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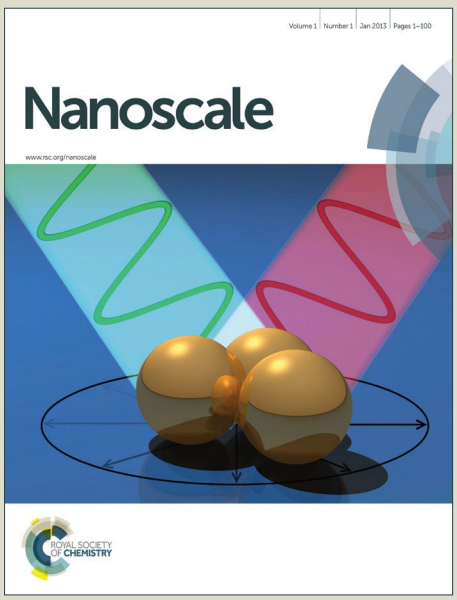

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ARTICLE

Refilling of Carbon Nanotube Cartridge for 3D Nanomanufacturing†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A metal-filled carbon nanotubes (CNTs) are known to be used as a pen-tip injectors for 3D manufacturing in nanoscale. However, a small volume of the CNT cartridge requests methods of refilling it to allow the fabrication of complex metallic structures. The strategy for refilling of CNT cartridges is suggested in this study. Controlled growth of gold nanowires in the interiors of isolated CNTs using a real-time manipulator installed in a transmission electron microscope is reported herein. The encapsulation process of discrete gold nanoparticles in the hollow spaces of open-ended multi-wall CNTs was evaluated in detail. The experimental results reveal that the serial loading of isolated gold nanoparticles allows the control of the length of the loaded nanowire with nanometer accuracy. Thermophoresis and the coalescence of gold nanoparticles are assumed to be the primary mechanisms responsible for gold loading into a CNT cartridge.

Introduction

Combining carbon nanotubes (CNTs) with nanoscale metal structures often leads to enhanced and novel functionalities. [1] This fact arose a great scientific interest and since early years after discovery of CNT [2] many groups have developed strategies to produce metal-filled CNT structures. Early reports proposed capillary-induced filling of low-melted-point metals [3] or metallic salts, [4] while later research focused on chemical and electrochemical filling, [5] filling through functionalization, [6] and in situ filling during the CNT production process. [7] Arrays of CNTs filled with metals such as nickel [7b, 8] and copper [7a] were obtained using these methods. Advances in the filling of CNT with metals made these structures potential candidates for various applications: resonant optical antennas, [9] nano-optical tweezers, [10] electrical nanocables, [11] nanomagnets, [12] nanoswitches, [13] etc. A capability to withdraw loaded material from the CNT container has opened a new trend in nanofabrication technology: application of the metal filled CNTs structures for 3D manufacturing as a pen-tip injector. [14] A controlled metal deposition made by metal-filled CNT injector has been demonstrated in Ref. 14. A metal filled CNT fabricated by a thermal CVD method [15] was bridged and biased between two electrodes; metal was ejected from the CNT due to combination of forces originated from the Joule heating of the created system.

Despite the promising results, fabrication of 3D metal nanostructure is still a technical challenge. One of the biggest problems arise from the fact that CNT container cannot accumulate enough material to fabricate complex metallic nanostructures. [14a] Therefore a method of refilling of the CNT container need to be developed. It is important to understand mass-transport mechanisms in the CNTs caused by Joule heating to fabricate a refillable CNT cartridge for 3D nanofabrication. Many studies on the mass-transport effects in copper or iron-filled CNTs have been carried out. [16] For a metal-filled multi-walled CNT (MWCNT) bridged between two electrodes under an electric bias, three primary mass transport mechanisms have been considered: thermal evaporation, thermomigration, and electromigration. [16a] Recent advances in in situ TEM have allowed the realization of the Joule heat-induced melting of the metal electrode (Au, Pt, Ag) followed by the filling of the inner channel of the CNT with a liquid electrode material driven by electromigration force. [17] In Ref. 17, using a real-time manipulator, an individual MWCNT was placed in contact with two noble metal electrodes to form a circuit. A bias voltage was then applied, causing the temperature on the CNT circuit to increase due to Joule heating. The gold electrode melted close to the gold–CNT interface, and the melt entered the CNT channel along the direction opposite to the current flow after a few minutes of biasing. This method can be applied for refilling the CNT cartridge for 3D nanofabrication what was demonstrated by Fan et al. [14a] However it is clearly seen from the result presented in his work that CNT cartridge was severely damaged by heating of the CNT over the sublimation temperatures. [18]

