

Research Report

Deterministic manipulation of carbon nanotubes for optical devices

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When device scaling reaches the limit imposed by atoms, technology based on atomically precise structures is expected to emerge. In this technology, the assembly of building blocks with identified atomic arrangements without contamination plays a key role. We propose a transfer technique for deterministic fabrication of carbon-nanotube-based optical devices. By using single-crystalline anthracene as a medium, which can form large-area thin films, clean nanotubes are placed on a wide range of substrates. Under in-situ optical monitoring, nanotubes of desired chirality can be placed onto the desired location with sub-micron accuracy. This paper introduces the details of the transfer technique, followed by a few examples of the deterministic construction of heterostructures consisting of nanotubes with defined atomic arrangements and other nanomaterials/nanostructures.

Received July 31, 2022; Accepted August 30, 2022

Translated from Oyo Buturi 91, 736 (2022) DOI: https://doi.org/10.11470/oubutsu.91.12_736

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1. Overview

Ever since Feynman proposed the concept of nanotechnology in his 1959 lecture [1], miniaturization of devices has been a driving force of technological innovation. Driven by scientific curiosity and a desire for better technology, the trend of miniaturization is expected to continue until devices are composed of materials and interfaces that are controlled at the atomic level. That destination is likely to be full of rich phenomena beyond our expectations. An example is the two-dimensional van der Waals heterostructure combining atomic layer materials such as graphene and transition metal dicalcogenides. This heterostructure is attracting attention because of the many completely new physical phenomena that emerge when the materials are stacked by controlling the number of layers and angle of rotation of materials with structures defined at atomic scale [2–4]. In cases where stacking materials in layers does not give sufficient combinatorial freedom, it is desirable to combine and use materials of different dimensions. However, building blocks such as single atoms and molecules whose structure is defined at atomic scale [5] are difficult to maintain and manipulate under room temperature or ambient conditions [6]. Conversely, in semiconductor nanostructures such as quantum dots [7], it is difficult to obtain the same structure repeatedly at atomic level.

From this perspective, the carbon nanotube (CNT) can be an ideal material for constructing technologies controlled at atomic level. The reason is that the same atomic arrangement can be reproduced repeatedly by specifying a pair of integers (n, m) called chirality. To date, researchers have demonstrated the ability to find a single CNT with the desired chirality, measured its optical properties [8], and built transistors [9], light-emitting diodes [10], and other devices by post-processing. However, combining CNTs with other nanostructures and nanomaterials to provide higher-order functionality and integration requires a technique for precisely arranging CNTs with identified structures at the desired location. For example, when the light emission of a CNT is controlled by a optical

microcavity [11] that functions only at a specific wavelength, the positions and wavelengths of both must be matched, and if this process is left to brute-force search, the time and effort increase quadratically. Polymer-mediated transfer technology [12,13] and the like offer the advantage of a wider choice of surface shapes and materials for the substrates on which the devices are constructed, but care must be taken to ensure that clean surfaces and interfaces can be maintained.

Based on the stamping method [14], which has been applied to two-dimensional materials in a number of reports, we have implemented a new technique to transfer nanotubes cleanly to the desired location by using single-crystalline anthracene, which readily sublimates, as a mediating film [15]. Furthermore, by simultaneously performing microspectroscopy during this transfer process, we are able to position the nanotubes, which have a uniquely identifiable structure, with high accuracy while monitoring their position. To explain the details of this method and demonstrate its usefulness, in this paper we present the results of an experiment on deterministically coupling CNT emission to a photonic crystal cavity and an experiment on forming cross-junctions of CNTs with the desired chirality.

2. Key methods

2.1 Stamp transfer via organic molecular crystals

In order to keep CNTs clean and transferable to a variety of substrates, it is desirable to use a medium that forms a large-area, high-strength thin film and that readily sublimates at room temperature and atmospheric pressure. To meet this requirement, we focused on anthracene [16], which consists of three benzene rings, and used single-crystalline anthracene as a sacrificial layer on the surface of a poly(dimethylsiloxane) (PDMS) stamp. Given that anthracene has a molecular structure similar to that of CNTs, one would expect it to have a high ability to pick up CNTs through strong π - π interactions [17].

