Near-infrared magneto-optical study of excitonic states in single-walled carbon nanotubes under ultra-high magnetic fields

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Abstract. Singlet excitonic states at the first subband-edge in single-walled carbon nanotubes (SWCNTs) have been studied through near-infrared magneto-absorption spectroscopy under magnetic fields to 105.9 T. Well-resolved absorption spectra of stretch-aligned SWCNT(CoMoCAT)-gelatin films were obtained above 100 T. By the application of magnetic fields in parallel to the alignment of SWCNTs, peak shift toward the lower energy was observed for (8, 4) and (7, 6) tubes and the opposite behavior was observed for (7, 5) and (6, 5) tubes. Above 28.8 T, new peaks emerged at the higher energy side of the peak for the (8, 4) and (7, 6) tubes, and at the lower energy side of the peaks for the (7, 5) and (6, 5) tubes. The magnetic splitting between the existing peak and the new peak was symmetric for every tube, which is in line with the energy splitting due to the Aharonov-Bohm effect. Judging from the energetic positions where the new peaks emerged, the singlet dark excitonic state locates at the lower energy than the singlet bright one in the (7, 5) and (6, 5) tubes while it is suggested strongly that the bright one locates at the lower energy in the (8, 4) and (7, 6) tubes.

1. Introduction

Single-walled carbon nanotube (SWCNT) is one of the ideal materials to study one-dimensional excitonic states. The edges of the conduction bands and the valence bands in this material locate at K and K' points which are degenerate. This feature brings exctionic states at the points 16-fold degeneracy. It is predicted theoretically that the degenerate states is split into two singlet states and twelve triplet states and only the bonding state of the singlet exciton is optically active (bright exciton) and the others are all inactive (dark exciton) due to intra- and inter-valley mixing at K and K' points (K-K' coupling) [1]. As the optical properties of one-dimensional materials are governed strongly by the excitons, their energetic states, especially energetic configuration of the singlet bright and dark excitons, have been studied intensively.

Experimental investigations for this issue have been conducted through photoluminescence (PL) measurements including micro PL spectroscopy under magnetic fields at low temperatures [2, 3]. In these studies, lifting of the degeneracy at the K and K' points due to the Aharonov-Bohm effect by the

application of magnetic fields along the tube axis [4] is utilized to cause brightening of the singlet dark exciton. The authors all concluded that the lower singlet state was assigned to a dark one for every investigated SWCNT, taking into consideration emergence of a new PL peak at the lower energy side of a PL peak dominant at zero tesla. However, PL is not a crucial approach to identify the excitonic states as the PL intensity does not reflect the density of states directly. While the magneto-absorption spectroscopy is more preferable, application of higher magnetic fields is required as the absorption peaks become broad to such an extent in SWCNTs that it is difficult to distinguish spectral changes at conventional magnetic fields.

We have recently developed a near-infrared (NIR) spectroscopy system for absorption measurements under very fast megagauss fields [5]. The system enables us to obtain absorption spectra associated with the first subband-edge excitons in SWCNTs above 100 T. In this paper, we report well-resolved infrared absorption spectra of SWCNTs in the megagauss region and discuss the energetic configuration of the excitonic states.

2. Experimental details

In the absorption measurement system, a xenon short-arc flash lamp (Eagle corp., 600 V, 30 J) was employed as a light source and operated at the discharge voltage of 450 V. The light was delivered to an optical probe through a visible-NIR optical fiber. Transmission measurements were conducted in the Voigt configuration by sandwiching a sample with two right-angled prisms made of BK7 at room temperature. Transmission light was conveyed to a 0.3 m spectrometer (Acton SpectraPro-2300i) with gold coated mirrors through another visible-NIR optical fiber. These employed fibers were of the graded-indexed type with a core of 800 μm in diameter. Spectral light intensities were detected with an InGaAs photodiode array (Xenics, XLIN 1.7, 0.9-1.7 μm, 512 pixels of 25 μm in pitch and 500 μm in height). The detector was cooled down to 260 K thermo-electrically during the measurements.

