Nanostructures

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Hole-Doped Single-Walled Carbon Nanotubes: Ornamenting with Gold Nanoparticles in Water**

*Dong Sik Kim, Takhee Lee, and Kurt E. Geckeler**

Since the discovery of carbon nanotubes,[1] intensive studies of their unique electronic and mechanical properties have been performed,[2] and considerable potential applications in nanotechnology have been suggested.[3] It is advantageous or required to modify carbon nanotubes by physical or chemical methods to optimize their use in many applications. Nanohybrid materials based on carbon nanotubes with metal nanoparticles are promising materials because of their exciting features (which are different from their intrinsic physical properties) such as catalytic activity,[4] enhanced conductivity,[5] and hydrogen-sensing ability.[6] These properties of hybrid nanostructures could hold promise for a bright future in electronic, optical, and magnetic applications.[7]

A variety of different methods, such as physical evaporation,[8] thermal decomposition,[9] electroless deposition,[10] chemical immobilization using covalent coupling[11] and hydrophobic anchoring,[12] and polymer-assisted hybridization,[7] have been explored to obtain hybrids of carbon nanotubes and metal nanoparticles.

Recently, Au nanoparticles were generated on single-walled carbon nanotubes (SWNTs) through direct redox reactions by the immersion of SWNTs grown on a SiO_2 substrate in a solution of Au^{3+} ions.[5] This method is an attractive approach because it opens up a direct way to prepare Au nanoparticles on SWNTs without using high-temperature treatment, reducing agents, or anchoring functional groups. However, the reaction took place on a solid support and the final hybrid material was not soluble. In addition, the size of the nanoparticles was not uniform and the poorly wetted surface of the as-produced SWNTs required the use of an ethanol/water (1:1) mixture.

Herein, we report for the first time a simple and facile method to prepare water-soluble hybrid materials of Au nanoparticles and hole-doped SWNTs.[13] The SWNTs with uniformly arranged Au nanoparticles were obtained by the addition of metal salts to surfactant-suspended SWNTs in water by using the solution-phase dispersion technique.[14]

[*] D. S. Kim, Dr. T. Lee, Prof. Dr. Dr. K. E. Geckeler
Department of Materials Science and Engineering
Gwangju Institute of Science and Technology (GIST)
1 Oryong-dong, Buk-gu, Gwangju 500-712 (South Korea)
Fax: (+82) 62-970-2338
E-mail: keg@gist.ac.kr

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The method reported here is easy to scale-up and a uniform size of nanoparticles can be prepared. More importantly, as the method yields water-soluble products, a much greater variety of applications can be envisaged.

In a typical experiment, commercially available, highly pure SWNTs (1 mg, from Iljin Nanotech) were dispersed in an aqueous solution of the surfactant Tween-80 (0.1 wt%, 10 mL) by using an ultrasonic tip for 10 minutes. The dispersion was then ultracentrifuged at 80000 g for 3 h and the supernatant collected. The final concentration of nanotubes was determined to be 48 mg L^{-1} by UV/Vis spectroscopy. Subsequently, $KAuCl_4$ (0.3 mg) was added to the black solution of carbon nanotubes (1.2 mL) to yield the carbon nanotube/Au nanoparticle hybrid, which was comfirmed by Raman spectroscopy and transmission electron microscopy (TEM) images (see the Supporting Information). Furthermore, an optimized procedure for the high-resolution transmission electron microscopy (HRTEM) sample was used, in which the sample was incubated at 60°C for 1 h to yield uniformly distributed Au nanoparticles on the SWNTs.

As shown in Figure 1, the TEM studies confirmed the successful formation of the Au nanoparticles on the sidewalls of carbon nanotubes. Well-dispersed and isolated Au nanoparticles can be seen to decorate the walls of the nanotubes quite uniformly. The energy dispersive X-ray (EDX) spectrum (see the Supporting Information) identified the black dots as gold. No nanoparticles were observed in a blank experiment without treatment with the metal salt. The high-resolution TEM image (Figure 1b) indicates an average size of the Au nanoparticles of 2.94 ± 0.75 nm, which was determined from a statistical study with 36 nanoparticles. On the basis of the dimensions of the SWNT (length: 300 nm, diameter: 1.4 nm) and the assumption of a spherical shape of the nanoparticles, it can be calculated that 7.5×10^{-17} g of gold is coated on one individual nanotube and one tube contains about 300 Au nanoparticles. More interesting results were observed after increasing the metal salt concentration in the solution of the carbon nanotubes to 3.5 mM. Figure 2 shows the TEM image with Au nanoparticles of 9-nm diameter aligned on the carbon nanotubes.

