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ARTICLE TYPE

A novel method to encapsulate a Au nanorods array in 15 nm radius multiwalled carbon nanotubes

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In this paper we demonstrate a novel complex array structure comprising well-aligned Au nano-rods (10 nm in diameter) encapsulated inside 15nm radius multiwalled carbon nanotubes (MWCNTs). A pre-aligned and open-ended nano-porous MWCNT membrane is used as the starting material. Au nano-rods are precisely deposited and aligned inside the hollow channels of CNTs by inter-diffusing HAuCl₄ precursor and the reductant solution. Ultra-long Au nano-wires and spherical Au nano particles are also observed in the CNT cavity with the same diameter in special case. By using high-resolution TEM(HRTEM), Scanning transmission electron microscopy(STEM), 3-dimensional TEM(3D-TEM) and Energy dispersive X-ray spectroscopy(EDX), the precious location and composition of the encapsulated Au components with various structures are confirmed. This aligned Au@CNT endohedral material has important potential applications in nano-catalysis, waveguides, as well as novel plasmonic devices.

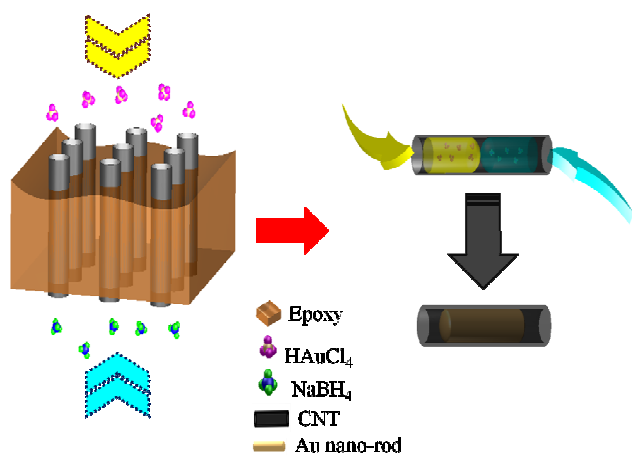
Introduction

Carbon nanotubes (CNTs) composed of single or multiple rolled graphene sheets form a well-defined hollow pore with nanometer scale. Such one-dimensional confined space has been utilized for both tiny material storage and transportation.^{1,2} The so-called endohedral CNT materials have shown quite unique properties as compared to the bulk, such as molecular packing, orientation, translation and reactivity, due to the nano-confinement effect and the interaction between the fillers and CNTs.³⁻⁶ Many promising applications have emerged for this endohedral CNT materials including bio-imaging, drug delivery, efficient catalysis as well as photonic devices.⁷⁻¹⁰ CNTs encapsulated with metals, alloys, semiconductors, insulators and some organic species like DNAs and proteins have been achieved using different synthesis approaches including melting-phase capillary filling, solvent extraction (wet-infilling) and chemical vapor deposition.¹¹⁻¹³ To improve the filling efficiency high temperature, high vacuum or pressure conditions are normally required.^{14,15} Meanwhile the CNTs need to be cut and shortened in advance.⁹ However, the wetting and filling of the inner pore of CNTs are still challenging for the CNTs with diameters below 30nm due to the significant decrease in the capillarity of narrow nanotubes as compared to CNTs with large inner diameter and cavity size.^{2,16} Another obstacle for traditional filling method is the poor selective modification on the inner pore of CNTs due to extreme similarity in chemical properties between the inside and outside CNT walls.¹⁷ A mixture of inner and outside modified sample brings extra difficulty to study the nano-confinement effect.¹²

