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We have investigated a selective attachment of functionalized single-walled carbon nanotubes (SWNTs) on templates. Our efforts have been concentrated on both functionalization of carbon nanotubes and their binding onto templates such as Si-wafer and gold. The alignment of SWNTs was performed by modifying the SWNTs with carboxylic acid, carboxylic chloride and alkyl thiol groups. Functionalized SWNTs were selectively immobilized through the formation of amide bonds using a coupling reagent onto prepatterned nanostructures by a self-assembly method. The characterization of chemically attached carbon nanotubes has been investigated using various surface characterization tools like AFM, TEM, SEM, and FT-IR.

Keywords: AFM; carbon nanotube; chemical attachment; nanosphere

INTRODUCTION

A carbon nanotube has been widely investigated as an essential component for fabrication of nanoelectronic devices and its numerous

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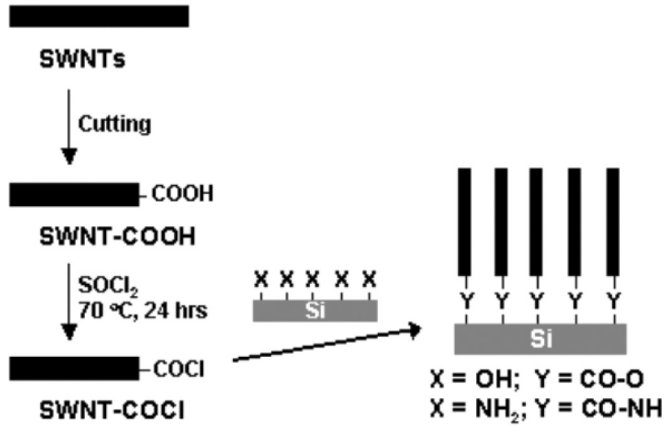
applications [1]. Especially, well-arrayed carbon nanotubes are highly desired to prepare chemical sensors [2], nanoprobes for scanning probe microscopy [3], field emitter devices [4], etc. Besides their capabilities as functional components, carbon nanotubes are good building blocks for organizing 3-D nanostructure which is another important factor in molecular electronics [5]. In this study, we have investigated a selective attachment of chemically-functionalized single-walled carbon nanotubes (SWNTs) on modified templates by a covalent bonding. If high selectivity of a specific chemical reaction can be controlled, we can design an effective 3-D nanostructure for nano-sized devices using SWNTs as a main frame of the structure. To induce a selective attachment of SWNTs, AFM anodization lithography was engaged in patterning the nanostructures on templates. As another approach to achieving this goal, chemically-modified nanosphere was also used to combine with SWNTs to form the effective nanostructure. Nanosphere lithography has been thought as a great tool to fabricate a periodic array of nanostructure. Therefore, it would be expected to realize the SWNTs nanostructures if the nanosphere is chemically attached to SWNTs.

EXPERIMENT

The purified single-walled carbon nanotubes were purchased from Carbon Nanotechnologies Inc. (HiPCO SWNTs), and were used without further purification processes. The $-NH_2$ modified polystyrene (PS) nanosphere with an average diameter of 190 nm and silicon nanosphere of 400 nm (purchased from Bangs Laboratories, Inc.) were also used as received. The carboxylic acid groups-terminated SWNTs (SWNT-COOH) were prepared by shortening and etching processes using ultrasonification in mixed acids according to the reported procedure [6]. To consider further chemical reaction with chemically modified surface, the carboxylic acid groups on SWNTs were converted into acid chloride groups by treatment with thionylchloride. The acid chloride-functionalized SWNTs (SWNT-COCl) were dispersed in dimethylformamide (DMF) by ultrasonic agitation and were immediately reacted with chemically functionalized surfaces [7]. The formation of functional groups on SWNTs was confirmed by FT-IR [8]. We prepared two kinds of Si surfaces: (i) the surface containing hydroxyl groups (–OH), simply prepared by piranha treatment [9] and (ii) the $-NH_2$ surface by a self-assembly method using 3-(aminopropyl) triethoxymethylsilane [10]. The modified SWNTs were reacted with the two surfaces in DMF suspension of SWNT-COCl for a given time in order to accomplish their chemical attachments (Scheme 1). After completing the attachment, the reacted substrates were rinsed with deionized



SCHEME 1 Schematic view of chemical attachments of SWNTs on modified template.

water under sonication and were dried under a stream of nitrogen. Non-contact mode atomic force microscopy (XE-100, PSIA Inc.) was exploited to characterize the surface morphologies modified with SWNTs.

RESULTS AND DISCUSSION

In the cutting operation of single-walled carbon nanotubes (SWNTs), the 3:1 concentrated H_2SO_4:HNO_3 mixture was used as the oxidizing acid. The shortened nanotubes, having diameters ranging from 700 nm to 1 μm and lengths from 40 nm to 80 nm, could be produced by ultrasonication in the oxidizing acid at 50°C for 6 hr. Figure 1 shows a typical atomic force microscope (AFM) image of the shortened SWNTs which is usually aggregated each other because of van der Waals interaction. SWNTs aggregates are shown including small carbon particles and catalysts as impurities. Cutting time of 6 hr was chosen in order to reduce the most of these impurities such that chemically-functionalized SWNTs could react easily with templates or nanospheres.

