Fabrication of Hg-Carbon Nanotubes Composite Materials in Solution

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Carbon nanotubes (CNTs) have excellent electronic properties, good chemical stability, and large surface area.[1-3] These unique properties make CNTs promising substrates for supporting metal nanostructures. CNTs-metal nanostructures assemblies can be useful in many potential applications including catalysts, electrochemical sensors, and fuel cells.[4,5] Previous approaches to metal functionalization of nanotubes include physical evaporation,[5] attachment after chemical modification of nanotubes,[6] solid-state reaction with metal salts at elevated temperatures,[7] and electroless deposition from salt solutions.[8,9] Recently, Lee *et al.* reported that metal nanostructure-CNTs assemblies can also be formed by the CNTs-mediated self-assembly of metal nanoparticles at the liquid/liquid interface.[10]

In this study, we present a novel solution-phase synthetic method for the fabrication of Hg-CNTs assemblies. Upon injection of CNTs solution into aqueous solution of mercury salt, Hg-CNTs composite materials with unusual superstructure were formed by spontaneous reduction of metal ions around the sidewalls of CNTs. This work is motivated by recent observations that nano-sized metal particles form spontaneously on the sidewalls of CNTs in solutions containing metal ions.[8,9] The deposition of particles proceeds without the aid of reducing agents or catalysts. Experimental results show that the present method is facile and simple with high preparation success rates. Hg-CNTs composites were characterized with field-emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectroscopy (EDS), and Raman spectroscopy, In particular, Raman spectroscopy permits distinguishing charge transfer between CNTs and mercury.

Experimental Section

The method for the preparation of multi-walled CNTs (MWCNTs) and single-walled CNTs (SWCNTs) was reported previously.[10] The CNTs were cleaned by sequentially sonicating in toluene, acetone, and diethyl ether. Hg-CNTs composites were fabricated as follows. The 5.0 mL of the freshly prepared Hg salt (Hg(NO$_3$)$_2$, HgCl$_2$, and Hg(CH$_3$COO)$_2$) aqueous solution (1 mM) was taken in a vial. When preparing Hg salt solution, HNO$_3$ was added to acidify the solution in order to prevent the formation of HgO. To the aqueous solution of mercury salt, 1.0 mL of a solution of CNTs (SWCNTs or MWCNTs) in acetone was injected and the solution was stirred for 20 min. And then, 4.0 mL of diethyl ether was added to the aqueous solution resulting in a biphasic mixture with organic part on top and aqueous solution below. Hg-CNTs composites were then immediately transferred to the aqueous/organic interface.

The scanning electron micrographs and the EDS data of the samples were taken with field emission scanning electron microscope (FESEM, Phillips Model XL30 S FEG). Raman spectra were obtained using a Jobin Yvon/HORIBA LabRAM spectrometer equipped with an integral microscope (Olympus BX 41). The 632.8 nm line of an air-cooled He/Ne laser was used as an excitation source. Raman scattering was detected with 180° geometry using a thermoelectrically cooled 1024 × 256 pixel CCD detector.

Results and Discussion

Acetone solution of CNTs was added to the freshly prepared Hg salt solution, and resultant solution was shaken gently for 20 min. When making a biphasic mixture by taking diethyl ether to the aqueous solution, a thin film was immediately formed at the aqueous/organic interface. In a control experiment, same process was performed with only acetone. However, nothing was fabricated at the interface. Therefore, the acetone does not influence the formation of interfacial films. The interfacial film is a composite material consists of Hg metal and CNTs (vide infra). The aqueous/organic biphasic system was used as a medium in the formation of composite materials because CNTs and related materials can be readily assembled at the aqueous/organic interface by decorating the surface of CNTs by appropriate materials.[9,10] From this interfacial entrapment process, the composite materials can be easily collected without further purification step such as centrifugation. The interfacial films were collected by transferring them to solid substrates. In fact, the biphasic mixture was poured into a Petri dish and the diethyl ether phase evaporated to leave a uniform thin film on the surface of water. This film was lifted onto mica substrates for further analysis. The transferred films were very stable for prolonged time. The physicochemical characteristics of these films were examined by various analytical tools such as SEM, EDS, and Raman spectroscopy.

