

# Facile “Scratching” Method with Common Metal Objects To Generate Large-Scale Catalyst Patterns Used for Growth of Single-Walled Carbon Nanotubes

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**ABSTRACT** A facile “scratching” method to pattern a catalyst with commonly used metal objects, such as blade, pen cover, tweezers, watchband, knife, key, clamp, and coin, was developed. The single-walled carbon nanotube (SWCNT) networks and well-aligned SWCNT arrays successfully grew by chemical vapor deposition on the scratched catalyst patterns on Si/SiO<sub>x</sub> and quartz, respectively. This method provides an extremely simple and nearly zero-cost way to fabricate large-scale catalyst patterns used for controlled growth of SWCNT arrays, which could have potential applications in the fabrication of CNT-based devices.

**KEYWORDS:** catalyst • single-walled carbon nanotubes • arrays • chemical vapor deposition • scratching

On the basis of their unique structure and mechanical and electrical properties, single-walled carbon nanotubes (SWCNTs) have attracted intensive attention because of their potential applications, such as in electronics, sensors, drug delivery systems, etc. (1–6). To fulfill the unique properties of SWCNTs in large-scale devices, pre patterning of a catalyst in a controlled fashion used for subsequent growth of SWCNTs is of great importance. Many techniques, such as microcontact printing ( $\mu$ CP) (7–10), photolithography (11), e-beam lithography (12) and dip-pen nanolithography (DPN) (13–37), can be used to pattern the catalyst. However, all of them have their own limitations. For example, although  $\mu$ CP is a low-cost and high-throughput technique, the fabrication of a new pattern requires the redesign of the master. This is quite expensive. The process of photolithography is quite complicated. Also, the photoresists are harmful to the environment. E-beam lithography is operated under strict conditions, such as in a high-voltage and -vacuum environment, which restricts its use. DPN is an efficient technique to prepare catalyst patterns in a controllable manner (15); however, achieving a high throughput of catalyst patterns in a short time is still a challenging task even with the latest developed multipen DPN (17, 18) and polymer pen lithography (38).

Recently, we developed a facile, nearly no-cost, and environmentally friendly “needle-scratching” method (NSM) to generate catalyst patterns on solid substrates, which are successfully used for the controlled growth of well-aligned SWCNTs on quartz with high density (up to 10 tubes/ $\mu$ m) and ultralong length (up to 0.5 mm) (39). Although Cheng et al. (40) and Huang et al. (41) have reported that SWCNTs can grow on the scratched catalyst patterns on Si/SiO<sub>2</sub> by using a diamond blade or the sharp edge of a Si/SiO<sub>2</sub> wafer, i.e., nonmetal objects, the density of the grown SWCNTs is quite low. Moreover, Liu et al. (42) used carbon steel and tungsten carbide blades to scratch the quartz to generate catalyst patterns for growth of aligned SWCNTs, but the quality of SWCNTs is lower than that obtained by us (39). In this letter, our study reveals that the “scratching” tool used in NSM (39), i.e., the common syringe needle, can be replaced by a number of inexpensive and common metal objects, such as blade, pen cover, tweezers, watchband, knife, key, clamp, and coin. This finding provides a universal, one-step, fast, nearly zero-cost, no special equipment required, and environmentally friendly method to pattern the catalyst on Si/SiO<sub>x</sub> and quartz substrates for the controlled growth of SWCNTs, which would benefit the fabrication of CNT-based devices for future researches and applications.

After a Si/SiO<sub>x</sub> substrate was scratched by the aforementioned metal objects [their elements were characterized by energy-dispersive spectrometry (EDS); see Figure S1 in the Supporting Information], it was subsequently used to grow CNTs by chemical vapor deposition (CVD). Figure 1 shows the typical scanning electron microscopy (SEM) images of CNTs grown on the scratched Si/SiO<sub>x</sub> wafer. The CNT networks are observed on the catalyst patterns generated

