Steady state photoinduced absorption of PbS quantum dots film

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We have measured steady state photoinduced absorption (PIA) of PbS quantum dot (QD) film in an energy range of interband electronic transitions at low temperature. PIA spectra show both positive and negative PIAs corresponding to five consecutive interband transitions. The close resemblance between PIA spectrum and the second derivative of the linear optical absorption strongly suggests that these steady state PIAs may be caused by photoinduced local electric field, i.e., the linear Stark effect. We postulate this local electric field be generated by the trapped charges under laser excitations. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2907492]

Lead chalcogenide (PbS, PbSe, and PbTe) quantum dots (QDs) have attracted enormous attention in recent years due to many of their merits: (1) strong quantum confinement arisen from the large exciton Bohr radius (e.g., $a_B = 20$ nm for PbS); (2) size-tunable optical band gaps (E_g) covering wide spectral range from near infrared to visible, originated from their small E_g in bulk (e.g., $E_g = 0.41$ eV for bulk PbS at room temperature); and (3) flexibility and versatility associated with colloidal synthesis. These unique features have accounted for extensive studies in PbS and PbSe QD-based optoelectronic applications.[1–4] Recently, multiple exciton generation (MEG) has been observed in these QDs.[5,6] This discovery has stimulated further research activities in academic and industrial societies since MEG may lead to advances for single-junction solar cells beyond the Shockley–Queisser limit.[7]

Particularly, lead sulfide (PbS) QDs are nanocrystals having rock salt crystal symmetry, with sizes tunable between 1 and 10 nm. Due to the huge surface to volume ratio, these QDs have to be passivated by certain surfactants (or organic ligands) to avoid aggregations. Therefore, the optical and electronic properties of QDs are not only determined by their confined nanocrystal structure but are also largely influenced by their surface properties. Previous studies have shown that surface passivation is usually complete with only one type of atom.[8] Due to the high chemical reactivity, the left unpassivated atoms can be easily oxidized and lead to poor photostability,[9] or directly serve as trapping sites for excitons and charges. The existence of surface trapping states greatly affect the performance of optoelectronic devices based on these QDs.[1–4]

Previous transient absorption (TA) studies showed linear Stark effect caused by local photoinduced charges,[10,11] and these photoinduced charges were thought to be short lived; thus, they are only observed by fast TA measurements. In this paper, we demonstrate that similar Stark effect can be observed in continuous wave (cw) or steady state photoinduced absorption (PIA) measurement without external electric field modulation. Our results indicate that these photoinduced charges are trapped and long lived. Both PIAs and photobleachings (PBs) related to five consecutive interband transitions are observed in PIA spectra. The remarkable simi-larity between PIA spectrum and the second derivative of optical absorption indicates that these steady state PIA features may be caused by linear Stark effect, in agreement with early time (approximately picoseconds to nanoseconds) TA spectra.[10,11]

The colloidal PbS QDs studied here were obtained from Evident Technologies, Inc. These oleic acids capped PbS QDs have sizes tunable from 4 to 7 nm in diameter. Thin film containing one size of PbS QD was made by drop casting from chloroform solution onto a glass substrate. The average film thickness was around 500 nm with optical density of 0.8 at 488 nm. The as-cast film was left in a glovebox for overnight drying, then kept in dynamic vacuum for 2 h before mounting onto the cryostat sample holder. PIA measurement was taken at 10 K unless otherwise specified.

The PIA technique has been widely used for studying long-lived, subgap photoexcitations.[12] Two light beams (pump and probe) are used in PIA, a cw Ar$^+$ laser (pump) excites the sample film, whereas a tungsten-halogen lamp is used to probe the modulated changes ΔT in transmission T. PIA is calculated by $-\Delta T/T = \Delta \alpha d$. A lock-in amplifier is employed with an optical chopper for photomodulation. A variety of diffraction gratings, optical filters, and solid state detectors (silicon and indium antimonides) was used to span the probe photon energy from 0.3 to 3 eV. Absorption and photoluminescence (PL) measurement are carried out using the same setup. In this report, the 488 nm line of the Ar$^+$ laser was used with an output intensity of 250 mW and the modulation frequency is 400 Hz, detected also at this frequency. The spot size of the laser beam after expansion is 5×15 mm^2 with an intensity of 150 mW/cm^2 on sample film, which is quite stable under illumination.