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† Electronic Supplementary Information (ESI) available: variations of loading of the initial nanoparticle into the CNT, movies demonstrating processes of the loading of initial nanoparticle and elongation of encapsulated nanowire. See DOI: 10.1039/x0xx00000x

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In the presence of a temperature gradient, small particles are known to experience a force in the direction from the hot side of the medium to the cold side. [19] Previous studies [14a,17] demonstrated that the thermomigration force generated by the thermal gradient between the central part of the host MWCNT and its tip counteracts the gold encapsulation process. However, under certain conditions, the effect of thermomigration can be used to fill the interiors of CNTs.

Herein we propose to use an isolated MWCNT as a container for the consequent loading of metal to make a refillable cartridge for 3D nanofabrication. We developed an in situ TEM method that utilizes the effect of thermomigration for the length-selective growth of gold nanowires in the interiors of isolated MWCNTs. A TEM holder combining standard TEM imaging characteristics with manipulation capabilities allowed the realization of positioning with sub-nanometer accuracy, and a connection between an open-ended MWCNT and an isolated gold nanoparticle located on a thin supportive CNT was made. This geometry of the experimental setup shifts the point of the highest temperature from the host open-ended MWCNT to the supportive CNT while a current passes through the system. The temperature gradient created between the host open-ended MWCNT and the supportive CNT forces a gold nanoparticle to move away from the hottest point of the system via thermophoresis. We can direct the driving force of thermophoresis toward the host MWCNT to assist the gold encapsulation process by adjusting the physical dimensions of both the host and supportive CNTs. The desired length of the encapsulated nanowire can be obtained by the serial loading and coalescence of several discrete gold nanoparticles. The distinct advantages of this proposed scheme are: i) a handling of individual particles, which allows precise control of the length of the encapsulated nanowire with nanometer accuracy; ii) shift of the highest temperature point from the host CNT to the supportive CNT what preserve a CNT cartridge from the temperature-induced damage.

Experimental section

Preparation of supportive gold-decorated double-walled CNTs (DWCNTs)

Purified DWCNTs fabricated using DC arc discharge [20] were placed onto a flat surface acting as a holder. The DWCNTs were then adhered and aligned on the tip of a platinum-covered knife-edged silicon wafer by moving this wafer with the tip being kept in contact with the surface of holder. [21] Gold nanoparticles with typical diameters in the range of 3–6 nm were deposited on the adhered DWCNTs using an ion sputterer (Hitachi E-1030).

Preparation of CNT container for refillable cartridge

A container for loading gold was fabricated from MWCNTs produced by DC arc discharge [20] with external diameters in the range of 10–16 nm and inner diameters of 1–2 nm. An isolated MWCNT was attached to the tip of a cantilever using a manipulator installed in a scanning electron microscope in accordance with procedures reported previously. [22] The isolated MWCNT was fixed rigidly to the tip by the deposition of amorphous carbon assisted by electron beam irradiation and cut by applying current. [23] The tip opening of the MWCNT was performed inside a high-resolution transmission electron microscope (JEOL JEM-2500SE) operated at 90 kV to reduce the structural changes in the carbon material caused by electron irradiation. The microscope was equipped with a piezo-driven manipulator system consisting of two stages (Sanyu Electron Co., Ltd). The cantilever with the mounted MWCNT was placed at one stage of the manipulator, and the tip of the MWCNT was bridged with the second stage of the piezo-manipulator. A bias voltage was applied between the electrodes to pass a current through the MWCNT using a source meter (Keithley 2410). The central part of the MWCNT was heated locally to the sublimation temperature of 3200 K [18] due to Joule heat, [24] and several outer layers peeled off step-by-step due to the sublimation of carbon atoms. [25] The peeling was stopped when the outer diameter of the remaining layers reached the desired value (i.e., the value consistent with the diameter of the gold nanowire we wanted to load into the CNT cartridge). Subsequently, one of the electrodes was moved in the axial direction of the MWCNT, and the inner core of the MWCNT was pulled out. As a result, we obtained an open-ended MWCNT with an inner diameter of 3–8 nm, as shown in Figs. 1b and 4a.

