# ALIGNED CARBON NANOTUBES FOR MULTIFUNCTIONAL NANOCOMPOSITES AND NANODEVICES:

## Multicomponent Micropatterned Aligned Carbon Nanotube Devices with Reversibly Switchable Electronic Properties for Multifunctional Applications

Liangti Qu and Liming Dai*

*Department of Chemical and Materials Engineering, School of Engineering, University of Dayton, 300 College Park, Dayton, Ohio 45469, USA*
*Corresponding Author. E-mail: ldai@udayton.edu

**ABSTRACT**

A simple, but effective and versatile, double contact transfer method was developed for controlled fabrication of three-dimensional (3D) multicomponent micropatterns of vertically-aligned carbon nanotubes. Using our reported dry contact transfer technique,[12] we first built a micropattern of vertically-aligned multiwalled carbon nanotubes (VA-MWNTs) onto a Scotch tape. The pre-transferred VA-MWNT pattern was then used as a new physical mask for the second dry contact transfer of vertically-aligned single-walled carbon nanotubes (VA-SWNTs) of a different length. The resultant 3D micropatterns with VA-SWNTs interposed into the VA-MWNT patterned structure was demonstrated to show reversible electrical responses of potential applications in various electronic devices, ranging from touch sensors to electronic switches.

**KEYWORDS**

Vertically-aligned carbon nanotube, contact transfer, 3-D micropattern, switchable electronics

Carbon nanotubes (CNTs) in an aligned and micropatterned form are highly desirable for many device applications, ranging from nanoscale sensors to electronic circuits [1-3]. Although various micropatterning methods, including photolithography [4-6], soft lithography [7, 8], and electron or laser beam lithography [9, 10], have been devised for producing single component vertically-aligned CNT micropatterns for some years, the formation of multicomponent vertically-aligned CNT micropatterns is a recent development. In this context, we have reported the preparation of multicomponent micropatterns of VA-MWNTs interposed with nanoparticles [11], self-assembled nonaligned CNTs [12], or VA-SWNTs [13]. In the present study, we developed a double contact transfer technique by using a patterned structure of VA-MWNTs pre-transferred onto a Scotch tape [11] as a physical mask for the second dry contact transfer of, for example, vertically-aligned single-walled carbon nanotubes (VA-SWNTs) of a different length to produce three-dimensional (3D) aligned CNT micropatterns with VA-SWNTs interposed into the VA-MWNT patterned structure. Here, we report the detailed procedures of the newly-developed double contact transfer technique for the formation of 3D multicomponent micropatterns with VA-SWNTs interposed into the VA-MWNT patterned structure, and demonstrate their potential applications in micro-/nano-electronic devices.

Figure 1 shows a schematic representation of the procedures for fabricating 3D VA-SWNT/VA-MWNT multicomponent micropatterns by the newly-developed double contact transfer technique. To start with, we synthesized nonpatterned VA-MWNT films with a homogenous tube length of ~5 μm on a quartz glass plate by pyrolysis of iron phthalocyanine (FePc) in $Ar/H_2$ atmosphere at 1100$^{o}$C [14]. Nonpatterned VA-SWNT films with a uniform length of about 10-15 μm were also synthesized by plasma enhanced chemical vapor deposition according to an earlier publication [15].

