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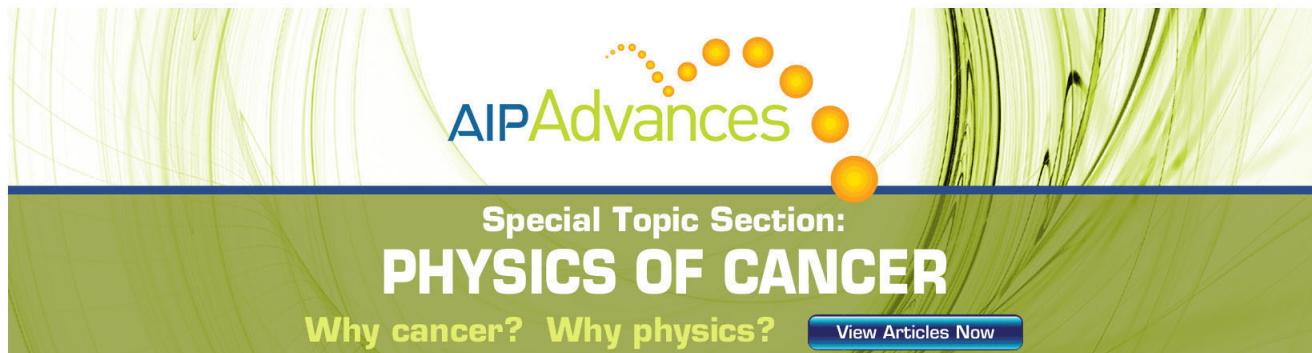
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Fast electron transfer from PbSe quantum dots to TiO₂

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Fast electron transfer from PbSe quantum dots (QDs) to the porous anatase TiO₂ film was observed in transient absorption and luminescence, when the lowest unoccupied molecular orbital level of PbSe QDs is higher than that of TiO₂. In PbSe QDs 2.7 nm in diameter linked to the TiO₂ film the bleaching recovery and the luminescence decay shortened to 1 ps and 4.2 ns from 650 ps and 1.3 μ s observed in the non-linked PbSe QDs, respectively. The electron transfer from both the quantum state and the localized state in PbSe QDs to TiO₂ takes place fast and efficiently. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729881>]

Quantum dots (QDs) have recently attracted much attention as a light harvesting element in solar cells. Quantum size effect changes both the highest occupied molecular orbital (HOMO) level and the lowest unoccupied molecular orbital (LUMO) level, and the HOMO-LUMO gap of PbSe and PbS QDs covers the solar spectrum ranging from the visible region to the infrared region. Strong spatial confinement of electrons in QDs enhances the Coulomb interaction among electrons and holes and carrier multiplication followed by the absorption of a high energy photon.¹ A highly efficient solar cell of layered PbSe QDs having Schottky barriers and *p-n* junctions was reported.² A Grätzel-type solar cell sensitized by PbS QDs was also reported.³ Solar cells sensitized by QDs are based on efficient charge transfer from QDs to transparent conducting oxides like dye-sensitized solar cells. Especially efficient electron transfer from PbSe QDs to TiO₂ particles is expected in the same manner as dye-sensitized solar cells, if the LUMO level of PbSe QDs is higher than that of TiO₂. Fast electron transfer assures efficient electron transfer. Fast electron transfer from PbSe and PbS QDs to TiO₂ particles is expected through the linker molecules but the transfer times reported so far are scattered depending on interfaces between QDs and TiO₂. Electron transfer from PbS QDs to TiO₂ particles was reported to be slow in 100 ns range⁴ or to take place in 1.2 ns,⁵ while hot electron transfer from PbSe QDs to a TiO₂ crystal was reported to take place in subpicosecond.⁶ In this report we show the electron transfer from PbSe QDs to the porous TiO₂ film takes place in picosecond range which is much faster than the electron-hole recombination time.