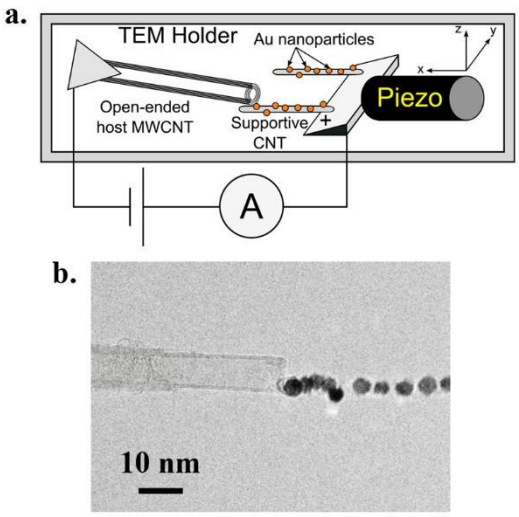

Fig. 1 Schematic drawing (a) and TEM image (b) of the circuit used for filling CNT interiors.

Setup for gold loading

Gold was loaded into the interior of the MWCNTs using in situ TEM. A schematic of the setup utilized in our experiment and a corresponding TEM image are shown in Fig. 1. An open-ended MWCNT that had been mounted to the tip of one electrode was bridged with a gold-decorated DWCNT secured to a second (opposite) electrode. We established a contact between the open end of the MWCNT and one gold nanoparticle on the supportive DWCNT. Gradually increasing the current passing through the contact then induced Joule

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heating, which led to the melting of the gold nanoparticles and their encapsulation in the MWCNT. In all the experiments applied voltage and correspondingly current was increased from low to higher values.

Sequential movies of the TEM experiment were recorded using a slow-scan camera (Gatan USC 1000) with a frame rate of 0.3 s/frame. TEM images illustrating the dynamics of the gold-filling processes were then extracted from the movies.

Results and discussion

Applying a voltage to a CNT bridged between two electrodes will increase the temperature of the CNT via Joule heating. According to the classical equation of heat conduction, for a simple two-terminal connection, the temperature distribution on the CNT bridge has a parabolic shape with a maximum located near the middle of the CNT bridge. [18, 24] In this situation, a strong temperature gradient directed toward the electrode pushes metal particles or melts in the same direction. This may prevent metal loading into the CNT and may lead to the destruction of the host CNT. To eliminate the negative effects of the thermal gradient, we proposed the experimental setup described above. The most important advantage of this configuration is that the point of highest temperature during Joule heating is on the supportive DWCNT and not on the host MWCNT when the diameter of the supportive DWCNT is smaller than that of the host MWCNT. This enables us to create a temperature gradient that is always directed toward the open end of the host CNT, ensuring that thermophoresis promotes rather than hinders the metal loading process. This arrangement also prevents the Joule heat-induced damage of the host CNT.

The process of CNT cartridge filling is conventionally separated into two steps: first, the loading of the first nanoparticle into the open end of a hollow CNT (i.e., the nucleation of the encapsulated nanowire); and second, the posterior growth of the nanowire via its connection with other nanoparticles. In the first step, there are several possible ways in which the initial gold nanoparticle can be loaded inside the host MWCNT (supplementary information: section S1 and Movies S1-S5), although the loading mechanisms are still under consideration. A typical procedure for the first nanoparticle loading is described below, and a scheme for this process is presented in Fig. 2a.

