Photoconductive Hybrid Films via Directional Self-Assembly of C₆₀ on Aligned Carbon Nanotubes


Hybrid nanostructured materials can exhibit different properties than their constituent components, and can enable decoupled engineering of energy conversion and transport functions. Novel means of building hybrid assemblies of crystalline C₆₀ and carbon nanotubes (CNTs) are presented, wherein aligned CNT films direct the crystallization and orientation of C₆₀ rods from solution. In these hybrid films, the C₆₀ rods are oriented parallel to the direction of the CNTs throughout the thickness of the film. High-resolution imaging shows that the crystals incorporate CNTs during growth, yet grazing-incidence X-ray diffraction (GIXD) shows that the crystal structure of the C₆₀ rods is not perturbed by the CNTs. Growth kinetics of the C₆₀ rods are enhanced 8-fold on CNTs compared to bare Si, emphasizing the importance of the aligned, porous morphology of the CNT films as well as the selective surface interactions between C₆₀ and CNTs. Finally, it is shown how hybrid C₆₀–CNT films can be integrated electrically and employed as UV detectors with a high photoconductive gain and a responsivity of 10⁴ A W⁻¹ at low biases (± 0.5 V). The finding that CNTs can induce rapid, directional crystallization of molecules from solution may have broader implications to the science and applications of crystal growth, such as for inorganic nanocrystals, proteins, and synthetic polymers.

1. Introduction

Fullerenes (C₆₀) are a uniquely monodisperse nanoscale building block and can be assembled into nano- and microscale crystals with diverse and controllable sizes and shapes using evaporation of dispersions.[1–6] Crystalline C₆₀ is a direct-band gap semiconductor,[7] an excellent electron acceptor,[7,8] and calculations show that contacts between C₆₀ molecules in a closely packed crystal have very low thermal conductance.[9] These features make C₆₀ attractive for applications including diodes,[8,10] field-effect transistors,[11] photovoltaics,[12,13] and thermoelectrics.[14,15] C₆₀ crystals are generally made in bulk or deposited randomly on substrates; however, directed placement, alignment, and interconnection of C₆₀ crystals is typically necessary for their utilization in devices, and this remains a challenge. We demonstrate that aligned carbon nanotube (CNT) films can spatially direct the crystallization of C₆₀ from solution, therefore enabling integration of hybrid thin-film devices by combining standard photolithography and two-step capillary self-assembly process. Uniquely, we find that C₆₀ rods crystallize preferentially parallel to films of horizontally aligned CNTs, thus creating a self-organized directional assembly, wherein C₆₀ crystals are pierced and interconnected by CNT conduits. We find that the kinetics of C₆₀ crystallization are 8-fold faster on CNTs than on bare Si, but the dimensions of the rods are the same. The resultant hybrid film is advantageous for energy devices, especially considering that C₆₀ crystals alone are poor electrical conductors. To this end, we demonstrate that the C₆₀–CNT hybrid films have high photoconductive gain under UV irradiation with a responsivity as high as 10⁴ A W⁻¹ at low biases (± 0.5 V). Overall, the rational design and fabrication of templates that induce ordered crystallization, and the understanding of how nanostructured surfaces affect crystallization kinetics, are important topics for applications including organic electronics,[13] composite materials, and protein science.[14,15]

