

# Alternating patterns on single-walled carbon nanotubes

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**Scientific and technological interest in one-dimensional nano-materials, in particular carbon nanotubes<sup>1,2</sup>, is a result of their fascinating properties and their ability to serve as templates for directed assembly. For applications in nanoelectronics it is necessary to create ordered arrays of nanotubes for large-scale integrated circuits, an area in which there has been significant progress<sup>3-7</sup>, and to produce controllable patterns on individual nanotubes so that multiple transistors can be fabricated on them, an area where progress has been slower<sup>8-14</sup>. Here, we show that judiciously selected crystalline block copolymers can be periodically decorated along carbon nanotubes, leading to amphiphilic, alternating patterns with a period of ~12 nm. In addition, end-functionalization of the block copolymers allowed gold nanoparticles to be periodically attached to the nanotubes. This approach provides a facile technique for the periodic patterning of one-dimensional nanomaterials.**

The functionalization of carbon nanotubes is of great interest from both scientific and technological viewpoints<sup>15</sup>. Periodically functionalized carbon nanotubes can directly lead to the creation of controlled two- or three-dimensional carbon nanotube supra-structures, which is an essential step towards building future carbon nanotube-based nanodevices. Very few reports have addressed periodic functionalization/patterning on carbon nanotubes<sup>10-13</sup>. Regarding the patterning on the carbon nanotube surface, all the reported periodic patterns to date have suffered from limitations such as the locality of the pattern or poor periodicity. Here, we report the use of low-molecular-weight polyethylene-*b*-poly(ethylene oxide) (PE-*b*-PEO) block copolymer to obtain uniform, periodic patterns on carbon nanotubes. This unique hybrid structure holds promise for a variety of nanoelectronic and biomedical applications<sup>16</sup>.

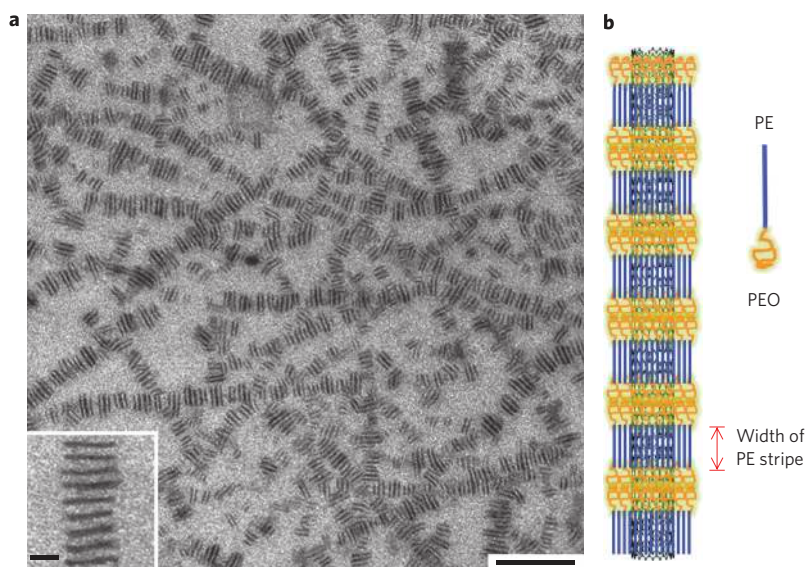
A single-walled carbon nanotube (SWNT)/dichlorobenzene solution was dropcast on a carbon-coated nickel grid and dried at ambient temperature. The fractionated PE-*b*-PEO (molecular weight 1,700 g mol<sup>-1</sup>; 50 wt% PE) was dissolved in chloroform and the solution was then spincoated onto the SWNT-loaded grid. The sample was stained with ruthenium tetroxide (RuO<sub>4</sub>) to enhance the contrast. Figure 1a shows a transmission electron microscopy (TEM) image of the resultant block copolymer/SWNT hybrid. Numerous elongated 'worm-like' structures with dark and bright stripes are clearly visible. Their average length is ~1 μm and their width ~50 nm. The stripes are phase-separated block copolymers; the dark stripes are PEO and the bright ones PE blocks. The inset of Fig. 1a shows an enlarged area. Because of their small size and the coverage of block copolymers, no carbon nanotubes can be clearly identified in the image. However, the consistent orientations of the adjacent stripes and the aspect ratio of this unique worm-like morphology indicate that the axes of the underlying SWNTs are perpendicular to the stripes, as shown in Fig. 1b. This can also be supported by our

