

Exciton dynamics in luminescent carbon nanodots: Electron–hole exchange interaction

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Received: 22 July 2015

Revised: 29 October 2015

Accepted: 30 October 2015

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KEYWORDS

carbon dots, photoluminescence, pyrolysis, electron–hole exchange interaction, energy splitting

ABSTRACT

The electron–hole exchange interaction significantly influences the optical properties of excitons and radiative decay. However, exciton dynamics in luminescent carbon dots (Cdots) is still not clear. In this study, we have developed a simple and efficient one-step strategy to synthesize luminescent Cdots using the pyrolysis of oleylamine. The sp^2 clusters of a few aromatic rings are responsible for the observed blue photoluminescence. The size of these clusters can be tuned by controlling the reaction time, and the energy gap between the π – π^* states of the sp^2 domains decreases as the sp^2 cluster size increases. More importantly, the strong electron–hole exchange interaction results in the splitting of the exciton states of the sp^2 clusters into the singlet-bright and triplet-dark states with an energy difference ΔE , which decreases with increasing sp^2 cluster size owing to the reduction of the confinement energy and the suppression of the electron–hole exchange interaction.

1 Introduction

As a new fascinating class of carbon nanomaterials, luminescent carbon dots (Cdots) have attracted sig-

nificant attention owing to their favorable properties of good biocompatibility, low toxicity, and low cost, which offer the opportunity to substitute highly toxic semiconductor quantum dots (like CdSe and CdTe)

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in bio-imaging applications and light-emitting diodes (LEDs) [1–5]. After the development of an electrophoretic method to purify fluorescent carbon materials from arc-discharge soot [6], the past few years have witnessed considerable progress in developing physical and chemical preparation methods for Cdots. For instance, graphite has been cut into ultra-small luminescent Cdots using a laser ablation approach [7], electrochemical synthesis [8], and a hydrothermal cutting method [9]. Furthermore, the soot from burning candles or natural gas has been oxidized to synthesize Cdots [10, 11]. The pyrolysis approach has been employed using carbohydrates, citric acid, and ethylenediaminetetraacetic acid as carbon precursors [12–15]. Previous reports have demonstrated that carbon architectures show similar photoluminescence (PL) behavior, whether they are carbon nanotubes [16] or amorphous [17] and crystalline [18] carbon particles. Based on the study of luminescent Cdots fabricated by cutting graphite/graphene sheets, three main explanations have been proposed for the origin of PL: emissive surface defects [12, 17], localized electron–hole pairs from π – π^* states in sp^2 clusters [19], and zigzag sites with a carbene-like triplet ground state [9, 13]. However, the mechanism of exciton dynamics in Cdots has not yet been studied.

Herein, we demonstrate a simple one-step method for the synthesis of luminescent Cdots by the pyrolysis of oleylamine. This approach can be extended to other alkylamines and silanes. In the synthetic system, oleylamine is the only chemical, acting simultaneously as a solvent, a precursor, and a passivation agent. We synthesized different luminescent Cdots by controlling the reaction time and further investigated their exciton dynamics. Fourier-transform infrared (FTIR), Raman, nuclear magnetic resonance (^1H NMR) spectroscopy, and X-ray photoelectron spectroscopy (XPS) data confirmed that the alkylamines were oxidized into sp^2 domains. Our experimental data demonstrated that the absorption and PL position of the Cdots were red-shifted owing to the decrease of the energy gap between the π – π^* states of the sp^2 domains as the reaction time increased, which resulted in an increasing sp^2 cluster size. Furthermore, the exciton dynamics in Cdots showed that the electron–hole exchange interaction in the sp^2 domains generated a large

splitting between optically active (singlet-bright) and optically passive (triplet-dark) electrons (electron–hole excitations). The electron–hole exchange interaction and confinement energy decreased with increasing sp^2 cluster size.

2 Experimental

2.1 Synthesis of carbon dots

Photoluminescent Cdots were synthesized by the carbonization of one organic solvent. First, 8-mL glass vials were heated at 380 °C for 10 min and then 50 μL oleylamine was quickly added to the vials. The reaction time was set at 1, 5, 10, 20, and 30 min. After cooling to room temperature, the obtained Cdots were directly dispersed in 4 mL hexane. 0.2 mL of Cdots dispersion solution were extracted and diluted by hexane to 2 mL for the absorption and PL measurements. Oleylamine can be substituted by other organic sources, such as octadecanethiol, dodecanethiol, hexadecyltrimethoxysilane (HDTMSi), hexadecylamine, dodecylamine, 3-aminopropyltrimethoxysilane (APTMS), and N-(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AEPTMS).

