Functional Materials Science and Engineering Research Section

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1. Introduction

Our research section focuses on the physical properties, functions, and energy applications of quantum materials that exhibit significant quantum mechanical effects, such as carbon nanotubes (CNT) and recently discovered topological materials. The aim is to create new technologies for highly efficient use of solar light/thermal energy that will contribute to the realization of a sustainable energy society. To understand the unique physical properties of these materials from the fundamental principles and extract superior functions that exceed the limits of conventional materials, we are promoting interdisciplinary research that covers basic sciences, including condensed matter physics and materials synthesis, as well as thermal, mechanical, electronic, and optical engineering along with the fabrication of integrated nanomaterials. Followings are main research achievements in the year of 2021.

2. Development of theory of exciton thermal radiation in semiconducting single-walled carbon nanotubes

As one of the advanced application technologies of thermal radiation, thermophotovoltaic power generation technology is under development. In this power generation method, thermal radiation generated from a hot object is used as an input to a photovoltaic cell to generate electricity (Figure 1a). In principle, the energy conversion efficiency is high when the radiation energy is concentrated in the near-infrared wavelength region near the band gap of the photovoltaic cell, and therefore, materials with high emissivity only in the near-infrared region and high thermal stability are suitable as materials for thermal radiation generating components called wavelength selective emitters.

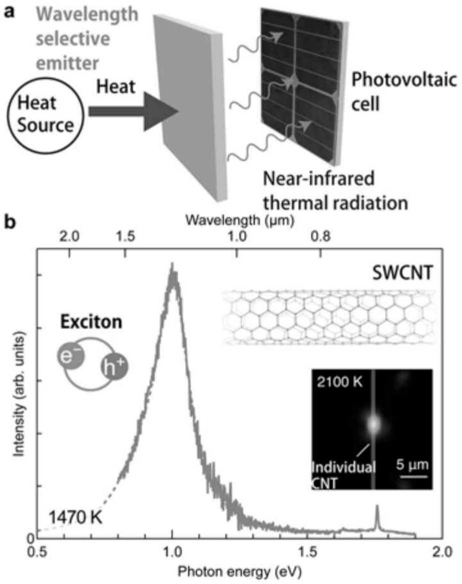

Fig. 1 (a) Schematic of thermophotovoltaic power generation. (b) Thermal radiation spectrum of a single suspended SWCNT. Inset shows an example of an SWCNT structure (top) and microscopy image of the thermal radiation at 2100 K from an individual SWCNT.

Single-walled carbon nanotubes (SWCNTs), which are nanoscale materials (nanomaterials) composed of a single layer of graphene sheet rolled up into a cylindrical shape with a diameter of the order of 1 nm, are promising materials with such characteristics. Previously, we revealed that SWCNTs show significantly narrow-band near-infrared thermal radiation in the near infrared wavelength range (Figure 1b) [1] based on the direct observation of the thermal radiation from an individual suspended SWCNTs heated to temperatures above 1000 K using dark-field microscopy in vacuum. Recently, we have theoretically clarified that this narrow bandwidth is a consequence of the very strong Coulomb interaction between electrons (negative charge) and holes (positive charge) in SWCNTs. Unlike in conventional materials, the electrons and holes are bound to each other and move in a correlated manner in SWCNTs. Therefore, thermal excitation of an electron and a hole leads to formation of a hydrogen atom-like quantum state called exciton. The exciton has a discrete energy level structure similar to that of a hydrogen atom, and thus has well-defined energy, and the annihilation of the exciton generates a narrow-band thermal radiation reflecting the exciton energy. To theoretically investigate light emission due to thermal excitons, we used fluctuational electromagnetics to derive a simple and practical formula for emissivity $e(\omega)$ that appropriately incorporates the structure of SWCNTs and exciton effect

$$e(\omega) = \frac{\omega d}{3c}\mathrm{Im}[\varepsilon(\omega)],$$

where d is the diameter, c is the speed of light, and $\varepsilon(\omega)$ is the dielectric function. With this formula, the emissivity can be easily obtained given the diameter and dielectric function of the SWCNTs, allowing us to study the thermal radiation due to thermal excitons at various diameters.

