSSION**

The TEM image reveals that the CQDs are nearly spherical in shape and about 1–6 nm in size with the most probable diameter of 3.2 nm (Figure 1a and b). The size distribution diagram was obtained through counting 400 particles in Figure S1a in the Supporting Information. The representative high-resolution TEM image is shown in the inset of Figure 1a and Figure S1b in the Supporting Information. The CQDs are highly crystalline, and the two different lattice fringes correspond to the (002) and (100) faces of hexagonal graphite, respectively. The crystalline state of the CQDs can also be judged from the SAED pattern (Figure S1c in the Supporting Information), which shows polycrystalline structure of the sample.

Figure 2a shows the PL spectra acquired from the CQD suspension at pH of 7 excited by different wavelengths. The spectra can be divided into two parts: excitation wavelength independent blue emission and excitation wavelength dependent LW emission. According to the previously reported mechanism concerning PL from CQDs, the blue emission can be ascribed to carbon defects such as carbon vacancies or irregular carbon rings, whereas the LW emission stems from the radiative recombination of electron–hole pairs confined in CQDs.\(^{16,17}\) The red-shift observed from the LW emission with increasing excitation wavelength can be attributed to quantum confinement in the carbon dots. The PL intensity change is related to the size distribution of the CQDs, or in other words, the band gap of the most probable diameter of the CQDs determines the optimal emission wavelength. With regard to the LW emission, the intensity of the PL peak at about 505 nm reaches a maximum when excited by 400 nm. According to the relationship between the size and band gap of the CQDs,\(^{17–19}\) the band gap which corresponds to the most probable CQD diameter (3.2 nm) is calculated to be about 2.43 eV (~510 nm), which is in good agreement with our experiment results. This indicates that the red shift in the LW emission with increasing excitation wavelength arises from quantum confinement in the CQDs.

Figure 2b,c and Figure S2 in the Supporting Information show the pH-dependent PL spectra excited by wavelengths of 360 and 440 nm, respectively. The peak excited by 440 nm is almost pinned at 520 nm as the pH increases. However, with increasing pH, the emission spectrum excited by 360 nm broadens gradually and becomes more asymmetrical. The PL emission spectral changes with increasing pH are consistent with those reported previously.\(^{10}\)

The PL intensity reaches a maximum at pH = 4 under excitation by the two different wavelengths. This is different from the previous report that the PL intensity changes monotonically with pH. The reason for the intensity change has been considered to be due to protonation and deprotonation of carboxylate.\(^{6,12}\) To clarify this point, FTIR spectra were acquired from the CQDs at different pH (Figure 3). The spectrum for pH = 3 shows an apparent absorption peak related to –OH groups at about 3430 cm\(^{-1}\); the band at 1720 cm\(^{-1}\) indicates C–O vibration;\(^{8,20}\) and another strong peak at 1368 cm\(^{-1}\) is attributed to –COOH.\(^{13}\) The results imply that the CQDs are oxidized graphite with abundant –COOH groups on the surface. The absorption peak at 1617 cm\(^{-1}\) can be assigned to C–C vibration,\(^{5,7}\) and its intensity changes slightly with pH. Relative to the intensity of the C–C vibration, the intensity of the band at 1368 cm\(^{-1}\) decreases with increasing pH. The intensity ratios of –COOH to C–C vibrations versus pH are shown in Figure 3b. The vibration intensity ratios diminish gradually with increasing pH, indicating gradual deprotonation of –COOH. However, similar to results obtained from other experiments,\(^{6,13}\) our results show that the PL intensity does not vary monotonically with pH. That is, protonation or deprotonation of –COOH is not the main factor affecting the PL spectrum as the pH changes. Furthermore, this cannot explain the broadening or shifting of the PL spectrum with increasing pH, as shown in Figure 2b.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** (a) TEM and HR-TEM images (inset) of the CQDs and (b) size distribution of the CQDs calculated from the TEM image. The most probable diameter is 3.2 nm.
Kozawa et al. \(^2\) have explained the emission wavelength shift of graphene oxide by the DFT-based many-body perturbation theory and demonstrated that carboxylate protonation blue-shifts the PL whereas deprotonation redshifts the PL. However, this explanation also fails to describe our experimental results. That is, the PL spectrum acquired from the CQDs blueshifts and becomes asymmetrical as the pH goes up.

In low-dimensional structures, one prominent characteristic is the strong correlation between carriers due to quantum confinement. Electron–electron repulsive and electron–hole attractive interactions play important roles in the electronic and optical properties in carbon-based nanomaterials such as single-wall carbon nanotubes (SWCNTs) and graphene oxide. \(^2\)–\(^4\) Trion (charged exciton), a bound state of two holes and one electron (or two electrons and a hole), also affects the optical properties of carrier-doped low-dimensional semiconductors. \(^2\)–\(^4\) Adding HCl (H\(^+\)) into the SWNT dispersion can achieve hole doping to form positive trions in SWCNTs. \(^2\)–\(^4\) In our experiments, after adding HCl to the CQDs solution, hydrogen ions extract electrons from the CQDs, and holes are injected into the CQDs. Theoretical analysis and experiments indicate that the excitons and doped holes tend to localize around the disorder structures. \(^2\)–\(^4\) Hence, it is reasonable to consider that the excitons and doped holes are localized around the carbon topological defect sites in this case. When a defect-bound exciton encounters a chemically induced hole before radiative recombination, they may form a positive trion. The variation of the PL spectra excited by a wavelength of 360 nm at different pH may be related to the positive trions. However, the electron–hole pairs confined in the CQDs are not susceptible to the doped hole, and this is the reason the peak position in the PL emission excited by a wavelength of 440 nm hardly changes (Figure 2c).