Samples investigated in this study are chemically synthesized PbSe QDs capped by oleic acid with the lowest clear optical absorption band. PbSe QDs capped by oleic acid in trichloroethylene (TCE) solvent, PbSe QDs linked to either TiO₂ particles through bifunctional linker molecules, 3-mercaptopropionic acid (MPA), in TCE solvent or porous anatase TiO₂ film through MPA were studied.⁷ Absorption spectra and photoluminescence (PL) spectra under the excitation at 635 nm were measured by a spectrophotometer and a Fourier transform infrared spectrometer, respectively. The

absorption spectra and PL spectra of 2 samples of PbSe QDs are shown in Fig. 1. The smaller PbSe QDs show the lowest-energy absorption peak at 1070 nm (1.16 eV) and a PL peak at 1145 nm (1.08 eV). Small Stokes shift of the PL suggests the localization of electron-hole pairs. The average diameter, *D*, of PbSe QDs is evaluated to be 2.7 nm on the basis of the relationship $E_{H-L} = 0.278 + 1/(0.016D^2 + 0.209D)$ between the HOMO-LUMO gap energy, E_{H-L} (eV), equal to the absorption peak energy and the diameter, *D*(nm), which fits well experimental PbSe data from many studies.⁸ The larger PbSe QDs show the lowest-energy absorption peak at 1471 nm (0.843 eV) and a PL peak at 1475 nm (0.840 eV). The average diameter of PbSe QDs is evaluated to be 4.7 nm.

Femtosecond pump-probe measurement was done at the room temperature by means of a 250 kHz optical parametric amplifier (OPA) pumped by a Ti:sapphire regenerative amplifier (REGA) system. Pump pulses at 802 nm (band width = 9 nm) were the output of REGA and probe pulses (band width = 20–30 nm) coming from OPA were resonant to the absorption peak of the lowest $1s_e - 1s_h$ transition of PbSe QDs. Excitation densities of the pump and the probe were 22–52 μ J/cm² and 0.8–4 μ J/cm², respectively. The pulse width was 225 fs. Sub-nanosecond time-resolved

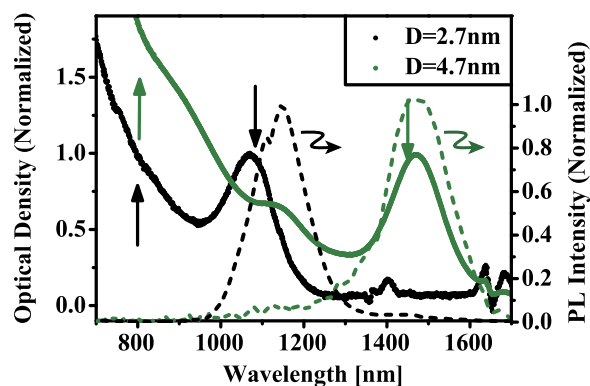


FIG. 1. Absorption and photoluminescence (PL) spectra of 2 samples of PbSe quantum dots shown by black lines and green lines, respectively. The pump photon energy and the probe photon energy in the pump-probe experiment are shown by upward arrows and downward arrows, respectively. The PL detection wavelength (energy) in the time-correlated single photon counting experiment is 1120 nm (1.11 eV). Small structures in the absorption spectrum around 1350–1400 nm and 1620–1700 nm come from the subtraction error of the absorption of trichloroethylene.

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luminescence measurement was done by the time-correlated single photon counting with an infrared InP/InGaAsP photomultiplier and a 70 ps semiconductor laser emitting at 653 nm. Time resolution of the time-correlated single photon counting was 1 ns.

Size-dependent LUMO and HOMO energy levels of PbSe QDs are calculated on the four-band effective-mass model,¹¹ although the calculated HOMO-LUMO gap and the relationship between E_{H-L} and D shown above are used to derive the diameter of PbSe QDs. Size-dependent LUMO and HOMO levels of PbSe QDs relative to the vacuum level are plotted in Fig. 2, where the electron affinity of bulk PbSe is assumed to be -4.85 eV.⁴ The LUMO level of the porous anatase TiO₂ film is considered to be -4.45 eV, which is shifted from -3.9 eV of the LUMO level of TiO₂ particles in organic solvent.^{9,10} Energy crossing is expected around $D = 4$ nm. According to the Marcus theory,¹² electron transfer between two states is dominated by the difference of the free energy between the two states and later the Marcus theory is applied to electron transfer from dyes to continuous LUMO state of semiconductors.¹³ Similarly the theory allows the electron transfer, when the LUMO level of QDs is higher than that of TiO₂. Therefore, we can expect electron transfer from PbSe QDs to the anatase TiO₂ film, if D of QDs is smaller than 4 nm.