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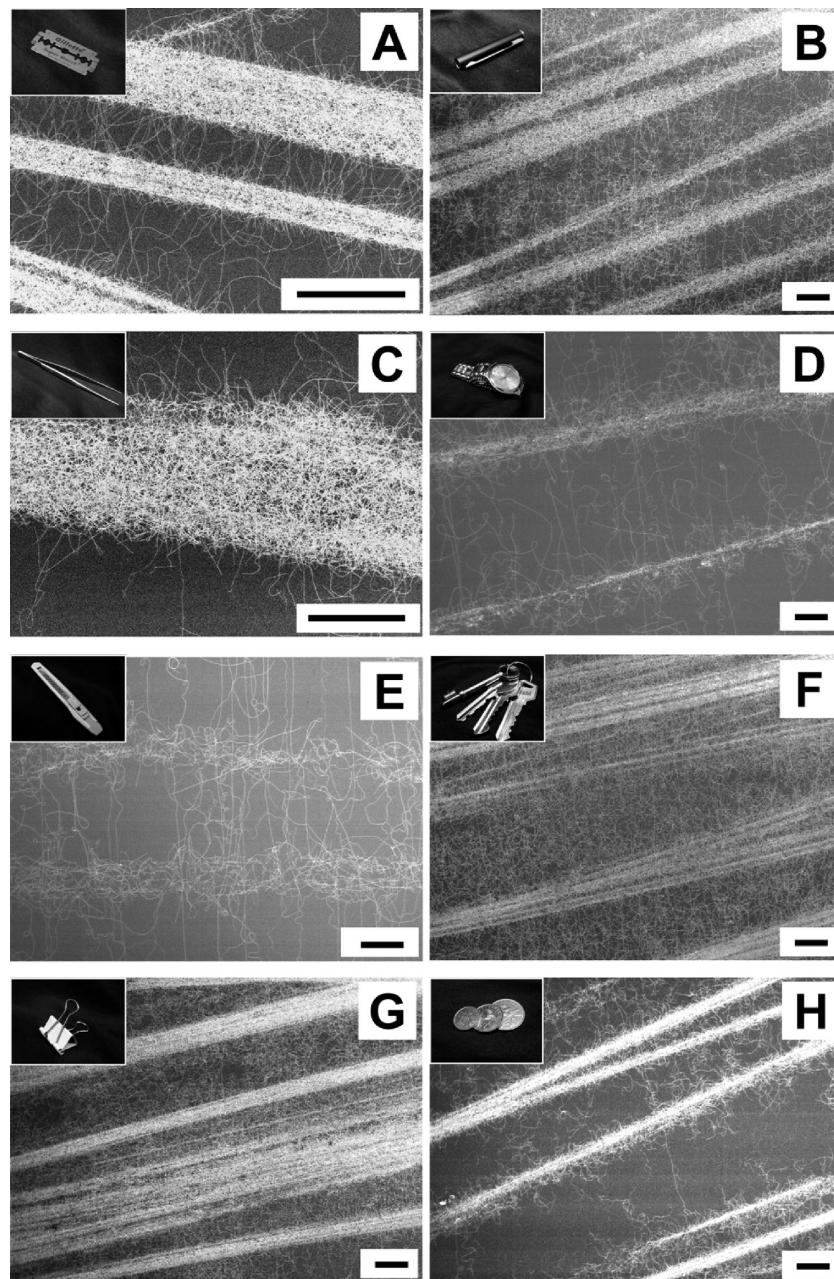


FIGURE 1. SEM images of SWCNTs grown on catalyst patterns on Si/SiO<sub>x</sub> scratched by (A) blade, (B) pen cover, (C) tweezers, (D) watchband, (E) knife, (F) key, (G) clamp, and (H) coin, respectively. Scale bar = 25 μm. Insets: pictures of the respective “scratching” tools used in the experiments.

by scratching of the Si/SiO<sub>x</sub> surface with a blade (Figure 1A), pen cover (Figure 1B), tweezers (Figure 1C), watchband (Figure 1D), knife (Figure 1E), key (Figure 1F), clamp (Figure 1G), and coin (Figure 1H), respectively. The as-grown CNTs were characterized by Raman spectra (Figure 2), where the distinct radial breath mode (RBM) peaks are observed in all CNT samples in Figure 1, which indicates that the as-grown CNTs are SWCNTs with diameters of 1.2–1.6 nm calculated by using  $\omega_{\text{RBM}} (\text{cm}^{-1}) = 248/d (\text{nm})$  (43). The relatively low D band reveals that high-quality SWCNTs were obtained (44). These results show that the metal-object-based “scratching” method is efficient to generate catalyst patterns, which can be used for the growth of high-quality SWCNTs.