2. Synthesis of C₆₀–CNTs Hybrid Films

Directed crystallization of C₆₀ on CNTs is achieved, as shown in Figure 1. First, vertically aligned CNT “forests” are grown from lithographically patterned catalyst on silicon wafers using a standard catalytic chemical vapor deposition (CVD) process.[16,17] The forests comprise multi-walled CNTs with a mean diameter of 11 ± 2.8 nm.[18] Next, the vertical CNTs are
transformed to a horizontal orientation via capillary folding by condensation of acetone onto the substrate.\textsuperscript{[19,20]} Because the direction of capillary folding depends on the geometry of the CNT microstructures,\textsuperscript{[20]} capillary folding enables fabrication of not only unidirectional films (Figure 2c) but also multidirectional CNT patterns, such as radially oriented (not shown) and adjacent perpendicular CNT films that overlap during capillary folding (Figure 2c). This method results in uniform-thickness CNT films with high packing fraction (\(\approx 0.2\))\textsuperscript{[19]} and high in-plane anisotropy. Further, the CNT films can be folded such that they bridge a set of prepatterned electrodes (in this case TiN). This provides a straightforward and robust method for electrical integration of the C\textsubscript{60}-CNT hybrids into sensors or other devices requiring electrical read-out. The in-plane anisotropy of the folded CNT sheets was previously quantified by X-ray scattering\textsuperscript{[19]} and electrical resistance measurements. Finally, C\textsubscript{60} dispersed in \textit{m}-xylene (without surfactants)\textsuperscript{[1,4,6]} is deposited by drop-casting onto the CNT films. The solution infiltrates the CNT film by capillary action and then is allowed to evaporate under ambient conditions. C\textsubscript{60} rods crystallize on and within the CNT film during wetting and evaporation. Additional experimental details can be found in the Supporting Information.

3. Characterization of Alignment and Structure

We observe that the major axis (length) of each C\textsubscript{60} rod is oriented along the direction of CNTs within the film, in both unidirectional and multidirectional sheets. This is shown in Figure 2b–c. In comparison, alignment is not observed in a control experiment where C\textsubscript{60} crystallization is performed on the polished side of a bare (100) silicon wafer (Figure 2b). We quantify the average orientation of the C\textsubscript{60} rods by the mean square cosine

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**Figure 1.** Fabrication of C\textsubscript{60}-CNT hybrid films and device integration: a) process sequence involving CNT growth on patterned TiN electrodes and folding of vertical CNTs to produce horizontally oriented films, followed by wetting and drying with C\textsubscript{60} dispersion in \textit{m}-xylene. I–V characterization with and without UV exposure is performed before and after C\textsubscript{60} crystallization.

**Figure 2.** Scanning electron microscopy (SEM) images after synthesis of C\textsubscript{60} rods on bare silicon (a), unidirectional CNT film (b), and bidirectional CNT film (c). Accompanying histograms are below each SEM, showing distribution of rod orientation relative to axis indicated by black dashed lines.
\[ \cos^2 \theta \], where \( \theta \) is the orientation angle of each rod relative to a reference axis (dashed line). This parameter has been used to quantify the order of other anisotropic structures including polymer chains,[21] liquid crystals,[22] and CNTs.[23] Note that \( \cos^2 \theta = 1 \) corresponds to perfect parallel alignment of the rods with the CNTs, while \( \cos^2 \theta = 1/2 \) represents random order. The C60 rods are randomly oriented when crystallized on bare silicon (Figure 2a; \( \cos^2 \theta = 0.54 \)), while those crystallized on CNTs are strongly correlated to the direction of CNT alignment (Figure 2b, 2c; \( \cos^2 \theta > 0.8 \)). On bare silicon, we occasionally observe areas where the solvent droplet becomes pinned to the substrate during evaporation. This causes a locally higher density of rods to form in arrangements that resemble drying rings, as in the “coffee stain” phenomenon (see the Supporting Information, Figure S1).[24] At these locations, the pinned meniscus does slightly influence local rod orientation, resulting in \( \cos^2 \theta < 0.7 \). This likely occurs due to capillary forces that orient the rods as well as fluid flow and solute concentration gradients near the meniscus.[24,25] Thus, pinning of the meniscus on a flat substrate is not as uniformly effective in aligning the rods as compared to the CNT templates, albeit by a different mechanism.

Further investigation by electron microscopy shows that the C60 rods penetrate beneath the surface of the CNT films, and that CNTs pierce through the C60 crystals. A magnified view of the hierarchical, aligned morphology of the CNTs and CNT bundles is shown in Figure 3a–b. The existence of rods both on top and beneath the CNTs (Figure 3c) suggests that C60 rods can nucleate and grow on the surface of the CNT film and/or within the film. In both cases the rod growth direction is influenced by the CNTs. As seen here and in Figure 3d, the CNTs are laced through the C60 rods, forming a true hybrid material, where up to \( \approx 10^5 \) CNTs may be incorporated into a single C60 crystal (\( \approx 1 \mu m \) width), based on the packing density of the CNT film. Transmission electron microscopy (TEM) confirms that individual CNTs are connected to the side facet of the C60 rod (Figure 3e) and that the crystal structure of the rod is not disrupted by the CNTs (Figure 3f), which we later substantiate by X-ray diffraction.

