

Cite this: DOI: 10.1039/c1cc13359d

www.rsc.org/chemcomm

## Poptube approach for ultrafast carbon nanotube growth†

Zhen Liu,<sup>a</sup> Jialai Wang,<sup>b</sup> Vinod Kushvaha,<sup>c</sup> Selcuk Poyraz,<sup>a</sup> Hareesh Tippur,<sup>c</sup> Seongyong Park,<sup>d</sup> Moon Kim,<sup>d</sup> Yang Liu,<sup>a</sup> Johannes Bar,<sup>a</sup> Hang Chen<sup>e</sup> and Xinyu Zhang<sup>\*a</sup>

Received 6th June 2011, Accepted 21st July 2011

DOI: 10.1039/c1cc13359d

**Microwave irradiation can be used to heat conductive materials and metallocene precursors to initiate ultrafast CNT growth. It takes only 15–30 seconds to grow CNTs at room temperature in air, without the need for any inert gas protection and additional feed stock gases.**

Carbon nanotubes (CNTs) have drawn a great deal of attention since Iijima discovered this new class of allotropes of carbon.<sup>1</sup> Due to their extraordinary mechanical, thermal and electrical properties, CNTs have huge potential in the applications of composite materials,<sup>2</sup> smart structures,<sup>3</sup> chemical sensors,<sup>4</sup> energy storage<sup>5</sup> and nano-electronic devices.<sup>6</sup> However, the challenges remain in the high cost of CNT raw materials and the difficulty in their processing and applications. For example, vacuum or inert gas protection, high temperature and/or high energy density are always needed for the production of CNT, *e.g.*, arc-discharge,<sup>7</sup> laser ablation<sup>8</sup> and chemical vapor deposition (CVD)<sup>9</sup> approaches, which make the cost of the as-produced CNTs to remain high. In addition, strong van der Waals force induced poor solubility/dispersibility is another factor that restricts the application of CNTs, especially in reinforcing composite materials.<sup>10</sup>

As an attempt to address the challenges mentioned above, some reports discussed on embedding CNTs into carbon fibers through the conventional thermal heating process,<sup>11</sup> and CVD methods,<sup>12</sup> which can partially solve the dispersibility issue, but the reaction setup is still costly and complicated, and the process is time-consuming and energy inefficient due to the target-less volumetric heating. As previously developed by our group, conducting polymers can be heated to very high temperature in a short time, and converted to graphitic nanocarbons.<sup>13</sup> Based on this finding, we can use conducting polymers as heating sources towards growth of CNTs through the microwave approach.

In a typical process, microwave Poptube precursors, such as ferrocene powder,<sup>14–16</sup> were physically mixed in the solid state with conductive materials, namely conducting polymers, Indium Tin Oxide (ITO) nano-powders, graphite powders, and carbon fibers. Upon microwave irradiation of the conducting materials, they will be heated to spark, arc and rapidly reach the temperature above 1100 °C,<sup>13,17</sup> where the ferrocene could be decomposed to an iron catalyst<sup>18</sup> and cyclopentadienyl that could serve as the carbon source. The microwave initiated CNT growth will take only 15–30 seconds under the microwave irradiation at room temperature in air, without the need for any inert gas protection, and additional feed stock gases, usually required in the CVD approach and other methods. To the best of our knowledge, this is the fastest CNT growth in terms of process duration, and probably the only approach that can be done under ambient conditions.

The SEM images revealed the morphologies of the CNTs made from conducting polypyrrole-Cl powder (PPy-Cl) and ITO nanopowders (Fig. 1A and B). Spaghetti-like, hollow CNTs were observed with a few micrometres long (Fig. 1B), when conducting PPy-Cl was used as the heating layer, with outer diameter in the range of 30–50 nm. However, rod-like CNTs with bamboo-shaped inner hollow structures were obtained when ITO nanopowders were used as the heating layer (Fig. 1C and D and the inset), having outer diameters in the range of 150–200 nm. The nature of the conducting layers could play a significant role in controlling the morphology of the CNTs, *e.g.*, the crystallinity and conductivity of the heating layers could affect the crystallinity and dimension of the iron catalyst nanoparticles. The multi-walled nature of the CNTs was evidenced by high resolution TEM (HRTEM, Fig. 1E and F), confirming that the CNTs are composed of ~20 layers of coaxially folded graphene sheets. Other metallocenes and derivatives can be used as precursors, such as cobaltocene, nickelocene and 1,1'-bis-(diphenylphosphino) ferrocene, which are evidenced by the SEM images in Fig. S2 (ESI†). Compared to ferrocene, the 1,1'-bis-(diphenylphosphino) derivative has more conjugated rings (four benzene rings) in the structures, which could contribute to the more rigid structures (Fig. S2B, ESI†).