Based on chemical reactions of the modified SWNTs with functionalized surfaces, we tried selective attachments of SWNTs on patterned surfaces as shown in Figure 2(a). We chose self-assembled monolayer (SAM) of hexamethyldisilane (HMDS) as a resist whose surface was covered by methyl groups (–CH_3). Since there is no reaction between chemically modified SWNTs and CH_3 groups, SWNT-COCl will be reacted only with the patterned area containing –OH groups. In

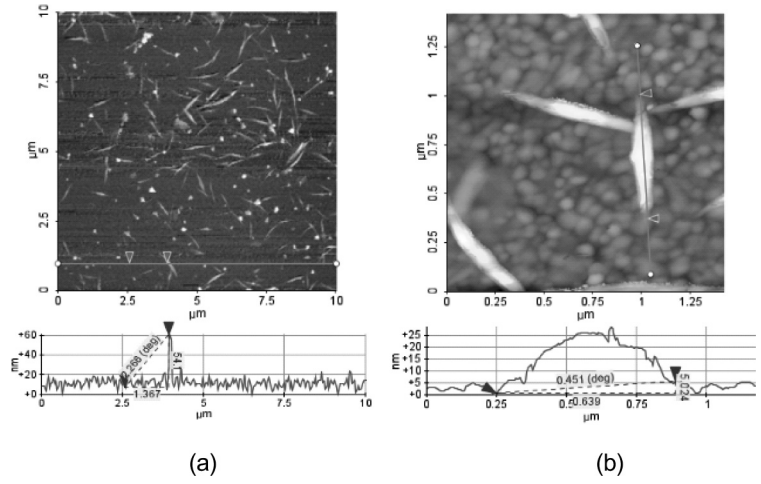


FIGURE 1 Typical AFM images of the shortened SWNTs: (a) in large area, and (b) in small area, and their profiles for: (a) diameter, and (b) length of representative SWNTs.

AFM anodization lithography, patterning was achieved by the growth of silicon oxide which contained –OH groups as shown in Figure 2(b, top). As a result, the patterned area is covered by –OH group while

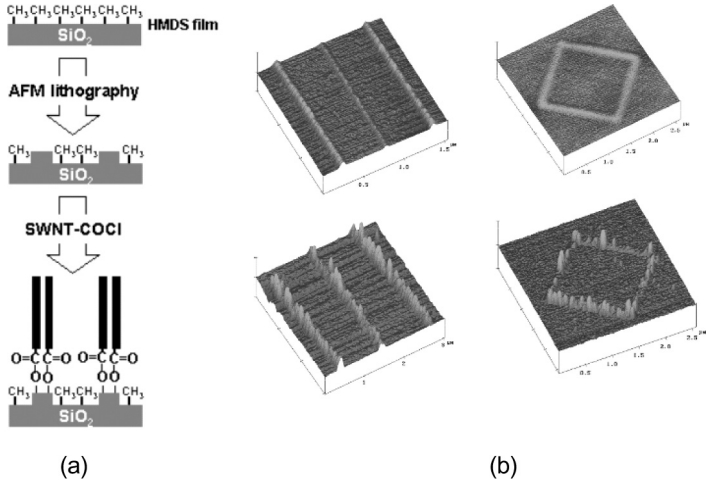


FIGURE 2 (a) Schematic for selective attachments of SWNTs on prepatterned surfaces, representative tapping mode AFM images of patterned HAMD SAM, (b, top) before, and (b, bottom) after reaction with SWNTs.

unpatterned area is covered by $-CH_3$ group. Figure 2(b, bottom) shows selectively attached SWNTs on the protruded SiO_2 region. The height of attached SWNTs on patterned surfaces ranges from 6 nm to 18 nm which are too low for these values to be regarded as those of SWNTs. In fact, the materials attached on line patterns are a kind of carbon which can be clearly confirmed by phase mode AFM. Moreover, in Figure 2(b, bottom), what it was selectively attached means that the chemical reaction occurred only on patterned area. Hence, it can be suggested that line patterns containing –OH groups react rapidly with very thin SWNTs-COCl separated from the aggregates as well as carbon particles also modified with –COCl since their mobility is better than bulkily-aggregated SWNTs in solution. The similar selective attachment of SWNTs was observed on the various types of patterns.

As another selective attachment of SWNTs, chemical binding of nanospheres-NH_2 with SWNTs-COCl was conducted to fabricate effective nanostructure. Figure 3 shows wonderful images of nanospheres selectively combined with a bunch of SWNTs. In the cutting process of SWNTs using the oxidizing acid, many defects are produced on the side wall of SWNTs, analogous to both ends of SWNTs. These defects also are terminated with $-COOH$ groups which can be active sites to react with substitutes. To date, it has been focused on improving physical, chemical, and electrical properties of SWNTs through chemical attachments of useful substances on the side defects of SWNTs from many research groups. The alignment of carbon nanotubes also has been critical issue to apply them to the area of molecular electronics, field emission display, etc. As shown in Figure 3, the PS nanospheres attached on the SWNTs would not seem to change much the properties of SWNTs and also to improve the alignment greatly. However, it is very important to selectively attach nanospheres onto SWNTs because these basic structures have quite a possibility to be used to make a practical application of SWNTs.