Au@CNT structure has fascinated scientists recently because the thermal stability and transition behaviour of Au significantly varies as the diameter of the CNTs decreases based on theoretical simulations.¹⁸ The regular anodic aluminum oxide (AAO) template can be used to fabricate 1D composite nano structures.¹⁹ However the diameter of the AAO template is usually larger than 30nm which provides limited confinement on the fillers.⁴ Chu *et al.* synthesized Au nano particles@CNT composite by refluxing the CNTs with the HAuCl₄ followed by a thermal decomposition reaction.²⁰ In their study, they did not provide detailed characterization on the location of the enclosed Au nano-particles except 2-D TEM. Rao *et al.* prepared Au nanowires inside SWNTs by a sealed-tube reaction under a high vacuum and temperature but cannot avoid decoration of metal nanoparticles on the external wall of the CNT.²¹

To achieve an efficient and selective Au encapsulation, it is necessary to protect the external wall of CNTs during the deposition and provide enough driving force to guide the mass efficiently into the channel. Hinds *et al.* developed a “nano-porous MWCNT membrane”, which have vertically aligned CNT array embedded into a polymer matrix with open ends to study the mass nano-transportation and drug-delivery behaviour.^{22,23} In this paper we choose similar nano-porous MWCNT membrane as the platform to selectively deposit Au nano particles inside the hollow CNT channels with a diameter less than 15nm in a mild condition. The HAuCl₄ and the reductant solution diffuse into nano pores from opposite sides of a CNT membrane, which avoids the reaction outside the CNTs. As they meet inside the CNT pores, the HAuCl₄ is reduced and Au grows simultaneously inside CNT channels as shown in scheme 1. Au nano-rods with

10nm radii (aspect ratio is from 2.5-5) are observed to align inside the MWCNT hollow pores with tens of nanometers gap between each other. The Au nano-wire with aspect ratio over 20 and Au spherical particles are also observed inside MWCNTs. The HRTEM, STEM, 3D-TEM and EDX analysis confirm Au@CNT structures, locations and the composition. The rupture of a long Au nanowire or the growth of Au in a non-continuous phase of the reactants through Ostwald ripening might be responsible for the formation of nanorods array. This Au nano-rods@CNT array material may have potentials in selective catalysis, plasmonic devices and waveguides.



Scheme 1. Schematic representation of Au-nanorods growth inside a CNT channel of nano-porous MWCNT membrane through an inter-diffusing-reducing reaction.

Results and Discussion

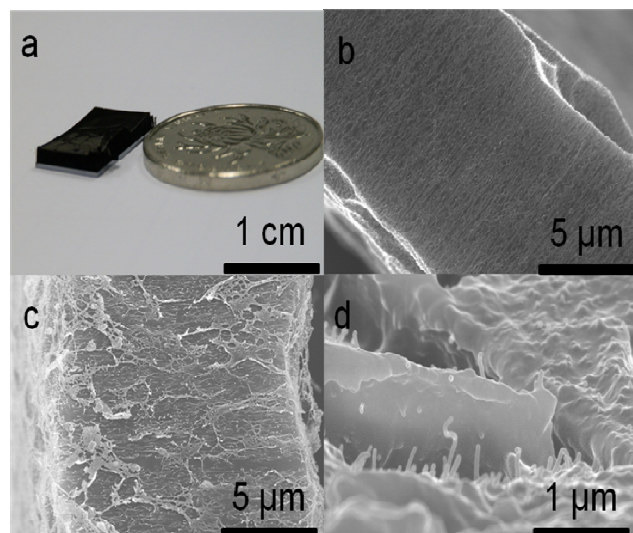


Figure 1. a) Photograph of 1.5mm-high CNT array with a Chinese coin used as reference; b) SEM image of a microtome-cut film of CNT array (10±2µm thick) embedded in Epoxy resin; c) Side-view and d) Top-view of a CNT array/epoxy composite film after plasma etching.

The CNT array is prepared through a CVD method with the height in the range of 1mm - 1cm by tuning the growth

parameters. Fig.1a shows a SEM image of a typical 1.5mm-high CNT array film with a Chinese coin as reference. After the epoxy embedment and microtome-cut, the CNT array in the polymer matrix remains its original orientation as shown in Fig. 1b. Fig. 1c and 1d show the side-view and top-view SEM image of a microtome-cut CNT composite membrane after O₂ plasma etching treatment respectively. An inspection of these images indicates that some carbon nanotubes (or bundles) protrude from the polymer matrix.