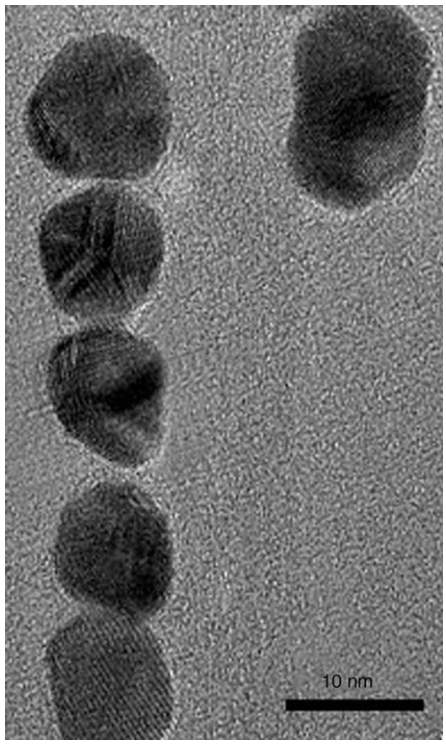

Figure 2. High-resolution TEM image of the carbon nanotube/Au nanoparticle hybrid obtained from a solution of carbon nanotubes suspended in Tween 80 (3.5 mM of $KAuCl_4$).

A frontier orbital picture describing the chemistry of carbon nanotubes suggested by Joselevich[15] could be used to explain these surprising experimental results. Carbon nanotubes have a rich electronic structure that stems from the quantization of the wave vector of the carbon nanotube along the circumferential direction. When $(n-m)/3$ is an integer (where both integers n and m define the nanotube chirality), the carbon nanotube is metallic, otherwise it is semiconducting. The frontier orbitals of semiconducting nanotubes are related to the first van Hove singularities in the valence and conduction bands, whereas those of metallic nanotubes correspond to the orbitals near the Fermi level. The frontier orbital picture of the reduction reaction of $AuCl_4^-$ at the surface of a carbon nanotube can be represented as shown in Figure 3. It is well known that the electrochemical potential measured with respect to a reference electrode is related to the absolute potential relative to the vacuum level. The potential scale versus the vacuum level can be calculated using the equation: V_{abs}(versus vacuum

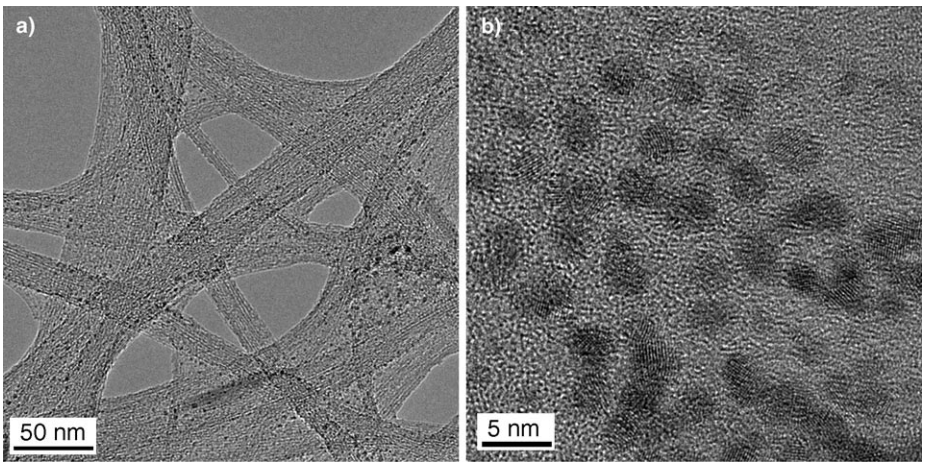

Figure 1. TEM images of the carbon nanotube/Au nanoparticle hybrid (a), and high-resolution TEM image of the carbon nanotube/Au nanoparticle hybrid (b) obtained from a solution of carbon nanotubes suspended in Tween 80 (0.46 mM of $KAuCl_4$; focusing on the Au nanoparticles prevents visibility of the SWNTs, Figure 1b).

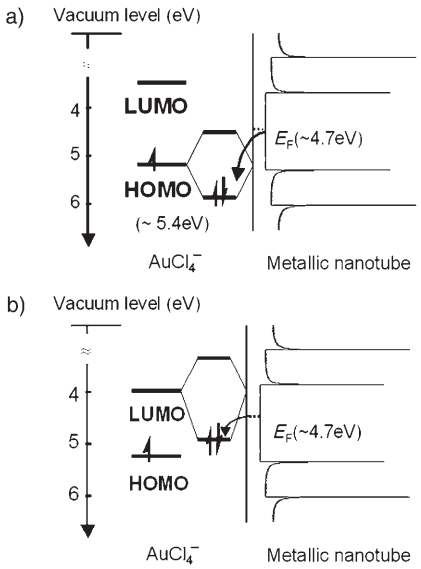

Figure 3. Frontier-orbital picture representation of four-electron interactions (a) and zero-electron interactions (b) between $AuCl_4^-$ and a metallic carbon nanotube. The $AuCl_4^-$ frontier orbitals are designated as HOMO and LUMO, and the nanotube orbitals are represented by the density of states plots. A similar picture can be applied for semiconducting carbon nanotubes (not shown). E_F = fermi level.

