

Site-Specific Deposition of Gold Nanoparticles on SWNTs

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A simple strategy was developed to site-specifically deposit gold nanoparticles on single-walled carbon nanotubes (SWNTs) using dip-pen nanolithography (DPN) or electrochemical dip-pen nanolithography (E-DPN). As-grown SWNTs on SiO_x/Si substrates were directly used without any pretreatment. By adjusting the writing velocity, tip voltage bias, and the times of seeded growth processes, gold nanoparticles with sizes from several nanometers to tens of nanometers could be controllably deposited on SWNTs. E-DPN provided a route for in situ monitoring the deposition of gold nanoparticles. Without any extra processing step in solution, this route resulted in clean gold nanoparticles/SWNT heterostructures. This DPN-based strategy may find potential application for the fabrication of site-defined nanoscaled heterostructures, site-specific microelectrodes on SWNTs, and room-temperature single-electron transistors.

1. Introduction

Single-walled carbon nanotubes (SWNTs) decorated with metal nanoparticles have shown potential applications as sensors,^{1–9} electrocatalysts in fuel cells,^{10,11} nanoelectrodes,¹² and single-electron transistors or memories.^{13–15} This kind of composite has been considered as model material for studying the electronic interactions between the SWNTs and nanoparticles.^{2,16–18} However, it remains a great challenge to deposit metal nanoparticles at preselected locations on SWNTs. Site-specific decoration of metal nanoparticles on SWNTs will not only allow fabrication of nanoelectrodes on SWNTs,¹² but also facilitate better control over the single-electron transport behavior.¹⁴ The deposited metal nanoparticles may also serve as active sites for site-defined modification or growth of mesostructures.¹⁹

Various methods have been developed to decorate SWNTs with metal nanoparticles,²⁰ including physical evaporation,^{3–5,21–24} directed assembly driven by hydrophobic interaction,^{16,19,25} attachment of nanoparticles to modified SWNTs,^{26–32} and reduction of the adsorbed metal salts at elevated temperatures.³³ Particularly, electroless and electrochemical deposition have been found as better alternatives because of their flexibility in controlling the size and coverage of the metal nanoparticles.^{1,2,6,12,34–41} However, there were few reports about the site-specific deposition of metal nanoparticles on carbon nanotubes (CNTs). Ramanath and co-workers used focused ion beam to site-selectively create defects on multiwalled carbon nanotubes, which were subsequently used to trap metal nanoparticles onto the tubes.⁴² This approach needs state-of-the-art techniques, and the condition is very harsh; therefore, it is not suitable for nondestructive modification of SWNTs. Quinn and Lemay deposited one single particle at the exposed end of each SWNT with electrochemical method.¹² Additionally, scanning probes were used to move gold nanoparticles onto the nearby SWNTs,^{13,15} but it is very difficult to handle very small nanoparticles of a few nanometers by scanning-probe manipulation. However, the small size of the nanoparticles is essential

for building room-temperature single-electron transistors.¹³ Furthermore, this method often results in bad contact between nanoparticles and SWNTs.¹⁵ Up to now, developing nondestructive methods for in situ site-specific deposition of metal nanoparticles on SWNTs was still a big challenge.

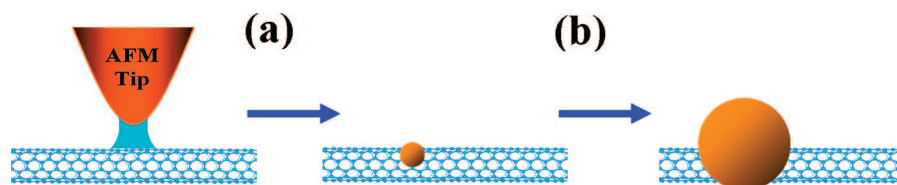
Dip-pen nanolithography (DPN)-based techniques are ideally suited for site-specific modification of nanomaterials while keeping other places clean because the position of the atomic force microscope (AFM) tip can be controlled at nanometer accuracy.^{43–52} For example, Liu et al. site-specifically oxidized GaN nanowires to form GaN/gallium oxide heterostructures using electrochemical dip-pen nanolithography (E-DPN).⁴⁶ In this article, we present a strategy for site-specific deposition of gold nanoparticles on SWNTs using DPN or E-DPN. For the DPN approach, the gold nanoparticles were visible by AFM only after the seeded growth process. Alternatively, direct deposition of visible gold nanoparticles on SWNTs could be achieved by the E-DPN approach. Neither approach was destructive to the SWNTs, and the gold nanoparticles could be deposited at any designed sites on the side walls of SWNTs. When the two methods were combined, gold nanoparticles with sizes from several nanometers to tens of nanometers could be controllably deposited on SWNTs.