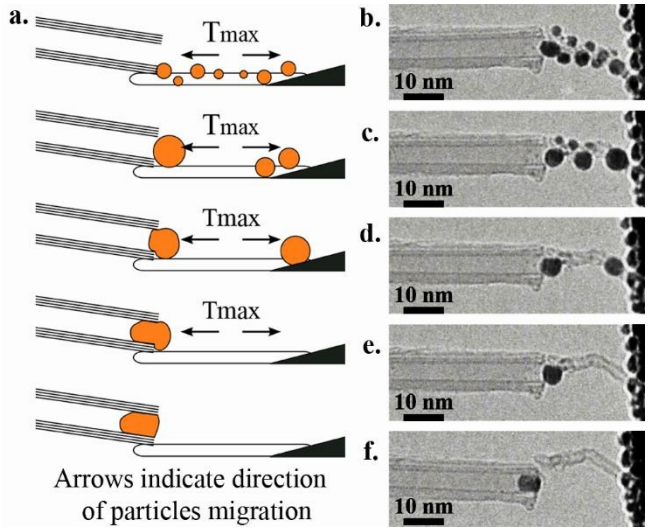

Fig. 2 Encapsulation of gold nanoparticles. Scheme (a) and TEM pictures (b–f) of the process.

After establishing a contact between the open-ended host MWCNT and the supportive DWCNT (Fig. 2b), voltage was applied and increased until the gold nanoparticles began to coalesce on the DWCNT. This typically occurred when the current flowing through the contact reached 5–10 μA. At these values of current, the gold nanoparticles coalesced and reached diameters roughly matching or slightly larger than the inner diameter of the open-ended MWCNT (typically 6–8 nm). At the same time, the contact angle between the gold nanoparticles and DWCNT increased (i.e., the surface area of the Au–DWCNT interface decreased, causing the interaction force between the gold nanoparticles and supportive DWCNT to decrease). After nanoparticle formation, we slightly adjusted the positioning of the open tip of the host MWCNT so that it was located in front of a gold nanoparticle (Fig. 2c). The voltage was then increased until molten gold particles migrated and entered inside the opened MWCNT driven by the impact of thermal gradient (Figs. 2d, e, and f). At this step, a short gold nanowire with a length of 6–8 nm encapsulated in CNT was formed (Fig. 2f).

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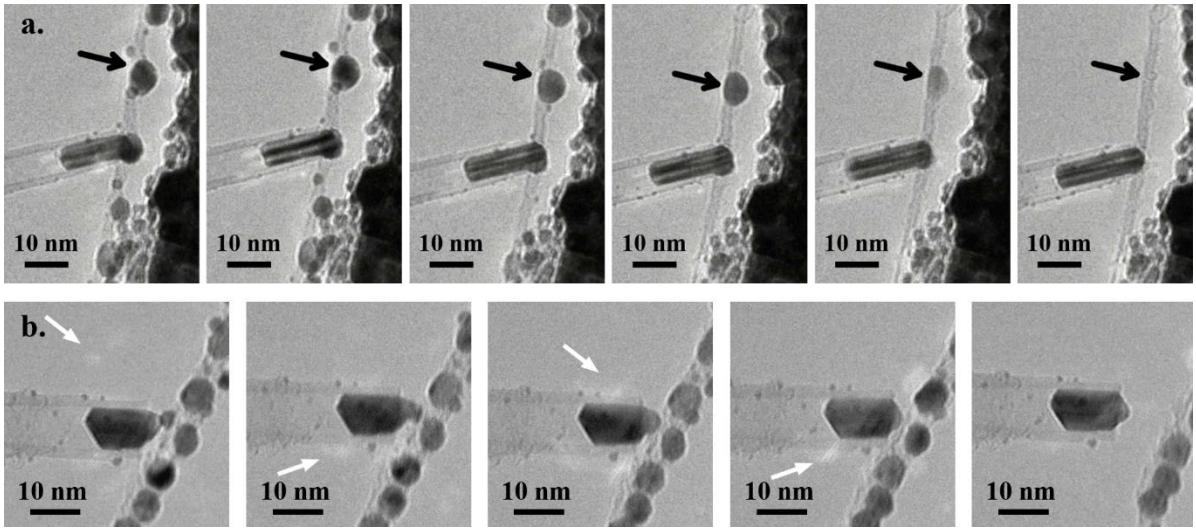

Fig. 3 Series of TEM images illustrating the elongation processes of a gold nanowire caused by: (a) strong thermal gradient ("forced" method) and (b) coalescence of gold nanoparticles ("mild" method). Black arrows indicate sublimating nanoparticles; white arrows indicate the diffraction shadows.

