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Femtosecond transient absorption spectroscopy of nanocrystalline polydiacetylene colloids

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Femtosecond transient absorption spectral measurements have been performed for size-controlled polydiacetylene microcrystals (30, 100, and 150 nm mean diameter) dispersed in water. Ultrafast relaxation processes within 5 ps after excitation were attributed to formation and decay of self-trapped exciton, which was independent on the size. A time-dependent spectral shift of transient bleaching, corresponding to the stationary excitonic absorption band, was observed in the time region from 10 ps to a few ns. It is explained as a thermalization of absorbed light energy within the microcrystal and the succeeding cooling by comparing transient absorption spectra with temperature difference spectra of the ground state absorption. Size-dependent cooling dynamics of a 'hot' microcrystal was successfully demonstrated; the time constant increases with the crystal size.

Keywords microcrystals; polydiacetylene; femtosecond absorption spectroscopy; cooling dynamics; size dependence

INTRODUCTION

Nano-sized organic and inorganic crystals have attracted increasing interests in investigations on photophysics and photochemistry in mesoscopic spatial scale; much lager than molecular size but much smaller compared to bulk. In the present work, we investigate ultrafast relaxation dynamics after photoexcitation of size-controlled polydiacetylene (poly[1,6-di(N-carbazolyl)-2,4-hexadiyne], poly-DCHD) microcrystals (30, 100, and 150 nm mean diameter) in water by means of femtosecond transient absorption spectroscopy. Polydiacetylenes are well known as an organic material having

large third-order nonlinear susceptibility coefficient with a fast temporal response. Also, the ultrafast relaxation processes after photoexcitation have been studied extensively for thin films and single crystals.[1-3] Comparing the present results with them, we discuss the size-dependent photophysical dynamics of the microcrystal, including not only the excited dynamics but also the following transient heating and cooling in the ground state.

EXPERIMENTAL

The poly-DCHD microcrystals were prepared by solid-state polymerization of size-controlled DCHD microcrystals dispersed in water, which was fabricated by the reprecipitation method described in ref. 4 and 5. The size of poly-DCHD microcrystals was evaluated by means of dynamic light scattering (Otsuka Electronics DLS-7000) and scanning electron microscopy (Hitachi S-900). The colloidal water solution (about 0.01 wt% of poly-DCHD) was contained in a quartz cell (2 mm optical path length), and used as a sample of spectroscopic measurements. Transient absorption spectra and their time profiles were measured by our femtosecond transient absorption spectroscopic system.[6] The excitation light pulse was the second harmonic of an amplified fs Ti: sapphire laser pulse (170 fs fwhm, 780 nm), and the probe light pulse is a fs white-light continuum generated by focusing the fundamental laser pulse into water. Excitation pulse energy was about 1.3 mJ/cm^2, and the measurements were performed at room temperature in air.

RESULTS and DISCUSSION

Femtosecond transient absorption spectra

Transient absorption spectra of 100 nm microcrystals are shown in Figure 1. There are three negative peaks (647, 592, 575 nm) corresponding to the ground state absorption to the 1^1B_u excitonic state. These peaks can be attributed to the zero-phonon band (647 nm) and one-phonon side bands coupled to the C=C and C≡C stretching modes, respectively. Also, two positive absorptino changes were observed; one with a peak around 680 nm shows an ultrafast decay dynamics, and the other peaking at longer than 850 nm is almost constant over 5 ns. Time profiles of transient absorption observed at several wavelengths are shown in Figure 2. By referring transient

absorption spectral data of thin films and single crystals of polydiacetylenes[1-3], we can safely assign the short- and long-lived transients to self-trapped and triplet excitons, respectively. Similar spectral features and time profiles were also observed for microcrystals with other sizes.

