

Assembling nanoparticle catalysts with nanospheres for periodic carbon nanotube structure growth

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Abstract

We have developed a novel method to grow carbon nanotubes in a periodic structure using a simple one-step self-assembly process. In this approach, monodispersed nanospheres are utilized to assemble smaller nanoparticle catalysts into an ordered periodic pattern. Using this process, we have grown carbon nanotube bundles into a honeycomb structure. The proposed method eliminates the need for lithography and material deposition, greatly reducing the fabrication complexity and cost.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years there has been significant interest in a new class of 1D nanostructured materials, including carbon nanotubes (CNT) [1], zinc oxide (ZnO) [2], and silicon nanowires [3]. These materials have many interesting properties, and significant research effort has been dedicated to processes that can reliably control structure attributes such as their growth site location, orientation, and size distribution. However, common processes for CNT growth, such as arc discharge [4], laser vaporization [5], and plasma-enhanced chemical vapor deposition (PECVD) [6], result in random nanotube forests with limited or no control over the growth site. The ability to arrange these nanotubes and nanowires in periodic structures can potentially lead to powerful applications in photonics, optoelectronics, biosensor arrays, and field emission devices.

The most direct method to grow periodic structures of nanotubes/nanowires is to utilize catalyst seed layers that are lithographically patterned into ordered geometries. Recently,

various groups have used processes such as electron-beam [7], interference [8], and nanosphere lithography [9–11] to grow ordered structures of CNT and/or ZnO nanowires. These methods generate a periodic template, which then directly determines where the nanotubes can grow. To achieve this periodic layer formation step, these fabrication techniques typically employ multiple processes that include lithography, deposition of catalyst material, and lift-off.

Here we report a novel one-step self-assembly process for fabricating periodic catalyst layers for CNT growth. In this scheme colloidal nanoparticles assemble around an ordered cluster array of larger nanospheres by spincoating. CNT growth subsequently takes place at the sites of the colloidal nanoparticles. The catalyst layer essentially self-assembles on the substrate by using a simple low-cost process. This method eliminates the need for lithography and catalyst deposition, which require expensive equipment.

The advantage of the proposed process is that it employs a single spincoating step before nanotube growth, thus presenting itself as a practical nanomanufacturing process of significantly lower complexity than existing approaches. Using this method, we have successfully fabricated CNT bundles

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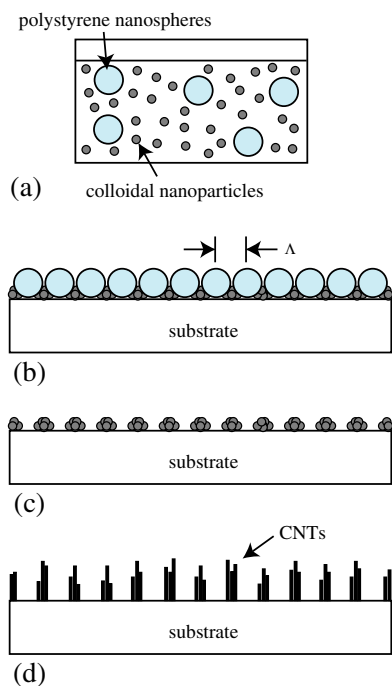


Figure 1. Process diagram for the proposed process. (a) A solution containing both monodispersed nanospheres and colloidal nanoparticle is synthesized. (b) The solution is spincoated on the substrate, and the spheres act as a template and assemble the particles into periodic clusters. After (c) removing the polymer spheres the remaining nanoparticle array can be used (d) for nanotube growth in a CVD process.

arranged in a 2D honeycomb structure with 450 nm lattice spacing. This honeycomb geometry can be especially useful in photonic structures, as it has complete (both TE and TM) energy bandgaps [12]. Even though we limited the scope of this work to periodic CNT structures, the process can be extended to grow ZnO or silicon nanowires by selecting other nanoparticle catalyst materials and optimizing process conditions.