In the second step, the length of the short nanowire was grown by connecting it with other gold nanoparticles located on the supportive DWCNT in one of the following two ways: "forced" and "mild" (Movies S6 and S7, respectively). In the "forced" strategy, a gold nanoparticle on the supportive DWCNT was forced to move into the interior of the host MWCNT by applying a relatively high voltage, which induced intensive Joule heat and a strong temperature gradient. In the "mild" method, gold loading was carried out at a significantly lower current value using a delicate combination of chemical interatomic interactions and mass-transport effects. The "forced" method is essentially the sequential reiteration of the steps described above for the loading of the first nanoparticle. However, this strategy has at least two evident disadvantages. First, it is difficult to precisely control the length of loading; the accuracy is 5–10 nm because the gold nanoparticles coalesce into relatively large volumes prior to loading. Second, most of the gold nanoparticles sublimate or move away from the host CNT driven by the temperature gradient (Fig. 3a), which leads to losses of material and requires a large quantity of Au-decorated supportive DWCNT.

Thus, it is preferable to carry out the gold loading using the "mild" method as follows. In the "mild" method, it is essential to establish a contact between the host MWCNT and the Au-decorated DWCNT to create an interface between the loaded gold wire in the host CNT and one of the gold nanoparticles on the supportive DWCNT. The nanowire and nanoparticle are joined by an applying voltage (0.1–0.5 V), and a neck forms at the boundary. In this case, the voltage is significantly lower than that applied for melting gold nanoparticles; thus, we suppose that an atomic-scale solid-state direct bonding process takes place. Through the created boundary, the gold nanoparticle then coalesces with the nanowire loaded into the host MWCNT when electrical current was passed through the circuit. Kizuka et al. [26] reported similar bonding under intense electron irradiation; in that study, a crystallographic boundary formed after the spontaneous contact of two nanometer-sized gold tips approached each other at a distance of few atomic layers. [26]

In most cases, after the process of coalescence is finished some amount of gold remains outside of the inner channel of the CNT container (Fig. 3b). To realize the complete loading of gold inside the CNT, it is necessary to increase the voltage to create a temperature gradient that pushes the gold into the interior of the MWCNT. For small gold nanoparticles (less than 2 nm in diameter), bonding and coalescence occur even without applying voltage and flowing current. Grain boundaries are clearly visible on the loaded gold nanowire during the loading process. This fact in addition to the diffraction contrasts on the gold crystal suggests that the gold nanowire is in a solid state during the loading process. Diffraction contrast appears because TEM image formed from direct and diffracted beams. Beam diffracted on the solid crystal is visible as white shadows on TEM picture.

