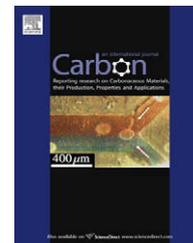


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/carbon

Carbon nanocages grown by gold templating

Renyun Zhang^{*}, Magnus Hummelgård, Håkan Olin

Department of Natural Sciences, Engineering and Mathematics, Mid Sweden University, SE-851 70 Sundsvall, Sweden

ARTICLE INFO

Article history:

Received 4 June 2009

Accepted 17 September 2009

Available online 19 September 2009

ABSTRACT

A method for growing carbon cages using gold nanoparticles as templates is reported. Gold nanoparticles were deposited on carbon nanotubes (CNTs). The nanocages were grown on the gold particles by electrical Joule heating of the CNT. The gold was subsequently evaporated, leaving the cages intact. A special in situ TEM-holder equipped with a small scanning tunneling microscope was used as an electrical probe to drive current through the CNT, while the TEM was used for imaging of the entire growth process. The method might provide a general way for making carbon structures limited only by the shapes allowed by the fabrication methods of the gold nanostructures.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Nanocages are nanosized hollow particles [1]. They are of importance in a number of applications including rechargeable batteries, hydrogen production and storage, catalysis, sensing, and drug and gene delivery [1,2]. It is the large fraction of void space of the hollow cages that is used in several different ways: encapsulating of sensitive materials such as DNA, to lower the density, to modulate the refractive index, or to increase the active area for catalysis.

To fabricate these nanocages, the most common methods are conventional hard-templating, sacrificial templating, soft templating, and template free method [1]. To remove the template, typically selective etching or calcinations at high temperature are used [1]. An early example of nanocage fabrication is the colloidal templating synthesis of hollow silica spheres [3], but nanocages are made in many different materials including gold [4], palladium [5], and boron nitride [6].

Carbon as a material in nanocages is attractive for several reasons [1], but the most well investigated carbon nanocages are smaller ones, such as C₆₀ [7] or carbon onions [8–9]. Arc discharge [10] and resistive heating [11] have been used for synthesizing small carbon capsules or carbon nanoparticles. Attempts to make larger carbon nanocages have resulted in foam-like structures with relatively thick walls [12] or by a

method [13] that do not easily permit controllable sizes. Another kind of flower-like structures, called carbon nanohorns, with an average diameter of about 80 nm [14], are hollow particles and could be used in some nanocage applications such as for gas storage and as drug carriers [15]. However, for applications of nanocages there is still a need for alternative methods that allow carbon cages to be fabricated with determined size and shape.

Several different methods are used for growing carbon structures. To study the growth mechanism, in situ electron microscopy of electron beam induced growth has been used [22–24]. Laser vaporization, arc discharge, and chemical vapor deposition (CVD) are the commonly used methods for CNT synthesis [16–18]. Metal nanoparticles, usually Fe, Co and Ni [19–21], catalyze the deposition of carbon atoms in the CVD method. Gold nanoparticles have recently been found to catalyze the growth of CNT, and the enhanced catalytic activity of gold nanoparticles is now well established [25]. Gold nanoparticles could be attractive template materials for nanocage synthesis due to the good control of the size and shape in the synthesis process, as well as for its resistance to oxidation [26]. Additionally, gold can be encapsulated or removed from carbon nanocages [9]. Gold nanoparticles might thus act as suitable templates for fabricating carbon nanocages.

Here, we report on a method to grow large carbon cages, using gold nanoparticles on CNTs as templates. The

^{*} Corresponding author. Fax: +46 60 148802.

E-mail address: renyun.zhang@miun.se (R.Y. Zhang).

0008-6223/\$ - see front matter © 2009 Elsevier Ltd. All rights reserved.

doi:10.1016/j.carbon.2009.09.056

experiments were done inside a TEM using a special in situ holder with movable electrical probes, allowing a detailed observation and control of the entire process. The cages were grown on the gold nanoparticles under electrical Joule heating. The gold was subsequently evaporated, leaving the cages intact. The templating gold nanoparticles could be made in different sizes allowing size adjustments of the resulting carbon nanocages. The method may serve as new strategy to fabricate designed carbon materials, and the obtained carbon nanocages may have wide applications including drug delivery and hydrogen storage [2].

2. Experimental

2.1. Materials

CNTs (diameter 110–170 nm) were purchased from SIGMA. Sodium citrate and HAuCl_4 , both purchased from SIGMA, were diluted in doubly distilled water at the concentration of 1.0 wt.%.

