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Communication

Patterned Assembly of Shortened Single-Walled Carbon Nanotubes on Gold Surface*

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Abstract Patterned arrays of shortened single-walled carbon nanotubes(s-SWNTs) on gold were prepared using a surface reaction method. Under the existence of a condensation reagent, dicyclohexyl carbodiimide (DCC), s-SWNTs terminated with carboxylic groups were found to react with the $NH_2(CH_2)_{11}SH$ self-assembled monolayers (SAMs) on gold readily, but could rarely be adsorbed on a CH_3-terminated surface. Thus by using a patterned surface with both NH_2 and CH_3 groups, s-SWNTs were immobilized only on NH_2 areas, resulting in a patterned array of s-SWNTs.

Keywords: Shortened single-walled carbon nanotubes (s-SWNTs), Surface reaction, Patterned assembly, Gold surface

With the accumulation of the knowledge on carbon nanotubes, these new members of the fullerene family, especially the single-walled carbon nanotubes (SWNTs), are being exploited more and more widely because of their potential as new materials. For most property investigations and real applications, it is highly desirable to organize the as-prepared tangled and bulky carbon nanotubes in a well-ordered fashion. Much work toward this direction has been done, either by an external force[1, 2], or by growing SWNTs on a pre-defined surface with catalysts[3]. The SWNTs in these cases were very long, mostly in the order of several micrometers, far longer than what can be used in nanosized devices.

Liu *et al*. opened the door for chemists to manipulate SWNTs by cutting the as-prepared long entangled SWNTs into short pipes, which produces –COOH groups at the open ends[4]. These shortened SWNTs(s-SWNTs) behave like small carboxylic molecules in many aspects[5-8]. One successful attempt was made by Chen *et al*[5]. By reacting with a long-chain amine, an alkyl chain is introduced into the s-SWNT "molecule", which will greatly increase the solubility of the s-SWNTs in polar solvents.

Recently work[9], we have succeeded in immobilizing s-SWNTs on gold using a surface reaction method. With the aid of DCC (dicyclohexyl carbodiimide), s-SWNTs were found to react with an NH_2-terminated SAM easily. By using this surface reaction method, we have prepared patterned s-SWNTs assembly on solid surface. When a patterned SAM of amino undecanethiol and dodecanethiol on gold is used, s-SWNTs are found to combine selectively with the NH_2-terminated areas, resulting in a patterned array of s-SWNTs.

1 Experimental

The s-SWNTs were prepared by an arc-discharge method, followed by an oxidative cutting using mixed acid[7-9]. As expected, they are terminated by carboxylic groups at both ends and well dispersible in water, ethanol, acetone and *N, N*-dime-thyl formamide

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(DMF)[8].

About 2mg s-SWNTs and 5 mg of dicyclo carbodiimide (DCC, A R, Shanghai Reagent Co.) were dissolved in 10mL DMF (A R, Beijing Reagent Co). The mixture was ultrasonicated for 10 min followed by nitrogen bubbling for 5 min to get rid of the dissolved oxygen before use. The amino undecanethiol (AUDT, Dojindo Laboratory, Japan) SAM was prepared by immersing a clean gold substrate (sputtered on Si(100), treated in piranha solution *i. e.* H_2SO_4: H_2O_2, $V/V=7:3$, at 90 ℃ for 10 min) into the AUDT ethanol solution(0.5 mmol·mol^{-1}) for 5 h then rinsed with ethanol thoroughly and dried in high-purity nitrogen stream. The resulting sample was immersed into the nanotube suspension and treated at 50 ℃ for ca 12 h. All the samples were rinsed thoroughly with ultrapure water and sonicated in ethanol for 5 ~ 10 s before characterization if not specifically noted. Patterned SAMs of AUDT and dodecanethiol (DDT, Aldrich, USA) were prepared using a microcontact printing (μCP) technique[10].

Raman characterizations were conducted on Renishaw System 1000 Raman imaging system (Renishaw plc, UK), equipped with a 632.8 nm, 25 mW He-Ne laser(Spectra Physics, USA) and a BH-2 microscope (Olympus, Japan). The incident light was less than 2 μm in diameter with a power of no more than 5 mW. Exposure times are 10 s × 3 in all cases. Optical micrographs were taken on a PM-10AK3 automatic exposure photographic system attached to the above BH-2 microscope.