2.2 Characterization

Transmission electron microscopy (TEM) investigations were performed using a JEOL1400 transmission electron microscope with an accelerating voltage of 100 kV. Ultraviolet–visual (UV–Vis) absorption spectra were recorded at room temperature using a Lambda 950 spectrophotometer. Room-temperature steady-state PL spectra were recorded by a home-built optical setup using 457-, 488-, 532-, and 633-nm lasers for excitation. FTIR spectra were recorded by a Bruker Vertex 80v at room temperature in a continuous vacuum environment with typically 256 scans per loop and 4 cm^{-1} resolution in the transmission and reflection mode. Raman scattering spectroscopy was performed using a micro-Raman spectrometer (Horiba-JY T64, 000) excited with a solid-state laser ($\lambda = 514 \text{ nm}$) in the backscattering configuration. The backscattered signal was collected through a 100 \times objective and dispersed by a 1,800- $\text{g}\cdot\text{mm}^{-1}$ grating; the laser power on the sample surface was measured to be approximately 1.0 mW.

The typical measurement time was 30 s. The XPS data were acquired using an Omicron EA125 analyzer with monochromatic Al K alpha ($h\nu = 1,486.7$ eV) radiation. The room-temperature time-resolved PL spectra were obtained by a Becker-Hickl DCS-120 confocal scanning fluorescence lifetime imaging microscopy (FLIM) system, with excitation from a laser diode operating at 375 nm. The ^1H NMR spectra of the oleylamine and Cdots were recorded by a Bruker BioSpin GmbH NMR300. To detect the feature peak of sp^2 at 7.2 ppm, the Cdots were dispersed in CD_2Cl_2 .

3 Results and discussion

3.1 UV-Vis absorption and PL properties of Cdots

Figure 1(a) shows the UV-Vis absorption spectrum of Cdots synthesized by the pyrolysis of oleylamine with a reaction time of 10 min. The typical feature at ~ 230 nm is attributed to the $\pi-\pi^*$ transition of aromatic sp^2 domains and the two absorption shoulders at ~ 275 and ~ 300 nm to the $n-\pi^*$ transition [20]. The insets in Fig. 1(a) show the dispersion of Cdots with blue fluorescence under 254 nm UV light illumination.

Figure 1(b) presents the TEM image of the Cdots. The results reveal that the Cdots were mostly irregularly sphere with diameters in the range 4–13 nm. Their PL properties show an excitation-dependent behavior. The PL emission shifts to longer wavelengths and its intensity decreases with the increase of the excitation wavelength, which agrees with previous reports [1, 9, 17, 21]. The emission band maximum was 554, 560, 580, and 656 nm of the Cdots excited by 457-, 488-, 532-, and 633-nm lasers, respectively. The Cdots were dispersed in hexane and the laser power on the sample surface was measured to be approximately 80 mW. However, the PL intensity decreased drastically when the sample was excited with the 532- and 633-nm lasers. Until now, several mechanisms have been proposed to explain this excitation-dependent behavior, such as the presence of several different fluorophores within the carbogenic network [17] and a distribution of different emissive sites and sizes [10, 22]. However, the essence of the excitation-dependent behavior is debatable. Using our approach, other mercaptans, alkylamines, and silanes, such as octadecanethiol, dodecanethiol, HDTMSi, hexadecylamine, dodecylamine, APTMS, and AEPTMS, can

