

Subpicosecond coherent nonlinear optical response of isolated single-walled carbon nanotubes

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We report an excitation-energy dependence of ultrafast changes of exciton absorptions in isolated semiconducting single-walled carbon nanotubes. For a photoexcitation far below the exciton transition, a blueshift of exciton absorptions originating from the optical Stark effect due to exciton-photon coupling was observed. Under near-resonant excitation conditions, a broadening of exciton absorptions was discriminated from a blueshift signal in the time and frequency domains. The broadening can be attributed to virtual exciton-real exciton scattering, which is considered to be characteristic of strongly confined excitons in nanotubes.

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In quasi-one-dimensional (1D) semiconductors, the inverse-square-root divergence of the density of states and the large excitonic effect cause a concentration of oscillator strength on band-edge excitons. This can give rise to large third-order nonlinear optical (NLO) responses. In typical 1D semiconductors of conjugated polymers such as polydiacetylene¹ and polysilane,² and halogen-bridged platinum-chain compounds³ with strong excitonic effects, considerably enhanced third-order nonlinear susceptibility $\chi^{(3)}$ has been observed near exciton transitions. A single-walled carbon nanotube (SWNT) is another typical example of a 1D electronic system. Recent theoretical and experimental studies have demonstrated that in semiconducting (SC)-SWNTs, a primary photoexcited state is also an exciton, and the binding energy E_b of an electron and a hole in the exciton reaches ~ 400 meV in a tube with a diameter of ~ 1 nm,⁴ which is comparable to E_b in the above conjugated polymers and platinum-chain compounds. Therefore, a SC-SWNT can be a good NLO material.

Early studies of NLO responses in SWNTs were performed on bundled tubes from the viewpoint of large absorption saturation of band-edge excitons and their rapid recovery.^{5,6} It was reported that $\chi^{(3)}$ reaches 10^{-10} – 10^{-7} esu, and the decay time of the excitons is on the order of 1 picosecond (ps).^{6,7} Subsequently, transient absorption studies were performed on isolated SWNTs, revealing that a typical decay time of excitons in isolated SWNTs is on the order of 10 ps and is much longer than in bundled SWNTs.⁸ These results suggest the presence of an ultrafast nonradiative decay mechanism of excitons in bundled SWNTs, which is considered to be a rapid exciton- and/or charge transfer from SC-SWNTs to metallic ones.

More recently, detailed transient absorption spectroscopy of a band-edge exciton (a so-called S1 peak) was performed on bundled SWNTs. The results indicate that SC-SWNTs show large and ultrafast optical nonlinearity ($\text{Im } \chi^{(3)} = 4.2 \times 10^{-6}$ esu) under resonant excitation conditions, the response time of which is independent of recombination and intertube-transfer processes of excitons and charges.^{9,10} This response was attributed to the optical Stark effect (OSE), which is a coherent response with no dissipation detected only during irradiation by a strong laser pulse^{11,12} and characterized by a photoinduced shift of an

excitonic transition due to exciton-photon coupling. The OSE is one of the most typical third-order optical nonlinearities, and is sometimes observed in atoms in gas phases and excitons in semiconductor quantum wells. In isolated SWNTs, more systematic and advanced studies of coherent optical nonlinearity are expected to be possible, but such studies have not yet been performed.

In this Rapid Communication, we report coherent NLO responses in isolated SC-SWNTs. To detect these responses, real excitations of excitons and charge carriers were suppressed, because the absorption saturation due to the real excitations would obscure coherent responses. For this purpose, in our study, excitation energies were set below the S1 transitions. Using femtosecond (fs) pump-probe spectroscopy, we observed transient absorption changes due to coherent NLO responses in SC-SWNTs. The responses could not be produced by a spectral shift induced by the conventional OSE alone, but can be explained accounting for an additional modulation of the exciton absorption due to exciton-exciton scatterings. The mechanisms of these responses will be discussed on the basis of the detuning energy dependence of transient absorption changes.