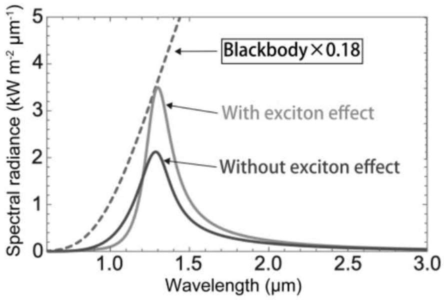

Fig. 2 Theoretically calculated thermal radiation spectra of an SWCNT at 1300 K with and without considering the excitonic effect. Dashed curve indicates 0.18-multiplied black body radiation spectrum at 1300 K.

Figure 2 shows the calculated thermal radiation spectra of an SWCNT with a diameter of 1.1 nm at 1300 K with and without exciton effect (the dotted line is the blackbody radiation spectrum at 1300 K). It is clearly shown that the exciton effect increases the thermal radiation intensity and narrows the line width. Also, compared to the blackbody thermal radiation spectrum, the thermal radiation from an SWCNT has a very narrow line width. This result is in good agreement with the experimental result shown in Figure 1b and proves the correctness of the thermal radiation theory of thermal excitons obtained in this study [2].

2. Complex refractive index measurement of carbon nanotube membranes - Toward wavelength selective radiation and absorption applications

In order to design thermo-optic devices such as wavelength-selective emitters that require precise control of spectral emissivity, information on the complex refractive index spectrum, which defines the macroscopic optical properties of the material, is necessary. In particular, the complex refractive index spectra of SWCNT membranes with a well-defined chiral structure are required because there exist variety of nanotube species with different chiral structures reflecting the degree of freedom in the wrapping of graphene, and the exciton energy is determined by the structure of the SWCNTs. However, broadband complex refractive index spectra of single chiral structure SWCNT membranes have not been reported so far, which has hindered the development of SWCNT-based optical devices, including wavelength selective emitters.

Response functions, such as optical susceptibility describing the response of a material to light, are generally complex numbers. Therefore, physical properties such as the refractive index obtained from the susceptibility are also generally expressed in terms of complex numbers that depend on the frequency. In this study, we determined the complex refractive index spectra of membranes of five different chiral structures. The results are summarized in Figure 3, which shows similar spectral shapes except for the difference in the resonance energy of the exciton peak sensitive to the nanotube chiral structure (chirality) indicated by two integers. From this similarity, we further examined whether the complex refractive index spectra can be reproduced simply by using only the average values of the parameters obtained from the five types of SWCNT membranes. The gray shaded area in Figure 3b shows the reproduced values, and it is found that most of the experimental data can be covered by taking into account an error of ±20%. This result implies that the complex refractive index spectra of SWCNT membranes other than these five types of chirality could also be predicted to some extent by extrapolation. Using the empirical formula for the complex refractive index spectrum, now one can design various optical and thermo-optical devices such as wavelength-selective emitters matching the band gap of photovoltaic cells, wavelength-selective absorber films, and dielectric multilayers combining SWCNTs and other materials [3].

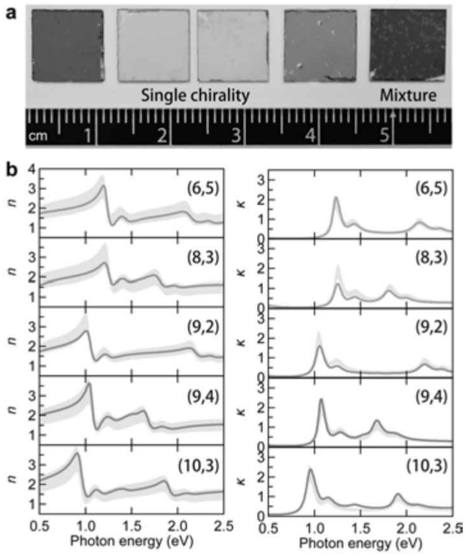

Fig. 3 (a) Photograph of single chirality (left four samples) and mixed chirality SWCNT membrane (right). (b) Real (left) and imaginary (right) parts of the complex refractive index spectra of five different SWCNT membranes.

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