Laser Lithography of a Tube-in-a-Tube Nanostructure

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Supporting Information

ABSTRACT: Carbon nanotubes hold vast potential for device innovations because their optical and electronic properties can be synthetically tailored at a length scale unattainable by lithographic techniques. However, lithographic patterning of carbon nanotubes with electronic-type control remains one of the major problems for the integration of these nanomaterials for practical device applications. In this work, we propose a laser lithography method for direct-write patterning of devices on thin films of outer wall selectively functionalized double-walled carbon nanotubes (Tube^2). This method is enabled by the reversible removal of surface functional groups with a laser tuned into resonance with the inner tube of Tube^2. We show that it is possible to directly create patterned dot arrays and conductive pathways and circuits on insulating Tube^2 thin films by tuning the resonance of the direct-writing laser with the electronic type of the inner tube (i.e., metallic or semiconducting). The successful patterning was unambiguously confirmed with in situ Raman spectral imaging and electrical characterization. This work suggests the possibility of developing a nanostructure-specific nanofabrication technology reminiscent of thermal printing.

KEYWORDS: nanomaterials, double-walled carbon nanotube, device chemistry, optical selectivity, nanofabrication, thin film

Carbon nanomaterials, such as single-walled carbon nanotubes (SWCNTs) and graphene, possess remarkable optical, electrical, and mechanical properties, which hold vast potential for innovation in biotechnology, electronic, optoelectronic, and other applications. In recent decades, photolithography has been commonly used to pattern extremely small features, producing increasingly sophisticated integrated circuits. However, in the case of CNTs, the critical issues of the mixed populations of and limited control on CNT electronic structures (i.e., metallic or semiconducting) prevent circuits from being turned on completely, creating the necessity for a patterning technique with both high spatial precision as well as structural and electronic-type selectivity. Powerful CNT sorting strategies have been developed for achieving high semiconductor yields, but combination of these sorting techniques with existing patterning technology is often lengthy and it is difficult to integrate both semiconducting and metallic nanostructures within the same device. Other innovative patterning techniques that combine patterning of CNTs with electronic specificity, such as directed assembly and guided growth, have also been proposed. Each of these methods possesses distinct advantages but is still too sophisticated for practical applications. For instance, while directed assembly is capable of creating structure-specific patterns, it necessitates the substrate to be prepatterned physically and chemically, requiring extensive lithography and chemical synthesis steps. On the other hand, guided growth produces highly aligned arrays of CNTs but often utilizes quartz substrates that are not suitable for electronics fabrication, therefore requiring cumbersome transfer processes. A simple, scalable, and rapid technique for integrating CNTs into electronic devices remains an unmet, challenging goal.

In this study, we demonstrate a CNT lithography method that is capable of patterning both semiconducting channels and electrically conductive pathways directly on an insulating nanotube thin film. This method is enabled by a tube-in-a-tube (Tube^2) structure, which was created synthetically through outer tube selective functionalization of double-walled carbon nanotubes (DWCNTs). Nonfunctionalized DWCNT thin films (pristine) are normally conductive, with a sheet conductance of 5–7 S μm−1 for metallic films and an electron mobility of 1.5 cm2 V−1 s−1 for semiconducting films, but functional groups that are covalently attached to the outer tube of Tube^2 prevent electrical contact between the individual nanostructures, making the nanotube thin film insulating. By optical excitation of the Tube^2 with a laser tuned to the resonance of the electronic transitions of the inner tube, the functional groups on the outer tube, where the excited inner tube is nested, are selectively removed (Figure 1a). The removal of the surface functional groups restores the DWCNT
structure and reinstates \( \pi \)-conjugation, thus a conductive pathway can be generated in the otherwise insulating thin film. By this direct-write method, it is possible to directly create functional electronic circuits in thin films, as unambiguously confirmed by Raman spectroscopy and electrical characterization. By using two different lasers that selectively excite metallic and semiconducting inner tubes, we show that both metallic and semiconducting patterns can be created, suggesting a possible path to overcome the critical barrier toward the integration of CNTs for electronics applications.