Purified CoMoCAT SWNTs (Ref. 13) (Nanotechnologies Inc.) were isolated in water with 1 wt% sodium cholate hydrate, and then mixed with gelatin.¹⁴ The solution was dried on a SiO₂ substrate to obtain a homogeneous thin film for the optical measurements. To perform fs pump-probe absorption spectroscopy, two optical parametric amplifiers excited by the outputs of a Ti:Al₂O₃ regenerative amplifier [785 nm (1.58 eV) and repetition of 1 kHz] were employed as sources of pump and probe pulses. The temporal and spectral width of the pulse was 130 fs and 25 meV, respectively. The time resolution of the system was ~ 180 fs. All measurements were performed at room temperature.

An absorption [optical density (OD)] spectrum of a film sample of isolated SWNTs is shown in Fig. 1(a) (a solid line). The structures at 1.15–1.3 eV are reproduced by the sum of the three Lorentz functions shown by broken lines, which are the S1 exciton absorptions of SC-SWNTs with chiralities of (7, 5), (6, 5), and (8, 3).¹³ The main component is the absorption of (6, 5) tubes, which peaks at $E_{\text{ex}} = 1.25$ eV. The ratio of the (6, 5) tubes was $\sim 60\%$ in SC-SWNTs.

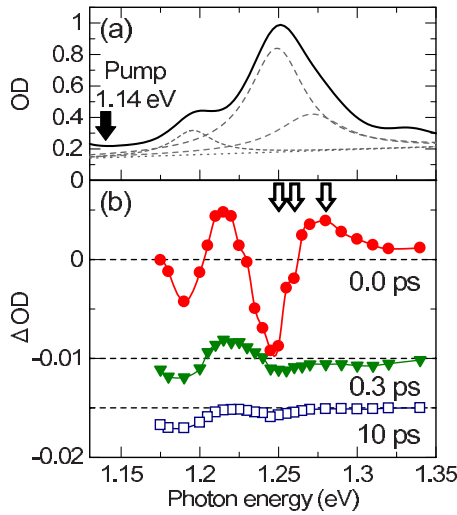


FIG. 1. (Color online) (a) Absorption (OD) spectrum and (b) photoinduced absorption (ΔOD) spectra in the SWNT film. The OD spectrum was decomposed into the three Lorentz functions shown by dotted lines. The pump energy is indicated by a solid arrow.

Spectra of photoinduced absorption changes ΔOD for a pump energy $E_p = 1.14$ eV (off-resonant excitation) are shown in Fig. 1(b). The excitation photon density x_{ph} was 6×10^{13} photons (ph)/ cm^2 . The ΔOD spectra show the oscillatory structures and the dynamics of ΔOD strongly depend on probe energy, as seen in Figs. 2(a)–2(c). For all probe energies, however, a spike-like instantaneous response was observed at $t_d \sim 0$ ps, as indicated with shading in the figures. The magnitude of this instantaneous response was proportional to x_{ph} . It is therefore attributable to third-order optical nonlinearity.

To derive the spectral and time characteristics of the instantaneous response, we calculated differential absorption spectra $\delta OD(t_d) = [\Delta OD(t_d) - \Delta OD(0.3 \text{ ps})]$ of $\Delta OD(t_d)$ at

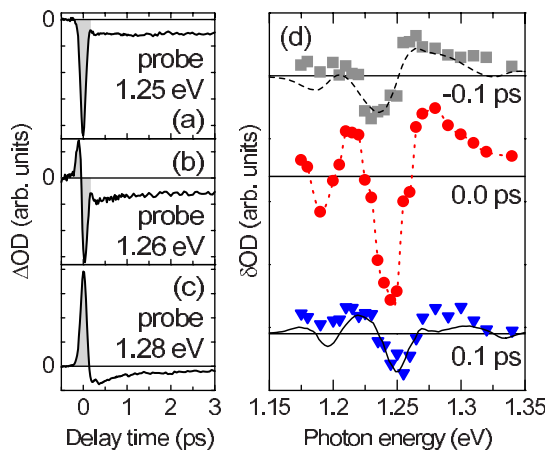


FIG. 2. (Color online) (a–c) Time characteristics of ΔOD . The probe energies are indicated by open arrows in Fig. 1(b). The shaded regions show instantaneous responses. (d) The differential ΔOD spectra, $\delta OD(t_d) = [\Delta OD(t_d) - \Delta OD(0.3 \text{ ps})]$, for $t_d = -0.1, 0,$ and 0.1 ps. The broken and the solid line show the first derivative and the second derivative of the OD spectrum, respectively. The dotted line is a visual guide.