As shown in Fig. 1(a), we constructed a nanomaterial transfer system in which the substrate and the stamp can be moved independently by two three-dimensional feedback

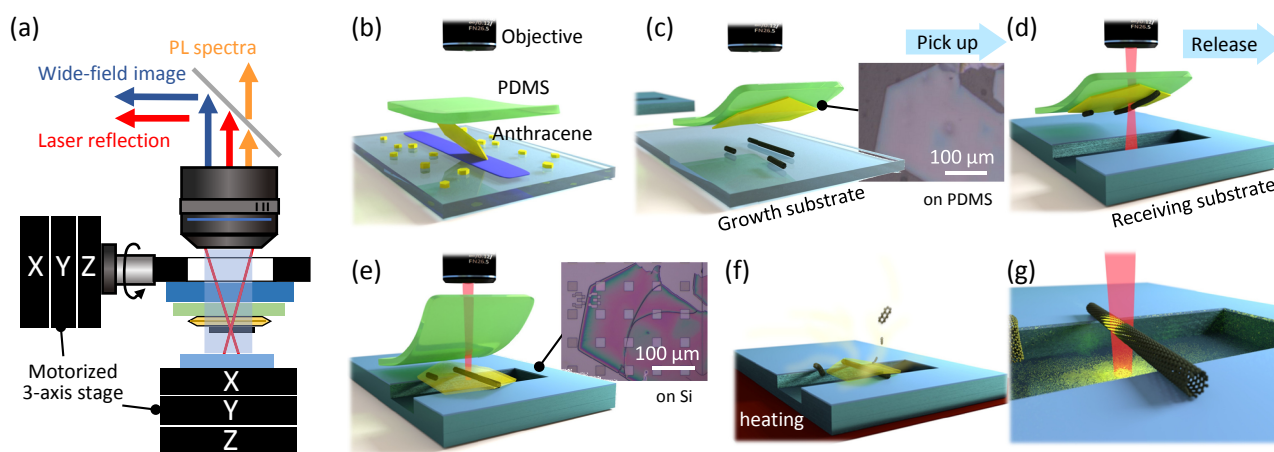


Fig. 1. (a) Schematic of the transfer system that can monitor the photoluminescence from CNTs, the reflected laser, and the wide-field optical images. (b) Single-crystalline anthracene grown on glass is picked up with a PDMS stamp. (c) The PDMS/anthracene stamp is used to pick up CNTs, (d) followed by a PL measurement to locate a desired CNT. (e) Anthracene/CNTs are transferred on a receiving substrate. (f) By heating the substrate to sublime the anthracene crystal, (g) a CNT alone remains. Insets in (c, e) display the optical image of an anthracene crystal transferred on a silicon chip with square pits.

stages. The first step is to attach the grown anthracene single crystal on the surface of the PDMS sheet (Fig. 1(b)). By pressing the flat surface of the anthracene crystal against the substrate on which the CNTs are synthesized and quickly pulling it away, a large number of CNTs can be picked up on its surface (Fig. 1(c)). Then, by pressing the stamp against the transfer destination substrate and slowly peeling it off, the CNTs are left on the substrate together with the anthracene crystals [18] (Figs. 1(d) and 1(e)). When the substrate is heated in air, the anthracene sublimates (Fig. 1(f)), resulting in the transfer of only the CNTs.

Anthracene can be easily grown as a large-area single crystal, and given that it forms a mechanically stable thin film, it is easy to transfer to substrates with trenches and pits. In addition, given that the anthracene sublimates in approximately 10 min at 100 °C or in a few days at room temperature, the CNTs attached to the anthracene surface can be transferred to any location. Transfer methods involving the dissolution or melting of polymers [12,13] are unable to keep single CNTs suspended across (over) a trench. However, given that anthracene does not exert capillary force during sublimation, it is suitable for forming air-suspended structures (Fig. 1(g)), and can be expected to produce high-efficiency light emission unaffected by the substrate.

