# Surface Selective One-Step Fabrication of Carbon Nanotube Thin Films with High Density

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ABSTRACT Thin films of carbon nanotubes (CNTs) are fabricated from solution using a one-step directed assembly strategy. Very high surface selectivity and exceptionally high CNT densities can be observed in small features with complex shapes. This directed assembly technique makes use of minimum amounts of CNTs and low toxicity solvents, and can be applied to metallic, semiconducting and mixed CNTs for fabrication of thin films over macroscopic areas.

The thin films obtained with this approach are used for thin-film transistor (TFT) fabrication, and their electrical characterization is described.
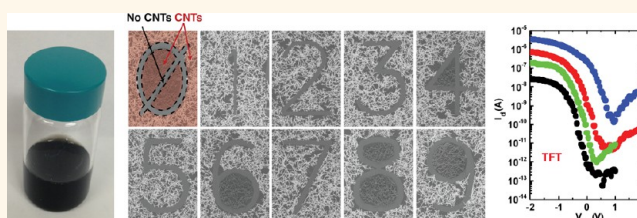
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Carbon nanomaterials are currently being aggressively investigated to meet many of the current and future needs in the fields of computing, security, energy, life sciences and healthcare.[1] Among them, carbon nanotubes (CNTs)[2] in particular are a promising and interesting group of materials due to their unique optical, electronic, and mechanical properties, as well as their chemical versatility.[3] CNT thin films have been demonstrated in numerous applications in different fields,[4] such as sensing,[5−10] catalysis,[11] energy,[12] electronics,[13] and digital logic.[14] However, the manufacturing and commercialization of CNT thin film-based technologies has met limited success, mainly due to the difficulties in processing these materials by adapting traditional solution-based fabrication methods, while keeping processes environmentally friendly and cost-efficient.[8] Ideally, CNT thin films would be deposited from solution to obtain complex thin-film shapes in narrow features in the nano/microscale, while using low toxicity solvents or no solvent at all and minimizing the amount of CNTs and solvent wasted in the process.

As-synthesized CNTs have very low solubility in organic and aqueous solvents.[15,16] Many chemical strategies have been described to modify the surface of CNTs with the purpose of increasing their long-term solubility and adding extra functionality,[2,17] which can also be used as a vehicle for the fabrication of CNT thin films with very high degrees of surface selectivity.[18,19] These solubilization strategies improve CNT surface interaction with the solvent of choice and can take one of two approaches: covalent modification of the CNTs surface[20,21] or use of surfactants to bring CNTs into solution.[19,22] Methods for CNT thin film fabrication by either covalent or surfactant-based approaches typically have one or several of the following limitations: (1) the substrate surface needs to be modified prior to CNT deposition, which increases the number of fabrication steps and cost and can lead to irreproducibility; (2) the density of CNTs in the thin film is too low for practical applications, which usually require densities above the CNT percolation threshold; (3) a large amount of CNTs/solvent is consumed during the fabrication process; (4) the fabrication method is not surface-selective, and complex shapes cannot be obtained; (5) the CNT film features that can be obtained are too large for the desired application.