control experiment, in which block copolymer alone was spincoated on the carbon-coated grid. In such a case, random alternating stripes and/or lozenge-shaped single crystals were formed (see Supplementary Fig. S1).

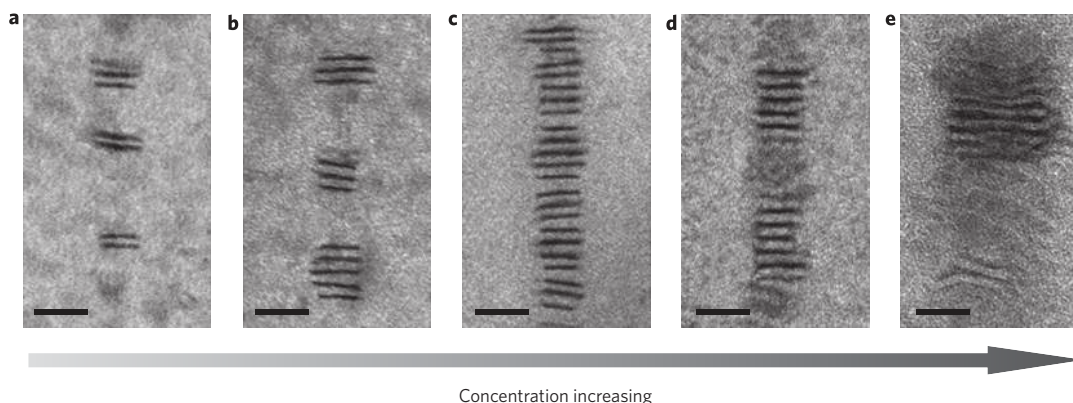
Observing this regular pattern on carbon nanotubes at a scale of ~12 nm is intriguing and the formation of this structure is related to the interplay between block copolymer phase separation and carbon nanotube-induced polymer crystallization. Block copolymers are known to be able to phase separate into ordered microstructures at a scale of ~10–100 nm (refs 17–19). As they are dissolved in solvents, block copolymers can be considered as macromolecular surfactants<sup>20,21</sup>. In a carbon nanotube/block copolymer system, if one segment of the block copolymer is crystalline and is able to form single crystals on carbon nanotubes, the block copolymer phase separation and the carbon nanotube-induced crystallization should affect each other. Depending on the block copolymer/nanotube/solvent interaction parameters, a few scenarios are possible: (i) the block copolymers form micelles (or other aggregates), which separate from the carbon nanotubes; (ii) the block copolymers form micelles that wrap around the carbon nanotubes; and (iii) one segment of the block copolymer crystallizes on the carbon nanotubes, leading to nanotube-induced block copolymer phase separation. The morphology of the block copolymer/SWNT hybrid in Fig. 1 clearly indicates that the phase separation of PE-*b*-PEO is directed by the underlying SWNTs, suggesting that scenario (iii) is the dominant physical process in the present system. Note that there are some other possible mechanisms that might lead to the formation of similar structures. For instance, if both blocks of a block copolymer are neutral to the surface of a carbon nanotube, a similar phase-separated structure could be formed along the nanotube. Other researchers have also shown that topological pre-patterned lines could guide a block copolymer-containing hybrid material to form an orthogonally aligned lamellar phase<sup>22</sup>. To demonstrate the role of PE crystallization in the formation of the present hybrid structures, we further conducted two control experiments. In the first control experiment, PE-*b*-PEO was replaced by polybutadiene(1,4 rich)-*b*-poly(ethylene oxide) (PB-*b*-PEO). In the second, a thin layer of amorphous carbon was deposited onto the SWNTs before spincoating. In both cases, alternating block copolymer patterns were not observed on the SWNTs (see Supplementary Fig. S2). These control experiments clearly demonstrate that nanotube-induced PE crystallization is critical to the formation of the alternating patterns on the carbon nanotubes. Note also that solvent selectivity is critical to solution crystallization of crystalline block copolymers<sup>20</sup>. Our preliminary work showed that as the solvent was switched from chloroform to dimethylformamide (DMF) or water, uniform and dense stripes were not observed. DMF and water are more selective for PEO, so micelles become more stable in the solution. As a result, crystalline stripes are not formed upon solidification. Recently, our laboratory reported that