The mechanism of the CNT growth is still unclear, although a tip-growth model could be proposed for this Poptube process. This is confirmed by the electron microscope images, since most of the catalyst particles are either at the tip or the middle part of the carbon nanotubes, indicating that the CNT

<sup>a</sup> Department of Polymer and Fiber Engineering, Auburn University, Auburn, AL 36849, USA. E-mail: xzz0004@auburn.edu; Fax: +1-334-844-4068; Tel: +1-334-844-5439

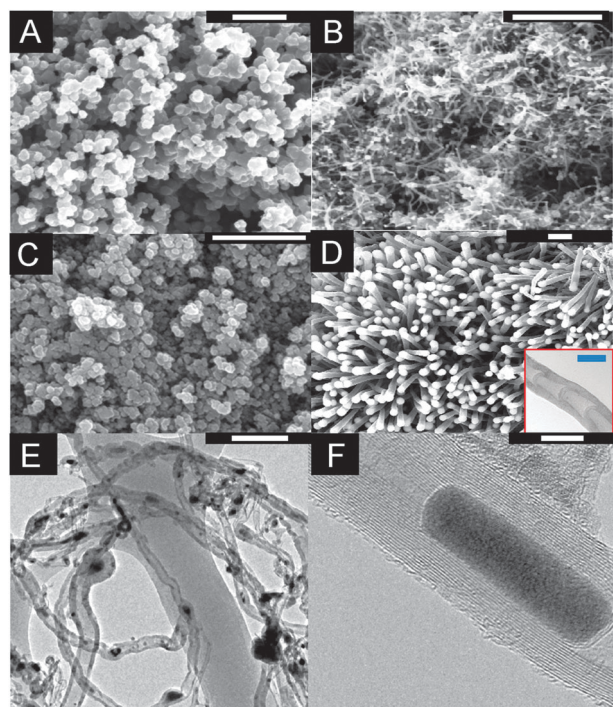
<sup>b</sup> Department of Civil, Construction, and Environmental Engineering, The University of Alabama, Tuscaloosa, AL 35487, USA

<sup>c</sup> Department of Mechanical Engineering, Auburn University, Auburn, AL 36849, USA

<sup>d</sup> Department of Materials Engineering, The University of Texas at Dallas, Richardson, TX 75080, USA

<sup>e</sup> Nanotechnology Research Center, Georgia Institute of Technology, Atlanta, GA 30332, USA

† Electronic supplementary information (ESI) available: Enlarged images and experimental details. See DOI: 10.1039/c1cc13359d

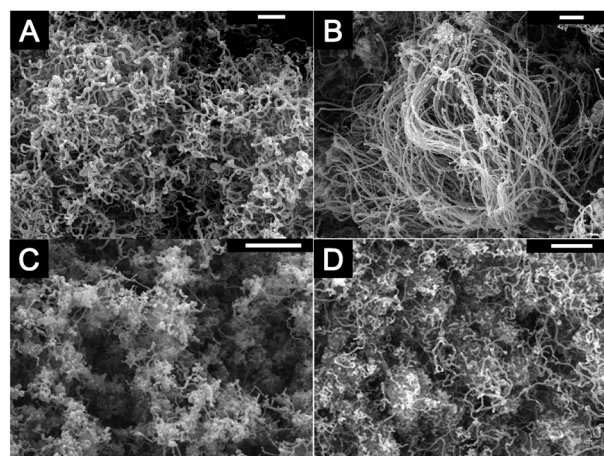


**Fig. 1** SEM images of (A) granular PPy-Cl; (B) CNTs grown on PPy-Cl granules; (C) ITO nanopowders; (D) CNTs grown on ITO nanopowders (scale bar for A–D: 1  $\mu\text{m}$ ), inset: the TEM image of an individual CNT grown on ITO nanopowders (scale bar: 100 nm); (E) TEM image of CNTs grown on PPy-Cl granules (scale bar: 200 nm); and (F) HRTEM of individual CNTs with trapped Fe catalyst particles (scale bar: 5 nm).

growth is following the tip-growth mode instead of the base-growth mode.<sup>19</sup> Actually, these tips are still active to promote further growth of CNTs. We actually have observed both growth in length and coverage density of the CNT on the substrates, by simply repeating the process cycles. For example, the initial length of the as-produced CNTs on PPy-Cl powders was in the range of 1–3  $\mu\text{m}$ . To the product from the first cycle, additional ferrocene was added in an equivalent amount, and followed by speed mixing and microwave heating. The second step mainly helps to increase the density of CNTs on the substrates (Fig. 2A), instead of the length. However, another cycle (3rd cycle) will increase the length dramatically (Fig. 2B), from 1–3  $\mu\text{m}$  to about 10–20  $\mu\text{m}$ . We speculate that CNT growth favors the substrate surfaces, which are very hot upon microwave heating, and ready to decompose the precursor for the CNT growth. And once the available lots are taken, the active tip will be the next favorable place to grow CNTs.

