Transient Absorption Kinetics Associated with Higher Exciton States in Semiconducting Single-Walled Carbon Nanotubes: Relaxation of Excitons and Phonons

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Differential absorption spectra with E_{22} exciton excitation for sample 1

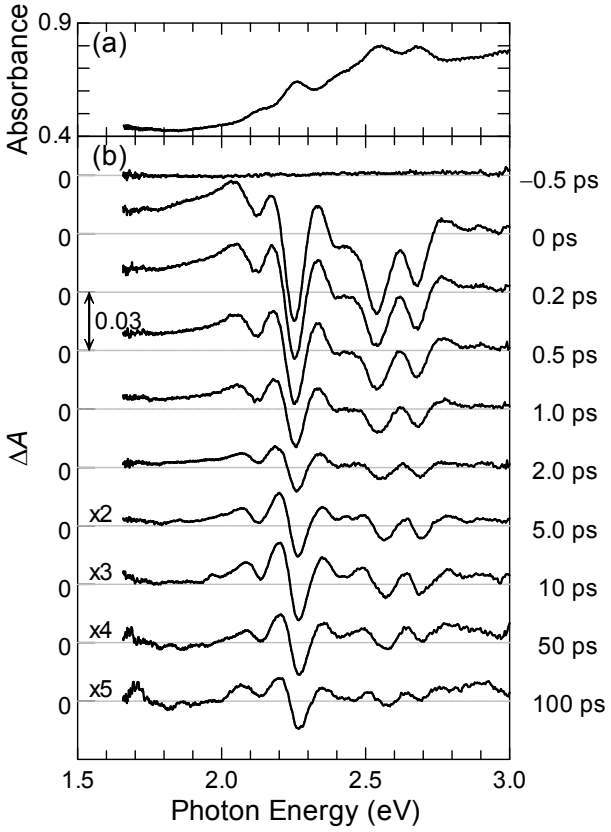

Figure S1. (a) Linear absorption spectrum of sample 1. (b) Differential absorption spectra at different delay times (indicated on the right of the figure) with the E_{22} exciton excitation at 1.27 eV. The pump fluence is 5.0×10^{15} photons cm^{-2} per pulse.

Differential absorption spectra and time evolutions with low pump fluences for sample 1 and sample 2