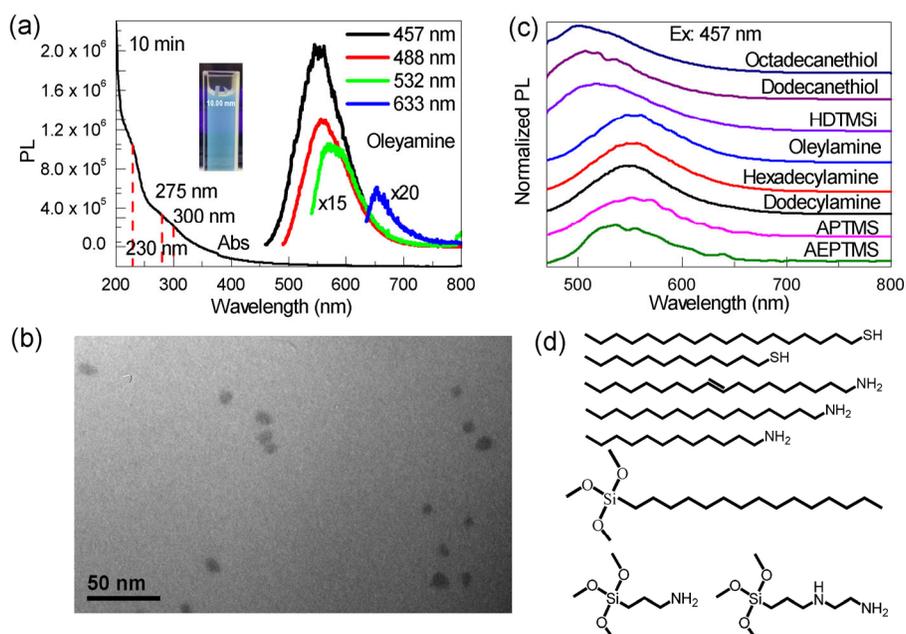


Figure 1 (a) PL spectra of Cdots in hexane excited with different lasers and the corresponding absorption spectrum. The insets show the dispersion of Cdots with blue fluorescence under 254-nm UV light. (b) Typical TEM image of Cdots. (c) Normalized PL spectra of Cdots synthesized from other mercaptans, alkylamines, and silanes: octadecanethiol, dodecanethiol, HDTMSi, hexadecylamine, dodecylamine, APTMS, and AEPTMS. (d) The chemical structure of the mercaptans, alkylamines, and silanes.

also be used as sources to synthesize Cdots. Figure 1(c) shows the PL spectra of Cdots using different sources under excitation with a 457-nm laser. Figure 1(d) displays the chemical structure of those alkylamines and silanes.

3.2 Mechanism of the pyrolysis of oleylamine to Cdots

The basic procedures to synthesize Cdots include the decomposition and pyrolysis of oleylamine in air. FTIR spectroscopy and ^1H NMR spectroscopy were used to confirm the reaction process. To eliminate the FTIR signal interference due to H_2O in the air, the Cdots were drop-casted on 50-nm-thick Au films to form thin films and then measured in a continuous vacuum environment in the reflection mode. The oleylamine liquid films were examined in a vacuum environment in the transmission mode. Figure 2(a) shows the FTIR spectra of the oleylamine and Cdots. The bands at 2,924 and 2,853 cm^{-1} can be ascribed to the symmetric and asymmetric stretching vibrations of the C–H bonds from CH_2 and CH_3 [23–26]. The peaks at 1,467 and 1,378 cm^{-1} can be assigned to the asymmetric in-plane and symmetric rocking mode of C–H [25]. The peaks at 1,306 and 1,073 cm^{-1} in the oleylamine spectrum are attributed to the stretching vibrations of $\text{CH}_2\text{--CH}_3$ and C–N. However, the direct FTIR analysis of the Cdots did not obtain detectable FTIR signals, indicating that $\text{CH}_2\text{--CH}_3$ and C– NH_2 were carbonized. The peak of oleylamine at 722 cm^{-1} corresponds to the in-plane rocking vibration of the CH_2 bond from $(\text{CH}_2)_n$ chains, where $n > 4$ [24]. However, the fractions of the peak at 722 cm^{-1} drastically decrease in Cdots, which indicates that the long chains of oleylamine are broken during carbonization. After carbonization, the stretching vibrations and in-plane rocking mode of N–H at 3,375, 1,571, and 796 cm^{-1} and the C–N stretch peak of oleylamine at 1,073 cm^{-1} disappear [27, 28], which indicates that the --C--NH_2 groups of oleylamine are oxidized. It is important to note that a new band appears at 1,710 and 1,600 cm^{-1} , which is assigned to the stretching vibrations of C=O and the ring stretching vibrations of the phenyl group, respectively. The oleylamine peaks at 3,005, 1,621, and 967 cm^{-1} can be assigned to the stretching vibrations of =C–H and --C=C-- and the