Characteristic Raman spectroscopy peaks of C60 and CNTs allow for their identification within the hybrid film. We profile a single C60 rod that is partially embedded in the CNT film, and has one end exposed (Figure 4a) with a focused beam of less than 1 \( \mu m \) at the sample. Initially at (1), where the C60 rod is fully exposed, the characteristic C60 peak at \( \approx 1468 \text{ cm}^{-1} \)[26] is strong and discernable in the presence of the weaker CNT peaks near 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\) (D- and G-bands, respectively).[27] The intensity of the C60 peak declines relative to the CNT G-band as the beam is scanned along the length of the rod (2],3] , matching with the transition of the rod into the CNT film. The peak position does not shift in frequency over the length of the rod, indicating that no chemical modification of the C60 molecules takes place before or during crystallization (e.g., via polymerization[28]). No spectroscopic features of the C60 are observed away from the rod at (4), confirming that the synthesis process leaves C60 highly localized around the crystals.

We determine the crystal structure of the C60 rods by grazing incidence X-ray diffraction (GIXD) measurements (Figure 4b) using synchrotron radiation and a 2D area detector. These measurements show the as-received C60 powder has a face-centered cubic (FCC) crystal structure with the lattice parameter \( a = 14.3 \text{ Å} \)[4,29] whereas the C60 rods grown on bare silicon and on CNT films both have a hexagonal structure \( (a = 23.4 \text{ Å}, c = 10.3 \text{ Å}) \), which is consistent with previous studies of C60 synthesized from m-xylene.[1,4,30] This change in packing from the higher-density FCC phase is due to the incorporation of trace solvent molecules at interstices,[4,6,10,31] where the C60:m-xylene composition is 3:2.[30] Solvent is incorporated with the crystal partially due to the strong association between the its aromatic structure and the electron-rich hexagonal faces of C60,[23] as well as kinetics of the crystallization process, both of which are discussed later. A large difference in the scattered X-ray intensity is observed when the beam is aligned parallel versus perpendicular to the CNTs, emphasizing the crystallographic anisotropy of the hybrid material. C60 rods synthesized from m-xylene are known to crystallize...
along the $c$-axis (001)\cite{16} and the crystal lattice spacing we measure from TEM (5.04 Å) in Figure 3f is approximately half of $c$ because there are two crystal planes per unit cell.

4. Enhanced Kinetics of C$_{60}$ Crystallization

Although the presence of CNTs does not alter the structure of the C$_{60}$ crystals, C$_{60}$ crystal growth on CNT films is significantly faster than on bare silicon. We use in situ optical microscopy to measure rod length versus time, as shown in Figure 5. The lengthening kinetics of C$_{60}$ rods on CNTs are 8.6 times faster than on bare silicon (average rates $\approx 1.8$ and 0.2 μm sec$^{-1}$, respectively), and growth terminates when the solvent fully evaporates from the substrate. After this occurs, the average length of the crystals is nearly identical on both substrates (16.1 and 15.5 μm, respectively), yet the standard deviation of length is smaller on CNTs (1.8 and 4.1 μm, respectively). The average width of the C$_{60}$ rods in both cases is 1.3 ± 0.4 μm when growth terminates. The length distribution broadens with time on Si, yet narrows with time on CNTs, suggesting that the CNT substrate also enables a more uniform delivery of C$_{60}$ to the growth sites. We also note that the rods do not move or rotate during observable stages of growth on CNT films, yet they remain straight and predominantly follow the CNT direction as growth proceeds. By guiding the delivery of the C$_{60}$ dispersion by motion of a razor blade at constant velocity and distance from the film, we verify that the direction of crystallization is determined by the CNTs and not by the direction of liquid infiltration. Indeed, while directed meniscus motion controls the alignment of C$_{60}$ rods on bare silicon, the rods always align to the CNTs even when the solvent is drawn over the CNTs in the perpendicular direction (see the Supporting Information, Figure S3).