As discussed above the CNT nano pores are the only paths for the mass transportation with the isolation of epoxy resin. The solute diffuses across the membrane driven by the concentration difference. We also consider the possibility of existence of voids in the epoxy matrix. First, we carried out the 20nm Au nanoparticle diffusion test and no voids bigger than 20nm in the membrane are detected. The porosity of the CNT membrane is measured to be $6\pm 2 \times 10^8$ by using KCl as the target species. Detailed information about this part is given in our previous paper.²⁴ To avoid the reduction of HAuCl₄ outside CNTs we use an inter-diffusion cell to separate the Au precursor and the reductant as shown in figure S1.

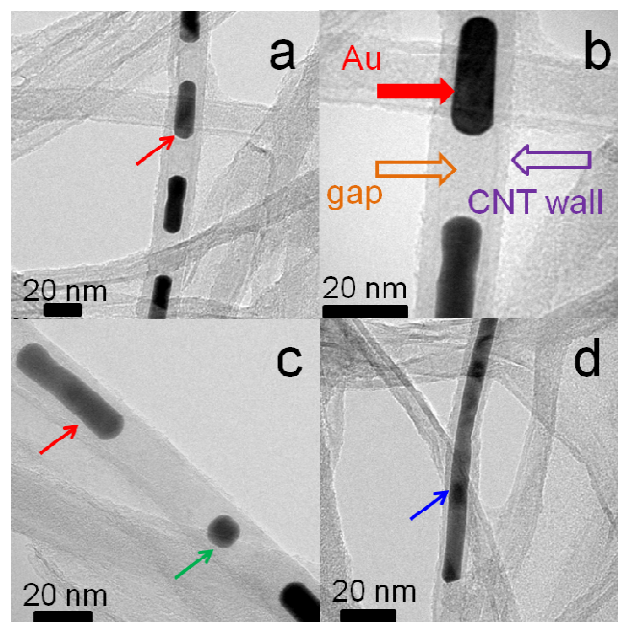


Figure 2. Typical 2D-TEM images from Au nano-rod (2a,b,c indicated by the red arrow), nano-sphere (2c, indicated by the green arrow), nano-wire (2d, indicated by the blue arrow) encapsulated inside a carbon nanotube with an inner diameter of 15nm

It is well known that mixing HAuCl₄ and NaBH₄ with CNTs in a solution induces a complex structure of Au nano-particles decorated on the CNT external surface. Au nanorods usually formed with the assists of the micelles formed by the surfactants.^{25,26} However by using the CNT nano-porous membrane a well-aligned Au-nanorod structure grows inside channel of the CNTs with the radii less than 15nm without the surfactants. Fig. 2a,b show the representative TEM images of a multiple Au nanorod-filled CNT structure with well alignment within CNT. Those nanorods with a dark contrast (as indicated by the red arrow in Fig. 2a,b,c) have the diameter of 10±1nm and the

aspect ratio about 2-5. A clear gap between two nano-rods varies from 20-100nm. The distance between the Au-nanorods and the CNT wall is measured to be 2 ± 1 nm. Except enclosed Au nanorods we also find two different Au nano structures inside the CNTs. In Fig. 2c a spherical Au particle (as indicated by the green arrow) with 10nm in diameter is found between two Au nano-rods. Fig. 2d exhibits a long continuous Au nanowire (as indicated by the blue arrow) inside CNT channels. The wire grows along the longitude direction of the CNT and almost fulfills the whole CNT cavity. This Au nanowire can grow as long as 300nm with the aspect ratio over 20.