CNT surface modification by covalent functionalization offers the advantages of long-term stability and chemical integrity of the CNT surface when compared to surfactant-based approaches, which tend to be dynamic systems where the surfactant
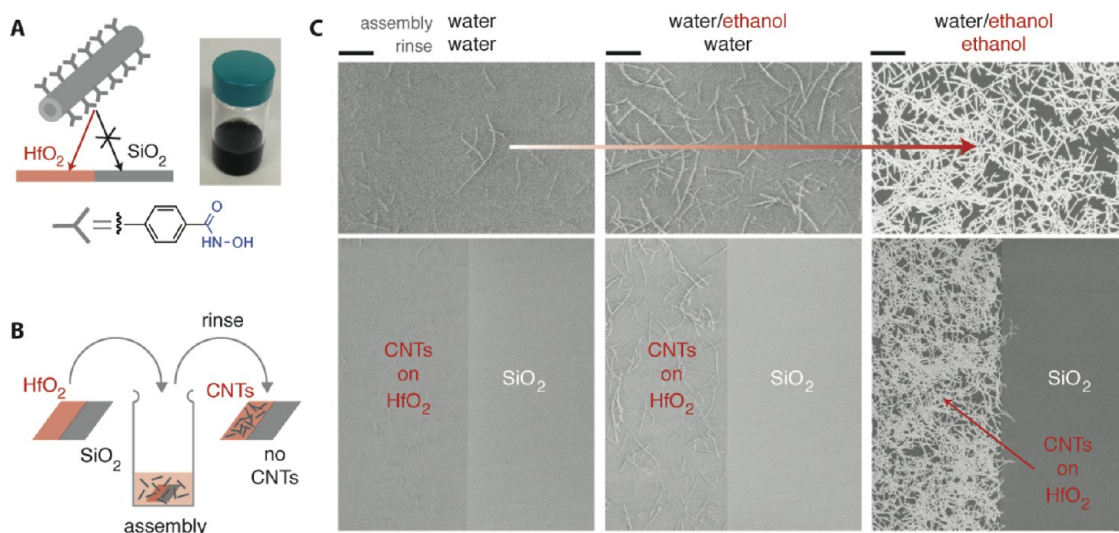
Figure 1. CNT assembly using functionalized CNTs. (A) Surface selectivity of CNTs functionalized with hydroxamic acid moieties. Inset: High concentration CNT solution in water after functionalization and organic moiety on the surface of the CNTs. (B) One-step assembly process: the substrate is exposed to a CNT solution of water/ethanol and then rinsed with water or ethanol followed by drying. (C) CNT thin film density and selectivity on substrates with surfaces of hafnium oxide (HfO$_2$) on silicon dioxide (SiO$_2$), using different solvents for the assembly/rinsing step. From left to right, an increasing amount of ethanol was used in the thin film fabrication process. When water is used as a solvent for the assembly and rinsing (left), the CNT density is relatively low. A much higher CNT density is observed when using a mixture of water/ethanol in the assembly process (middle), and the CNT density is even better when using ethanol as a solvent for rinsing instead of water (right). Scale bars: 1 μm.

is in equilibrium between a "bound state" on the surface of the CNTs and a "free state" in the solvent. This dynamic equilibrium of free/bound surfactant poses difficulties for the storage and use of CNT solutions in the long term. The electronic and optical properties of covalently functionalized CNTs can be recovered by thermal annealing or by chemical means once they have been deposited from solution. CNTs functionalized covalently with organic moieties bearing hydroxamic acids can be used for the selective assembly of CNTs from solution on hafnium oxide (HfO$_2$) surfaces without coating silicon dioxide (SiO$_2$) surfaces also present during the assembly, and no surface treatment prior to the assembly is required (Figure 1A).[23,24] The mechanism is based on the interaction of hydroxamic acids with dielectric materials that are relatively basic over surfaces showing a more acidic behavior.[25] This phenomenon has been used in the past to selectively coat HfO$_2$ surfaces over SiO$_2$ surfaces with hydroxamic acid-functionalized compounds without the need of depositing an initial monolayer.[18,19,23,24] However, the previously reported CNT thin film density using this chemical strategy was relatively low, of only a few CNTs in features that were several micrometers wide.[24]

In this work, we present a method for the fabrication of high-density thin films of CNTs based on covalently functionalized CNTs bearing hydroxamic acids, where only selected areas of a substrate are coated with CNTs with very high selectivity (Figure 1). This technique does not require any previous chemical modification of the surface, and only low toxicity solvents such as

water and ethanol were used. The fabrication and characterization of thin-film transistors (TFTs) with good electrical properties based on these CNT thin-films are also discussed. Since directed assembly techniques are used for film fabrication, very small amounts of CNTs are consumed during the fabrication process, and the solution used for the assembly can be reused.