**RESULTS AND DISCUSSION**

Tube^2 was synthetically created from DWCNTs by selectively functionalizing the outer tube with 4-nitrobenzenediazonium salt, as we previously reported,\(^{20}\) to the exclusion of the inner tube. The sodium dodecyl sulfate (SDS) surfactant that had been used to suspend the DWCNTs in aqueous solutions for the reaction was subsequently removed by vacuum filtration to make a thin film of Tube^2. The visible—NIR absorption spectra of the Tube^2 thin film confirmed that both the E_{11} and E_{22} inner tube absorption features remain after the diazonium reaction, while the outer tube E_{11} absorption greatly diminished compared with the nonfunctionalized DWCNT control (Figure 1b), suggesting successful functionalization of the outer tube selectively.

Raman spectroscopy also corroborated this conclusion (Figure 1c). A DWCNT is composed of one SWCNT nested within another; each tube gives rise to a set of Raman spectral features, including the radial breathing modes (RBM, 100−350 cm^−1), the tangential mode (G peak, ∼1590 cm^−1), and the disorder mode (D peak, ∼1350 cm^−1). The DWCNTs used in this study have two sets of RBMs, which are assigned to the outer (RBM_{outer}, 100−200 cm^−1, diameter ∼1.61 nm) and inner tubes (RBM_{inner}, 240−350 cm^−1, diameter ∼0.86 nm).\(^{23}\) Upon covalent sidewall functionalization of a DWCNT that converts it to Tube^2, both the RBM_{outer} and G peak of the outer tube diminished and the D peak intensity concomitantly increased due to the incorporation of sp\(^3\) defects on the outer tube (Figure S1). Using a laser to optically remove functional groups produces annealed DWCNT (\( \alpha \)-DWCNT), we observed the successful removal of the aryl groups from the outer tubes, as shown by the recovery of the RBM_{outer} and G peak, as well as by the concomitant decrease of the D peak intensity (Figure 1c). Removal of aryl groups from Tube^2 was also observed for \(-C_6H_4Br under the same conditions (excitation wavelength, exposure time, and power density), suggesting that this technique can be generally utilized to remove different functional groups (Figure S2).

We found that selective defunctionalization of the outer tube of Tube^2 required a threshold power density (Figure 2a), below which structural recovery to the DWCNT does not occur despite extended exposure to the 532 nm laser (Figure 2b). Below this threshold power density, the RBM_{outer} features were not recovered. This threshold feature allows us to characterize the annealed films with \textit{in situ} Raman spectroscopy by operating beneath the power threshold to ensure that defunctionalization does not occur. The existence of a threshold power density can be partially understood by the balance of laser-induced heating and heat dissipation. The inner tube of a Tube^2 converts photons to heat efficiently, while the substrate acts as a heat sink. The energy at the sharp transition in Figure 2a resembles the minimum power density required to locally defunctionalize Tube^2, structurally recovering the structure of DWCNT, the Tube^2 precursor. When the laser power density is higher than the threshold energy, resonant excitation of the inner tube defunctionalizes the outer tube, and
the extent of defunctionalization increases linearly as a function of irradiation time until 20 s, at which point ∼50% defunctionalization efficiency is achieved, followed by a negative exponential decay function with τ = 13 s. By 50 s, the defunctionalization approached ∼95% completeness (Figure 2b).

We further observed that this defunctionalization from Tube^2 is specific to its structure. Raman scattering shows that irradiation of Tube^2 by a 532 nm laser recovered its outer tube RBM peak, while under the same irradiation power and duration, a similarly functionalized SWCNT (f-SWCNT) thin film remained flat (Figure S3). We attribute this distinct difference to the presence of nonfunctionalized inner tube in Tube^2, which can be optically excited to defunctionalize the outer tube, while for f-SWCNT, functionalization of the lone nanotube resulted in the loss of the optical transitions that were needed to facilitate resonance-enhanced annealing. This control experiment confirms that the nonfunctionalized inner tube within Tube^2 is an enabling element for the observed laser-induced selective defunctionalization.

