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研究課題名（和文）Development of ultra-efficient terahertz devices by exploiting multiple exciton generation in single-walled carbon nanotubes

研究課題名（英文）Development of ultra-efficient terahertz devices by exploiting multiple exciton generation in single-walled carbon nanotubes

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研究成果の概要（和文）：私たちはプロジェクトの過程で次のマイルストーンを達成しました: (1) 光伝導アンテナデバイスへのカーボンナノチューブ (CNT) の統合の成功、(2) テラヘルツ (THz) エミッターとしての有望な効率の実証、(3) THz 放射 分光法は、低次元物質の準粒子ダイナミクスを解明する強力なツールです。

研究成果の学術的意義や社会的意義
We were able to get a clearer understanding of dynamics of free carriers and excitons in carbon nanotubes. From a scientific standpoint, this demonstrates the drastically different behavior of low-dimensional materials. It also brings us closer to their application in future optoelectronic devices.

研究成果の概要（英文）：We achieved the following milestones over the course of our project: (1) successful integration of carbon nanotubes (CNTs) in photoconductive antenna devices, (2) demonstrated their promising efficiencies as terahertz (THz) emitters, and (3) showed that THz emission spectroscopy is a powerful tool in unraveling quasiparticle dynamics in low dimensional materials.

研究分野：THz science and technology

キーワード：carbon nanotubes　terahertz emission　photocurrent

１．研究開始当初の背景

Carrier multiplication (CM), and similarly multiple exciton (electron-hole pair) generation (MEG), is the process where several carriers are generated upon the absorption of a single photon. This has been observed in many bulk semiconductors, and more recently in nanomaterial systems such as single-walled carbon nanotubes (SWCNT) (*Acc. Chem. Res*. **2013**, 46, 6, 1358). There are at least two proposed mechanisms for MEG in SWCNT - direct creation of multiple excitons after optical excitation (*Phys. Rev. Lett.* **2012**, 108, 227401) and impact excitation (bias-driven) due to energetic hot carriers (*Science* **2009**, 325, 1367). Although the fundamental mechanism of CM and MEG is still a controversy, it is clear that these processes are of great interest because of the prospect of developing next-generation solar cells and other light-harvesting technologies with conversion efficiencies way beyond the Schockley-Quisser limit.

２．研究の目的

The primary goal of the research is to develop ultra-efficient THz devices based on SWCNT, using device structure designs that exploit and/or enhance the MEG process. To achieve this goal, it is critical to understand the dynamics of quasiparticles (free carriers, excitons, phonons, etc.) in SWCNT. SWCNT is a 1-dimensional (1D) material, with behavior that differs drastically from conventional bulk semiconductors used in current technology.

３．研究の方法

We employed terahertz (THz) emission spectroscopy, together with photocurrent measurements and numerical simulations, to understand the quasiparticle dynamics under strong electric fields in SWCNT. We used highly-aligned and chirality-enriched SWCNT films prepared by the controlled vacuum filtration (CVF) method (*Nat. Nanotechnol.* **2016**, 11, 633; *Nano Lett.* **2020**, 20, 4, 2332). These films we then incorporated in standard photoconductive antenna (PCA) switches used as THz devices (Fig. 1). The overall alignment direction of SWCNTs was parallel to the direction of the

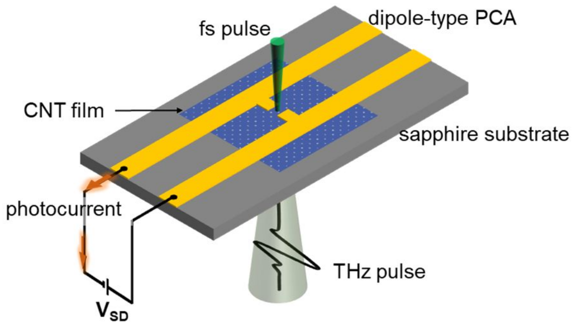

Fig. 1. Device and experimental schematic diagram.

applied electric field. For THz emission and photocurrent measurements, the samples were photoexcited with femtosecond pulses (~150fs) with energies between 1.65 to 2.53 eV. This allows excitation of excitons in the second band (E_{22}) for the (6,5) SWCNTs used in our work. The emitted THz radiation was then guided by a pair of off-axis parabolic mirrors into a separate PCA switch for detection. Biasing and measurement of the photocurrent were done using the same electrodes as illustrated in Fig. 1. Both THz emission and photocurrent were measured by lock-in detection. All the measurements were taken at vacuum conditions (~1×10-3 Pa). For theoretical simulations, we used a newly-developed numerical method that solves the Boltzmann transport and scattering equation while completely considering the strongly out-of-equilibrium scattering integrals. This allowed us to model the thermalization processes which is directly related to the THz emission process.