2. Experimental Section

2.1. Materials. All chemicals used were of analytical grade. Milli-Q water (18.2 MΩ cm) was used throughout the experiment. The nanotube samples used here were as-grown SWNTs on SiO_x/Si substrates. The CVD growth of SWNTs was performed in a procedure similar to that in our previous articles.^{53,54} Gold electrodes were thermally evaporated on one side of the SiO₂ substrates before the electrochemical DPN for direct deposition of gold nanoparticles on ultralong SWNTs.

2.2. Inking and DPN Process. The gold reflecting layer of AFM silicon probe (NSG11 purchased from NT-MDT Co.) was modified with 1-dodecylthiol by being immersed in its ethanol solution (1/1000, v/v) for 3 min. After being washed by ethanol and blown dry with high-purity nitrogen, the AFM probe was immersed in the 10 mM HAuCl₄ ethanol/water (3/1, v/v)

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SCHEME 1: Site-Specific Deposition of the Gold Nanoparticle on SWNT by DPN (a) and Subsequent Seeded Growth (b)

solution for 3 min and dried in air. After that, the probe was mounted on a SPA400 scanning probe microscope (SPM, Seiko Instrument, Inc.) for AFM imaging and lithography. The procedures of the DPN process were as follows. The locations of the SWNTs were found through tapping mode AFM imaging. Then the AFM tip was translated through the selected sites controllably. Finally, the resulting features were imaged with tapping mode AFM. The relative humidity (RH), measured with a digital hygrometer, was adjusted by a humidifier and a dehumidifier.

2.3. Seeded Growth. The seeded growth solution was prepared similarly as previously reported⁵⁵ with minor modification: 40 mL of 0.40 mM ascorbic acid solution was added to 60 mL of 0.17 mM H₂AuCl₄ solution under stirring. The silicon wafer was put upside down on the surface of the seeded growth solution for 1 h. Then the silicon wafer was rinsed gently with ethanol and water before AFM characterization.

3. Results and Discussion

3.1. DPN for Electroless Deposition of Gold Nanoparticles on SWNTs. Scheme 1 illustrates the DPN process and subsequent seeded growth process for site-specific deposition of gold nanoparticles on a SWNT. As could be seen from Figure 1a, the nanotube side walls were clean and uniform before the DPN process. The height of the SWNTs was 1.0–1.8 nm. During the DPN process, the AFM probe inked with H₂AuCl₄ was translated across the SWNTs along the route indicated by dashed arrows (Figure 1a). There was no obvious change in the topographical image after the DPN process. However, three nanoparticles appeared on the SWNTs after the seeded growth process (Figure 1b). The original heights of the upper two nanoparticles were 4.0 and 5.6 nm. Supposing the two nano-

particles sit on top of SWNTs, the actual heights of the nanoparticles were calculated by subtracting the heights of corresponding SWNTs. In contrast, the lowest particle was at the side of SWNT, and thus the actual height of the nanoparticle equaled the measured height. Therefore, the heights of the nanoparticles in Figure 1b were 2.5, 4.4, and 1.6 nm, respectively. The actual heights of nanoparticles on SWNTs listed below in this article were all obtained by similar methods. As could be seen from both the topographical image (Figure 1b) and phase image (Figure 1c), nanoparticles occurred only on the preselected sites of the SWNTs. As the Fermi level of the SWNTs was well above the reduction potential of AuCl₄⁻, the gold seeds were selectively formed on the SWNTs but not on the silica surface.³⁴ We noticed that the two SWNTs in the lower left corner in Figure 1a disappeared in Figure 1b. This may be due to the rinsing step after seeded growth. Comparative experiments at the same condition and procedure except using pure water instead of H₂AuCl₄ ink did not show gold nanoparticle deposition on SWNTs after being incubated in the seeded growth solution. This result shows that the predeposition of a hint amount of gold on the SWNTs by DPN is essential.