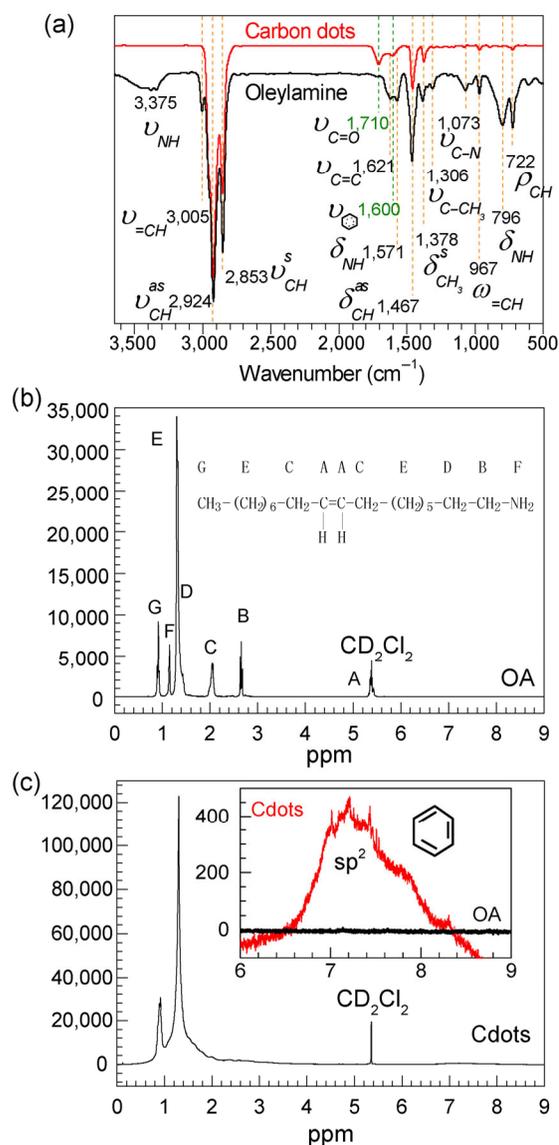


Figure 2 (a) FTIR spectra of oleylamine and Cdots, (b) and (c) ^1H NMR spectra of oleylamine and Cdots. The insets in (c) demonstrate the formation of sp^2 clusters in Cdots.

out-of-plane rocking mode of =C–H [25]. However, the peaks at 3,005 and 1,621 cm^{-1} disappear, which indicates that the CH=CH groups were broken and the left small peak at ~ 967 cm^{-1} is attributed to the C–O groups in Cdots. To further confirm the formation of sp^2 clusters, the ^1H NMR spectra of oleylamine and Cdots in CD_2Cl_2 solvent were examined, as shown in Figs. 2(b) and 2(c). It is important to note that the ^1H NMR feature peak of the phenyl group at ~ 7.2 ppm was detected in Cdots. However, it was not observed in oleylamine. Therefore, O_2 from air participated in the pyrolysis of oleylamine and sp^2 clusters or

fragments were formed in the Cdots. Oleylamines are oxidized into carbon compounds consisting of sp^2 clusters (phenyl group), C=O, C–O, $-CH_2-$, and $-CH_3$ species.

Raman spectroscopy and XPS were further used to investigate the composition of Cdots. Figure 3(a) shows the Raman spectra of Cdots excited with a 514-nm laser. Two fingerprint features of carbon, the D band and G band, are clearly observed at 1,347 and 1,586 cm^{-1} , respectively [29]. The D band is related to the presence of sp^3 defects and the G band corresponds to the in-plane stretching vibration of sp^2 carbon atoms, which is a doubly degenerate (TO and LO) phonon

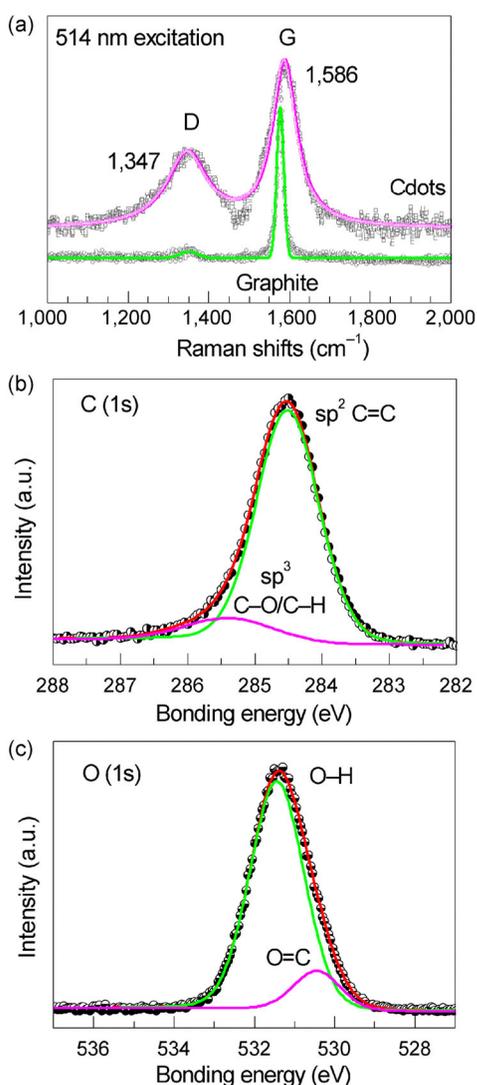


Figure 3 (a) Raman spectra of Cdots and graphite excited with a 514-nm laser, (b) and (c) XPS spectra of Cdots. The solid lines represent a fit to the data.