Magnetic fields were generated using a single-turn coil system with a fast capacitor bank (40 kV, 100 kJ) [6]. Though the single-turn coils made of copper were destroyed after discharge due to the strong Maxwell stress, the probe settled in the coil bore was not destroyed as the coil was destroyed outward. A pick-up coil for the measurement of magnetic fields was positioned away from the field center by 2.3 mm along the radial direction in the optical probe. The deviation of the measured field from the center field was estimated at 1.5% at most when a field coil with both the inner diameter and the width of 12 mm was used [7]. Magnetic fields with the peak field below 30 T were generated non-destructively with a single-turn coil reinforced with a collar made of iron.

A typical wave form of the magnetic fields is shown in Fig. 1. In this experiment, a pulsed field with the peak field of 108.3 T was generated using a coil with the diameter of 12 mm and a discharge
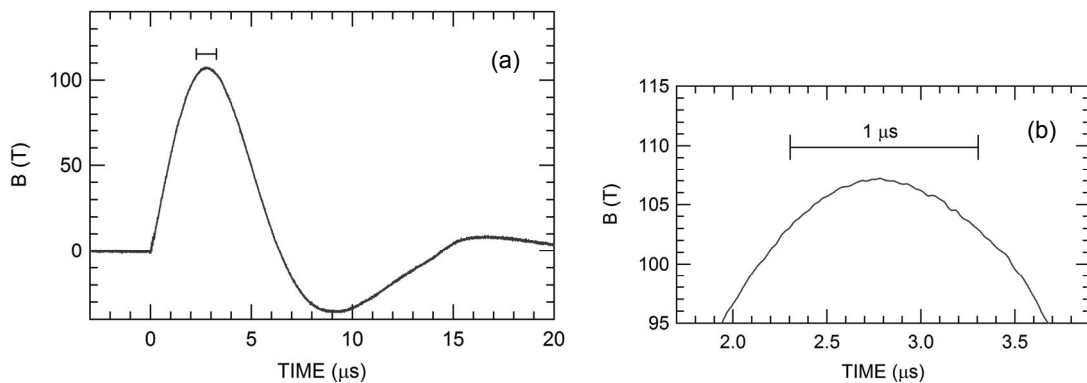

Figure 1. Wave form of a pulsed magnetic field generated using a copper coil with the diameter of 12 mm and a discharge voltage of 35 kV in the single-turn coil system. (a) The whole wave form of the pulsed field. (b) Enlarged view of the field pulse around the peak. The exposure period of the detector array is indicated with the horizontal lines.

voltage of 35 kV. In the absorption measurement, the InGaAs diode array was exposed to the spectral light for 1 μs while the pulsed field was almost maximal as exhibited in Fig. 1(b). Field variation during the exposure time was around 1.2%.

Absorption measurements were conducted for aligned SWCNT-gelatin composite films prepared in the same procedure reported previously. SWCNTs (CoMoCAT) were dispersed with sodium dodecylbenzene sulfonate (SDBS) in gelatin matrix and four times stretch-aligned along the plane of the films. Magnetic fields were applied either in parallel (hereafter, parallel configuration) or in perpendicular (perpendicular configuration) to the alignment of SWCNTs in the Voigt geometry. The light incident on the sample was also polarized in parallel to the alignment of SWCNTs with an NIR linear polarizer.

3. Results and discussion

Figure 2(a) displays magnetic field expansion of absorption spectra of a stretch-aligned SWCNT film in the parallel configuration. Three absorption peaks at the photon energies of 1.097, 1.203 and 1.256 eV were recognized at zero tesla. The peaks at 1.203 and 1.256 eV are assigned to the first subband-edge singlet bright excitons in SWCNTs with the chirality vectors of (7, 5) and (6, 5), respectively. As for the peak at 1.097 eV, those excitons in (8, 4) and (7, 6) tubes are thought to contribute to the absorption comparably. The small difference of about 9 meV between those exciton energies [8] made it difficult to distinguish the two corresponding absorption peaks.

