

# Macroporous carbon nanotube arrays with tunable pore sizes and their template applications

Huisheng Peng<sup>\*ab</sup> and Xuemei Sun<sup>a</sup>

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**This work reports the first synthesis of macroporous carbon nanotube arrays with tunable pore sizes, and these porous arrays provide simple and efficient templates for synthesizing composite carbon nanotube–polymer materials.**

Carbon nanotubes (CNTs) are among the most promising materials to impact future technologies.<sup>1</sup> Their unique structures and excellent physical properties make them very attractive for a broad range of applications. For instance, CNT–polymer composites have been used as electrostatic-discharge components in which CNTs enhance the electrical conductivity of plastics.<sup>2</sup> For these composite materials in many practical applications, CNTs are desired to be highly aligned to deliver the high conductivities of individual CNTs.<sup>3</sup> Therefore, the synthesis and direct use of aligned CNT arrays have been investigated recently.<sup>4</sup> Two successful systems of aligned CNT–poly(methyl methacrylate)<sup>5</sup> and CNT–polyaniline<sup>6</sup> have been synthesized by infiltrating monomers into the arrays, followed by *in situ* polymerization. For the above approach, however, it is difficult to control the structures and properties of the resulting composite materials by directly casting monomers onto the CNT arrays. Herein, we report the first synthesis of macroporous CNT arrays which are very useful to achieve aligned high-quality CNT–polymer or other CNT-based functional composite materials. In other words, the pore size can be tuned to control the composite structures and properties. We have further shown that, when polymers are cast into the pores, the resulting composite materials show much improved electrical conductivities.

Fig. 1 schematically shows the synthesis of macroporous CNT arrays. A dense CNT array which functions as the building block of the porous array is first synthesized by a chemical vapor deposition process. Fe/Al<sub>2</sub>O<sub>3</sub> serves as the catalyst system, and ethylene is used as the carbon source. More synthetic details are described in the experimental section.† The macroporous CNT array is then fabricated by dropcasting methyl acrylate into the as-synthesized dense array, followed by evaporation of methyl acrylate at a temperature between 45 and 55 °C.

Fig. 2a shows a typical scanning electron microscopy (SEM) image of a dense CNT array. The CNT is normal to the substrate with thickness of ~0.7 mm on silicon. Fig. 2b shows

that the CNTs are highly aligned in the array. The top surface of the array is smooth and clean (Fig. 2c). The inset transmission electron microscopy image in Fig. 2b demonstrates that the synthesized CNTs are multi-walled with a diameter of ~30 nm. Typical Raman spectra of dense CNT arrays have been reported elsewhere.<sup>7</sup> The density of the aligned CNTs in the array is higher than 10<sup>10</sup> cm<sup>-2</sup>.<sup>8</sup> After coating with methyl acrylate, the arrays shrank but maintained their original morphologies. Macropores with highly aligned CNTs in the vertical direction form following evaporation of methyl acrylate by thermal treatment (inset in Fig. 2d). The top surface of the array remains flat and clean. The pore size largely varies from 1 μm to 7 μm, and it mainly depends on the thermal treatment temperature and the thickness of the CNT array (Fig. 2e). Low temperatures produce relatively small pore sizes, while high temperatures favor the formation of big pores. For instance, thermal treatment of 1 mm-long dense CNT arrays at 45 °C and 55 °C produced pores with diameters in the range of 1.0–3.0 μm and 1.5–4.0 μm, respectively. Thermal treatment of 2 mm-long dense CNT arrays at 45 °C, 49 °C, and 55 °C produced pores with diameters in the range of 1.3–2.6 μm, 1.5–3.1 μm, and 2.5–6.5 μm, respectively. We have also found that the thickness of the array does not obviously affect the pore size if the thermal treatment is done at a temperature of 45 °C. The long array, on the other hand, favors the formation of big pores, *e.g.*, 1.5–4.0 μm for a 1 mm-long array and 2.5–6.5 μm for a 2 mm-long array at a thermal treatment temperature of 55 °C.