2.2. Synthesis of CNT/Au nanocomposites

The composites of CNT and gold nanoparticles were synthesized by a single step method [27]. Briefly, 4.0 mg CNTs (diameter 110–170 nm, Sigma) were mixed with 4.0 ml sodium citrate (1.0 wt.%) and treated with ultrasonication for 10 min. The solution was then diluted to 100 ml and heated to boil while stirring, 1.0 ml HAuCl_4 (1.0 wt.%) was added and kept boiling for 5–8 min until the color no longer changed. Samples were rinsed and collected using an 8000-rpm centrifuge. When growing the gold nanorod on CNTs (shown in Fig. 6 below), we mixed the above obtained CNT/Au nanocomposites with sodium citrate and stirred for 5 min without sonication, then diluted the solution to 100 ml and heated to the boiling point. HAuCl_4 was added after the solution was boiled and kept boiling for 5–8 min until the color no longer changed.

2.3. In situ TEM sample preparation

The in situ experiments were performed using an in situ TEM probe [28–30] (Nanofactory Instruments) inside a JEOL-2000FX TEM. This in situ probe is essentially a tiny scanning tunneling microscope incorporated with a side-entry TEM sample holder (a photo of the sample holder is shown in Supplementary materials). The holder system contains two electrodes; one is fixed while the other can be moved in three dimensions by a piezoelectric actuator. In our experiments, we used two 0.25 mm gold wires as electrodes. To attach the sample, we simply dipped one gold wire in conductive epoxy glue (Circuit Works, type 38017750 CW2400), and then into the dried CNT/Au nanocomposites. The wires were inserted into the holder and kept for 30 min at room temperature until the conductive glue was dried.

2.4. In situ TEM measurements

The TEM was a JEOL-2000FX operating at 160 kV using a LaB6 electron emitter. The pressure inside the TEM chamber was

3×10^{-7} mbar. To make the Joule heating experiment inside the TEM chamber roughly two steps were needed. The first step was to align and make an electrical contact between the probing tip and a selected carbon nanotube using the piezo-electric motor. The second step was to perform the actual Joule heating experiment, which was done by increasing the applied voltage between the probing electrode and the CNT. The voltage applied to the nanotube and the current measurements were done using a PXI-6228 16-bit AD/DA measurement card (National Instruments) and controlled with a LabView program. The applied voltages could be controlled manually or by the software. In each experiment, a movie of the TEM images was recorded using a digital camera at 10 frames/s. Each frame of the movie was displayed and saved with the corresponding measured current and applied voltage.

3. Results

3.1. The gold templating scheme

In our experiments, carbon cages were grown by heating gold nanoparticles on CNTs using the in situ TEM probe system (Fig. 1). The gold particles acted as templates for carbon cages

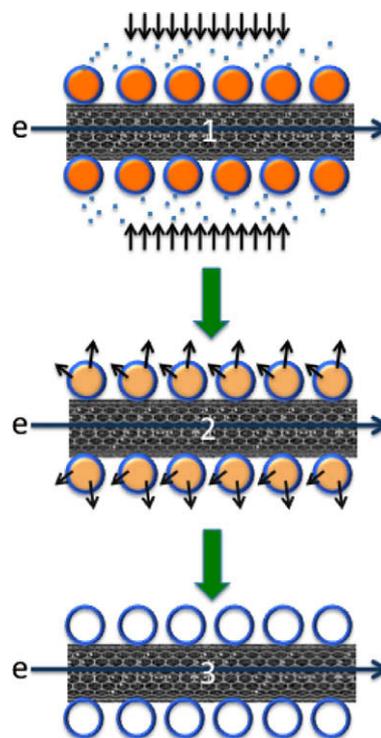


Fig. 1 – Schematic drawing of the growth process of carbon cages. The arrows labeled with an “e” indicate current passing through the carbon nanotube. (1) A composite of carbon nanotube and gold nanoparticle was contacted by two gold electrodes. An electrical current heated the composite to a temperature when the gold nanoparticles template the deposition of carbon atoms, (2) increasing the current and thus the temperature, lead to the evaporation of the gold nanoparticles, and (3) leaving the empty carbon cages intact.

