

Electric-Field-Enhanced Assembly of Single-Walled Carbon Nanotubes on a Solid Surface

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We report a novel electric-field-enhanced chemical assembly approach for fabricating highly aligned SWNT arrays on a solid surface with remarkably improved efficiency and packing density, which is very important for the real applications of carbon nanotube arrays. With the enhancement of the electric field, the assembling kinetics of SWNTs is remarkably speeded up to effectively decrease the assembling time, and the packing density can even exceed the saturated density of conventional assembly method by four times within only half an hour. The molecular dynamics simulation results illustrated the alignment of SWNTs with their long axes along the electric flux in solution, leading to the increase of packing density and efficiency through overcoming the steric hindrance of the “giant” carbon nanotubes.

Introduction

Highly oriented single-walled carbon nanotube (SWNT) arrays are crucial for improving the performance of nanotube-based devices, such as nanoprobe for scanning probe microscopy,¹ nanosensors,² field emitters,³ and nanoelectronic devices.⁴ Recently, many works have focused on the fabrication of vertically aligned SWNTs on a solid surface,^{5–10} as well as the applications of such nanotube assemblies.^{11,12} In our previous work, a wet chemical assembly technique was developed for organizing randomly tangled SWNTs into well-ordered arrays on a solid surface.^{5–7} Thus-prepared SWNT assemblies have been used as nanoelectrode arrays to fabricate aligned metal nanowires.¹¹ However, low surface coverage and long assembling time remain important issues. Efforts have been made to improve the coverage density using a metal-assisted self-assembly method,^{9,10} but the results are still not satisfactory because of the remarkable steric hindrance effect arising from the “giant” carbon nanotubes. Recently, the aligning effect of SWNTs at electrode edges has been observed under an electric field.^{14,15} This suggests a possibility of improving the efficiency of chemical assembly by combining the electric field in the assembling process. Herein, we report this electric-field-enhanced chemical assembly approach for fabricating highly aligned SWNT arrays on solid surfaces with remarkably improved efficiency and packing density.

Experimental Section

SWNTs were produced by the chemical vapor deposition (CVD) method. The chemical shortening and post-treatment of original SWNTs followed the procedure described in our previous publications.^{5,7} The short SWNTs were dispersed in ethanol under ultrasonication. The amino-terminated self-assembled monolayers (SAMs) on sputtered Au substrates were

prepared by immersing the substrates into an ethanol solution of $\text{NH}_2(\text{CH}_2)_{11}\text{SH}$ for 24 h. The SWNT assemblies were further made on the SAM-modified Au substrates by immersing the substrates into an ethanol solution of SWNTs without or with an electric field. The dc potential was applied by a regulated DC power supply (model PAB32-2A, Kikusui, Japan).

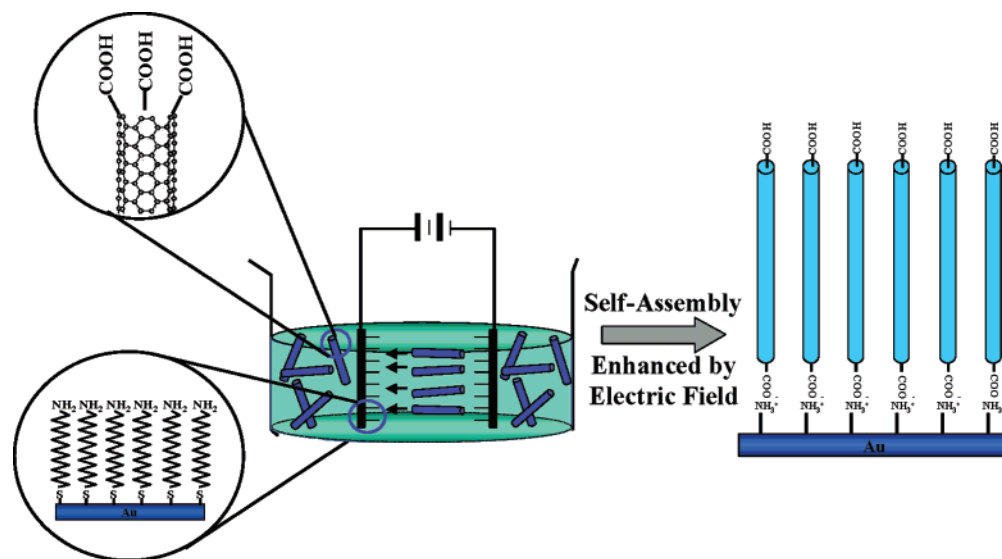
All the AFM characterizations were performed on a Nano-scope IIIa microscope (Digital Instruments, USA) in tapping mode. Raman spectroscopy was conducted on the Renishaw System 1000 Raman imaging system. All cyclic voltammetric experiments were carried out with a CHI 660A electrochemical workstation (USA) in a conventional three-electrode cell at room temperature. A saturated calomel electrode (SCE) and a Pt wire were employed as reference and counter electrodes, respectively.