2. Method and materials

The proposed approach for growing CNTs in an ordered structure is illustrated in figure 1. First, a solution containing monodispersed polystyrene (PS) nanospheres ($D \sim 450$ nm) and colloidal nanoparticles ($d \sim 10$ nm) is synthesized, shown in figure 1(a). The solution is then spincoated onto a silicon substrate. Upon drying, the nanospheres self-assemble into a close-packed hexagonal structure, arranging the smaller nanoparticles into a periodic cluster array, as shown in figure 1(b). In a single temperature anneal step, the polymer spheres are burnt away; the remaining nanoparticles are used as catalysts for CNT growth, as shown in figures 1(c) and (d). The lattice parameter Λ of the periodic CNT array is controlled by selecting the diameter of the spheres. This process essentially deposits and assembles the catalysts in an ordered structure using a single spincoating step.

In our experiments, we selected iron oxide as the catalyst material due to its low cost and easy accessibility. The iron oxide nanoparticles used were contained $\sim 3\%$ by volume in

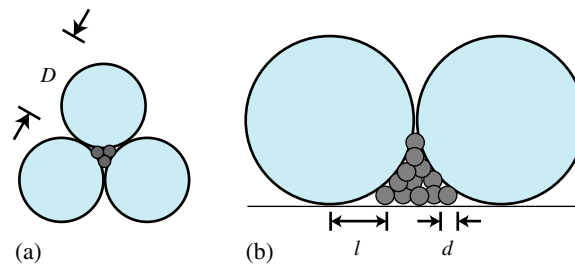


Figure 2. Desired assembly geometry in the proposed system. (a) Top view of the hexagonal close-packed nanospheres with nanoparticle clusters in the voids. (b) Side view of the assembly geometry, where l is the radius of the hollow core region in which the particles cannot assemble.

aqueous suspension (FerroTec Corporation, EMG707). The particles have an average diameter of 10 nm, and were coated by a surfactant to prevent agglomeration. The polystyrene nanospheres we used were contained $\sim 2.5\%$ by volume in aqueous suspension (Polysciences, Inc., 07307-15). The spheres had a mean diameter of 450 nm with a 3% coefficient of variance, as specified by the manufacturer. The experimental solution was synthesized by mixing aqueous suspensions of polystyrene spheres with iron oxide particles, and further diluting in compatible solvents such as ethanol.

The fill factor of the assembly can be controlled by varying the relative concentrations of particles to spheres based on geometry. In the desired assembly geometry where the nanoparticles cover half of the nanospheres, as illustrated in figure 2, the sphere-to-particle ratio is calculated to be approximately 3. Due to size constraints, the nanoparticles cannot assemble in the regions near the bottom of the spheres, resulting in an empty region. The radius l of the hollow core is given by

$$l = \sqrt{Dd}, \quad (1)$$

where d and D are the diameters of the iron oxide nanoparticles and polymer nanospheres, respectively. The parameter l outlines the boundary below which the particles cannot exist.

The silicon substrates used were pre-cleaned in a base RCA clean (1:1:5 solution of ammonium hydroxide, hydrogen peroxide, and water). The nanosphere/nanoparticle solution was spincoated on the substrate at low spin speeds, between 500 and 1000 RPM. The solution may also be applied by other assembly methods typically used in standard nanosphere lithography [9–11, 13, 14]. After drying, the polymer spheres were removed by a temperature cycle, and the residual nanoparticles were used as the catalyst layer for CNT growth. The CNTs were grown using a commercial PECVD system (Aixtron, Black Magic Pro), with the growth temperature at 700 °C and a 4:1 flow of ammonia and acetylene gases. Note that since the CNT growth process occurs at an elevated temperature, the polystyrene spheres can be removed simultaneously during the growth cycle. Therefore, the substrate can be placed in the CVD chamber immediately after spincoating without any additional processing.

3. Results and discussion

The assembly of nanoparticles after spincoating is illustrated in the top-view scanning electron micrograph (SEM) images