Figure 1(a) shows the absorption and PL spectra of a PbS (4 nm diameter, $E_g = 1.07$ eV) film at 10 K, with a Stokes shift of about 150 meV. Previously, there were similar reports about very large Stokes shift in PbS QDs, which was attributed to the presence of localized surface states or trap states.[13] A larger scale absorption spectrum and the negative of its second derivative (filled circle) are presented in Fig. 1(b). There are clearly five well-resolved peaks associated with various excitonic transitions. The first excitonic peak (a_1, at 1.073 eV) is from ^1S_h to ^1S_e, which is also the optical band gap E_g of this size PbS QD. Based on the relation between full width at half maximum (FWHM) of first excitonic transition and size distribution,[14] we estimate the size dispersion of the studied PbS QD is within 5%.

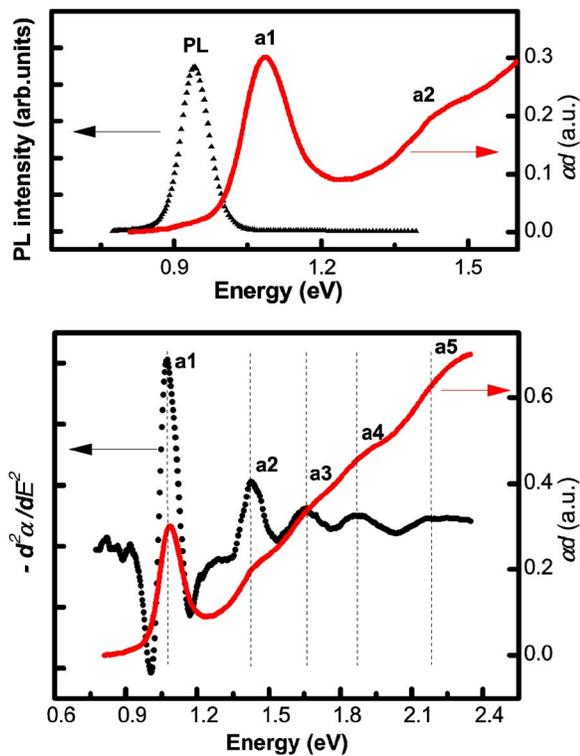[a]Author to whom correspondence should be addressed. Electronic mail: xjiang@cas.usf.edu.

FIG. 1. (Color online) (a) Absorption (solid line-right) and PL (filled triangle-left) spectra of PbS QD (4 nm diameter) film on glass, measured at $T = 10$ K. (b) Comparison between absorption spectrum and the negative of its second derivative. $a_1 - a_5$ denotes the first to the fifth excitonic transitions.

FIG. 2. (Color online) PIA spectrum (filled circle-left) of PbS QD (4 nm diameter) film at $T = 10$ K and modulation frequency 400 Hz. Laser excitation is 488 nm with 150 mW/cm^2 intensity on film. Solid line (right) is the second derivative of the absorption spectrum, also shown in Fig. 1. PBs stand for photobleaching bands ($\Delta \alpha < 0$), whereas PIAs are for photoinduced absorptions ($\Delta \alpha > 0$).

Though there has been debate over assignment of the second excitonic transition (a_2, at 1.428 eV),[6] we assign it as ^1P_h to ^1P_e. The third (a_3, at 1.660 eV), the fourth (a_4, at 1.868 eV), and the fifth rather broad peak (a_5, at 2.157 eV) are due to higher energy transitions from ^1D_h to ^1D_e, ^2S_h to ^2S_e, and ^2P_h to ^2P_e, respectively. Our result indicates that the energy levels are not equally spaced, with $\delta_1 = 0.178$ eV between ^1S_h and ^1P_h, $\delta_2 = 0.116$ eV between ^1P_h and ^1D_h, $\delta_3 = 0.104$ eV between ^1D_h and ^2S_h, and $\delta_4 = 0.145$ eV between ^2S_h and ^2P_h. This is in agreement with the recent report of electronic states in PbSe and PbS QDs.[15]