Results and Discussion

Scheme 1 illustrated the strategy of the electric-field-enhanced chemical assembly technique of SWNTs. The open ends of the SWNTs were modified with carboxyl groups formed in the process of oxidative shortening by mixed acid. The SAMs terminated by amino groups were prepared by immersing the gold-coated silicon substrate into $\text{NH}_2(\text{CH}_2)_{11}\text{SH}$ solution for 24 h. The assembly of SWNTs was obtained through the electrostatic interactions between the positively charged amino groups on the gold-coated substrate and the negatively charged carboxyl groups at the ends of carbon nanotubes. A dc electric field was applied to the two amino-terminated gold substrates, which was expected to induce the alignment of SWNTs along the electric field in the assembling solution.

Typical tapping mode (TM)-AFM images of the SWNT assemblies formed without and with the aid of an electric field are shown in Figure 1, parts a and b, respectively. The assembling time of SWNTs in ethanol solution was 0.5 h for both cases. The enhancement effect of an electric field is remarkable. As seen in Figure 1a, very few needlelike carbon nanotubes exist on the substrate surface when no electric field

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SCHEME 1: Schematic Illustration of the Electric-Field-Enhanced Chemical Assembly of Single-Walled Carbon Nanotubes on a Gold Surface^a

^a The distance between two gold electrodes was 100 μm ; the applied voltage was 10 V, that is, the applied electric field was 1×10^5 V/m.

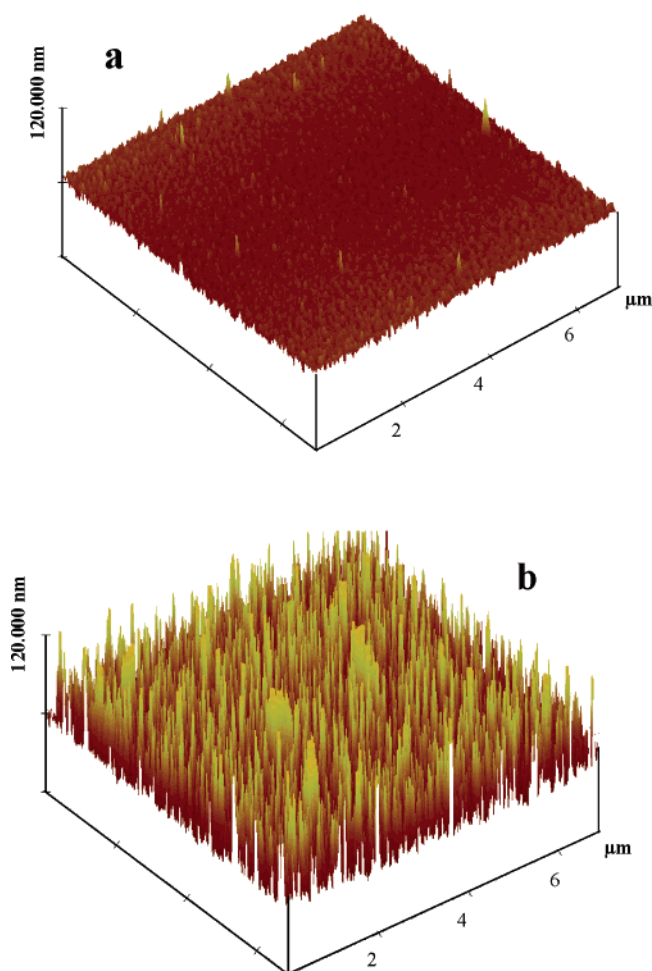


Figure 1. Typical TM-AFM images of SWNTs self-assembled on Au surfaces from the ethanol solution of SWNTs for 0.5 h without (a) and with (b) application of a 1×10^5 V/m electric field.

