# Biexcitonic spectral shift and quasi-type II carrier distribution in type I CdSe/CdS core/shell QDs

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【**Abstract**】Carrier distribution and mobility in semiconductor heteronanostructures are important for photovoltaic applications, which can be disclosed by transient absorption spectroscopies with selective excitation of compositions. Energy band alignment of CdSe (2.9 nm diameter) and CdSe/CdS core/shell quantum dots (QDs) with one and two monolayer CdS shells were confirmed to be type I even though the electron penetrated into the shell. Carrier trapping processes on the surface of CdS shells represented the elongated trapping time with shell coating generated by tunneling barriers. Related with hole trapping, biexcitonic induced spectral shift was observed in the whole spectral region. In the case of shell excitation, electron relaxed from high lying state of CdS shell (270 fs) to CdSe core, transferred from the lowest excitonic state of CdS shell (3.1 ps) to CdSe core and also partially localized in CdS shell, in which energy relaxation by electron-hole coupling played a dominant role.

【**Introduction**】Semiconductor heteronanostructures with a near unit quantum yield from surface passivation or long lifetime carriers from a charge separated state become hot topics owing to potential applications, such as solar cells, light emission diodes, and microlasers. CdSe QDs, one of the most studied II-VI semiconductors, are good candidates as cores for epitaxial growth of CdS with a ~4% small lattice mismatch to prepare CdSe/CdS heteronanostructures. Type I was expected for the energy band diagram of CdSe/CdS core/shell nanostructures based on the bulk properties.[1] However, several discussions exist on the band alignment. Energy band alignment of CdSe/CdS heterostructures was assigned to type I by scanning tunneling spectroscopy while quasi-type II and type II using time-resolved spectroscopic methods.[2,3]

In this paper, we performed transient absorption measurements for CdSe/CdS core/shell QDs with selective excitation of CdSe core and CdS shell. Type I band alignment of CdSe/CdS core/shell was determined while carrier distribution represented to be quasi-type II.

【**Experiments**】CdSe and CdSe/CdS core/shell QDs were prepared following reported procedures with slight modifications.[4,5] Steady-state absorption, luminescence, and scanning transmission electron microscopy were used to confirm the formation of CdS shells on CdSe cores. Time-resolved luminescence dynamics were measured by a time-correlated single-photon counting system. Transient absorption spectroscopy was performed with selective core or shell excitation and detected in visible region.

【**Results・Discussion**】Two different CdSe/CdS core/shell QDs with one and two monolayer CdS shells were prepared from 2.9 nm diameter CdSe core QDs. With coating of CdS shell, the lowest excitonic state of the QDs was gradually red-shifted from 543 to 575 nm (Fig. 1a) owing to electron penetration from CdSe core to CdS shell. With core excitation, carrier trapping time constants in the QDs with 0 to 0.6 nm shell thickness were elongated from 1.4 to 4.0 ps and 10 to ~100 ps for electron and hole, respectively (Fig. 1b), which may be induced by tunneling energy barriers between band edges of CdSe core and surface trapped states on CdS shell. With shell excitation, two-step build-up processes of the lowest excitonic
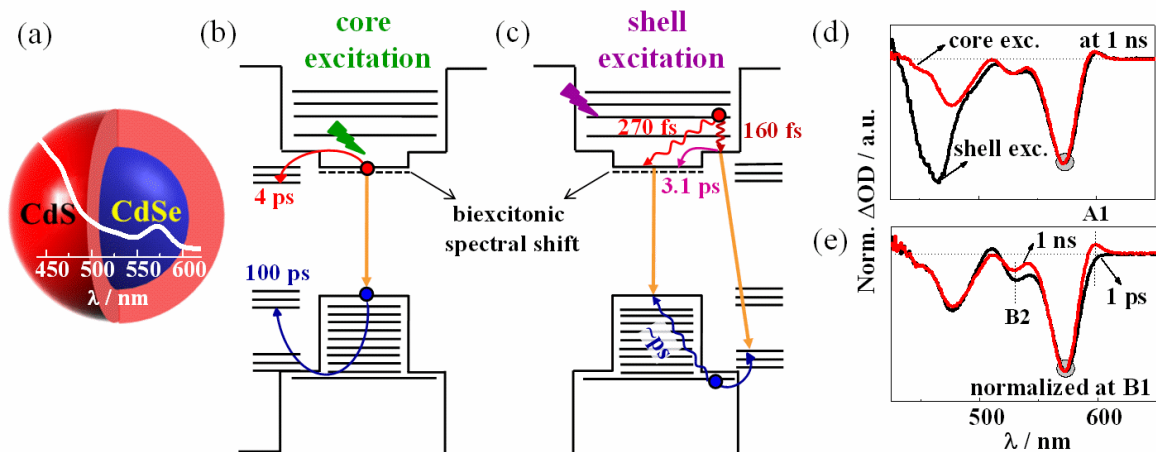
**Fig. 1.** (a) Schematic of CdSe/CdS core/shell QDs and their steady-state absorption spectrum with the lowest excitonic state at 575 nm, (b) carrier dynamics with core excitation: exciton localized in CdSe core and followed by surface trapping process after tunneling barriers of CdS shell or radiative recombination, (c) carrier dynamics with shell excitation: electron relaxed into CdSe core on subpicosecond time scale, transferred from CdS shell to CdSe core on ps time scale, or localized in CdS shell, finally recombined with hole localized in CdSe core or trapped on surface of CdS shell, (d) TA spectra of 1 ns delay time with selective excitation normalized at the lowest excitonic state B1, in which absorption specie of the lowest excitonic state of CdS shell was declared around 461 nm, and (e) TA spectra of 1 ps and 1 ns delay time after core excitation, in which biexcitonic induced spectra shift was observed at B2 and A1 and gave contribution in the whole spectral region.

state of the QDs, 270 fs and 3.1 ps, were assigned to hot electron relaxation started from high energy state and the lowest excitonic state of CdS shell, respectively (Fig. 1c). Long lifetime of electron population in CdS shell was resulted from the absence of efficient Auger-type electron transfer from CdS shell to CdSe core. This is probably due to the reduced overlap of electron and hole wavefunctions originated from the hole transfer from CdS shell to CdSe core with a relaxation rate of 0.4 eV/ps. Conduction band edge of CdSe core was located at a lower energy level than that of CdS shell, which was supported by electron localized in CdSe core with core excitation while delocalized in the whole QDs with shell excitation as shown in Fig. 1(d). CdSe/CdS core/shell QDs represented a quasi-type II carrier distribution while actually they had a type I energy band alignment. In Fig. 1e, the dynamics of $1S(e)-2S_{1/2}(h)$ transition (B2) always showed a ~100 ps decay component as compared to that of $1S(e)-1S_{3/2}(h)$ transition (B1) in CdSe/CdS core/shell QDs with core excitation. The additional decay was also observed with shell excitation. This decay component represented similar time constant with rising process of induced absorption (A1) on the red side of band edge. Hence, it was assigned to biexcitonic induced spectral shift coming from the probe pulse created exciton and the hole-trapping related surface trapped state. Our results provided a useful method to clarify band alignment of heteronanostructures and carrier distribution by transient absorption measurement with selective excitation of compositions, which could help to objectively extract charge carriers in photovoltaic applications.

## 【References】

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