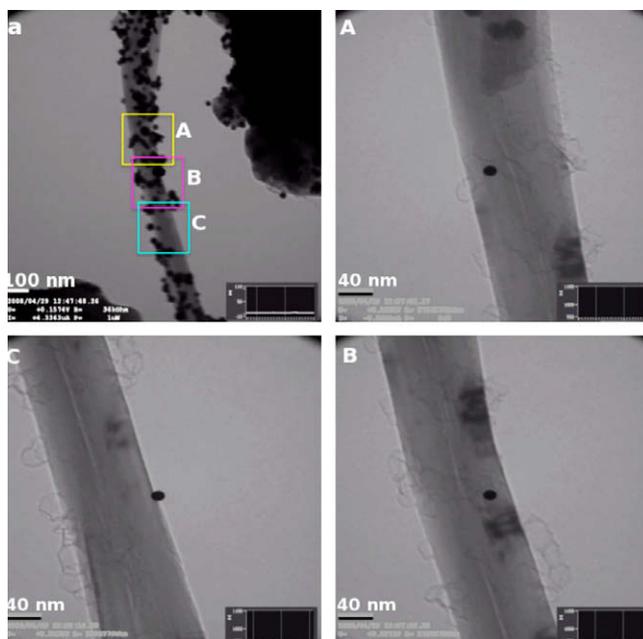


Fig. 2 – TEM images of the composites of carbon nanotube and gold nanoparticles before (a) and after (A, B and C) gold melting. A, B and C indicated the three parts on the carbon nanotube in (a) where carbon cages were grown.

growth and were later evaporated away, leaving carbon nanocages behind. Both the heating that is necessary for the growth and the evaporation was done using direct electrical Joule heating of the CNT. There were several reasons for choosing gold nanoparticles as templates, including easy control of size and shape, resistance to oxidation, and the possibility to empty the cages by evaporation of gold. The catalytic property of gold for growing CNT [25,31] was also considered in our choice, but we have not investigated whether this is the

case here. There are also other active metal nanoparticles [20,21,32,33] that might work, however, the low melting point of gold was attractive in our implementation.

3.2. In situ TEM images and electrical data of the growth process

Fig. 2 shows the TEM images of carbon cages that were grown on the CNT. Fig. 2a shows the CNT/Au nanocomposite before gold melting. Fig. 2A–C shows the three parts on the CNT after the gold melted and evaporated away, which corresponds to the three labeled squares in Fig. 2a. Fig. 2A–C shows that the cages were of similar sizes as the gold nanoparticles and localized at the same positions as the gold nanoparticles were before evaporation.

Fig. 3 shows a closer comparison of the gold nanoparticles and the carbon nanocages, showing the similarity between the cages and the earlier size and shape of the gold nanoparticles. A movie of growth process, showing how the gold nanoparticles on the carbon were melting is given in Supplementary material as SP1. A TEM figure of another nanocages with smaller size that similar to Fig. 3 is given in Supplementary material.

Fig. 4 shows the measured resistance of a CNT and the Joule heating power (from $P = RI^2$). The increase in applied voltage, leading to an increase in current, was controlled by software. There were three steps that we could identify during the process. During the first annealing step, the resistance decreased rapidly. This kind of annealing is common and has been observed earlier [28,29], and is due to curing of the contact resistances of the CNT to the electrodes. The current–voltage curves measured before and after the annealing step were all linear (see Supplementary material). After the contact annealing step, we heated the nanotube by increasing the current. By further increasing the heating current, the process moved to the evaporating step, when all the gold

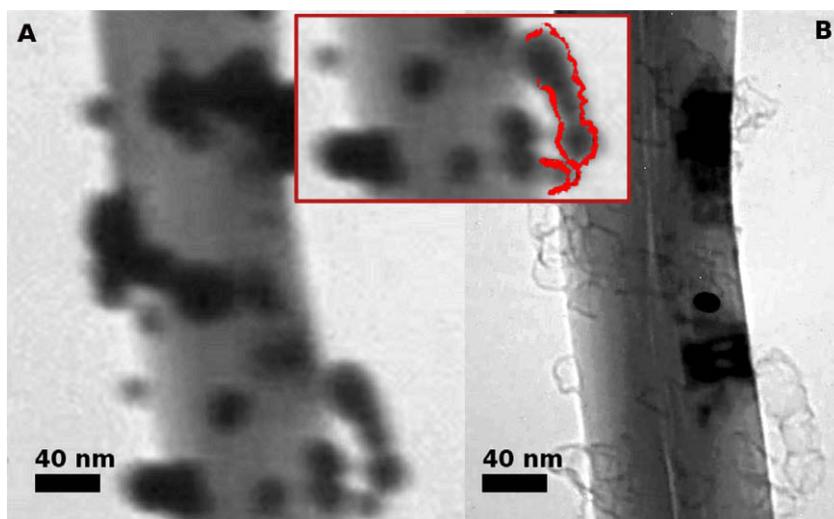


Fig. 3 – (A) Digital zoom of the TEM image in Fig. 2a showing the gold particles on the carbon nanotubes. (B) Corresponding TEM image of the carbon cages that were grown at the same place. The insert shows part of the cage image overlaid on the gold particles, where the cage image from part of B was colored in red. Note the close correspondence between the cages and the sites of gold.