Fast electron transfer from the quantum state of PbSe QDs to the porous TiO₂ film was observed in transient absorption. When the LUMO level of PbSe QDs ($D = 2.7$ nm) is higher than that of porous TiO₂ films (-4.45 eV), pump-probe transient absorption of PbSe QDs showed the recovery time of the bleaching becomes as short as 1 ps, as is shown in Fig. 3. The decay is well fitted by $0.98\exp(-t/0.95[\text{ps}]) + 0.02$. On the other hand, transient absorption bleaching of PbSe QDs ($D = 2.7$ nm) in TCE solution decays slowly. The decay is well fitted by $0.31\exp(-t/5.2[\text{ps}]) + 0.61\exp(-t/1.1[\text{ns}])$. The $1/e$ recovery time of the bleaching is 650 ps. These observation shows the electron transfer from quantum state in PbSe QDs to TiO₂ takes place in 1 ps evaluated by $1/(1/1[\text{ps}] - 1/650[\text{ps}])$.

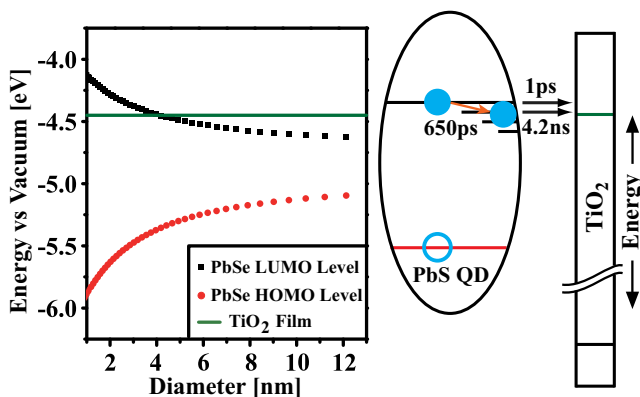


FIG. 2. Left figure: An energy diagram of LUMO and HOMO levels of diameter-dependent PbSe QDs and LUMO level of TiO₂ anatase porous film. Right figure: Horizontal arrows show electron transfer from the quantum state shown by an uppermost long line and the localized state shown by short marginal lines in PbSe QDs to LUMO level of anatase TiO₂. An inclined downward arrow shows the localization of electrons.

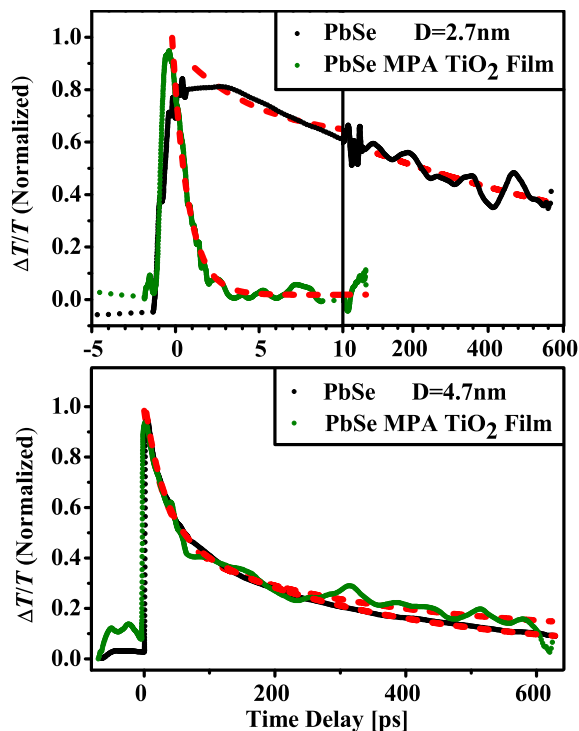


FIG. 3. Upper figure: Transient absorption time traces of PbSe QDs ($D = 2.7$ nm) linked to a TiO₂ porous film or in trichloroethylene solution. Decays are fitted by dashed lines. Lower figure: Transient absorption time traces of PbSe QDs ($D = 4.7$ nm) linked to a TiO₂ porous film and in trichloroethylene solution. Decays are fitted by dashed lines.

