

Functional Materials Science and Engineering Research Section

Y. Miyauchi, Professor

T. Nishihara, Junior Associate Professor

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, two-dimensional semiconductors, 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 materials synthesis and condensed matter physics, 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 2024.

2. Coalescence of carbon nanotubes while preserving the chiral angles

One of the most difficult challenges in the science of nanocarbons, such as carbon nanotubes and fullerenes, is the solid-state chemical reaction of sequentially cleaving and recombining numerous carbon-carbon bonds into new bonds with atomic-level precision. In particular, coalescing large nanocarbon molecules such as fullerenes and carbon nanotubes and converting them into even larger nanocarbon molecules (Figure 1) is known to be a difficult problem. For fullerenes, which are made up of 60 carbon atoms, it is known that two fullerenes can be coalesced together using a solid-state reaction (Figure 1(a)). Moreover, many fullerenes can be coalesced together and converted into nanotubes by confining them in a carbon nanotube and then heat-treating them at high temperatures. However, synthesizing many new nanotubes by coalescing carbon nanotubes together (Figure 1(b)), which are made up of several thousand to tens of thousands of carbon atoms, has been considered to be extremely difficult due to the large number of carbon-carbon bonds that have to be rearranged.

The electronic, optical, chemical, thermal, and mechanical properties of carbon nanotubes are strongly dependent on their geometric structure, which is defined by the diameter and chiral angle of the nanotube (Figure 1(a)). Therefore, to date, extensive research

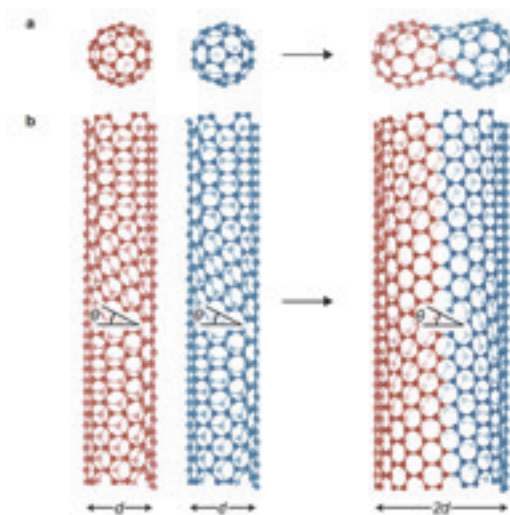


Fig. 1 Coalescence of fullerenes (a) and carbon nanotubes (b) into large coalesced molecules. θ and d in (b) are the chiral angle and diameter, respectively.

has been conducted to achieve complete structural control synthesis and structural separation of nanotubes. However, the methods known to date have only enabled structure-selective synthesis and separation on a macroscale for thin nanotubes with diameters of around or less than 1 nm. This is because, for relatively thick nanotubes with diameters of around 1.3 nm or more, there are a very large number of geometrically feasible nanotube structures with similar diameters and properties, making it difficult to create or separate specific structures. The precise atomic-level carbon nanotube coalescence achieved in this study could be one of the most promising approaches to solving this problem. Since it is possible to produce high-purity samples of thin nanotubes, if it is possible to cause efficient coalescence reactions in them, it will be possible to achieve structure-selective synthesis of thick nanotubes using thin nanotubes as precursors. Furthermore, by using this reaction, it will also be possible to cause partial coalescence reactions by performing post-processing on nanotube aggregates, and to form sp^2 covalent bonds between nanotubes. The technology of dramatically changing the macroscopic properties of nanotube assemblies through post-processing is expected to be very useful for various applications of nanotube assemblies on a macroscale.

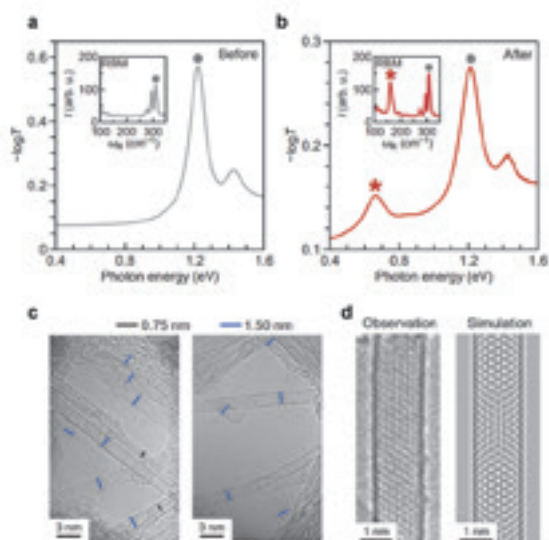


Fig. 2 Optical absorption ($-\log T$, where T is transmittance) spectra of (6,5) nanotube membranes before (a) and after (b) the vacuum heat treatment. The insets show the radial breathing mode (RBM) features of the Raman spectra. I and ω_R are intensity and Raman shift. The gray filled circles indicate the peaks corresponding to the (6,5) nanotubes with $d \approx 0.75$ nm and the chiral angle of $\approx 27^\circ$. (c) Transmission electron microscope (TEM) images obtained for the samples after vacuum heat treatment at 900°C . Bars with different colors indicates lengths corresponding to diameters of typical nanotubes found in the sample. (d) Comparison of the observed TEM image of the newly generated nanotube with $d \approx 1.5$ nm, and simulated one for a (12,10) nanotube with $d \approx 1.5$ nm and the chiral angle of $\approx 27^\circ$.