Because of requirements in high-performance CNT-based devices, SWCNTs in an aligned geometry are more attractive because they, especially in horizontal alignment, can avoid the overlapping of tubes and the resistance caused by tube junctions and preserve the unique physical and chemical properties of individual tubes (1, 45). Recently, some efforts have been made to prepare aligned SWCNT arrays, such as work with the assistance of an external electric field (46, 47), special substrates (11, 42, 48, 49) and gas flow (50–52). The substrate-lattice-induced growth of aligned SWCNT arrays has been demonstrated to be a highly efficient way. For example, Rogers et al. reported the generation of perfectly aligned

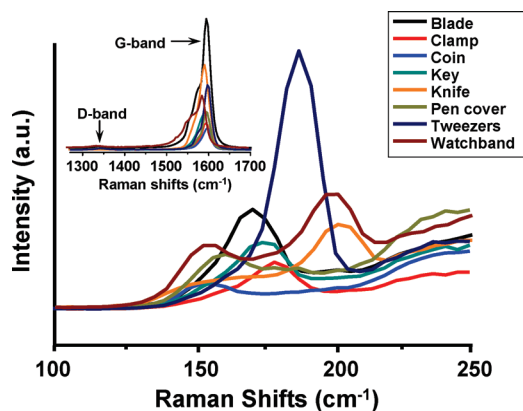


FIGURE 2. Raman spectra, in the RBM region, of SWCNTs in Figure 1. Inset: Raman spectra show D and G bands of SWCNTs in Figure 1. A 532 nm laser was used.

and highly dense SWCNT arrays on quartz, which were useful for high-performance transistors (11).

In order to grow large-scale aligned SWCNT arrays, similar experiments were performed on the stable-temperature-cut single-crystal quartz substrates, in which the common metal objects mentioned above were used to scratch the substrates (Scheme S1 in the Supporting Information). With the same CVD process as that used for the scratched Si/SiO<sub>x</sub> substrates mentioned above, the SWCNT arrays successfully grew on the scratched samples (Figure 3). Those SWCNTs grown in the patterned catalyst areas exhibit random network geometry, which is due to the adverse effects of unreacted catalyst particles and the disturbed interaction among tubes (11, 50). While outside the patterned catalyst areas, the well-aligned SWCNT arrays were formed along the [100] crystallographic direction of the quartz substrate (39). Note that the nonuniform space between two patterned lines arises from the handmade scratching process. This could be effectively improved by the mounting of these metal objects on a micromanipulator used in our recently developed NSM (39), where the movement of metal objects can be controlled accurately. Also, it should be noted that there are a few CNTs grown with an angle to the [100] crystallographic direction, as shown in Figure 3A,C. It is possible that these nanotubes were lifted up above the substrate during the initial growth stage, resulting in weak interactions between these nanotubes and the quartz surface. Hence, the gas flow, rather than the crystallographic direction of the quartz, dominates the growth direction of these CNTs. A similar phenomenon was also observed in the SWCNTs grown on the scratched Si/SiO<sub>x</sub> substrates (Figure 1D,E).

In order to study the mechanism of SWCNTs grown on the “scratched” patterns, atomic force microscopy (AFM) was used to characterize the scratched areas. Figure 4A shows that many nanoparticles (NPs) exist in the scratched area on quartz where CNTs grew. The measured NP size is  $4.8 \pm 2.9$  nm (Figure 4B). In our previous report (39), we have studied the mechanism of growth of SWCNTs on the NSM-generated patterns on Si/SiO<sub>x</sub> and quartz. It has been demonstrated that, after the solid substrates were scratched with “needles”, the catalyst NPs were generated and used

for growth of SWCNTs. Nonmetal objects, such as a diamond scribe and the sharp edge of a Si/SiO<sub>x</sub> wafer, were also chosen as “scratching” tools, but the density of the as-grown SWCNTs is low and the reproducibility is poor (39). Therefore, we concluded that SiO<sub>2</sub> NPs generated by NSM are used as catalysts for CNT growth. The trace amount of metal NPs may have also acted as a catalyst for CNT growth, but they only played a subordinate role in our experiments (39). We believe that this mechanism can also be applied to the experiments shown here. On the basis of previous reports (53, 54), the size and uniformity of catalyst particles highly affect the diameter and density of CNTs. Our results show that the small NPs,  $4.8 \pm 2.9$  nm, generated by our “scratching” method are very suitable for catalyzing the growth of high-quality SWCNTs.

