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LETTERS

Synthesis of Cu Nanoparticles and Microsized Fibers by Using Carbon Nanotubes as a Template

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Copper in the form of nanoparticles and microsized fibers was synthesized by using carbon nanotubes as a template. The size of the copper nanoparticles was controllable in the range between a few and tens of nanometers, depending on the diameter of carbon nanotubes and the preparation conditions. They could be detached from carbon nanotubes by ultrasonic treatment. Cu fibers with diameter ranging from 100 nm to several μm were obtained when increasing the amount of Cu coated onto carbon nanotubes, which in this case became undetectable under SEM and XRD observations. The electronic structure of these two forms of Cu materials was studied by XPS and UPS and compared with that of polycrystalline Cu metal. A negative core-level binding energy shift for Cu nanoparticles and an increase in work function for Cu fibers as compared with those of the polycrystalline Cu were observed and discussed in terms of size effect.

Since the discovery of carbon nanotubes, there have been intensive studies concerning the preparation, characterization, and application of this fascinating material.[1−4] Great interest in finding a way to use this material arises worldwide because of its superior properties. This includes using carbon nanotubes as nanodevices, gas absorbents, one-dimensional quantum wire, and nonlinear optical limiter among others.[5−8] In this study, carbon nanotubes were employed as templates to synthesize small-sized Cu which has been found to exhibit unusual properties as compared with the bulk material.[9,10]

Normally, Cu nanoparticles are prepared by wet chemistry methods which can provide Cu particles as small as several nanometers but may suffer from the uncontrollable size distribution.[11] An alternative preparation route is pulsed laser ablation, in which a Cu target is evaporated in an inert gas atmosphere, but for effectiveness several parameters need to be carefully controlled.[12] The method reported in this paper provides an easy and controllable way to synthesize nanoparticles. It also has an advantage in separating Cu nanoparticles from the template. Furthermore, a new form of Cu fibers with diameter ranging from 100 nm to several μm can be synthesized using the same method by increasing the amount of Cu added.

It has been found in our previous study that a size effect may manifest itself in the variation in the core level binding energy and in the work function.[13] In this study, XPS and UPS were applied to investigate and compare the electronic structure of Cu nanoparticles, Cu fibers, and polycrystalline Cu metal. As will be reported below, the results reveal that a similar size effect does exist among these three kinds of Cu.

Experimental Section

The carbon nanotubes used in this study were prepared by the decomposition of CH_4 on a $Ni_xMg_{1-x}O$ catalyst as described previously.[13,14] By changing catalyst composition, this method enabled us to produce carbon nanotubes with narrow and specific size distributions. When $x = 0.3$, approximately 90% (as measured from careful TEM inspection) of the tubes have diameters between 5 and 10 nm, while 80% of the tubes are

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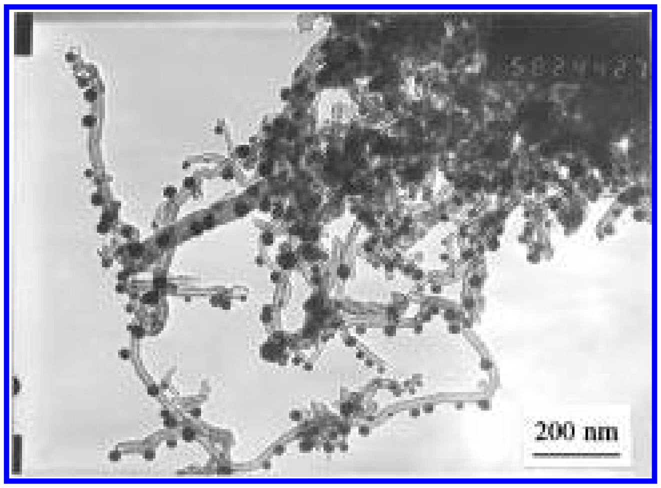

Figure 1. TEM image of Cu nanoparticles.

between 10 and 20 nm when $x = 0.4$, and 80% are between 25 and 35 nm when $x = 0.5$. Little (<10 wt %) nonnanotube material such as metal (catalyst) particles, amorphous carbon, disordered carbon etc. was observed from TEM and thermogravimetry (TG) study of high temperature hydrogen etching. The preparation procedure for Cu nanoparticles and fibers involved fully dispersing a certain amount of carbon nanotubes in water, followed by adding a desired amount of a Cu salt (normally 2 molar % for Cu nanoparticles, and 100 molar %, i.e., 1:1 Cu to carbon nanotubes molar ratio, for Cu fibers) to the suspension. The mixture was then strongly stirred at 373 K until the solvent was vaporized completely, and finally it was subjected to decomposition and reduction with H_2 at temperatures below 773 K.