With increasing the magnetic field, peak shift toward the lower energy was observed for the (8, 4) and (7, 6) tubes and that toward the higher energy was observed for the (7, 5) and (6, 5) tubes. Above 28.8 T, new peaks emerged at the higher energy side of the peak for the (8, 4) and (7, 6) tubes, and at the lower energy side of the peaks for the (7, 5) and (6, 5) tubes. In the perpendicular configuration, neither peak shift nor emergence of new peaks was recognized up to 105.2 T (Fig. 2(b)). Judging from these results, we have determined that the magnetically induced peak shift is attributed to the Aharonov-Bohm effect and that the emergence of new peaks is associated with brightening of the singlet dark exciton following the lifting of the degeneracy of the K and K' valleys due to the Aharonov-Bohm effect.
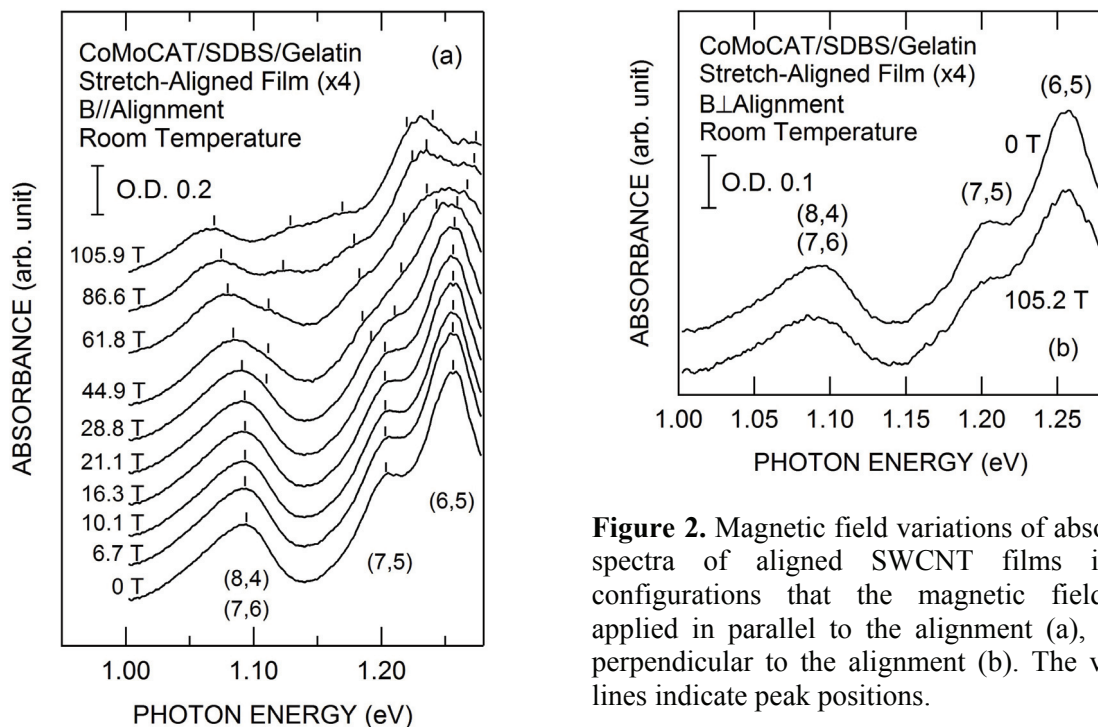

