Comparison between Copper and Iron as Catalyst for Chemical Vapor Deposition of Horizontally Aligned Ultralong Single-Walled Carbon Nanotubes on Silicon Substrates

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A careful comparison was performed between Cu and Fe as catalysts for the growth of horizontally aligned ultralong single-walled carbon nanotube (SWNT) arrays on SiO$_2$/Si substrates, and the mechanism of the difference was discussed. Cleaner and straighter SWNTs with smaller diameters and narrower size distribution were obtained using Cu as catalyst. It was also found that the SWNTs always grew from the edges of the substrates wherever the catalyst precursors were patterned when Cu was used, while SWNTs normally grew from the patterned catalysts when Fe was used. The size change of Fe and Cu nanoparticles along with the reduction processes shows that Cu nanoparticles were much easier to be vaporized, and the molecular mechanics calculations about the surface energy changes with the particle sizes indicate that the renucleation of Cu tends to form smaller nanoparticles than Fe. This is an important factor that leads to the different performance for Cu and Fe in SWNT growth. This argument was further proved by the fact that using polyvinylpyrrolidone to fix Cu nanoparticles resulted in similar growth behavior to that of Fe catalyst. This study is helpful for further understanding the growth mechanism of SWNTs and gaining more control over the growth of SWNTs.

Introduction

Single-walled carbon nanotubes (SWNTs) have caused intensive attention for their potential application in many fields, especially in carbon-based nanoelectronics. It is common sense that the controlled preparation of SWNTs is the foundation and essential issue for the application of SWNTs. However, the rational and precise control over the preparation process of SWNTs is still a goal on the road. Chemical vapor deposition (CVD) is the most widely used method for the preparation of SWNTs. The catalyst plays a key role in the CVD process. It is normally accepted that catalysts take responsibilities in the decomposition of carbon stocks and the nucleation and growth of SWNTs. Group VIII metals including iron, cobalt, and nickel are commonly used catalysts to decompose the carbon feedstock and initiate the formation of SWNTs. Especially, iron began to be used from the very beginning as the catalyst for CVD growth of SWNTs and has been the most intensively used one.

Copper had been considered as a bad catalyst for the growth of SWNTs in the past. However, it was found later that copper can be an efficient catalyst for the preparation of SWNTs both in our lab and by Homma’s group. In the subsequent reports, copper shows to be a superior catalyst for the growth of SWNT arrays. According to our experience, for the preparation of ultralong SWNT arrays on SiO$_2$/Si substrates, samples of higher quality (straight, clean, with smaller diameter) were normally obtained by using copper as catalysts. And the field effect transistors (FETs) built with SWNTs grown from copper also showed very high performance. A question arises from these facts: how is the difference between copper and iron as catalysts for the growth of SWNTs?

Here are some differences between copper and iron which we know from handbooks and the literature: copper has a much lower melting point than iron; copper has a lower catalytic activity for the decomposition of alkanes than iron; the interaction between copper and silica (substrate) is much lower than that between iron and silica. Then how do these differences we already know as well as those we still neglect affect the catalytic behavior of copper and iron? It is still an open question. In this paper, we make careful comparison between copper and iron as catalysts for the growth of horizontally aligned SWNT arrays and find that copper is indeed a better catalyst than iron in many aspects. We also make some theoretical analysis and discussion to explain the mechanism of the difference between copper and iron.

Experimental Section

Preparation of SWNT Arrays. Monodispersed Cu$_2$O nanoparticles (~10 nm) produced by the thermolysis of cupric formate in coordinating solvents, FeMo clusters, 0.1–1 mM FeCl$_3$ or CuCl$_2$ ethanol solutions, or CuCl$_2$ solution with polyvinylpyrrolidone (PVP) (1:20, molar ratio of Cu to PVP monomer) were patterned onto the silicon wafer by PDMS stamping. The wafer with catalyst was put into a horizontal quartz tube furnace and calcined in air at 600–700 °C for 5 min. Afterward, the wafer was pulled out of the center of the furnace and heated to 960 °C under Ar atmosphere. Then 320 sccm of CH$_4$ together with same flow of H$_2$ was introduced, and the silicon wafer with the catalyst was quickly transferred into the center of the heated furnace. After 15 min of growth, the system was cooled to room temperature under Ar.