mode (E_{2g} symmetry) at the center of the Brillouin zone [30, 31]. The increasing phenyl group units in the sp^2 domain result in a blue shift of the G band [32]. The XPS Cdots data of C1s are shown in Fig. 3(b). The peaks at 284.5 and 285.4 eV are assigned to sp^2 carbon (C=C) and sp^3 carbon (C–O/C–H) clusters, respectively, in agreement with previous FTIR, 1H NMR, and Raman spectroscopy results [30, 33, 34]. As shown in the O1s XPS data, the peak at 530.5 eV contains contributions from C=O groups whereas the peak at 531.4 eV is assigned to C–O and O–C–O groups [35–37], which further verifies the FTIR results. It is important to note that the possible contribution from water molecules can be excluded based on four arguments: (1) The Cdots are hydrophobic and passivated with long-chain alkyl groups, (2) the sample was extracted by centrifugation and washing in THF, (3) the sample was heated at 100 °C and pumped before XPS was performed, (4) the FTIR data measured in vacuum do not show any feature peaks of water molecules. Therefore, the Raman and XPS data confirm that the Cdots contain a mixture of sp^2 clusters and a few conjugated repeating units dispersed in an insulating sp^3 matrix, in which a fraction of the carbons are bonded with oxygen (C=O, O=C–OH groups); this is consistent with the UV–Vis, 1H NMR, and FTIR results.

3.3 Aromatic sp^2 domains for the observed blue PL

To understand the PL mechanism, we synthesized Cdots using different reaction times and further investigated the time dependence of their absorption, PL, and lifetime. As shown in Fig. 4(a), the UV absorption peak of the π – π^* transition of aromatic sp^2 domains is red-shifted from 217 to 230 nm as the reaction time increases from 1 to 10 min and further shifted slightly to 232 nm at 30 min. Li et al. calculated the dependence of the HOMO–LUMO gap on the size of graphene fragments and suggested that the gap decreases gradually as the size of the fragment increases [8]. Eda et al. calculated the energy gap between the π – π^* states, which decreases as the size of the sp^2 clusters or conjugation length increases [19]. Therefore, we propose that small sp^2 clusters or fragments of a few aromatic rings are responsible

for the observed blue PL of our Cdots, which were synthesized by the pyrolysis process. The red shift of the π - π^* transition absorption peak is attributed to the increased size of the sp^2 clusters. The broad absorption peak of the π - π^* transition indicates that the size distribution of the sp^2 cluster is inhomogeneous. The most obvious absorption peak line-shape at 5 min is probably due to the conjunction of sp^2 domains and C=O and -CH₃ groups, consistent with previous works [38]. The absorption peaks of the n - π^* transition at ~275 and 300 nm are attributed to the electronic transition of the C-OH and C=O groups, respectively. The FTIR and XPS data confirmed that the two groups, C-OH and C=O, are formed in the Cdots. The electronic orbital energy of the n state of the C-OH group is lower than that of the C=O group [39]. Therefore, the energy gap for the n - π^* transition of the C-OH group is larger than that of the C=O group, resulting in a blue shift of the absorption peak.

Theoretically, the n - π^* energy gap is independent of the size of the sp^2 clusters. Therefore, the absorption peaks of the n - π^* transition for our Cdots are not shifted as the reaction time increases from 1 to 30 min.

Figure 4(b) shows the normalized PL spectra of Cdots synthesized with different reaction times varying from 1 to 30 min, obtained using excitation by a 457-nm laser. It is clearly observed that the PL position is red-shifted from 544 to 553 nm when the reaction time increases from 1 to 30 min, which indicates that the energy gap between the π - π^* states decreases, in