As reported previously, small molecules such as hexane can be used as a carbon source to produce CNTs.<sup>20</sup> Although ferrocene can be the catalyst and carbon source combination, the addition of hexane to the system will improve the CNT growth due to the additional carbon source. As shown in Fig. 2C and D, the addition of hexane increased both the length and the coverage density of CNTs on graphite powders.

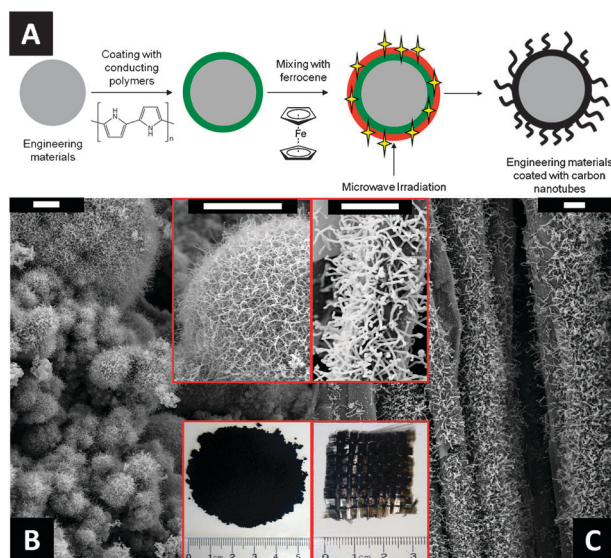
Besides the stand-alone conductive materials such as PPy-Cl or ITO nanopowders, these multi-walled CNTs (MWNTs) can also be grown on a variety of engineering materials, which are pre-coated with the conductive materials, such as carbon



**Fig. 2** SEM images of CNT (A) with polypyrrole coated fly ash via a two step CNT growth method, (B) with polypyrrole coated fly ash via a three step CNT growth method, (C) graphite powder and (D) graphite powder with addition of hexane (scale bar: 1  $\mu\text{m}$ ).

fibers. Actually, MWNTs were successfully grown on PPy-Cl coated fly ash powders, glass fibers, Kevlar, Basalt fibers, Kaolin powders, and commercial 3M glass microballoons through this microwave initiated Poptube approach, using ferrocene as the catalyst and carbon source combination (Fig. 3, Fig. S3 and S4 in ESI<sup>†</sup>). In this aspect, the Poptube approach can be considered as a “Universal” method due to the diverse precursors and the surfaces for which this method can be applied.

With an attempt to see the scalability of the Poptube process, we carried out experiments with powder and fabric materials. Conducting PPy-Cl coated fly ash and glass fiber cloth were selected as the substrate materials. We could easily produce 10 g powder of the fly ash–CNT nanocomposites



**Fig. 3** (A) Scheme: microwave initiated CNT growth on engineering materials; SEM images of the as-produced CNTs on (B) fly ash, insets: (top) zoom-in SEM image; (bottom) digital picture of 10 g CNT coated fly ash; and (C) glass fiber fabrics, inset: (top) zoom-in SEM image; (bottom) digital picture of 1 inch  $\times$  1 inch glass fiber fabric coated with CNT (scale bar: 5  $\mu\text{m}$ ).

using this Poptube approach within 10 minutes in the lab using a kitchen microwave, with excellent reproducibility (Fig. 3B, inset), and make CNT coated glass fiber fabrics with a dimension of 1 inch  $\times$  1 inch (Fig. 3C, inset), which depends on the size of the container in the microwave oven. It is to be noted that the production volume of the CNTs is proportional to the number of microwave ovens.

These CNT-coated engineering materials can be used as multifunctional fillers in a polymer matrix, or construction materials to build intelligent structures, in order to enhance the electrical and thermal conductivity and mechanical strength. Actually, we have observed enhancement in electrical conductivity, *i.e.*, the bulk four probe dc conductivity of CNT coated fly ash is  $\sim 0.87 \text{ S cm}^{-1}$ , compared to insulating bare fly ash. To demonstrate the improvement of the mechanical properties, we have tested epoxy resin based syntactic foam (SF) reinforced by glass microballoons with (nano-SF) and without CNT decoration (Fig. S4, ESI†).<sup>21</sup> Static fracture studies were carried out for conventional SF and nano-SF, containing 15 vol% undecorated/decorated microballoons respectively.

The three-point bending tests revealed an enhancement for the nano-SF in terms of critical fracture toughness and cross head displacement at  $\sim 17.0\%$  and  $\sim 7.5\%$ , respectively, compared to the conventional SF. To ensure the repeatability of experimental results, three specimens of each composite were tested under identical conditions. This finding confirmed that direct growth of CNTs will assist the improvement of the mechanical characteristics such as static toughness.