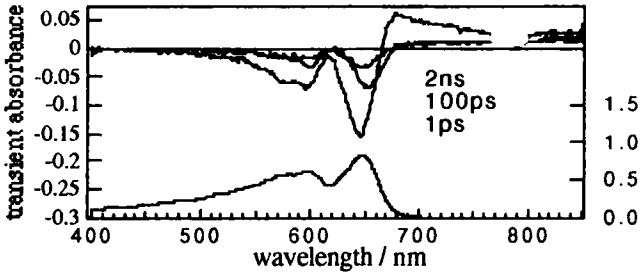

FIGURE 1 Transient absorption spectra and the ground state absorption spectrum of poly-DCHD microcrystals (100 nm mean diameter) dispersed in water.

Formation and decay dynamics of the self-trapped exciton

First, we describe the ultrafast relaxation dynamics within 5 ps after excitation. The transient absorption at 690 nm rises with a time constant of 150 ± 50 fs and decays with a lifetime of 1.2 ± 0.1 ps. The recovery dynamics of bleaching at 645 nm consists of fast and slow components and

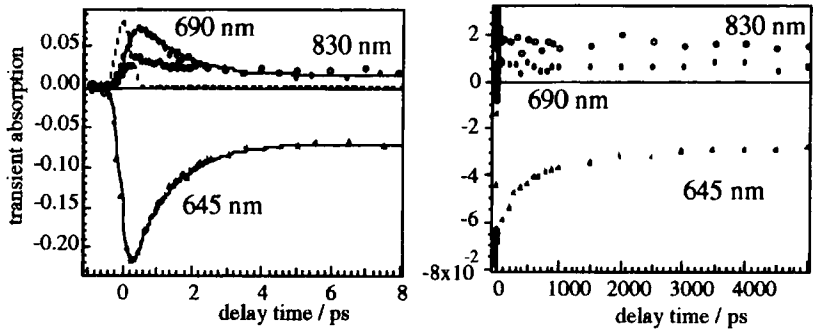

FIGURE 2 Temporal profiles of transient absorption of poly-DCHD microcrystals (100 nm mean diameter) dispersed in water. Solid curves are calculated transient absorption changes with the double-exponential function; 690 nm, 0.014 + 0.1{exp(- t / 1.15 ps) - exp (- t / 150 fs)}; 645 nm, -0.073 - 0.19 exp(- t / 1.15 ps) - 0.048 exp (- t / 150 fs). A broken curve is a cross-correlation of the excitation and the probe pulses.

the former is well fitted by using the same lifetime as shown in Figure 2. The rise and decay dynamics is quantitatively identical with that of a polycrystalline film of poly-DCHD.[3,4] Moreover, the same time constants were obtained within the experimental errors for 30, 100 and 150 nm microcrystals, independent with the crystalline size. This is in contrast to the fact that the peak of the exciton band was slightly red-shifted with the crystal size.[7] The common feature of ultrafast relaxation processes of several polydiacetylenes with different side chains (including poly-DCHD) has been discussed in terms of the self-trapped exciton; its formation from the free photogenerated exciton with a hundred to two hundred fs, and the following nonradiative relaxation of the self-trapped exciton to the ground state by a quantum mechanical tunneling with the time constant of a few ps. Also these processes are strongly coupled with vibrational stretching modes in the backbone chain. The present result can be explained along the above explanation. Namely, ultrafast relaxation processes regulated by the local vibrational motion and rapid localization of the exciton has no size dependence.

Thermalization of absorbed light energy and the following cooling of a microcrystal

In Figure 2b, a slow recovery of the bleaching signal at the peak wavelength of the excitonic absorption band (645 nm) is found in the time region from 10 ps to 2 ns. In Figure 3, the peak wavelengths of the transient bleaching are plotted