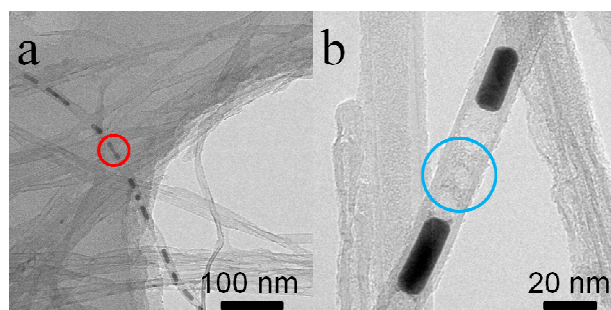


Figure 3. TEM images of special Au nanorods@CNT structure a) The dark area in the red circle indicates a dumbbell-shaped Au nanorod within a CNT cavity; 2b) The area in the cyan circle indicates a discontinuous liquid phase between two Au nanorods.

When we check other Au@CNT samples we find that some Au nano-rods show significant distortion in shape. For the dumbbell-shaped Au nano rod (as indicated in the red circle in fig 3a), it may be caused by fusion of two short nano rods or rupturing of a long Au nano wire. For the first mechanism the reduced small Au nano particles fuse into a longer wire through an Ostwald ripening.²⁷ As discussed above, the aqueous solution is difficult to wet and fulfill the CNT channel with small radii. When the reactant diffuses across the CNT channels, as driven by the concentration difference between the two sides of the film, the hydrophobic effect of the CNT inner wall may induce the aqueous precursor solution separated by air bubbles and form a discontinuous phase (as indicated by the cyan circle in Fig. 3b). This leads to the formation of isolated Au nano-rod structure. Continuous Au nano wire only forms in a continuous liquid phase. As is known the inner surface of traditional AAO template is hydrophilic and the channel diameter is larger as compared to our CNTs. The precursor solution is relatively easy to fulfill the whole AAO channel and leads to the formation of a continuous metal wire.¹⁹

On the other hand the rupturing of a pristine long and continuous Au nano-wire structure during hot acid etching and sonication treatment for the sample release from the epoxy matrix is another possibility for formation of nanorods. Guo *et al.* predicted the deformation behavior of gold-filled single-walled carbon nanotubes under axial compression by molecular dynamics simulation.²⁸ El-Sayed *et al.* observed thermal reshaping of Au nanorods in micelles due to instability of the micelles capping the longer gold nanorods.²⁹ In our case, the Au nano-wire may have low melting point and special interaction with the CNT which causes the rupture of Au structure. Herein we need to point out that our Au nano-rods are very stable under

high energy electron beam irradiation (200keV). We did not observe the obvious breakup of Au under e-beam irradiation which is found by Rao *et al.* in a SWNT.²¹

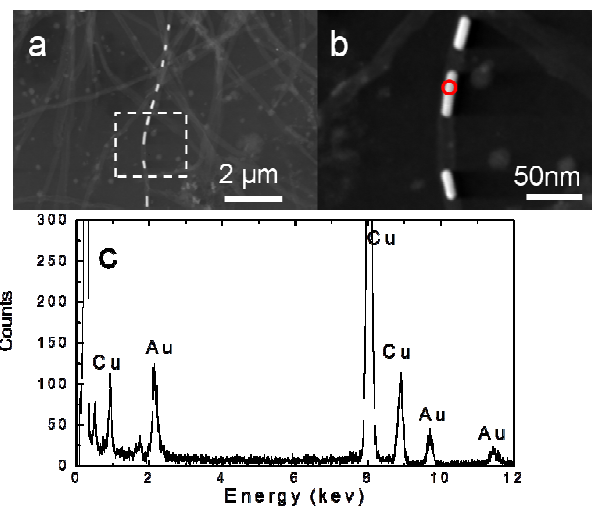


Figure 4. a,b) Typical STEM-HAADF image from a Au nano-rods encapsulated MWCNT with an inner diameter of 15nm. c) EDX analysis of the selected area (pointed by the red circle in fig 4b)