Atomic Force Microscopy(AFM) was performed on Nanoscope IIIa (Digital Instruments, USA).

2 Results and Discussion

2.1 Reactive deposition of s-SWNTs on AUDT SAMs

Raman spectroscopy has been shown to be a powerful tool in characterizing SWNTs. The three commonly noticed absorption bands of SWNTs are located around 150 – 250 cm^{-1}, 1330 cm^{-1} and 1590 cm^{-1}, among which the 150 – 250 cm^{-1} band is the most important one for distinguishing SWNTs from other forms of carbon, such as multi-walled carbon nanotubes (MWNTs), graphite and amorphous carbon. This band originates from the radial breathing mode (RBM) of SWNTs. It is determined by[11]

$$\omega = \frac{223.75}{d} \quad (1)$$

where ω is the peak center of the RBM band in cm^{-1}, and d is the diameter of the SWNTs in nm.

Fig. 1(a) and (b) show the Raman spectra of the AUDT SAMs on gold before and after reacting with the s-SWNTs, respectively. We can see clearly the characteristic RBM band of SWNTs at about 172 cm^{-1} in Fig. 1(b), while Fig. 1(a) gives no characteristic absorption bands at all, indicating the existence of s-SWNTs on gold after surface reaction. The diameter of s-SWNTs calculated using formula (1) is 1.30 nm, in well accordance with previous measurements.

To find out whether or not the s-SWNTs are immobilized onto AUDT SAMs *via* chemical bonding, blank experiments were carried out at the same time. Fig. 1(c) is the Raman spectrum of a DDT

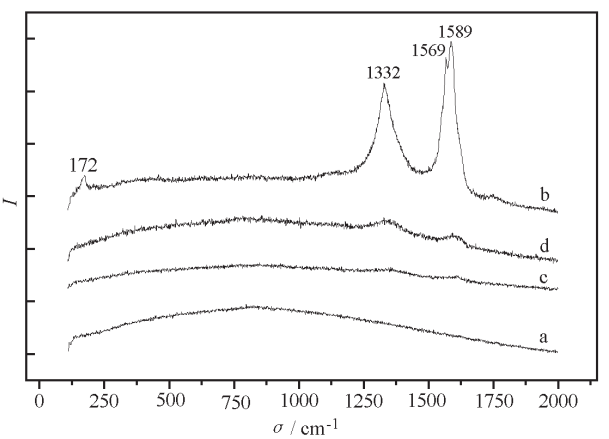

Fig. 1 Raman spectra of samples

a) AUDT SAMs on gold before reacting with s-SWNTs/DMF/DCC; b) AUDT SAMs on gold after reacting with s-SWNTs/DMF/DCC; c) DDT SAMs on gold immersed in s-SWNT/DMF/DCC; d) AUDT SAMs on gold immersed in s-SWNT/DMF suspension

SAMs after being immersed in s-SWNTs/DMF/DCC under the same condition as used by AUDT SAMs, and Fig. 1(d) is the Raman spectrum of a AUDT SAM immersed in s-SWNTs suspension at 50 ℃ for 12 h without DCC. Both of the samples were rinsed and sonicated in ethanol for 5 – 10 s after being pulled out from s-SWNTs suspension. Nothing can be seen in Fig. 1(c) and only very small peaks can be observed in Fig. 1(d), indicating that only a very small amount of s-SWNTs were adsorbed onto the surface when no DCC was added into the reaction system. So it is believed that the s-SWNTs are immobilized onto the surface by chemical reaction between COOH groups at the end of s-SWNTs and NH_2 groups of the AUDT SAMs.

2.2 s-SWNTs assembled on AUDT/DDT patterned SAMs

Microcontact printing(μ-CP) technique[12] has been widely used in preparing patterned surface structures. A patterned SAM of AUDT and DDT was prepared using this method. The resulting surface was imaged by AFM in friction force mode with a Si_3N_4 tip, as shown in Fig. 2(a), where the bright circles correspond to NH_2 groups covered regions. The distance between two bright circles is about 1.8 μm. No image contrast could be observed when imaging in height mode or using an optical microscope.