RESULTS AND DISCUSSION

Many factors can influence the assembly of molecules from solution, such as the surface chemistry, purity, concentration, and solvent. The polarity and surface tension of the solvent used for the assembly have a large effect mainly due to (1) differences in surface wetting and (2) the influence in the degree of interaction between the functional group used for the assembly and the surface/solvent. If substrate wettability is promoted, then the rate of assembly and the degree of interaction can be greatly increased, which can result in a denser molecular assembly. Similarly, if the degree of interaction between the solvent and the compound being assembled is decreased without causing the assembling compound to precipitate, a denser assembly of molecules can also be expected. Ethanol has a much lower polarity and surface tension than water (see Figure S1 in the Supporting Information for contact angle measurements using ethanol and water on typical substrates used for CNT assembly), while still having relatively low levels of toxicity and low cost, making the mixture of ethanol and water an attractive solvent system that can potentially improve the assembly of functionalized CNTs from solution.

The surface of carbon nanotubes was modified using diazonium salt functionalization chemistry,[20,21] which resulted in CNTs having a surface decorated with organic moieties bearing a hydroxamic acid functional group (see Supporting Information for details on the synthesis). Purification of these CNTs was carried out by several cycles of precipitation from a non-solvent such as acetone and by discarding the supernatant. CNTs functionalized with hydroxamic acids can be rendered soluble in water, which makes them suitable for purification by repeated cycles of filtration, washing, and resolubilization in water by resonication. By doing this additional purification step, any side-products and unreacted starting material were removed from the CNT residue. The resulting CNTs were highly soluble in water (Figure 1A), and solutions were stable over a period of months without any visible CNT sedimentation. Covalent functionalization of the CNT surface was confirmed by Raman spectroscopy:[26,27] an increase of the intensity of the defect (D) band at 1350 cm^{-1} relative to the G bands at 1590 cm^{-1} was observed, indicating a higher ratio of defects in the carbon nanotube surface due to the covalent attachment of organic moieties (Supporting Information Figure S4). Large amounts of ethanol of up to 10-fold were added to an aqueous solution of functionalized CNTs without any visible sedimentation of CNTs, and the solutions were also stable for months.

To coat a given substrate with CNTs using directed assembly, the substrate was directly exposed to a solvent carrying the CNTs without any prior modification and then quickly rinsed (Figure 1B). After the solvent used for rinsing was blow-dried, the assembly of CNTs was evaluated by scanning electron microscopy (SEM). When a substrate with patterns of HfO$_2$ on SiO$_2$ was exposed to a solution of functionalized CNTs in water and then rinsed with water, CNTs were selectively placed only on the HfO$_2$ regions of the substrate (Figure 1C, left), albeit the density of the CNT film deposited was low as evidenced by SEM measurements. For several applications including the case of TFT fabrication, a dense network of percolated CNTs is needed, so such low CNT densities below the percolation threshold are detrimental. On the other hand, when a solvent mixture of lower polarity and decreased surface tension (water/ethanol) was used for the assembly, a higher CNT density could be obtained due to the lower polarity and decreased surface tension of the solvent (Figure 1C, middle). This effect was even more pronounced when using ethanol for rinsing the substrate after the assembly instead of water (Figure 1C, right). Mild sonication of the substrates using a bath sonicator after the assembly helped remove CNTs that were nonselectively deposited on SiO$_2$ areas or CNTs that were partially deposited onto the SiO$_2$ regions. Dilution of the CNT solution by equal amounts of water instead of ethanol did not

improve the quality (density, homogeneity) of the CNT films. This technique purely based on assembly from solution contrasts with other CNT film fabrication techniques that rely on drying the CNT solution, which might lead to films with irreproducible CNT density/thickness and where the amount of CNTs used for each individual substrate is much higher. It is also worth noting that compared to popular drop casting methods that inevitably consume large quantities of CNTs, the amount of CNT solution used for each directed assembly run is negligible, and the initial CNT solution could be reused for coating other substrates in this approach. This is particularly important when using a solution of purified CNTs, which are typically more costly and time-consuming to produce.