2.2 In-situ monitoring of single-nanotube emission

To specify the chirality and orientation of the CNTs and place them in the desired location, we integrated the transfer device described above with an optical system that simultaneously acquires reflected laser light, wide-field microscope images, and photoluminescence (PL) from a single nanotube during the transfer process. Unexpectedly, we discovered that the luminous efficiency of the CNTs was maintained on anthracene crystals, and by measuring the PL in real time, we were able to determine the exact position of the CNTs. As a side note, pentacene, in which five benzene rings are connected in a linear structure, can also modulate its energy environment by means of the dielectric screening effect while suppressing non-radiative relaxation of excitons in the CNTs. Taking advantage of this, we reported that local modification of CNTs by pentacene nanoparticles controls the diffusion

of excitons and as a result is effective for single photon generation [19].

In Fig. 1(d), after the CNTs on the substrate used for synthesis were picked up on anthracene crystals, the chirality and coordinates of CNT were identified by scanning measurement using micro PL spectroscopy over several hundred square μm of the single-crystalline anthracene. The transfer destination was precisely aligned with the laser scan image, the CNTs to be transferred were moved on the laser optical axis based on the PL scan image, and finally the stamp was affixed to the substrate. In this way, the CNTs, which are not visible to a camera, became aligned with the destination.

3. Bright emission from clean transfer nanotubes

We first verified whether suspended CNTs with high luminescence intensity could be easily obtained as planned by applying single-crystalline anthracene-mediated transfer to CNTs grown on a quartz substrate [20]. When we transferred oriented CNTs to a SiO_2/Si substrate in which a 5- μm wide trench was etched, we obtained the isolated suspended CNTs shown in Fig. 2(a), indicating that removal by sublimation is effective. These CNTs were approximately 50 μm in length and extended to both sides of the trench, but only the suspended portions could be easily observed by scanning electron microscopy or confocal PL images (Fig. 2(b)). In Fig. 2(c), the red line is the PL spectrum from the suspended portion of the CNT, whereas the green line is the PL spectrum from the portion on the substrate. Comparing both, the luminous efficiency is approximately 250 times higher, the spectral line width is approximately 4 times narrower, and the luminous energy is 55 meV higher in the suspended part. All these numbers are explained by the presence or absence of contact with SiO_2 [21]. This is approximately 5000 times greater than the typical luminescence intensity on a quartz substrate immediately after synthesis, and corresponds to the top 0.1% in strength compared to CNTs suspended at the synthesis stage, thereby confirming that brightly luminescent suspended CNTs can be obtained by transfer via sublimating anthracene.

4. Chirality-on-demand cross-structure formation

Next, for the purpose of demonstrating that the position

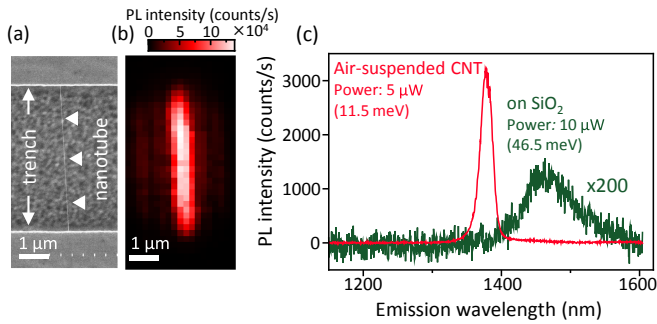


Fig. 2. (a) Scanning electron microscopy image (b) and the corresponding PL image of a transferred CNT over a trench. (c) PL spectra of the CNT measured at an air-suspended region (red) and at a region in contact with the substrate surface (green). Numbers in parentheses show the full width at half maximum.