The hypothesis that the nonfunctionalized inner tube is essential for laser-induced defunctionalization is corroborated by evidence that only selected outer tube populations are annealed when a particular inner tube chirality is excited (Figure 3). Each DWCNT has a pair of RBM peaks from the outer and inner tubes, whose positions are inversely proportional to tube diameter.4,25 When creating Tube^2 synthetically from a pristine DWCNT precursor solution, the outer tube of the DWCNT is selectively functionalized, resulting in the RBM_{outer} peaks being greatly diminished. This process occurs to all of the outer tube chiralities (both red and gray peaks) within a mixture. However, when these Tube^2 structures were annealed with a 532 nm laser, only the red-shaded RBM_{outer} (160 cm\(^{-1}\)) peak was restored whereas the gray-shaded RBM (147 cm\(^{-1}\)) peak was not.

The observed selective defunctionalization of a particular outer tube population can be understood based on resonant Raman excitation. The single Raman peak within the inner tube region is located at the 269 cm\(^{-1}\) peak, and the possible chiralities are (9,3) and (10,1) based on the Kataura plot. Since the (9,3) is located at the very edge of the resonance window, the 269 cm\(^{-1}\) peak should be predominantly due to the (10,1) chirality, which has a diameter of 0.825 nm. Given the van der Waals spacing in the DWCNTs investigated here (∼0.36 nm),20,23 the outer tube diameter associated with the (10,1) inner tube should be ∼1.55 nm, which translates to an RBM_{outer} peak at ∼160 cm\(^{-1}\). Based on this assignment, the outer tube associated with the red-shaded peak at ∼160 cm\(^{-1}\) is part of DWCNT structures containing the (10,1) inner tube. This is strong evidence that for defunctionalization to occur in an outer tube, the inner tube nested within it must be optically excited. This conclusion is corroborated by the lack of defunctionalization for the gray-shaded population of outer tubes (d ∼ 1.68 nm), whose inner tubes are not optically resonant with the 532 nm laser wavelength. Although the gray peak outer tube is also in resonance with the 532 nm laser, the associated inner tube for this outer tube is not in resonance. Therefore, the gray Raman peak disappears upon functionalization and does not recover by the 532 nm laser annealing.

In contrast, selective annealing of the outer tube may occur even more efficiently when both the inner tube and the recovering outer tube can be resonantly excited by the same laser, as evidenced by the synchronous increase of RBM intensity for both inner and outer tubes of the defunctionalized structures (Figure S4). The increase in RBM intensity for the inner tubes is not expected but may be due to functionalization-induced modification of the strong intrastuctural coupling between inner and outer tubes of a nonfunctionalized DWCNT structure.26−28

We attribute the observed defunctionalization of Tube^2 to thermal annealing effects.30 Tour et al. have demonstrated with thermogravimetric analysis that the temperature needed to thermally detach aryl groups from the CNT lattice is 400−500 °C.30 Although it is difficult to determine the exact defunctionalization temperature for Tube^2, qualitative evidence of thermal heating at increasing irradiation power densities can be derived from in situ Raman downshifts in G peak position (Figure S5). Right below the threshold power density, a downshift by 6−8 cm\(^{-1}\) was observed, corresponding to a temperature of ∼400−500 °C for locally excited nanotubes based on previous temperature-dependent Raman studies by Zhang et al. and Xie et al.31,32 Even upon defunctionalization, which provides a second G_{outer} contribution at high wave-numbers, the left shoulder peak corresponding to the G_{outer} shifts to lower wavenumbers in correlation to higher laser power densities. Furthermore, it has been shown that a high power density laser, such as that used here, is capable of heating CNTs to 300−800 °C.33,34

