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# Copper Catalyzing Growth of Single-Walled Carbon Nanotubes on Substrates

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**ABSTRACT**

**Metallic copper, which is normally considered as a contaminant in the growth of single-walled carbon nanotubes (SWNTs), was found to be an efficient catalyst to grow SWNTs under suitable conditions. It showed very high catalytic activity for the growth of both random SWNT networks and horizontally aligned SWNT arrays. Especially, high-quality SWNT arrays were obtained when monodispersed copper nanoparticles were used. The catalytic behavior of copper for the growth of SWNTs was discussed. The weaker interaction between the copper and silica surfaces plays an important role in the growth of high-quality horizontally aligned SWNT arrays. This new synthesis process of SWNTs with a non-ferromagnetic catalyst brings more convenience to the study of magnetic properties of SWNTs and gives more insight in structure-controlled synthesis of SWNTs.**

Single-walled carbon nanotubes (SWNTs) have been extensively studied as a typical one-dimensional system due to their unique electrical, chemical, optical, and mechanical properties.[1] It is well-known that transition-metal catalysts play dominant roles in chemical vapor deposition (CVD) processes for the growth of SWNTs. They catalyze the decomposition of carbon feedstock which leads to the supersaturated carbon precipitate and ultimately the formation of SWNTs according to vapor–liquid–solid (VLS) model.[2] In the past 10 years, many experimental[3,4] and theoretical[5–7] works were undertaken to understand the catalytic growth mechanism of carbon nanotubes (CNTs) and to find optimal catalysts. Various transition metals have been investigated, but only Fe, Co, Ni, Mo, and their alloys show high activity for the catalytic growth of SWNTs. Among other difficulties relating to these metals, the existence of the residual ferromagnetic catalysts particles in CNTs is the main obstacle for the research on the magnetic property of CNTs in situ.[8] Despite such problems, evidence of a narrow (*n*, *m*) distribution of SWNTs synthesized by Co–Mo catalysts has been reported,[9] indicating that the chirality distribution of SWNTs is related to the types of catalyst. These promote the motivation for exploring new catalysts for CVD growth of SWNTs.

In this Letter, we present the preparation of high-quality SWNTs on the surfaces of silicon wafers and silica microspheres via a Cu-catalyzed CVD method. So far, only a few references have reported that Cu can catalyze the growth of multiwalled carbon nanotubes[10] and carbon nanofibers.[11] Moreover, in comparative experiments and theoretical predictions Cu shows the poorest catalytic efficiency for the CNTs growth.[3,5] Our experimental results break the traditional paths for the surface synthesis of SWNTs, proving that Cu has high catalytic activity and can act as a new type of catalyst for the synthesis of SWNTs. The use of Cu as catalyst will greatly benefit the study of the intrinsic magnetic properties of SWNTs. Furthermore, we will show hereafter the distinctness of Cu-catalyzed CVD.

Monodispersed Cu nanoparticles synthesized by the reduction of $CuCl_2$ in the presence of CTAB[12] and $Cu_2O$ nanoparticles produced by the thermolysis of cupric formates in coordinating solvents[13] (both with the size of about 10 nm) were used as the catalysts. (See Supporting Information.) Or more simply, 0.01–10 mM $CuCl_2$ ethanol solutions were used as the catalytic precursors. Silicon wafers with 500 nm of silica layer or silica microspheres[14] were used as the substrates. The catalysts were put onto the substrate surfaces by dipping in or by PDMS stamping. Methane, ethanol, and 2-propanol were used as the carbon sources. Before the CVD process, the wafers were put into a horizontal quartz tube with 1.5 in. diameter and calcined in air at 700 °C for 5

