Photoluminescence upconversion in colloidal CdTe quantum dots

Xiaoyong Wang,1 W. William Yu,2 Jiayu Zhang,1 Jose Aldana,2 Xiaogang Peng,2 and Min Xiao1,*

1Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA
2Department of Physics, University of Arkansas, Fayetteville, Arkansas 72701, USA

(Received 16 December 2002; revised manuscript received 20 May 2003; published 22 September 2003)

Efficient photoluminescence (PL) up-conversion has been observed in colloidal CdTe quantum dots with an energy gain of as high as 360 meV. Compared with the normal PL, the peak energy of this up-converted PL (UCPL) shows a redshift of about 80 meV, and the corresponding radiative lifetime becomes nearly twice as long. This UCPL is attributed to the carrier recombination involving surface states mainly through a thermal excitation process.

DOI: 10.1103/PhysRevB.68.125318 PACS number(s): 78.47.+p, 78.67.Bf, 78.55.Et

Photoluminescence (PL) up-conversion, the observation of luminescence with energies higher than those of the excitation photons, has been widely observed in the bulk1 and heterostructures2–5 of semiconductors, quantum wells,6 porous silicon,7 self-assembled quantum dots (QDs),8 and colloidal QDs.9,10 It was proposed that the existence of intermediate states with energies resonant with or lower than those of the excitation photons is a prerequisite for these up-conversion states.9,10 It was proposed that the existence of intermediate states with energies resonant with or lower than those of the excitation photons is a prerequisite for these up-conversion states (UCPL) processes. Carriers must be excited to these intermediate states by the first excitation photon and further to the higher energy states through various underlying mechanisms such as Auger excitation,7 two-step two-photon absorption (TS TPA),1–3,5,6 or the thermal effect.9,10 Most of these intermediate states are "observable,"2–7 i.e., in addition to the UCPL emission, one can also see the normal PL emission from these states with energies lower than those of the excitation photons. However, in some cases of self-assembled and colloidal QDs, these intermediate states can hardly be observed since carriers cannot efficiently populate them by the above-band-gap excitation of normal PL.8 In a way, UCPL can provide a unique method for detecting the existence of these "defect" states in semiconductor quantum nanostructures and investigating their properties, which are usually different from those of the band-gap states.

Semiconductor colloidal QDs are characterized by a large surface-to-volume ratio due to their small particle sizes, as well as the surface complexity originating from the passivation ligands used to neutralize the surface dangling bonds. Surface states have long been invoked to be responsible for some complex phenomena that could not be explained by using the concept of band-gap states only. For example, the almost universal occurrence of a biexponential distribution in the radiative lifetime strongly implies the existence of surface states in colloidal QDs.11,12 In this sense, time-resolved measurements can provide one, but only indirect, way to probe the surface states in colloidal QDs, and consequently the existence of them is still controversial.13 However, if one can observe a UCPL signal from colloidal QDs, this problem will be easily resolved since the demand of intermediate states can only be fulfilled by the existence of surface states. Recently, UCPL signals were observed in colloidal InP,9 CdSe,9,10 and CdTe (Ref. 10) QDs, which have provided a strong proof of the existence of surface states in colloidal QDs and opened up a new opportunity for the systematic study of these surface states.

Here, we report on our optical studies of efficient UCPL in colloidal CdTe QDs with an energy gain of as high as 360 meV. Compared with the normal PL, the UCPL signal shows a redshift of about 80 meV in its peak energy, while the excitation spectroscopy of the UCPL (UCPLE) measurement at this peak energy showed a broad excitation band with energies below those of the band gap. Time-resolved measurements were utilized to study the time-resolved dynamics of this UCPL, whose radiative lifetime now becomes nearly twice as long as that of the normal PL. Finally this UCPL is attributed to the recombination of carriers from the band-gap states and surface states mainly through a thermal excitation process.