Fig. 4a shows a typical 2D STEM image from a multiple Au nano-rods array encapsulated CNT sample captured in a high angle annular dark-field mode (HAADF). There is a high contrast between the Au nano rods and the unfilled CNTs and amorphous carbon. Bright parts in fig 4a and 4b correspond to Au nano rods@CNT structure. Based on the selected area EDX analysis (indicated by the red circle in fig 4b), the characteristic Au signals are detected which verifies the nano-rods is composed of Au, as shown in fig 4c (The copper peaks come from the grid.). In our study, the fine structure of Au nano-rods cannot be observed by using HRTEM due to superimposition of the CNT wall and Au nano-rods which is accordance with the observation by Ersen *et al.*¹⁷

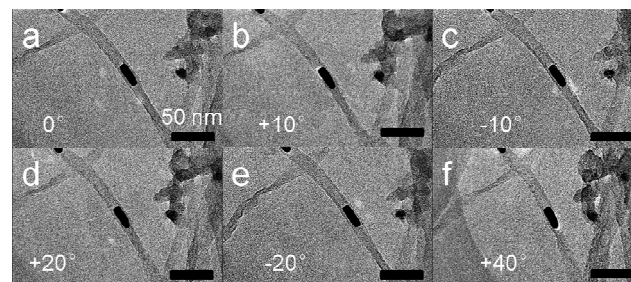


Figure 5. TEM tilt series (obtained by tilting the sample Au nano-rod@CNT from -20° to $+40^\circ$). (Scale bar: 50nm)

Tessonier *et al.* pointed out that 2D TEM imaging is not a powerful tool to locate the position of nano-particles, namely inside or outside the CNTs.¹⁶ We carry out 3D-TEM analysis to provide detailed information about the accurate position of the Au nano-structures. By rotating the sample, TEM image is captured at each angle. Those particles inside the tube will move with the tube but their motion is confined inside tubule. However,

those particles outside CNTs progressively move toward the outer wall and finally cross it.¹⁶ From Fig. 5, the Au nanorod stays inside the pore of CNT during one rotation process of sample, which indicates that Au nanorod is indeed located inside CNTs.

5 A video captured during the rotation of the sample from -60° to $+60^\circ$ is provided in the Supporting Information.

Our samples have a 10-20% filling efficiency estimated from TEM images. The relatively low filling efficiency might be ascribed to the blockage of the CNT channel by amorphous carbon or the Au nano-structures, which impede diffusion of the reactants and hence continuous growth of the Au nano-structures. It should be noticed that our CNTs are relatively long (over $10\mu\text{m}$) and such Au-enclosed structure may have small volume ratio in the whole CNTs, which may also decrease the filling efficiency.

Experimental Section

Materials

HAuCl₄, NaBH₄ and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. without further purification. SPI-Pon-812 monomer, curing agents DDSA and NMA, and DMP-30 as accelerator were supplied by SPI Supplies, Division of Structure Probe Inc. Au colloidal dispersion (20nm in diameter) was purchased from Ted Pella Inc. with the size distribution less than 5% and used to check the leakage of the membrane.

Characterization

TEM images were obtained with a Tecnai G²20 (FEI) microscope at 200 KV accelerating voltage. The tilt series for 3D-TEM experiments were recorded in dark-field mode on a Tecnai G²F20 microscope, running at 200 kV high-voltage with a specific tilt holder allowing a maximum tilt angle of $\pm 70^\circ$ around an axis perpendicular to the beam direction. The acquisition process was performed using the FEI Xplore3D acquisition software which is able to change automatically the tilt angle, to correct defocus and shift of the object, and to record and store 2D images. With tilt angles ranging from -60° to 60° at 1° increments, the tilt series consists of 120 images. A 2048×2048 pixels cooled CCD array detector (Gatan 832) was used to store these images with an exposure time of 2 s per image. No apparent irradiation damage on the specimen was observed during the total acquisition time of the tilt series.