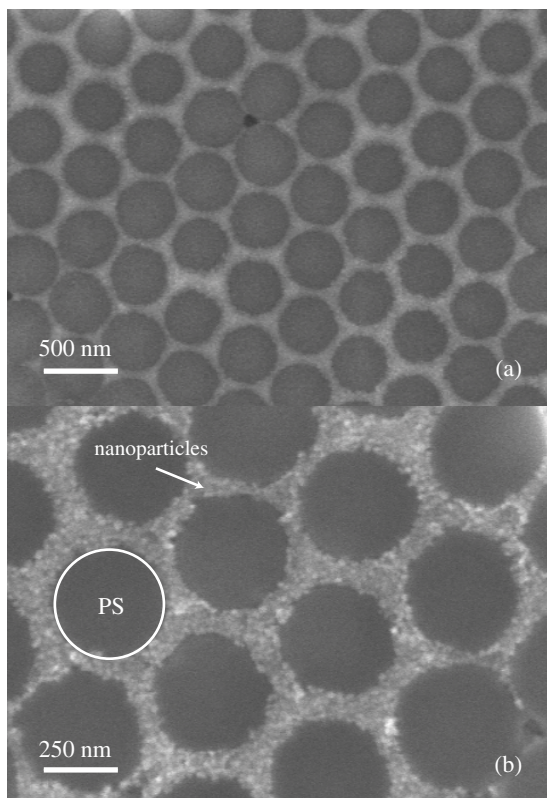


Figure 3. Top-view micrograph of (a) assembled nanosphere and nanoparticles. (b) Particle clusters filling in the void between the larger spheres.

of figure 3. The nanospheres assemble into hexagonal close-packed structures (dark tone), and the nanoparticle clusters (bright tone) fill the voids between the spheres. A typical assembly pattern is illustrated in figure 3(a), where the grain boundaries are in the order of $10\ \mu\text{m}$. A dark hole near the center of the micrograph indicates a defect where the nanoparticles did not fill the void. A higher magnification micrograph is depicted in figure 3(b), where individual nanoparticles can be resolved.

To examine the fidelity of the nanoparticle clusters, the PS spheres were removed by heating the sample to $500\ ^\circ\text{C}$ for 3 h. The residual nanoparticles assembled in a periodic honeycomb structure, as illustrated by the micrograph of figure 4. While the periodicity of the clusters is consistent, a number of hole defects can be observed in figure 4(a). This indicates that the colloidal nanoparticles did not fill all of the voids, possibly due to non-uniformity in the local particle density during assembly. One possible way of reducing the void defects is to lengthen the assembly time, which is currently in the order of seconds.

These results demonstrate that the nanoparticles do not assemble directly under the spheres due to size constraints, resulting in a hollow region. The radii of the hollow cores can be examined in the higher magnification micrograph shown in figure 4(b), and are around $l \sim 90\text{--}100\ \text{nm}$. This is slightly larger than the physical limit of $67\ \text{nm}$, calculated using equation (1). This indicates the nanoparticles are not tightly packed in the regions close to the bottom of the spheres. The micrograph also shows that there may be some polymer residue

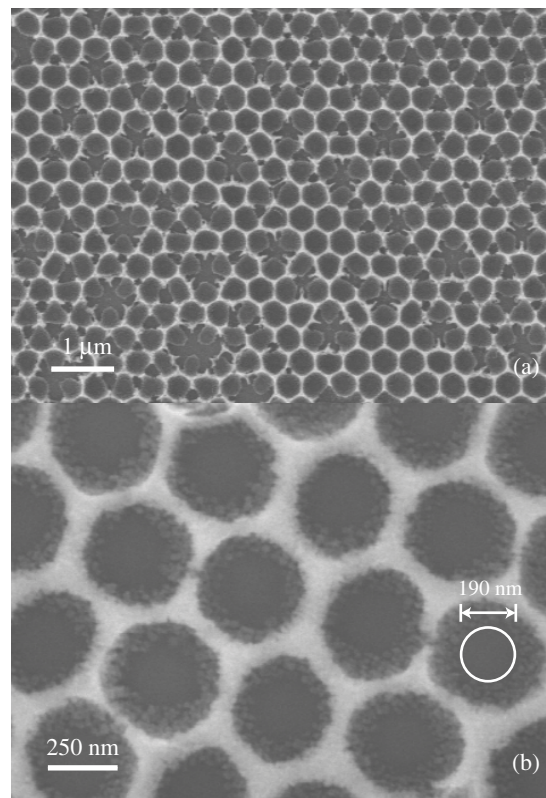


Figure 4. Top-view micrograph of (a) residual nanoparticle clusters in the honeycomb structure after removing the nanospheres. Void defects can be seen. (b) Individual particles can be observed with possible polymer residuals. The white circle represents the hollow core region where there is no particle assembly.

on the clusters. This is less of a concern because the higher temperature during CNT growth will result in removal of the polymer.