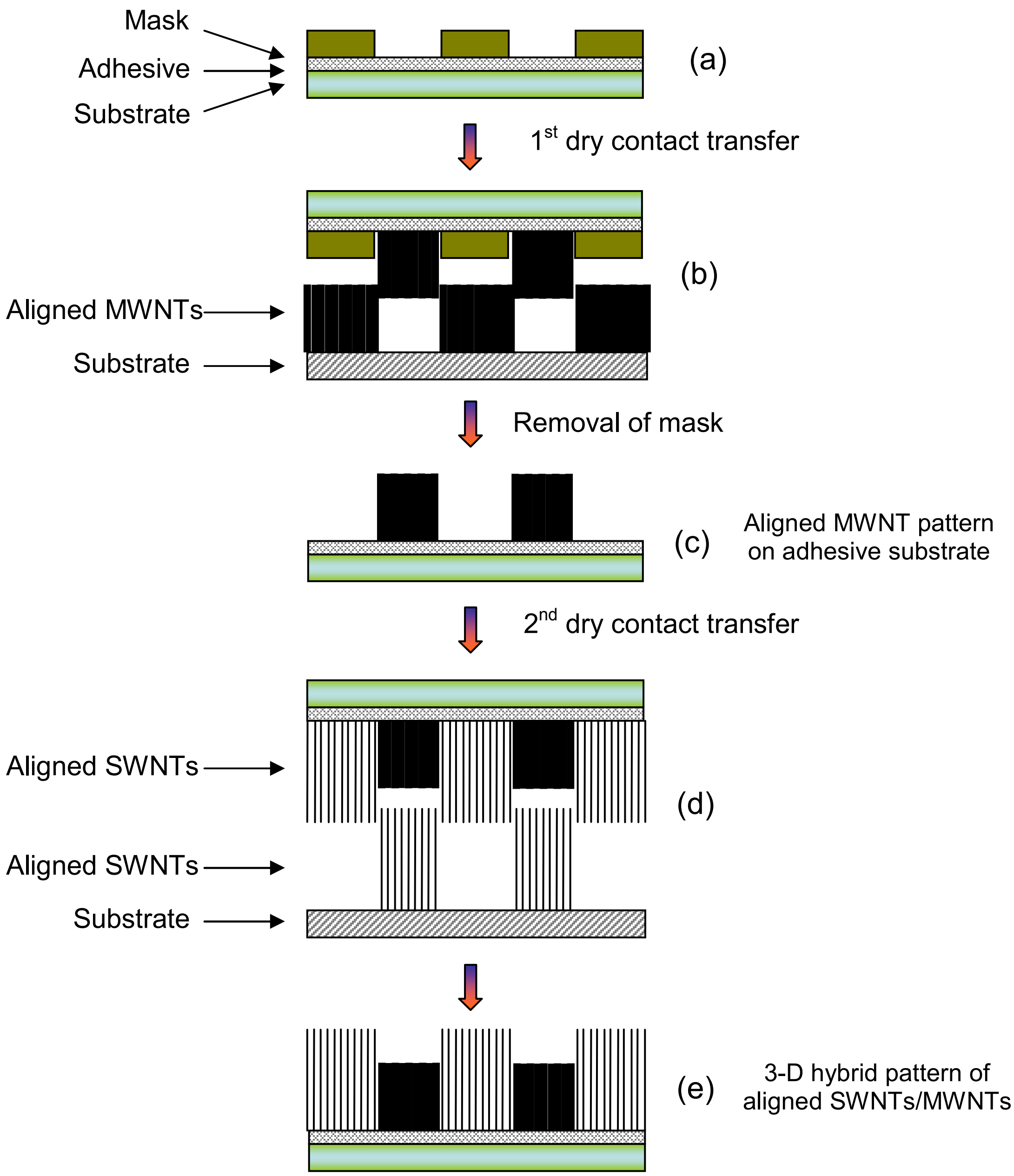


FIG. 1. A schematic illustration of the double contact transfer method.

Following a published procedure [12], we adhered a TEM grid consisting of square windows (*ca.*100-µm wide) onto a commercially available Scotch tape (3M, polypropylene-film-supported acrylic adhesive) as a physical mask (Fig. 1a) for the first dry contact transfer of VA-MWNT micropatterns from the *as-synthesized* nonpatterned VA-MWNT film (Fig. 1b) [11, 16]. After careful removal of the TEM grid, a VA-MWNT micropattern replicated the TEM grid structure formed on the Scotch tape (Fig. 1c), which was then used as a new physical mask for the second dry contact transfer of VA-SWNT micropatterns from the *as-synthesized* nonpatterned VA-SWNT film (Fig. 1d). Finally, a 3D multicomponent micropattern with VA-SWNTs interposed into the VA-MWNT patterned structure was obtained on the flexible Scotch tape (Fig. 1e). Figures 2a and b show the positive and negative VA-MWNT micropatterns on the original quartz plate and Scotch tape, respectively, formed by the first dry contact transfer (*cf.* Fig. 1b). Upon the second dry contact transfer by using the Scotch-tape-supported VA-MWNT micropattern (*i.e.* Fig. 2b) as a physical mask, a 3D multicomponent micropattern with VA-SWNTs interposed into the VA-MWNT patterned structure was formed on the flexible Scotch tape (Fig. 2d) whilst the VA-SWNTs in the regions covered by the nonadhsive VA-MWNT square patterns were left over on the quartz substrate used for the synthesis of VA-SWNTs (Figs. 2c & 1d). While Figure 2d clearly shows that both the contact-transferred VA-MWNTs and VA-SWNTs are well registered into their respective areas, the corresponding SEM images under higher magnifications (Figs. 2e & f) reveal that both the VA-MWNTs and VA-SWNTs remain perpendicularly-aligned in full lengths even after the contact transfer for twice. This is because aligned CNTs have been previously demonstrated to possess excellent mechanical flexibility [15, 17, 18] and the dry contact transfer did not cause any obvious detrimental effect on their alignment [11, 16].