In this study, we discovered that thin carbon nanotubes can be efficiently coalesced into thicker nanotubes with twice the diameter using a simple heat treatment. This process involves heating structurally separated carbon nanotube aggregates at $900\text{--}1000^\circ\text{C}$ under a reduced pressure of approximately 5×10^{-4} Pa (Figure 2). Furthermore, we found that in the presence of a trace amount of oxygen (around 10 Pa), oxygen acts as a catalyst and the temperature required for the coalescence reaction can be reduced to 600°C , which is more than 1000°C lower than the required heat treatment temperature reported in previous studies. The obtained thick nanotubes were confirmed by Raman scattering spectroscopy (Inset of Figure 2(a,b)) and aberration-corrected transmission electron microscopy (TEM, Figure 2(c,d)) to have doubled in diameter while maintaining the chiral angle of the precursor thin nanotubes. In addition, the measurement of the light absorption spectra confirmed that the nanotube coalescence reaction occurred efficiently throughout the entire nanotube film (Figure 2(a,b)). This study presents the first clear observation of exciton resonance peaks, demonstrating that the nanotubes synthesized through coalescence exhibit the characteristic

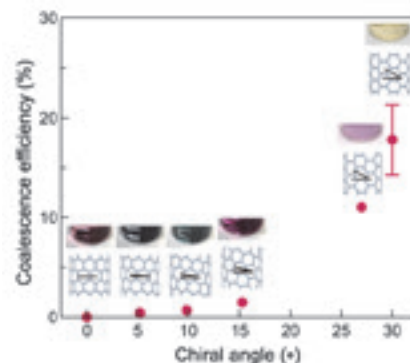


Fig. 3 Efficiency of the coalescence reaction as a function of chiral angle. The inset diagrams show photos (above) and partial structures (below) of the dispersion solution of thin carbon nanotubes (precursors). The angle between the black lines indicates the chiral angles of each nanotube structure.

optical properties of a specific carbon nanotube structure. This also clearly shows that the coalesced nanotubes exist in large numbers in the macroscopic sample, and that they actually have the electronic structure unique to a specific type of nanotube. It is noteworthy that only “armchair”-type and “near-armchair”-type nanotubes with a chiral angle of exactly or near 30° efficiently coalesce, and there is almost no coalescence of nanotubes with a small chiral angle (Figure 3). This result strongly indicates the structure dependence of the energy cost of coalescence reactions due to geometric factors. In this study, we also proposed a rational mechanism to understand the structure dependence of the observed nanotube coalescence efficiency.

This research has provided useful findings for various future applications of carbon nanotubes, such as the structure-selective synthesis of relatively thick carbon nanotubes, which has been difficult to achieve until now, and the modification of the physical properties of carbon nanotube aggregates through post-processing. Furthermore, from a broader perspective, this work presents a novel concept in nanomaterials science: macroscale materials with new physical properties can be created using precisely structure-controlled nanomaterials enabled by recent advances in nanotechnology.

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Collaboration Works

宮内雄平, 浙江大学 (中華人民共和国), 高純度半導体型カーボンナノチューブ試料の作製とヘテロ構造化

Financial Support

1. Grant-in-Aid for Scientific Research

宮内雄平, 基盤研究(S), エネルギー科学展開に向けた量子熱光物性の基盤構築

宮内雄平, 挑戦的研究 (開拓), 量子非平衡吸収体を用いた太陽光熱利用の原理的革新

西原大志, 基盤研究(B), 熱励起子ポラリトン状態の実現と熱放射制御原理の開拓

西原大志, 基盤研究(S), エネルギー科学展開に向けた量子熱光物性の基盤構築 (分担金)

Wu Hengkai, 特別研究員奨励費, カーボンナノチューブの量子熱光物性に基づく超高効率太陽光選択吸収体の実現

川上未央子, 特別研究員奨励費, 精密熱ふく射スペクトル制御に向けた異種ナノ物質薄膜の多重積層技術の開拓

2. Others

宮内雄平, (公財) 井上科学振興財団, 第 15 回エネルギー理工学研究所国際シンポジウム

西原大志, 科学技術振興機構 創発的研究支援, ナノシステム制御による太陽光利用の技術革新

Publications

A. Takakura, T. Nishihara, K. Harano, O. Cretu, T. Tanaka, H. Kataura, Y. Miyauchi, Coalescence of carbon nanotubes while preserving the chiral angles, *Nature Communications*, 16, 1093, 2025

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