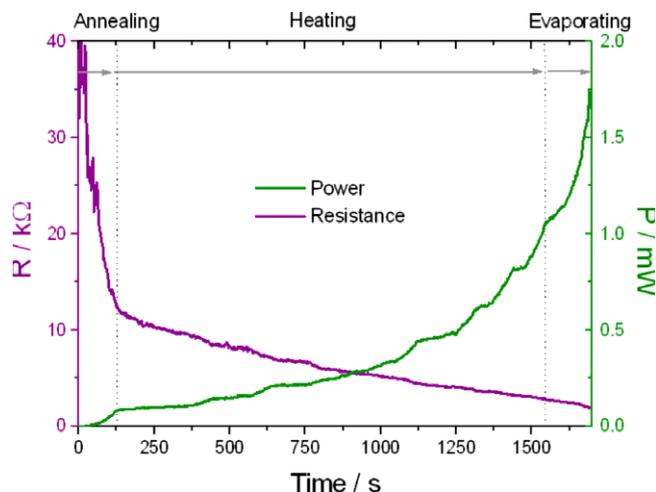


Fig. 4 – The annealing, heating and evaporation phases and the corresponding injected electrical power and resistance of the CNT/Au composite. The bias voltage was increased linearly with time in this experiment.

atoms were evaporated while the carbon cages remained on the CNT. As shown in the [Supplementary SP1](#) movie, the gold evaporating step was within a few seconds.

To observe how the gold nanoparticles melted, we controlled the bias voltage manually, and focused on a smaller part on the CNT at higher magnification and using a larger gold nanorod. The annealing and heating steps was shortened a little bit, as shown in [Fig. 5](#). When the temperature reached the melting point of the gold nanorod, the power was set around 1600 μW , and the gold nanorod was slowly evaporated. TEM images are shown in [Fig. 6](#) and a movie can be found in [Supplementary material](#) as SP2.

The power shown in [Figs. 4 and 5](#) is the total power inserted both to the CNT and to the contact resistances. As shown in [Supplementary](#), we can indirectly calculate the contact resistances by using a model of the temperature [34] and use the melting of gold as a calibration point. The modeling gave CNT resistances that were about 20% of the total resis-

tance and thus the Joule heating power is proportionally lower (As shown in [Table S1](#) in [Supplementary material](#)).

4. Discussion

Our idea of the growth mechanism of the carbon nanocages was that the electron beam radiation on the CNT would break the C–C bonds, possibly aided by the high temperature on the CNT due to Joule heating. These released carbon atoms would then serve as a source of carbon for a growth of the nanocages, templated by the gold nanoparticles at high temperature. Below we discuss this idea and possible extensions of the protocol.

4.1. Cage material

As discussed in [Section 4.3](#) below, no cages were found without a carbon source. It is thus highly likely that the material of the cages was carbon. In addition, if the cages were carbon cages they should have the same melting point as the CNT. To test this, we increased the bias voltage further, and after all the gold atoms were evaporated, we reached the melting point of carbon when the cages melted at the same time as the CNT (see the TEM images in [Supplementary material](#)). The corresponding resistance and power changes are shown in [Fig. 7](#). The CNT started to break from outside to inside, causing the resistance to increase until the nanotube broke. The calculated melting temperature of carbon cages was 3800 K (see [Table S1](#) in [Supplementary material](#)), which is close to the melting temperature of CNTs (3925 K, as given by SIGMA). We used the bulk value as the experimental reference point in these calculations, since gold nanoparticles that larger than 20 nm have a melting temperature close to the bulk value of 1300 K [35].