The assembled honeycomb nanoparticle cluster was then used as an ordered catalyst layer for CNT growth. The sample was first annealed at $700\ ^\circ\text{C}$ for 5 min, and then the CNTs were grown at 150 W DC plasma power for 20 min. Top-view and angle-view micrographs of the sample after the PECVD cycle are shown in figures 5(a) and (b), respectively. The CNT bundles have grown in a periodic honeycomb structure, determined by the assembled nanoparticle catalysts. The CNTs have lengths ranging from 500 to 1000 nm and diameters from 40 to 100 nm, as measured by SEM. More details of the grown CNTs can be observed in the higher magnification SEM image shown in figure 6(a). The tip of the nanotube is seen to be embedded by iron oxide nanoparticle catalysts. The transmission electron microscope (TEM) image of a single CNT further indicates that the grown CNTs are multi-walled and have outer diameters of around 50 nm, as illustrated in figure 6(b). The TEM image of a longer CNT with a 90 nm diameter and length of over $1\ \mu\text{m}$ is shown in figure 6(c).

To further investigate the overall quality of the grown CNTs, Raman spectra of the sample were measured using a Raman microscope (WITec CRM 200). A $20\times$ objective lens and excitation wavelength of 532 nm were used to characterize the sample. The Raman spectra, illustrated in

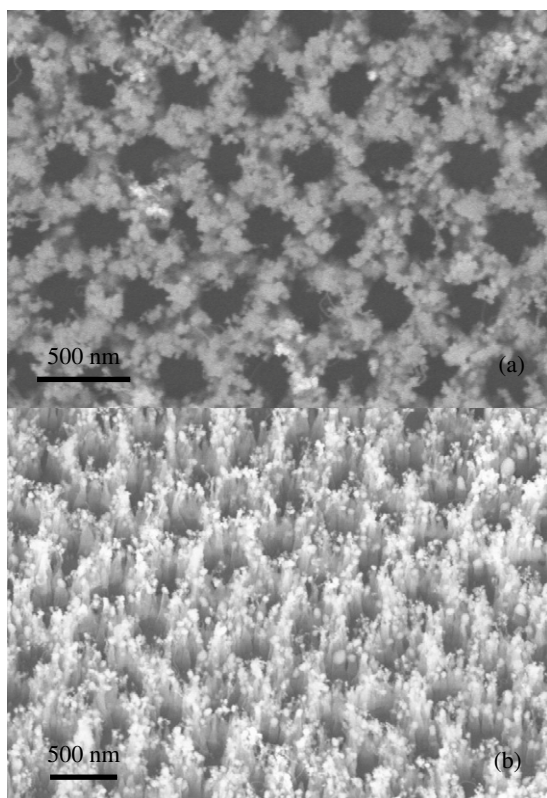


Figure 5. (a) Top-view and (b) angled-view micrographs of CNTs grown on a periodic honeycomb lattice using the assembled nanoparticles as catalyst layer.

figure 7, contain two main features. The first is a peak around 1350 cm^{-1} (D band), corresponding to defects in the CNT wall structure, and the second is a peak around 1590 cm^{-1} (G band), corresponding to the tangential graphitic structure of the CNT walls. The balanced peak intensities at the D and G bands indicate the grown CNTs are multi-walled with some amorphous impurities. The measured spectra are similar to those of multi-walled CNTs reported in the literature [15–17]. The spectra also have a first and second order peak of the silicon substrate at 520 and 960 cm^{-1} , as well as weak second order peaks at 2700 (2D) and 2940 cm^{-1} (D + G). The quality of the CNT is consistent with those previously grown using iron oxide nanoparticles that were uniformly coated [18].

As stated earlier, the spatial coherence length of the ordered CNT structure is in the order of $10\text{ }\mu\text{m}$, and is mainly limited by the coherence of the PS nanosphere self-assembly process. The defect-free structure area may be improved to macroscopic distances by adopting other assembly techniques used in standard nanosphere lithography, which has reported significantly longer coherence lengths [9–11, 13, 14].

