Carrier Multiplication in CdTe Quantum Dots by Single-photon Timing Spectroscopy

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Carrier multiplication (CM) was observed in CdTe quantum dots (QDs) capped with tetradecylphosphonic acid (TDPA) at $h\nu/E_g > 2.5$ by picosecond single-photon timing spectroscopy, where $h\nu$ and E_g are the excitation and the band gap energies, and the CM efficiency increased rapidly with the increase of $h\nu/E_g$. No CM was observed less than the threshold value of $h\nu/E_g \approx 2.5$, which is close to that of CdSe QDs. As compared to a previous report by Nair and Bawendi, our result suggests that CM is sensitive to the QD surface conditions.

Carrier multiplication (CM) in semiconductors is a process in which multiple excitons are generated by one photon absorption with an energy higher than the band gap energy of E_g. CM can potentially improve the performance of many semiconductor-based devices such as solar cells, photocatalysts, and optical amplifiers. CM in bulk materials was first observed in the 1950s; however, significantly higher energy is required for CM. For example, CM in bulk PbS has a threshold energy of ca. $5E_g$, and an efficiency of 170% is obtained at very high energy of ca. $9E_g$.[1] In 2004, Klimov et al. reported the highly efficient CM up to 700% in PbSe QDs by transient absorption spectroscopy.[2,3] Efficient CM has been reported for several semiconductor QDs: CdSe,[4] PbS,[5,6] and PbTe.[7] However, some reports have claimed that CM does not occur in CdSe, CdTe QDs,[8] and InAs/CdSe/ZnSe core/shell/shell QDs[9] and that CM efficieny of PbSe QDs is not as high as the first reported result.[10] These descrepancies may come from surface and environmental conditions of QDs. In the present study, we examined CM of CdTe QDs capped with tetradecylphosphonic acid (TDPA) by picosecond single-photon timing spectroscopy and found that CM was observed with a threshold energy of ca. $2.5E_g$.

Tetra-*n*-decylphosphonic acid (TDPA; 98%) was purchased from Alfa Aesar. 1-Octadecene (ODE; 90.0%) was obtained from Wako Pure Chemical Industries, Ltd. Tellurium (Te; 99.999%) and cadmium oxide (CdO, 99%) were purchased from Kojundo Chemical Laboratory and Kanto Chemical Co. respectively. *n*-Hexane, chloroform, and methanol were special grade from Kishida Chemical Co., Inc.

TDPA-capped CdTe QDs were prepared by high-temperature colloidal methods in organic solvents reported in the literature.[11] Aliquots of growing CdTe QDs at high temperature were taken out at different reaction times, mixed with *n*-hexane and stored under nitrogen. The synthesis was carried out under nitrogen. Unreacted cadmium precursors were separated by an extraction method.[11] After the extraction, QDs contained in hexane/ODE phase were precipitated with acetone. The precipitate was isolated by centrifugation and decantation. The final product was redissolved in hexane and used for absorption spectroscopy (U3210; Hitachi), luminescence spectroscopy (FluoroMax-2; Jobinyvon-Spex), and luminescence decay measurements. Luminescence decays were measured by using picosecond single-photon timing spectroscopy.[12] QDs were excited at 400 (3.10 eV) and 266 nm (4.67 eV) of a Ti:Sapphire laser with a repetition rate of 8 MHz. All measurements were performed at room temperature.

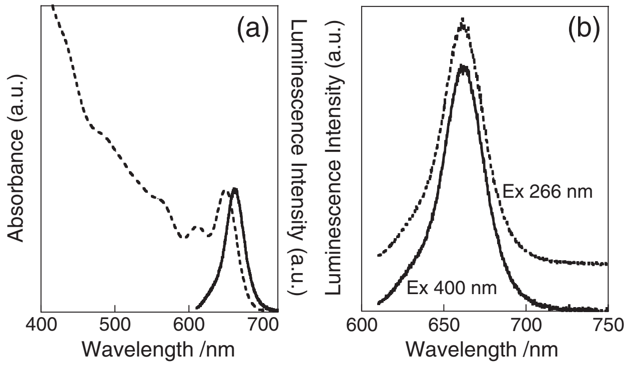

Figure 1. Typical absorption (dotted line) and luminescence spectra (solid line) of TDPA-capped CdTe QDs, $D = 4.3$ nm and $E_g = 1.83$ eV (a). Luminescence spactra excited at 266 nm (dotted line) and 400 nm (solid line) (b).

Typical absorption and luminescence spectra of TDPA-capped CdTe QDs are shown in Figure 1a. The first excitonic absorption peak was clearly observed at 649 nm. The diameter (D) and the band gap (E_g) were estimated from the first excitonic absorption peak and absorption edge, respectively. D and E_g of a series of CdTe QDs ranged from 3.6 to 5.4 nm and from 1.93 to 1.73 eV, respectively.[10] To examine the effect of the excitation energy on luminescence spectra, CdTe QDs were excited at 400 and 266 nm as illustrated in Figure 1b. As clearly shown in Figure 1b, both luminescence spectra were very similar irrespective of the excitation energy, suggesting that the effect of impurities on luminescence spectra is negligible and that luminescence decays can be compared at both excitation wavelengths. Excitation energy dependence on luminescence spectra was not detected for all CdTe QDs examined here.

