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In-Gap State of Lead Chalcogenides Quantum Dots

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1. Introduction

Lead selenide (PbSe) and lead sulfide (PbS) quantum dots (QDs) have many unique properties to make them promising materials for optoelectronic devices. Their bandgaps, ranging from 0.3~1.1eV, can be easily tuned via size control during synthesis, and their photo response in near infrared region promises their broad applications in bio-imaging [1], telecommunications [2], LEDs [3], lasers [4], photodetectors [5], and photovoltaic devices [6-8].

QDs are essentially nanocrystals consisting of tens to hundreds of atoms (Fig.1a). Due to the nanocrystal’s small size (smaller than the exciton Bohr radius of the bulk semiconductor), strong quantum confinement results in discrete energy levels and bigger bandgaps compared with the respective bulk semiconductor (Fig. 1b)[9]. \( E_1 \), \( E_2 \) and \( E_3 \) stand for the first, second and third excitonic transitions, respectively. \( E_1 \) is the optical bandgap of QD, which is correlated with the size of QD, as shown in the absorption spectra of a series of PbSe QDs (Fig. 1c). QDs studied here are synthesized by colloidal chemistry [10, 11], where the QDs are kept in hexane or toluene as a suspension. The transmission electron micrograph (TEM) shows the highly monodisperse PbSe QDs with average size of 9.6 nm, and the single crystal structure was clearly shown [50]. The crystal structure for PbSe or PbS QDs is rock salt crystal, the same as its bulk semiconductor. The lattice constant for bulk PbS is about 5.9 Å, and 6.1 Å for PbSe [12]. In order to prevent coalescence of QDs, surface passivation by appropriate ligands/surfactants is necessary. Oleic acid is a common ligand for lead chalcogenides such as PbSe or PbS QDs [11]. The passivation layer (ligands) can also modify the optical and electronic properties of the QDs.

Unlike in their bulk semiconductors, enhanced Coulomb interaction in QDs results in much more tightly bonded excitons, and the fate of excitons in these quantum dots is of great relevance to their device applications. Although the properties of excitonic states have been thoroughly studied in the past decade, mostly employing transient spectroscopies [13-17], relatively less attention has been paid to the states within the

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quantum dots bandgap. Conventionally, there are two types of in-gap states: one is the dark exciton state, which is due to the exchange splitting from confinement-enhanced exchange interaction [18, 19]; another type is trap state(s) associated with surface defects [20-22].

These in-gap states are of great importance since they affect the final destiny of excitons. We have previously reported a peculiar in-gap state that bears confinement dependence, with life time about 2 \( \mu \)s [23]. This single gap state (G.S) does not seem to fall into either one of the above conventional gap state categories. A detailed analysis of temperature dependence of photoluminescence (PL), absorption and photoinduced absorption (PA) reveals the unconventional G.S. is a new state of trapped exciton in QD film [24]. The importance of such gap state is illustrated below through the analysis of exciton loss mechanisms in QDs.

As can be seen in Figure 2, Auger recombination happens within sub-ps, followed by hot exciton cooling on the ps timescale [13]. Radiative recombination was surprisingly slow in these QDs, and was detected in the sub-\( \mu \)s range [25-27]. In contrast, relaxation to gap state(s) occurs much faster (<ns) [28]. Therefore, the final state of photogenerated carriers is likely to be the gap state. Due to its long lifetime, this state can be used to monitor charge transfer between QDs and polymers, similar to the case seen in \( \pi \)-conjugated polymer and fullerene systems [29, 30]. This feature also enables the investigation of charge transfer in hybrid composite of polymers and QDs using continuous wave photoinduced absorption (cw-PA) measurements of both constituents, and therefore provides a reliable and accurate study of charge transfer within the hybrid composite. This is especially useful when energy transfer is superimposed with charge transfer. As a matter of fact, the interplay of energy transfer and charge transfer in such composites has been one of the major obstacles that hinder the progress in QD/polymer solar cells. A thorough understanding of the gap state will help to identify photoinduced charge transfer between QDs and the polymer host, as will be illustrated in 2.3.