Even though iron oxide colloidal nanoparticles are cost effective, they may limit the quality of the CNTs grown in the honeycomb structure. One main reason is because iron oxide particles do not reflow during the anneal cycle, but instead agglomerate to form clumps with non-uniform sizes [18]. The quality of the catalyst may be improved by raising the anneal temperature, or by using other metallic nanoparticles such as gold or nickel, which can readily soften

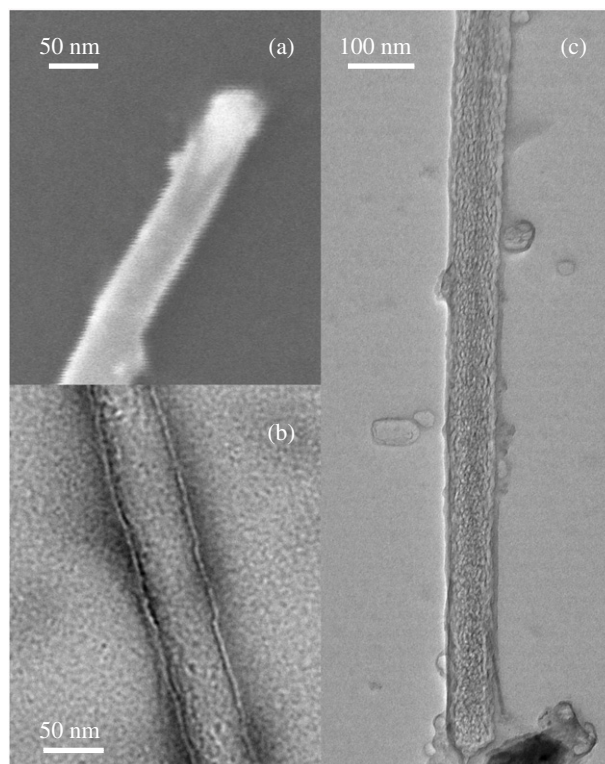


Figure 6. Higher resolution electron micrographs of the grown multi-walled CNT. (a) SEM image of a single CNT, with iron oxide nanoparticle catalyst embedded at the tip. (b) High resolution TEM images of a grown CNT with outer diameter around 50 nm , and (c) CNT with 90 nm diameter and over $1\text{ }\mu\text{m}$ length.

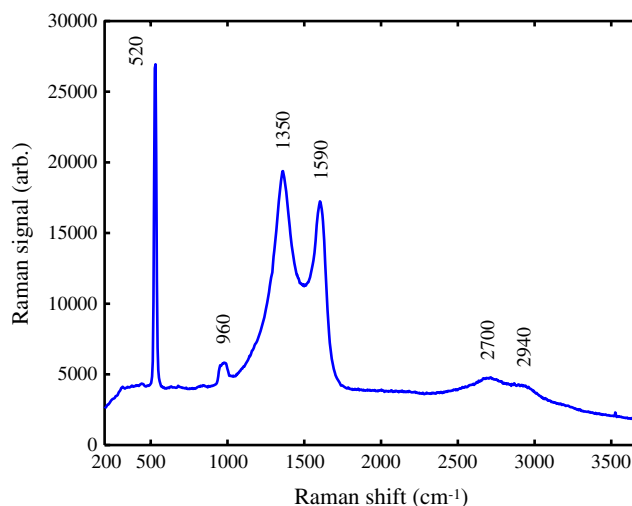


Figure 7. Measured Raman spectra of the honeycomb CNT bundle array using an excitation wavelength of 532 nm . The balanced D ($\sim 1350\text{ cm}^{-1}$) and G ($\sim 1590\text{ cm}^{-1}$) bands indicate the grown CNTs are multi-walled. The peaks at 520 and 960 cm^{-1} are due to the silicon substrate.

and reflow at the temperature range used [16, 18]. With this approach, the heat treatment cycle can be controlled to further improving the geometry of the growth site locations, possibly yielding isolated nanotube bundles. Using different

nanoparticle materials as catalysts may also allow using the proposed process to grow other nanowires such as ZnO and silicon.

In this work, we have exclusively examined CNT bundles in periodic honeycomb geometry; however, it may be possible to grow in other periodic structures by controlling various process parameters, such as the annealing and/or growth conditions, and the relative size and concentration between the templating spheres and particle catalysts.