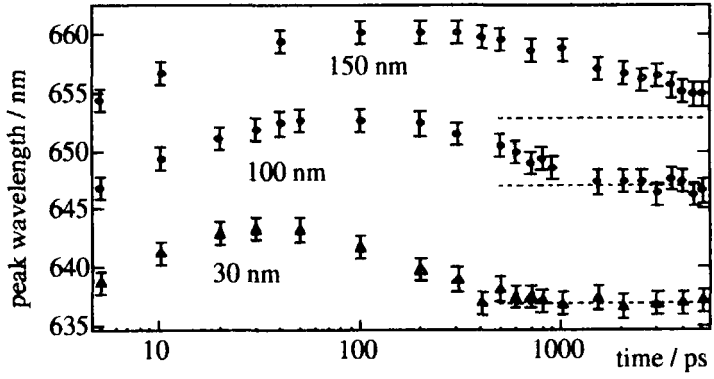

FIGURE 3 Temporal dependence of the negative peak of transient absorption spectra of poly-DCHD microcrystals with different sizes. Dotted lines represent the peak wavelength of the stationary absorption band at room temperature for each microcrystals.

against delay times for the samples with differed crystal sizes. Most interestingly, the negative peak wavelength changes with the delay time in this time region. The slow recovery and the time-dependent spectral shift will be attributed to some relaxation processes of the ground state itself, since the triplet exciton absorption band is almost constant up to 5 ns and no other decay of transient induced absorption corresponding to the slow recovery was observed. One possible explanation is due to heat generation by fs pulse excitation. Absorbed light energy of a fs excitation pulse is converted to heat (vibrational energy) within a few ps through the ultrafast relaxation of the excited state, resulting in formation of a 'hot' microcrystal. To examine the idea, we measured the ground state absorption spectra at several temperatures (24 to 52 Celsius degree). The peak of the zero-phonon excitonic absorption band was blue-sifted and the spectral width became slightly broad with temperature elevation. Temperature difference spectra, which are obtained by subtracting the high-temperature spectra from that at 24 degree, have a negative peak located at a longer wavelength than the absorption peak. Their spectral shape was almost unchanged, but the amplitude increased linearly with temperature. On the other hand, we subtracted a spectrum at 5 ns (the triplet exciton) from transient absorption spectra at the respective delay times, since the component of the triplet exciton is overlapped in transient absorption spectra at each delay time. The obtained transient absorption spectra at delay times of 50 ps to 1 ns were very similar to the temperature difference spectra. Hence, we conclude that the time-dependent spectral shift originates from a transient thermal effect in the microcrystal.

As shown in Figure 3, the negative peak shifts to a longer wavelength at first and then back to the position of the stationary excitonic absorption band with further increasing of the delay time, and their time constants strongly depend on the crystal size. The initial red-shift of the peak can be attributed to a thermalization process within a microcrystal as described above. It includes not only a energy redistribution process of molecular and intrachain vibrational modes as well as lattice phonon ones, but also a geometrical reorganization to a stable form of the microcrystal at a given high temperature. Since the former process takes place in a few ps, the time scale of the observed peak shift may correspond to the latter reorganization. A thermal diffusion within the microcrystal will not be effective, because the excitation light is homogeneously absorbed due to a rather weak absorption at 390 nm. It is notable that the time at which the amount of the peak shift becomes a

maximum value increases with the crystal size, although the further detailed analysis is necessary.

A hot microcrystal should cool down by a heat transfer to the surrounding water, which was observed here as a temporal blue-shift of the peak of transient bleaching at late stages. We here estimate the time constant for the microcrystals of three different sizes; 200 ps (30 nm mean diameter), 600 ps (100 nm), and 2 ns (150 nm). It increases with the crystal size. Qualitatively, this result is quite reasonable, since the heat transfer takes place at the interface of a microcrystal and water and the ratio of the surface area to the volume of the microcrystal increases with decreasing of its size. The present result will be a clue to reveal the mechanism and dynamics of heat transfer or diffusion in a nano-scale spatial region, which is necessary even for evaluating spectroscopic and optical properties.

CONCLUSION

No appreciable size dependence on the dynamics of a self-trapped exciton formation and its relaxation to the ground state of poly-DCHD microcrystals was observed for the crystal size from 30 to 150 nm. This is consistent with a localized character of the self-trapped exciton. A slow relaxation process depending on the size up to a ns time region has been found and well explained in terms of a temperature effect. Thermalization of absorbed light energy and cooling dynamics of a nano-sized organic crystal was clearly demonstrated by transient absorption spectroscopy.

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