Characterization. Scanning electron microscopy (SEM, S4800, Hitachi, Japan) was operated at 1 kV. Raman spectra were collected on a Jobin Yvon LabRam HR 800 micro-Raman spectrometer with the excitation wavelength of 632.8 nm and spot size of 1 μm, using a 100× air objective. The laser energy
Cui et al.

was carefully controlled to avoid any heat effect. Atomic force microscopy (AFM, SPI3800, operated at tapping mode) was used to measure the diameter of the SWNTs and the size of the catalyst particles. High-resolution transmission electron microscopy (HRTEM, Hitachi 9000) was operated at 100 kV.

**Molecular Simulation.** 1 ns molecular dynamics simulation on the Cu and Fe nanoparticles with different diameters was carried out. Molecular mechanics calculations were further performed on the fully relaxed nanoparticles and the bulk metal. The surface energy of the nanoparticles was obtained from the energy difference of the nanoparticles and the bulk metal.

Molecular simulation was conducted to make predictions for the interactions between Cu nanoparticle and the PVP under Accelrys’s MD program Discover using COMPASS force field. The van der Waals and Coulomb interactions were treated using the atom-base cutoff method with a cutoff radius of 20.0 Å. 500 ps molecular dynamics simulation was first performed to relax the Cu−PVP system to its equilibrium structure. Molecular mechanics simulation was then carried on the optimized Cu−PVP structure, the Cu nanoparticle, and the PVP. The binding energy is defined as the difference between the energy of the Cu−PVP structure and the sum of the energies of the Cu nanoparticle and the PVP.

**Results and Discussion**

Parts a, c, and e of Figure 1 show the SEM images of horizontally aligned arrays of SWNTs on SiO$_2$/Si substrates prepared using 1 mM monodispersed Cu$_2$O nanoparticles and 1 mM and 0.1 mM CuCl$_2$ ethanol solution as catalytic precursors, respectively. The lengths of the SWNTs are centimeters, limited only by the length of silicon wafer. We analyzed the length distribution of the sample corresponding to Figure 1c. 80%−90% of the SWNTs have the length greater than 5 mm and 70%−80% greater than 10 mm. Actually, many SWNTs could grow longer if the silicon wafer was long enough. The highest density we achieved using Cu as catalyst is 14 SWNTs/100 μm. The SWNTs are very straight and clean when using Cu$_2$O nanoparticles as the catalyst precursors (Figure 1a).

Comparatively, SWNTs were also grown using 1 mM FeMo clusters and 1 mM and 0.1 mM FeCl$_3$ ethanol solution as catalytic precursors, respectively (Figure 1b,d,f). The SWNTs as prepared are not very straight and well-aligned as those produced from Cu catalysts, and some of the tubes end their growth in the middle of the silicon wafer. As Fe has higher catalytic activity for the dissociation of alkanes than Cu, then the supply of carbon is faster. This might be unfavorable for the growth of ultralong SWNTs. When we decreased the concentration of FeCl$_3$−ethanol solution to 0.1 mM, the density and the quality of horizontally aligned arrays of SWNTs were obviously improved (Figure 1f) compared with those from 1 mM FeCl$_3$ solution but were still not as good as the arrays prepared with Cu catalysts. For the sample in Figure 1f, 60%−70% of the SWNTs are longer than 5 mm, but only 40%−50% are longer than 10 mm.

We have already known that Fe is very effective in catalyzing the decomposition of carbon stocks. However, the superfluous carbon feeding may cause many problems, for example, the formation of amorphous carbon and bundled SWNTs. The excessive carbon species may form a graphitic carbon layer covering the iron particle surface and deactivate the catalyst. The deactivation of catalyst particles will undoubtedly stop the growth of SWNTs. The plenteous supply of carbon can also lead to a very quick growth of SWNTs. When the growing speed is higher than gas flow rate, twisted tubes are formed. Twisted tubes may disturb their floating status and fall down to the substrates. Then due to the strong interaction of SWNTs with the silica substrates, the tubes will stick on the substrates and stop their growth. Therefore, the overabundant carbon feeding might be the reason when SWNTs stop grown at the middle of the substrates as shown in Figure 1d,f when Fe was used as the catalyst. By contrast, the weaker catalytic activity in carbon stock decomposition of Cu may be able to obtain optimized carbon feeding for growing high-quality SWNTs, and the weaker interaction between Cu and silica makes it easier to lift the Cu nanoparticles out of the substrates than Fe nanoparticles. This is also an advantage for using Cu as catalyst to grow horizontally aligned SWNT arrays via the “kite mechanism”.8,14