4.2. Cage size and shape

As shown in [Figs. 2 and 3](#), the sizes and shapes of the carbon cages were similar to the gold nanoparticles, although some-

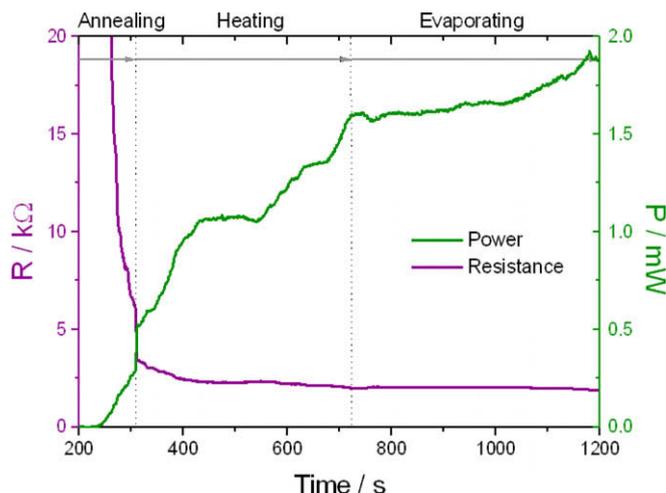


Fig. 5 – Resistance and Joule heating power during the melting process. The bias voltage was controlled manually in this experiment. At the beginning, bias was increased quickly to shorten the annealing step. In the evaporating step, the power was kept around 1.6 mW to slowly evaporate the gold atoms.

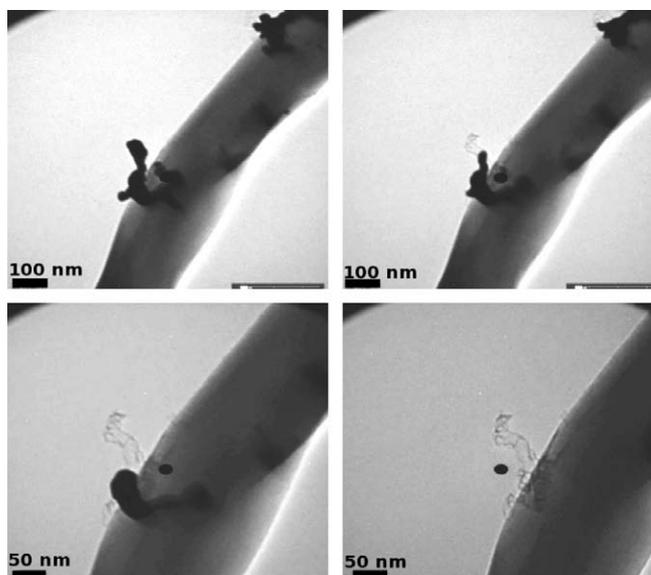


Fig. 6 – Sequence of in situ TEM images when a gold nanorod evaporates.

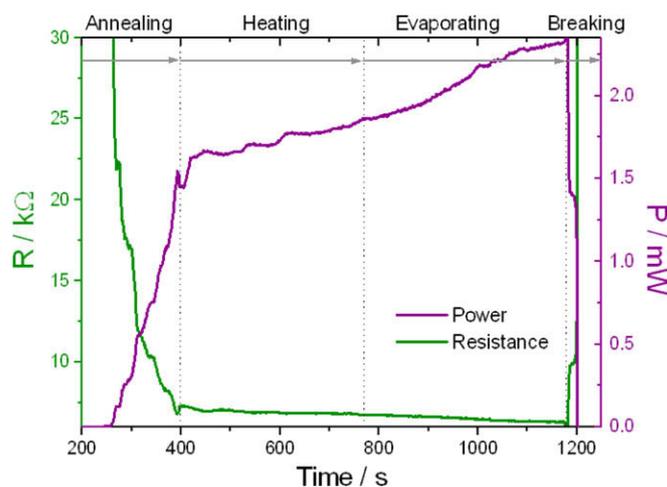


Fig. 7 – Resistance and power changes during the experiment to melt carbon cages and carbon nanotube. The bias was controlled manually in this experiment. A breaking step was shown here to distinguish from Figs. 4 to 5.

times, during the gold melting process, the cages changed slightly. This is thus consistent with our view that the carbon nanocages were templated by the gold nanoparticles. The thicknesses of the walls of those carbon cages were below 1–3 nm as measured by TEM, suggesting that only a few layers of carbon were grown. The reason for such a thin film thickness might be due to the low carbon atom concentration inside the vacuum, as well as the short carbon deposition time. If the CNT was acted as a carbon source, as argued below, the carbon atoms must be first released from the CNT by the electron beam and this production of free carbon atoms is low [8].