Luminescence decays of different size CdTe QDs ($D = 3.7$ and 5.4 nm), excited at 400 and 266 nm and probed at the wavelength of maximum intensity, are shown in Figure 2. The decay curve excited at 400 nm was normalized to 1 at the peak height of the curve, and the curve at 266 nm was normalized to the decay of 400 nm at the long time scale of 8 ns. In a sample whose $E_g = 1.93$ eV and $D = 3.7$ nm (Figure 2a), luminescence decays excited at 400 and 266 nm were very similar to each other. This result indicates that no CM occurs in this sample ($E_g = 1.93$ eV) even at 266 nm (4.67 eV). On the other hand, an additional fast decay component was detected for CdTe QDs ($E_g = 1.73$ eV, $D = 5.4$ nm) in the decay dynamics excited at 266 nm as compared with the decay at 400 nm (Figure 2b). When the multiple

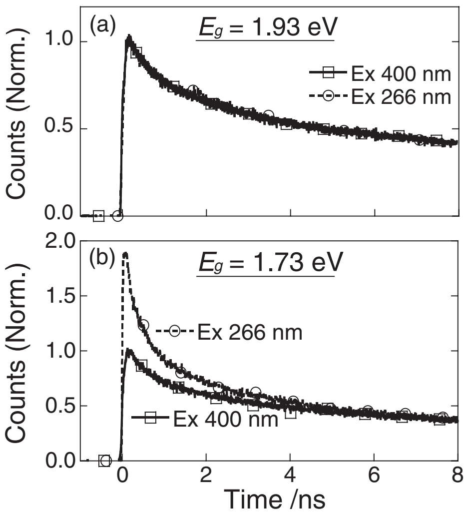

Figure 2. Luminescence decay dynamics of TDPA-capped CdTe QDs excited at 400 (solid line) and 266 nm (dotted line) whose $E_g = 1.93$ eV (a) and 1.73 eV (b).

carriers are formed in a single CdTe QD, Auger recombination easily occurs with a time constant of a few tens of ps to a few hundreds ps depending on the QD size and the QD surface conditions.[13] In our experimental results (Figure 2b), a faster decay of ca. 140 ps was observed as difference decay dynamics, in which the time constant is comparable with that of Auger recombination of ca. 5-nm CdTe QDs.[13] In addition, the excitation intensity of 266 nm is a few pJ/pulse, so the multiphoton absorption can be neglected. Thus the faster decay component detected at 266-nm excitation is most probably due to the carrier–carrier interaction of Auger recombination originating from CM.

CM efficiency that determines how many excitons are generated by one photon absorption can be calculated from the ratio of the maximum amplitudes of luminescence decays excited at 400 and 266 nm similar to a procedure by Klimov et al.[4] CM efficiency is plotted as a function of $h\nu/E_g$ in Figure 3. No CM was observed up to $h\nu/E_g \approx 2.5$, and then the CM efficiency increased rapidly at $h\nu/E_g > 2.5$. For large sized CdTe QDs ($E_g = 1.73$ eV) shown in Figure 2b, CM efficiency was calculated to be 190% at 266-nm excitation ($h\nu = 4.67$ eV). This result indicates that CM efficiency has a threshold of $h\nu/E_g \approx 2.5$ for TDPA-capped CdTe QDs. This threshold is very similar to that of CdSe QDs ($h\nu/E_g \approx 2.5$) and smaller than PbSe QDs ($h\nu/E_g \approx 3.0$).[3]

The threshold of CM efficiency has been interpreted in terms of simple bulk-semiconductor effective-mass arguments without invoking a precise structure of quantized states.[3] From energy conservation, the minimum photon energy required to produce CM ($h\nu_{CM}$) is determined by the following equation, $h\nu_{CM} = (2 + m_e/m_h)E_g$, where m_e and m_h are the effective mass of electrons and holes. In CdTe, $m_e{:}m_h = 1{:}4$,[14] and hence $h\nu_{CM}/E_g \approx 2.3$. This simple estimation explains the experimental result ($h\nu_{CM}/E_g \approx 2.5$) although the value is a little larger than the expectation.

In the previous report by Nair and Bawendi, CM has not been detected for CdSe/ZnS core/shell QDs and CdSe and CdTe QDs capped with trioctylphosphine.[8] In addition, recent transient absorption experiments on PbSe QDs suggest that CM is sensitive to the chemical and surface treatments of QDs.[15] The difference of surface conditions may be the reason why CM was not observed in trioctylphoshine-capped CdTe QDs and observed in TDPA-capped CdTe QDs.

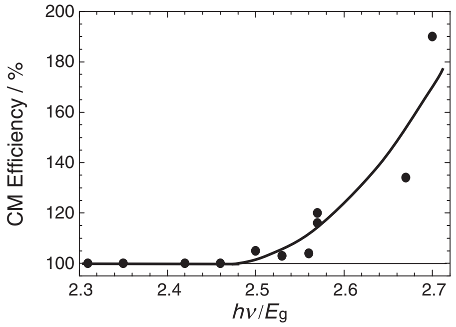

Figure 3. CM efficiency as a function of $h\nu/E_g$. The CM efficiency threshold of TDPA-capped CdTe QDs was around $h\nu/E_g \approx 2.5$. The solid line was fitted by hand.

In conclusion, CM was observed in TDPA-capped CdTe QDs at $h\nu/E_g > 2.5$ by picosecond single-photon timing spectroscopy, in which the threshold is close to that of CdSe QDs. As compared to the previous report, our result suggests that CM is sensitive to the QD surface conditions.

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