level) = V(versus normal hydrogen electrode (NHE))+4.44 V, as derived by Trasatti.[16] Since the reduction potential of $AuCl_4^-$ corresponds to 1.002 V,[17] the HOMO level is 5.44 eV. Here the work function of individual single-walled carbon nanotubes was chosen as approximately 4.7 eV.[18]

Since the relative position of the Fermi level of nanotubes with respect to the mixed metal ion/nanotube HOMO and LUMO is suitable for charge transfer, both semiconducting and metallic carbon nanotubes may establish attractive interactions with the metal ions, either by four-electron interactions involving two occupied orbitals (Figure 3a) or zero-electron interactions involving two empty orbitals (Figure 3b). It is worth noting that the HOMO level of $AuCl_4^-$ is partly occupied with electrons.

Figure 4a and b show the radial breathing mode (RBM) and tangential G-band of the Raman spectra, respectively, of carbon nanotubes suspended in Tween 80 after the successive addition of $KAuCl_4$ (excited at 532 nm). An increase in the concentration of the metal salt results in both the RBM and tangential G-band decaying significantly as a consequence of a depletion of singular features in the density of states of the carbon nanotubes. This observation is a strong indication of the removal of electrons from the conduction band of carbon nanotubes following the reduction of metal ions at the surface of nanotubes. Similar behavior was reported for chemical[19] and electrochemical redox doping.[20] It is also interesting to note that the peak of the tangential G-band shifted to a higher frequency. This shift can be interpreted as a stiffening of the graphene mode, caused by the introduction of holes into the conduction band of nanotubes as a result of the charge-transfer interaction.[20]

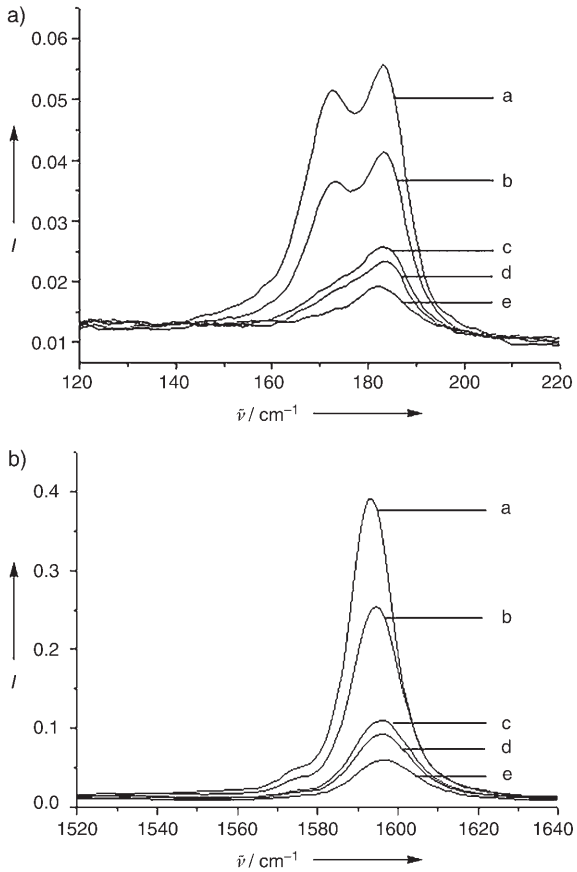

Figure 4. Raman spectra of SWNTs suspended in Tween 80 after the addition of various amounts of metal salt (0 mM, 0.1 mM, 0.5 mM, 1 mM, and 5 mM of $KAuCl_4$ (a–e)) with excitation at 532 nm. The plots display the region of RBM mode (a) and the region of tangential G-band (b). I = intensity, arbitrary units.

In summary, a novel carbon nanotube/Au nanoparticle hybrid material was prepared in a homogeneous phase by using the reduction reaction of gold salts with surfactant-suspended carbon nanotubes in water. It has been observed that well-dispersed Au nanoparticles were formed quite uniformly on the side walls of nanotubes. Frontier orbital pictures can explain this phenomenon. The process is easy to scale up and the size can be controlled. More importantly, a water-soluble and processable product is obtained. Further study is underway to align metal nanoparticles on individual carbon nanotubes, which is an attractive challenge in the generation of nanoscale building blocks.

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