Figure 3. Raman spectral evidence of inner tube selectivity. The RBMs of pristine DWCNT, Tube^2, and α-DWCNT samples are shown for direct comparison. The top panel displays a Kataura plot in the resonant window of the 532 nm excitation. The laser excitation energy is marked by the solid green line, and the window of resonant excitation is defined by the pair of dashed green lines. In the Raman spectra, the peak in the RBM_{outer} region was deconvoluted into two Lorentzian peak shapes, which are shaded in red and gray for clarity. The possible chiralities for each outer and inner tube peak are highlighted in the Kataura plot.
exhibited a strong dependence on the Tube^2 film thickness. We found that for a thicker film, a lower power density was required to induce laser writing (Figure S6). For thicker Tube^2 films, it is more difficult to selectively defunctionalize the intended outer tube chiralities, while thinner Tube^2 films were much easier to control. We hypothesize that this difference is a result of heat transfer within the nanotube network. At a higher nanotube density, more inner tubes are available to absorb and dissipate the heat, and there is also a greater amount of tube–tube interactions within the network, which results in a higher chance of thermal cross-talk between the nanotubes to generate greater nonselective defunctionalization. We also note that laser annealing of f-SWCNTs can occur at much higher power densities for denser films. However, not being a resonant excitation, defunctionalization of the relatively more transparent f-SWCNT structures is much less efficient compared to inner tube resonant annealing in Tube^2 thin films. We note that the high power density (~50 mW/μm^2) is less desirable for practical, large-scale applications. However, significant reduction of the power density is possible by using DWCNT precursors with tighter structure distribution as separation techniques advance and light sources that are in resonant with the larger inner tube populations of interest. Since the annealing is an optically resonant process, irradiation at a laser wavelength closer to resonant chiral nanostructure’s maximum absorption cross section would result in a lower power density threshold, as indicated also in previous works on thermal destruction of CNTs.

This resonant laser-induced defunctionalization phenomenon provides us with direct-write capability to pattern CNT structures. As a demonstration, we used a 532 nm laser with a power density that exceeded the power threshold (~50 mW/μm^2) to “write” a 2 × 2 array of 2.5 μm diameter dots separated by 5 μm on a Tube^2 thin film (Figure 4). The pattern was subsequently “read” in situ in 0.5 μm steps over a 10 μm × 10 μm area using micro-Raman mapping with the same laser at a lower power density (0.5 mW/μm^2) to avoid further defunctionalization as the spectra were measured. Removal of the functional groups from the outer tubes was unambiguously confirmed by the recovery of the RBM outer and G peaks as well as the diminished D peak. The sharp contrast between the patterned dot array and the unpatterned areas on the Raman maps demonstrates the strong localization effects of resonant laser-induced defunctionalization of Tube^2 structures within a thin film.

We further explored this lithography technique using two different laser excitations: 532 and 633 nm. Using either the 532 or 633 nm laser, we wrote dot arrays on the Tube^2 films and then read both sets of patterns using 532 and 633 nm excitation lines at a lower power density (Figure 5). The result in Figure 5 demonstrates that only the Tube^2 structures with inner tubes that were in resonance with the laser were selectively defunctionalized (indicated by arrow pointing to recovered RBM outer), further corroborating that annealing occurs as a result of optical excitation of the inner tube. Additionally, after writing the Tube^2 thin film using the 532 nm laser, recovery of the outer tube RBM was confirmed by subsequently reading the pattern using the same 532 nm laser at a lower power density, and consistently, the pattern could not be observed when read with the 633 nm laser, which is beyond

Figure 4. In situ Raman mapping confirmed the fabrication of a 2 × 2 dot array on a thin film of Tube^2 by direct laser patterning. The array was written using a 532 nm laser at a power density of 50 mW/μm^2. Next, the Raman spectra were read using the same 532 nm laser at 0.5 mW/μm^2, which was lower than the threshold power density required for annealing/writing. The Raman maps unambiguously confirm the recovery of the DWCNT characteristics, as evidenced by the recovery of the RBM outer and the diminishing D peaks at the patterned dots.
the contrast within SEM images between the interface of covered and exposed areas.

Conductance measurements show that the film was originally insulating with a conductivity 0.4 $\mu S$ (Figure 6e, black open circles), which was attributed to the functional groups of the outer tube preventing the intertube contact needed for a conductive percolating pathway. Upon laser exposure, the Tube*2 structures within the patterned line were defunctionalized, allowing intertube contact between neighboring nanostructures. In this manner, we fabricated a 17 $\mu m$ wide conductive pathway by laser writing. These patterned channels possessed a conductance of 87 $\mu S$, which is over a 200-fold improvement in conductivity (Figure 6e, red filled circles). The conductance of the patterned channel increases linearly with the channel width (Figure 6f). We note that the conductance restored is only 5% of the starting, nonfunctionalized DWCNT film (Figure S8), further supporting optically selective defunctionalization.

