PD Research Report for the 2018 year

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Research Theme　半導体ナノ微粒子系の多励起子素過程の解明と光応答分子システムへの応用
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Semiconductor nanostructures are expected to provide multiexciton generation for photo-switchable systems. In semiconductor-metal hybrid nanosystems, metal components may influence exciton dynamics by charge separation. Carrier dynamics in metal and semiconductor nanostructures provide basic information to design high efficiency photo-switch systems.

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

Transient absorption measurements of CdSe/CdS core/shell quantum dots (QDs) were performed with state selective excitation of CdSe core or CdS shell to declare assignment of spectral species and monitor distribution of charge carriers. Two different CdSe/CdS core/shell QDs with one− and two−monolayer (ML) CdS shells were prepared from 2.9 nm diameter CdSe core QDs. CdSe/CdS core/shell QDs represented a quasi-type II carrier distribution according to red-shifted spectra, increased quantum yields, and elongated luminescence lifetimes. However, a type I band alignment of the core/shell QDs was supported by electron localized in CdSe core with core excitation while delocalized in the whole QDs with shell excitation. By state selective excitations, overlapped spectral species of 1S(e)-1$S_{3/2}$(h) transition of CdS shell and 1S(e)-2$S_{1/2}$(h) of CdSe core became distinguishable, and biexcitonic spectral was found to be existed in all transitions to 1S(e) electronic state. Elongated trapping time constants of both electron and hole were observed with core excitation, which was induced by tunnel effect through energy barrier, CdS shell. Our results by transient absorption spectroscopy with state selective excitation of compositions are useful to clarify band alignment and carrier distribution of heteronanostructures, which could help to objectively extract charge carriers in photovoltaic applications.

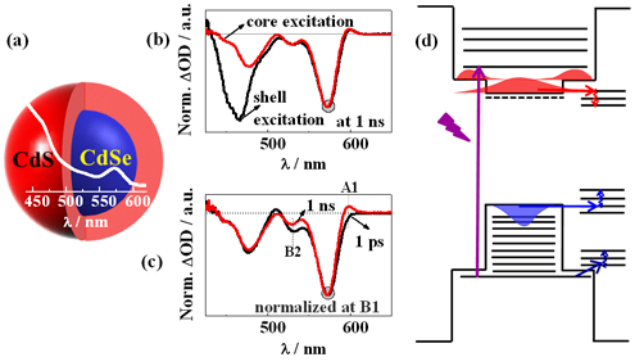

Figure 1. Absorption spectrum (a), transient absorption spectra with shell (black) and core (red) excitation at 1 ns delay time normalized at 575 nm (b), transient absorption spectra with core excitation at 1 ps (black) and 1 ns (red) delay times normalized at 575 nm (c), and the carrier relaxation diagram with shell excitation (d) of CdSe/CdS core/shell QDs with the lowest excitonic state at 575 nm.

2. Coherent acoustic phonon vibration of Au nanocubes, nanoctahedrons, and nanocuboctahedrons.

Metal nanoparticles with the unique property of localized surface plasmon resonance (LSPR) provide tunable optical property, surface enhanced electromagnetic field, high frequency mechanical resonance, and nano-sized heat source. Their applications have been explored as light collectors for solar cells, as efficient catalysts in photocatalysis, supplying enhanced electric fields for non-destructive spectroscopies, as resonators for detecting mechanical properties of surrounding environments, and as target heaters in photothermal therapies. Coherent acoustic phonon vibration can be detected when its displacement is sensitive to the plasmon mode.

Coherent acoustic phonon vibrational mode of Au nanopolyhedrons including nanocubes, nano-octahedrons, and nanocubeoctahedrons were analyzed. As shown in Table 1, for modes I and II, their phases are less than π/10 difference but π/2 out-of-phase for mode III of Au nano-octahedrons. Morover, similar quality factors for modes I and II while that for mode III is much smaller. Hence, modes I and II were driven by lattice heating while mode III was generated by impulsive electron pressure. The vibrational modes were simulated by finite element method (FEM) with bulk elastic properties based on continuum elastic theory. The calculated frequencies f_{FEM} are in good agreement with the experimental results. Reverse spectral shift for expansion of the two modes has been reported for Ag nanocubes. The similar phases for mode I and mode II represent reverse displacement of modes I and II, that means expansion of mode I is combined with shrinkage of mode II

Table 1. Parameters for coherent acoustic vibrational modes of Au nanocubes, nanooctahedrons, and nanocuboctahedrons.φ and f are phase and frequency of vibrational mode. f_{FEM} is vibrational frequency calculated by COMSOL with bulk properties. Q is quality factor of the mode.

Au	mode	φ (π)	f (GHz)	f_{FEM} (GHz)	Q ($\pi\tau f$)
Cube	I	-0.02 ± 0.01	29.9 ± 0.6	27.8	16.7
	II	0.02 ± 0.03	46.8 ± 0.3	42.7	16.5
Octa	I	0.1 ± 0.1	30.4 ± 0.2	30.8	19.7
	II	0.2 ± 0.1	53.7 ± 0.3	52.3	23.1
	III	-0.3 ± 0.1	68.1 ± 0.3	-	0.9
Cub-octa	I	0.05 ± 0.03	51.4	43.2	22.4
	II	0.09 ± 0.03	57.8	51.3	21.2

Conferences:

1) Li Wang, Kouhei Nonaka, Tomoki Okuhata, Naoto Tamai, "Biexcitonic spectral shift and quasi-type II carrier distribution in type I CdSe/CdS core/shell QDs", 第 11 回分子科学討論会 2017 仙台, 4B10

Publications:

1) L. Wang, K. Nonaka, T. Okuhata, K. Tetsuro, and N. Tamai, "Quasi-Type II Carrier Distribution in CdSe/CdS Core/Shell Quantum Dots with Type I Band Alignment" (submitted)
2) L. Wang, S. Takeda, T. Okuhata, R. Sato, T. Teranishi, and N. Tamai, "Ultrafast Spectroscopy and Coherent Acoustic Phonon of Au Nanopolyhedrons" (in draft)