The morphologies and microstructures of the as-prepared interfacial films were studied by means of SEM. Figure 1a shows a typical SEM image of the film obtained with
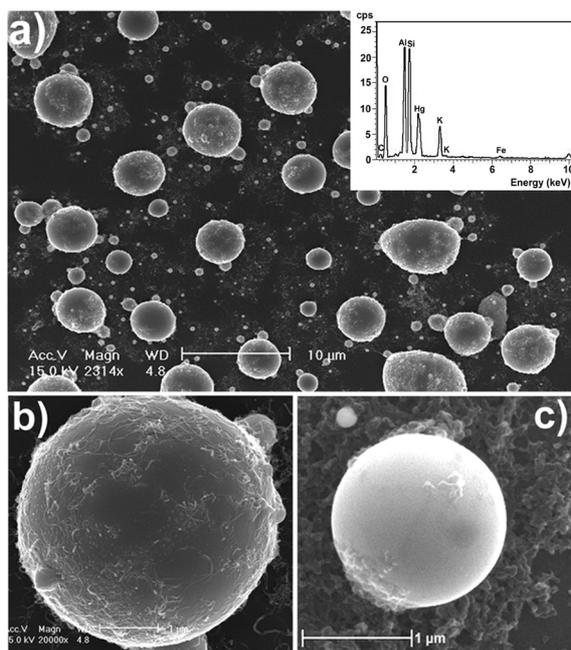
Figure 1. (a) SEM image of the Hg-MWCNTs composites. Inset shows EDS spectrum of the composites. High magnification SEM images of (b) the Hg-MWCNTs and (c) the Hg-SWCNTs composites.

Figure 2. SEM images of Hg-MWCNTs composites at the different stage of reaction: (a) 1, (b) 5, (c) 15, and (d) 20 min after the injection of MWCNTs solution to aqueous solution of mercury salt.

MWCNTs and $Hg(NO_3)_2$. The image shows that the interfacial film is composed of certain superstructured materials with mostly spherical shape. The average size of the superstructure is 4.3 ± 1.3 μm. The higher magnification SEM image of the materials presented in Figure 1b indicates that the superstructure is a composite material formed by assembly of mercury and MWCNTs. The presence of Hg and CNTs in the sample was further confirmed by EDS analysis during the SEM observation (inset of Figure 1a). The EDS spectrum shows the peaks of Hg and C, along with peaks for O, Al, Si, Fe, and K arising from the mica substrate. We also observed the formation of superstructures at the liquid/liquid interface when using SWCNTs (Figure 1c). Moreover, similar composite materials could be fabricated with other Hg salts such as $HgCl_2$ and $Hg(CH_3COO)_2$ instead of $Hg(NO_3)_2$.

From the SEM measurements for a series of samples prepared by the present method with different time, the formation and evolution of superstructures could be monitored. Figure 2 shows the typical SEM images of Hg-MWCNTs samples taken after reaction for 1, 5, 15, and 20 min, respectively. Within 1 min, Hg selectively coated the sidewalls of CNTs. Along the reaction proceeds, nano-sized Hg structures were formed and then grew and some of them attached together. After reaction time prolonged to 20 min, many superstructures were found as the result of evolution of the Hg nanostructures (Figure 2d). Same experiment with higher (5 mM) or lower (0.5 mM) concentration of Hg salt solution gave the similar results. These results show that Hg-CNTs composite materials with unusual superstructure can be readily prepared by our simple aqueous phase synthetic
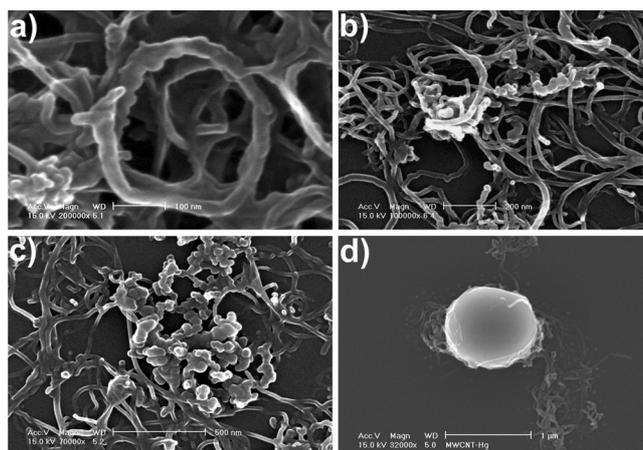
method. Indeed, the construction of superstructures made of CNTs is one of the challenges in nanotube chemistry.[11]