Fig. 1. (Color online) (a) Rock salt crystal structure of a PbSe quantum dot. (b) Quantized energy levels of a PbSe quantum dot (QD). The dashed line represents the gap state energy level found on IV-VI quantum dots. (c) Absorption spectra of variously sized PbSe QDs. \( E_1 \) is the optical gap of QD.

![Figure 1](image-url)
2. Experimental observation of in-gap state in lead sulfide quantum dots

2.1 Experimental methodology

The main experimental method to study the in-gap state is Continuous Wave Photoinduced Absorption (cw-PA) spectroscopy. Continuous Wave Photoinduced Absorption (cw-PA) is also called pump & probe or photomodulation spectroscopy (Fig.3). A cw Ar⁺ laser (pump), with its energy larger than the optical gap of the investigated material, excites the sample film and generates long-lived photoexcitations; a tungsten-halogen lamp is used to probe the modulated changes $\Delta T$ in transmission $T$ among the interested energy range, usually the subgap regime. A lock-in amplifier is employed with an optical chopper for photomodulation. A series of solid-state photodetectors are coupled with light sources and optical components to span the detection range from UV to NIR. The advantages of cw-PA are that both neutral and charged excitations may be studied and there is no need to introduce dopants into the film [31].
Fig. 3. (Color online) Continuous wave photoinduced absorption (cw-PA) spectroscopy. A regular absorption spectrum of a quantum dot is modified by pump-populating a gap state. This gives rise to a new absorption peak $\Delta E$, whose intensity is directly proportional to the electron density on the gap state.

The pump (cw Ar$^+$ laser) excites the semiconductor sample with photons of an energy larger than the optical gap of the semiconductor (for example, $E_g = 1.07\text{eV}$ for a 4nm PbS QD). The excited electrons thermalize into a long lived gap state(s) caused by defects in the semiconductors. This changes the absorption spectrum since now the transition $\Delta E$ becomes possible. A new peak arises in the spectrum at a wavelength commensurable with $\Delta E$ (for example $\Delta E = 0.33\text{eV}$ for a 4nm PbS QD), as being schematically indicated in Figure 3. The important feature of this measurement is that the magnitude of this absorption peak is linearly proportional to the density of the electrons occupying this gap state:

$$PA = \frac{\Delta T}{T} = -\Delta ad = \sigma n_c d$$  \hspace{1cm} (1)

with $n_c$ the density of photoexcitations, $d$ the sample thickness, and $\sigma$ the excited state optical cross section.

Previously several groups have been using cw-PA to investigate photophysics of CdSe and CdS quantum dots [32, 33]. Recently, we have applied this method to PbS and PbSe quantum dots system [23, 24, 34]. This methodology is very useful to study long-lived, in-gap states and their associated photoexcitations.

2.2 Spectral signature of charged species

We have measured cw photoinduced absorption (cw-PA) of PbS QD film in an energy range of interband electronic transitions at low temperature (10K) [34]. At photon energy near and above the QD bandgap, $E_g$, five photoinduced absorption (PA) peaks are clearly observed,
and four photoinduced absorption bleaching (PB) valleys are also present (Fig. 4a). Figure 4b shows the five interband transitions involved. The close resemblance between PA spectrum (Fig. 4a, black circle) and the second derivative of the linear optical absorption (Fig. 4a, red line) strongly suggests that these steady state PAs may be caused by photoinduced local electric field, and therefore resemble the linear Stark effect [35]. Heretofore, there have been reports about QD charging associated with photoexcitation [36-38].

Fig. 4. (Color online) (a) Photoinduced absorption (PA) spectrum (filled circle, black) of PbS nanocrystal (4.2 nm in diameter) film at T=10K and modulation frequency 400 Hz. Laser excitation is 488 nm with 150 mW/cm² intensity on film. The second derivative of the absorption spectrum (solid line, red) is also shown. PBs stand for photo bleaching bands (Δα<0), whereas PAs are for photoinduced absorptions (Δα>0). [Reprinted with permission from [34]. J. Zhang et al., Appl. Phys. Lett. 2008, 92, 14118. Copyright (2008), American Physical Society]. (b) A schematic drawing of the five interband transitions involved.