To cross-check our argument, we made pump-probe measurement of the larger PbSe QDs whose LUMO level is not higher than that of porous anatase TiO₂ film. The LUMO level of PbSe QDs 4.7 nm in diameter is not higher than that of the porous TiO₂ films (-4.45 eV). The pump-probe transient absorption shows little difference between PbSe QDs in TCE solution and PbSe QDs linked to the porous anatase TiO₂ film, as is shown in Fig. 3. For PbSe QDs in TCE solution the decay is well fitted by $0.03 + 0.52\exp(-t/30[\text{ps}]) + 0.49\exp(-t/300[\text{ps}])$, while for PbSe QDs linked to the porous anatase TiO₂ film the decay is well fitted by $0.10 + 0.52\exp(-t/35[\text{ps}]) + 0.36\exp(-t/300[\text{ps}])$. Transient absorption time trace for PbSe QDs in TCE solution almost coincides with that for PbSe QDs linked to the porous anatase TiO₂ film through MPA. This observation shows that electron transfer from the quantum state of PbSe QDs ($D = 4.7$ nm) to the porous TiO₂ film does not take place. At the same time pump-probe transient absorption of PbSe QDs ($D = 4.7$ nm) shows that the 1 ps recovery of transient absorption observed for PbSe QDs ($D = 2.7$ nm) linked to the porous anatase TiO₂ film is ascribed to fast electron transfer from PbSe QDs to the porous anatase TiO₂ film and is not to the nonradiative decay caused by the oxidation.

The pump-probe transient absorption shows little difference between PbSe QDs ($D = 2.4$ nm) in TCE solution and PbSe QDs linked to TiO₂ particles in TCE solution. This is because electron transfer from PbSe QDs ($D = 2.4$ nm) to TiO₂ particles in organic solution is difficult because of the relative LUMO energies of them. The LUMO level of the PbSe QDs is still lower than that of TiO₂ particles in TCE (-3.9 eV), even if electrostatic energy shift of the charged

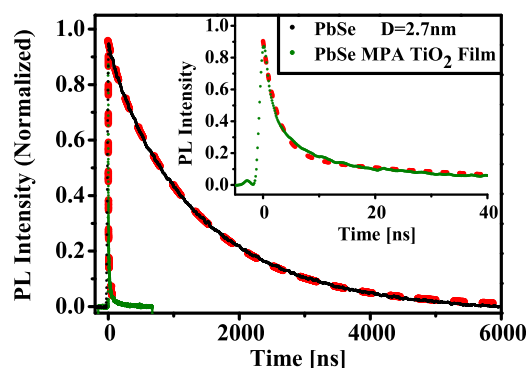


FIG. 4. PL decay of PbSe QDs ($D=2.7$ nm) linked to a TiO_2 porous film and in trichloroethylene solution. In the inset initial part of PL of PbSe QDs linked to a TiO_2 porous film is enlarged and displayed. Decays are fitted by dashed lines.

dielectric sphere is included.^{4,14,15} Then pump-probe transient absorption of PbSe QDs showed the recovery time of bleaching is longer than 1 ns.

Time-correlated single photon counting of PL gives the lifetime of localized electron-hole pairs in PbSe QDs ($D=2.7$ nm) linked to a TiO_2 porous film and in TCE solution. For both the samples, the experimental data are well fitted by the double exponential decay, as shown in Fig. 4. The PL decay of PbSe QDs in TCE solution is fitted by $0.06\exp(-t/142[\text{ns}]) + 0.89\exp(-t/1.4[\mu\text{s}])$, while the PL decay of PbSe QDs linked to a porous TiO_2 films is fitted by $0.73\exp(-t/2.9[\text{ns}]) + 0.16\exp(-t/45[\text{ns}])$. The PL of PbSe QDs linked to a porous TiO_2 films decays in the $1/e$ time of 4.2 ns, while the PL of the PbSe QDs in TCE decays in the $1/e$ time of 1.3 μs . The shortening of PL decay, $1/(1/4.2[\text{ns}]-1/1.3[\mu\text{s}])$, indicates the electron transfer from the localized state in PbSe QDs to TiO_2 takes place in 4.2 ns.

We consider the localization of electron-hole pairs in PbSe QDs shortens the lifetime of the quantum state of PbSe QDs and supplies PL. We show the electron transfer from the quantum state and the localized state of PbSe QDs to the porous TiO_2 film takes place in the picosecond and nanosecond ranges which are much faster than the lifetime of the quantum state in the subnanosecond range and the electron-

hole recombination time in the microsecond range, respectively. It means the electron transfer efficiency is as high as 1.

In summary, we have studied the energy transfer from PbSe QDs to TiO_2 particles by means of transient recovery of absorption bleaching and PL decay. We demonstrated the efficient electron transfer from PbSe QDs to the porous anatase TiO_2 films, when the LUMO level of PbSe QDs is higher than that of porous anatase TiO_2 . The observed transfer time is 1 ps which is much shorter than the lifetime of the quantum state of 650 ps and the recombination time of 1.3 μs . It means the transfer efficiency is 1.

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