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**Figure 1 | The alternating pattern of PE-*b*-PEO block copolymers formed on SWNTs.** **a**, TEM image of the PE-*b*-PEO decorated SWNTs. The dark and bright stripes are the PEO and PE domains, respectively. The formation of this unique structure is attributed to the subtle interplay between carbon nanotube-induced polymer crystallization and block copolymer phase separation (scale bar, 200 nm). The inset shows an enlarged area (scale bar, 20 nm). **b**, Schematic representation of the arrangement of the PE-*b*-PEO molecules along a SWNT.



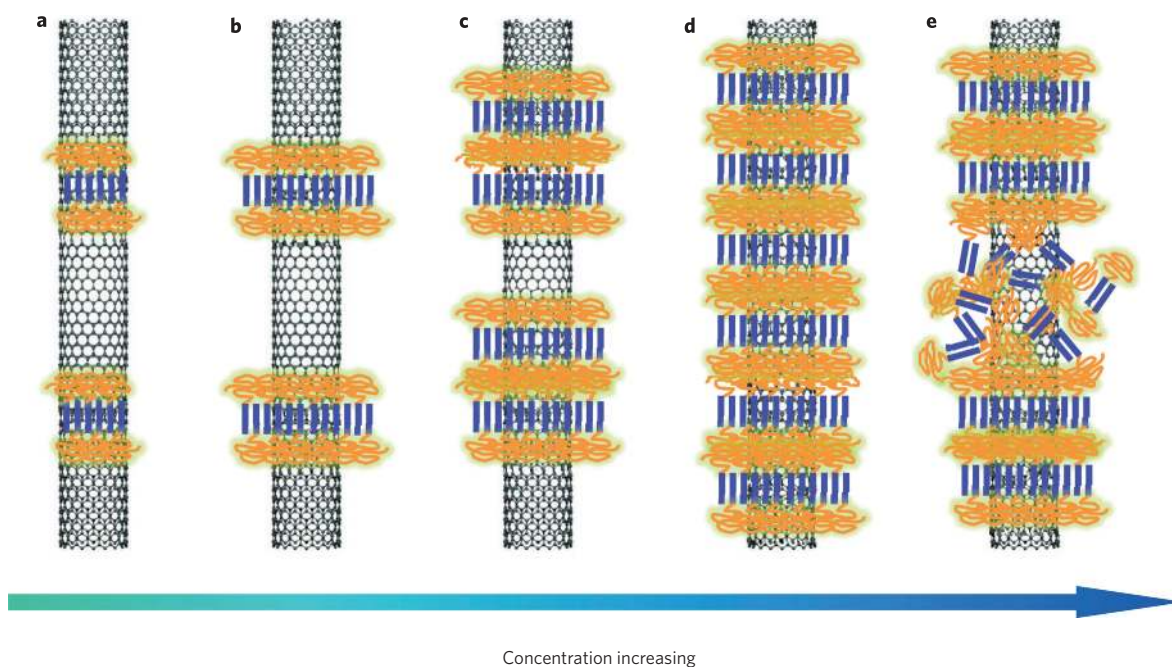
**Figure 2 | TEM images of the five different morphologies of the block copolymer/SWNT hybrid at various block copolymer concentrations.** **a-e**, TEM images for concentrations of the block copolymer solution of 0.001 wt% (**a**), 0.002 wt% (**b**), 0.005 wt% (**c**), 0.020 wt% (**d**), 0.050 wt% (**e**). Scale bars, 50 nm.