To understand the PL spectral changes at different pH excited by a wavelength of 360 nm (Figure 2b), we divide these PL spectra by Gaussian line shape. The fitted results are shown in Figure 4a–f and Figure S3 in the Supporting Information.
ering the unnoticeable LW emission change in the peak position with increasing pH (Figure 2c), we fix the positions and full-width at half-maximum (fwhm) of EmB when these PL spectra are decomposed. The fwhm of EmB is large because of the wide size distribution (1–6 nm) of the CQDs (Figure 1). All the PL spectra are reproduced well by the sum of the three peak components.

Figure 4g shows the peak position of the three divided emissions (EmA1, EmA2, and EmB) versus pH. The theoretically calculated EmA2 intensity versus pH is obtained by solving the rate equations. (i) Integral intensity ratio of EmA2 and EmA1 \[ \frac{I(EmA2)}{I(EmA1)} \] versus pH.

Figure 4. (a–f) Gaussian fitting of the PL spectra excitation by 360 nm at pH values of 2, 4, 6, 8, 10, and 12. The fitting results for pH of 3, 5, 7, 9, 11, and 13 are shown in Figure S3 in the Supporting Information. (g) Peak positions of the three divided emissions (EmA1, EmA2, and EmB) versus pH. (h) Integral intensities of the whole PL spectrum from Figure 2c, EmB, EmA2, and EmA1 versus pH. The theoretically calculated EmA2 intensity versus pH is obtained by solving the rate equations. (i) Integral intensity ratio of EmA2 and EmA1 \[ \frac{I(EmA2)}{I(EmA1)} \] versus pH.

No PL intensity fluctuation is observed, and this also indicates that the maximum PL intensity observed at the pH of 4 has very little to do with both EmA1 and EmA2.

To explain the PL intensity at the pH of 4, the PL mechanism at three pH values is illustrated in Figure 5. It is important to note that in our experimental system the hydrogen ion (H+) has two effects: One is to extract electrons from the CQDs, that is, to inject holes to the CQDs. The other is to passivate the surface of CQDs. A dynamic equilibrium occurs among the H+, defect-bound exciton, and defect-bound trion. When the pH is larger than 4, there are a certain amount of COO\(^{-}\) groups on the surface of the CQDs, and so the CQDs are negatively charged. After the CQDs are photoexcited to produce electron–hole pairs, some holes will be captured by the negative charge centers on the surface. The more abundant is COO\(^{-}\) on the surface, the more holes will be captured. Hence, the emission intensity related to the size effect is enhanced when the pH decreases to about 4 because of enhanced H\(^{+}\) surface passivation (Figure 2c). The −COOH group is weakly acidic. When pH is 4, the COO\(^{-}\) is completely neutralized by H\(^{+}\), and the surface of the CQDs no longer has a net charge. That is, the surface of the CQDs is optimally passivated, and the PL intensity reaches a maximum at pH of 4. If the pH is reduced further, −COOH changes to −COOH\(^{+}\). When the photoexcited electron–hole pairs are generated, some electrons will be captured by the positively charged
centers on the surface, and this explains why, at pH < 4, the PL intensity diminishes gradually with further pH decrease.

It is difficult to accomplish high electron doping at normal temperature and pressure, and so it is difficult to form negative trions in carbon nanostructures. With the reduction of temperature and pressure, and so it is difficult to form negative trions in carbon nanostructures. However, hydrocarbon ions in the current CQD solution, the formation rate of trions declines. We theoretically calculate the PL intensity from trions (EmA2) by solving the rate equations (see eqs 1−4 and 6 below). As shown in Figure 4b, the calculated PL intensity monotonically decreases with increasing pH. This indicates that with increasing pH the trion emission is quenched, and the exciton emission (LW emission) is slightly recovered. The total peak shows a multipeak structure when the pH is large enough (Figure 2b). When the pH is larger than 8, the small amount of H+ has a small effect on the formation rate of positive trions. However, OH− cannot transfer the electron to the CQDs efficiently in the solution to form the electron dopant. That is, it is difficult to form negative trions in this system, and so the intensity ratio of the trion PL to exciton PL changes slowly when the pH varies from 8 to 13 (Figure 4i).