We systematically studied the effect of translation rate and relative humidity on the resultant gold nanoparticles on SWNTs. As it takes time for the reduction of the H₂AuCl₄ by carbon nanotube, the translation rate of the AFM tip should not be too fast in the DPN process. We found that gold nanoparticles were hardly attained when the translation rate was faster than 50 nm/s. The slower translation of the AFM tip elongated the contact time between the tip and the carbon nanotube; thus, the deposition of the gold seeds could be much enhanced, and it would be good for getting larger gold nanoparticles. To deposit enough gold on SWNTs for the efficient seeded growth, the

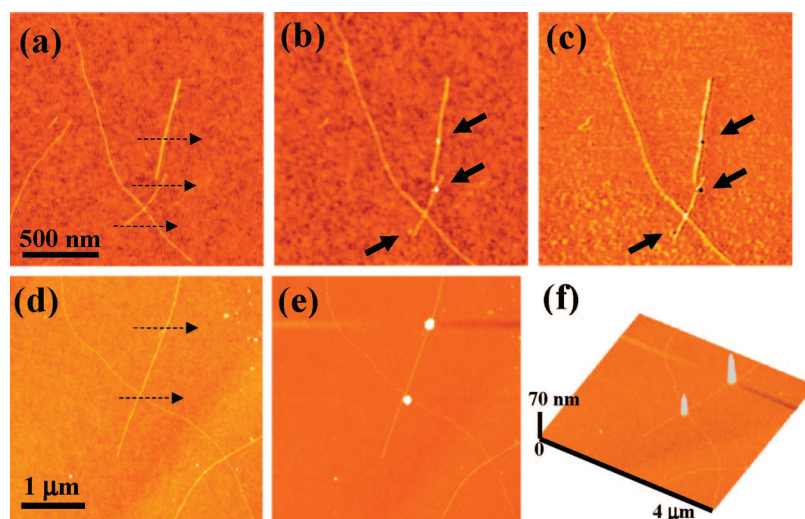


Figure 1. (a–c) Topographical images of carbon nanotubes before (a) and after (b) DPN at the translation rate of 50 nm/s (RH was 55%) followed by seeded growth once. (c) The corresponding phase image of (b). The heights of the nanoparticles (indicated by dashed arrows) are 2.5, 4.4, and 1.6 nm, respectively. (d–f) Topographical images of carbon nanotubes before (d) and after (e) DPN at the translation rate of 20 nm/s (RH was 46%) followed by seeded growth for three times. (f) The corresponding 3D image of (e). The heights of the nanoparticles are 67 and 48 nm.

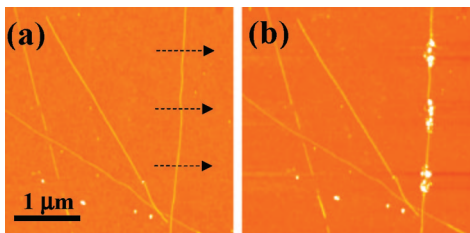
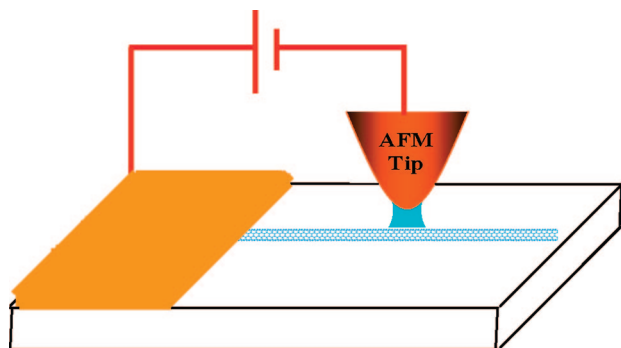


Figure 2. Topographical images of the carbon nanotubes before (a) and after (b) E-DPN process in which the AFM tip was translated across the rightmost nanotube at voltage bias of 9 V. RH was 49%.

SCHEME 2: Electrochemical DPN for Direct Deposition of Gold Nanoparticles on Ultralong SWNTs



DPN process should be conducted at RH between 40 and 60%. Gold nanoparticles were hardly attained when the RH was lower than 40% during the DPN process. However, too high RH would increase the nonspecific deposition of gold nanoparticles (Figure S2 in Supporting Information).

