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Selective Attachment of Gold Nanoparticles to Ionic Liquids Adsorbed Multiwalled Carbon Nanotubes

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Abstract: Room temperature ionic liquids were adsorbed on the surface of the multiwalled carbon nanotubes (MWCNTs) by electrostatic interaction between carboxyl groups on the chemically oxidized MWCNTs surface and room temperature ionic liquids. The cations of ionic liquids and carboxyl groups on the carbon nanotube surface are put into a one-to-one correspondence by the electrostatic interaction. Negatively charged 15 nm gold nanoparticles are subsequently anchored to the surface of the MWCNTs through the electrostatic interaction between the ionic liquids and the gold nanoparticles. Gold nanoparticles are selectively attached to chemically functionalized surface sites of carbon nanotubes. This approach provides an efficient method to attach other nanostructures to carbon nanotubes and can be used as an illustrative detection of the functional groups on carbon nanotube surfaces.

Keywords: Carbon nanotubes, surface treatment, gold nanoparticles, modification, ionic liquids.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], a great amount of research work on CNTs and related nanostructures has been carried out due to their unique electronic structure, molecular dimensions, and shape, making them attractive in nanotechnology and materials science. Their potential applications include nanodevices [2], quantum wires [3], ultrahigh-strength engineering fibers [4], sensors [5], and catalyst support [6]. To optimize the use of nanotubes, many times there is a need to attach functional groups to their surface and then assemble the nanotubes into structures or attach other nanostructures to the nanotubes [7].

These unique properties make carbon nanotubes very useful for supporting metal nanoparticles in many potential applications, ranging from advanced catalytic systems through very sensitive electro-chemical sensors to highly efficient fuel cells. Consequently, the functionalization of carbon nanotubes with metal nanoparticles has attracted great interest in recent years. And a few interesting routes have now been devised for either covalently or noncovalently attaching certain metal nanoparticles onto carbon nanotubes. In addition, there is a need to attach functional groups to the carbon nanotube surface and then assemble the nanotubes into structures or attach other nanostructures to the nanotubes [8-14].

Room temperature ionic liquids (ILs), which are composed of cation and anion, are widely used as an excellent green reaction media. We have reported the modification of MWCNTs with ionic liquids to improve their compatibility and stability, creating more opportunity for applications of MWCNTs in sensors and actuators by improving the electrical contact with bulky media. As the ionic liquids are composed of micromolecular cation, such as quaternary ammonium, dialkylimidazolium, tetra-alkylphosphonium, and anions, such as Br-, BF4-, PF6-, the electrostatic interaction between carboxyl groups on the nanotube surface and cations of ionic liquids are put into a one-to-one correspondence. Here we report a method to functionalize carbon nanotubes by the electrostatic interaction between carboxyl groups on the chemically oxidized nanotube surface and ionic liquids, and to attach gold nanoparticles from a gold colloid suspension to the surface of the nanotubes through the electrostatic interaction between the ionic liquids and the nanoparticles. It can be used for illustrative detection of the functional groups on carbon nanotube surfaces. And it can be of better use for illustrative detection of the functional groups on carbon nanotube surfaces [15]. In the present study, a new and simple method to attach gold nanoparticles on the surface of carbon nanotubes is introduced.

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2. Experimental Section

The MWCNTs material consists of structures containing highly oriented nanotubes of diameter 40-100 nm. According to the reference [16], the carbon nanotubes are modified by acid-treatment, which results in carboxyl, carbonyl and hydroxyl on the carbon nanotubes. The ionic liquid chosen in this reaction is 1-methy-3- hexylimidazolium bromide. The nanotubes suspension was mixed with ionic liquids aqueous solution for 120 mins at room temperature. Ionic liquids were adsorbed to the surface of the nanotubes because of the electrostatic interaction between the carboxyl groups and the cations of ionic liquids. After filtrating and thoroughly washing with deionized water, the nanotubes were dispersed in water again, and mixed with a gold colloid (15 nm) for 30 mins by stirring. The negatively charged gold nanoparticles (NPs) were anchored to the surface of the nanotubes through the electrostatic interaction between the cations of ionic liquids and the nanoparticles. After filtrating and thoroughly washing with deionized water, TEM samples were prepared by dispersing the nanotubes in water. The complete scheme for the modification of the nanotube surface and the attachment process of the gold nanoparticle on the nanotube surfaces is shown in Figure 1.

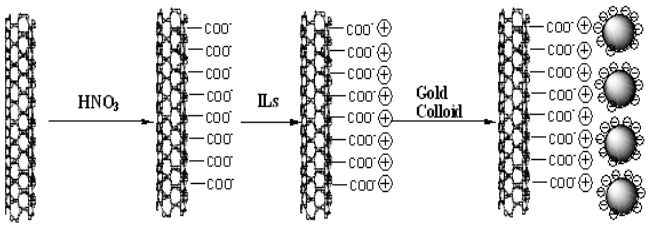

Figure 1 Schematic view of the process for anchoring gold nanoparticles to nanotubes.