The photoinduced local electric field may be created by the trapped charges at the QD surface states. In cw-PA measurement, the laser is being modulated, which is equivalent to the modulation of the local electric field. As a result, the excitonic energy levels shifts and causes change of linear absorption, similar to that observed in electroabsorption spectrum [39]. Therefore, the electroabsorption (EA) feature above the QD bandgap is an indicator of charged species.

2.3 Spectral signature of neutral species

We have extended the cw-PA measurement to photon energy below the QD bandgap. A single PA band (called IR-PA) was observed in the near infrared range. The lifetime of this photoexcitation is about several microseconds, and the peak position of this band has correspondence with the QD size [23]. This photoexcitation was due to a transition from a gap state (G.S) to the second level of exciton excited state 1Pₓ (Fig. 1b). Two different
scenarios could each partially explain our observations. Scenario 1 is that this G.S belongs to a certain trap state, and this could explain the large Stokes shift. Trap states in PbS or PbSe QDs have been previously observed [20, 40]. However, the characteristics of a conventional trap state do not completely go with the confinement-dependence, narrow emission band and short lifetime observed here. Furthermore, the temperature dependence of PL intensity (Fig. 5) shows no thermal activation behavior typical for trap state emission [40]. The lack of thermal activation also indicates there is negligible non-radiative recombination due to defects or aggregates in the films. Large Stokes shift from 100 to nearly 300 meV was observed [23]. The inset of Figure 5b plots the PL energy, $E_{PL}$ vs. $1^{st}$ excitonic peak ($E_1$). Dotted line shows the zero Stokes line (i.e., $E_{PL} = E_1$), which has a slope of 1.0. The linear fitting slope of $E_{PL} \sim E_1$ is 0.75, which is larger than 0.50, meaning the emission state or G.S is not fixed with respect to the bottom of the bulk conduction band, as previously reported for an in-gap hybrid state [41].

We also rule out G.S to be a dark exciton state in PbS quantum dots, since the gap state is too ‘deep’ for dark exciton state from exchange splitting, which was calculated to be less than 10 meV below the lowest bright exciton for a 4.2 nm PbS QD [18], on the other hand, the activation energy of G.S was measured to be about 20 meV [24]. In terms of Stokes shift, even counting the total splitting due to exchange and intervalley interactions, the calculated value was less than 80 meV, whereas the Stokes shift we measured is 332 meV for this size QD [24]. These inconsistencies mean that G.S is not the dark exciton state.
To further validate this claim, we measured the temperature dependences of PL energy, $E_{PL}$ (solid circle, black) and the first excitonic absorption, $E_i$ (open triangle, red) of a 4.2 nm QD film (Fig. 6). Above $T = 50$ K, a linear increase of $dE_i/dT = 0.05$ meV·K$^{-1}$ was obtained from fitting of the absorption experimental data. On the other hand, a temperature coefficient of $dE_{PL}/dT = 0.3$ meV·K$^{-1}$ was derived from fitting of $E_{PL}$ data. $dE_i/dT << dE_{PL}/dT$ indicates that emission is not originated from a band edge splitting state such as a dark exciton state.

Fig. 6. (Color online) Temperature dependences of PL energy, $E_{PL}$ (solid circle, black) and the first excitonic absorption $E_i$ (open triangle, red) of a 4.2 nm QD film. Black line is a linear fit for $E_{PL}$ data and red line is a fit for $E_i$ at $T > 50$ K. [Reprinted with permission from [24]. J E Lewis et al., Nanotechnology 2010, 21, 455402. doi:10.1088/0957-4484/21/45/455402. Copyright (2010), IOP Publishing Ltd].