When different solvents with a lower polarity/surface tension (e.g., 2-propanol, tetrahydrofuran, or acetone) were used for the final rinsing step, similarly high CNT densities were observed. This methodology could also be extended to purified and isolated semiconducting CNTs and metallic CNTs to obtain films with high CNT densities beyond the percolation threshold only on the HfO$_2$ parts of the substrate. While the reactivity of semiconducting CNTs is expected to be lower than that of metallic CNTs, and thus the number of anchoring chemical moieties (hydroxamic acids in this case) would be lower, CNT film densities beyond the percolation threshold were also observed.

Very dense films of CNTs can be obtained both over large areas (of several centimeters) and on smaller features of a few hundred nanometers while still maintaining the surface selectivity (Figure 2A−C). The density of these CNT films is comparable to record methods for CNT coverage of large areas,[18] and much higher than previous reports using covalently functionalized CNTs.[24] This assembly strategy can be used to deposit CNTs without covering smaller features such as the ones delineated by SiO$_2$ on the substrates on Figure 2D, which is difficult to achieve when the attractive surface is elevated and the surface that does not interact with the CNTs is a narrow trench, due to the fact that CNTs can cross over the trenches due to their large aspect ratio. Complex curved shapes of CNT thin-films can be achieved by using this methodology, which is interesting for certain applications such as RFID antennas or advanced sensor design layouts.

The assembly of CNTs was also studied on narrower features of HfO$_2$ (ridges) surrounded by trenches of SiO$_2$ (Figure 2E). CNTs on the HfO$_2$ parts of the substrate were still attached to the substrate even after bath sonication in a solution of water or ethanol. The ridge width was 400 nm for the substrate shown in Figure 2E, and the observed CNT density in these narrower features exceeds the densities previously reported using similar CNTs by orders of magnitude. Similar CNT selectivities and densities were observed throughout different areas of the same substrate (see Figure S2 in the Supporting Information).
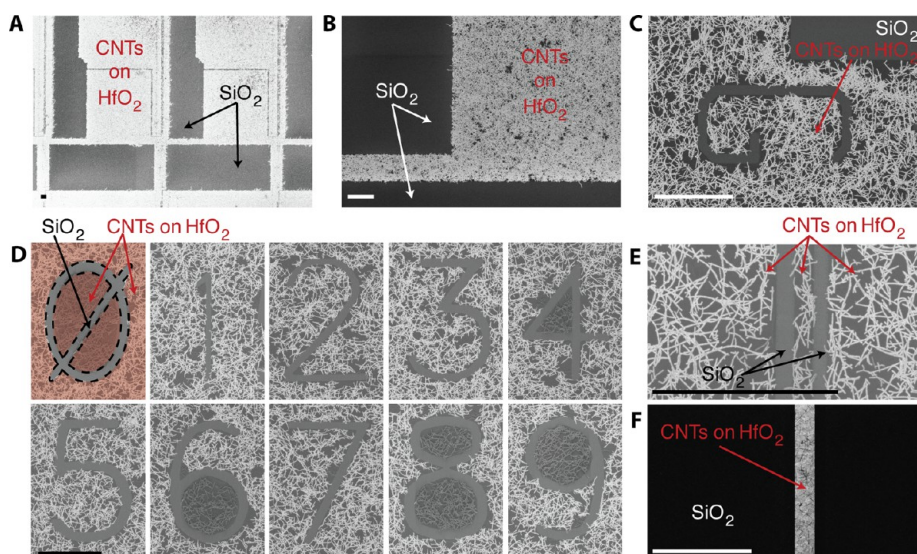
Figure 2. SEM images of CNT thin films on HfO_2/SiO_2 substrates with different features at various length scales. From A to B to C: images showing increased magnification for the same substrate. (D) CNT assembly on a substrate that contains narrow SiO_2 features. HfO_2 areas are completely covered in CNTs and highlighted in red, while SiO_2 trenches are defining the numbers. (E) CNT assembly on narrow HfO_2 ridges. (F) CNT assembly on narrow HfO_2 trenches. Good selectivity is observed while retaining very high CNT densities. Scale bars: 5 μm.