agreement with the absorption data. Therefore, the size of the sp^2 clusters increases as the reaction time increases. All luminescent Cdots have a quantum efficiency of ~3%. It is important to note that the PL and absorbance measurement conditions for all Cdots were approximately the same, which ensured that the comparisons of the PL and absorbance absolute intensities are convincing. As shown from the absolute intensity PL spectra (the inset in Fig. 4(b)), the PL intensity monotonously increases to a maximum at 10 min and then decreases with increasing reaction time from 10 to 30 min. The absorption data in the inset in Fig. 4(a) show that the absorption intensity of the π - π^* transition first increases, reaches a maximum at 20 min, and then drastically decreases at 30 min; this indicates that the concentration of luminescent sp^2 clusters in the Cdots becomes maximum at ~20 min. Therefore, the observed increase in the PL intensity is attributed to the increased concentration of the strongly localized sp^2 sites. Although the concentration of the sp^2 sites at 20 min is larger than that at 10 min, the PL intensity at 20 min is smaller than at 10 min. Therefore, the subsequent PL intensity decrease at 20 min is due to the percolation between the sp^2 configurations, which facilitates the transport of excitons to nonradiative recombination sites and thus leads to PL quenching [19]. With a longer reaction time, excessive carbonization occurs, which results in the drastically decreased concentration of luminescent Cdots. Therefore, the absorption and PL intensity drastically decrease.

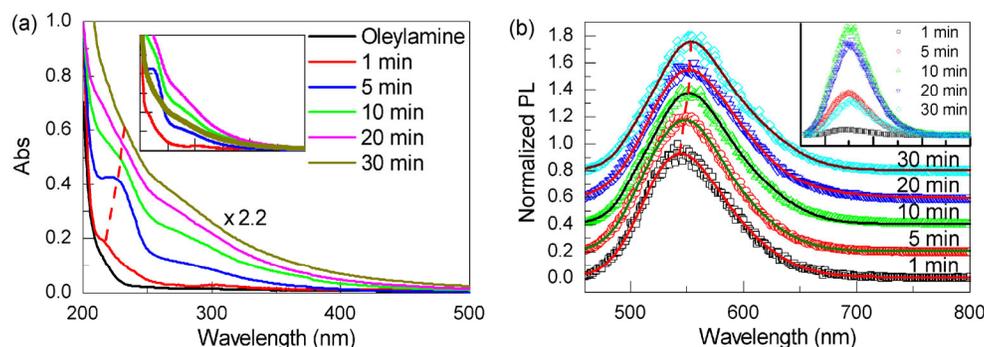


Figure 4 (a) UV-Vis absorption spectra of oleylamine and Cdots at different reaction times between 1 and 30 min. To clearly show the red shift of the absorption peak, the absorption intensity of the Cdots at 30 min was multiplied by 2.2. The inset shows the original absorption intensity data. (b) Normalized PL spectra of Cdots excited with a 457-nm laser. The solid lines are fitting curves to the data using the Gaussian peak function. The inset displays the non-normalized PL spectra of the Cdots.

However, it is important to note that both the absorption and PL data clearly show that the size of the sp^2 clusters increases with increasing reaction time. The absorption and PL intensity depend on the concentration of the formed sp^2 clusters. However, a high concentration facilitates the percolation between sp^2 clusters, leading to nonradiative energy transfer and thus PL quenching, which is similar to in the behavior of CdSe/ZnS quantum dot films [40].

3.4 Electron–hole exchange interaction

The time-resolved PL spectra of luminescent Cd dot drop-casted films were recorded by a confocal scanning fluorescence lifetime imaging microscopy system and are shown in Fig. 5(a) [41, 42]. The time-resolved PL decay curve is well fitted by the biexponential function, $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, with two time constants: a fast decay (τ_1), accompanied by a long-living emission (τ_2), where $I(t)$ is the PL intensity [43, 44]. Because of the inhomogeneous

distribution of sp^2 cluster lifetimes, the emission kinetics shows a multiexponential behavior distributed over a large time scale [45]. The lifetime of the long-lived decay component is assumed to correspond to the lifetime of the film samples [46], which was determined to be dependent on the reaction time. As the reaction time increases, the lifetime of the Cdots decreases. The fluorescence lifetimes τ_1 are 1.2 ± 0.06 , 0.7 ± 0.01 , 0.5 ± 0.01 , 0.4 ± 0.01 , and 0.3 ± 0.01 ns and the τ_2 ones are 6.5 ± 0.01 , 3.9 ± 0.02 , 2.5 ± 0.02 , 1.9 ± 0.02 , and 1.2 ± 0.02 ns for the reaction times 1, 5, 10, 20, and 30 min, respectively. The absorption and PL data of the Cdots show that the size of the sp^2 clusters increases with increasing reaction time. Therefore, we propose that an electron–hole exchange interaction occurs in the luminescent Cdots, leading to the splitting of the excitonic states and thus the size dependence of their lifetimes, which is consistent with previous reports [46, 47]. Donegá et al. [48] and Brongersma et al. [49] investigated the size dependence of the band-