4. Conclusion

We have introduced a novel process to assemble colloidal nanoparticles into a honeycomb structure, which can be used as the catalyst layer for the growth of periodic CNT bundles. The proposed process consists of a simple spincoating process and eliminates the need for expensive lithography and catalyst deposition tools, thus greatly reducing fabrication complexity. We have demonstrated CNTs grown in a honeycomb structure with 450 nm lattice spacing. Future work will be to examine other colloidal nanoparticle materials such as gold, reduce pattern defects by optimizing assembly conditions, explore other periodic geometries, and extend this process to grow other types of nanowires.

Acknowledgments

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References

- [1] Iijima S 1991 Helical microtubules of graphitic carbon *Nature* **354** 56–8
- [2] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 Catalytic growth of zinc oxide nanowires by vapor transport *Adv. Mater.* **13** 113–6
- [3] Westwater J, Gosain D P, Tomiya S, Usui S and Ruda H 1997 Growth of silicon nanowires via gold/silane vapor–liquid–solid reaction *J. Vac. Sci. Technol. B* **15** 554–7
- [4] Ebbesen T W and Ajayan P M 1992 Large-scale synthesis of carbon nanotubes *Nature* **358** 220–2
- [5] Guo T, Nikolaev P, Thess A, Colbert D and Smalley R 1995 Catalytic growth of single-walled nanotubes by laser vaporization *Chem. Phys. Lett.* **243** 49–54
- [6] Ren Z F, Huang Z P, Xu J W, Wang J H, Bush P, Siegal M P and Provencio P N 1998 Synthesis of large arrays of well-aligned carbon nanotubes on glass *Science* **282** 1105–8
- [7] Ren Z F, Huang Z P, Wang D Z, Wen J G, Xu J W, Wang J H, Calvet L E, Chen J, Klemic J F and Reed M A 1999 Growth of a single freestanding multiwall carbon nanotube on each nanonickel dot *Appl. Phys. Lett.* **75** 1086–8
- [8] Krishnan R, Nguyen H Q, Thompson C V, Choi W K and Foo Y L 2005 Wafer-level ordered arrays of aligned carbon nanotubes with controlled size and spacing on silicon *Nanotechnology* **16** 841–5
- [9] Huang Z P, Carnahan D L, Rybczynski J, Giersig M, Sennett M, Wang D Z, Wen J G, Kempa K and Ren Z F 2003 Growth of large periodic arrays of carbon nanotubes *Appl. Phys. Lett.* **82** 460–2
- [10] Kempa K *et al* 2003 Photonic crystals based on periodic arrays of aligned carbon nanotubes *Nano Lett.* **3** 13–8
- [11] Wang X, Summers C J and Wang Z L 2004 Large-scale hexagonal-patterned growth of aligned ZnO nanorods for nano-optoelectronics and nanosensor arrays *Nano Lett.* **4** 423–6
- [12] Chern R L, Chung Chang C, Chang C C and Hwang R R 2003 Large full band gaps for photonic crystals in two dimensions computed by an inverse method with multigrid acceleration *Phys. Rev. E* **68** 026704
- [13] Hultheen J C and Van Duyne R P 1995 Nanosphere lithography: a materials general fabrication process for periodic particle array surfaces *J. Vac. Sci. Technol. A* **13** 1553–8
- [14] Rybczynski J, Ebels U and Giersig M 2003 Large-scale, 2D arrays of magnetic nanoparticles *Colloids Surf. A* **219** 1–6
- [15] Li W, Zhang H, Wang C, Zhang Y, Xu L, Zhu K and Xie S 1997 Raman characterization of aligned carbon nanotubes produced by thermal decomposition of hydrocarbon vapor *Appl. Phys. Lett.* **70** 2684–6
- [16] Chhowalla M, Teo K B K, Ducati C, Rupesinghe N L, Amaratunga G A J, Ferrari A C, Roy D, Robertson J and Milne W I 2001 Growth process conditions of vertically aligned carbon nanotubes using plasma enhanced chemical vapor deposition *J. Appl. Phys.* **90** 5308–17
- [17] Griffiths H, Xu C, Barrass T, Cooke M, Iacopi F, Vereecken P and Esconjauregui S 2007 Plasma assisted growth of nanotubes and nanowires *Surf. Coat. Technol.* **201** 9215–20
- [18] Choi G S, Cho Y S, Son K H and Kim D J 2003 Mass production of carbon nanotubes using spin-coating of nanoparticles *Microelectron. Eng.* **66** 77–82