The CdTe QD samples were synthesized in a non-coordinating solvent 1-octadecene (ODE) with controllable sizes. A mixture of CdO, tetradecylphosphonic acid, and technologically-grade ODE was heated to 300 °C to get a clear solution. A solution of tellurium dissolved in tributylphosphine and ODE was quickly injected into this hot solution, and then the reaction mixture was allowed to cool to 240 °C for the growth of CdTe QDs. The unconverted cadmium and tellurium precursors and ODE were carefully separated out before the optical measurements. Typically, the size distribution was between 5% and 8% determined by using the transmission electron microscopy. Here we selected the sample with the diameter of 4.3 nm, which has a normal PL peak around 660 nm, for our optical measurements. The solution containing the QDs in chloroform (CHCl3) solvent was sealed in an ultraviolet-visible (UV-Vis) cuvette initially under nitrogen gas environment to prevent photo-oxidation for further measurements at room temperature. The absorption spectrum, as shown in the inset of Fig. 1, gives the optical densities at different wavelengths, from which we estimate the QD density in this sample to be \( \sim 2.7 \times 10^{-6} \text{ M}^{-1} \). A Ti:sapphire pulsed laser (\( \sim 1\)-ps duration, 0.05 \( \mu \text{J} \) pulse, and a 16.4-MHz repetition rate) with the photon energy varying from 1.442 eV (860 nm) to 1.699 eV (730 nm) was used as the excitation source for the UCPL measurement, while its second-harmonic light beam (at 365 nm) was used for the normal PL measurement. The UCPLE spectrum was ob-
obtained from a fluorescence spectrophotometer (Model F-2500, Hitachi) and corrected for the excitation source spectrum of the xenon lamp. It should be mentioned that the UCPL spectrum obtained from this fluorescence spectrophotometer was similar to those excited by the Ti:sapphire laser as presented here, but these signals were much weaker because of the xenon lamp used as the excitation source. The PL and UCPL time-resolved dynamics were obtained by using a time-correlated photon-counting system with a time resolution down to ~400 ps.

In Fig. 1, the normal PL spectrum of this CdTe QD sample, with a peak energy of 1.879 eV (660 nm) excited by the photons of wavelength 365 nm, can be fitted well by a single Gaussian distribution, which is due to the band-gap recombination. No obvious emission involving the surface states was observed in the long-wavelength side. The photon energy of the excitation laser was then tuned between 1.442 eV (860 nm) and 1.699 eV (730 nm) to probe the UCPL signal. Figure 1 shows four typical UCPL spectra with the excitation photon energies of 1.632 eV (760 nm), 1.653 eV (750 nm), 1.676 eV (740 nm), and 1.699 eV (730 nm), respectively. The normal PL intensity has been scaled down by a factor of ~10 with the same excitation power density of the excitation laser. The intensity of the UCPL signal is shown by the inset in Fig. 1. The UCPL signal for the colloidal CdTe QDs used in the experiment.

FIG. 1. Normal PL spectrum excited at a photon energy of 3.397 eV (365 nm) and UCPL spectra excited at photon energies of (a) 1.632 eV (760 nm), (b) 1.653 eV (750 nm), (c) 1.676 eV (740 nm), and (d) 1.699 eV (730 nm), respectively. The UCPL spectra show similar shapes and the peaks are nearly fixed at 1.800 eV (689 nm) with a peak energy of 1.879 eV (660 nm). A broad excitation band centered at 1.722 eV (720 nm) was clearly detected, which was unambiguously related to the intermediate states required for the observed UCPL process. The energy gain of the UCPL is defined as the difference between the excitation energy and the energy value at which a low-wavelength wing of the UCPL spectrum crosses the average background noise level. If we take into account the fact that the UCPL signal begins to emerge at an excitation photon energy of 1.621 eV (765 nm) and extends to an energy as high as 1.984 eV (625 nm), the energy gain of this efficient UCPL has reached a value of ~360 meV, which is consistent with the previously reported values for colloidal CdSe and CdTe QDs.