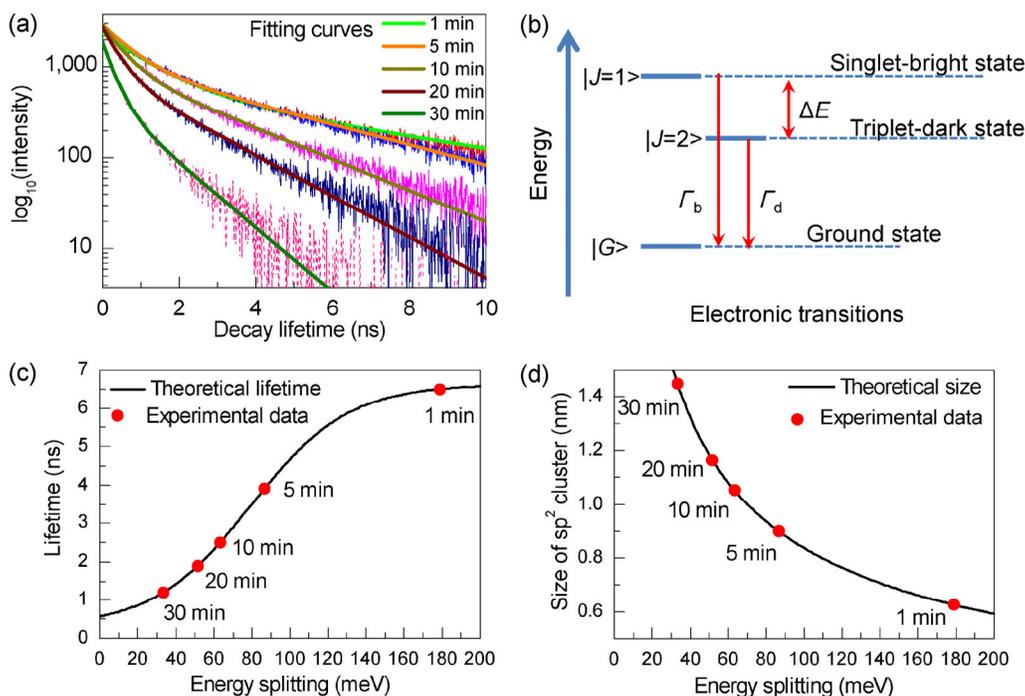


Figure 5 (a) Time-resolved PL spectra of Cdots synthesized using different reaction times. The lifetime decreases as the reaction time increases. The solid lines are fitting curves to the data using a biexponential function. (b) Schematic diagram of a three-level model with the singlet-bright, triplet-dark, and ground states. (c) Lifetime as a function of the energy splitting between the singlet-bright and triplet-dark states (ΔE). The red solid circles are the experimental long-living emission lifetime, extracted from (a), and the black solid line is a fit to the data using Eq. (2), as described in the text. (d) Size of sp^2 clusters (d) vs. energy splitting (ΔE). The red solid circles denote the energy splitting extracted from (c) and the black solid curve is a fit to the data using Eq. (3).

edge PL decay of CdSe quantum dots with diameters ranging from 1.7 to 6.3 nm and Si nanocrystals with diameters in the range of 2 to 5.5 nm. Both works were based on a three-level system consisting of a zero-exciton ground level and excitonic singlet and triplet states. These studies demonstrated that the lifetime decreases with increasing quantum-dot size owing to the decreased electron–hole exchange interaction, which results in the decrease of the energy gap between the excitonic singlet and triplet states. For the electronic states of the graphene structure, 16 exciton states have been proposed that originate from the spin and degeneracy of band structures in the K and K' valleys in the momentum space. However, the optical transition from only one exciton state to the ground state is dipole allowed and is defined as the singlet-bright exciton state. The other 15 exciton states are optically forbidden and are defined as triplet-dark exciton states [47]. Therefore, the exciton states of the sp^2 clusters can be classified into singlet and triplet states of the electron–hole spin configuration. Figure 5(b) shows a schematic of a three-level model with singlet-bright ($J = 1$) and triplet-dark ($J = 2$) excitonic states and a zero-exciton ground state (G). The dark state lies below the bright state with an energy splitting ΔE . Γ_b and Γ_d are the radiative rates from the singlet-bright ($J = 1$) and the triplet-dark ($J = 2$) states to the ground state (G), respectively. The $|J = 1\rangle \rightarrow |J = 2\rangle$ and $|J = 2\rangle \rightarrow |J = 1\rangle$ rates are, respectively, $\gamma_b = \gamma_0(N_B + 1)$ and $\gamma_d = \gamma_0 N_B$, where $N_B = [\exp(\Delta E/k_B T) - 1]^{-1}$ is the Bose-Einstein phonon number at temperature T , γ_0 is the relaxation rate of the $|J = 1\rangle \rightarrow |J = 2\rangle$ transition at zero temperature [45], and $\gamma_b n_b = \gamma_d n_d$, where n_b and n_d are the numbers of excitons at the singlet-bright and triplet-dark states, respectively. Therefore, we can obtain $n_b \exp(\Delta E/k_B T) = n_d$. By defining $N = n_b + n_d$ as the total number of excitons, the decay rate (Γ) of the excitons is given by [46, 50]