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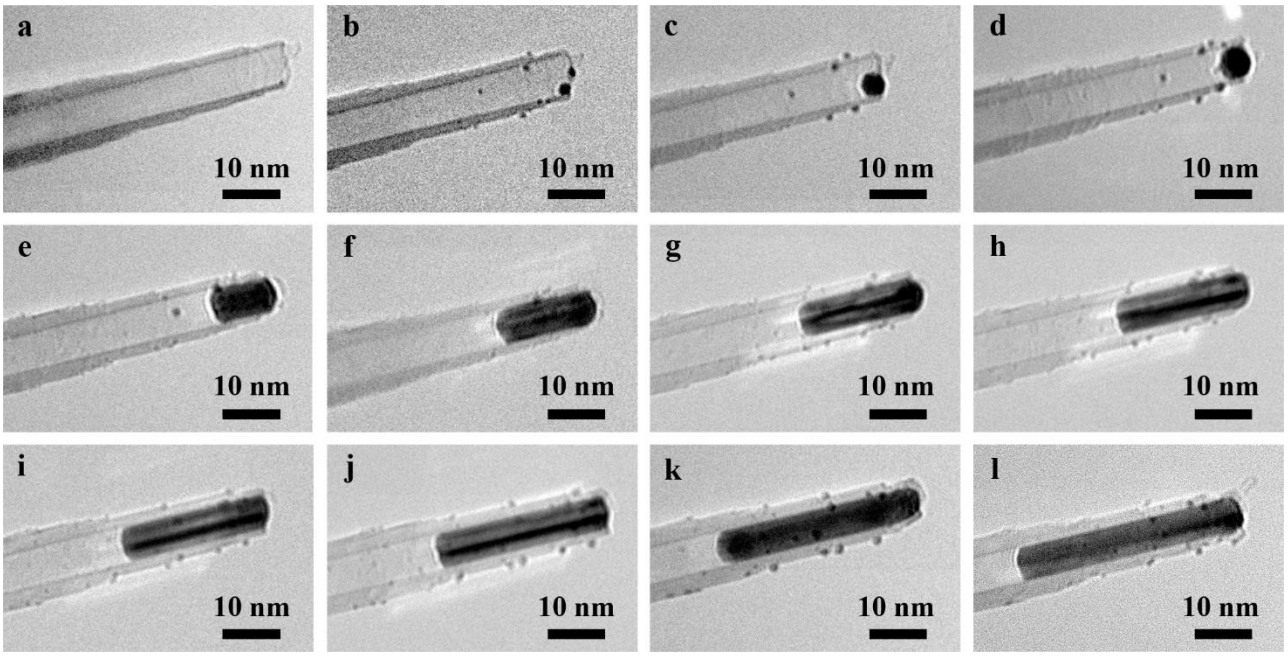

Fig. 4 Length-selective growth of the gold nanowire achieved by serial loadings of discrete gold nanoparticles: (a-e) nucleation and (f-l) elongation of the encapsulated gold nanowire.

It is possible to collect all gold nanoparticles from the supporting DWCNT using the proposed technique because the Joule heat induced by a relatively low current does not increase the temperature to above the melting point of the gold nanoparticles. [27] The encapsulated nanowire can be grown to the desired length by the serial loading of discrete gold nanoparticles (Fig. 4). As shown in Fig. 4l, the length of the encapsulated gold nanowire can reach 45 nm. Based on the number of loaded nanoparticles, their diameters, and the elongation value, we determined that loading individual nanoparticles with an average diameter of 4.8 nm into an MWCNT with an inner diameter of 5.5 nm caused the encapsulated nanowire to elongate by 2.4 nm per nanoparticle. The inner diameter of the MWCNT and diameters of the initial nanoparticles are variables, allowing us to control the elongation of the encapsulated nanowire within the range of 0.5–5 nm. For example, increasing the inner diameter of the host CNT to 8 nm and reducing the average diameter of the loaded nanoparticles to 3.9 nm gives us much more precise control over nanowire length; the loading of one nanoparticle in this case gives an elongation of ~0.66 nm.

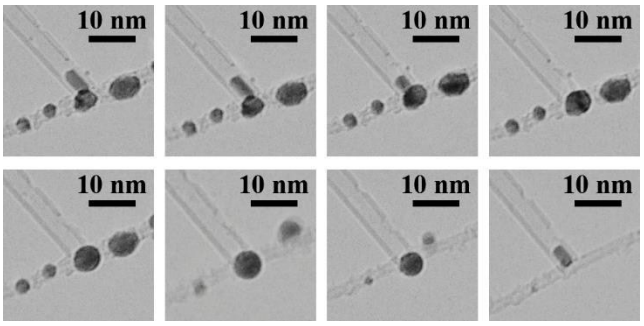

Fig. 5 Effects of capillarity and thermophoresis on the process of gold loading.

Below, we consider the mechanism of gold loading into the hollow CNT container. The most likely mechanisms are electromigration, capillarity, and thermomigration. [15] Two experiments using manipulators with different electrical polarities were conducted to determine if electromigration was the primary cause of gold filling. In one experiment, the electromigration force was directed toward the open-ended CNT; in the other experiment, the force was directed in the opposite direction. In both experiments, gold nanoparticles were loaded inside the hollow CNT, and a gold nanowire was formed in the interior of the MWCNT. The results suggested that the electromigration force was insignificant in our experiment and can be neglected from further consideration. This conclusion differs from that of Zou et al., who determined electromigration to be the primary mechanism of loading; [17] however, this discrepancy can be attributed to principal differences between the proposed experimental setups; in their report, the host CNT was connected directly to the gold electrode, causing the temperature to be the highest in the central part of the host CNT. [18, 24] Consequently, the thermophoresis force was directed toward the direction opposite to that of gold loading.