Placement of CNTs *via* directed assembly was also studied on substrates where the attractive HfO_2 surface was a trench instead of a ridge (the underlying surface being HfO_2 and the upper layer SiO_2, Figure 2F). The contrast of this SEM image is different due to the inverted surface composition, with lighter HfO_2 and darker SiO_2 in this particular substrate. Comparable selectivity and densities were also observed for these substrates, even for narrower trench features (see Figure S3 in the Supporting Information for additional SEM images).

To further confirm the homogeneity and reproducibility of this assembly technique, the CNT density was inspected in a feature that could be found across the substrate. In this case, several images of a feature in the shape of a "zero", delineated by SiO_2 trenches, were taken on different parts of the substrate over an area of several square centimeters, and similar CNT densities could be observed as shown in Figure 3. The CNT film density was extremely high while still showing very good selectivity for the HfO_2 areas of the substrate as observed in previous cases.

Previous studies of the electronic properties of functionalized CNTs have shown that well-behaved transistors of isolated CNTs can be obtained,[24] but the CNT film densities in these cases were not good enough to fabricate TFTs where the CNTs form a fully connected network between the source and the drain over larger areas. To test whether this CNT thin film fabrication strategy is suitable for TFT applications, we fabricated and characterized transistors using a thin film of functionalized single-walled carbon nanotubes (SWCNTs) with ~90% semiconducting purity (purchased from NanoIntegris) as the channel. Before device fabrication

and after film assembly, a thermal annealing step was used to remove the ancillary organic moieties bearing hydroxamic acids used to bind the CNTs to the substrate surface.[24] The recovery of the conjugated structure of the semiconducting SWCNTs was studied using Raman spectroscopy: different annealing times and temperatures were tested and the annealing progress was monitored by tracking the intensity of the D band (see Figure 4). Measurements showed that the optoelectronic structure of the CNTs can be fully recovered by annealing at 400 °C under ultrahigh vacuum for 7 min, or just in 30 s at 600 °C.