The most distinct feature of this UCPL is the redshift of ~80 meV in its peak energy relative to that of the normal PL. The similar redshift of ~80 meV was observed in recent UCPL experiments on both colloidal CdTe and CdSe/ZnS QDs. A larger redshift of ~100–200 meV was also observed in porous Si (Ref. 7) and attributed to the resonant excitation of electron-hole pairs spatially separated in neighboring crystals, followed by the subsequent excitation of a second pair in the larger of the two crystals and Auger ejection of a carrier into the smaller one. This is obviously not the case in our experiment, since the nearly infinite energy barrier and relatively large distance between neighboring QDs in solution prevent a direct carrier transfer. This redshift in colloidal CdTe QDs strongly implies the involvement of other energy states within the band gap in this UCPL process. These energy states are more likely to be of the surface nature than, e.g., the deep-center states inside the crystal, although we currently do not have any direct evidence for the exact chemical origin of them. Consequently, the UCPL signal can be assigned to the recombination process.
tion of carriers from the band-gap states and the surface states, as will be discussed later. Another useful information we can deduce from this redshift is the existence of both electron surface states (ESSs) and hole surface states (HSSs) within the band gap, as shown in Fig. 3. This is due to the fact that, if there exists only one kind of surface states, electrons will be excited by the excitation photons from the valence band to these states, and further to the conduction band under various mechanisms, resulting in UCPL by recombination without the participation of intermediate states, and consequently with no red-shift relative to that of the normal PL. Therefore, we can conclude that the excitation band of Fig. 2 from the UCPL measurement corresponds to the excitation of electrons from the HSSs to the ESSs, as shown in Fig. 3.

In order to further explore the origin and nature of this redshifted UCPL, we performed time-resolved measurements at the peak energies of both the normal PL and the UCPL. As shown in Fig. 4(a), the normal PL decay curve can be fitted pretty well by a single-exponential function with the radiative lifetime of ~16.7 ns, which corresponds to a single decay channel for the excited carriers and is consistent with the results from one recent report. As mentioned before, usually one distinct feature for the PL decay of colloidal QDs, such as CdSe, is the almost universal occurrence of a bi-exponential distribution in the radiative lifetime. The shorter lifetime is dominant and can be attributed to the intrinsic recombination of initially populated band-gap states, while the longer lifetime is closely related to the surface states due to the poor overlap of electron and hole wave functions. So this single-exponential decay gives a strong proof that few surface states were involved in the normal PL, which can only be realized by the condition that both electron and hole surface states are far enough from the band-gap states so that they cannot be efficiently populated by thermal excitation at room temperature. We also measured the decay time distribution over the whole normal PL band. The PL decay dynamics showed nearly no change when we scanned the whole PL spectrum from the blue side to the red side, which is similar to the results reported recently for colloidal CdSe QDs in solution. This wavelength-independent time decay of the normal PL further excludes the contribution of surface states or shallow-trap states to this normal PL, in which case the decay time should be longer in the red side of the normal PL spectrum. Due to the limited time resolution of 400 ps in our current photon-counting system, the rise time of the normal PL cannot be resolved, which implies a fast carrier formation and relaxation process under the excitation of above-band-gap photon energies.

Figure 4(b) shows the time-resolved dynamics of the UCPL excited at a photon energy of 1.699 eV (730 nm). Compared with the normal PL, the UCPL possesses more complicated time-resolved behaviors, i.e., a clearly discern-
able rise time and a biexponential decay with a shorter lifetime of 3.6 ns and a longer lifetime of 26.2 ns, respectively. This delayed rise time of $\sim 1.5$ ns from a single-exponential fit reflects a much longer generation process of the UCPL excitons than that of the normal PL. In Refs. 9 and 10, the UCPL process was described under a thermal model, in which the extra energy needed for the UCPL process was obtained by phonon absorption. Up-conversion with an energy gain from the phonon bath can definitely occur for thermal energies much lower than the energy gain obtained (360 meV), which results from the different densities of states of the initial and the final states. This thermal model is also applicable in our case since we also observed an enhanced UCPL intensity at higher temperatures, as shown in the inset of Fig. 2. The thermal population can easily explain the finite rise time of 1.5 ns as the time required for establishing thermodynamic equilibrium.