Figure 2 shows PIA spectrum (filled circle) of the same PbS QD film at 10 K. Five PIA peaks are clearly observed, and four PA bleaching valleys are also present. This is a somewhat a surprising result because steady state PIAs from higher transitions above the band gap cannot be observed due to fast intraband relaxation (approximately subnanoseconds). Normally, only PB$_1$ (bleaching of the first excitonic transition) shows up in steady state PIA spectra above E$_g$. For comparison, the second derivative of linear absorption ($\partial^2 \alpha / \partial E^2$) (solid line) was also shown in Fig. 2 and the dips (below zero) represent these five resolved excitonic transitions. The close matches between the dips in $\partial^2 \alpha / \partial E^2$ (i.e., linear optical transitions) and related PBs in the PIA spectrum, as well as the one to one correlation between peaks of $\partial^2 \alpha / \partial E^2$ and PIAs, are striking. This kind of similarities was previously observed in early time (approximately picoseconds) TA spectra of CdS QD and was explained by charge-induced linear Stark Effect.[10] We tentatively interpreted it as linear Stark effect due to the photoinduced electric field localized at each individual QD and the modulation of laser light is equivalent to the modulation of local electric field. Local electric field causes excitonic energy level shifts and
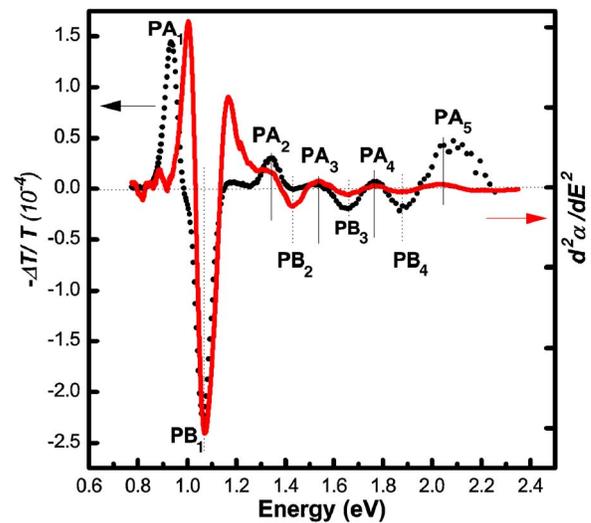
the resultant absorption changes are manifested as PIAs and PBs in our PIA spectra above the band gap, similar to that observed in the electroabsorption spectra. Close matched lineshapes between the PIA spectrum and the second derivative of absorption indicate that this Stark effect is dominant by randomized permanent dipoles, and it is a linear effect.[16] This linear Stark effect has also been observed in electroabsorption measurement of similar PbS QDs film.[17]

One could argue that temperature-dependent transition broadening would result in 2nd-derivativelike features. However, we exclude temperature effect as a possible explanation for the observed PIA features, mainly due to two reasons: one, thermal effect is a relatively slow process, with the modulation frequency chosen (400 Hz), periodic heating effect is minimized, and our measurement at 20 KHz revealed the same spectra features; two, we measured temperature dependence of absorption spectra and the first excitonic transition has the same FWHM of 130 nm from 10 to 300 K, therefore, no thermal broadening was observed.

Regarding the mechanism of photoinduced local electric field, we postulate the following scenario: following the photoexcitation, one of the carriers was trapped at the surface states located at each individual QD surface, a local electric field was created at each dot, causing the observed PIAs and PBs.

Figure 3 shows the temperature dependence of the PIA spectrum. All PIAs and PBs decrease with increased temperature. At $T > 200$ K, all PIAs and higher energy PBs have vanished, and the only remaining feature is PB$_1$. This indicates that these surface traps are relatively shallow and thermal activation helps the escape of trapped carriers, as well as smears out the higher energy states. At room temperature, only the bleaching from ^1S transition (a_1) survives, whereas the PIAs, due to Stark effect, have rapidly decayed along with the diminishing local electric field.

Heretofore, there have been reports about QD charging associated with photoexcitation.[18–20] We tend to elucidate our result as related to trapped photoinduced carriers. However, other mechanisms, such as polarization of PbS by local
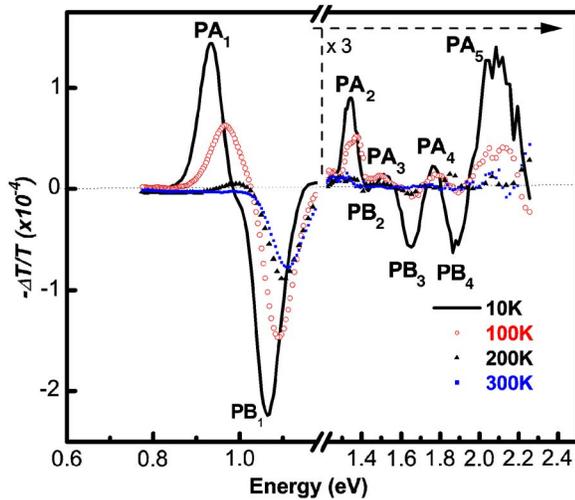
FIG. 3. (Color online) PIA spectra of PbS QD film taken at four different temperatures. Various PIAs and PBs are labeled for clarity. There is a scale change at 1.20 eV (shown as break in the figure).

static electric field from the substrate,[21] can also be possible to account for the unusual PIA feature reported here.