The size and morphology of the final gold particles on carbon nanotubes could be adjusted by varying the seeded growth condition. For example, the gold nanoparticles deposited on carbon nanotubes would get remarkably bigger if we repeated the seeded growth process twice more (Figure 1d–f). The heights of the nanoparticles increased to as large as 67 and 48 nm, respectively. The succeeded seeded growth processes should

be conducted continuously. Otherwise, the nanoparticles would not grow bigger because of the deactivation of the surface of the nanoparticles.

Although the gold seeds deposited by the DPN process were too small for direct AFM height measurement, some gold seeds were visible in phase image (Figure S2 in Supporting Information). Moreover, they could be “seen” after the adsorption of 1-dodecylthiol molecules. After the DPN process, the silicon wafer was immersed in the ethanol solution of 1-dodecylthiol (v/v, 1/1000) for 3 min and rinsed by ethanol followed by being blown dry with high-purity nitrogen. Topographical and phase images (Figure S3 in Supporting Information) showed that the deposition site on the SWNT was covered by 1-dodecylthiol. The other sections on the same SWNT and the silica substrate were still clean. This indicates the effective site-specific deposition of gold on the SWNT.

3.2. E-DPN for Direct Deposition of Visible Gold Nanoparticles onto SWNTs on Silicon Wafer with Thin Top SiO₂ Layer. The main disadvantage of the electroless DPN approach is that the gold nanoparticles were too small before seeded growth. Though the seeded growth can enlarge the gold nanoparticles, however, the reproducibility of this process is highly dependent on the reaction condition. The Ostwald ripening of the gold nanoparticles during the growth is also a big problem. Furthermore, nonspecific deposition due to further nucleation in the seeded growth process would contaminate the surface (Figure S4 in Supporting Information).⁵⁵ Thus, the direct deposition of gold nanoparticles on SWNTs should be explored. It was found that gold nanoparticles could be deposited directly on SWNTs grown on silicon wafers with thin thermal oxide layers (~10 nm in thickness) by the E-DPN approach. After the AFM probe inked with HAuCl₄ was translated across the SWNT at a tip voltage bias of 9 V (Figure 2a), 14–17 nanoparticles with heights of 5–20 nm were generated on each side of the three deposited places on the SWNT (Figure 2b). The nanoparticles were selectively formed on the side wall of the SWNT other than the silica substrate. Compared with the DPN approach, this E-DPN method is more reproducible for site-specific deposition of gold nanoparticles on SWNTs.

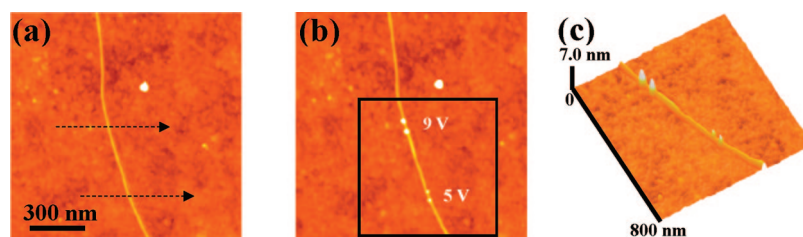


Figure 3. Topographical images of the carbon nanotube before (a) and after (b) the E-DPN process in which the AFM tip was translated across the nanotube along the two dashed lines under different tip voltage bias at the translation rate of 2 nm/s. RH was 46%. (c) The enlarged 3D image of the selected area in (b). The heights of the four deposited nanoparticles are 4.5, 4.4, 1.3, 2.2 nm, respectively.

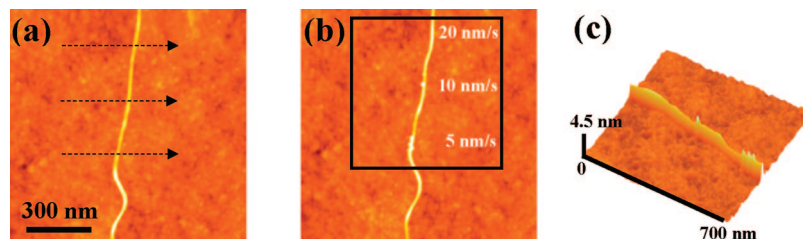


Figure 4. Topographical images of the carbon nanotube before (a) and after (b) the E-DPN process in which the AFM tip was translated across the nanotube along the three lines at different translation rates. RH was 46%, and tip voltage bias was 9 V. (c) The enlarged 3D image of the selected area in (b). The heights of the carbon nanotube and the deposited nanoparticles are 1.7 and 0.8 nm (20 nm/s), 0.6 and 1.6 nm (10 nm/s), 1.5, 1.8, and 1.7 nm (5 nm/s), respectively.