It should be also noted that not all CNT arrays can form porous structures by this approach. It has been reported that wetting CNT arrays either caused them to lay down on the substrate and re-organize into cellular structures<sup>9</sup> or collapse into the packed solids<sup>10</sup> or foams<sup>11</sup>. Although the CNTs were highly aligned, no pores were observed in the resulting materials.<sup>9–11</sup> This phenomenon may be related to the rigidity and density of the CNT arrays. Softer and less organized

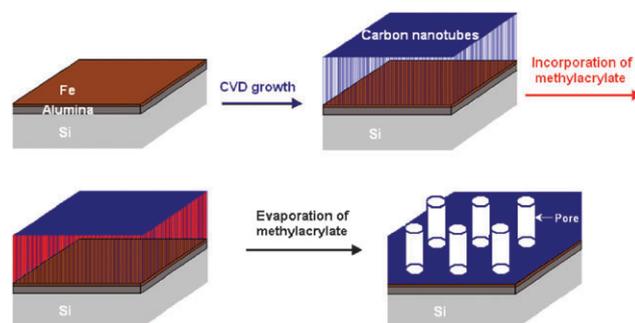
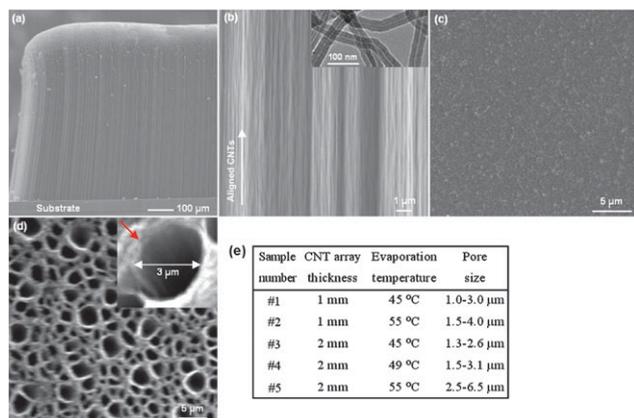


Fig. 1 Synthesis of macroporous CNT arrays.

<sup>a</sup> Laboratory of Advanced Materials and Department of Macromolecular Science, Fudan University, Shanghai 200438, China. E-mail: penghs@fudan.edu.cn; Fax: 86-21-51630316; Tel: 86-21-51630316

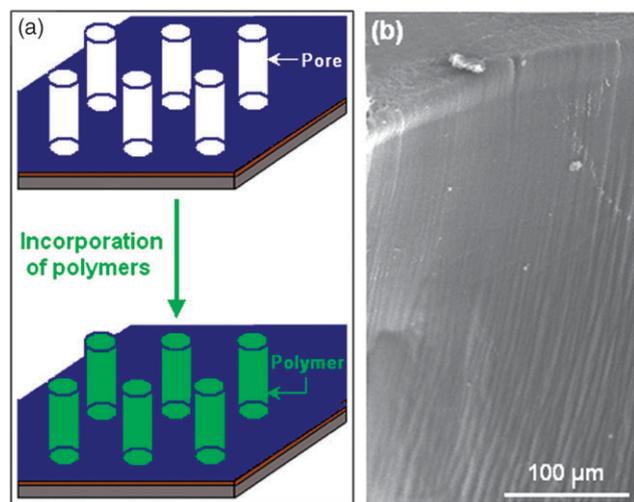
<sup>b</sup> Los Alamos National Laboratory, Los Alamos, NM 87545, USA



**Fig. 2** Scanning electron microscopy (SEM) images of a dense CNT array and its derived macroporous CNT array. (a) and (b) Side views of the dense array under different magnifications (the inset in (b) shows the transmission electron microscopy image of CNTs). (c) Top view of the dense array. (d) Macropores formed in the CNT array (the inset shows a pore with diameter of  $\sim 3 \mu\text{m}$ ). The red arrow shows highly aligned CNTs between the pores. (e) Porous CNT arrays with tunable pore sizes by varying the thickness of the CNT arrays and the thermal treatment temperatures.

CNT arrays tend to lay down or collapse much more easily. In our system, the dense and vertically aligned arrays are rigid enough to largely maintain their original vertical orientations. The formation of pores is due to the re-organization of CNTs.<sup>9-11</sup>