In conclusion, we have observed above-the-gap PIAs and PBs of PbS QD film using cw PIA technique. This anomalous PIA spectrum bears a great resemblance with the second derivative of linear absorption and it is also similar to a TA spectrum of CdS QD.[10] We interpret this anomalous PIA as carrier-induced linear Stark effect due to photogenerated local electric field, caused by trapped charges at the QD surface states. The same PIA feature was also observed in QDs of different sizes and was repeatable within a duration of several weeks. Our report indicates the presence of long-lived trap states, which cause photogenerated excitons to dissociate and be trapped. These long-lived charges could potentially be utilized to enhance photovoltaic effect upon realization of charge transfer mechanism and formation of separate charge transport channels to electrodes.

[1] S. A. McDonald, G. Konstantatos, S. Zhang, P. W. Cyr, E. J. D. Klem, L. Levina, and E. H. Sargent, Nat. Mater. **4**, 138 (2005).
[2] A. A. R. Watt, D. Blake, J. H. Warner, E. A. Thomsen, E. L. Tavenner, H. Rubinsztein-Dunlop, and P. Meredith, J. Phys. D **38**, 2006 (2005).
[3] X. Jiang, S. B. Lee, I. B. Altfeder, A. A. Zakhidov, R. D. Schaller, J. M. Pietryga, and V. I. Klimov, Proc. SPIE **5938**, 59381F (2005).
[4] X. Jiang, R. D. Schaller, S. B. Lee, J. M. Pietryga, A. A. Zakhidov, and V. I. Klimov, J. Mater. Res. **22**, 2204 (2007).
[5] R. D. Schaller and V. I. Klimov, Phys. Rev. Lett. **92**, 186601 (2004).
[6] R. J. Ellingson, M. C. Beard, J. C. Johnson, P. Yu, O. I. Micic, A. J. Nozik, A. Shabaev, and A. L. Efros, Nano Lett. **5**, 865 (2005).
[7] M. C. Hanna and A. J. Nozik, J. Appl. Phys. **100**, 074510 (2006).
[8] A. Lobo, T. Möller, M. Nagel, H. Borchert, S. G. Hickey, and H. Weller, J. Phys. Chem. B **109**, 17422 (2005).
[9] J. S. Steckel, S. Coe-Sullivan, V. Bulovic, and M. G. Bawendi, Adv. Mater. (Weinheim, Ger.) **15**, 1862 (2003).
[10] V. I. Klimov, *Semiconductor Nanocrystals: From Basic Principles to Applications*, edited by A. L. Efros, D. J. Lockwood, and L. Tsybeskov (Kluwer Academic, New York, 2003), Chap. 3, pp. 79–82.
[11] D. J. Norris, A. Sacra, C. B. Murray, and M. G. Bawendi, Phys. Rev. Lett. **72**, 2612 (1994).
[12] Z. V. Vardeny and X. Wei, *Handbook of Conducting Polymers II* (Marcel Dekker, New York, 1997), Chap. 22.
[13] M. J. Fernée, E. Thomsen, P. Jensen, and H. Rubinsztein-Dunlop, Nanotechnology **17**, 956 (2006).
[14] W.-Y. Wu, J. N. Schulman, T. Y. Hsu, and U. Efron, Appl. Phys. Lett. **51**, 710 (1987).
[15] J. M. An, A. Franceschetti, S. V. Dudiy, and A. Zunger, Nano Lett. **6**, 2728 (2006).
[16] V. L. Colvin, K. L. Cunningham, and A. P. Alivisatos, J. Chem. Phys. **101**, 7122 (1994).
[17] E. J. D. Klem, L. Levina, and E. H. Sargent, Appl. Phys. Lett. **87**, 053101 (2005).
[18] S. A. Empedocles and M. G. Bawendi, Science **278**, 2114 (1997).
[19] K. Zhang, H. Chang, A. Fu, A. P. Alivisatos, and H. Yang, Nano Lett. **6**, 843 (2006).
[20] T. D. Krauss, S. O'Brien, and L. E. Brus, J. Phys. Chem. B **105**, 1725 (2001).
[21] C. H. Ben-Porat, O. Cherniavskaya, L. Brus, K.-S. Cho, and C. B. Murray, J. Phys. Chem. A **108**, 7814 (2004).