4.3. Carbon source

There are three possible sources of carbon: from the CNT, the chamber, and the citrate group. We will argue below that, most likely, the main source of carbon is the CNT. First, we just note that the cages were not present before the growth

process. The original CNTs we obtained from SIGMA had clean surfaces (as shown in [Supplementary materials](#)).

The view that CNTs may act as a carbon source is consistent with observations that the electron beam inside the TEM breaks the C–C bond and generates free carbon atoms [8,9]. In our experiments, the CNTs were heated and this elevated temperature might provide additional aid in releasing carbon atoms. However, the main argument for CNTs as the carbon source was from a control experiment using a non-carbon nanowire. We synthesized a $\text{Mo}_6\text{S}_3\text{I}_6$ –gold nanocomposite (as shown in [Supplementary material](#)) and repeated the same procedure as above, but no cages were found on the $\text{Mo}_6\text{S}_3\text{I}_6$ nanowires after the evaporation of gold nanoparticles. Gold nanoparticles were deposited on the $\text{Mo}_6\text{S}_3\text{I}_6$ wire with the same method as we used for CNT. The diameter of the $\text{Mo}_6\text{S}_3\text{I}_6$ wire was 320 nm and with a length of 34 μm . The experimental results showed that we have not observed any cages without an additional carbon source.

The second possible source is the citrate group. Sodium citrate was used to reduce Au^{3+} in our experiment and some citrate group could cover the surface of gold nanoparticles. But the citrate has a low melting point of 573 K and will probably be evaporated early in the Joule heating process. In addition the test using $\text{Mo}_6\text{S}_3\text{I}_6$ showed no carbon cages despite the similar gold nanoparticles deposition procedure. This source is therefore less likely to be of any major importance.

The third possibility is that the carbon comes from the electron microscope chamber, for example from the diffusion pump oil or other environmental contaminations. It is well known that carbon structures may be deposited inside electron microscopes under ordinary operating pressure, a technique known as electron beam induced deposition (EBID) [36]. The electron beam dissociates adsorbed molecules into fragments: one part that is nonvolatile, which will be deposited, and another part that is volatile, which will be pumped away [37]. The important parameters are the exposure time, electron beam current density, and pressure. Our pressure was the standard 3×10^{-7} mBar and we imaged under standard current densities (typically below 20 A cm^{-2}). Typical imaging time in the experiments was 20–60 min. These conditions might lead to deposition of carbon, but as shown recently, the temperature of the nanowires should not be too high [38]. Using the same kind of Joule heating by in situ TEM probing as in our study, the deposition rate was shown to decrease at higher temperature and approached zero above 400 K [38]. In our case, the temperature is well above 400 K, resulting in a cleaning of the surfaces of the nanowires from amorphous carbon contaminants. Thus, this kind of carbon source is also less likely to be of any major importance.

4.4. Growing larger amounts of carbon nanocages and applications

To grow bulk amount of carbon cages using this method, a slightly different approach could be used. Instead of using the electron beam from the TEM to release carbon from CNTs, one could use another carbon source, and instead of the laborious arrangement with an in situ TEM probe for Joule heating a simple vacuum furnace should have the same effect. Fig. S6 in Supplementary material describes a possible way. First, gold nanoparticles could be deposited on a substrate and placed inside a vacuum furnace, then a small amount of carbon should be injected and heated to the catalytic temperature for a short time, and, by increasing the temperature, evaporate the gold and empty the cages. Since the size and shape of the carbon cages are depended on the gold nanoparticles, one could design and grow different carbon cages with different size and shape. Furthermore, it may be used to grow 3D carbon composite by depositing multi-layers of gold nanoparticles on the substrate, to grow similar structure as in the theoretical studied hydrogen storage [2]. Several other applications of carbon cages have been suggested. C_{60} might be used in cancer therapy [39], but the perfectly closed structure and small size [40], makes it hard to fill them with therapeutics agents. By using larger cages, which are filled with drug molecules, the effect may be enhanced. Another application for cages may be in fuel cells [41]. The new system shown in

this paper may thus serve as a new platform for physical, chemical, and biomedical applications.

5. Conclusions

In summary, a method for growing carbon cages using gold templates based on CNT/Au nanocomposites is described. The carbon cages were grown on gold nanoparticles using electric Joule heating on CNTs. The Joule heating was also used to remove the gold nanoparticles by evaporation, leaving the carbon cages intact. In situ TEM probing was used both for controlling and characterizing the entire growth process of carbon cages. The likely mechanism of this growth process was that the CNTs served as a carbon source and the growth was templated by the gold particles. The gold template method might provide a general way for fabricating carbon nanostructures of predetermined shape, which might have application in many fields like fuel cell, drug carrier, or hydrogen storage.