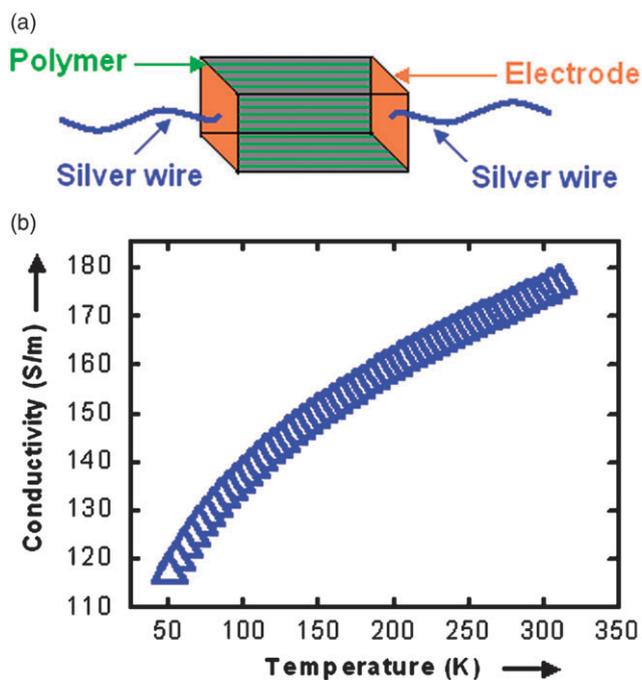
Porous materials have been widely used as templates to synthesize functional composite materials.<sup>12</sup> As CNTs are highly aligned in the porous CNT arrays, we can use them as templates to fabricate CNT-based composite materials with much improved physical properties. For example, Fig. 3a schematically shows an approach that can be effectively used to incorporate polymers into the pores of the porous CNT array through a simple solution process.



**Fig. 3** (a) Schematic illustration of the synthesis of composite materials using macroporous CNT arrays as templates. (b) Side view of a CNT-polystyrene composite. The white contrast corresponds to the polystyrene moiety.

CNT-polymer composites have been extensively investigated due to their potential applications, such as cost-effective electrodes.<sup>2</sup> Three main fabrication approaches have been explored, *i.e.*, solution blending, melt blending, and *in situ* polymerization.<sup>6</sup> A common yet significant barrier is the aggregation and random dispersion of CNTs in polymer matrices, which greatly limits the performance of composites.<sup>7b</sup> For example, the electrical conductivity of such composites is extremely low.<sup>13</sup> CNT-poly(methyl methacrylate) composites synthesized by a melt spinning process shows a conductivity less than  $10^{-4} \text{ S m}^{-1}$ .<sup>14</sup> By introducing polymers into porous CNT arrays, we have synthesized highly aligned CNT-polymer composites with a wide variety of polymers, designed structures, and much enhanced conductivities. Fig. 3b shows the side view of a CNT-polystyrene composite. The pore part is filled with polystyrene (white contrast), and the array almost maintains the original morphology. In other words, the vertically aligned CNTs remain in the composite. The derived CNT-polystyrene composite shows an electrical conductivity of  $175 \text{ S m}^{-1}$  at room temperature measured by a two-probe method (Fig. 4a). Fig. 4b further shows the temperature dependence of the conductivity for the CNT-polystyrene composite between 50 K and 310 K. The conductivity increases with temperature, suggesting a semiconducting behavior.<sup>15</sup>

In summary, this work reports the first synthesis of highly aligned macroporous CNT arrays with tunable pore sizes. Second phase materials, such as polymers, can be incorporated into the pores through a simple solution process. Compared with traditional fabrication methods, the highly aligned CNT-polymer composites synthesized by this approach show much improved conductivities.



**Fig. 4** (a) Schematic illustration of the conductivity measurement by a two-probe method. The electrode is a coated thin layer of Au/Pt. (b) Temperature dependence of the conductivity of a CNT-polystyrene composite.

## Notes and references

† *Synthesis of CNT arrays*: CNT arrays were synthesized in a quartz tube furnace with a diameter of 2.54 cm. Ethylene served as the carbon source, and Ar with 6% H<sub>2</sub> was used as the carrier gas. The catalysts used in this study were Fe (0.3–1.0 nm)/Al<sub>2</sub>O<sub>3</sub> (10 nm) on silicon. More experimental details have been reported elsewhere.<sup>16</sup>

*Synthesis of macroporous CNT arrays*: macroporous CNT arrays were fabricated by dropcasting methyl acrylate (99%, from Fisher Scientific) into as-synthesized dense CNT arrays, followed by evaporation of methyl acrylate at different thermal treatment temperatures. All operations were processed in a hood with the environmental temperature of ~22 °C.

*Synthesis of CNT-polymer composites*: polystyrene (number-average molecular weight of  $1.4 \times 10^5$  g mol<sup>-1</sup> and weight-average molecular weight of  $2.3 \times 10^5$  g mol<sup>-1</sup> from Aldrich) was first dissolved in tetrahydrofuran with a concentration of 133 mg mL<sup>-1</sup>. The resulting solution was dropped into porous CNT arrays at room temperature. CNT-polymer composites were then produced after evaporation of tetrahydrofuran.