To further understand the behavior of the PL intensity ratio of EmA2 and EmA1, a three-level model of the topological defect state is shown in Figure 5 (right side), in which X represents the defect-bound exciton state and T stands for the defect-bound trion state. G refers to the generation rate of defect-bound excitons; γX and γXT denote the radiative decay rate and nonradiative exciton decay rate, respectively; and γXT represents the trion formation rate. The trions also decay via radiative (γT) and nonradiative (γnr) processes. It is supposed that the trions are formed from excitons. This can be verified by the PL excitation (PLE) spectra as shown in Figure 2d which are acquired by monitoring at 410 nm (defect-bound exciton emission, EmA1) and 450 nm (trion emission, EmA2) at the pH of 6. The PLE spectrum of trions shows no new peak compared to the PLE spectrum of defect-bound excitons. The results are similar to those obtained from samples at other pH values, suggesting that the trions are formed via excitons.

The rate equations for the population of exciton N_X and trion N_T are expressed as

\[
\frac{dN_X}{dt} = G - (\gamma'_X + \gamma'^{nr}_X + \gamma_X)N_X
\]  
(1)

and

\[
\frac{dN_T}{dt} = \gamma_X N_X - (\gamma'_T + \gamma'^{nr}_T)N_T
\]  
(2)

N_X and N_T can be derived from the steady-state solutions of the above two equations

\[
N_X = \frac{G}{\gamma'_X + \gamma'^{nr}_X + \gamma_X}
\]  
(3)

and

\[
N_T = \frac{\gamma_X}{\gamma'_T + \gamma'^{nr}_T + \gamma_T} \frac{G}{\gamma_X N_X - (\gamma'_T + \gamma'^{nr}_T)N_T}
\]  
(4)

Regarding the PL intensity of the exciton (I_X) and trion (I_T) as a function of the adsorption probability (a) and [H+]

\[
I_T/I_X = \frac{\gamma'_T\gamma_X(m)}{\gamma'_X(\gamma'_T + \gamma'^{nr}_T)} \left(1 - \frac{sm}{1 + m}\right)
\]  
(5)

where m denotes the pH. For simplicity, the changes of \(\gamma'_X\) and \(\gamma'_T + \gamma'^{nr}_T\) with chemical doping are assumed to be small and neglected in the analysis.

Assuming that the absorption rate of H+ onto CQDs obeys Langmuir’s law, the trion formation rate from the excitons \((\gamma_{XT}(m))\) at different pH can be described as

\[
\gamma_{XT}(m) = K_0 \left(1 - \frac{sf(a, [H^+] + 1)}{f(a, [H^+])}\right)
\]  
(6)

where \(K_0\) is the trion formation rate with slight H+ and s reflects the charge transfer ability from H+ to CQDs. \([H^+]\) refers to the effective number of hydrogen ions in the system, and \(f(a, [H^+])\) is a function related to the adsorption probability (a) and \([H^+]\). It is found that when \(f(a, [H^+]) = n\) the calculated PL intensity ratio of the trion and exciton is consistent with the experimental data. That is, from expressions 5 and 6, \((I_T/I_X)\) can be expressed as

\[
\frac{I_T}{I_X} = \frac{\gamma'^{K_0}X}{\gamma'_X(\gamma'_T + \gamma'^{nr}_T)} \left(1 - \frac{sm}{1 + m}\right)
\]  
(7)
On the basis of Eq. 7, the calculated PL ratio of the trions to excitons with the assumed constant radiative decay rates is presented by the red solid line in Figure 4i. It is in line with the experimental data.

It has recently been observed that the lifetime (inverse of radiative decay rate) of trions is longer than that of excitons because of the mixed characteristics of the singlet and triplet states.\(^\text{25}\) Accordingly, the time-resolved PL of excitons and trions at pH of 7 is monitored, and the corresponding results are shown in Figure 6. According to the three-level model, the lifetime of the trion can be expressed as

\[
\tau = \sum_{i} \alpha_{i} \tau \exp(-t/\tau_{i})
\]

where \(\tau_{i}\) is the single decay time; \(\alpha_{i}\) represents the amplitude of the components at \(t = 0\); \(n\) is the number of decay time; and \(A\) is the background offset (a fitting parameter). The fitted results are presented in Figure 6. The average lifetime of the trion is 6.73 ns, and that of the exciton is 4.57 ns. This also verifies the validity of the defect-bound trion model. All in all, the multipeak structure exhibited by the blue emission can be explained well by the model involving defect-bound trions.

**CONCLUSIONS**

CQDs exhibiting blue emission that is excitation wavelength independent and LW emission that depends on the excitation wavelength are produced and studied. The blue emission becomes more asymmetrical at high pH, whereas the peak position of the LW emission is hardly affected by the pH change. A model based on defect-bound trions is proposed to explain the phenomenon, and the calculated PL intensity ratio of trions to excitons is consistent with the experimental results. The intensities of the two emissions are consistent at different pH values with the maximum observed from the CQD system at the pH of 4. This phenomenon can be explained by the evolution of surface charges.

**REFERENCES**


(10) Qiao, Z. A.; Wang, Y. F.; Gao, Y.; Li, H. W.; Dai, T. Y.; Liu, Y. L.; Huo, Q. S. Commercially Activated Carbon as the Source for