carbon nanotubes were able to induce polymer crystallization<sup>23–25</sup>. PE single crystals have been controlled to grow on carbon nanotubes, and the growth mechanism is size-dependent soft epitaxy. In the present block copolymer/SWNT hybrids, upon crystallization, PE chains aligned parallel to the SWNT axis, forming the bright stripes. The observed alternating stripes are thus perpendicular to the SWNT axes. Compared with the crystal patterns formed in carbon nanotube-induced homopolymer crystallization, the present alternating pattern formed by the block copolymer is far more uniform. In Fig. 1a, the period of the alternating pattern is  $11.9 \pm 0.9$  nm. The width of the bright stripes along the carbon nanotube axes is  $5.9 \pm 0.7$  nm. Comparing this number with the extended chain length of the PE block suggests that each PE domain is made of one layer of interdigitated extended PE chains. Note that sodium dodecyl sulphate (SDS)-wrapped carbon nanotubes have also been reported to have periodic patterns<sup>12</sup>. The formation mechanism in the SDS/carbon nanotube case was first attributed to the hemisphere micelles formed along the carbon nanotube. Molecular simulation conducted by others have shown, however, that the hydrophobic tail of SDS aligned parallel to the tube axis, forming multiple layers on

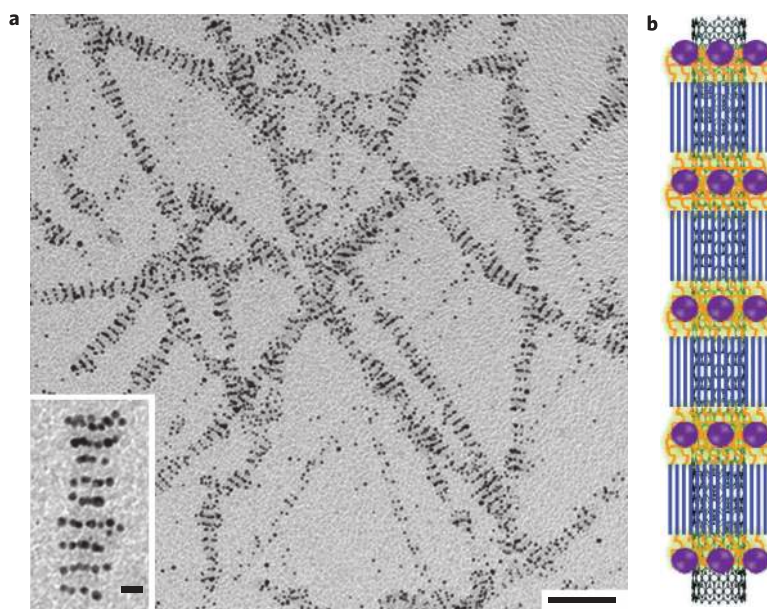
the carbon nanotube surface<sup>26</sup>. The parallel packing of the SDS tails may resemble the crystallization of the PE segments in PE-*b*-PEO.

The block copolymer concentration around the SWNT has an important role in the formation of the alternating pattern. Figure 2 shows five different morphologies of block copolymer/SWNT hybrids formed at various block copolymer concentrations. At a relatively low block copolymer concentration, the SWNTs are decorated by discrete patches of stripes (Fig. 2a). There is no block copolymer present in the intervals between the adjacent patches. As the block copolymer concentration rises, the number of stripes in each patch increases (Fig. 2b). When the block copolymer concentration reaches a certain value, the intervals between patches are completely filled with stripes, and uniform, alternating stripes are found along the entire SWNTs (Fig. 2c). As the block copolymer concentration increases further, new ‘intervals’ seemingly appear along the tubes (Fig. 2d). These new intervals are made of block copolymers. The area looks greyish because the orientation of the phase-separated block copolymer is not uniform. As the concentration increases further, the lateral dimension of the patches increases dramatically (Fig. 2e).