As to the biexponential decay part of the time-resolved dynamics in Fig. 4(b), we attribute the shorter-lifetime component to the nonradiative carrier depopulation from the surface states, as will be discussed later. While the longer lifetime of the UCPL decay, which is almost twice as long as that of the normal PL, is consistent with the previous conclusion that surface states were involved in the UCPL process. Under the thermal excitation model, as shown in the energy-level diagram of Fig. 3(a), the electrons are first excited from the HSSs to the ESSs, followed by thermal excitation of the holes in the HSSs to the valence band maximum (VBM), while the subsequent recombination of electrons and holes from the ESSs and VBM results in the UCPL signal with an elongated lifetime compared with that of the normal PL.

To exclude the possibility that TS-TPA (Refs. 1–3, 5, and 6) might contribute to this UCPL process, we approximately calculated the number of absorbed photons (or generated excitons when assuming a 100% quantum yield) per QD, considering a laser spot diameter of 200 $\mu$m and a maximum laser power density of 25.5 kW/cm$^2$ on the samples in our experiment. Using the complex refractive index for bulk CdTe (Ref. 19) at 730 nm and the formulas from Ref. 20, we got an absorption cross section of $10^{-16}$ cm$^2$ for the used CdTe QDs with a diameter of 4.3 nm. Then the number of absorbed photons per QD was calculated to be $\sim 0.184$, which is far below the limit for the TS-TPA to occur. We should also note the fact that the UCPL signal can actually be observed under much lower excitation laser intensities, as represented in the inset of Fig. 5. On the other hand, if we consider the fact that the UCPL conversion efficiency in our experiment is pretty high (10% of that of the normal PL under the same excitation power density), while the Auger excitation often has a very low efficiency, we can safely rule out Auger excitation as the underlying mechanism for the observed UCPL. The above conclusions were further confirmed by the fact that the UCPL intensity shows a linear dependence on the excitation laser intensity, as shown in the inset of Fig. 5. For a TS-TPA process, high excitation intensities and long lifetimes of the surface states would be required. However, the lifetimes of the surface states are apparently short in our case, then a TS-TPA process should exhibit a square-law dependence on the excitation intensity and the Auger process even a cubic dependence.

Now if we consider the center energies of the normal PL (1.879 eV), UCPL (1.800 eV), and UCPL (1.722 eV), and assume that the UCPL results from the carrier recombination from the ESSs and the VBM, a simple calculation will give the energy difference of 79 meV between the ESSs and the CBM, and 78 meV between the HSSs and the VBM, as shown in Fig. 3. From the evaluation under thermodynamic equilibrium, at a distance of 78 meV between the HSSs and the VBM without consideration of the degeneracy multiplicity, about 4% of all holes (with a Fermi distribution) will be thermally excited to the VBM level at room temperature, which is comparable to the observed $\sim 10\%$ conversion efficiency of the UCPL relative to that of the normal PL.

So far we have only considered the possibility that holes can be thermally excited from the HSSs to the VBM. However, in reality, the electrons should have an equal chance to be thermally excited from the ESSs to the CBM, as shown in Fig. 3(b). Then the observed UCPL should result from a recombination of electrons and holes from the ESSs and the VBM, as well as from the CBM and HSSs, respectively. Since the ESSs and HSSs have nearly the same energy separations from the VBM and CBM, we cannot resolve two separate peaks in the UCPL spectra of Fig. 1. It should be noted here that, in the energy-level diagram of Fig. 3, electrons from the CBM and holes from the VBM can also recombine to give the emission involving only band-gap states (normal PL). Since PL is proportional to the product of the electron and hole occupation numbers, assuming $\sim 4\%$ of the initially generated electrons (holes) would populate the CBM (VBM) under thermodynamic equilibrium, the UCPL intensity at the normal PL peak energy (1.879 eV) should be...
\(~1/48\) of that at the UCPL peak energy \((1.800 \text{ eV})\) from a simple calculation. This is consistent with the experimentally observed value of \(~1/51\) in the UCPL spectrum (d) of Fig. 1.

