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Attachment of Gold Nanoparticles to Carbon Nanotubes

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Abstract: Carbon nanotubes were initially chemically modified with an H_2SO_4-HNO_3 treatment, and subsequently activated with Pd-Sn catalytic nuclei *via* a one-step activation approach. These activated nanotubes were used as precursors for obtaining gold nanoparticles-attached nanotubes *via* simple electroless plating. This approach provides an efficient method for attachment of metal nanostructures to carbon nanotubes. Such novel hybrid nanostructures are attractive for many applications.

Keywords: Carbon nanotubes, gold nanoparticle, electroless plating.

Since their discovery in 1991[1], carbon nanotubes have been of great interest because of their unique structural, electrical, and mechanical properties. Their potential applications include nanodevices, quantum wires, ultrahigh-strength engineering fibers, sensors, and catalyst supports[2-4]. For optimizing the uses of nanotubes in many of these applications, it is necessary to attach the functional groups to their surfaces and then assemble the nanotubes into desired structures or attach other nanostructures to the nanotubes[5-7]. In the present study, a simple electroless plating method for attachment of gold nanoparticles to the surfaces of carbon nanotubes is introduced. Multiwalled carbon nanotubes (MWNTs) produced by using a catalytic decomposition of acetylene method were initially modified chemically with H_2SO_4-HNO_3 and subsequently activated *via* a one-step activation approach[8]. When the activated MWNTs were immersed in an electroless plating bath, metal deposition occurred at the catalytic sites. The deposited metal clusters then further catalyzed metal deposition on the tube surfaces (autocatalytic process). Novel hybrid nanostructures with homoge neously distributed gold nanoparticles on MWNT resulted.

To the best of our knowledge, this is the first report of attachment of gold nanoparticles to carbon nanotubes *via* electroless plating.

The MWNTs were synthesized by silica-supported cobalt-based catalytic decomposition of acetylene (C_2H_2) at 900℃ in an N_2 atmosphere. The as-produced MWNTs displays uniform outer diameter (40-50 nm) and length (40-60 μm) under transmission electron microscope (TEM). The as-produced MWNTs were suspended in a

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concentrated sulfuric acid/nitric acid mixture (3:1 v/v) and refluxed at 140℃ for about 6 h, then thoroughly washed with distilled water, and dried at 100℃. In the previous research on MWNTs[9], this acid-treatment was reported to result in carboxyl, carbonyl, hydroxyl, and sulfate groups on the carbon nanotubes, but their locations were unknown. In the present work, with the diffusion reflectance infrared fourier transform (DRIFT) spectroscopy, we studied the raw and acid-treated MWNTs (as shown in Figure 1), and confirmed that these functional groups: carbonyl and carboxyl groups (1600-1700 cm^{-1}), hydroxyl and phenolic groups (3300-3500 cm^{-1}) were presented on MWNTs. Because these functional groups are hydrophilic, the MWNTs can be dispersed easily in water.

The nanotubes were then activated *via* a one-step activation approach by stirring the acid-treated tubes in a $PdCl_2/SnCl_2$ colloid solution for 10 min. Pd-Sn catalytic seeds protected by the Sn colloidal layer were introduced onto the surfaces of the acid-treated tubes. The functional groups of the surfaces and the $PdCl_2/SnCl_2$ colloid solution interacted. The activated tubes were then washed with 1 mol/L HCl and distilled water in turn to preferentially dissolve the Sn protective layer, exposing the catalytic Pd-Sn nuclei to a greater extent.

Gold nanoparticles attached carbon nanotubes were obtained by immersing the activated tubes in the gold electroless-plating bath for 5 min. When the activated tubes were immersed in the electroless plating bath, gold deposition occurred at the catalytic sites. The deposited clusters of metal atoms then further catalyzed gold deposition on the tube surfaces (autocatalytic process). The resultant materials were then separated by centrifugation and washed with distilled water. The gold electroless plating bath was

Figure 1 DRIFT spectra of (a) the raw carbon nanotubes material and (b) H_2SO_4-HNO_3 treated samples