The diameter distribution comparison was carried out on the horizontally aligned SWNTs arrays prepared using Cu and Fe catalysts with the samples in Figure 1c,f according to the feature heights in AFM images. For SWNT array prepared with Cu catalyst, the diameter distribution is quite narrow and more than 85% of the tubes (100 of 117) present diameters smaller than 3 nm (Figure 2e). We further performed the size distribution analysis of the features with the heights below 3 nm in the AFM images. The mean diameter is 1.5 ± 0.5 nm. For SWNT array prepared with Fe catalyst, the diameter distribution is wider, and only 58% of the tubes (76 of 131) have the diameters below 3 nm (Figure 2f). The mean diameter is 2.1 ± 0.6 nm. The diameter distribution analyzed above points out that it is much easier to prepare individual ultralong SWNTs with smaller diameter when using Cu catalyst compared with Fe catalyst.

During the AFM imaging process, we also found that the samples of SWNT arrays prepared with Cu catalyst are normally very clean, and small particles are scarcely seen on the silicon wafers (Figure 2a,b). But for the SWNT array samples prepared with Fe catalyst, abundant particles appear on the substrates and sometimes on the tubes, which is adverse for the charac-
terization and application of the as-prepared SWNTs. We also used HRTEM to investigate the specific structure of SWNTs. SWNTs grown on substrates bind tightly with the substrate surface. Polymers are normally used to peel the SWNTs off from the substrate and transfer the tubes onto the TEM grids. However, polymer residues always exist on the tubes even by very harsh treatments. Here we placed a few silica spheres on silicon wafer outside the catalyst region before the growth; then the as-grown SWNTs can be transferred into ethanol solution directly by ultrasonication and ready for being dropped onto TEM grids. HRTEM characterization of SWNTs offered direct proof that the SWNT catalyzed by Cu catalyst (Figure 2c) possesses a clean surface while there is some dirt on the surface of the SWNT obtained by Fe catalyst (Figure 2d). Figure 2g,h shows the typical Raman spectra of SWNTs from copper and iron. The quite weak intensity of the D-band shows the high quality of the obtained SWNTs. RBM bands at 140 and 129 cm\(^{-1}\) in the Raman spectra show the diameters of SWNTs are 1.77 and 1.92 nm, respectively.

We also found that SWNTs catalyzed by Fe grow from the area where the catalyst precursors were patterned (Figure 3a), while SWNTs catalyzed by Cu always grow from the edges of the silicon wafers instead of the area where catalyst precursors were patterned (Figure 3b). It is known that Cu is much easier to be vaporized on SiO\(_x\)/Si substrates than Fe due to the lower melting and boiling points of Cu, and Cu is more mobile than Fe for the weaker interaction between Cu and silica.\(^{33}\) We studied the size change of Fe and Cu on SiO\(_x\)/Si substrates during the reducing process with H\(_2\) at 900 °C. We measured the heights of Fe and Cu nanoparticles on SiO\(_x\)/Si substrates in the AFM images. After being reduced with H\(_2\) for 15 min at 900 °C, the same areas of the substrates were imaged again and the heights of the particles were measured. For Fe, the nanoparticles are still at the same place though the sizes of the particles are remarkably decreased after 15 min of reduction (Figure 3c,d). But for Cu, most of the nanoparticles are disappeared (Figure 3e,f).

