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Transforming carbon nanotube forest from darkest absorber to reflective mirror

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Carbon nanotube (CNT) forests are known to be among the darkest materials on earth. They can absorb the entire visible range of electromagnetic wave more efficiently than any other known black material. We have attempted controlled mechanical processing of the CNTs and, surprisingly, observed mirror-like reflection from the processed area with 10%–15% reflectivity, a level higher than typical reflectivity of pure forests by over two orders of magnitude, for a wide range of the spectrum (570–1100 nm). Patterning of micro mirrors in the forest is demonstrated to show its potential application for producing monolithically integrated reflector-absorber arrays in the material. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4744429]

Researchers have shown the application of carbon nanotube (CNT, both single-walled and multi-walled) forests as a near perfect black body absorber.[1–4] However, other types of optical applications of CNT forests have also been demonstrated. Hsieh *et al.*[5] showed that, if the height of a CNT forest was short enough (<500 nm), light could transmit through the forest and be reflected from the substrate underneath to produce a colorful iridescence effect. De Heer *et al.*[6] demonstrated that CNTs aligned on a surface are birefringent, having different dielectric function along and perpendicular to the nanotubes' axis. Zhao *et al.*[7] studied the anisotropic optical behavior of aligned single-walled CNT forests for photonic applications. They also showed, similar to De Heer *et al.*,[6] that the dielectric function had different values for light polarized along the nanotube axis and light polarized perpendicular to the nanotube axis. Lee *et al.*[8] investigated the reflectance spectra of aligned single-walled CNT films and demonstrated that they had a strong anisotropic behavior at a 3.1-eV photon energy. Kempa *et al.*[9] fabricated honeycomb-structure arrays of vertically aligned CNTs and observed strong colorful diffraction from the nanotubes because of their high metallicity (i.e., low dielectric loss). Vinten *et al.*[10] reported visible iridescence from the sidewalls of CNT forests due to the ripples present on the sidewalls. Shoji *et al.*[11] developed an optical polarizer made of aligned single-walled CNTs. Photoluminescence of CNTs was also demonstrated and studied.[12,13] Here, we mechanically manipulated vertically aligned CNTs in a forest to bend the CNTs locally and create micro-scale regions of flattened nanotubes. We observed a significant optical transformation in the bent-CNT region: the black-body CNT forest became an optically reflective mirror.

We grew multi-walled CNT (MWCNT) forests on highly doped silicon substrates (⟨100⟩n-type, resistivity 0.008-0.015 Ω cm) using atmospheric pressure chemical vapor deposition (ethylene-based with iron catalyst) with a recipe described in our earlier work.[14] A typical as-grown sample of the forest is shown in Fig. 1(a). Fig. 1(b) illustrates the concept of mechanical processing of the CNT forest that