To further demonstrate the inner tube selectivity of this resonance-enhanced annealing and extend the applicability of this patterning technique to semiconducting features, we refunctionalize the patterned Tube*2 thin film with the same outer wall selective chemistry. This refunctionalization selectively functionalizes the outer tubes of the laser annealed DWCNT structures to reproduce Tube*2 (labeled as “a-Tube*2” for the fact of the optical de-functionalization step) but does not functionalize the junction areas where the neighboring tubes are in strong van der Waals contact preventing functionalization of the contact (Figure 6a). As a result, refunctionalization once again removes the optical and electrical contributions of the outer tube but preserves the electrical intertube contact that was established by laser annealing as shown in our previous works. By removing the electronic contributions of the outer wall through refunctionalization, the desired inner tube properties, which can be selected by laser wavelength excitation, dominate the overall electrical transport. Using a 532 nm laser, with the ability to selectively excite metallic inner tubes and a 561 nm laser that is resonant with semiconducting inner tube populations, we show that semiconducting and metallic lines can be drawn, respectively (Figure 6g). $I_{ON}−V_T$ curves determined that predominantly metallic inner tube features ($I_{ON}/I_{OFF} = 5$) were created with the 532 nm laser, while p-type semiconducting inner tube ($I_{ON}/I_{OFF} = 50$) features were created upon annealing with the 561 nm laser, which demonstrate that by proper selection of laser excitation energies electronic-type specificity can be achieved. While high ON/OFF ratios are needed for logic circuits, the ON/OFF ratios obtained through the technique proposed here are sufficient for many CNT-based semiconductor devices, such as thin film field-effect transistor sensors, which have demonstrated picomolar sensitivity of DNA sequences with ON/OFF ratios lower than those shown here. We anticipate based on the inner tube optical transitions that the semiconducting selectivity can be further improved by using a laser with greater resonance to semiconducting populations, although such a laser was currently not accessible to us. Furthermore, because the outer tube can be covalently functionalized to such a high degree that a semiconducting inner tube can be chemically gated solely by surface functional groups without the need of a physical gating electrode, transistor sensors in previously unattainable device architectures may be created in a straightforward fashion using this laser lithography method.

Figure 5. Optical patterning is specific to the electronic structure of inner tube. The Tube*2 thin film was written with one laser and subsequently read at a lower power density using Raman spectroscopy. Two laser lines, 532 and 633 nm, were used for the writing (at a power density above the threshold) and reading (at a power density below the threshold), resulting in four spectral combinations. The Raman spectra, before (dashed lines) and after (solid lines) laser annealing, are shown for comparison. The RBM$_{inner}$ peaks that are restored upon annealing are highlighted by red and blue arrows.
CONCLUSIONS

We demonstrate that Tube^2, a DWCNT, and a-Tube^2 thin films. Dotted line and arrows represent electrical transport within the network. The channels are patterned across parallel arrays of gold electrodes (source and drain) deposited on a doped Si wafer, which acts as a global gate. (c) SEM image resolving laser-written channel and insulating Tube^2 film. The laser used here is 561 nm. (d) Periodic intensity profiles of the Raman D/G ratio and the RBM_outer peak intensity revealed for a Tube^2 film patterned using a 532 nm laser. A parallel array of written channels is shown, as indicated by the arrows. (e) I–V curves of a 17 μm wide channel on a Tube^2 film before and after laser writing and (f) current vs channel width of the pathways written using a 532 nm laser. (g) Transport characterization (V_{SD} = −0.1 V) of a Tube^2 film (black) and a-Tube^2 circuits made with 561 nm (green) and 532 nm (red) lasers and then refunctionalized.