and orientation of CNTs with the desired chirality can be controlled and transferred, we formed two CNT crossing structures with different chirality and investigated their exciton behavior by PL monitoring during the transfer process. Here, we focus on (10, 5) and (13, 5) as combinations of chirality (n, m) with moderately different absorption and emission wavelengths. First, we transferred CNTs via anthracene crystals onto a Si substrate coated with poly-methyl methacrylate. This is because CNTs in contact with certain polymers emit light brightly, albeit with an efficiency of approximately 10–50% of that of CNTs suspended in air [21,22]. After searching the transferred CNT for a one with chirality (10, 5), we adjusted the position and angle of the (13, 5) nanotube newly picked up on the anthracene crystal, and then transferred it in such a way that they intersected each other. When we measured the PL spectrum while scanning the excitation wavelength (at position *b) on the (13, 5) nanotube approximately 1 μm away from the intersection shown in the schematic diagram of Fig. 3(a) (the PL excitation spectrum), we observed peaks only at the absorption and emission energies specific to the (13, 5) nanotube, as shown in Fig. 3(b). By contrast, for the smaller-diameter (10, 5) nanotube, we focused on the PLE spectrum measured at position *c, approximately 500 nm away from the intersection. In addition to the absorption and emission peaks of each CNT, we observed light emission up to 1510 nm corresponding to the (13, 5) nanotube at excitation near 800 nm (horizontal dashed line), which corresponds to the absorption of the

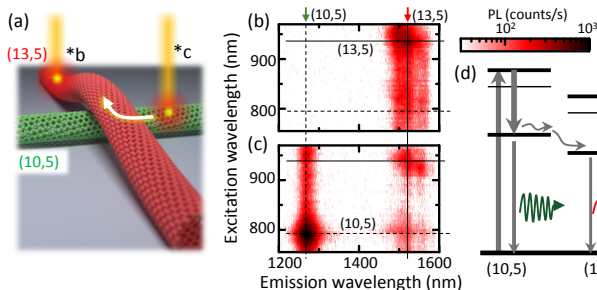


Fig. 3. (a) Schematic showing the cross junction of two CNTs with chiral indices of (10,5) and (13,5). (b, c) PL excitation maps measured at the positions corresponding to *b (b) and *c (c) in the schematic. Horizontal and vertical lines in the maps show the peak positions for absorption and emission, respectively, of the two CNTs. (d) Schematic of energy diagram for the cross-junction structure.

(10, 5) nanotube (Fig. 3(c)). This can be attributed to the process indicated in Fig. 3(d): E₂₂ excitons generated in the (10, 5) nanotube relax to the E₁₁ level, which is followed by diffusion to the CNT intersection, transfer to the other CNT, and recombination. In an appropriate combination of chirality, the exciton energies of both CNTs will coincide, and we can expect to observe resonant and highly efficient exciton transfer [23]. In addition to opening new vistas in basic research, this will lead to the development of new device functions through construction of the desired hetero-structures.

5. Deterministic optical coupling with a optical microcavity

To further demonstrate the effectiveness of chirality selection and position control by this method from the viewpoint of device fabrication, here we present the results of an experiment on deterministically coupling the emission from a single CNT to a photonic crystal optical microcavity. The function of the optical microcavity is to confine light of a specific wavelength in a very small volume. In this study, we used a cavity with a one-dimensional Si nanobeam structure with periodic air holes [11,24,25], as shown in Fig. 4(a). This structure requires the CNTs that match the specific modes and emission wavelengths of the nanobeam cavity—that is, CNTs of specific (n, m)—to be arranged orthogonally. Furthermore, given that the out-of-plane leakage of the electric field is small, the CNTs must be placed very close to the cavity in the z -direction as well. However, if the CNT comes into contact with the Si cavity, almost all its excitons undergo non-radiative relaxation (see Fig. 2). To overcome this trade-off, we used hexagonal boron nitride (hBN) with a thickness of ~30 nm as a spacer. In a previous study, we showed that hBN, which can adopt any thickness based on the number of layers, is also an ideal substrate for maintaining the luminescence intensity of CNTs [26].