Additional control experiments reinforce that both the physical and chemical characteristics of CNTs influence the rapid, directed crystallization of C$_{60}$ (data not shown). First, we observe a very low density of rods on highly ordered pyrolytic graphite (HOPG), which presents similar chemical compatibility to C$_{60}$ as CNTs. This is due to the smooth surface of HOPG and the strong wetting of m-xylene on HOPG, which accelerate evaporation and inhibit prolonged crystal growth. Therefore, the topography of the CNT film is important for a high nucleation density. Second, to preserve the physical texture and porosity of the CNT film while changing the surface chemistry, we conformally coated CNTs with alumina by atomic-layer deposition (ALD). On alumina-coated CNT films, rods form at low densities and are not aligned with the CNTs. This demonstrates that both the native surface chemistry and texture of the aligned CNT films are needed for directional crystallization. Third, instead of crystallizing C$_{60}$ directly on CNTs, we alternatively prepared C$_{60}$ rods in solution by liquid–liquid interface precipitation (LLIP)\cite{13} and then drop-cast these rods onto CNT films. Even though the CNTs influence the motion of the meniscus during evaporation, the rods made by LLIP are not oriented with the same fidelity as those crystallized directly on the CNT films ($\cos^2 \theta = 0.72$ versus 0.93), and they do not penetrate into the CNT film. Therefore, in situ crystallization on CNT templates is necessary to direct the rod orientation. This finding also emphasizes how the present work is different than previous approaches to align pre-made nanostructures by directional wetting.\cite{23,34}

We interpret these findings based on the anisotropic morphology of the CNT films as well as the physical interactions...
Although the CNT packing fraction increases by as much as a factor of two during evaporation of the solvent,[19] the solvent and C$_{60}$ clusters can still penetrate the CNT film because the size of the C$_{60}$ clusters in solution (14.1 ± 2.9 nm, measured by dynamic light scattering, Figure S4) is less than the mean CNT–CNT nearest-neighbor spacing (i.e., pore size), which is approximately 20 nm for a packing fraction of 0.2. Also, the carbon atoms in both CNTs and C$_{60}$ are sp$^2$-hybridized, although they differ in aromaticity due to the presence of pentagonal faces in addition to hexagonal ones in C$_{60}$. Calculations show that the binding energy between a single C$_{60}$ molecule and the outer wall of a CNT (0.537 eV)[35] exceeds that for either C$_{60}$–C$_{60}$ (0.277 eV)[36] or solvent–CNT interactions (0.232 eV).[37] Therefore, C$_{60}$ in solution should be strongly attracted to the surface of CNTs.

Precedence in literature indicates that nanoscale roughness and porosity promote nucleation of C$_{60}$ crystals[38] as well as other materials[15,39] Thus, favorable crystallization of C$_{60}$ on CNTs is a specific case of a more general behavior, whereby nanostructured templates can assist crystallization via both fluidic and surface effects. Because of the strong C$_{60}$–CNT interaction, we hypothesize that rods nucleate when C$_{60}$ clusters adhere to the CNTs while in solution, and then the crystal grows along CNTs by precipitation of the solute in a similar templating fashion previously observed in crystallization of polymers on CNTs.[40] This may be aided by adsorption and migration of C$_{60}$ clusters along the CNTs, and the strong capillary action within the CNT film.[41] Surface defects are well known to act as favorable nucleation sites by restricting the mobility of adsorbed precursors, such as in vapor–solid growth of nanowires,[42] including formation of oxide nanostructures on CNT forests.[43] Thus, we expect the defect density of CNTs influences C$_{60}$ crystal nucleation, and experiments with CNTs of different diameters (i.e., single-walled CNTs, which can have fewer defects) will be insightful. Likewise, the micro- and nanometer-scale surface texture of the CNT film (determined by the waviness and bundling of the CNTs) and the pore size (CNT spacing) within the film depend on the diameters and packing configuration of the CNTs, so controlling these characteristics may be a route to achieve enhanced control of selective crystal growth. For instance, previous studies found that bundles of CNTs selectively aid crystallization of organic molecules,[13] which Pan, et al. suggest is due at least in part to favorable adsorption sites created by interstitial pores between CNT bundles.[44]