Considering that the SWNTs catalyzed by Cu all grow from the edges of silicon wafers other than the places where Cu was originally patterned (Figure 3b) and the disappearance of Cu nanoparticles under H\(_2\) flow (Figure 3f), it can be deduced that Cu was vaporized and renucleated at the silicon wafer edges where nanoparticles nucleate more easily due to the obvious surface roughness. These re-formed Cu nanoparticles act as the catalysts for the growth of SWNTs. In order to prove our inference, we designed the following experiment. First, Cu catalyst was evaporated to the center of inner walls of quartz tube rather than imprinted on the surface of silicon wafer (Figure 3a, e) and Fe (b, f, h) catalysts corresponding to the samples in Figure 1c,f, respectively. (c, d) HRTEM image of an individual SWNT catalyzed by Cu catalyst and Fe catalyst at the same growth conditions corresponding to the samples in Figure 1c,f.
4a), and then SWNTs were grown using the same growing conditions as before. Well-aligned SWNTs are still grown from the edge of the substrate where no catalyst precursors have been patterned (Figure 4b). This shows that Cu was vaporized from the inner surface of the quartz tube and renucleated at the edges of silicon wafer, acting as the catalysts for the growth of SWNTs. Cu might remove from the area where it was patterned to the silicon wafer edges. However, we have not found convective evidence for this hypothesis yet.

From above discussion, the nucleation of Cu nanoparticles is very important for the catalytic growth of SWNTs in the CVD process. Therefore, we calculated the surface energy change with the particle size using molecular mechanics (MM) simulation. As shown in Figure 5, the surface energy per atom for Fe particle increases sharply with the decrease of particle size. But that for Cu is much lower and increases more gently than Fe. This result indicates that it is energetically more favorable for Cu to form smaller nanoparticles than Fe. Hence, the vaporized Cu can nucleate into smaller nanoparticles. Catalyzed by these smaller particles, SWNTs of smaller diameter should be obtained. This might be the reason why Cu catalysts can produce SWNTs with smaller diameters than Fe.

As analyzed above, we considered that the weaker interaction with the substrate and the easiness in vaporization take important roles for Cu to behavior different with Fe in catalyzing the growth of SWNTs. If this is true, Cu should act similarly with Fe when we find a way to increase its interaction with the substrate and to reduce its volatility. Then we used PVP to fix Cu nanoparticles on the substrates. Molecular mechanics calculations were conducted to make predictions for the inter-
actions between catalyst nanoparticles and the PVP. The catalyst nanoparticles consist of 1043 metal copper atoms. The optimized structure is shown in Figure 6a. An energy decrease of 2042.5 kcal/mol is obtained for the Cu–PVP system in comparison with bare Cu. This means that the presence of PVP greatly increase the stability of Cu nanoparticle. Using PVP, the interaction between the particle and the substrate should be also increased. Obviously, the enwrapping of Cu nanoparticles can depress the evaporation of Cu. Though PVP can be burned in the step of calcining (Cu/PVP) at 600–700 °C for 5 min, the thorough elimination of PVP is very difficult. Therefore, the residues of PVP can still take effect. As shown in Figure 6b, most of SWNTs grow from the area where Cu (with PVP) has been originally patterned, which is very similar to the situation when Fe was used as the catalysts (Figure 3a), and the diameters of SWNTs catalyzed by Cu/PVP are remarkably larger (Figure 6c–e). Figure 6c shows the AFM image of two tubes with the heights of 4.6 and 6.1 nm. According to the analysis based on 34 tubes measured in AFM images, the size distribution is much broader (Figure 6e). The heights of the features are mostly between 2 and 5 nm with the mean value at 4.5 nm. These results give further support for our analysis about the reason why Cu exhibits unique behavior in catalyzing the growth of SWNTs.

In conclusion, we found that copper is a better catalyst than iron in catalyzing the growth of horizontally aligned ultralong SWNT arrays on SiO$_2$/Si substrates. Using copper as catalyst, SWNTs with bigger lengths, smaller diameters, narrower diameter distribution, and less amorphous carbon were obtained. These characters of the SWNT samples from copper catalyst are believed to be reasons responsible for the superior performance of copper catalysts. The comparison of catalytic behavior of copper and iron catalysts will be helpful for both in-depth studies of growth mechanism of SWNTs and controllable growth of SWNTs.

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References and Notes