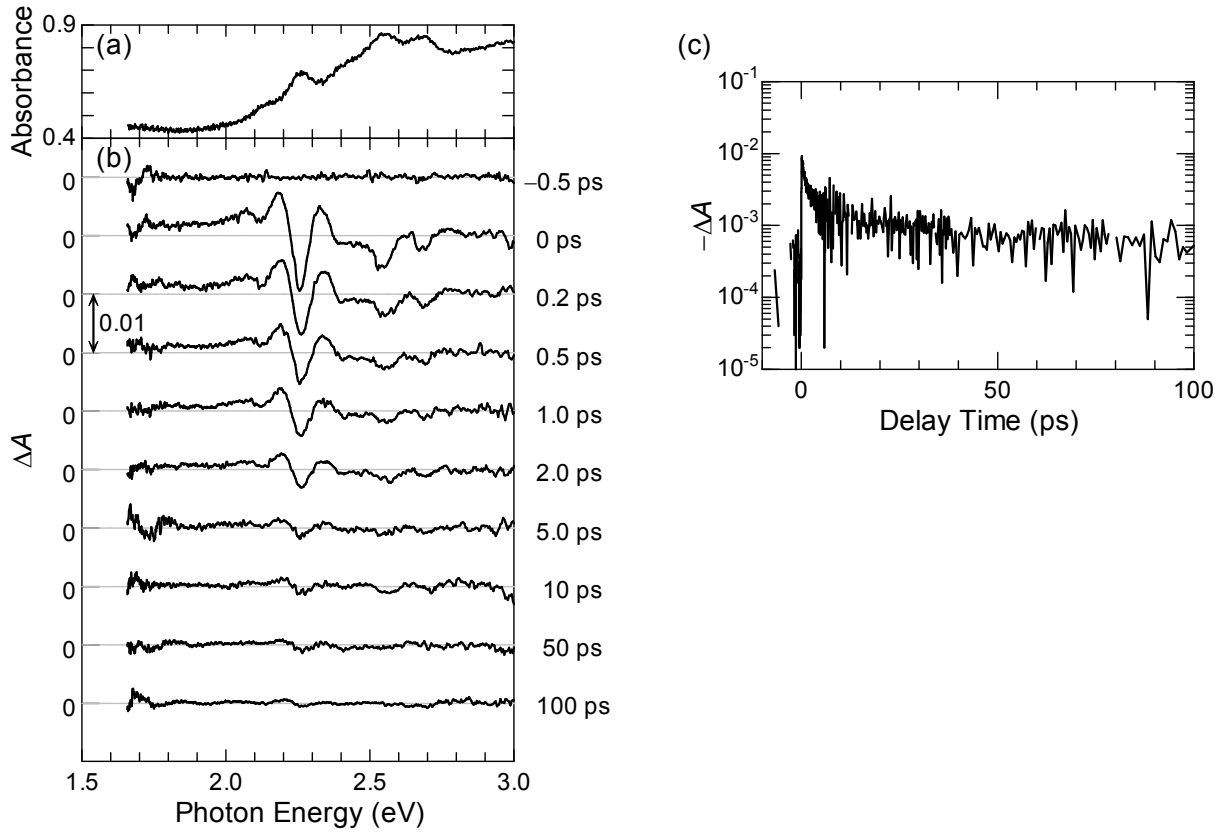

Figure S2. (a) Linear absorption spectrum of sample 1. (b) Differential absorption spectra at different delay times as indicated on the right of the figure. (c) Time evolution of differential absorption at 2.26 eV corresponding to the E_{33} exciton band. The excitation photon energy is 0.73 eV corresponding to the E_{11} exciton band, and the pump fluence is 1.9×10^{14} photons cm^{-2} per pulse.

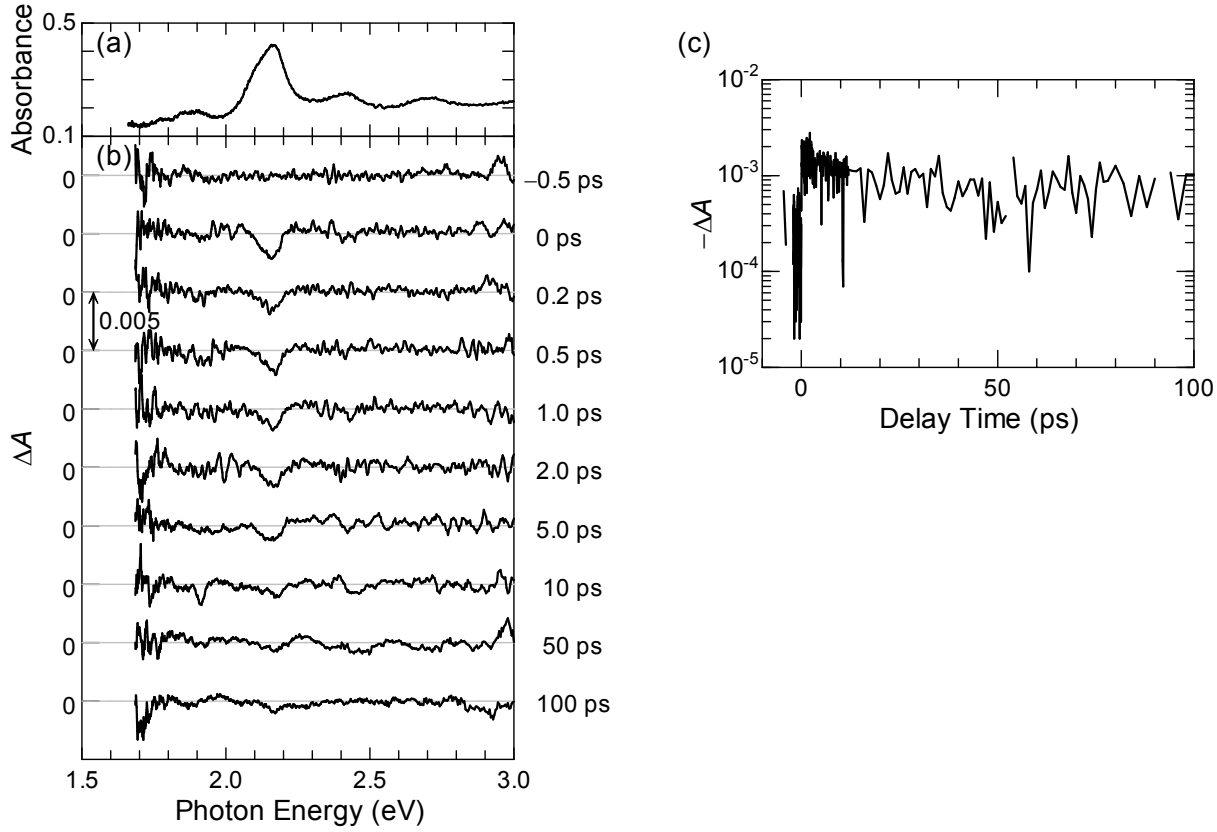

Figure S3. (a) Linear absorption spectrum of sample 2. (b) Differential absorption spectra at different delay times as indicated on the right of the figure. (c) Time evolution of differential absorption at 2.16 eV corresponding to the E_{22} exciton band. The excitation photon energy is 1.27 eV corresponding to the E_{11} exciton band, and the pump fluence is 5.0×10^{13} photons cm^{-2} per pulse.