Unlike the 3D single-component VA-MWNT micropatterns [16], the *newly-prepared* 3D multicomponent micropattern with VA-SWNTs region-selectively interposed into the VA-MWNT patterned structure showed interesting region-specific electronic properties characteristic of the micropatterned *semiconducting* SWNTs and *metallic* MWNTs, respectively [13]. Therefore, these 3D VA-MWNT/VA-SWNT micropatterns should be useful for the development of various novel electronic devices for a wide range of potential applications.

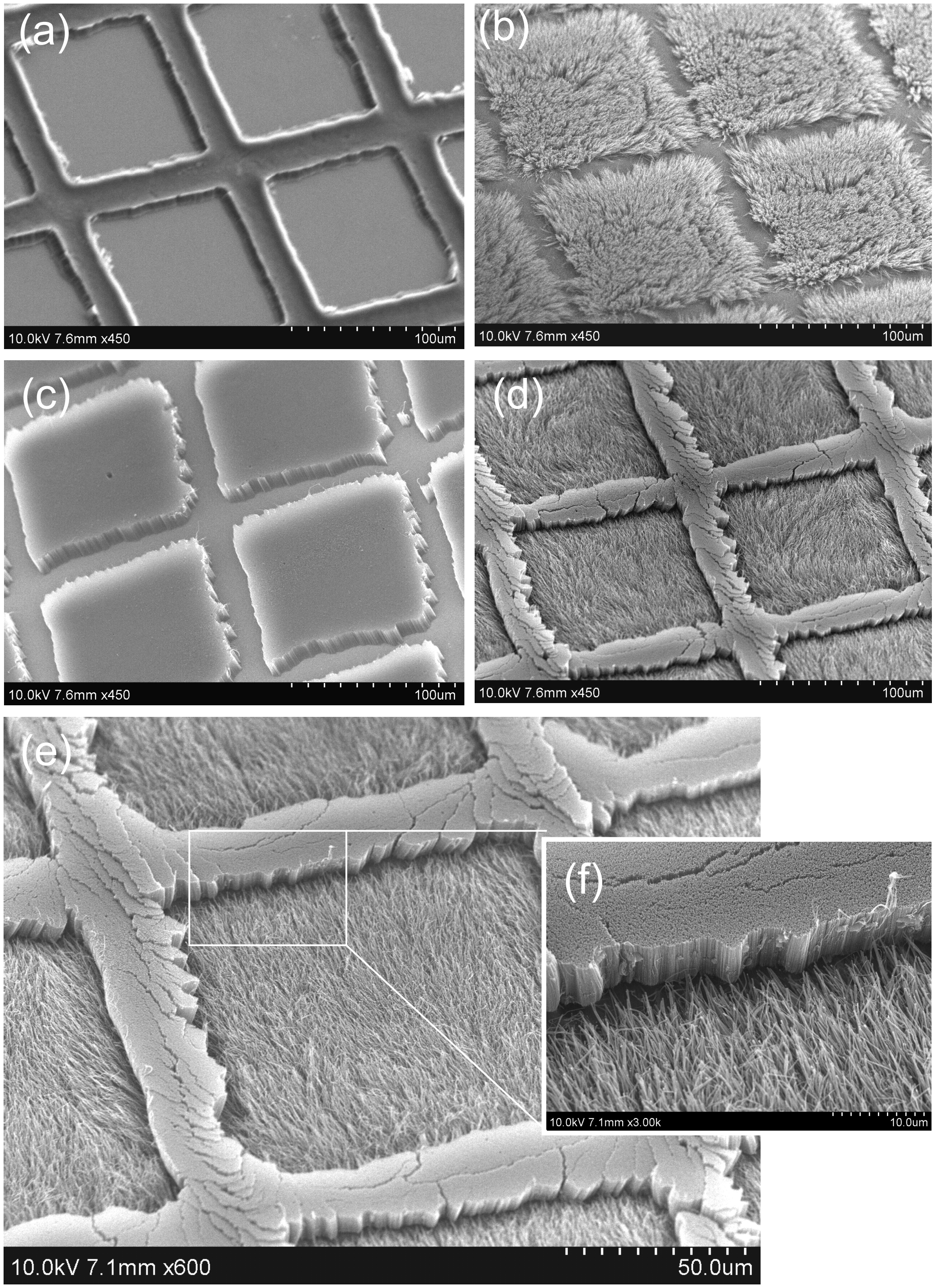


FIG. 2. SEM images of the aligned MWNTs left over on the quartz substrate (a) and transferred onto the Scotch tape (b) after the 1$^{st}$ dry contact transfer; the aligned SWNTs left over on the quartz substrate (c) and the hybrid pattern of aligned SWNTs/MWNTs transferred onto the Scotch tape (d) after the 2$^{nd}$ dry contact transfer. (e, f) as for (d) under higher magnifications.

To demonstrate potential applications for the newly-prepared 3D VA-MWNT/VA-SWNT multicomponent micropatterns, we replaced the Scotch tape with a conductive adhesive tape *(e.g.* copper conducting adhesive tape, 3M) for the double contact transfer (Fig. 1) and placed a conducting ITO glass plate on the top surface of the resultant 3D nanotube pattern to form the top electrode (Fig. 3a). As the VA-SWNTs are longer than the interposed VA-MWNTs, a current (*I*) – voltage (*V*) curve characteristic of the semiconducting VA-SWNTs was observed initially (curve i in Fig. 3c). Upon compression by pressing down the ITO glass (*ca.*100g loading, Fig. 3b), an effective contact between the VA-MWNTs and ITO glass was made while the VA-SWNTs were mechanically compressed [15]. As a result, an Ohmic *I* - *V* behavior was obtained (curve ii in Fig. 3c) as the metallic VA-MWNTs supported the major current flow between the two electrodes in the compression state. Due to the reversible mechanical compressibility of the VA-SWNTs [15, 17, 18], we found that *I* - *V* characteristics of the 3D multicomponent micropattern with the shorter VA-MWNTs interposed into the longer VA-SWNTs can be reversibly switched between the metallic and semiconducting states during the compression-decompression cycles. Under a constant voltage (say, 5 V), a strong current response (by a fact of 2) to compression-decompression cycles was observed, which is apparently very fast with a good repeatability (Fig. 3d). Inset of Fig. 3d shows an enlarged view for a small portion of the current response curve. The peak current intensity and response time can be tuned by developing the 3D VA-MWNT/VA-SWNT multicomponent micropatterns with various patterned geometries and/or nanotube length differences. These *newly-developed* 3D multicomponent VA-MWNT/VA-SWNT micropatterns with reversibly switchable electronic properties can be potentially useful for many device applications, including touch sensors, memory storages, and electronic switches.