Arrays of global back-gated TFTs with a channel width of 10 μm and varying channel lengths (L_g) were then fabricated on a Si substrate with 10 nm HfO_2 as gate dielectric (Figure 5A). The 20 nm Pd/20 nm Au source/drain electrodes are patterned using ebeam lithography, metallization, and lift-off process to enable high quality contacts for hole transport. The fabrication is completed by defining the channel regions with oxygen plasma etch. Representative transfer and output characteristics for devices with 1 and 10 μm long channels are shown in Figure 5B, top and bottom, respectively. At drain bias (V_{ds}) of -0.1 V, the device with $L_g = 10$ μm exhibits good performance with an on/off ratio of $\sim10^7$ and a subthreshold swing of ~155 mV/dec. Increasing V_{ds} to -1 V or reducing L_g to 1 μm both increase on current (I_{on}) by $>10\times$ while reducing on/off ratio to $\sim10^5$. The measured on/off ratios are on par with previously reported CNT transistors with similar channel lengths.[28] It is worth noting that the gate bias required to operate these TFTs is very low compared with previous reports due to a very thin gate dielectric (10 nm HfO_2) employed
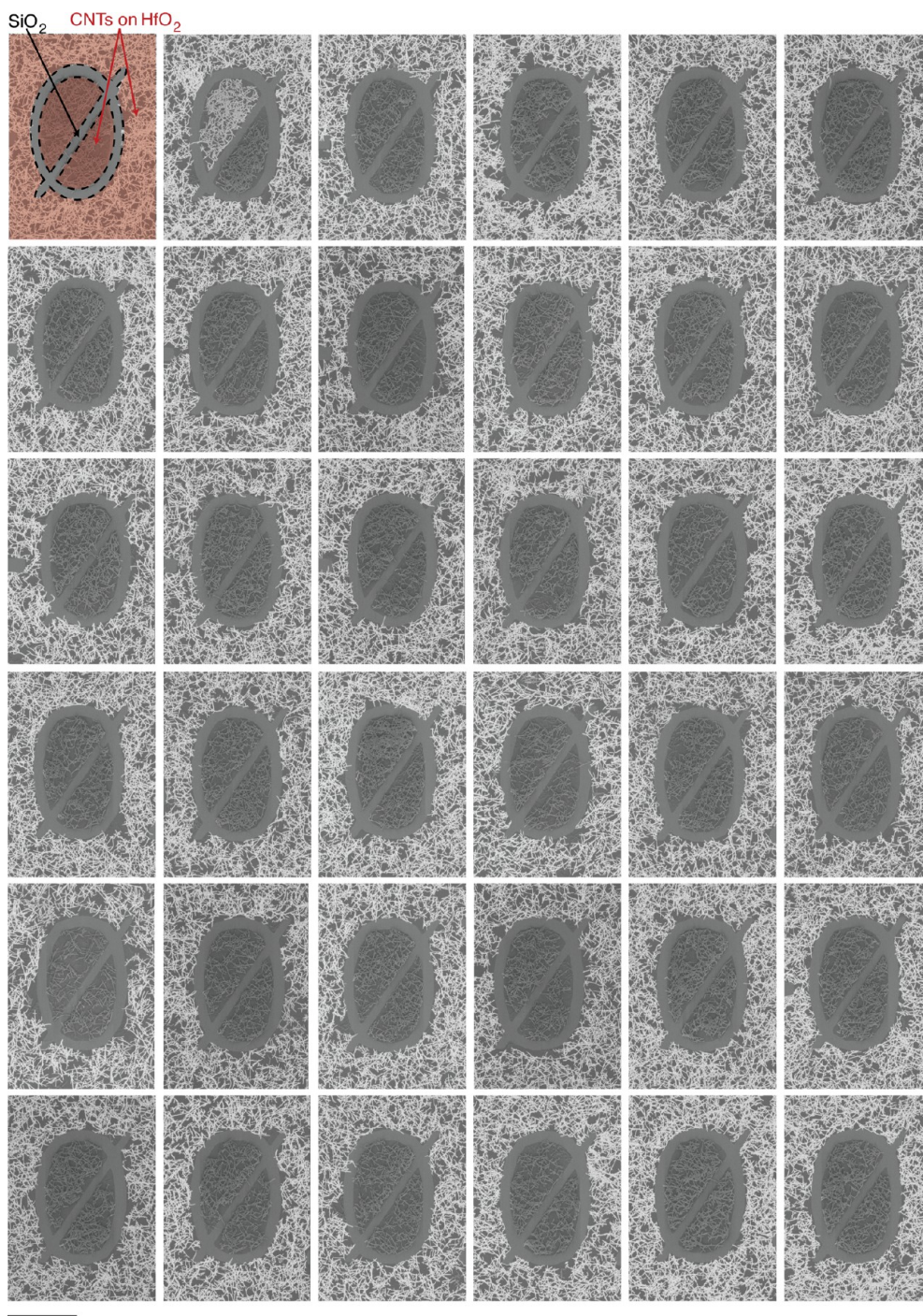
Figure 3. SEM images of CNT assembly on different parts of a substrate with HfO_2/SiO_2 features. The SiO_2 trenches defining the numbers are not covered by CNTs, whereas the HfO_2 areas show very high CNT densities while retaining the selectivity. Scale bar: 5 μm.