**Figure 3** | Growth mechanism of the alternating stripes on a SWNT. **a**, Heterogeneous nucleation of the PE segments on a SWNT. **b-e**, The growth patterns of the stripes at various block copolymer concentrations, where concentration increases from **b** to **e**.



**Figure 4** | Periodic immobilization of 5-nm gold nanoparticles on the block copolymer/SWNT hybrid. **a**, TEM image of the gold nanoparticle-decorated block copolymer/SWNT hybrid. The block copolymer is end-functionalized with a thiol group (scale bar, 100 nm). The inset shows an enlarged area (scale bar, 10 nm). **b**, Schematic representation of the arrangement of the gold nanoparticles and the block copolymer chains along an SWNT.

Based on the above observations, we propose a growth mechanism for the formation of the alternating stripes on SWNTs (Fig. 3). During spincoating, the block copolymer molecules randomly adsorb onto the SWNT surface due to the favourable interaction between the PE segments and the SWNTs, leading to heterogeneous nucleation (Fig. 3a). After the formation of a stable nucleus, the PE crystal starts to grow, following the soft epitaxy mechanism<sup>23</sup>. At an extremely low block copolymer concentration, the block copolymer molecules crystallize only to the initially formed nuclei. Because of the local concentration gradient generated at the crystal growth front, the stripes grow laterally on the carbon film with a

perpendicular orientation to the tube axis (Fig. 3b). The above process is driven by carbon nanotube-induced PE crystallization. As the block copolymer concentration increases, more crystals start to appear. The tethered PEO chains at the crystal edges, dangling in the solution, attract PEO segments of the free block copolymer molecules to the adjacent region, and facilitate crystallization of the block copolymer at a certain distance away from the initially formed nuclei on the SWNT, where the distance depends on the length of the PEO block. This process is governed by the phase separation of the block copolymer. Repetition of the process leads to the formation of patches of alternating block

copolymer stripes along the SWNT (Fig. 3c). As the block copolymer concentration reaches a critical point, the patches are long enough to connect with each other, leading to continuous, alternating stripes spanning the entire SWNT (Fig. 3d). As the concentration further increases, there are so many block copolymer molecules depositing on the SWNTs that they do not have enough time and space to align themselves into a well-defined structure. As a result, the block copolymer molecules accumulated at the intervals do not show a clearly phase-separated pattern (Fig. 3e).

This uniformly patterned hybrid structure represents a unique nanoscale complex architecture that has not been achieved previously. Because PE is hydrophobic and PEO is hydrophilic, this system features a hybrid structure on individual carbon nanotubes that has alternating amphiphilicity with a  $\sim 12$ -nm period. The domain size can be controlled by changing the block copolymer molecular weight. Our preliminary data show that as the PE molecular weight decreased from 850 to 730  $\text{g mol}^{-1}$  (the molecular weight of the PEO block ranging from 850 to 970  $\text{g mol}^{-1}$ , respectively), the width of the bright stripes dropped from  $5.9 \pm 0.7$  nm to  $4.6 \pm 0.7$  nm. This structure is also similar to multicompartamental block copolymer structures, which can be used as a drug delivery system with the capability to deliver multiple drugs<sup>27,28</sup>. Furthermore, the PEO domains can be modified with various functional groups so that periodic functionalization of carbon nanotubes may be achieved. As a proof of concept, we synthesized thiol-terminated PE-*b*-PEO (see Supplementary Fig. S3). Following the same experimental procedure, SWNTs were periodically decorated by the block copolymer with thiol groups present in the PEO stripes (see Supplementary Fig. S4). The resultant product was then incubated with a gold colloid (5 nm in diameter). Figure 4a is a TEM image of the gold nanoparticle-decorated block copolymer/SWNT hybrid. The gold nanoparticles were patterned periodically along the SWNTs, with a period the same as that of the block copolymer/SWNT hybrid. This is because the thiol-terminated PEO stripes immobilized gold nanoparticles on their surface by means of sulphur-gold bonds, as shown in Fig. 4b (ref. 29). Note that the number of gold nanoparticles on each PEO stripe can be tuned by controlling the lateral dimension of the block copolymer stripes on the carbon nanotube surface. This periodic gold nanoparticle/SWNT hybrid is of great interest in various areas of nanoelectronics and single-electron devices.