Preparation of nano-porous MCNT membrane

We use the modified chemical vapor deposition (CVD) method to grow the vertically aligned MCNT arrays on Si wafer which is pre-coated with 100nm SiO_x layer and a Fe/Al catalyst layer. The as-prepared aligned CNT arrays have a height of 1-10mm and an inner diameter of 15 nm.

The as-prepared CNT arrays are then mixed with epoxy precursor solution and cured in a vacuum oven. The composite film is cleaved by HF etching and cut into $10\mu\text{m}$ thick membranes through a microtome technique (RMC, Boeckeler Instruments, Inc.). The residual polymer is removed via further O₂ plasma etching treatment (PDC-32G, Harrick Plasma Inc. 18W for 20min, O₂, 500 mtorr). Details can be referred to our

previous work.²⁴

Encapsulation of Au nano structures inside CNTs

For the inter-diffusion reduction of Au inside CNTs, a piece of CNT nano porous membrane is mounted between two pieces of silicon panels in a diffusion cell (Supporting information, fig S1). The feeding side contains 15ml degassed HAuCl₄ (0.5mM) aqueous solution. The permeate side is filled with 15ml Milli-Q water. After twelve hours' diffusion, the reducing agent NaBH₄ (20mM) was added to the permeate side. The diffusion cell was held at ambient condition for an additional 12 hours to grow the Au nanostructure in the CNT nano channel. The membrane was finally disassembled and rinsed by DI water thoroughly. To release the Au@CNT from the epoxy matrix, an acid etchant solution containing concentrated sulfuric acid and hydrogen peroxide (2:1 in volume) was used to dissolve the organics at 50°C for 5 days. The suspension of Au@CNT was filtered by a PTFE membrane ($5\mu\text{m}$ pore size) and washed with DI water thoroughly.

Conclusions

In conclusion, we prepared a novel array material comprising Au-nanostructures encapsulated in CNTs with diameters smaller than 15nm. Au nano rods with diameters around 10nm are verified to be aligned inside the CNT cavity by 3D TEM. The embedding of nano-porous aligned CNT in the epoxy matrix enables the hollow CNT inner channels to be the only path for the diffusion of the reactants and the formation of the enclosed Au nano-structures. Our method is versatile and convenient to fabricate complex endohedral CNT materials, which applies to develop new class of catalysts and plasmonic devices.

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Notes and references

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Electronic Supplementary Information (ESI) available: a photograph of the inter-diffusing cell and a nano-porous MCNT membrane into which Au-nanorods are impregnated, a video obtained from TEM tilt series shown here. See DOI: 10.1039/b000000x/

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Notes

This work is dedicated to Professor Weixiao Cao, Peking University, China, for his 80th birthday in November 2014