*Characterization*: for the measurement of the electrical conductivity, the two ends of the CNT-polystyrene composite were first coated with thin Au/Pt layers through a mask technology, *i.e.*, the other parts of the array were covered with a paper. Silver wires were then connected to the electrodes using silver paint. We thank Dr M. Jain for the help with the conductivity measurements.

- (a) A. N. Khlobystov, D. A. Britz and G. A. D. Briggs, *Acc. Chem. Res.*, 2005, **38**, 901; (b) M. Zhang, K. R. Atkinson and R. H. Baughman, *Science*, 2004, **306**, 1358; (c) X. Zhang, K. Jiang, C. Feng, P. Liu, L. Zhang, J. Kong, T. Zhang, Q. Li and S. Fan, *Adv. Mater.*, 2006, **18**, 1505; (d) H. Dai, *Acc. Chem. Res.*, 2002, **35**, 1035.
- P. M. Ajayan and J. M. Tour, *Nature*, 2007, **447**, 1066.
- M. Moniruzzaman and K. I. Winey, *Macromolecules*, 2006, **39**, 5194.
- (a) C. Wei, L. Dai, A. Roy and T. B. Tolle, *J. Am. Chem. Soc.*, 2006, **128**, 1412; (b) T. Sun, H. Liu, W. Song, X. Wang, L. Jiang, L. Li and D. Zhu, *Angew. Chem., Int. Ed.*, 2004, **43**, 4663.
- (a) N. R. Raravikar, L. S. Schadler, A. Vijayaraghavan, Y. Zhao, B. Wei and P. M. Ajayan, *Chem. Mater.*, 2005, **17**, 974; (b) N. R. Raravikar, A. S. Vijayaraghavan, P. Koblinski, L. S. Schadler and P. M. Ajayan, *Small*, 2005, **1**, 317.
- W. Feng, X. D. Bai, Y. Q. Lian, J. Liang, X. G. Wang and K. Yoshino, *Carbon*, 2003, **41**, 1551.
- (a) H. S. Peng, J. Menka, D. E. Peterson, Y. T. Zhu and Q. X. Jia, *Small*, 2008, **4**, 1964; (b) H. S. Peng, *J. Am. Chem. Soc.*, 2008, **130**, 42.
- Y. Tu, Z. P. Huang, D. Z. Wang, J. G. Wen and Z. F. Ren, *Appl. Phys. Lett.*, 2002, **80**, 4018.
- Q. W. Li, R. Depaula, X. Zhang, L. Zheng, P. N. Arendt, F. M. Mueller, Y. T. Zhu and Y. Tu, *Nanotechnology*, 2006, **17**, 4533.
- D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura and S. Iijima, *Nat. Mater.*, 2006, **5**, 987.
- N. Chakrapani, B. Wei, A. Canillo, P. M. Ajayan and R. S. Kane, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 4009.
- (a) X. Chen, M. Steinhart, C. Hess and U. Gosele, *Adv. Mater.*, 2006, **18**, 2153; (b) D. Wang, H. Luo, R. Kou, M. P. Gil, S. Xiao, V. O. Golub, Z. Yang, C. J. Brinker and Y. Lu, *Angew. Chem., Int. Ed.*, 2004, **43**, 6169; (c) A. T. Rodriguez, M. Chen, Z. Chen, C. J. Brinker and H. Y. Fan, *J. Am. Chem. Soc.*, 2006, **128**, 9276.
- W. Zhou, J. Vavro, C. Guthy, K. I. Winey, J. E. Fischer, L. M. Ericson, S. Ramesh, R. Saini, V. A. Davis, C. Kittrell, M. Pasquali, R. H. Hauge and R. E. Smalley, *J. Appl. Phys.*, 2004, **95**, 649.
- F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer and K. I. Winey, *Macromolecules*, 2004, **37**, 9048.
- (a) H. S. Peng, M. Jain, Q. W. Li, D. E. Peterson, Y. T. Zhu and Q. X. Jia, *J. Am. Chem. Soc.*, 2008, **130**, 1130; (b) H. S. Peng, D. Y. Chen, J. Y. Huang, S. B. Chikkannanavar, J. Hanisch, D. E. Peterson, S. K. Doorn, Y. F. Lu, Y. T. Zhu and Q. X. Jia, *Phys. Rev. Lett.*, 2008, **101**, 145501.
- Q. Li, X. Zhang, R. F. DePaula, L. Zheng, Y. Zhao, L. Stan, T. G. Holesinger, P. N. Arendt, D. E. Peterson and Y. T. Zhu, *Adv. Mater.*, 2006, **18**, 3160.