Acknowledgements

We thank the Sundsvall Community for financial support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.carbon.2009.09.056](https://doi.org/10.1016/j.carbon.2009.09.056).

REFERENCES

- [1] Lou XW, Archer LA, Yang ZH. Hollow micro-/nanostructures synthesis and applications. *Adv Mater* 2008;20(21):3987–4019.
- [2] Dimitrakakis GK, Tylianakis E, Froudakis GF. Pillared graphene: a new 3-D network nanostructure for enhanced hydrogen storage. *Nano Lett* 2008;8(10):3166–70.
- [3] Caruso F, Caruso RA, Möhwald H. Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating. *Science* 1998;282(5391):1111–4.
- [4] Skrabalak SE, Chen JY, Au L, Lu XM, Li XD, Xia YN. Gold nanocages for biomedical applications. *Adv Mater* 2007;19(20):3177–84.
- [5] Xiong YJ, Wiley B, Chen JY, Li ZY, Yin YD, Xia YN. Corrosion-based synthesis of single-crystal Pd nanoboxes and nanocages and their surface plasmon properties. *Angew Chem Int Ed* 2005;44(48):7913–7.
- [6] Oku T, Kusunose T, Niihara K, Suganuma K. Chemical synthesis of silver nanoparticles encapsulated in boron nitride nanocages. *J Mater Chem* 2000;10:255–7.
- [7] Kratschmer W, Lamb LD, Fostiropoulos K, Huffman DR. Solid C_{60} : a new form of carbon. *Nature* 1990;347(6282):354–8.
- [8] Ugarte D. Curling and closure of graphitic networks under electron-beam irradiation. *Nature* 1992;359(6397):707–9.
- [9] Banhart F, Redlich Ph, Ajayan PM. The migration of metal atoms through carbon onions. *Chem Phys Lett* 1998;292(4–6):554–60.
- [10] Saito Y. Nanoparticles and filled nanocapsules. *Carbon* 1995;33(7):979–88.
- [11] Kizuka T, Kato R, Miyazawa K. Structure of hollow carbon nanocapsules synthesized by resistive heating. *Carbon* 2009;47(1):138–44.