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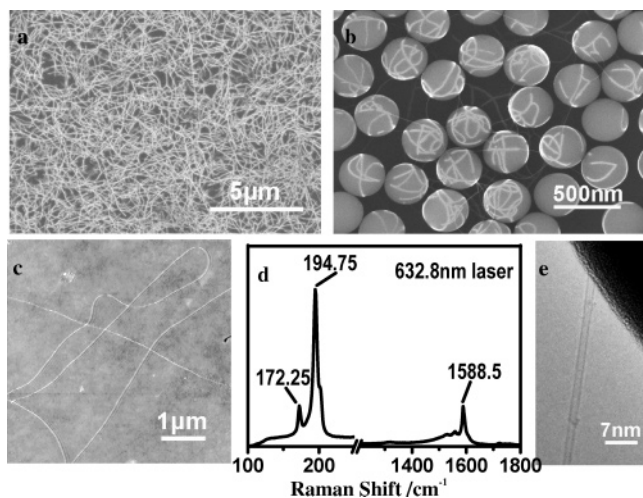‡ National Laboratory of Rare Earth Material Chemistry and Application.

**Figure 1.** (a) SEM image of random networks of SWNTs grown by using 1 mM $CuCl_2$ ethanol solution as catalytic precursor on a silicon wafer. (b) SEM image of SWNTs grown from the surface of silica microspheres with Cu catalyst. (c) AFM image of random networks of SWNTs grown by using $CuCl_2$ catalyst precursor on silicon wafer. (d) Raman spectrum of the SWNTs sample corresponding to (b). (e) HRTEM image of the SWNTs sample corresponding to (b).



**Figure 2.** (a) SEM image of a high-density aligned array of SWNTs grown on silicon wafer. (b) SEM image of another sample of a low-density aligned array of SWNTs. (c) AFM image of aligned SWNTs with the diameter of about 2.0 nm grown on a silicon wafer. (d) Typical Raman spectrum of an isolated long SWNT. Bars in inserted images of (a) and (b) both represent 20 $\mu$m.

min. Subsequently, the substrates were slowly heated to 825−850 °C in an Ar atmosphere, and then the catalyst was reduced using $H_2$. The flow of $CH_4$ (800 sccm) or ethanol (or isopropanol) vapor carried by Ar and/or $H_2$ was then introduced. After 15 min of growth, the system was cooled to room temperature under Ar. We also proceeded fast-heating CVD.[15] The silicon wafers with monodispersed Cu nanoparticles were quickly heated to 925 °C, and a relatively high total flow of the $CH_4/H_2$ mixture gas (800 sccm/700 sccm) was introduced to guide the orientation of SWNTs grown on the substrates. Scanning electron microscopy (SEM, FEI XL30 S-FEG, operated at 10 kV or 1 kV), high-resolution transmission electron microscopy (HRTEM, Hitachi 9000, operated at 100 kV), micro-Raman spectroscopy (Renishaw 2000, with the excitation wavelength of 632.8 nm), and atomic force microscopy (AFM, SPI3800, operated at tapping-mode.) were used to characterize the produced SWNTs.