In summary, we have produced nanoscale alternating patterns of block copolymer along SWNTs. The period of the patterns was  $\sim 12$  nm along the SWNT axis. The mechanism of formation was attributed to the interplay of carbon nanotube-induced PE crystallization and the block copolymer phase separation. By end-functionalizing the block copolymer with a thiol group, gold nanoparticles were immobilized along the SWNTs, replicating the ordered block copolymer structure. This work therefore demonstrates a facile method to achieve periodic patterning on SWNTs, a key step towards using one-dimensional nanomaterials in nanodevice applications.

## Methods

**Materials.** Purified HiPco SWNTs were purchased from Carbon Nanotechnologies. Dichlorobenzene (DCB), tetraoctylammonium bromide (TOAB), pentyl acetate, thioglycolic acid, sulphuric acid (98%), isopropyl ether, dichloromethane, 5-nm gold/water colloid, toluene and chloroform were purchased from Sigma-Aldrich and used as received. Polyethylene-*b*-poly(ethylene oxide) (PE-*b*-PEO) (molecular weight 1,400  $\text{g mol}^{-1}$ , 50 wt% PE) was purchased from Sigma-Aldrich and was fractionated before usage. Polybutadiene(1,4 rich)-*b*-poly(ethylene oxide) (PB-*b*-PEO) (molecular weight 930–1,020  $\text{g mol}^{-1}$ ) was purchased from Polymer Source and used as received.

**Instruments.** The Branso Ultrasonic Cleaner was used for sonication. Spincoating was performed on the Specialty Coating Systems Spin Coater—G3P12. The Fisher Scientific Centrifuge Marathon 21000 was used as the centrifuge. TEM experiments were conducted on a JEOL 2000FX TEM with an accelerating voltage of 120 kV. The polydispersity index of PE-*b*-PEO was characterized by gel permeation

chromatography (GPC) at 40 °C using tetrahydrofuran as the eluent at a flow rate of 1.0  $\text{ml min}^{-1}$ . Data were collected by the Refractive Index Detector 2414 and analysed using the software provided by Waters. The calibration curve was constructed with narrowly distributed PEO standards. Proton nuclear magnetic resonance (<sup>1</sup>H NMR) was measured on a Unitynova 500 MHz NMR spectrometer. The Fourier transform infrared (FTIR) spectra were obtained on a Varian Excalibur FTS-3000. Vacuum evaporation of carbon was conducted on a Polaron Range E6300 Vacuum Evaporator.

**Fractionation of PE-*b*-PEO.** PE-*b*-PEO (10 g) was dissolved in 50 ml dichloromethane and 100 ml isopropyl ether was added to the solution subsequently. The mixture was then placed in a vacuum chamber to gradually remove the solvents. The block copolymers with the highest PE percentage precipitated out first. The precipitated block copolymer was collected and labelled as fraction 1 to 6 in time order. Fraction 4 was chosen to be used in this research.

The GPC spectrum (see Supplementary Fig. S5) showed that the polydispersity index of the fractionated block copolymer was 1.15. From the end-group analysis using <sup>1</sup>H NMR (see Supplementary Fig. S6), the molecular weight was 1,700  $\text{g mol}^{-1}$  and the PE block 50 wt%.

**Crystallization of block copolymer on SWNTs.** SWNTs (0.02 mg) were dissolved in 1.0 g DCB by means of sonication for 1 h. The SWNT/DCB solution was dropcast on the carbon-coated nickel grids and dried at ambient temperature. Block copolymer/chloroform solution was spincoated on the SWNT-loaded grids at 3,000 rpm for 30 s. The concentrations of the solutions varied from 0.001 to 0.050 wt%. The samples were stained by RuO<sub>4</sub> before TEM observation.