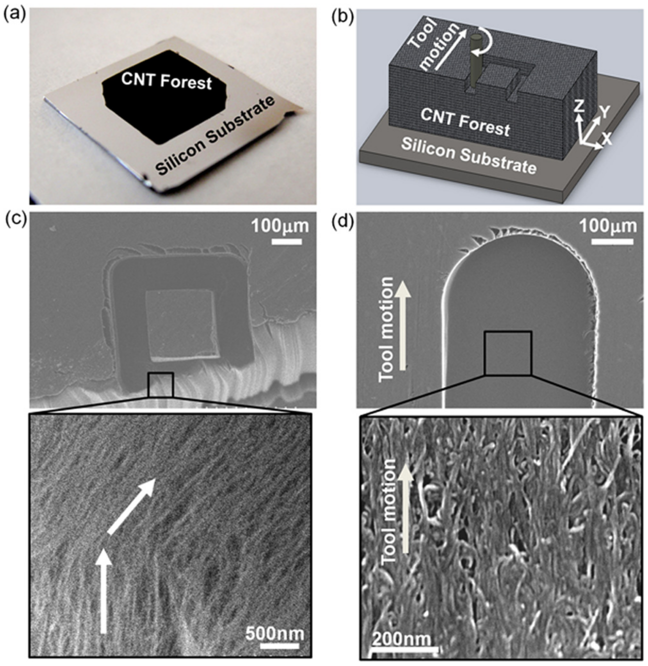

FIG. 1. (a) As-grown MWCNT forest (height > 700 μm) on a Si substrate. (b) The concept of CNT-forest patterning by physical bending of CNTs. A rotating tool (3000 rpm) moves in the X-Y plane (1 mm/min) as shown while moving downwards in the Z direction in steps (1 μm/step). (c) SEM image of a patterned structure showing bent CNTs on its surface. The arrows indicate the directions of vertical and bent portions of the CNTs. (d) High resolution FE-SEM image showing the alignment of CNTs along the scan direction of the tool.

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is locally bent by scanning a microscopic metallic tool; a cylindrical piece of tungsten (diameter $\leq 300\,\mu$m) rotating at a speed of 3000 rpm is moved along the X, Y, and Z directions to carry out the process. The movement in the Z direction was performed in the step mode with a step size of $1\,\mu$m, and the back-and-forth scanning speed in X and Y directions was 1 mm/min. This technique was used to create patterned structures in bare CNT forests by the local mechanical manipulation of the CNTs. Fig. 1(c) shows a scanning electron microscope (SEM) image of a sample pattern of bent CNTs obtained after this process. The magnified view in Fig. 1(c) shows a corner region where the CNTs are bent, indicating that the orientation of the nanotubes has been changed from vertical to horizontal. Fig. 1(d) further shows that the bent nanotubes are aligned in the direction parallel to the scan direction of the tool, which has an interesting application as discussed later.

The most interesting and significant result of this experiment is that the patterned area started to reflect light like a mirror as shown in Fig. 2(a). This phenomenon was further characterized by quantifying the reflectivity of the bent-CNT surfaces. The result shown in Fig. 2(b) indicates that the typical reflectivity of the bent-CNT surfaces is approximately 10%–15% for the visible to the infra-red band of unpolarized light. In order to confirm that the reflection is not coming from the substrate (which is essentially a polished silicon wafer), we partly dry etched the substrate while holding the CNT forest (with reflective patterns) by depositing a thin film of Parylene-C, a transparent polymer, on top of the forest.[15] This CNT forest sample without the substrate also exhibited the same reflective feature, verifying that the reflection is from the patterned region of the CNT forest and not from the substrate. An attempt was also made to determine the reflectance of the bare forest; however, the reflection was so low that it fell within the noise level of the measuring instrument. Previous reported data suggest a typical MWCNT forest reflects light only by 0.045%,[4] while this processing technique optically transforms the forest to increase the reflectivity by over two orders of magnitude.

The probable reason behind the observed phenomenon is as follows. The CNT forests grown in this study are essentially comprised of metallic MWCNTs. When these metallic nanotubes are bent and flattened controllably as described earlier, the resultant surface texture becomes considerably smoother, providing an average roughness (R_a) of 10–30 nm. This level of surface roughness is considered optical surface quality and, because of the conductive behavior of the nanotubes, the surface exhibits mirror-like reflection, with a reflectivity of 10%–15%. Another interesting finding was white light diffraction from the bent-CNT area. Figs. 2(c) and 2(d) show blue and red light diffracted from narrow regions of processed patterns observed with different incident angles of white light, respectively. Figs. 2(e) and 2(f) compare SEM images between a processed surface that did not show this diffraction effect and a surface that showed the effect. A notable difference can be observed from this comparison; the surface in Fig. 2(e) is completely flat, whereas the one in Fig. 2(f) has periodic, grating-like patterns of bundled nanotubes with $\sim$200-nm spacing, which is the most likely cause of the observed diffraction phenomenon (Figs. 2(c) and 2(d)). The formation of these periodic structures on the processed surfaces could be related