in our devices.[29−31] Figure 5D shows the channel length dependence of I_{on} (left) as well as typical hysteresis from 1 μm long device measured at V_{ds} of −1 V (right). The hysteresis (∼0.7 V) can be further reduced by properly passivating the tube and substrate surfaces with hydrophobic monolayers such as hexamethyl-disilazane (HMDS)[32] or dielectrics such as Al_2O_3.[29] The field-effect mobility can be calculated as $(L_g$gm$)/$ $(V_{ds}C_{gate}W)$, where gm is the device transconductance

and C_{gate} is the gate oxide capacitance including the electrostatic coupling between nanotubes and the quantum capacitance.[32] At V_{ds} = −0.55 V, the calculated mobilities are ∼18 and ∼17 cm^2 V^{-1} s^{-1} for 1 and 10 μm long devices, respectively, which are in agreement with the electronic properties described in previous reports and further proves that the structure of the CNTs is recovered upon thermal annealing.
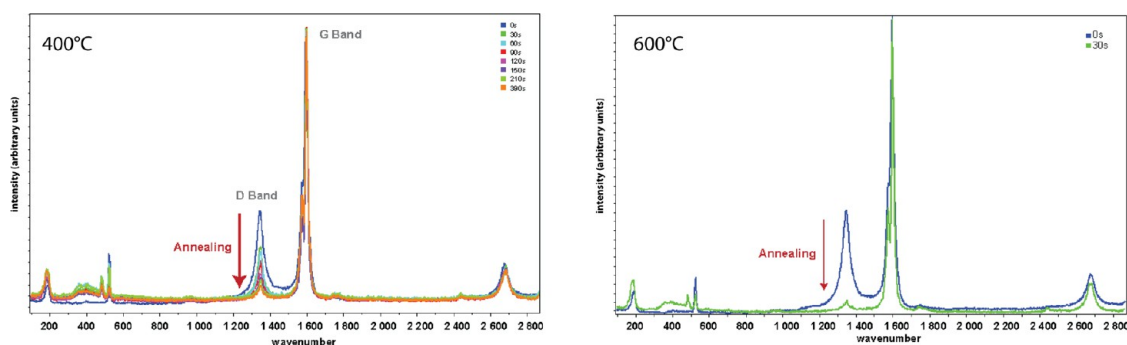
Figure 4. Raman spectra of CNT films after annealing under vacuum at 400 °C (left) and at 600 °C (right). The relative intensity of the D band goes back to comparable values to those of unfunctionalized CNTs after 7 and 0.5 min, respectively.
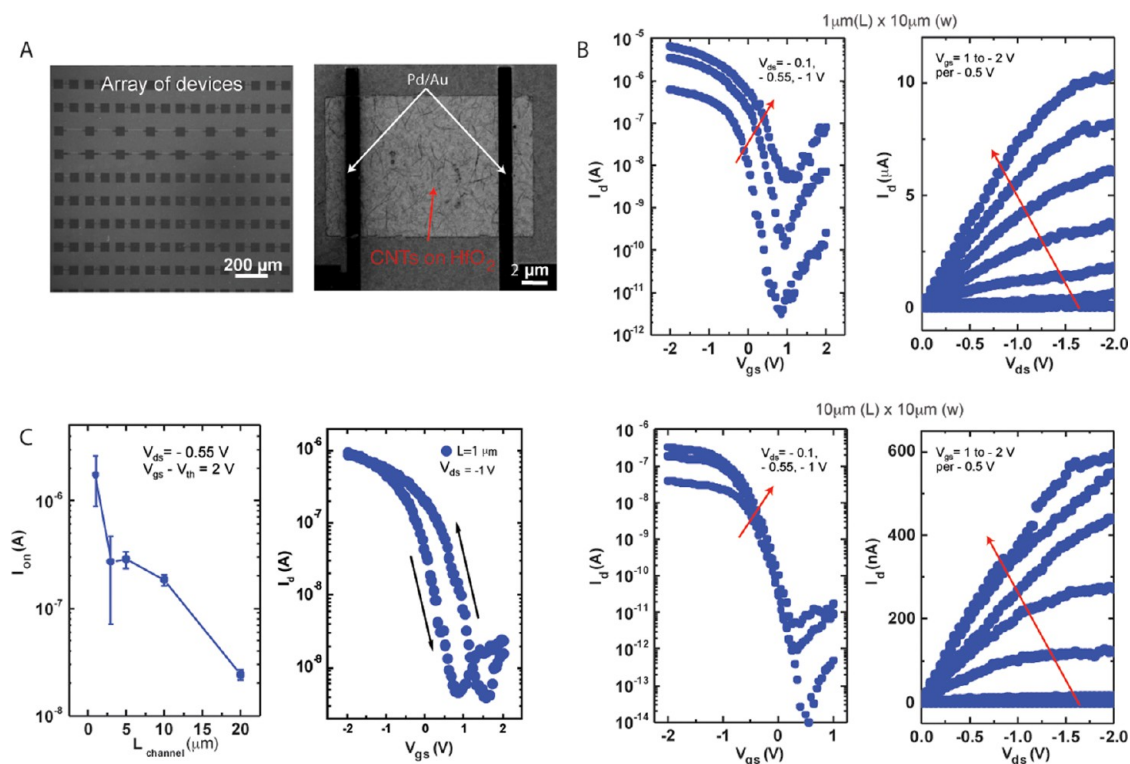