$$-\frac{dN}{dt} = n_b \Gamma_b + n_d \Gamma_d \quad (1)$$

$$\Gamma = \frac{1}{\tau} = \frac{\Gamma_b + \Gamma_d e^{\Delta E/k_B T}}{1 + e^{\Delta E/k_B T}} \quad (2)$$

where τ is the lifetime and k_B is the Boltzmann constant, $8.617 \times 10^{-5} \text{ eV}\cdot\text{K}^{-1}$. The temperature T was 298 K

in our experiments. Using Eq. (2), the experimental long-living emission lifetime data were fitted, as shown in Fig. 5(c). As the lifetime increases, ΔE increases. The calculated energy splitting ΔE was 179, 86.6, 63.3, 51.7, and 33.4 meV, respectively, for reaction times 1, 5, 10, 20, and 30 min. Previous reports have shown that the energy splitting ΔE and the exciton lifetime increase with decreasing size of luminescent nanoparticles [45, 47, 49]. Brovelli et al. investigated the strong electron–hole exchange interaction in CdSe/CdS core–shell semiconductor nanocrystals and demonstrated that the relationship between the bright–dark energy splitting and the nanocrystal size can be fitted by the equation $70/d_1^2$ meV, where d_1 is the diameter of the nanocrystals in nanometers [46]. Matsunaga et al. determined the tube-diameter dependence of the energy splitting for carbon nanotubes, $\Delta E = 70/d_2^2$ (meV), where d_2 is the diameter of the carbon nanotubes in nanometers [51]. Therefore, the size of the sp^2 clusters, d , is defined as

$$d = \sqrt{70 / \Delta E} \quad (3)$$

where the units of d and ΔE are nanometers and millielectronvolts, respectively. Figure 5(d) shows the fitting curve. The size of the sp^2 clusters increases with the decrease of the energy splitting. The sp^2 cluster size is 0.6, 0.9, 1.1, 1.2, and 1.4 nm for reaction time 1, 5, 10, 20, and 30 min, respectively, which is in good agreement with the absorption and PL data. The decrease of the sp^2 cluster size produces an increasing confinement energy and a stronger electron–hole exchange interaction [48]. Therefore, the energy splitting ΔE increases, resulting in an increased lifetime.

4 Conclusions

In summary, luminescent Cdots have been synthesized by the simple one-step method of the pyrolysis of oleylamine, which is the only involved chemical, acting simultaneously as a solvent, a precursor, and a passivation agent in the synthetic system. FTIR data showed that oleylamines are oxidized into carbon compounds, including (C=C) $_n$, C–O, O–H, and C–H species. ^1H NMR, Raman, and XPS data confirmed

that the sp^2 clusters are formed and dispersed in an insulating sp^3 matrix. The absorption peaks of the $\pi-\pi^*$ transition and PL peaks of the Cdots are red-shifted as the reaction time increases. Therefore, the sp^2 clusters are responsible for the observed blue PL and the sp^2 cluster size increases with increasing reaction time. The exciton states of the sp^2 clusters are classified into singlet-bright and triplet-dark states. The bright-dark energy splitting decreases as the sp^2 cluster size increases, as a result of the decreasing confinement energy and weaker electron-hole exchange interaction, which results in the decreased decay lifetime of the Cdots.

Acknowledgements

Q. H. X. gratefully thanks the strong support from Singapore National Research Foundation through a Competitive Research Program (No. NRF-CRP-6-2010-2), and Singapore Ministry of Education via two Tier2 grants (Nos. MOE2011-T2-2-051 and MOE2011-T2-2-085) and a Tier1 grant (No. 2013-T1-002-232).

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