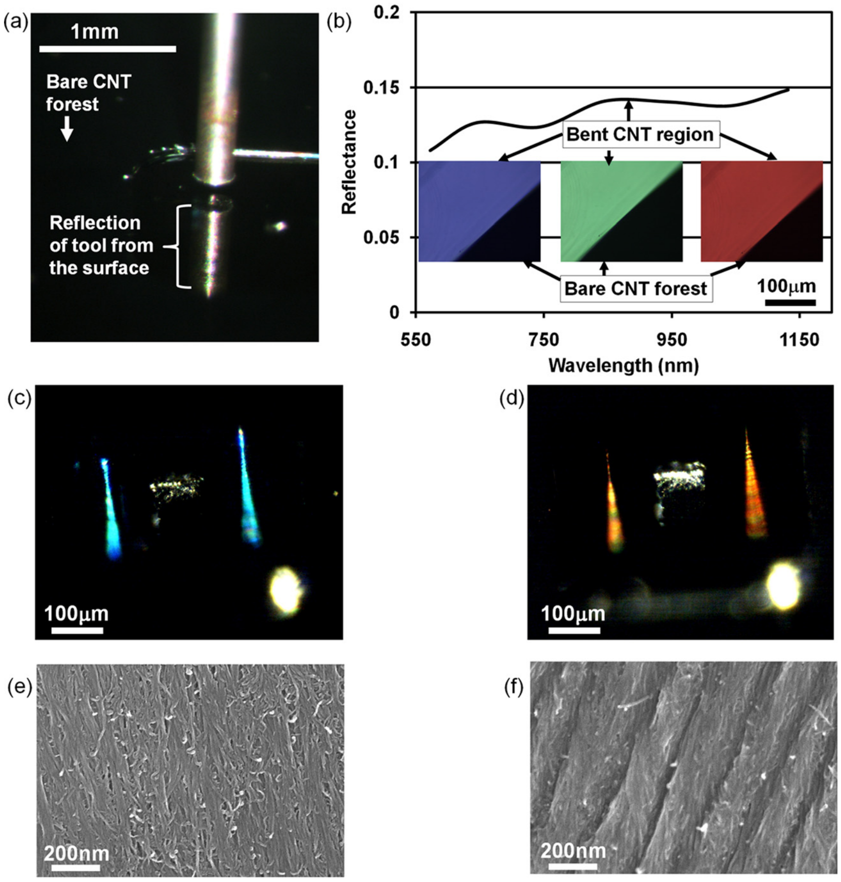

FIG. 2. (a) Optical image showing the reflected image of the tool on the bent-CNT surface. (b) Measured normal-incidence spectral reflectance of the surface (averaged) for visible-near infra red light accompanied by images of red, green, and blue light reflection from the processed surface. Repeatability of measured reflectance is estimated to be 2.5%–3%. (c) and (d) show blue and red light diffraction resulting from incident white light obtained with different incident angles ($\sim$45° to 60°), respectively. (e) FE-SEM image of the flat portion of the processed CNT surface that reflects light like a mirror. (f) FE-SEM image of the portion of the processed CNT surface that has developed a grating pattern, which is likely the source of the diffraction effect shown in (c) and (d).

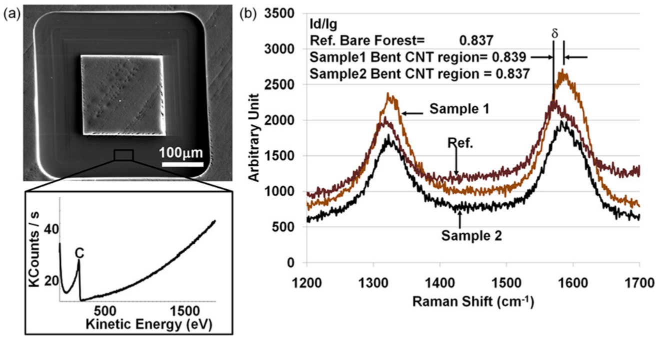

FIG. 3. Surface characterization of the bent CNT region. (a) SEM image of a pattern of bent CNTs with a result from SAM, suggesting that there is only carbon present on the surface of the processed region. (b) Raman spectroscopy results obtained using a Renishaw inVia Raman microscope show no evidence of crystalline defects in the bent CNTs.

to a combination of the morphology of the tool's bottom surface and the machining condition (scanning speed, tool's rotation speed, etc.) used for the mechanical manipulation. However, the patterning of these grating-like structures is not fully controllable yet in terms of spacing and repeatability of the periodic pattern.