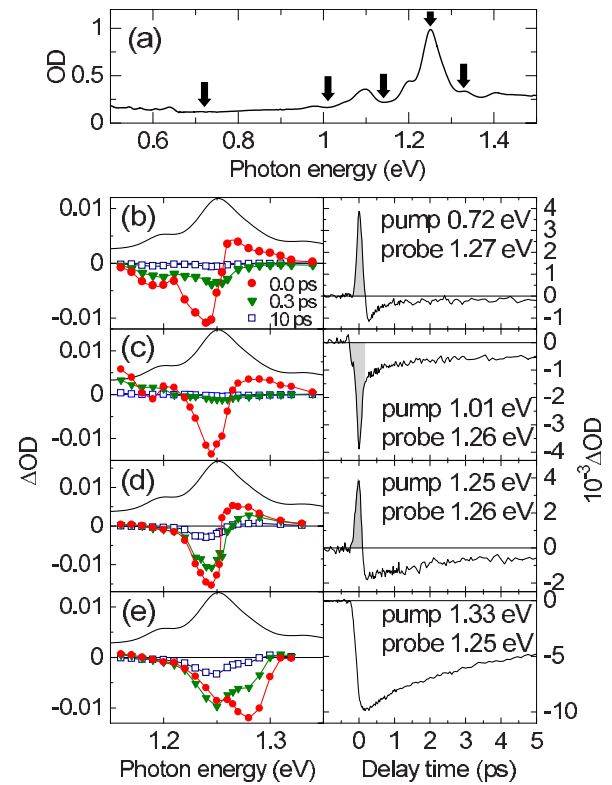


FIG. 3. (Color online) (a) The OD spectrum and the pump energies (arrows). (b)–(e) ΔOD spectra and their time characteristics around E_{ex} for pump energies of (b) 0.72, (c) 1.01, (d) 1.25, and (e) 1.33 eV.

$t_d = -0.1, 0.0$ or 0.1 ps, and $\Delta OD(t_d)$ at $t_d = 0.3$ ps, which are shown in Fig. 2(d). $\delta OD(-0.1 \text{ ps})$ and $\delta OD(0.1 \text{ ps})$ were almost equal to the first and second derivative of the original OD spectrum, shown by the broken and solid lines, respectively. Thus, there were two kinds of instantaneous responses, and the spectral shape of δOD changed from the first to the second derivative of the original absorption within ~ 0.2 ps.

To investigate the pump energy (E_p) dependence of the instantaneous response, we measured ΔOD spectra with $E_p = 0.72$ (5×10^{14} ph/ cm^2), 1.01 (1×10^{14} ph/ cm^2), 1.25 (9×10^{11} ph/ cm^2), and 1.33 eV (6×10^{12} ph/ cm^2), which are shown in Figs. 3(b)–3(e) with the time characteristics of ΔOD around E_{ex} . The pump energies are indicated by arrows in Fig. 3(a). The 1.25-eV pump corresponds to a resonant excitation. For the pump energies of 0.72, 1.01, and 1.25 eV, ΔOD spectra showed characteristic minus-plus structures and the time profiles showed spike-like responses similar to those observed for the 1.14-eV pump, as shown in Figs. 3(b)–3(d). In all cases, the magnitudes of the instantaneous responses were proportional to x_{ph} , and the instantaneous response was observed even for $E_p = 0.72$ eV much lower than E_{ex} . Therefore, these can be assigned to coherent third-order NLO responses such as OSE. For $E_p = 1.33$ eV higher than E_{ex} , the ΔOD around E_{ex} showed neither an oscillatory structure nor an instantaneous response. The signal is attributable mainly to absorption saturation by real exciton excitations. According to the time characteristics of ΔOD in Fig. 3(e),