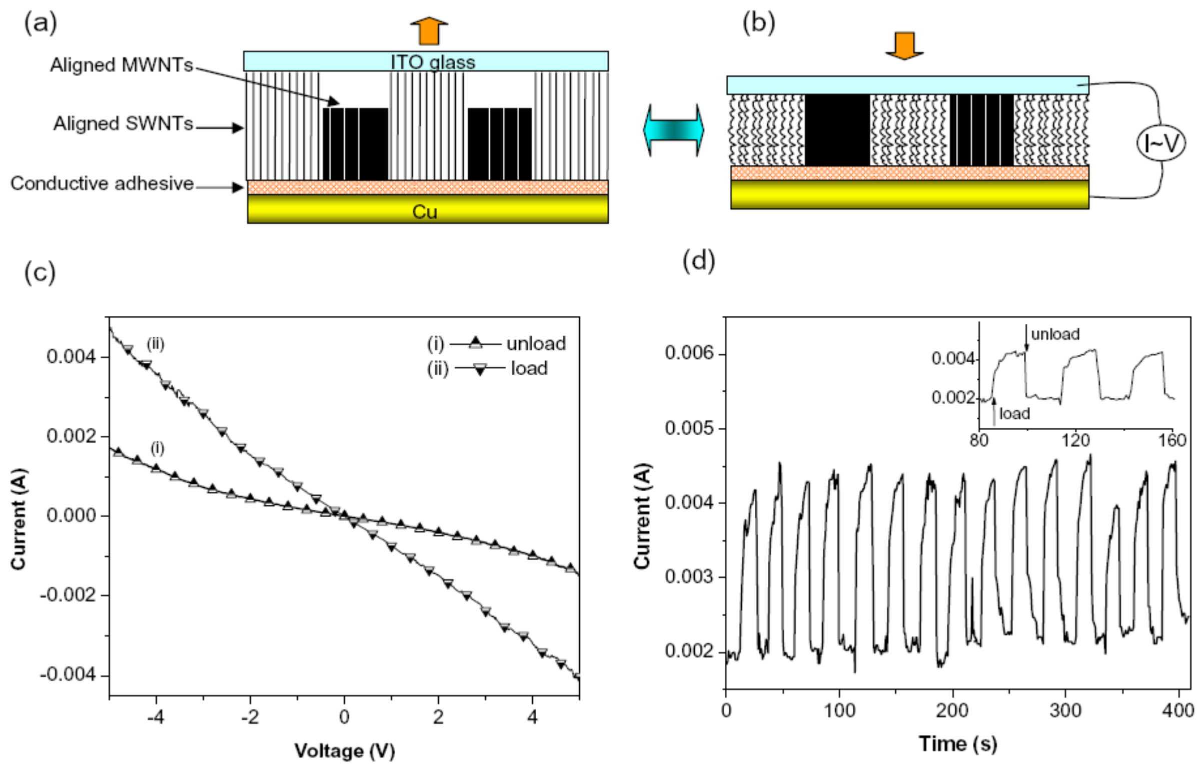


FIG. 3. (a & b) Schematic illustrations of the 3D VA-MWNT/VA-SWNT multicomponent micropatterns at the decompression and compression state, respectively, (c) Current-voltage response corresponding to (a) and (b), and (d) Current response to the compression-decompression cycles at a voltage of 5 V. Tested pattern area: 1mm$^2$.

In summary, we have developed a simple, but very versatile, double contact dry transfer technique for controlled fabrication of 3D multicomponent micropatterns with VA-SWNTs interposed into the VA-MWNT patterned structure. The resultant 3D VA-MWNT/VA-SWMT multicomponent micropatterns with region-specific nanotube lengths can be reversibly switched between a semiconducting and metallic state characteristic of the semiconducting VA-SWNTs and metallic VA-MWNTs, respectively. The observed fast and highly reversible pulsed current response to compression-decompression cycles at a constant voltage clearly indicate that these *newly-developed* 3D VA-MWNT/VA-SWNT multicomponent micropatterns are useful in a large variety of micro-/nano-electronic devices, ranging from electronic switches through memory storages to touch sensors. Furthermore, the double contact transfer concept developed in this study should be applicable for interposing a large variety of multiconmponent elements (*e.g.* nanotubes, nanowires, quantum dots, photonic crystals, metal oxides) onto a single chip for various multifunctional device applications.

**Acknowledgements**

This work was partially supported by NSF (CMS-0609077; CMMI-0708055) and AFOSR.

**References**

[1] Dresselhaus, M.S.; Dai, H.J. Recent advances in methods of forming carbon nanotubes. *MRS Bulletin* **2004**, *29*, 244-250.

[2] Qu, L.; Peng, Q.; Dai, L.; Spinks, G.M.; Wallace, G.G.; Baughman, R.H. Carbon nanotube electroactive polymer materials: Opportunities and challenges. *MRS Bulletin* **2008**, *33*, 215-224.