Voigt function used for curve fitting of linear absorption spectrum

We performed curve fitting of the linear absorption spectrum of sample 2 in the E_{22} band region. The spectrum is composed of (i) the E_{22} exciton absorption component due to semiconducting SWNTs, (ii) the M_{11} exciton absorption component due to metallic SWNTs, and (iii) the background component due to π-plasmon absorption in SWNTs and absorption and scattering by impurities such as amorphous carbons. The E_{22} exciton absorption component is fitted using a Voigt function, which is the convolution of Lorentz and Gauss functions. The Lorentz function represents an absorption band with homogeneous broadening of individual SWNT, and the Gauss function represents that with inhomogeneous broadening of SWNT ensemble. The width (full width at half maximum) Γ of the Lorentz function is set to 50 meV [S1], and the width Γ_{inh} of the Gauss function is an adjustable parameter for all SWNTs. The spectral weight S_i of the Voigt function for each chirality i is an adjustable parameter. The peak energy E_i of the E_{22} exciton absorption band for each chirality i is shifted from the reported value in ref [S2] (Since the surfactant used in this study (sodium cholate) is different from that used in ref [S2], the peak energies of exciton absorption bands are slightly shifted due to the environment effect [S3]). The shift value ΔE_i is an adjustable parameter for all SWNTs. The exciton absorption peak in SWNTs is accompanied by sidebands on both low and high energy sides [S4–8]. The high-energy sideband is relatively strong and its spectral weight is about 10% of that of the main exciton absorption band [S4]. Thus, we take into account the high-energy sideband. In the E_{22} band region of (7,5) SWNT [S4], the peak energy of this sideband is situated above the main exciton absorption peak by $\Delta E_{\mathrm{s}} \sim 220$ meV, and its width is equivalent to the main exciton absorption band. We assume that these values are common to all SWNTs. The M_{11} exciton absorption component is fitted using two Gauss functions with the same width. The width γ and spectral weight B_j are adjustable parameters. The background component is fitted using a linear function, where the slope a and intercept b are adjustable.

The total fitting function is expressed as follows:

$$\sum_i S_i\left[F_{\Gamma,\Gamma_{\text{inh}}}(\hbar\omega - E_i - \Delta E_i) + 0.1F_{\Gamma,\Gamma_{\text{inh}}}(\hbar\omega - E_i - \Delta E_i - \Delta E_{\text{s}})\right] + \sum_{j=1,2} B_j G_\gamma(\hbar\omega - M_j) + a\hbar\omega + b,$$

where

$$F_{\Gamma_0,\Gamma}(x) = \int_{-\infty}^{\infty} \frac{1}{\pi}\frac{\Gamma/2}{(x-X)^2 + (\Gamma/2)^2} \times \sqrt{\frac{\ln 2}{\pi}}\frac{1}{\Gamma_{\text{inh}}/2}\exp\left[-\frac{X^2}{(\Gamma_{\text{inh}}/2)^2}\ln 2\right]dX,$$

$$G_\gamma(x) = \sqrt{\frac{\ln 2}{\pi}}\frac{1}{\gamma/2}\exp\left[-\frac{x^2}{(\gamma/2)^2}\ln 2\right].$$

The fitted values of the adjustable parameters are listed in Table S1.

Table S1. Fitted Values of Adjustable Parameters in Curve Fitting of Linear Absorption Spectrum

i	(6,4)	(6,5)	(7,3)	(7,5)	(8,3)	(8,4)	(9,1)	(10,0)
S_i	1.84	34.87	5.04	9.64	1.63	9.81	7.86	3.64

Γ_{inh} (meV)	ΔE_i (meV)	M_1	M_2	B_1	B_2	γ (meV)	a (eV^{-1})	b
80	–27.8	2.40	2.70	4.42	7.58	200	0.1	–0.075

Calculated dependence of the total E_{22}-exciton number on the initial E_{11}-exciton number

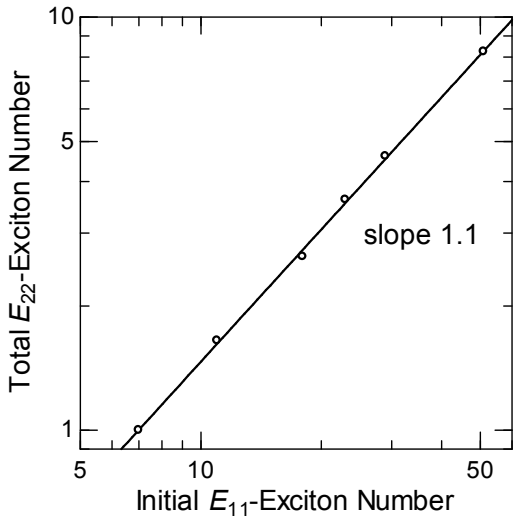

Figure S4. Total E_{22}-exciton number vs. initial E_{11}-exciton number. The ordinate is normalized by setting the minimum value of total E_{22}-exciton number to 1. The solid line is a least-square fit.

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