Cu samples for TEM observation were dispersed in water and subjected to ultrasonic treatment. A little drop of the suspension was then deposited onto carbon TEM grids. TEM and SEM observations were conducted on a JEM-100CX electron microscope; XRD measurement was performed on a Philips PW 1710 diffractometer. Both XPS and UPS measurements were performed on a VG ESCALAB Mk II machine at a vacuum better than 3×10^{-9} Torr. To avoid charging, samples for XPS/UPS measurements were first dispersed in acetone, dropped to the top of sample stubs, and then dried to secure a good contact with the sample stub. Samples were pretreated in purified H_2 at 573 K for 4 h to remove oxygen followed by Ar ion sputtering to ensure that the sample surface was free of oxygen and other impurities. The analyzer pass energy used in the XPS measurement was 5.0 eV, and the scan step was selected at 0.025 eV to improve resolution. The work function was measured by UPS using He(I) (21.2 eV) as an ionization source and a 10 eV bias was applied to make a clear cutoff of the secondary electron tail.

Results

Figure 1 is the TEM image of the Cu nanoparticles attached on the carbon nanotubes, which was prepared from 2 molar % Cu on the carbon nanotubes with diameters of 25−35 nm. It can be seen that the Cu particles are in the form of round dots stuck on the surface of carbon nanotubes, with diameter less than that of carbon nanotubes, i.e., less than 35 nm. It has been found that the size of Cu particles can be controlled by the templates: the smaller the diameter of carbon nanotubes template, the smaller the size of Cu particles prepared. When carbon nanotubes with diameter of 5∼10 nm were used, all of the Cu particles synthesized were found to be under 10 nm in diameter. Furthermore, the preparation conditions including the amount of Cu salt added and the decomposition/reduction temperature can also play important roles in controlling the size of Cu particles. By reducing the amount of the Cu salt from 2 molar % to <1 molar % while keeping other conditions identical, Cu nanoparticles synthesized have smaller size, 70% in the range of 5−10 nm. Also, if the decomposition/reduction temperature is high, close to the melting point of Cu, the size of Cu particles will be large, since Cu atoms at such high temperatures are prone to merge into large particles to reduce surface energy. Figure 2 shows Cu particles prepared under optimum conditions with diameters less than 5 nm. The TEM image also shows that the sticking of the Cu particles to the carbon nanotubes is not strong, with a large number of particles being dropped off from the tube surface and spread on the TEM grids after ultrasonic treatment. This provides an easy way for separating Cu particles from carbon nanotubes.

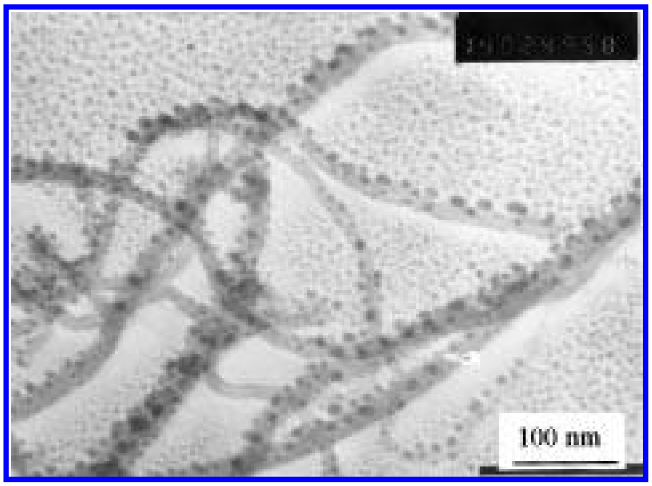

Figure 2. TEM image of Cu nanoparticles prepared under optimum conditions.

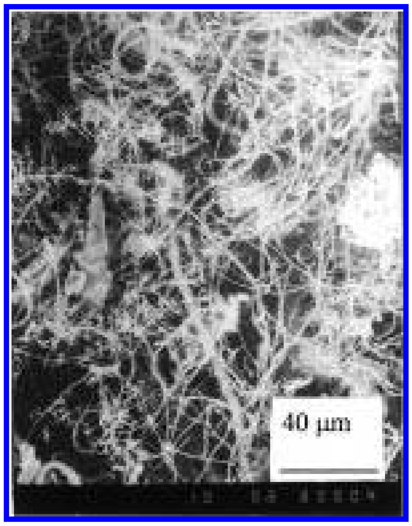

Figure 3. SEM image of Cu fibers.