In summary, G.S is not a trap state based on lifetime and confinement dependence, nor it a dark exciton state based on its different characteristics as oppose to free excitons, i.e., the energy level within the bandgap, its temperature dependence and large Stokes shift. We therefore assign G.S a state for trapped exciton. Such a state, due to its long lifetime (~ several μs), is relevant to exciton dissociation and carrier extraction processes in QD/polymer composite, a material system potentially can be utilized for low-cost high efficiency solar cells [7,42].

3. Implication of in-gap state for quantum dots solar cells

Figure 7 is a schematic drawing of a QD/polymer composite. The absorption of photons by both moieties create excitons, with favorable type II (‘staggered’) energy level alignment, exciton dissociation could happen, with electron being transferred to the QD from the polymer, and holes to the polymer from the QD.
Fig. 7. (Color online) Schematic drawing of QD/polymer composite. QDs (green balls) were shown embedded in polymer matrix (blue). Upper left panel shows the creation of excitons upon light absorption; upper right panel shows the charge transfer process with type II (‘staggered’) energy level alignment between QDs and polymer.

Photoluminescence quenching has been primarily used to identify possible charge transfer between QD and polymer [32,43]. Figure 8a shows the absorption of a 2nm PbS QD film and PL of a poly(3-hexyl) thiophene (P3HT) film, both measured at T=10K. Because of the overlap between the absorption of QD (guest material) and the photoluminescence of polymer (host material), energy transfer (including Förster energy transfer and radiative energy transfer) can occur, which quenches the polymer PL. On the other hand, charge transfer between the polymer (host) and QD (guest) can also eliminate PL of the polymer (Fig. 8b). Unfortunately PL quenching itself cannot distinguish these two mechanisms.

Figure 8c shows the PL of QD/P3HT composite films with different weight ratio of QDs. It is clearly shown that energy transfer is quite efficient at high weight ratio of QDs, and the emission from QD came at a price of P3HT photoluminescence quench. However, comparing with the case of polymer/C$_{60}$ composite, where <10% weight ratio of C$_{60}$ completely quenches the PL of polymer [30], with 200% of QDs the magnitude of PL of P3HT was only reduced by a factor of 5 (inset of Fig. 8c). This indicates that the charge transfer (CT) is not efficient in PbS QD/P3HT composite, as previously reported in CdSe QD/polymer blend [32].
Fig. 8. (Color online) (a) PL spectrum of P3HT film (red line) and absorption spectrum of a 2nm PbS QD film (black line) measured at T=10K. (b) schematic drawing of energy transfer (ET) and charge transfer (CT) processes in QD/polymer composite when the energy level alignment is type II (staggered, left) and type I (‘straddled’, right). (c) PL spectra of neat P3HT film (black half-filled square) and QD/P3HT composite with various weight ratios of QDs. The inset is a blow-up at short wavelength range.

Unlike in the case of CdSe and CdS QDs, with the spectral features we have discovered in PbS QDs, namely, IR-PA and EA (see sections 2.2&2.3 for details), we could qualitatively study charge transfer between PbS or PbSe QDs and polymers, without the complications from energy transfer which often occur in the composites. This is demonstrated in Figure 9. In Figure 9a, when the so-called type I alignment (“straddled”) is present between energy levels of QDs and polymers, the energetics would be in favor of energy transfer, IR-PA signal should increase since now there are more excitons generated on polymer being transferred and eventually trapped on the gap state of QD. In this case, since negligible charges are added to the QDs, the EA feature at energy higher than the QD bandgap is expected to remain the same.

On the other hand, in Figure 9b, when the energy alignment is type II (“staggered”), charge transfer could become more favorable, with hole being transferred to the polymer, the number of excitons originally trapped at the gap state would diminish, and therefore IR-PA signal is expected to decrease, and EA feature will increase due to enhanced QD charging.