Sometimes, several nanoparticles often appeared at one writing site on the SWNTs. This may be caused by the more violent reaction taking place under the electrochemical condition.

However, this E-DPN approach works well only with carbon nanotubes grown on silicon wafers with thin oxide layers. If the oxide layers were thicker than 100 nm, because of the insulation, no deposition of gold nanoparticles on SWNTs was found. However, SWNTs grown on thick thermal oxide layers were much more useful in applications such as nanotube field-effect transistors and chemical sensors.^{56–58}

3.3. E-DPN for Direct Deposition of Visible Gold Nanoparticles onto Ultralong SWNTs on Thick SiO₂. Scheme 2 illustrates the E-DPN process for site-specific deposition of gold nanoparticles on an individual SWNT on a thick SiO₂ layer. The ultralong SWNTs, which were grown on silicon wafers with ~500-nm-thick thermal oxide layers, acted as both conducting wires and electrodeposition templates. As the nanotube was a one-dimensional wire on an insulating substrate, deposition of gold nanoparticles was confined only on the nanotube. The deposition position was also very flexible from nanometers to millimeters away from the gold electrode.

Compared with electroless deposition of metal nanoparticles on SWNTs, the electrochemical approach showed better control in particle size and density by varying the potential, deposition time, and metal salt concentration. It is also very convenient to monitor the deposition of gold nanoparticles in situ. When the translation rate of the AFM tip remained constant in the E-DPN process, the height of the deposited particles was found to generally increase with increasing deposition potential. Representative images are given in Figure 3. Voltage bias below 4 V was not high enough for E-DPN deposition of visible nanoparticles. Voltage bias above 5 V was able to deposit visible gold nanoparticles via E-DPN. Two small nanoparticles (1.3 and 2.2 nm, respectively) were formed on the tube side wall at tip voltage bias of 5 V. The size of the nanoparticles increased (4.5 and 4.4 nm, respectively) when the tip voltage bias was increased to 9 V. As the contact resistances in the circuit and the resistance of the ultralong SWNTs consumed much potential drop,^{38,45,59} the potential applied here was much higher than that in electrochemical deposition of gold nanoparticles in solution (typically <1.0 V).³⁷ While the deposition potential was kept constant at 9 V, the slower translation rate would result in more and bigger nanoparticle deposition (Figure 4).

The reproducibility of E-DPN is much better than that for DPN for deposition of gold nanoparticles on SWNTs. In particular, periodic gold dot array was deposited on SWNTs at the translation rate of 20 nm/s with tip voltage bias of 12 V (Figure S5 in Supporting Information).

Because of the high chemical inertness of both gold and pristine SWNTs, the interaction between gold and pristine SWNTs is presumably van der Waals in nature.²² Although we could not get spectroscopic data such as X-ray photoelectron spectra with such a small amount of gold deposited by DPN or E-DPN, these gold nanoparticles are supposed to be physically linked to SWNTs.

4. Conclusions

We developed two methods based on DPN and E-DPN to site-specifically deposit gold nanoparticles on SWNTs. Gold nanoparticles could be site-selectively deposited at any predetermined locations of the SWNTs. It is expected that the contact resistance between the in situ formed nanoparticles and SWNTs is much smaller than that between nanoparticles and SWNTs via AFM manipulation.¹⁵ The size of the gold nanoparticles

could be alternated from several to tens of nanometers by varying the experimental conditions. Moreover, E-DPN provides a way for modification of SWNTs “as grown” (i.e., in pristine condition, without any extra processing step in solution). This is very important to eliminate the property change of SWNTs due to the contamination in the solution treatment process.⁶⁰ Additionally, the methods could be extended to deposit other noble metal nanoparticles such as Ag, Pt, Pd, and Rh. These methods may have potential application in fabricating room-temperature single-electron transistors, site-defined heterostructures, and site-specific microelectrodes on SWNTs.

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Supporting Information Available: AFM images of carbon nanotubes before and after DPN deposition of gold nanoparticles at high RH followed by seeded growth, the 1-dodecylthiol modification showing the gold deposition after DPN, and the nanoparticle arrays on SWNT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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