In the normal-heating CVD experiments, the high-quality random SWNTs were successfully synthesized. Parts a and c of Figure 1 show the SEM and AFM images, respectively, of the clean random networks of SWNTs grown on silicon wafers using 1 mM $CuCl_2$ ethanol solution as catalytic precursor by methane CVD. Figure 1b displays many SWNTs grown from the surface of silica spheres. The diameter of the SWNTs in Figure 1c is about 1.0 nm. HRTEM characterization of silica spheres with SWNTs (shown in Figure 1e) offered direct proof of the formation of SWNTs. The D band in the Raman spectrum of Figure 1d is so weak that it can hardly be observed. This shows that few defects exist in the SWNTs obtained by Cu catalysts. Interestingly, an abnormal high-intensity ratio of radial breathing mode (RBM) band to G band was often observed in the Raman spectra of the SWNTs samples grown from silica spheres. It had been reported that such a phenomenon
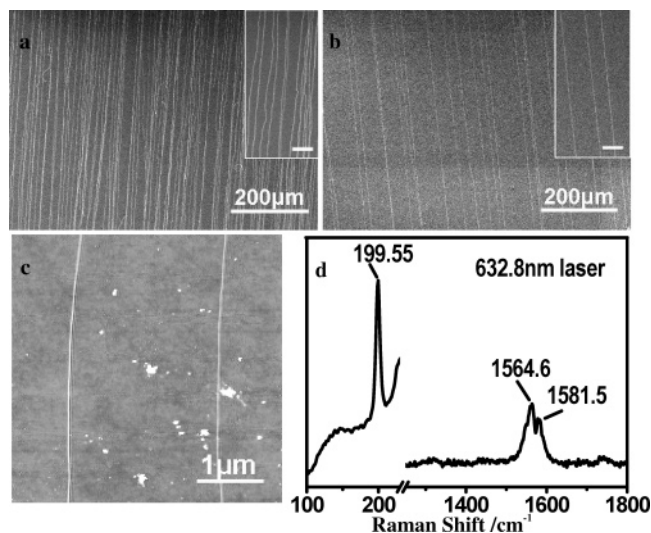
is characteristic of metallic SWNTs.[16] This indicates that there might be a higher percentage of metallic SWNTs in the Cu-catalyzed samples. The typical asymmetry Breit−Wigner−Fano (BWF) line shape of the tangential G band[17] also confirms that the SWNTs are metallic. Note that we are more interested in the Raman spectra collected from the samples of SWNTs grown on silica spheres. This is because suspended SWNTs exist in such samples; these suspended tubes provide stronger and more intrinsic Raman signals in comparison to SWNTs lying on a flat surface.[18] When ethanol and 2-propanol were used as the carbon sources, similar results were obtained. (See Supporting Information.)

Furthermore, we found that Cu nanoparticles have high catalytic efficiency for the growth of horizontally aligned arrays of SWNTs. By fast-heating methane CVD, or by the pyrolysis of ethanol vapors, the ultralong SWNTs (up to a centimeter) were synthesized on silicon wafers. Figure 2a shows a large area of aligned arrays of SWNTs without any random short SWNTs. The density of the array can achieve 2−3 SWNTs/10 $\mu$m. Though this density is lower than those of aligned SWNT arrays grown on quartz[19] and sapphire,[20] it is still very high among reports of horizontally aligned arrays of SWNTs on silicon wafers.[21−23] Although the SWNTs show a few twists in the high-density samples, the SWNTs in the low-density arrays are very straight (Figure 2b). The AFM measurement (Figure 2c) shows that the diameter of SWNTs is about 1.5 nm. The small diameter and the typical RBM in the Raman spectrum (Figure 2d) both support that SWNT arrays were synthesized. Moreover, a high-intensity ratio of the RBM band to G band was also detected. This shows again that metallic SWNTs were obtained.

The horizontally aligned arrays of SWNTs can also be prepared by the pyrolysis of ethanol vapor with Cu catalysts in the non-fast-heating CVD process. Figure 3 presents the
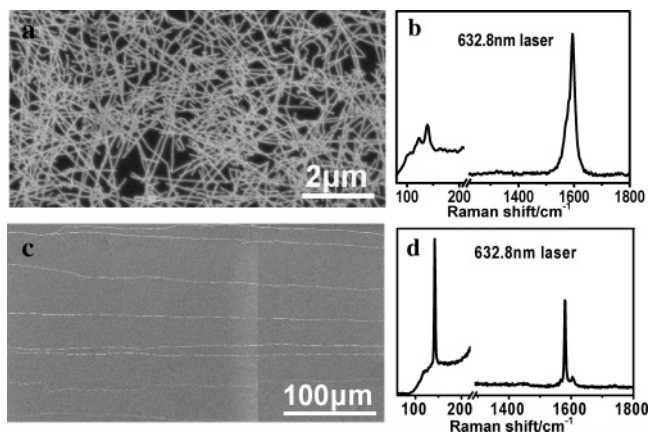
**Figure 3.** SEM images of random SWNT networks catalyzed by FeMo clusters (a) and ultralong SWNTs catalyzed by Cu nanoparticles on silicon wafers by pyrolysis of ethanol (c). (b) and (d) are Raman spectra corresponding to (a) and (c), respectively.