Figure 2. Magnetic field variations of absorption spectra of aligned SWCNT films in the configurations that the magnetic fields are applied in parallel to the alignment (a), and in perpendicular to the alignment (b). The vertical lines indicate peak positions.
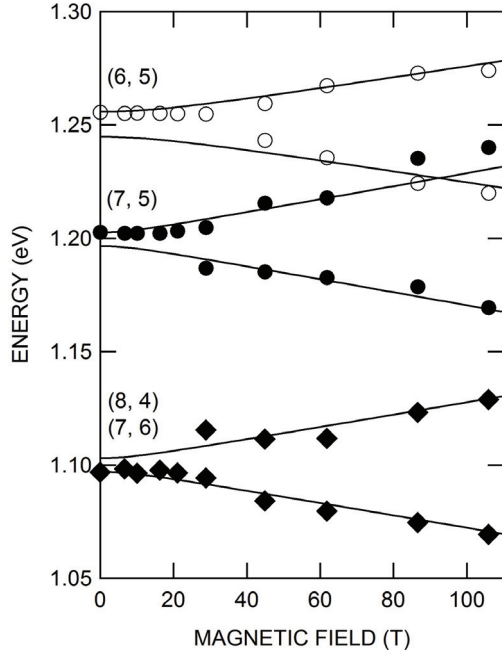
Figure 3. Magnetic field dependence of energies of absorption peaks in the configurations that the magnetic fields are applied in parallel to the alignment of SWCNTs. Lines indicate the results of the perturbation calculation fitted to the experimental data.

Table 1. The diameter calculated assuming the C-C bond length to be 0.144 nm, the energy gap between the first subbands without the K-K' coupling, the splitting energy between the singlet bright and dark excitonic states Δ_{bd}, lower singlet excitonic state in SWCNTs with chiral vectors investigated in this study.

Chirality	Diameter (nm)	Energy gap (eV)	Δ_{bd} (meV)	Lower state
(6, 5)	0.756	1.250	11	Dark
(7, 5)	0.827	1.200	6	Dark
(8, 4), (7, 6)	0.839, 0.893	1.100	6	Bright (tentative)

The absorption spectra for the parallel configuration were deconvolved with Gaussian functions to determine the peak energies precisely. Magnetic field dependence of the peak energies is exhibited in Fig. 3. It is clearly recognized that the splitting between the absorption peak dominant at zero tesla and the new peak emerging in higher fields is symmetric for the (8, 4), (7, 6), (7, 5) and (6, 5) tubes, which is theoretically predicted [1]. This feature was missing in the micro-PL experiments reported previously [2, 3]. Therefore, it would be more conclusive to determine the excitonic states using magneto-absorption techniques. Judging from the relative energy position of the emergence of new peaks, the energetic configuration of the singlet bright and dark excitonic states can be determined for each SWCNT as listed in Table 1. We have analyzed the magnetic field dependence of the peak energies using the perturbation theory where the splitting energy between the singlet bright and dark excitonic states Δ_{bd} (bright-dark splitting energy) is introduced to the off-diagonal terms of a 2×2 matrix and the splitting of energy levels due to the Aharonov-Bohm effect is incorporated. The experimental results were reproduced quantitatively as shown in Fig. 3, and the first subband gap energy without the K-K' coupling and the bright-dark splitting energy were derived for each SWCNT as listed in Table 1. The tendency that the bright-dark splitting energy becomes smaller with increasing the tube diameter is admitted for the (6, 5) and (7, 5) tubes, which is in line with the previous PL works [2, 3].

As for the (8, 4) and (7, 6) tubes, the magnetic behavior of their absorption peaks could not be distinguished in this study. The possibility that the two energy branches of the absorption is corresponding to a magnetic splitting of the bright excitonic states in these tubes would be denied. The magnetic enhancement of the upper energy branch of the absorption suggests strongly that the branch

is corresponding to a dark excitonic state. We assign the lower singlet excitonic state as the bright state for both tubes tentatively. However, further study using, for example, samples in which the (8, 4) or (7, 6) tubes are isolated is required to confirm the assignment.

4. Conclusion
The successful observation of the symmetric splitting of the exciton energies has proved that the NIR magneto-absorption spectroscopy of aligned SWCNT films to the megagauss region is a conclusive approach to determine the energy states of the first subband-edge singlet excitons in SWCNT. As reported in the previous micro-PL studies, the tendency that the splitting energy between the singlet bright and dark excitonic states becomes smaller with increasing the tube diameter is admitted for the (6, 5) and (7, 5) tubes. The lower singlet excitonic state is also confirmed to be dark for the (6, 5) and (7, 5) tubes. As for the (8, 4) and (7, 6) tubes, the possibility that the lower state is the bright one is strongly suggested.

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