Although the gold nanoparticles in our experiment were in the solid state, gold melting occurred under some conditions (e.g., when we attempted to load rather large nanoparticles (≥10 nm) or when the diameter of the supportive DWCNT exceeded that of the host MWCNT). In these situations, the capillary effect due to wetting from molten gold requires careful consideration. On one hand, only low-tension melts can be drawn into the inner cavity of the host CNT through capillary

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action. [13b] On the other hand, non-wetting liquid nanoparticles can be absorbed by the capillary effect of the CNT using Laplace pressure due to droplet surface tension (i.e., a sufficiently small liquid droplet can be drawn inside the CNT via capillary action even at contact angles higher than 90°). [28] To evaluate the role of capillarity in the process of gold nanowire growth, we considered the behavior of the initially loaded gold nanowire during serial contacts with the Au-decorated supportive DWCNT. Joule heating can easily melt a small amount of gold inside the host MWCNT (<10 nm), and the capillary effect became evident. As shown in Fig. 5, the molten gold tended to be withdrawn from the open end of the host CNT during the initial stage of contact. Further increasing the voltage, and consequently the current, increased the temperature gradient between the host CNT and the Au-decorated CNT, forcing the gold nanodroplet to move back inside the host CNT. Therefore, capillarity caused by wetting negatively affects the gold loading process and should be avoided by adjusting the current. In contrast, thermophoresis is one of the strongest effects responsible for the process of loading. However, note that the ejection of loaded gold from the interior of the MWCNT usually occurs when the volume of the loaded nanowire is smaller than that of the nanoparticle that is being loaded. This can be explained by the coalescence of gold nanoparticles caused by grain boundary diffusion. [29] Diffusion can also explain the above-described process of elongation of encapsulated gold nanowires under "mild" conditions. Therefore, we can conclude that the processes of gold loading and ejection can be attributed to a combination of multiple and sometimes competitive mass-transport effects.

Conclusions

In summary, we have suggested a strategy to refill a CNT cartridge for 3D manufacturing. Mechanisms of the gold filling have also been studied. The Joule heat-assisted loading of gold nanoparticles inside a hollow CNT was demonstrated in this study. We successfully grew a 45-nm-long gold nanowire in the interior of an MWCNT and demonstrated that the length of the nanowire can be precisely controlled by the number of serial contacts with gold nanoparticles located on a supportive DWCNT with an accuracy of less than 1 nm. The process of CNT cartridge refilling can be conventionally separated into two steps: the nucleation of the encapsulated nanowire and its posterior growth. We proposed two strategies to realize the second step: "forced" and "mild". It has been demonstrated that in the "forced" way, a strong thermal gradient forces nanoparticle to move from supportive CNT into the interior of host CNT. Under the "mild" condition, elongation of the encapsulated nanowire occurs mainly due to coalescence of gold nanoparticles. Moderate thermal gradient is created in order to assist and speed up the process of coalescence. Therefore the process of gold loading cannot be explained by only one mechanism; in this study, gold loading was caused by a dedicated combination of multiple mass-transport effects. Thermophoresis, along with the coalescence of gold nanoparticles caused by grain boundary diffusion, was the major mass-transport mechanism responsible for gold loading into the interior of the MWCNT in this study. We also demonstrated that the effect of electromigration is very small in comparison with the mechanisms mentioned above; thus, electromigration can be omitted from further consideration. While the role of the capillary effect due to wetting is not clear because it appears only in combination with the other, more prominent effects, it might have a negative effect on the process of gold nanowire growth and must be avoided.

Acknowledgments

A part of this work was supported by "Advanced Characterization Nanotechnology Platform, Nanotechnology Platform Program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan" at the Research Center for Ultra-High Voltage Electron Microscopy (Nanotechnology Open Facilities) in Osaka University. The authors would like to thank Enago (www.enago.jp) for the English language review.

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