We also investigated possible contamination by foreign materials and the crystalline defects of the bent CNTs. Scanning Auger microscopy (SAM) showed that the surface is not contaminated with the tool material (tungsten) as a result of this mechanical processing (Fig. 3(a)). SAM was carried out using an Auger electron spectrometer (Microlab 350, Thermo Electron Corp.) that was equipped with a field-emission source and a hemispherical energy analyzer. In SAM, the electron beam was rastered across a selected area for average surface composition with the primary electron beam set at 10 keV and 3.5 nA, and the analyzer was operated in the constant retardation ratio mode (CRR = 4.0). Fig. 3(b) shows a comparison of Raman spectra between an original bare forest and a mechanically bent forest. It is clear from this comparison that the I_d/I_g ratio is similar for both cases, suggesting that the developed micro mechanical process does not cause crystalline defects in the CNTs. Sandler *et al.*[16] reported that a compressive stress on the MWCNTs could cause a shift in the G band of the Raman spectra; this may explain the shift (δ indicated in Fig. 3(b)) observed in our case because of the stress induced in the CNTs during the mechanical bending process.

The mechanical process can be easily used to create arbitrary mirror patterns on CNT forest surfaces by scanning the tool in the desired patterns, as demonstrated in Figs. 4(a) and 4(b) that show optical images of created patterns as examples of coexisting arrangement of optical super absorber and mirror reflector. Figs. 4(c) and 4(d) are SEM images of the mirror patterns shown in Figs. 4(a) and 4(b), respectively. This type of microstructure may be used to create arrays of a mirror-absorber combination that provide high optical contrasts for light manipulation and switching applications in the micro domain.

Many researchers have attempted to produce CNTs in bulk with different orientations and alignments,[17–20] rather than only in the vertical direction. As discussed earlier (with Fig. 1(d)), CNTs processed using our technique are bent and arranged in a direction parallel to the motion of the tool. This observation suggests that manipulating CNT forests in this manner could be useful to define the alignment of the CNTs in a forest in desired directions.

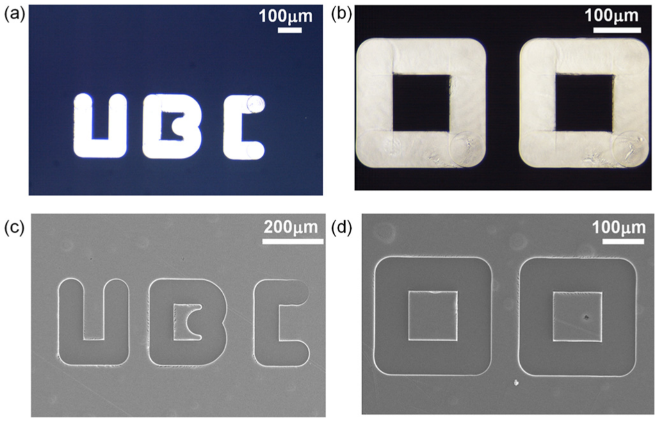

FIG. 4. Patterning micro mirrors in the CNT forest. (a) Optical image of reflective channels with letter patterns (UBC) created on a bare CNT forest. (b) Optical image of an alternating array of optical super absorber and reflector. (c) and (d) SEM images of the structures in (a) and (b), respectively, showing the structural integrity and smoothness of the surface texture for the resultant patterns.