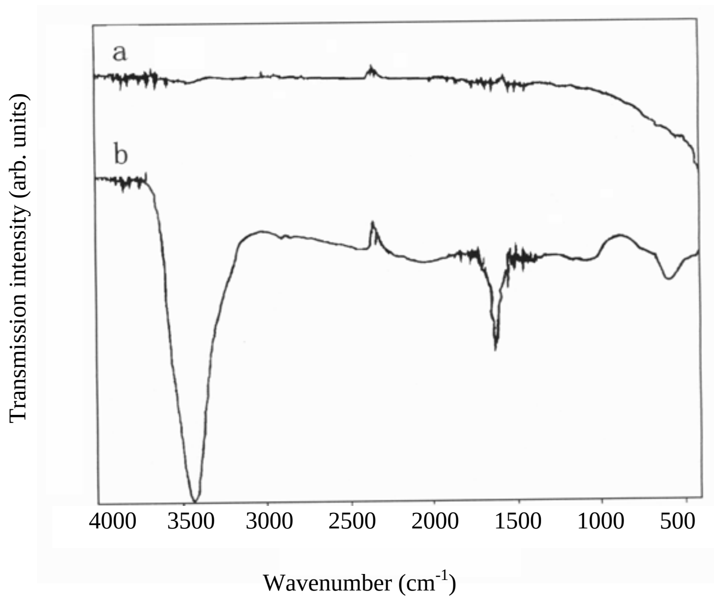


Figure 2 HRTEM micrographs showing gold nanoparticles-attached carbon nanotubes

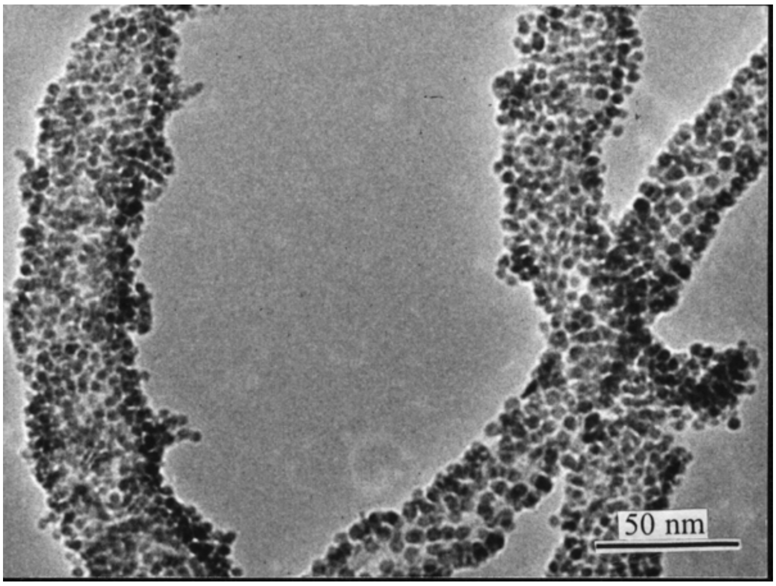
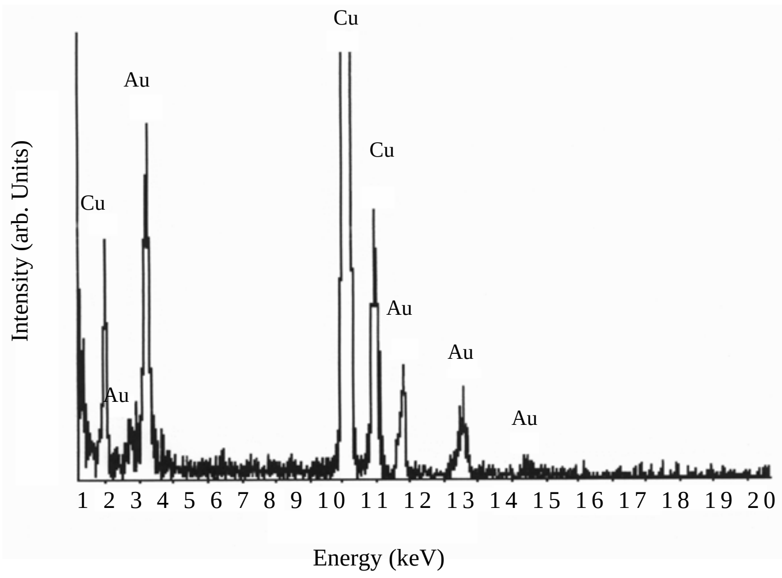


Figure 3 EDX spectrum of an gold-attached carbon nanotubes



composed of 0.7 g/L $KAu(CN)_2$, 5.5 g/L KCN, 5.6 g/L KOH, 5.0 g/L KBH_4 , 2.5 g/L Na_2EDTA, 25 mL/L glycolic amide, the pH was adjusted to 11 with diluted aqueous NaOH solution, at bath temperature of 20℃. After deposition and thorough washing with distilled water, HRTEM (high-resolution transmission electron microscopy) samples were prepared by dispersing the nanotubes in alcohol.

HRTEM studies confirmed the success of the attachment of gold nanoparticles to MWNTs, as shown in **Figure 2**. Well-dispersed gold nanoparticles decorate the walls and ends of the nanotubes quite uniformly, with a particle size distribution sharply centered at around 3-4 nm of diameter. EDX (energy dispersive X-ray spectroscopy) microanalysis studies of the nanoparticles evidenced the presence of Au when the electron beam was focused on the decorated areas (**Figure 3**) (the peaks of Cu come from the Cu support grid). It is also noted that the interaction between the gold nanoparticles and nanotubes is quite strong, even repeated washing and vigorous ultrasonication cannot remove them.

As a contrast, acid-treated MWNTs (without activation treatment) were immersed in the gold electroless plating bath, and almost no gold nanoparticles were found on the nanotubes. This indicates that activation plays a key role in the attachment; it acts as a bridge to connect gold nanopartcles with nanotubes.

In summery, gold nanoparticles were anchored to the surfaces of MWNTs by a simple electroless plating method. Through acid-treatment and one-step activation, the surfaces of carbon nanotubes can be tailored to be catalytic; so many other metal nanoparticles can be attached to the surfaces of nanotubes. These heterostructures decorated nanotubes could be used in catalytic, electronic, optical, and magnetic applications.

References

1. S. Iijima, *Nature*, **1991**, *354*, 56.
2. P. G. Collins, A. Zettl, H. Bando, *et al.*, *Science*, **1997**, *278*, 100.
3. S. J. Tans, M. H. Devoret, H. J. Dai, *et al.*, *Nature*, **1997**, *386*, 474.
4. J. Kong, N. R. Franklin, C. W. Zhou, *et al.*, *Science*, **2000**, *287*, 622.
5. Q. Chen, L. Dai, M. Gao, S. Huang, A. Mau, *J. Phys. Chem. B*, **2001**, *105*, 618.
6. R. J. Chen, Y. Zhang, D. Wang, H. J. Dai, *J. Am. Chem. Soc.*, **2001**, *123*, 3838.
7. S. Fullam, D. Cottell, H. Rensmo, D. Fitzmaurice, *Adv. Mater.*, **2000**, *12*, 1430.
8. L. M. Ang, T. S. A. Hor, G. Q Xu, *et al.*, *Chem. Mater.*, **1999**, *11*, 2115.
9. R. Yu, L. Chen, Q. Liu, *et al.*, *Chem. Mater.*, **1998**, *10*, 718.

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