From all the above discussions, we can tentatively attribute the fast component in the biexponential UCPL decay of Fig. 4(b) to the carrier depopulation from the surface states. In Fig. 3, after the holes are thermally excited from the HSSs to the VBM, they will recombine with the electrons in the ESSs. Meanwhile, the electrons in the ESSs may endure a fast depopulation to the CBM under thermal excitation. Similarly, when the holes in the HSSs recombine with the electrons in the CBM, they could also possess a fast thermal depopulation to the VBM. This fast decay of \(~3.6\) ns is compatible with the \(~1.5\)-ns rise time required for establishing thermodynamic equilibrium. However, a quantitative and confirmative analysis of such processes can only be realized by utilizing other high-resolution time-resolved systems. Another possible origin of this fast decay component is the nonradiative carrier depopulation from the surface states (both ESSs and HSSs) to the surface defect traps.\(^{21,22}\) whose energies also fall within the band gap. One previous time-resolved measurement\(^9\) in long-range-ordered (LRO) GaInP/GaAs heterointerface also showed that the UCPL could be described by a rapid decay and a slower decay, while the rapid decay agreed well with a rapid capture of carriers into some nonradiative decay channels in LRO GaInP.\(^{23}\) However, if we consider the fact that carrier capture by the surface defect traps usually happens within the time scale from several to tens of picoseconds,\(^{21}\) this kind of carrier depopulation may only play a minor role in this fast decay component (a few nanoseconds).

To show conclusively that the energy-level model, as shown in Fig. 3, can indeed describe the observed UCPL process, we show an interesting result in Fig. 5 from one additional experiment of making use of photo-oxidation to change the size, and consequently to tailor the band gap of the CdTe QDs. After being purposely exposed to the ambient air environment for several days, these QDs suffered a blue-shift of \(~68\) meV from \(1.879\) eV \((660 \text{ nm})\) to \(1.947\) eV \((637\) nm) in the normal PL peak energy, which was a clear indication that the band-gap energy had been increased due to the shrinkage in the diameter of the QDs by photo-oxidation.\(^{24}\) However, the UCPL peak energy changed only from \(1.800\) eV \((689 \text{ nm})\) to \(1.821\) eV \((681 \text{ nm})\) resulting in a much smaller blueshift of \(21\) meV. This provides another strong proof that the UCPL emission cannot be merely originated from band-gap states. As shown in Fig. 3, the UCPL signal results from the recombination of carriers from the ESSs (HSSs) and the VBM (CBM), so this blueshift of \(21\) meV can be attributed to the combined changes of the ESSs (HSSs) and the VBM (CBM) with the decreased QD size. The contribution of the changing band-gap states (CBM and VBM) might be dominant in this process if we consider the fact that the energy positions of the surface states (ESSs and HSSs) only change slightly with the size of colloidal QDs.\(^9,25\)

In summary, we have observed efficient UCPL in colloidal CdTe QDs with an energy gain as high as \(360\) meV. We attribute this UCPL to the recombination of carriers from the band-gap states and the surface states, which is similar to the conduction-band-to-deep-acceptor process described in a bulk GaAs system.\(^{26}\) The existence of both ESSs and HSSs was confirmed by the broad excitation band detected from the UCPL measurement, and was closely correlated to the \(~80\)-meV redshift of peak energy and the elongation of radiative lifetime for this UCPL signal. The existence of surface states within the band gap has provided us with new perspectives on these colloidal CdTe QDs, e.g., as four-energy-level systems. Our future work will be centered around the experimental determination of the size dependence of these surface states, while a similar theoretical calculation like that in Ref. 25 will be conducted to resolve the chemical origin and nature of these surface states.

The authors acknowledge the funding support from the National Science Foundation (through Grant No. PHY-0099496 and MRSEC Program No. DMR-0080054) and the Office of Naval Research. We thank H. Fu for stimulating discussions.

---

\(^{8}\)Email address: mxiao@mail.uark.edu


\(^{15}\)This single-exponential decay was observed in most of the as-
prepared CdTe QD samples. We are currently working on experiments in both chemical synthesis and optical measurements to verify if this behavior is intrinsic or synthesis dependent in CdTe QDs.