was applied, consistent with the extremely sluggish assembling kinetics of the “giant” carbon nanotubes.⁷ However, when 10 V of dc electric voltage was applied across two amino-terminated gold substrates with a gap of 100 μm , which is equivalent to an electric field of 1×10^5 V/m, SWNTs were

found to be densely assembled onto the anode surface with vertical orientation within the same assembling time. Because the carboxylic carbon nanotubes were negatively charged with a Z-potential in ethanol of -12 mV, the self-assembling effect was preferentially observed on the anode surface. Therefore all the characterizations were conducted with the anode substrate if not specifically notified. The apparent lengths of SWNTs seen in Figure 1b range from 30 to 80 nm, and mostly around 50 nm. The real tube lengths would be longer because of the difficulty in imaging narrow and deep features using the commercial Si AFM tips. The above observation clearly demonstrates that the electric field can greatly enhance the chemical assembly of SWNTs on a solid surface. It is noted that some longer nanotubes were also observed to be flatly aligned on the surface. However, the number of such kinds of nanotubes was greatly decreased as compared to the previous work performed without an electric field,^{5,7} which could be attributed to the electric field-induced alignment of SWNTs before being assembled on the substrate surface. The assembling kinetics of SWNTs was remarkably speeded up under the electric field (see Figure S1 in Supporting Information). The enhancement effect of an electric field may be attributed to two different reasons. First, the drifting velocity of the negatively charged SWNTs in ethanol solution would be increased under the electric field, leading to the fast gathering of nanotubes onto the anode surface. In contrast, the SWNTs can only reach the substrate surface via free diffusion without an electric field, and the “giant” nanotubes would obviously result in a sluggish diffusion rate. Second, alignment of SWNTs in solution along the electric flux is expected,¹⁴ which makes it easier to overcome the steric hindrance of the “giant” carbon nanotubes on the surface assembling process. The alignment of SWNTs and the increase of their drifting velocity under an electric field lead to the fast and dense assembly of nanotubes on solid surfaces. The following over-saturation assembly experiment provided further evidence of the above explanation. The saturated density of SWNTs can be obtained after 4h assembly without an electric field at the present experimental conditions (refer to Figure S1 in Supporting Information). Figure 2a shows the saturated packing density of SWNTs assembled without an electric field for 48 h, which was yet very low as a result of the severe steric

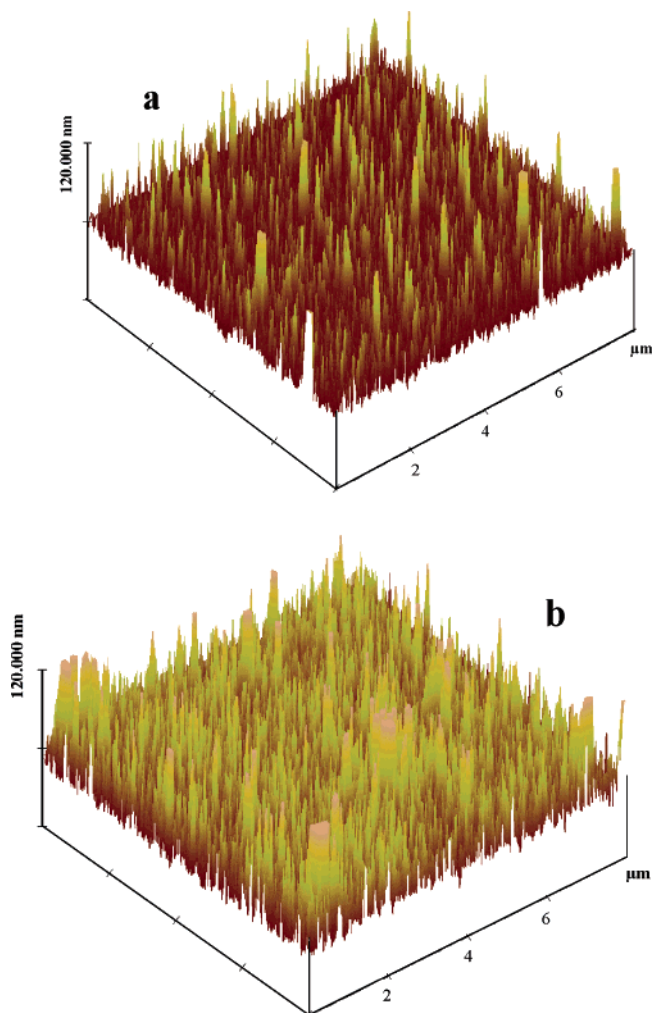


Figure 2. TM-AFM images of (a) a saturated SWNT assembly obtained from ethanol solution for 48 h without electric field, and (b) an over-saturated SWNT assembly obtained after an additional 0.5 h.

hindrance. However, when an electric field was applied, further assembling occurred on the saturated assembly, and the packing density was found to be greatly increased from circa $40/\mu\text{m}^2$ to about $150/\mu\text{m}^2$ within only half an hour, as seen in Figure 2b. This can be easily understood if alignment of carbon nanotubes in ethanol occurred under an electric field. The aligned nanotubes were filling up the empty space between the pre-assembled SWNTs, leading to the increase of packing density.