SWNTs produced by using FeMo nanoclusters[24] and mono-dispersed Cu nanoparticles as the catalysts, respectively. In both processes, ethanol was introduced into the system by Ar (200 sccm) and $H_2$ (300 sccm). No fast-heating process was used, and the gas flow was small compared with the normally used thousands of sccm.[15,23] In the FeMo case, random networks of SWNTs were obtained as predicted. However, ultra-long-aligned SWNTs were obtained when Cu nanoparticles were used as the catalysts. Though the quality of the SWNT arrays is not as high as those prepared by fast-heating methane CVD, it is still of interest because of its independence of fast heating.

It is somewhat surprising that Cu can catalyze the growth of SWNTs. Then in order to clear up the possibility of the presence of Fe contamination before and during the CVD process and to ensure that it is Cu that acts as the catalyst, we took many careful investigations. First, we used new quartz tubes for the Cu-catalyzed CVD experiments to avoid contamination. Second, we repeatedly did experiments of blank samples without catalysts and did not find any trace of the formation of SWNTs. Third, we carried out parallel experiments using other chlorides instead of $CuCl_2$ and found that still no carbon nanotubes were formed when NaCl, $MgCl_2$, $CaCl_2$, and $AlCl_3$ were used. Finally, the energy-dispersive X-ray spectra (EDS) in Figure 4 give evidence that no Fe or other metal elements which normally can catalyze the SWNTs' growth exists in our samples. No other transition metal than Cu exists in our catalysts (Figure 4b) and after the CVD process no new element appears (Figure 4d). From all above, we proved that it is Cu that catalyzed the growth of SWNTs.

On the basis of the previous studies, Cu is not suitable for SWNT growth. However, it is reasonable that Cu can catalyze the growth of SWNTs in theory. The Cu−C binary phase diagram[3] shows that carbon has some solubility in the Cu solid solution. This ensures that carbon atoms can dissolve into the Cu nanoparticles and precipitate out to form graphitic structures according to the VLS mechanism.

However, there are a few differences between Cu and Fe. The solubility of C in Cu is much lower than that in Fe. This indicates that C can precipitate out more easily. As a result, the CVD conditions of the Cu-catalyzed processes should be distinct from those catalyzed by Fe. In addition, Cu has lower catalytic activity for the dissociation of alkanes than Fe, and then the supply of carbon in the CVD process is slower. This may be an advantage for reducing the
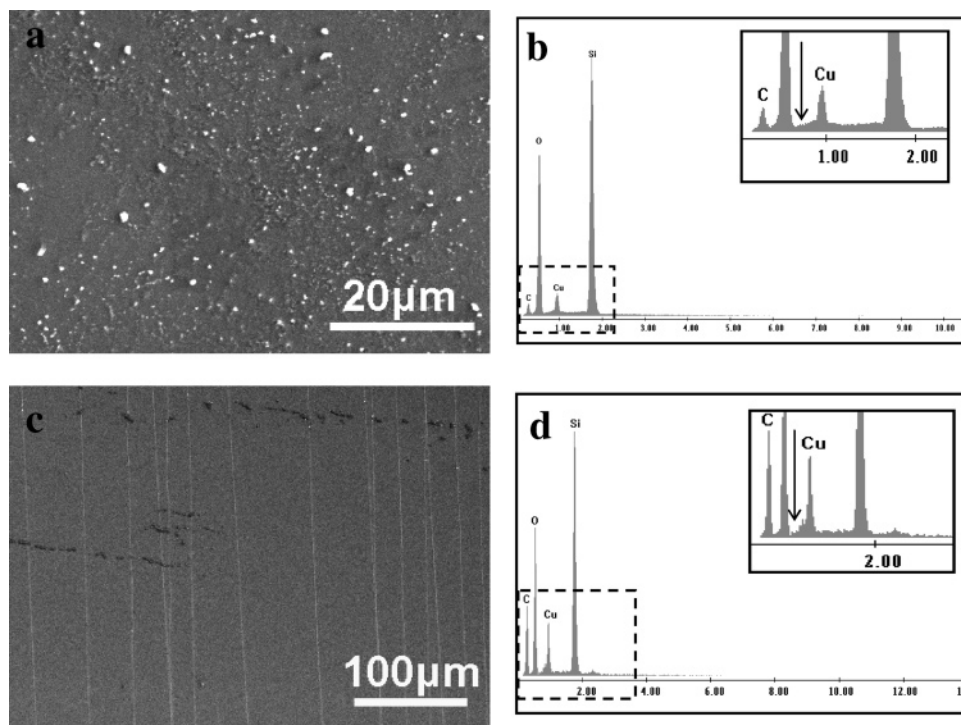