Fig. 2(b) shows an AFM height mode image of the patterned SAM on gold, after reacting with the s-SWNTs suspension containing DCC in DMF at 50 ℃ for 10 h. Similar images can be obtained with scanning electron microscope (SEM) and friction force mode AFM (data not shown). Bright cirlces, which cannot be observed in height mode AFM image before reaction, were of the same diameter as those in Fig. 2(a), strongly indicating that s-SWNTs were immobilized selectively onto the NH_2-covered areas during reaction. We also observed the large-scale array of s-SWNTs using an optical microscope with good contrast, as shown in Fig. 2(c), where the dark dots are s-SWNTs. Fig. 3(a) and (b) are the Raman spectra taken at the dark points and the bright areas, respectively. The sample was sonicated for 5 – 10 s to remove physically adsorbed species. In well agreement with our previous results on individual SAMs, no or only small peaks can be observed in the bright areas of Fig. 2(c), while the dark dots give out rather strong characteristic peaks of s-SWNTs. Thus

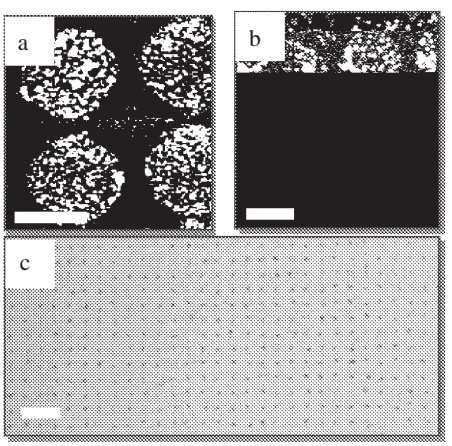

Fig. 2 AFM **image of sample**

a) AUDT/DDT patterned SAM with friction force mode. White circles stand for NH_2 areas; b) AFM image of the s-SWNTs pattern with height mode; c) An optical image of patterned s-SWNTs array. The scale bars in a, b, c are 1 μm, 1 μm and 4 μm, respectively

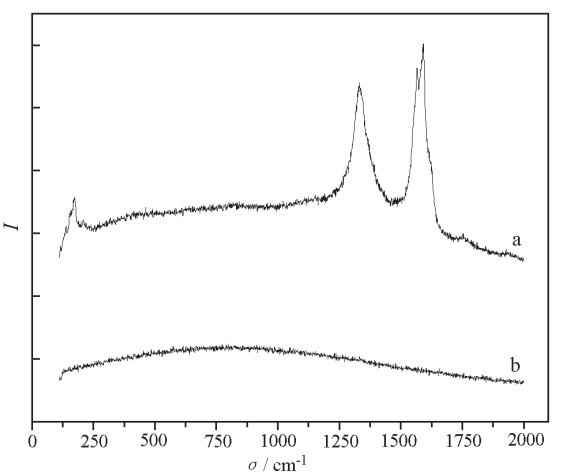

Fig. 3 **Typical Raman spectra of sample**

a) the dark dots in Fig. 2(c);

b) the blank areas in Fig. 2(c)

s-SWNTs have been immobilized only on the NH_2 areas, forming a regular array of s-SWNTs on gold.

In summary, we have successfully prepared a patterned array of SWNTs on gold by using a surface reaction method. As compared with the method developed by others[1-3], our approach has more freedom of controllability. By selecting a suitable coupling SAM and by designing the nanotube ends, we can expect to make patterned SWNTs on various surfaces.

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单壁碳纳米管在金表面的图形化组装

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摘要 利用湿法化学组装技术在金表面得到了图形化的单壁碳纳米管阵列. 在混酸氧化条件下, 初合成的交缠状态的单壁纳米管被截短成带有羧基等功能化末端的短管. 这些功能化的短管在缩合剂 DCC 的作用下与氨基/甲基图形化表面进行缩合反应时, 纳米管将选择性地结合到氨基区域从而形成规则的纳米管阵列.

关键词: 单壁碳纳米管, 表面反应, 图形化组装, 金表面

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