[3] Dai, L. (Ed.), *"Carbon Nanotechnology: Recent Developments in Chemistry, Physics, Materials Science and Device Applications*", Elsevier: Amsterdam, 2006.

[4] Fan, S.; Chapline, M.G.; Franklin, N.R.; Tombler, T.W.; Cassell, A.M.; Dai, H.J. Self-oriented regular arrays of carbon nanotubes and their field emission properties. *Science* **1999**, *283*, 512-514.

[5] Yang, Y.; Huang, S.; He, H.; Mau, A. W. H.; Dai, L. Patterned growth of well-aligned carbon nanotubes: A photolithographic approach. *J. Am. Chem. Soc.* **1999**, *121*, 10832-10833.

[6] Zhang, Z. J.; Wei, B. Q.; Ramanath, G.; Ajayan, P. M. Substrate-site selective growth of aligned carbon nanotubes. *Appl. Phys. Lett.* **2000**, *77*, 3764-3766.

[7] Xia, Y.; Whitesides, G. M. Soft lithography. *Angew. Chem. Int. Ed.* **1998**, *37*, 551-575.

[8] Huang, S.; Mau, A. W. H.; Turney, T. W.; White, P. A.; Dai, L. Patterned growth of well-aligned carbon nanotubes: A soft-lithographic approach. *J. Phys. Chem. B* **2000**, *104*, 2193-2196.

[9] Wei, H.; Kim, S. N.; Marcus, H. L.; Papadimitrakopoulos, F. Preferential forest assembly of single-wall carbon nanotubes on low-energy electron-beam patterned nafion films . *Chem. Mater.* **2006**, *18*, 1100-1106.

[10] Hung, W. H.; Kumar, R.; Bushmaker, A.; Cronin, S. B.; Bronikowski, M. J. Rapid prototyping of three-dimensional microstructures from multiwalled carbon nanotubes. *Appl. Phys. Lett.* **2007**, *91*, 093121.

[11] Yang, J.; Qu, L.; Zhao, Y.; Zhang, Q.; Dai, L.; Baur, J. W.; Maruyama, B.; Vaia, R. A.; Shin, E.; Murray, P. T.; Luo, H.; Guo, Z. Multicomponent and multidimensional carbon nanotube micropatterns by dry contact transfer. *J. Nanosci. Nanotechnol.* **2007**, *7*, 1573-1580.

[12] Yang, J.; Dai, L.; Vaia, R. A. Multicomponent interposed carbon nanotube micropatterns by region-specific contact transfer and self-assembling. *J. Phys. Chem. B* **2003**, *107*, 12387-12390.

[13] Qu, L. T.; Dai, L. Direct growth of three-dimensional multicomponent micropatterns of vertically aligned single-walled carbon nanotubes interposed with their multi-walled counterparts on Al-activated iron substrates. *J. Mater. Chem.* **2007**, *17*, 3401-3405.

[14] Huang, S.; Dai, L.; Mau, A. W. H. Patterned growth and contact transfer of well-aligned carbon nanotube films. *J. Phys. Chem.B* **1999**, ***103***, 4223-.

[15] Qu, L.T.; Dai, L. Gecko-foot-mimetic aligned single-walled carbon nanotube dry adhesives with unique electrical and thermal properties. *Adv. Mater.* **2007**, *19*, 3844-3849.

[16] Patil, A.; Ohashi, T.; Buldum, A.; Dai, L. Controlled preparation and electron emission properties of three-dimensional micropatterned aligned carbon nanotubes. *Appl. Phys. Lett.* **2006**, *89*, 103103.

[17] Cao, A. Y.; Dickrell, P. L.; Sawyer, W. G.; Ghasemi-Nejhad, M. N.; Ajayan, P. M. Super-compressible foamlike carbon nanotube films. *Science* **2005**, *310*, 1307-1310.

[18] Suhr, J.; Victor, P.; Sreekala, L. C. S.; Zhang, X.; Nalamasu, O.; Ajayan, P. M. Fatigue resistance of aligned carbon nanotube arrays under cyclic compression. *Nat. Nanotech.* **2007**, *2*, 417-421.

***Back to Programme*** ***Back to Topic*** ***Next Paper***