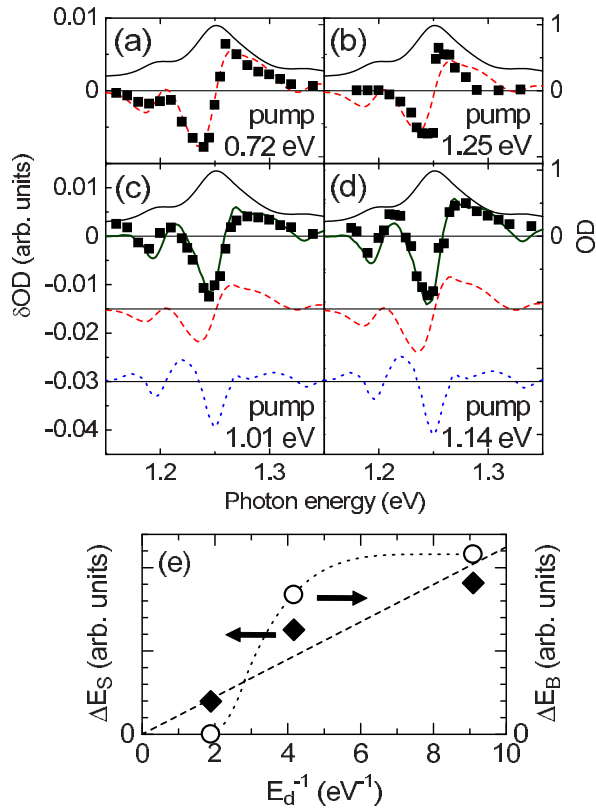


FIG. 4. (Color online) The differential ΔOD spectra, $\delta OD(0.0 \text{ ps}) = [\Delta OD(0.0 \text{ ps}) - \Delta OD(0.3 \text{ ps})]$, for pump energies of (a) 0.72, (b) 1.25, (c) 1.01, and (d) 1.14 eV. The upper solid lines show the OD spectrum. Broken and dotted lines show the first and second derivatives of the OD spectrum, respectively. Thin solid lines show the sum of the first and second derivatives. (e) Magnitudes of the photoinduced shift ΔE_S and broadening ΔE_B as a function of the inverse of the detuning energy E_d . The broken line shows the linear relation for $\mu = 4.4$ (eÅ). The dotted line is a visual guide.

the decay time of the excitons was roughly 10 ps. Disappearance of the instantaneous response was reasonable, since the real exciton excitations sometimes obscured coherent NLO responses.

To investigate the detuning-energy ($E_d = E_{ex} - E_p$) dependence of the instantaneous responses, we calculated $\delta OD(0.0 \text{ ps}) = [\Delta OD(0.0 \text{ ps}) - \Delta OD(0.3 \text{ ps})]$ for various pump energies (Fig. 4). The spectra for $E_p = 1.25$ eV (resonant) and 0.72 eV (off-resonant) showed minus-plus structures, which were in good agreement with the first derivative of the OD spectrum shown by broken lines in Figs. 4(a) and 4(b). For the near-resonant excitation with $E_p = 1.01$ eV, as well as 1.14 eV, the instantaneous component of ΔOD [Figs. 4(c) and 4(d)] can be reproduced by a sum (thin solid lines) of the first (broken lines) and second derivatives (dotted lines) of the OD spectrum. The first derivative of OD corresponds to a blueshift of the exciton transition, which can be reasonably attributed to OSE. The second derivative of OD can be considered a combination of blueshift and redshifts of related transitions due to two kinds of coherent optical nonlinearities or a broadening of the original OD spectrum.

Here, we discuss possible mechanisms for the second-derivative-type responses. Previous studies of inorganic

semiconductors revealed that in the presence of a biexciton, the OSE can cause both blueshift and redshifts of absorptions depending on the magnitude of coupling between an exciton and a biexciton.¹⁵ For example, in CuCl, a redshift of an exciton absorption was observed by photoirradiation just below the biexciton resonance. This phenomenon can be interpreted as repulsive shifts of an exciton and a biexciton level. Theoretical studies suggested that biexciton states of SC-SWNTs are located ~ 50 – 100 meV below twice the exciton energy.^{16,17} Therefore, a similar photo-modulation of exciton levels associated with a biexciton may give rise to a second-derivative-type response. As seen in Figs. 4(c) and 4(d), however, two similar second-derivative signals in ΔOD were observed at different pump energies, 1.14 and 1.01 eV. Therefore, they cannot arise from a resonance effect of the pump pulse on the exciton-biexciton transition. A similar resonance to a transition between an S1 exciton and a higher-energy exciton may be possible. In (6, 5) tubes, however, this possibility can also be excluded, since the energy difference $\Delta E (< E_b)$ between an S1 exciton and a higher-energy exciton in the same sub-band and $\Delta E (\sim 0.92 \text{ eV})$ between the S1 exciton and an exciton in the second-lowest sub-band are much smaller than the pump energies. Thus, we cannot interpret the second-derivative-type spectral changes as a superposition of blueshift and redshifts of the absorption due to OSEs.