Figure 5. (A) SEM images showing the arrays of devices. (B) I_d vs V_{gs} at various drain biases and I_d vs V_{ds} at various gate biases for CNT TFTs with a channel width of 10 μm and a channel length of 1 μm (top) and 10 μm (bottom). The curves show saturation behavior at high bias and ohmic behavior at low bias. (C) Channel length dependence of average I_{ON} for different TFT devices (left), and hysteresis curve for I_d vs V_{gs} (right).

CONCLUSIONS

In summary, we have shown a simple and inexpensive way to obtain thin films of CNTs by using low-cost, low toxicity solvents, which are environmentally friendly. By controlling the exact conditions and solvent composition, thin films can be fabricated with a CNT density orders of magnitude higher in narrower features compared to previous reports using similar approaches. The key is to use low polarity solvents that increase the surface wetting and promote CNT interaction with the substrate surface, rendering high-density CNT films while retaining selectivity. From the standpoint of large-scale fabrication, thin film deposition performed by directed assembly from solution poses an important advantage of making use of almost all of the CNTs dispersed in solution since only a small amount of CNTs is used for every film and the solution can be reused.

METHODS

Materials. All chemicals and anhydrous solvents were obtained from Sigma-Aldrich and were used as received. SWCNTs (ASP, synthesized by arc-discharge using Fe-based metal catalysts) were obtained from Hanwah Nanotech and used as received. Semiconducting CNTs (90% purity) were purchased from NanoIntegris and used as received.

Instruments. NMR spectra were obtained on a Bruker Avance (400 MHz). NMR chemical shifts are given in parts per million (ppm) referenced to CHCl$_3$/TMS (7.24 ppm for ^{1}H). SEM images were obtained using a LEO 1560 at 1 keV, 20 mm aperture. Substrates were cleaned by rinsing with water and 2-propanol and dried with a nitrogen gun, followed by cleaning with a plasma cleaner from Harrick Plasma, model PDC-32G. MiliQ water was obtained using a Q-Pod from Milipore. The probe sonicator used for these experiments was a SONICS from Vibra Cell (90% Amplitude, 1 s pulse). CNT bundles were removed by centrifugation using an IEC Centra CL2 at 3500 rpm (RCF = 137). Contact angle measurements were carried out using a VCA optima instrument. Raman spectra were acquired using a Horiba Jobin Yvon Raman microscope.

CNT Assembly. Untreated substrates were exposed to a solution containing functionalized CNTs. Solutions were sonicated prior to the assembly, and they were stable for a period of months. For experiments where the solvent was a mixture of water and ethanol, a 10-fold excess of ethanol was added to the aqueous solution of SWCNTs. Substrates were typically exposed for 3 h, after which the substrate was removed form solution and quickly dipped into the rinsing solvent of choice (water or ethanol). The substrates were then carefully dried with a stream of nitrogen. Substrates were sometimes mildly sonicated in a water solution using a bath sonicator to remove nonspecifically bound CNTs.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Conditions for CNT functionalization and device fabrication, contact angle measurements, additional SEM images, Raman spectra. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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