**Figure 4.** SEM images of Cu NPs on silicon wafer before CVD (a) and the as-grown SWNTs (c). (b) and (d) are the EDS spectra corresponding to (a) and (c), respectively. The insets of (b) and (d) are the magnified plots of the parts in the dashed rectangles. The arrows denote the energy position of Fe element, and no signal was found in the corresponding position in both samples.

formation of amorphous carbon. Matching the supply of carbon and the formation of nanotubes will produce SWNTs of high quality.[25] This is proved by the extremely high intensity ratio of G to D bands of our SWNT samples produced by Cu-catalyzed CVD.

Another difference is that Cu has a much lower melting point. This indicates that the Cu-catalyzed CVD might be able to proceed at lower temperatures. This is demonstrated in our experiment. Nevertheless, low temperatures can inhibit the crystallization of C and the formation of SWNTs. Therefore, the optimized temperature has been shown to be around 825−850 °C. The boiling point of Cu is also very low. Thus, the evaporation of Cu at high temperatures is very remarkable. As a result, it is very delicate work to control the size of Cu particles at high temperature, especially when Cu is loaded on bulk catalyst supports. It needs a careful control of the reduction condition to obtain Cu nanoparticles with proper size to catalyze the growth of SWNTs on surfaces. (See Supporting Information.) Yet, until now we have not found the proper condition to get high-quality SWNTs with Cu in the bulk system. This might explain why people normally think that Cu is not a good catalyst for SWNTs.

In order to further understand the function of Cu in the synthesis of horizontally aligned arrays of SWNTs, we did molecular dynamics calculations. We found that the interaction between Cu and $SiO_2$ is much lower than that between Fe and $SiO_2$. (See Supporting Information.) This is consistent with the previous study.[26] In the previous growth processes of horizontally aligned SWNTs with Fe catalysts, the most important step is to lift up the catalyst nanoparticles by overcoming their interactions with the substrate surface and allow them to float with a tube tailor.[15,23] The fast-heating procedure and large gas flow benefit this.[23] As the interaction of Cu nanoparticles is much lower, the growing efficiency of oriented long SWNTs can be greatly improved by using Cu instead of Fe as the catalyst in fast-heating method, even though no fast heating and high gas flow are needed for the growth of oriented long SWNTs with Cu nanoparticle when ethanol was used as carbon source.

In conclusion, Cu is a good catalyst for the growth of SWNTs on silicon wafers or silica spheres, especially for the preparation of long horizontal arrays of SWNTs. We can get high-quality SWNT networks or horizontally aligned arrays by Cu-catalyzed CVD. These SWNTs may present special properties. The Raman spectra give evidence of a higher percentage of metallic SWNTs produced via the Cu-catalyzed CVD. More detailed spectroscopic studies and electrical measurements are ongoing in our lab.

**Supporting Information Available:** Characterization of Cu catalyst particles, more CVD experimental details, and the Molecular Dynamics calculation process. This material is available free of charge via the Internet at http://pubs.acs.org.

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