Another possible mechanism is a broadening of exciton absorption, which can originate from exciton-exciton scattering. Previous photoluminescence studies on isolated SWNTs revealed that a rapid bimolecular Auger recombination process of excitons, that is a kind of exciton-exciton scattering process, is enhanced due to large exciton binding energies and is the dominant annihilation mechanism at high exciton densities.¹⁸ However, the instantaneous response observed here was proportional to x_{ph} so that a bimolecular recombination process of real excitons does not occur. In addition, the response was observed even for pump energies much lower than E_{ex} , so that it was not induced by real exciton generations. Therefore, the most plausible origin for the observed response is considered to be *virtual* exciton-*real* exciton scattering.

The OSE due to exciton-photon coupling should be detected only during the duration of a pump pulse. In fact, the blueshift (first-derivative) signal was observed as a pulsed response. On the other hand, broadening due to *virtual* exciton-*real* exciton scattering can be observed during the presence of the virtual exciton. Therefore, the decay of the broadening signal will be determined by a phase relaxation time τ_p of an exciton. τ_p was evaluated to be ~ 88 fs in a SC-SWNT with a diameter of 0.8 nm from a width of a PL band (~ 15 meV).¹⁹ In this case, the decay time of the second-derivative-type absorption change due to exciton-exciton scattering will be slightly longer than that of the first-derivative-type due to exciton-photon coupling. This explains well the spectral changes of ΔOD from the first-derivative-type to the second-derivative-type shown in Fig. 2(d).

Effects of real exciton-exciton scattering to exciton dephasing kinetics have been observed as modulation of the dephasing time of excitons in semiconductor quantum struc-

tures. In quantum wires,²⁰ it was reported that the exciton-exciton scattering rate increases with decreasing wire width, and is proportional to the exciton density. However, broadening-type spectral changes due to coherent responses, which dominate ΔOD spectra in our study, have not been detected to date. The isolation of SWNTs has made it possible to detect the broadening-type coherent response for the first time.

In Fig. 4(e), we show the detuning-energy (E_d) dependence of the blueshift ΔE_S (diamonds) and broadening ΔE_B (circles) of the exciton absorption for (6, 5) tubes at $t_d=0$ ps. ΔE_S and ΔE_B are defined as coefficients of the first and second derivatives of the absorption spectrum per unit light intensity. In the dressed exciton picture, ΔE_S in an off-resonant excitation is inversely proportional to E_d , and is expressed by the following formula,¹²

$$\Delta E_S = \frac{\mu^2 F^2}{2E_d}. \quad (1)$$

Here, μ is the transition dipole moment, and F is the electric field of the pump light. The experimental results (diamonds) approximate this formula with $\mu=4.4$ (eÅ), as shown by the

broken line in Fig. 4(e). On the other hand, a magnitude of ΔE_B (circles in Fig. 4(e)) shows steeper detuning-energy dependence than that of ΔE_S . The result demonstrates again that the coherent response characterized by the broadening was caused by a different mechanism from the OSE. To understand the detuning-energy dependence of ΔE_B , further theoretical studies should be necessary.

In summary, we investigated the pump-energy dependence of ultrafast photoinduced changes of exciton absorption in isolated semiconducting-SWNTs. In the case of a pump energy far below the exciton energy, the absorption change was caused only by a blueshift due to the optical Stark effect. In near-resonant excitation conditions, the absorption changes originated from a broadening due to exciton-exciton scattering as well as a blueshift. These results clearly demonstrate the importance of exciton-exciton scattering in ultrafast optical nonlinearity associated with excitons in SWNTs.

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