４．研究成果

Figure 2 summarizes the key findings in our research project. The key processes occurring after the initial excitation of E_{22} excitons are depicted in Fig. 2a while Fig. 2b shows the population in the electronic and excitonic bands at the different time scales indicated in Fig. 2a . The excitons, which are charge-neutral and therefore not affected by the electric field, undergo the usual phonon scattering processes, they lose energy and decay to the bottom band where they survive for a long period before recombining. A portion of the initial E_{22} excitons become free carriers through a process of spontaneous exciton autoionization. These carriers are then accelerated, creating a burst of THz radiation in the process. Some of the electrons gain enough kinetic energy which allows them to create additional excitons by exciton impact generation. This process becomes stronger with bias, and thus the total number of excitons has a component that also increases with bias (the other component being the one directly excited by the laser). The additional current produced by the slow thermal autoionization (Fig. 2a) of these excitons then is responsible for the superlinear behavior of photocurrent with bias (Fig. 2c). The linear dependence of THz amplitude with bias stems from the fact that only the free carriers generated in the beginning contribute to the THz generation.

Our results provide a clear understanding of the microscopic process leading to THz and photocurrent generation in SWCNTs. This pushes us a bit closer to the realization of advanced optoelectronic devices based on low-dimensional materials that can potentially outperform existing technologies.

The main results of this project are published at this journal:

Journal: ACS Nano Letters
Title:“Terahertz Excitonics in Carbon Nanotubes: Exciton Autoionization and Multiplication”
Authors: Filchito Renee G. Bagsican, Michael Wais, Natsumi Komatsu, Weilu Gao, Lincoln W. Weber, Kazunori Serita, Hironaru Murakami, Karsten Held, Frank A. Hegmann, Masayoshi Tonouchi, Junichiro Kono, Iwao Kawayama and Marco Battiato
Publication date: March 31, 2020
Doi: https://doi.org/10.1021/acs.nanolett.9b05082

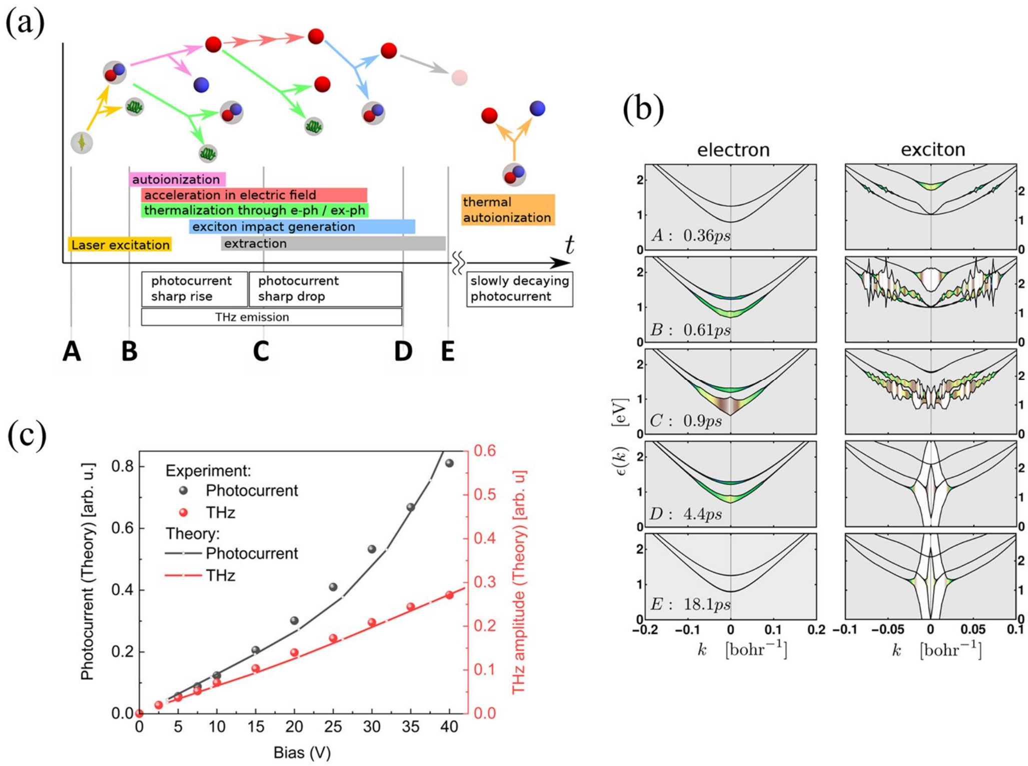

Fig. 2. (a) Qualitative description of the most influential scattering processes at different time scales. (b) Time snapshots of the electronic and excitonic band populations displayed over the dispersion at different time scales indicated in (a). (c) Comparison of the computed peak amplitude of the THz emission and photocurrent with experimental results.