**Preparation of amorphous carbon-coated SWNTs.** The SWNT-loaded grids were placed in a vacuum evaporator. A layer of amorphous carbon was deposited on the SWNTs by thermally evaporated a small amount of carbon from a graphite rod.

**Synthesis of thiol-terminated PE-*b*-PEO.** The PEO segment of the fractionated block copolymer is terminated with a hydroxyl group. Thiol-terminated PE-*b*-PEO was synthesized by reacting the hydroxyl terminated PE-*b*-PEO with thioglycolic acid as described by Brash<sup>30</sup>. Briefly, a drop of sulphuric acid, 5 g of PE-*b*-PEO, and a stoichiometric amount of thioglycolic acid were added to 20 ml of toluene preheated to 80 °C. The reaction proceeded at 110 °C under nitrogen for 3 h and was driven forward by the continuous removal of the water produced. The modified polymer was purified by precipitation in isopropyl ether and subsequent dissolution in dichloromethane. This sequence was repeated three times. The reaction product was then dried under vacuum at ambient temperature for 2 days.

**Preparation of 5-nm gold/pentyl acetate colloid.** The detailed procedure can be found in ref. 29.

**Immobilization of gold nanoparticles on a block copolymer/SWNT hybrid.** Thiol-terminated PE-*b*-PEO/chloroform solution (0.005 wt%) was spincoated on a SWNT-loaded grid at 3,000 rpm for 30 s. The grid was then incubated with the 5-nm gold/pentyl acetate colloid for 1 h. The grid was rinsed with pentyl acetate and dried at ambient temperature.

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## References

- Dresselhaus, M. S., Dresselhaus, G. & Avouris, P. *Carbon Nanotubes: Synthesis, Structure, Properties and Applications* (Springer, 2001).
- Baughman, R. H., Zakhidov, A. A. & de Heer, W. A. Carbon nanotubes—the route toward applications. *Science* **297**, 787–792 (2002).
- Rao, S. G., Huang, L., Setyawan, W. & Hong, S. Large-scale assembly of carbon nanotubes. *Nature* **425**, 36–37 (2003).
- Ahn, J. H. *et al.* Heterogeneous three-dimensional electronics by use of printed semiconductor nanomaterials. *Science* **314**, 1754–1757 (2006).
- Kang, S. J. *et al.* High-performance electronics using dense, perfectly aligned arrays of single-walled carbon nanotubes. *Nature Nanotech.* **2**, 230–236 (2007).
- Li, X. L. *et al.* Langmuir–Blodgett assembly of densely aligned single-walled carbon nanotubes from bulk materials. *J. Am. Chem. Soc.* **129**, 4890–4891 (2007).
- LeMieux, M. C. *et al.* Self-sorted, aligned nanotube networks for thin-film transistors. *Science* **321**, 101–104 (2008).
- Bachtold, A., Hadley, P., Nakanishi, T. & Dekker, C. Logic circuits with carbon nanotube transistors. *Science* **294**, 1317–1320 (2001).
- Keren, K., Berman, R. S., Buchstab, E., Sivan, U. & Braun, E. DNA-templated carbon nanotube field-effect transistor. *Science* **302**, 1380–1382 (2003).
- Czerw, R., Guo, Z., Ajayan, P. M., Sun, Y. P. & Carroll, D. L. Organization of polymers onto carbon nanotubes: a route to nanoscale assembly. *Nano Lett.* **1**, 423–427 (2001).
- Zheng, M. *et al.* Structure-based carbon nanotube sorting by sequence-dependent DNA assembly. *Science* **302**, 1545–1548 (2003).