The procedure for the transfer of hBN and CNT, which is rather complex, is summarized in Fig. 4(b). First, we observed that the fundamental mode of the test nanobeam cavity was redshifted by approximately 28 nm after the transfer of the

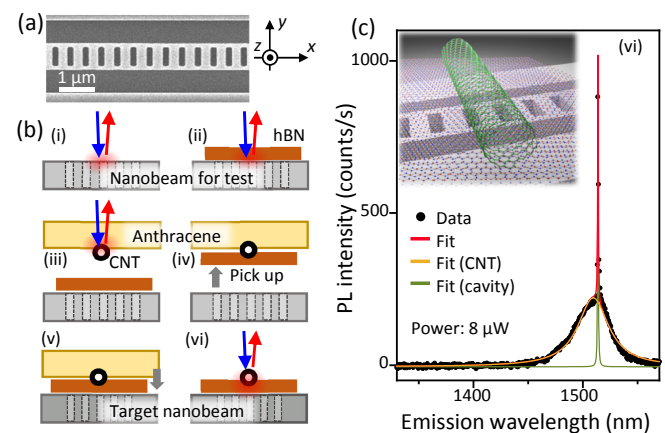


Fig. 4. (a) Typical SEM image of a nanobeam cavity. (b) Schematics showing the procedures for deterministic transfer of a CNT/hBN stacked structure onto a nanobeam cavity. (c) PL spectra of the CNT coupled to the nanobeam cavity through hBN spacer. Black dots are data and solid lines show the Lorentzian multi-peak fits. Inset: Schematic of the CNT/hBN/nanobeam cavity device.

hBN flake used in this study (i–ii). For further details on cavity mode shifts associated with 2D material stacking with different dielectric constants, please refer to a recent study of ours [27]. Next, we found a (13,5) nanotube on the anthracene crystal (iii), took the above-mentioned hBN flake, and formed a laminated structure of anthracene/CNT/hBN (iv). Knowing in advance that the emission wavelength of (13,5) nanotubes on hBN shifts to 1502 nm [25], we selected a cavity such that a mode appears near 1502 nm when the hBN flake is stacked. While monitoring the PL and reflected laser light, we aligned the CNT and cavity and transferred the layered structure described above (v). After sublimation of the anthracene, we made the PL measurements (vi). As shown in Fig. 4(c), in addition to the broad peak from the CNTs, we obtained an extremely narrow emission line coupled to the cavity. In scanning and measuring thousands of cavities, in the past we were able to find only a few instances of CNT-coupled light emission [24]. However, this method succeeded at deterministic coupling with a 75% probability, thereby demonstrating the effectiveness of spatial and spectral selection from the viewpoint of device fabrication. It should be noted that the anthracene crystals, which are notably flat, exhibit high affinity not only for CNTs but also for two-dimensional materials [26], which also played an important role in this experiment.

6. Conclusions

In this study, we demonstrated that by using single-crystalline anthracene as a transfer medium, it is possible to monitor the emission of a single nanotube with a uniquely defined structure and to precisely place it at the desired position and angle. Our method is also effective at keeping the surface of CNTs clean and forming suspended structures with high luminous efficiency. The method is not limited to one-dimensional nanotubes, but is also effective for two-dimensional materials such as hBN and tungsten diselenide, and we expect it to be applicable to other nanostructures and material groups as well. In the future, we hope to expand this research to observe new phenomena and achieve novel device functionalities by freely combining building blocks with identified atomic arrangements to construct higher-order structures, regardless of their dimensions.

Acknowledgments

This research is the result of collaborative research with Dr. Nan Fang and Dr. Daiki Yamashita of RIKEN, and Dr. Takashi Taniguchi and Dr. Kenji Watanabe of the National Institute for Materials Science. We thank Prof. Shigeo Maruyama and Prof. Kosuke Nagashio of the University of Tokyo and Assistant Prof. Taiki Inoue of Osaka University for their assistance in sample synthesis and measurements. This research was partially supported by Japan Society for the Promotion of Science (JSPS) Grants-in-Aid for Scientific Research (JP20H02558, JP19J00894, JP20K15137), the Ministry of Internal Affairs and Communications (SCOPE JP191503001), and the Ministry of Education, Culture, Sports, Science and Technology Nanotechnology Platform Project (Microfabrication Platform JPMXP09F19UT0075).

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Profile



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