We have described for the first time (i) an ultrafast microwave approach to CNT growth in air at room temperature within 15–30 seconds; (ii) that CNTs can be directly grown on a wide selection of engineering materials including glass fibers, carbon fibers, fly ash and glass microballoons *etc.*; (iii) that the incorporation of CNT decorated glass microballoons enhanced the toughness of syntactic foam. This novel Poptube approach also provides a possible solution for the existing challenges in CNT applications, such as high cost, low dispersibility and small scale production. Due to the high-efficiency and selective heating of microwave irradiation, this Poptube method can be considered as a “green and sustainable” technology. In addition, with proper precursors, this Poptube approach may be able to grow nanostructured metal oxides or

new carbon allotropes such as graphene, which were mainly produced by CVD approaches.

We gratefully acknowledge financial support from National Science Foundation Awards CMMI-1000491 and CMMI-1000580, Department of Commerce, Auburn University.

## Notes and references

- 1 S. Iijima, *Nature*, 1991, **354**, 56–58.
- 2 B. Dalton Alan, S. Collins, E. Munoz, M. Razal Joselito, H. Ebron Von, P. Ferraris John, N. Coleman Jonathan, G. Kim Bog and H. Baughman Ray, *Nature*, 2003, **423**, 703.
- 3 L. Rakesh, B. A. Howell, M. Chai, A. Mueller, M. Kujawski, D. Fan, S. Ravi and C. Slominski, *Nanomedicine*, 2008, **3**, 719–739.
- 4 J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dault, *Science*, 2000, **287**, 622–625.
- 5 R. H. Baughman, A. A. Zakhidov and W. A. de Heer, *Science*, 2002, **297**, 787–792.
- 6 A. G. Rinzler, *Nat. Nanotechnol.*, 2006, **1**, 17–18.
- 7 C. Journet, W. K. Maser, P. Bernier, A. Loiseau, M. Lamy de la Chapells, S. Lefrant, P. Deniard, R. Lee and J. E. Fischer, *Nature*, 1997, **388**, 756–758.
- 8 J. E. Fischer, H. Dai, A. Thess, R. Lee, N. M. Hanjani, D. L. Dehaas and R. E. Smalley, *Phys. Rev. B: Condens. Matter*, 1997, **55**, R4921–R4924.
- 9 B. Baykal, V. Ibrahimova, G. Er, E. Bengue and D. Tuncel, *Chem. Commun.*, 2010, **46**, 6762–6764.
- 10 D. Abusch-Magder, T. Someya, J. Wang, E. Laskowski, A. Dodabalapur, Z. Bao, D. M. Tennant, arXiv:cond-mat, 2002, 0210332.
- 11 A. Fraczek-Szczypta, M. Bogun and S. Blazewicz, *J. Mater. Sci.*, 2009, **44**, 4721–4727.
- 12 J. Zhao, L. Liu, Q. Guo, J. Shi, G. Zhai, J. Song and Z. Liu, *Carbon*, 2008, **46**, 380–383.
- 13 X. Zhang and K. Manohar Sanjeev, *Chem. Commun.*, 2006, 2477–2479.
- 14 X. Gui, J. Wei, K. Wang, A. Cao, H. Zhu, Y. Jia, Q. Shu and D. Wu, *Adv. Mater.*, 2010, **22**, 617–621.
- 15 Y.-L. Li, I. A. Kinloch and A. H. Windle, *Science*, 2004, **304**, 276–278.
- 16 H. Shiozawa, T. Pichler, A. Grueneis, R. Pfeiffer, H. Kuzmany, Z. Liu, K. Suenaga and H. Kataura, *Adv. Mater.*, 2008, **20**, 1443–1449.
- 17 Y.-L. Hsin, C.-F. Lin, Y.-C. Liang, K. C. Hwang, J.-C. Horng, J.-a. A. Ho, C.-C. Lin and J. R. Hwu, *Adv. Funct. Mater.*, 2008, **18**, 2048–2056.
- 18 A. S. Anisimov, A. G. Nasibulin, H. Jiang, P. Launois, J. Cambedouzou, S. D. Shandakov and E. I. Kauppinen, *Carbon*, 2009, **48**, 380–388.
- 19 L. J. Ci, Z. G. Zhao and J. B. Bai, *Carbon*, 2005, **43**, 883–886.
- 20 H. W. Zhu, C. L. Xu, D. H. Wu, B. Q. Wei, R. Vajtai and P. M. Ajayan, *Science*, 2002, **296**, 884–886.
- 21 H. S. Kim and H. H. Oh, *J. Appl. Polym. Sci.*, 2000, **76**, 1324–1328.