12. Richard, C., Balavoine, F., Schultz, P., Ebbesen, T. W. & Mioskowski, C. Supramolecular self-assembly of lipid derivatives on carbon nanotubes. *Science* **300**, 775–778 (2003).
13. Worsley, K. A., Moonosawmy, K. R. & Kruse, P. Long-range periodicity in carbon nanotube sidewall functionalization. *Nano Lett.* **4**, 1541–1546 (2004).
14. Mackiewicz, N. *et al.* Supramolecular self-assembly of amphiphiles on carbon nanotubes: A versatile strategy for the construction of CNT/metal nanohybrids, application to electrocatalysis. *J. Am. Chem. Soc.* **130**, 8110–8111 (2008).
15. Star, A. *et al.* Preparation and properties of polymer-wrapped single-walled carbon nanotubes. *Angew Chem. Int. Ed.* **40**, 1721–1725 (2001).
16. Kam, N. W. S., O'Connell, M., Wisdom, J. A. & Dai, H. Carbon nanotubes as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction. *Proc. Natl Acad. Sci. USA* **102**, 11600–11605 (2005).
17. Bates, F. S. & Fredrickson, G. H. Block copolymers—designer soft materials. *Phys. Today* **52**, 32–38 (1999).
18. Hawker, C. J. & Russell, T. P. Block copolymer lithography: merging 'bottom-up' with 'top-down' processes. *MRS Bull.* **30**, 952–966 (2005).
19. Cheng, J. Y., Ross, C. A., Smith, H. I. & Thomas, E. L. Templated self-assembly of block copolymers: top-down helps bottom-up. *Adv. Mater.* **18**, 2505–2521 (2006).
20. Hamley, I. W. *Block Copolymers in Solution Fundamentals and Applications* (Wiley, 2005).
21. Kang, Y. J. & Taton, T. A. Micelle-encapsulated carbon nanotubes: a route to nanotube composites. *J. Am. Chem. Soc.* **125**, 5650–5651 (2003).
22. Kim, H. C., Rettner, C. T. & Sundstrom L. Fabrication of 20 nm half-pitch gratings by corrugation-directed self-assembly. *Nanotechnology* **19**, 235301 (2008).
23. Li, C. Y., Li, L. Y., Cai, W. W., Kodjie, S. L. & Tenneti, K. K. Nanohybrid shish-kebabs: periodically functionalized carbon nanotubes. *Adv. Mater.* **17**, 1198–1202 (2005).
24. Li, L., Li, C. Y. & Ni, C. Polymer crystallization-driven, periodic patterning on carbon nanotubes. *J. Am. Chem. Soc.* **128**, 1692–1699 (2006).
25. Li, L. Y. *et al.* Patterning polyethylene oligomers on carbon nanotubes using physical vapor deposition. *Nano Lett.* **6**, 1007–1012 (2006).
26. Qiao, R. & Ke, P. C. Lipid-carbon nanotube self-assembly in aqueous solution. *J. Am. Chem. Soc.* **128**, 13656–13657 (2006).
27. Li, Z. B., Kesselman, E., Talmon, Y., Hillmyer, M. A. & Lodge, T. P. Multicompartment micelles from ABC miktoarm stars in water. *Science* **306**, 98–101 (2004).
28. Cui, H. G., Chen, Z. Y., Zhong, S., Wooley, K. L. & Pochan, D. J. Block copolymer assembly via kinetic control. *Science* **317**, 647–650 (2007).
29. Li, B. & Li, C. Y. Immobilizing Au nanoparticles with polymer single crystals, patterning and asymmetric functionalization. *J. Am. Chem. Soc.* **129**, 12–13 (2007).
30. Du, Y. J. & Brash, J. L. Synthesis and characterization of thiol-terminated poly(ethylene oxide) for chemisorption to gold surface. *J. Appl. Polym. Sci.* **90**, 594–607 (2003).

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### Author contributions

C.L. and B.L. conceived and designed the experiments. B.L. performed the experiments, with help from L.L. and B.W. B.L. and C.L. co-wrote the paper. All authors discussed the results and commented on the manuscript.

### Additional information

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