3. Results and Discussion

The attachment of gold NPs on MWCNTs is confirmed by the TEM image. Figure 2 shows the TEM image of the MWNTs modified with gold particles. It can be seen that the gold particles preferentially adhere to the surfaces of MWNTs rather than to other regions without MWNTs. And the interaction between the gold nanoparticles and nanotubes is quite strong, because thorough washing does not remove them. Figure 3 represents the XPS signal of the Au 4f for the MWCNTs-Au. The binding energies of the doublet for Au $4f_{7/2}$ and $4f_{5/2}$ are 83.2 and 86.9 eV, respectively, which are consistent with Au^0 oxidation state. The above results indicate that those assembled Au particles are predominantly Au^0 at the surface.

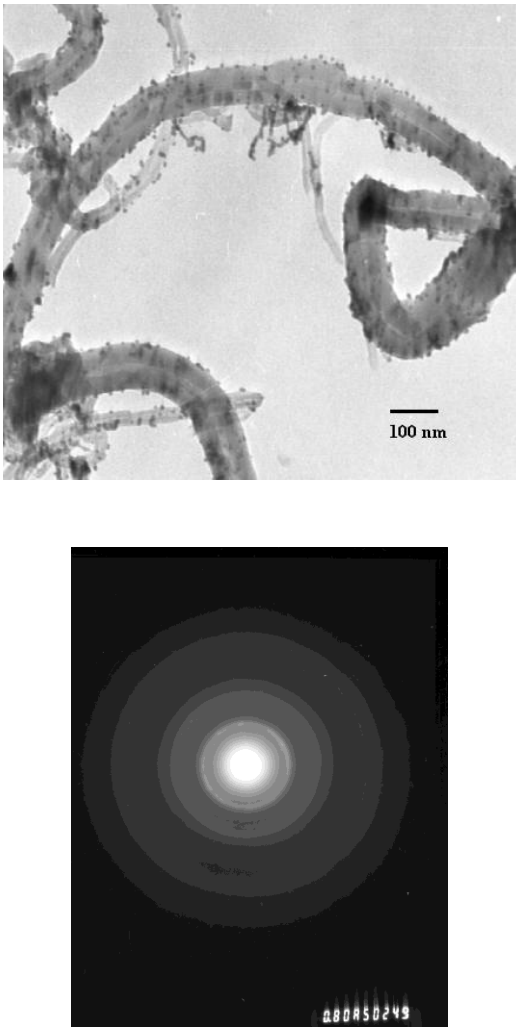

Figure 2 TEM and TED images of gold nanoparticles supported on undoped MWCNTs.

Single acid-treated MWCNTs (without ionic liquids treatment) were also mixed with gold colloid, and no gold nanoparticles were found on the nanotubes. This indicates that ionic liquid acts as a bridge to connect gold nanoparticles with MWCNTs nanotubes. Subsequent treatment with ionic liquids at room temperature and exposure to negatively charged gold nanoparticles showed that the carboxyl functional groups were present at the ends of the nanotubes. So it acts as an excellent method for monitoring the presence of carboxyl chemical groups on the surfaces of nanotubes [14].

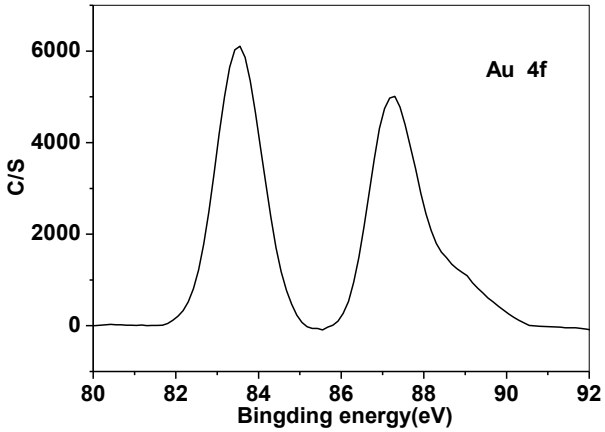

Figure 3 The narrow XPS spectra of the Au 4f region for MWCNTs–gold nanoparticles.

4. Conclusion

In summary, gold nanoparticles were anchored to the surfaces of MWCNTs nanotubes by a simple electrostatic adsorption. On account of the design ability of ionic liquids, some functional radical, such as hydrosulfuryl, amino, carboxyl and hydroxyl, etc., can be introduced into the ionic liquids by the molecular design. By choosing different kinds of functional ionic liquids, the surfaces of carbon nanotubes can be tailored to be negatively or positively charged, so many other nanoparticles, such as metal nanoparticles, semiconductor nanocrystals, magnetic nanoparticles, etc., can be selectively attached to the surfaces of nanotubes. Hopefully it opens up a new research branch of selective attachment of different nanoparticles on the surface of carbon nanotubes. And these nanoparticle-decorated nanotube heterostructures could be used in catalytic, electronic, optical, and magnetic applications. In addition, compared with the polyelectrolyte, ionic liquid is a simple micromolecule and the designability, as well as the method of decorating nanotubes by ionic liquids will be a more efficient way to be used to identify the location of functional groups.

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