In this letter, we have reported that CNT forests are not only a super dark material but also able to reflect light like a mirror when the CNTs in the forests are mechanically bent and flattened with proper control. We have also quantified the reflection of the mirror surfaces and showed that the reflectivity is approximately 10%–15%, more than two orders of magnitude higher than that of the bare forest surface as reported earlier.[4] This remarkable mirror reflection at the bent-CNT region is most probably due to the conductive nature of the CNTs and the smooth surface texture in the bent-CNT zone. Material characterization confirms that the surfaces of the processed CNT zone are not contaminated with the tool material and that the process does not introduce crystalline defects to the CNTs. This property of CNT forests could be useful in making matrices of light absorbers and reflectors with high optical contrasts.

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[1] K. Mizuno, J. Ishii, H. Kishida, Y. Hayamizu, S. Yasuda, D. N. Futaba, M. Yumura, and K. Hata, Proc. Natl. Acad. Sci. U.S.A. **106**, 6044 (2009).
[2] H. F. Shi, J. G. Ok, H. W. Baac, and L. J. Guo, Appl. Phys. Lett. **99**, 211103 (2011).
[3] X. J. Wang, L. P. Wang, O. S. Adewuyi, B. A. Cola, and Z. M. Zhang, Appl. Phys. Lett. **97**(16), 163116 (2010).
[4] Z. P. Yang, L. Ci, J. A. Bur, S. Y. Lin, and P. M. Ajayan, Nano Lett. **8**, 446 (2008).
[5] K. C. Hsieh, T. Y. Tsai, D. Wan, H. L. Chen, and N. H. Tai, ACS Nano **4**, 1327 (2010).
[6] W. A. Deheer, W. S. Bacsa, A. Chatelain, T. Gerfin, R. Humphrey-Baker, L. Forro, and D. Ugarte, Science **268**, 845 (1995).
[7] G. L. Zhao, D. Bagayoko, and L. Yang, J. Appl. Phys. **99**, 114311 (2006).
[8] H. Lee, T. D. Kang, K. H. An, D. J. Bae, and Y. H. Lee, Jpn. J. Appl. Phys. Part 1 **42**, 5880 (2003).

[9] K. Kempa, B. Kimball, J. Rybczynski, Z. P. Huang, P. F. Wu, D. Steeves, M. Sennett, M. Giersig, D. V. G. L. N. Rao, D. L. Carnahan, D. Z. Wang, J. Y. Lao, W. Z. Li, and Z. F. Ren, Nano Lett. **3**, 13 (2003).

[10] P. Vinten, J. Lefebvre, and P. Finnie, Appl. Phys. Lett. **97**, 101901 (2010).

[11] S. Shoji, H. Suzuki, R. P. Zaccaria, Z. Sekkat, and S. Kawata, Phys. Rev. B **77**, 153407 (2008).

[12] Y. Kim, N. Minami, and S. Kazaoui, Appl. Phys. Lett. **86**, 073103 (2005).

[13] S. W. Yang, A. N. Parks, S. A. Saba, P. L. Ferguson, and J. Liu, Nano Lett. **11**, 4405 (2011).

[14] T. Saleh, M. Dahmardeh, A. Bsoul, A. Nojeh, and K. Takahata, J. Appl. Phys. **110**, 103305 (2011).

[15] A. Bsoul, M. S. Mohamed Ali, and K. Takahata, Electron. Lett. **47**, 807 (2011).

[16] J. Sandler, M. S. P. Shaffer, A. H. Windle, M. P. Halsall, M. A. Montes-Moran, C. A. Cooper, and R. J. Young, Phys. Rev. B **67**, 035417 (2003).

[17] S. Huang and L. Dai, J. Nanopart. Res. **4**, 145 (2002).

[18] L. H. Lu and W. Chen, ACS Nano **4**, 1042 (2010).

[19] C. T. Wirth, S. Hofmann, and J. Robertson, Diamond Relat. Mater. **17**, 1518 (2008).

[20] B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath, and P. M. Ajayan, Nature **416**, 495 (2002).