The advantages of our “scratching” method are obvious. First, all of the metal objects used for patterning of the catalyst are quite common and easily accessible in our daily life. Second, the catalyst patterns can be prepared in one step by directly scratching the solid substrates, without the need of any complex procedure or sophisticated equipment. Third, besides the metal objects mentioned here, in principle, any metal objects could also be applied to our “scratching” method. We believe that our “scratching” method is applicable to the fabrication of large-scale devices with aligned SWCNTs or random SWCNT networks as electronic elements.

In summary, we developed a convenient, nearly zero-cost, and one-step “scratching” method for the patterning of large-scale catalysts on solid substrates with common metal objects. The scratched catalyst patterns are successfully used for growth of SWCNTs. In principle, any metal object could be used to scratch any solid substrate based on our method to generate catalyst patterns, which can be used for the growth of CNTs. We believe that the capability of patterning of the catalyst in such a straightforward way will open up an avenue for the fast fabrication of large-scale aligned SWCNT arrays used for electronic devices.

## METHODS

**Substrate Preparation.** The Si/SiO<sub>x</sub> (with a 300 nm SiO<sub>x</sub> layer) and quartz substrates were ultrasonicated in a mixture of acetone, water, and ethanol (1:1:1, v/v/v) for 10 min and rinsed with Milli-Q water. Then the substrates were immersed in a piranha solution [H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> = 7:3 (v/v)] at 100 °C for 30 min, subsequently rinsed with Milli-Q water, and dried with a nitrogen flow. Thus, cleaned substrates were immediately used for catalyst patterning and then growth of CNTs by CVD.

**Catalyst Patterning and Growth of SWCNTs by CVD.** Scheme S1 in the Supporting Information illustrates the experimental procedures. A catalyst stripe was created on a solid substrate by simply scratching with a metal object, such as the blade, pen cover, tweezers, watchband, knife, key, clamp, and coin used in our experiment. Similar to the CVD process reported in our recently developed NSM (39), the scratched substrates were placed in the center of a 20-mm-diameter quartz tube furnace and heated in air at 850 °C for 10 min. Then, the furnace temperature was increased to 900 °C in an argon atmosphere. After 2 min, hydrogen gas (H<sub>2</sub>) was introduced, and the flow rate ratio of H<sub>2</sub>:Ar at 2:1 (100 sccm of H<sub>2</sub>/