- 10 1. P. M. Ajayan, S. Iijima, *Nature* 1993, **361**, 333.
2. D. Ugarte, T. Stockli, J. M. Bonard, A. Chatelain, W. A. De Heer, *Appl. Phys. A-Mater. Sci. & Proc.* 1998, **67**, 101.
3. K. Koga, G. T. Gao, H. Tanaka, X. C. Zeng, *Nature* 2001, **412**, 802.
4. Z. W. Liu, Y. Bando, M. Mitome, J. H. Zhan, *Phys. Rev. Lett.* 2004, **93**, 095504.
- 15 5. S. Chen, G. Wu, M. Sha, S. Huang, *J. Am. Chem. Soc.* 2007, **129**, 2416.
6. V. C. Holmberg, M. G. Panthani, B. A. Korgel, *Science* 2009, **326**, 405.
- 20 7. S. Y. Hong, G. Tobias, K. T. Al-Jamal, B. Ballesteros, H. Ali-Boucetta, S. Lozano-Perez, P. D. Nellist, R. B. Sim, C. Finucane, S. J. Mather, M. L. H. Green, K. Kostarelos, B. G. Davis, *Nat. Mater.* 2010, **9**, 485.
8. S. Hampel, D. Kunze, D. Haase, K. Kraemer, M. Rauschenbach, M. Ritschel, A. Leonhardt, J. Thomas, S. Oswald, V. Hoffmann, B. Buechner, *Nanomedicine* 2008, **3**, 175.
- 25 9. X. Pan, Z. Fan, W. Chen, Y. Ding, H. Luo, X. Bao, *Nat. Mater.* 2007, **6**, 507.
10. M. A. Loi, J. Gao, F. Cordella, P. Blondeau, E. Menna, B. Bartova, C. Hebert, S. Lazar, G. A. Botton, M. Milko, C. Ambrosch-Draxl, *Adv. Mater.* 2010, **22**, 1635.
- 30 11. D. Eder, *Chem. Rev.* 2010, **110**, 1348.
12. U. K. Gautam, P. M. F. J. Costa, Y. Bando, X. Fang, L. Li, M. Imura, D. Golberg, *Sci. Tech. Adv. Mater.* 2010, **11**, 054501
- 35 13. D. Tasis, N. Tagmatarchis, A. Bianco, M. Prato, *Chem. Rev.* 2006, **106**, 1105.
14. M. Monthieux, *Carbon* 2002, **40**, 1809.
15. X. R. Ye, Y. H. Lin, C. M. Wang, C. M. Wai, *Adv. Mater.* 2003, **15**, 316.
- 40 16. J.-P. Tessonier, O. Ersen, G. Weinberg, C. Pham-Huu, D. S. Su, R. Schloegl, *ACS Nano* 2009, **3**, 2081.
17. O. Ersen, J. Werckmann, M. Houille, M.-J. Ledoux, C. Pham-Huu, *Nano Lett.* 2007, **7**, 1898.
18. S. Arcidiacono, J. H. Walther, D. Poulikakos, D. Passerone, P. Koumoutsakos, *Phys. Rev. Lett.* 2005, **94**, 105502.
- 45 19. J. C. Bao, C. Tie, Z. Xu, Z. Y. Suo, Q. F. Zhou, J. M. Hong, *Adv. Mater.* 2002, **14**, 1483.
20. A. Chu, J. Cook, R. J. R. Heesom, J. L. Hutchison, M. L. H. Green, J. Sloan, *Chem. Mater.* 1996, **8**, 2751.
- 50 21. A. Govindaraj, B. C. Satishkumar, M. Nath, C. N. R. Rao, *Chem. Mater.* 2000, **12**, 202.
22. B. J. Hinds, N. Chopra, T. Rantell, R. Andrews, V. Gavalas, L. G. Bachas, *Science* 2004, **303**, 62.
23. J. Wu, K. S. Paudel, C. Strasinger, D. Hammell, A. L. Stinchcomb, B. J. Hinds, *Proc. Natl. Acad. Sci. U.S.A.* 2010, **107**, 11698.
- 55 24. Z. Liu, G. Liao, S. Li, Y. Pan, X. Wang, Y. Weng, X. Zhang, Z. Yang, *J. Mater. Chem. A* 2013, **1**, 13321.
25. N. R. Jana, L. Gearheart, C. J. Murphy, *Adv. Mater.* 2001, **13**, 1389.
26. B. Nikoobakht, M. A. El-Sayed, *Chem. Mater.* 2003, **15**, 1957.
- 60 27. X. W. Lou, C. Yuan, E. Rhoades, Q. Zhang, L. A. Archer, *Adv. Func. Mater.* 2006, **16**, 1679.
28. S. H. Guo, B. E. Zhu, X. D. Ou, Z. Y. Pan, Y. X. Wang, *Carbon* 2010, **48**, 4129.
29. M. B. Mohamed, K. Z. Ismail, S. Link, M. A. El-Sayed, *J. Phys. Chem. B* 1998, **102**, 9370.
- 65