５．主な発表論文等

〔雑誌論文〕　計2件（うち査読付論文　2件／うち国際共著　2件／うちオープンアクセス　2件）

１．著者名 Filchito Renee G. Bagsican, Michael Wais, Natsumi Komatsu, Weilu Gao, Lincoln W. Weber, Kazunori Serita, Hironaru Murakami, Karsten Held, Frank A. Hegmann, Masayoshi Tonouchi, Junichiro Kono, Iwao Kawayama, and Marco Battiato	４．巻 20, 05
２．論文標題 Terahertz Excitonics in Carbon Nanotubes: Exciton Autoionization and Multiplication	５．発行年 2020年
３．雑誌名 ACS Nano Letters	６．最初と最後の頁 3098-3105
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.nanolett.9b05082	査読の有無 有
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１．著者名 Mannan Abdul、Bagsican Filchito Renee G.、Yamahara Kota、Kawayama Iwao、Murakami Hironaru、Bremers Heiko、Rossow Uwe、Hangleiter Andreas、Turchinovich Dmitry、Tonouchi Masayoshi	４．巻 n/a
２．論文標題 Ultrafast Terahertz Nanoseismology of GaInN/GaN Multiple Quantum Wells	５．発行年 2021年
３．雑誌名 Advanced Optical Materials	６．最初と最後の頁 2100258～2100258
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/adom.202100258	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

〔学会発表〕　計6件（うち招待講演　3件／うち国際学会　6件）

１．発表者名 Filchito Renee G. Bagsican, Iwao Kawayama, Hironaru Murakami, and Masayoshi Tonouchi
２．発表標題 Terahertz science and technology: exploring the last frontier of the electromagnetic spectrum
３．学会等名 21st SPVM National Physics Conference, and 2019 Int’l. Conference on Advanced Functional Materials and Nanotechnology（招待講演）（国際学会）
４．発表年 2019年

１．発表者名 Filchito Renee G. Bagsican, Iwao Kawayama, Michael Wais, Natsumi Komatsu, Kazunori Serita, Weilu Gao, Lincoln Weber, Marco Battiato, Hironaru Murakami, Frank A. Hegmann, Junichiro Kono and Masayoshi Tonouchi
２．発表標題 Probing photocarrier dyamics in semiconducting carbon nanotubes by terahertz emission spectroscopy
３．学会等名 21st SPVM National Physics Conference, and 2019 Int’l. Conference on Advanced Functional Materials and Nanotechnology（招待講演）（国際学会）
４．発表年 2019年

１．発表者名 Filchito Renee G. Bagsican, Iwao Kawayama, Hironaru Murakami, and Masayoshi Tonouchi
２．発表標題 Laser terahertz emission microscopy as an investigative tool for low-dimensional materials
３．学会等名 The 1st International Conference in Science and Mathematics (ICSM 2019)（招待講演）（国際学会）
４．発表年 2019年

１．発表者名 F.R. Bagsican, I. Kawayama, M. Wais, N. Komatsu, K. Serita, W. Gao, L. Weber, M. Battiato, H. Murakami, F.A. Hegmann, J. Kono, and M. Tonouchi
２．発表標題 Terahertz Emission from a Photoconductive Antenna Switch Based on Aligned Single-Chirality Semiconducting Carbon Nanotubes
３．学会等名 The 21st International Conference on Electron Dynamics in Semiconductors, Optoelectronics and Nanostructures (EDISON21)（国際学会）
４．発表年 2019年

１．発表者名 F.R. Bagsican, I. Kawayama, M. Wais, N. Komatsu, K. Serita, W. Gao, L. Weber, M. Battiato, H. Murakami, F.A. Hegmann, J. Kono, and M. Tonouchi
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３．学会等名 Optical Terahertz Science & Technology Conference (OTST)（国際学会）
４．発表年 2019年

１．発表者名 Filchito Bagsican, Michael Wais, Natsumi Komatsu, Weilu Gao, Kazunori Serita, Hironaru Murakami, Karsten Held, Iwao Kawayama, Junichiro Kono, Masayoshi Tonouchi, Marco Battiato
２．発表標題 Ultrafast Exciton Dynamics in Semiconducting Carbon Nanotubes Probed by Terahertz Emission and Photocurrent Spectroscopy
３．学会等名 The 81st JSAP Autumn Meeting（国際学会（国際学会）
４．発表年 2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
米国	Rice University			
シンガポール	Nanyang Technological University			