5. Device Integration and Photocurrent Measurements

Finally, we electrically integrate CNT films as two-terminal devices to characterize the photoresponse of our material in the UV range. Our fabrication method (Figure 1) is scalable because it employs standard photolithography of TiN electrodes that are compatible with high-temperature CVD of CNTs, and because capillary folding and drop-casting of C$_{60}$ are straightforward solvent processes. Figure 6a demonstrates that the photocurrent of the hybrid C$_{60}$–CNT device is substantially greater than either CNTs alone or C$_{60}$ rods alone. The linear I–V characteristics indicate that the hybrid device is a photoconductor.
and for instance, the resistance at 400 nm decreases by more than 20 times after integrating C\textsubscript{60} rods with the CNT device. The responsivity of the hybrid device is $10^{3}$–$10^{4}$ A W\textsuperscript{-1} in the range of 400–200 nm irradiation (Figure 6b), respectively. This exceeds recent benchmarks for nanostructured photodetectors (e.g., ZnO or PbS quantum dots),\cite{45} while our bias remains relatively low (0.5 V). Although the CNT device has an appreciable responsivity in this wavelength range (likely due to heat-induced changes in resistivity resulting from absorption of light\cite{46}), the addition of C\textsubscript{60} enhances the responsivity by approximately an order of magnitude.

The high photoconductivity of the hybrid film is the result of the interplay between the electronic structures of C\textsubscript{60} and CNTs, as well as their hierarchical organization. We expect C\textsubscript{60} crystals to generate excitons when illuminated by light with energy greater than the band gap of solid C\textsubscript{60}, which is about 2.3 eV (540 nm)\cite{47}. Others have shown that individual C\textsubscript{60} crystals with\cite{48} or without\cite{49} interstitial solvent molecules can generate photocurrent. The hierarchical structure of our hybrid film allows charge carriers to be injected into the multi-walled CNTs, which are metallic, and charge separation is also aided by the strong tendency of C\textsubscript{60} to accept electrons.\cite{7,8} Thus, holes are likely the injected charge carrier, and can pass through the circuit many times under the influence of the applied electric field (bias) before recombining with trapped electrons. While the absorption properties of C\textsubscript{60}/m-xylene crystals in the tested wavelength range is relatively constant,\cite{49} multi-walled CNTs show increased absorption toward 200 nm,\cite{50} which explains the upward trend in responsivity we observe in both the CNT and C\textsubscript{60}–CNT devices. The large surface-area-to-volume ratio of the hybrid films also plays a role in the large responsivity, increasing absorption and increasing the abundance of surfaces and interfaces, which can trap charge carriers, delay recombination, and thus increase the responsivity of the device.\cite{45,51} Recent studies have also demonstrated the advantages of combining C\textsubscript{60} with CNTs in various devices to enhance the performance of photodetectors\cite{48} and photovoltaics.\cite{52} While some of these examples also incorporate other materials, such as effective electron donors, the addition of C\textsubscript{60} to these complexes is key, and our CNT template technology could be combined with these previously studied materials to achieve new device architectures.

6. Conclusions

We show that CNT films promote rapid crystallization of C\textsubscript{60} from solution, and we harness the strong influence of the CNT direction to create multidirectional films. The C\textsubscript{60} CNTs are interconnected by CNTs, and the CNTs provide a conducting pathway to the C\textsubscript{60} crystals, making a unique hybrid material, which shows utility and promise as an organic UV photodetector with high responsivity. We assert that our methods and findings have general importance to the science and applications of crystal growth of other materials, including aromatic hydrocarbons, synthetic polymers, and biomolecules. In the future, more complex multi-directional CNT architectures\cite{53} may find use as scaffolds for spatially programmable 3D self-assembly, where the formation and organization of crystals is predetermined by the nanoscale texture of the CNTs and their microscale form factor.