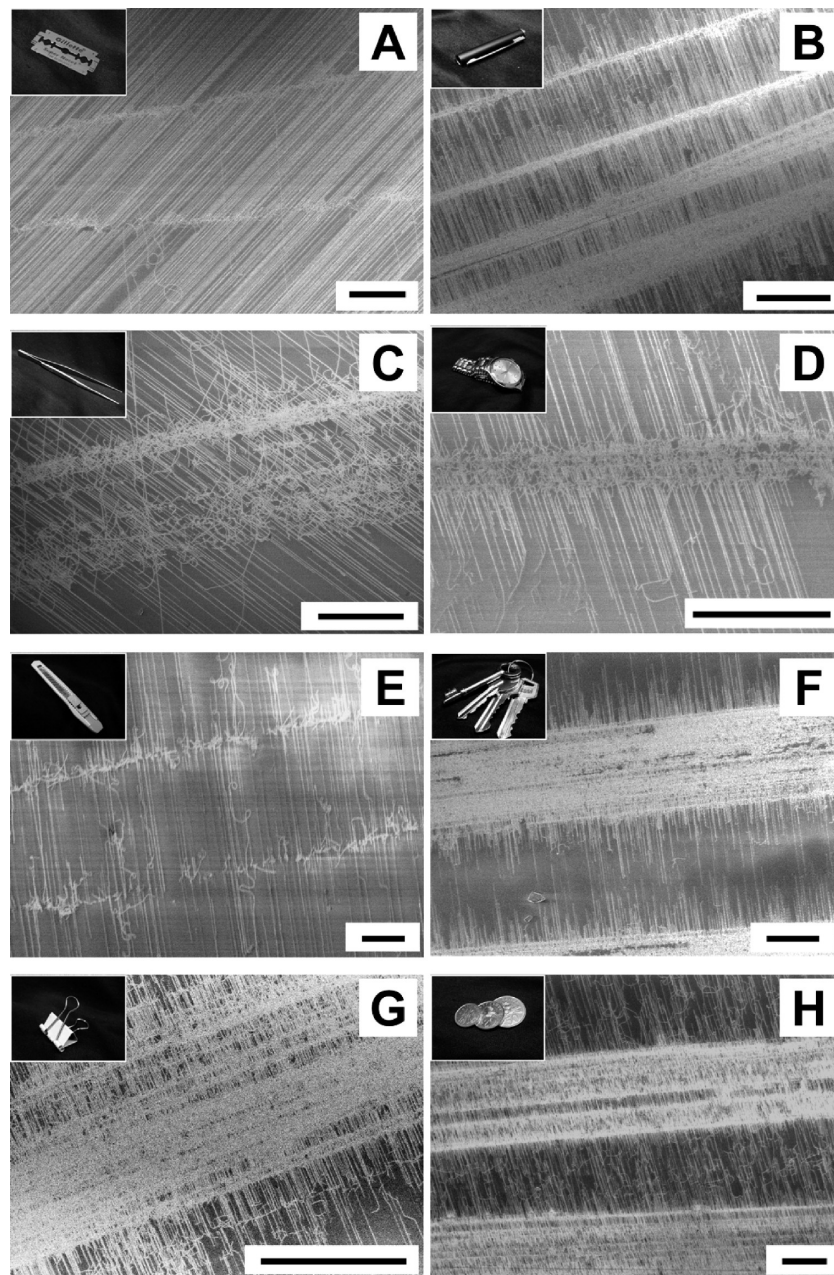


FIGURE 3. SEM images of SWCNTs grown on catalyst patterns on quartz scratched by (A) blade, (B) pen cover, (C) tweezers, (D) watchband, (E) knife, (F) key, (G) clamp, and (H) coin, respectively. Scale bar = 50  $\mu\text{m}$ . Insets: pictures of the respective “scratching” tools used in the experiments.

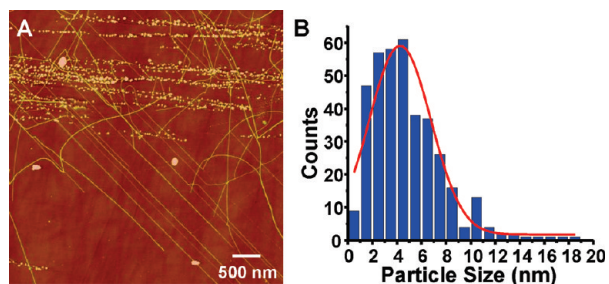


FIGURE 4. (A) AFM image of a blade-scratched area on the quartz in Figure 3A. SWCNTs and catalyst NPs are observed. (B) Histogram of the size distribution of 379 catalyst NPs measured by AFM. The Gaussian fitting curve gives a NP size of  $4.8 \pm 2.9$  nm.

50 sccm of Ar) was fixed. After 10 min, ethanol as the carbon source was bubbled into the quartz tube by gas mixtures of 40

sccm of  $\text{H}_2$  and 80 sccm of Ar. After growth for 30 min, the furnace was cooled to room temperature under argon protection.

**Characterization.** Field-emission SEM was carried out on a microscope (a JEOL model JSM-6700) at an accelerating voltage of 0.5–1.0 keV. Tapping-mode AFM images were obtained with a Dimension 3100 atomic force microscope (Veeco, Fremont, CA). The Raman spectra were performed with a WITEC CRM200 Raman System (532 nm laser, 2.33 eV).

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**Supporting Information Available:** Scheme of the experimental procedures and EDS spectra of the metal objects

used. This material is available free of charge via the Internet at <http://pubs.acs.org> or from the author.

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