The formation of Hg nanostructures around the sidewalls of CNTs can be ascribed to the result of direct redox reaction between metal ions and nanotubes. Metal cations can be spontaneously reduced on the surface of CNTs because of the difference in reduction potential between metal cations and CNTs. H. Dai *et al.* reported that the relative potential levels rationalize the spontaneous electron transfer from the nanotube to the metal ions.[8] Since CNT has a reduction potential of about +0.5 V vs SHE (standard hydrogen electrode),[8,9] it can reduce Hg^{2+} (Hg^{2+}/Hg, +0.851 V *vs.* SHE)[12] into metal nanostructures through a galvanic displacement reaction without the aid of a reducing agent. To validate the mechanism of the formation of nanostructures, we have performed the same experiments using other heavy metal ions of a reduction potential lower than that of CNTs, *i.e.*, Pb^{2+} (Pb^{2+}/Pb, −0.126 V vs SHE), Cd^{2+} (Cd^{2+}/Cd, −0.403 V *vs* SHE).[12] As expected, Pb and Cd structures have not been formed on nanotubes via spontaneous reduction of the metal ions by CNTs.
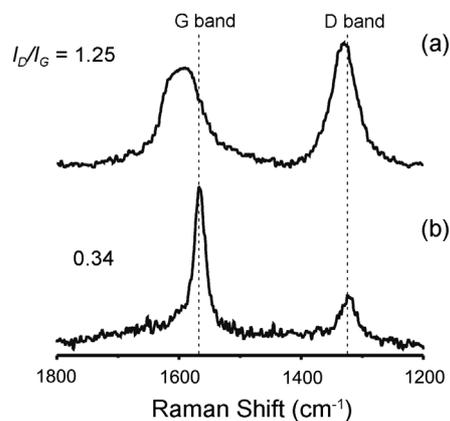

Figure 3. Raman spectra of (a) the Hg-MWCNTs composites and (b) the pristine MWCNTs.

To gain insight into the nature of the Hg-CNTs composite materials, Raman spectra of Hg-CNTs composites on mica were measured. Figure 3 shows the Raman spectra of the films of Hg-MWCNTs composites and pristine MWCNTs. As shown in Figure 3, representative Raman peaks such as a tangential G band and D band of CNTs were observed in the Hg-MWCNTs composites.[13] Comparison of the Raman spectrum of the Hg-MWCNTs composites with that of the pristine MWCNTs shows some noticeable features. The D band intensity remarkably increases in the case of the composites. This is reflected in the increase in the I_D/I_G value (intensity ratio of D band relative to the G band) (see Figure 3). There was also an increase in the bandwidth of G band. The increases in the I_D/I_G ratio and bandwidth of G band are an indication of an increase of the defects in the nanotube lattice.[13,14] Besides, the formation of composites has a great effect on the peak position of G band of the nanotubes. The G band is significantly shifted upward by 24 cm^{-1}. In the previous reports on the functionalization of the CNTs, the upward shift of G band has been explained to be the result of functionalization affecting the phonon structure and coupling to isoenergetic electronic states above the shifted Fermi level through the charge transfer interaction between the CNTs and the addend.[14,15] All the observed Raman spectral features indicate that certain structural changes of nanotubes surely occur on the formation of Hg-CNTs composites. This appears to relate to the above mentioned mechanism of the formation of composites; metallic structures are spontaneously formed on the sidewalls of CNTs by electron transfer from CNTs to metal ions. The observed structural changes of CNTs reveal that the prepared samples should be composite materials instead of simple mixtures.

Conclusions

We have developed a new solution-phase method for synthesis of Hg-CNTs assemblies. By injection of CNTs solution into the aqueous solution of mercury salt, Hg-CNTs composite materials with a novel superstructure can be prepared. From interfacial entrapment process, the composite materials can be easily collected without further purification step. The composites have spontaneously formed through direct redox reaction between CNTs and Hg cations. This phenomenon has been probed by SEM, EDS, and Raman spectroscopy.

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