Polarized Raman spectroscopy has been shown to be a powerful tool in characterizing the orientation of SWNTs on solid surfaces.^{9,11} Figure 3 shows the polarized Raman spectra of the SWNT assembly made by the electric-field-enhanced assembly technique. The polarization of the incident light was perpendicular (Figure 3a) and parallel (Figure 3b) to the surface normal, respectively. The characteristic bands of SWNTs centered around 217 and 1590 cm^{-1} , which can be assigned to the radial breathing mode (RBM) peak and the G band of the SWNTs, are clearly visible in the spectra. The diameter of SWNTs is estimated to be approximately 1.03 nm from the RBM peak.¹⁶ Previous work has shown that the polarized Raman spectrum shows the maximum intensity of the G band when the nanotubes are aligned parallel to the polarization of the incident laser light.¹⁷ As seen from Figure 3, the Raman intensity obtained with light polarization parallel to the surface normal is remarkably larger than that obtained with light polarization perpendicular to the surface normal. This strongly suggests that

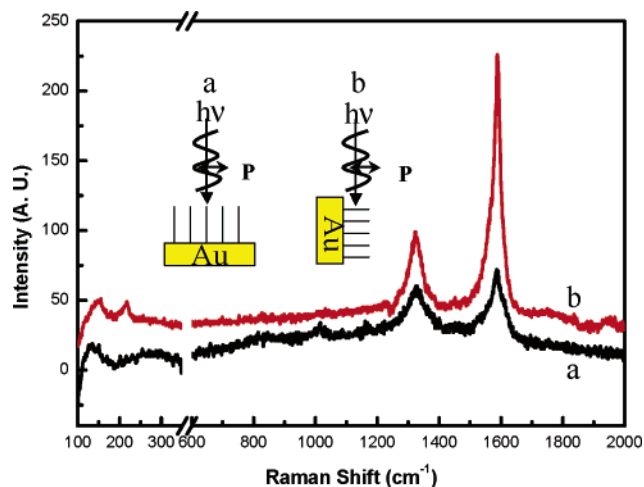


Figure 3. Polarized Raman spectra of the SWNTs assembled on Au surfaces using an electric-field-enhanced assembly method. The polarization of the incident light is (a) perpendicular, and (b) parallel to the surface normal.

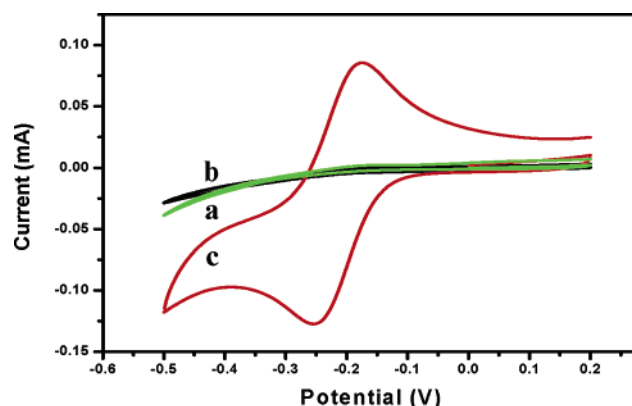


Figure 4. Cyclic voltammograms of Au electrodes covered by (a) NH_2 -SAM, (b) and (c) NH_2 -SAM/SWNTs self-assembled without and with the electric field, in 1 M KCl aqueous solution containing 5 mM $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$. Scan rate is 100 mV/s.

the SWNTs in the chemical assembly are oriented normal to the substrate surface, as expected.

The cyclic voltammetric studies provided additional evidence of the enhanced assembling effect of SWNTs under an electric field. Figure 4 shows the cyclic voltammograms (CVs) of a NH_2 -SAM-modified Au electrode (a), and the SWNTs assembly modified Au electrodes prepared without (b) and with (c) the electric field, in an aqueous solution containing $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$. No redox peaks were observed at the NH_2 -SAM electrode (Figure 4a) because of the blocking effect of the positively charged $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions and the underlying Au electrode.^{11,18} A similar result was obtained with the SWNTs assembly electrode prepared without an electric field (Figure 4b), suggesting that few SWNTs were assembled onto the electrode and the NH_2 -SAM kept almost intact.¹¹ A dramatic change was observed in Figure 4c, which exhibited the large characteristic redox peaks of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions. This indicates that a great number of SWNTs have been assembled onto the electrode surface with the aid of an electric field, working as the ensemble of nanoelectrodes. The negatively charged carboxylic SWNTs facilitate the access of positively charged $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions to the electrode, allowing the occurrence of electron transfer.^{11,18}