- [12] Wang JN, Zhang L, Niu JJ, Sheng ZM, Zhao YZ, Chang H, et al. Synthesis of high surface area water-dispersible graphitic carbon nanocages by an in situ template approach. *Chem Mater* 2007;19:453–9.
- [13] Saito Y, Matsumoto T. Carbon nano-cages created as cubes. *Nature* 1998;392(6664):237.
- [14] Murata K, Kaneko K, Steele WA, Kokai F, Takahashi K, Kasuya D, et al. Molecular potential structures of heat-treated single-wall carbon nanohorn assemblies. *J Phys Chem B* 2001;105(42):10210–6.
- [15] Ajima K, Yudasaka M, Murakami T, Maigne A, Shiba K, Iijima S. Carbon nanohorns as anticancer drug carriers. *Mol Pharm* 2005;2(6):475–80.
- [16] Thess A, Nikolaev P, Dai HJ, Robert PJ, Xu CH, Lee YH, et al. Crystalline ropes of metallic carbon nanotubes. *Science* 1996;273(5274):483–7.
- [17] Journet C, Maser WK, Bernier P, Loiseau A, Delachjapelle ML, Lefrant S, et al. Large-scale production of single-walled carbon nanotubes by the electric-arc technique. *Nature* 1997;388(6644):756–8.
- [18] Cassell AM, Raymakers JA, Kong J, Dai HJ. Large scale CVD synthesis of single-walled carbon nanotubes. *J Phys Chem B* 1999;103(31):6484–92.
- [19] Andrews R, Jacques D, Rao AM, Derbyshire F, Qian D, Fan X, et al. Continuous production of aligned carbon nanotubes: a step closer to commercial realization. *Chem Phys Lett* 1999;303(5–6):467–74.
- [20] Bower C, Zhou O, Zhu W, Werder DJ, Jin S. Nucleation and growth of carbon nanotubes by microwave plasma chemical vapor deposition. *Appl Phys Lett* 2000;77(17):2767–9.
- [21] Yudasaka M, Kikuchi R, Matsui T, Ohki Y, Yoshimura, S. Specific conditions for Ni catalyzed carbon nanotube growth by chemical vapor deposition. *Appl Phys Lett* 1995;67(17):2477–9.
- [22] Rodríguez-manzo JA, Terrones M, Terrones H, Kroto HW, Sun LT, Banhart F. In situ nucleation of carbon nanotubes by the injection of carbon atoms into metal particles. *Nat Nanotechnol* 2007;2(5):307–11.
- [23] Helveg S, López-cartes C, Sehested J, Hansen PL, Clausen BS, Rostrup-Nielsen JR, et al. Atomic-scale imaging of carbon nanofibre growth. *Nature* 2004;427(6973):426–9.
- [24] Lin M, Tan JPY, Boothroyd C, Loh KP, Tok ES, Foo YL. Direct observation of single-walled carbon nanotube growth at the atomistic scale. *Nano Lett* 2006;6:449–52.
- [25] Bhaviripudi S, Mile E, Steiner III SA, Zare AT, Dresselhaus MS, Belcher AM, et al. CVD synthesis of single-walled carbon nanotubes from gold nanoparticle catalysts. *J Am Chem Soc* 2007;129(6):1516–7.
- [26] Luo CX, Liu L, Jiang KL, Zhang LN, Li QQ, Fan SS. Growth mechanism of Y-junctions and related carbon nanotube junctions synthesized by Au-catalyzed chemical vapor deposition. *Carbon* 2008;46(3):440–4.
- [27] Zhang RY, Hummelgård M, Olin H. Simple and efficient gold nanoparticles deposition on carbon nanotubes with controllable particle sizes. *Mater Sci Eng B* 2009;158(1–3):48–52.
- [28] Svensson K, Jompol Y, Olin H, Olsson E. Compact design of a transmission electron microscope-scanning tunneling microscope holder with three-dimensional coarse motion. *Rev Sci Instrum* 2003;74(11):4945–7.
- [29] Svensson K, Olin H, Olsson E. Nanopipettes for metal transport. *Phys Rev Lett* 2004;93(14):145901.
- [30] Ziegler KJ, Lyons DM, Holmes JD, Erts D, Polyakov B, Olin H, et al. Bistable nanoelectromechanical devices. *Appl Phys Lett* 2004;84(20):4074–6.
- [31] Lee SY, Yamada M, Miyake M. Synthesis of carbon nanotubes over gold nanoparticles supported catalysts. *Carbon* 2005;43(13):2654–63.
- [32] Franklin NR, Li YM, Chen RJ, Javey A, Dai HJ. Patterned growth of single-walled carbon nanotubes on full 4-inch wafers. *Appl Phys Lett* 2001;79(27):4571–3.
- [33] Nikolaev P, Bronikowshi MJ, Bradley RK, Rohmund F, Colbert DT, Smith KA, et al. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chem Phys Lett* 1999;313(1–2):91–7.
- [34] Vincent P, Purcell ST, Journet C, Binh VT. Modelization of resistive heating of carbon nanotubes during field emission. *Phys Rev B* 2002;66(7):75406.
- [35] Koga K, Ikeshoji T, Sugawara K. Size- and temperature-dependent structure transitions in gold nanoparticles. *Phys Rev Lett* 2004;92(11):115507.
- [36] Broers AN, Molzen WW, Cuomo JJ, Wittels ND. Electron-beam fabrication of 80-Å metal structures. *Appl Phys Lett* 1976;29(9):596–8.
- [37] Silvis-Cividjian N, Hagen CW, Kruit P, vd Stam MAJ, Groen HB. Direct fabrication of nanowires in an electron microscope. *Appl Phys Lett* 2003;82(20):3514–6.
- [38] Wei XL, Liu Y, Chen Q, Peng LM. Controlling electron-beam-induced carbon deposition on carbon nanotubes by Joule heating. *Nanotechnology* 2008;19:355304.
- [39] Sayes CM, Fortner JD, Guo W, Lyon D, Boyd AM, Ausman KD, et al. The differential cytotoxicity of water-soluble fullerenes. *Nano Lett* 2004;4(10):1881–7.
- [40] Ahn JS, Suzuki K, Iwasa Y, Mitani T. Photoluminescence of C60 aggregates in solution. *J Lumin* 1997;72–74:464–6.
- [41] Hinokuma K, Ata M. Fullerene proton conductors. *Chem Phys Lett* 2001;341(5–6):442–6.