Excited-state Dynamics of CdTe Nanocrystals by Ultrafast Laser Spectroscopy

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Much attention has been recently paid for semiconductor nanocrystals that show interesting size-tunable optical and electrical properties due to the confinement of their electronic wavefunctions. Because of their unique properties, nanoparticles are likely to play a key role in the emerging new field of nanoscience and nanotechnology in applications ranging from optoelectronic and nonlinear devices and lasers to biological fluorescent marking [1,2].

CdTe nanocrystals prepared by using water-soluble thiol compounds are highly photoluminescent and photochemically stable [3]. However, only little is known on the excited-state dynamics of CdTe nanocrystals. Recently, Wuister et al. have reported luminescence decays of CdTe quantum dots prepared in TOP/DDA method showing monoexponential decays and no observable defect-related emission [4], although size-dependent luminescence dynamics has not been reported yet. In the present study, we have prepared CdTe nanocrystals with various sizes by the similar method reported previously [3], and examined excited-state dynamics of CdTe nanocrystals as a function of sizes by various time-resolved laser spectroscopies. Luminescence properties, electron-hole recombination dynamics, and hot-electron relaxation dynamics in CdTe nanocrystals have been studied in detail.

Briefly, H_2Te gas is introduced into $Cd(ClO_4)_2$ solution containing thioglycolic acid under nitrogen atmosphere. The resulted CdTe precursor solution is further refluxed at ~ 100˚C to form CdTe nanocrystals and the solution is taken out as a function of reflux time [3]. Picosecond-single photon timing, transient absorption, and four-wave mixing spectroscpies have been applied for CdTe nanocrystals.

Fig. 1 is a photograph of several CdTe nanocrystals, in which the colors are ranging from yellow to dark red. The corresponding absorption spectra have peaks at 430 nm to 600 nm, suggesting the band-gap control with reflux time. The band-gap (E_g) was estimated by the analysis of absorption spectrum. The size of CdTe nanocrystals was also estimated from the relationship between E_g and nanocrystal diameter [5], and the size of CdTe is ranging from 2.8 (E_g = 2.46eV) to 4.9 nm (E_g = 1.92eV). As similar to absorption, luminescence spectrum in Fig. 2 also shows size-dependent red shift of the spectrum: 510 nm (E_g = 2.46eV) to 640 nm (E_g = 1.92eV). Time-resolved luminescence decay curves of respective nanocrystals were measured at various wavelengths, and time-resolved spectra were reconstructed. The analyses of the luminescence decays at peak wavelengths reveal the following: (a) the relaxation time of excited-state CdTe becomes longer with increasing the size of nanocrystal, (b) luminescence decay is not single exponential even in large-sized nanocrystals. The average lifetimes are 2.3 ns (size 2.8 nm) to 24 ns (size 4.9 nm). The average radiative rate constants of CdTe nanocrystals analyzed by the luminescence quantum yield and lifetime decreased with increasing the size, which is in accordance with the absorption coefficient although some anomaly is observed.

Femtosecond transient absorption spectra of CdTe nanocrystals show mainly ground-state bleaching. It was found that an ultrafast rise component is observed in the bleaching wavelength, especially for small E_g nanocrystals, and the rise component is not detected for large Eg nanocrystal (Eg = 2.46eV): τ_r = 130fs for E_g = 2.24eV and τ_r = 320fs for E_g = 1.97eV. These results suggest that the stimulated emission is superimposed in the bleaching signal, and the rise component is probably originated from the relaxation of hot electron due to electron-phonon scattering. The excitation energy dependence on the relaxation of hot electron and the carrier dynamics in CdTe nanocrystals will be also discussed.

References

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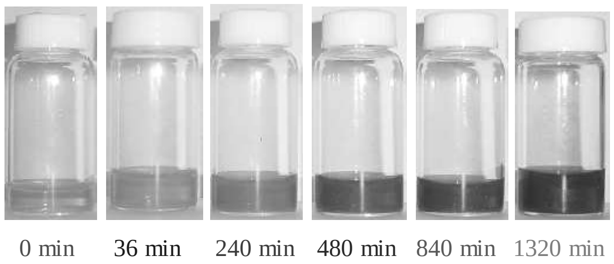

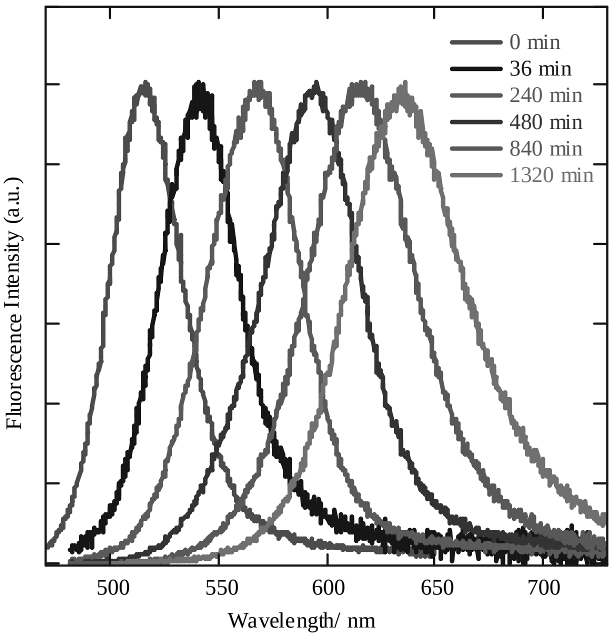

Fig.2 Luminescence spectra of thiol-capped CdTe nanocrystals as a function of reflux time.