The molecular dynamics simulation was performed to understand the aligning phenomenon of SWNTs in ethanol under

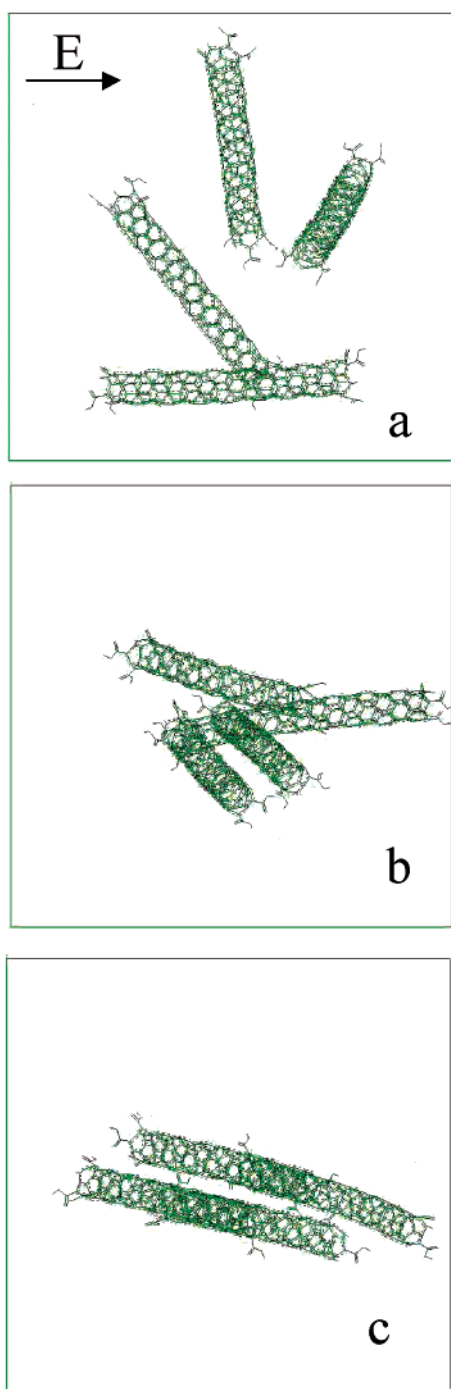


Figure 5. Molecular dynamics simulation of the electric-field-induced alignment of SWNTs in ethanol solution. (a), (b), and (c) exhibit the initial random state, intermediate state, and aligned state, respectively, after application of an electric field.

an electric field. The simulations were carried out at fixed temperature (300 K) and pressure (1 atm) (the so-called NPT ensemble) using the Langevin piston method.¹⁹ The systems were solvated in a box (79.17, 65.75, 102.51) of ethanol molecules (previously equilibrated under normal pressure at 300 K with the NAMD program,²⁰ using the CHARMM22 force field²¹) with periodic boundary conditions, involving 4467 ethanol molecules. The carbon nanotubes were assumed to be 50 nm long, with a 1.1 nm diameter, and well dispersed in ethanol into individual tubes with 3 negative charges. The simulation result is given in Figure 5. At the beginning, the carbon nanotubes were randomly oriented (Figure 5a). Directed by the electric field, the nanotubes were partially oriented in

the intermediate state (Figure 5b) and highly aligned along the electric flux at the end (Figure 5c). This indicates that the alignment of carbon nanotubes has been completed in ethanol solution before they arrived at the substrate surface. As a result, the steric hindrance of SWNTs on the assembling process would be greatly overcome. According to Henry's theory,²² the drifting velocity of nanotubes aligned parallel to the electric field is higher than the perpendicular ones by a factor of 2, which implies that the assembling time would be shortened with aligned SWNTs. All these predictions are consistent with the experimental observations.

In summary, our results demonstrate that the application of an electric field could greatly enhance the chemical assembly of SWNTs on a solid surface. Under an electric field, the SWNTs are aligned with their long axes along the electric flux and drift toward the anode substrate with higher velocity, leading to the increase of packing density through overcoming the steric hindrance of the "giant" carbon nanotubes and the effective decrease of assembling time. This simple approach may also be extended to other nanotubes and nanowires, which will be our future target.

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Supporting Information Available: The assembling kinetics of SWNTs on a gold surface without and with an electric field of 1×10^5 V/m was illustrated in Figure S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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