Noticeably in both cases, PL quenching of polymer would occur, therefore the conventional way of measuring PL quenching alone is not sufficient to distinguish between whether or not charge transfer has occurred. Furthermore, in the QD/polymer composite, detection of the charge transfer process can be determined from PA measurements performed on the individual constituents (i.e. QDs and polymer), and the mixed composite. The relative change of $\Delta E$ in QDs and the change of polaron absorption in polymers would give direct insight into the charge transfer within the system. The possible overlap of the lower polaron PA band ($P_1$, usually at 0.5 eV) and IR-PA for QDs can be easily avoided by choosing different QD size and different polymers.

The fact that the IR-PA feature has strong temperature dependence does not prevent it being used to study relevant device physics at room temperature. A previous example in polymer/fullerene composite has shown polaron absorption, which almost vanishes at room temperature, could have implications for organic solar cells efficiency [44].
Fig. 9. (Color online) Schematic drawing of how energy transfer and charge transfer affect IR-PA and EA (not shown here). (a) When energy transfer dominates, the IR-PA signal increases, EA signal remains the same. (b) When charge transfer dominates, the IR-PA signal diminishes, accompanied by increased EA signal.

Figure 10a shows the PA spectra of neat QD and P3HT, as well as the QD/P3HT composite with 1:1 weight ratio. As can be seen, the polaron population ($P_2$) in P3HT shows slight increase, whereas the density of interchain excitons (IEX) was greatly enhanced due to morphology change of P3HT upon adding the QDs [45]. On the other hand, the EA signal of QDs remains the same in the composite film comparing with in neat QD film, with a slight increase of IR-PA signal, which means that charge transfer was inefficient between QD and polymer P3HT, combining with PL quenching (Fig. 11), we can draw the conclusion that energy transfer dominates the photoexcitation process in QD/polymer composite film. Similar result was recently reported [46]. Further improvement of charge transfer can be done by ligands manipulation of QD, i.e., ligand exchange with shorter surfactant groups [49], or ligand removal [43, 48, 49], to improve the interfacial properties between QD and polymer, and to facilitate charge transfer occurrence.
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Fig. 10. (Color online) (a) Photoinduced absorption (PA) spectra of P3HT (black line), PbS QD (2.5nm) film (half-filled circle, red) and P3HT/PbS QD composite film (black line + red half-filled circle) measured at T =10K. The gap state is revealed as the near IR band (IR-PA), whereas the polaron absorption from P3HT is marked P. IEX stands for interchain exciton [45]; (b) Molecular structures of P3HT and PbS QD. (Courtesy of Dr. J. Lewis).

4. Conclusion

In conclusion, using photoinduced absorption (PA) spectroscopy, we have investigated the characteristics of a peculiar gap state (G.S) in films of PbS QDs with different sizes. Large Stokes shift was attributed to the difference from first excitonic absorption and emission from a gap state (G.S.) which bears quantum confinement dependence. A detailed analysis of temperature dependence of PL absorption and photoinduced absorption reveals the unconventional G.S. is a new state of trapped exciton in QD film. This gap state is directly relevant to exciton dissociation and carrier extractions in this class of semiconductor quantum dots.

The spectral features of PA of PbS QD include an induced absorption band (IR-PA) at near infrared range, and electroabsorption peaks (EA) above the QD bandgap. Both features can be utilized to characterize charge transfer process between QD and conducting polymers such as poly (3-hexyl)thiophene (P3HT), a widely used electron donor in organic photovoltaics. The methodology developed in our work could separate the contributions of energy transfer from that of the charge transfer in QD/polymer composite, therefore solve the current difficulty of independently evaluating the role of charge transfer useful in hybrid photovoltaic devices built on QD/polymer mixture.

5. Acknowledgment

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6. References

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The book "Fingerprints in the optical and transport properties of quantum dots" provides novel and efficient methods for the calculation and investigating of the optical and transport properties of quantum dot systems. This book is divided into two sections. In section 1 includes ten chapters where novel optical properties are discussed. In section 2 involve eight chapters that investigate and model the most important effects of transport and electronics properties of quantum dot systems. This is a collaborative book sharing and providing fundamental research such as the one conducted in Physics, Chemistry, Material Science, with a base text that could serve as a reference in research by presenting up-to-date research work on the field of quantum dot systems.

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