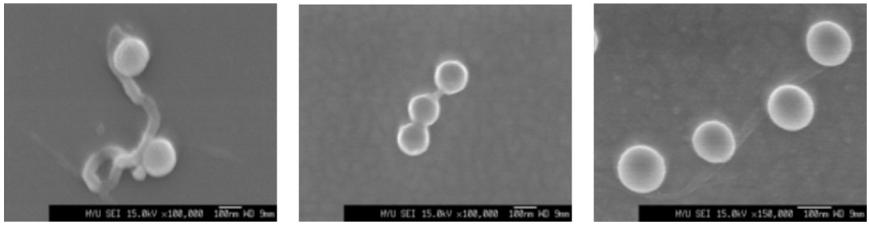
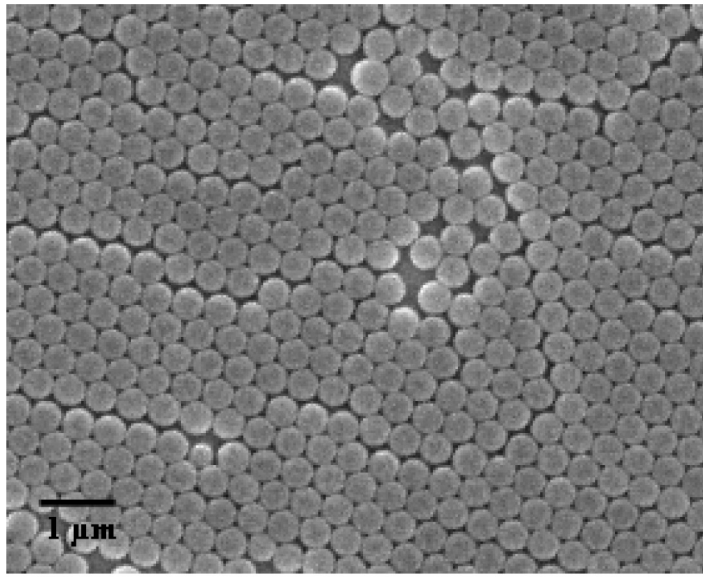
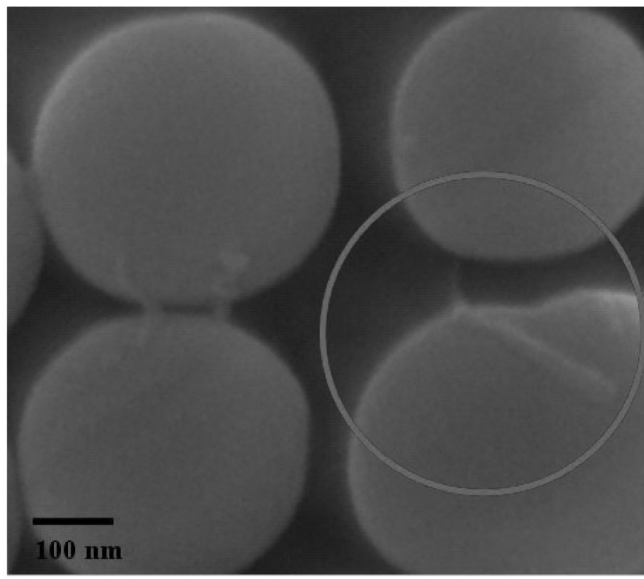


FIGURE 3 Scanning Electron Microscope (SEM) images of 190 nm of PS nanospheres chemically attached on the SWNTs.



(a)



(b)

FIGURE 4 SEM images of (a) the array of Si nanospheres on gold template, and (b) vertically-attached SWNT to gold template using the nanosphere as a supporter.

Figure 4 shows us an important example for SWNTs to be able to form the 3-D nanostructure in combination with nanospheres. 400 nm of Si nanospheres with no functional group were arrayed as a monolayer on gold substrate as shown in Figure 4(a). Then, SWNTs-COOH were chemically attached to $-NH_2$ modified gold substrate which was exposed only in the gap between Si nanospheres. In Figure 4(b), one end of the shortened SWNT is leaning against Si nanosphere due to an intrinsic flexibility of carbon nanotubes and the other end of that is being clearly attached to the gold substrate. This means that the SWNT is standing vertically such that the 3-D nanostructure is formed by using both nanospheres and SWNTs. These results demonstrate critically that the chemical attachments can be used easily to succeed in fabricating the nanostructures.

CONCLUSION

In conclusion, we have demonstrated selective attachments of chemically functionalized SWNTs on modified templates by using AFM and nanosphere lithography. This work will contribute to develop the fabrication of 3-D nanostructures on various substrates. Furthermore, it enables us to develop nanotube-based electronic devices.

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