7. Experimental Section

Fabrication of C\textsubscript{60}/CNT Hybrid Films: CNT growth was performed using both a horizontal quartz tube furnace (Thermo-Fisher Mini-Mite, 22 mm inner diameter, 12 inch heated length). The catalyst substrate comprises a 10 nm Al\textsubscript{2}O\textsubscript{3} underlayer and 1 nm Fe is deposited on (100) silicon wafers using e-beam evaporation, and patterned by lithography and lift-off.\cite{46} For lithography, we used a SPR 220-3.0 photomask. The lift-off was done by sonication in acetone followed by rinsing in isopropanol and evaporation using dry N\textsubscript{2}. After installing the substrate and purging the reactor, the substrate was heated to the growth temperature in flowing H\textsubscript{2}/He (100/400 sccm), and then C\textsubscript{60}H\textsubscript{4} (100 sccm) was added for the growth duration. To prepare the laterally oriented (LO) CNTs, vertically aligned CNTs are grown from parallel catalyst lines with 20 μm width and 200 μm spacing. The CNT line patterns are then mechanically rolled using a 300 μm diameter stainless steel roller in a
custom-built force-controlled rolling machine.[19] To prepare radially oriented (RO) CNTs, acetone vapor is generated by boiling acetone in a flask and condensing the vapor onto vertically aligned CNT patterns (rings as shown in Figure 1). The capillary forces exerted by the acetone during condensation from the CNTs mechanically fold the CNTs into RO CNT films.[19] Optionally, atomic layer deposition (ALD) of Al₂O₃ is done in an Oxford ALD system with trimethylaluminum (TMA) and water as precursors. A deposition temperature of 200 °C for 100 cycles results in ~10 nm of conformal coating of Al₂O₃ on the CNTs.

The C₆₀ dispersion was prepared using m-xylene and C₆₀ powder (99.5% purity; MTR, Ltd.) with a concentration of 1 mg mL⁻¹, which is below the solubility limit of C₆₀ in m-xylene. The mixture was sonicated for 30 min immediately after the addition of the powder to the solvent. During sonication, C₆₀ was observed to disperse uniformly without the formation of aggregates. The solvent was allowed to completely evaporate from the substrate under ambient conditions. Real-time videos were recorded with a 3.1 megapixel CMOS color camera (Lumenra Infinity 1:3C) at 15 frames per second, and snapshots at specified time intervals were selected for processing and measurements.

Materials Characterization: A Malvern Zetasizer Nanoseries was used to perform dynamic light scattering for estimation of the C₆₀ cluster size in m-xylene. SEM was performed using a Philips XL30-SEQ and a FEI Nova Nanolab, and TEM was performed on a JEOL 3011 HREM. Micro-Raman spectroscopy was performed using a Renishaw inVia Raman microscope equipped with a Leica microscope, RenCam CCD detector, 514 nm He–Ne laser. The spot size was <1 μm. In Figure 4a, peaks in the C₆₀ powder spectrum at approximately 470 cm⁻¹ and 1468 cm⁻¹ represent the radial breathing and pentagonal-pinch vibrational modes of C₆₀, respectively.[19] Characteristic peaks of multi-wall CNTs appear near 1350 cm⁻¹ and 1580 cm⁻¹ corresponding to the D- and G-bands, respectively.

Grazing incidence X-ray diffraction (GIXD) measurements were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) using beamline 11–3 with a photon wavelength of 0.09758 nm. The incidence angle was chosen in the range of 0.10°–0.12° to optimize the signal-to-background ratio. The beam size was 50 μm × 150 μm, which resulted in a beam footprint on sample 150 μm wide over the entire length of the S–10 mm long sample. The data were distortion-corrected (θ-dependent image distortion introduced by planar detector surface) before performing quantitative analysis on the images. The overall resolution in the GIXD experiments, dominated by the sample size, was about 0.08 Å⁻¹.

The samples are loaded into a probe station measuring the I–V characteristics of the material as it was illuminated at wavelengths ranging from 200 to 400 nm using a Sutter Instruments Co. Lambda 10-2 source. We measure the difference in current in dark conditions and during UV exposure for C₆₀ rods, CNT sheets and the C₆₀-CNT hybrids with an applied bias of ±0.5 V at an illumination power range of 8.4–131 μW cm⁻² for 200–400 nm, respectively. Normalizing the change in current (IUV−Idark/Idark) shows an increase in current of 5% in the case C₆₀-CNT hybrids, while this is more than 10 fold of pure CNT sheets or pure C₆₀ in our setup.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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