When the amount of the Cu salt added to carbon nanotubes was increased (from 2 molar % as mentioned above for nanoparticles) to 1:1 molar ratio, a spongelike yellow-brown product was obtained following the procedure described in the Experimental Section. The SEM image in Figure 3 reveals that this spongelike Cu is actually the piling up of microsized Cu fibers with diameters ranging from 100 nm to 5 μm, and lengths up to hundreds of μm. XRD measurement can hardly detect the graphitelike diffraction peaks, which are regularly detected from carbon nanotubes prior to Cu coating.[13,15] Only diffraction

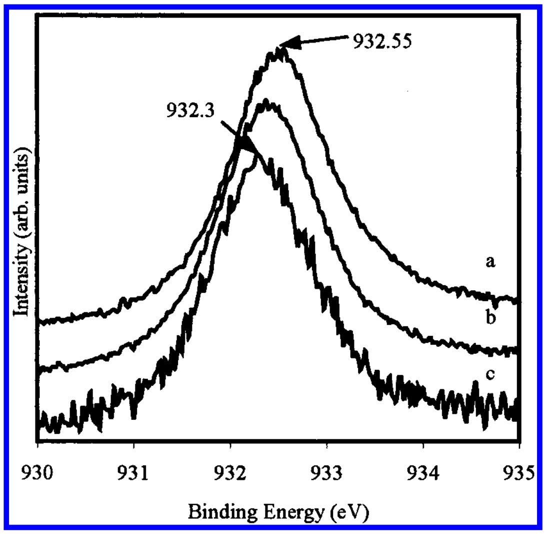

Figure 4. XPS core-level spectra of: (a) polycrystalline Cu, (b) Cu fibers, and (c) Cu nanoparticles.

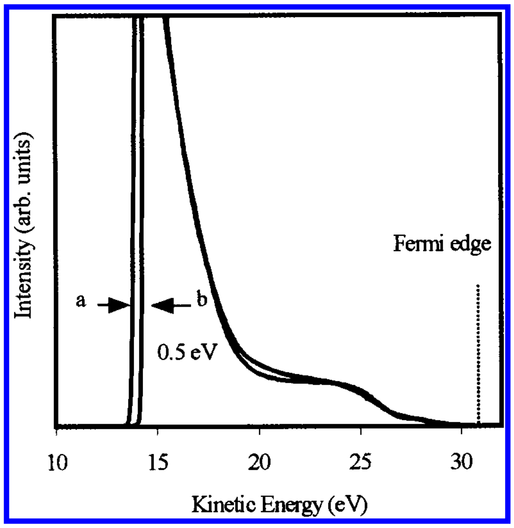

Figure 5. UPS (He(I)) spectra of (a) polycrystalline Cu and (b) Cu fibers.

of Cu metal is observable (spectrum not shown), indicating a thick coating of Cu on carbon nanotubes. The diameter of the Cu fibers can be controlled by changing the amount of Cu added. Nanosized Cu fibers with diameters around 100 nm can be obtained if the Cu salt added is less than 40 molar %. In this case Cu nanoparticles would coexist.

Figure 4 displays the XPS core-level spectra in the Cu $2p_{3/2}$ energy region obtained from Cu nanoparticles, Cu fibers, and polycrystalline Cu. It can be found that the binding energy of Cu ($2p_{3/2}$) for the copper powder stays at the normal value of 932.6 eV, but it shifts to 932.3 eV for the Cu nanoparticles. A slight negative shift for that of Cu fiber can also be observed. It is interesting to note that our previous study concerning the difference in electronic structure between carbon nanotubes and graphite also came to the same conclusion, i.e., as the particle size reduces to nanoscale, the core-level binding energy shifts to smaller values as compared with that of bulk one.

The electronic structure of the valence band of these three Cu materials was measured by UPS. As shown in Figure 1, Cu nanoparticles coexist with carbon nanotubes, so that their valence band spectrum shows characteristics both of Cu and the dominant carbon. The work function measured is also close to that of carbon nanotubes. As for Cu fibers, the carbon nanotubes have been shown by SEM and XRD observations to be fully coated by Cu, consequently the UPS spectrum obtained from the Cu fibers is characteristic of metallic Cu, different from that of carbon nanotubes. It can be found (see Figure 5) that there is a notable change in the energy position of secondary electron tails for Cu fibers and polycrystalline Cu. As the Fermi edges of the Cu fibers and polycrystalline Cu coincide at the same point, the change in the position of the secondary electron tail reflects the variation of the work function. The work function for polycrystalline Cu is measured to be 3.9 eV, the same as that which has been previously reported, but 4.4 eV is obtained for the Cu fibers giving an increase of 0.5 eV. The increase in work function means the energy barrier for an electron in the solid to escape to the vacuum is enhanced. Since low-index surfaces normally possess higher work functions than do high-index surfaces of the same identity, it may be inferred that microsized Cu fibers expose mainly low-index surfaces and have therefore fewer defects as compared with polycrystalline Cu metal.

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