METHODS

Preparation of DWCNT Solution. High-purity DWCNTs were separated from a chemical vapor deposition grown sample (Unidym DW411UA) using density gradient ultracentrifugation, as previously reported. The sorted DWCNTs have an average diameter of 0.86 and 1.61 nm for the inner and outer tubes, respectively. One milliliter of the DWCNT solution was dialyzed (Spectra/Por Float-A-Lyzer G2 100 kDa) against 500 mL of 1 wt % SDS/water solution (freshly changed at 2, 12, and 24 h) for a total of 48 h. The DWCNT solution was then diluted with and suspended in 1 wt % SDS/water to a final concentration at which the optical absorbance (o.d.) was 0.2 at 1000 nm.

Diazonium Salt Preparation and Synthesis of Tube^2 Solutions. 4-Nitrobenzenediazonium tetrafluoroborate was synthesized and functionalized to the exclusion of the inner tube, as we previously reported. The salts were stored at 4 °C and used within a week after synthesis. Exposure to light was limited by covering the vial with aluminum foil. Afterward, solutions were diluted to a tube density of 1 mg/L.

Creation of Insulating Tube^2 Film. Thin films were prepared using a vacuum filtration setup in which 1.5 mL of the diluted Tube^2
solution was created using a 47 mm Whatman Anodisc aluminum oxide membrane to filter out surfactants and unreacted reagents. Following filtration, 500 mL of nanopure water was added to remove the residual surfactant. We then carefully loaded the Tube^2 thin film/AAO membrane in a Petri dish containing 40 mL of 3 M sodium hydroxide (Sigma-Aldrich) solution. The thin film was left in the sodium hydroxide solution for 15 min to dissolve the membrane, leaving the Tube^2 thin film floating in solution. The film was delicately transferred to nanopure water four times to rinse the surface and afterward picked up with a clean substrate. The film was then dried on the substrate overnight at room temperature in vacuum. The film thickness could be tuned by controlling concentration and volume of the Tube^2 solution.

**Device Fabrication.** A 10 nm chromium adhesion layer and 50 nm gold were deposited through electron beam deposition on a Tube^2 thin film transferred on an n-type silicon substrate with a 300 nm silicon oxide dielectric layer (Silicon Quest International). Photolithography was then used to pattern electrodes on the Tube^2 thin film, which was 100 μm long and 1500 μm wide, separated by 15 μm to define the channel length.

**Laser Writing on Tube^2 Films.** Arrays of dots and lines were directly written on Tube^2 films using a laser. The exposure time for each dot was 50 s. To extend from discrete spots to lines, the laser was drawn with a step resolution equal to half of the laser spot size. The laser power was tuned by changing the percentage of the power output using optical filters.

Larger scale arrays of conductive pathways were patterned on Tube^2 thin films using a 4 in. chrome photomask on glass (Front Range Photo Mask LLC) and a 561 nm Cobalt Jive laser. The photomask was clamped to the substrate after aligning it to circular pathways, with a channel length of 15 μm, were written across the electrode arrays to form circuits.

**Characterization.** Raman spectra and maps were collected on an Aramis model LabRAM Raman microscope (Horiba Jobin Yvon) using the available excitation lines, 633 and 532 nm. The output of the 633 and 532 nm lasers was 10 and 100 mW, respectively. The laser power was tunable by changing the percentage of the power output using optical filters.

Absorption spectra were measured using a PerkinElmer Lambda 1050 UV−vis−NIR spectrophotometer equipped with a photo-multiplier tube (σ = 2.03% over 48 h of continuous use) and a broad-band InGaAs detector (σ = 1.56% over 48 h of continuous use). The instrument was warmed up for 15 min prior to each use. Electrical measurements were performed using a Keithley 4200-SCS analyzer. For gated measurements, the devices were back-gated using the silicon substrate.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b00624.

Figures S1–S8; Raman spectra and outer tube selectivity correlation, nanostructure specific annealing, correlated evolution of the inner and outer tube RBM peaks, Tube^2 film thickness versus threshold laser power density for annealing, Tube^2 Raman spectra collected at different laser power density, nanolithography patterning using a photomask, and additional electrical measurement results (PDF)

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**Notes**

The authors declare no competing financial interest.

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