Characterization of metal-carbon nanotube composites prepared by electrostatic interaction

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Nanocomposites of novel metals (gold and silver) and multi-walled carbon nanotubes (MWNTs) were prepared by electrostatic interaction. Both gold and silver nanoparticles were stabilized by sodium dodecyl sulfate (SDS), poly (sodium 4-styrene sulfonate) (PSS) and poly (4-vinylpyrrolidone) (PVP) in aqueous medium, and MWNTs were modified by poly(diallydimethylammonium) chloride (PDDA) in water. The as-prepared nanocomposites were structurally and electrically characterized by transmission electron microscopy (TEM), Field Emission Scanning Electron Microscopy (FESEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and UV/Vis spectroscopy.

1. Introduction

Carbon nanotubes (CNTs) have continuously attracted much interest because of their outstanding mechanical, chemical and electric properties (Unger et al., 2003). However, high agglomeration tendency caused by strong inherent attractive van der Waals interaction makes a difficulty in their applications (Zhao et al., 2002; Star and Stoddart, 2002; Thess et al., 1996; Ausman et al., 2000). To overcome the problem and improve the processibilty, CNTs have been treated with either strong acids or some surfactants (Hirsch, 2002; Dyke and Tour, 2004). Nanoparticles of metal, metal oxide, and semiconductor are also of great interest due to their potential applications as microelectronics, optoelectronics, catalysis, and information storage (Feldheim and Foss, 2000; Gopidas et al., 2003; Georgakilas et al., 2007).

Combining two characteristic nanostructured materials is expected to provide a versatile building block for the construction of modern nanodevices. For instance, the decoration of CNTs with some nanoparticles expands their applications from CNT-assisted catalytic systems to complex conductor networks in microelectronics (Unger et al., 2003; Georgakilas et al., 2007). Especially, nanoparticle-deposited CNTs are important due to their potential applications as broad-band optical emitters (Chin et al., 2005), electrodes (Guo and Li, 2005) and catalysts (Xue et al., 2001).

The introduction of nanoparticles to the sidewalls of CNTs is mainly

stimulated by their characteristic interactions, leading to nano-sized composites of nanoparticles and CNTs (Yang and Sacher, 2005; Bittencourt et al., 2007). In order to prepare the nanocomposites consisted of CNTs and nanoparticles, it is required to disperse CNTs well in solution and improve physical or chemical interactions between CNTs and nanoparticles. In our previous work (Rabbani et al., in press) we investigated the effect of dispersion agents on MWNT's dispersion in water. In this work we have studied the variation effect of surfactants on nanocomposites prepared with MWNTs and metal (gold and silver) nanoparticles. Sodium dodecyl sulfate (SDS), poly (sodium 4-styrene sulfonate) (PSS) and polyvinylpyrrolidone (PVP) were used as stabilizer to prepare both gold and silver nanoparticles in water, and MWNTs were modified with poly(diallydimethylammonium) chloride (PDDA) in water to develop the positively-charged surfaces.

2. Materials and Methods

To prepare Au-MWNT composite, 3 ml aqueous solution of gold nanoparticles (GNPs) stabilized by PVP was mixed with 1 ml of PDDA-treated MWNT aqueous dispersion. All the mixture dispersions were agitated well to prepare metal-MWNT nanocomposites. According to the same method as above, gold and silver nanoparticles stabilized by PSS and SDS were also mixed with PDDA-treated MWNTs aqueous dispersion separately. The metal/MWNT nanocomposites were precipitated by centrifugation and washed by distilled water. Prior to prepare nanocomposites, a series of negatively-charged metal nanoparticles, which were stabilized by PVP, PSS, and SDS, were prepared by the methods described in literatures (Hao and Lian, 2000). Carboxylated MWNTs were used to prepare positively-charged MWNTs via treatment of PDDA (Wen et al., 2007).

UV/Vis spectra were collected using an S-3100 Scinco spectrophotometer in single-beam mode and in the range of 400 - 800 nm with water as blank. Transmission electron microscopic images were obtained in JEOL 2010F microscope. TEM samples were prepared on carbon grids of 400 mesh by dip-coating in dilute solutions (1.0 wt% solid content). X-ray photoelectron spectroscopy (XPS) measurement was carried out by VG Scientific Escalab 250 at KBSI (Busan, Korea). The detailed nanocomposite structures were analyzed by FESEM (Quanta, FEG model, operated at 25 kV) and x-ray diffractometer (PANalytical X'pert Pro MPD) equipped with a reflection geometry and a fixed anode x-ray generator of a CuK_α radiation source.

3. Results and Discussion

Metal nanoparticles show a characteristic absorption peak, called as surface plasmon band, as measured by UV/Vis spectrometer (Gittins and Caruso, 2001; Lee et al., 2008). Generally surface plasmon in nanoparticles is caused by the fluctuations of electron density surrounded in nano-sized metal, and dependent on the size and the shape of nanoparticles (Link and El-Sayed, 1999). Figure 1 shows the absorption spectra of (a) gold nanoparticles (GNPs) and (b) silver nanoparticles (SNPs), which were stabilized by various surfactants such as PVP, PSS, and SDS. All the spectra showed the characteristic absorptions caused by surface plasmon. Peak position of the absorption slightly changed according to the surfactant used for preparation of nanoparticles. The use of PVP shifted to the shorter absorption position compared to the others. As shown in figure 1(b), the absorption positions of SNPs (ca. 400 nm) were

shorter than those of GNPs (ca. 520 nm). This indicates that the sizes of as-synthesized SNPs in a solution are smaller than those of GNP analogues. An abnormal shoulder in higher wavelength region of Ag(SDS) is caused by the broad size distribution of the as-synthesized SNPs.
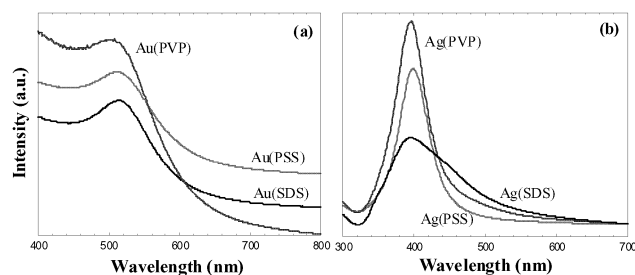

Figure 1. *UV/vis absorption spectra of (a) gold nanoparticles and (b) silver nanoparticles in aqueous solution. The notation of each spectrum in the parenthesis indicates the gold or silver nanoparticles stabilized by PVP, PSS, and SDS, respectively.*

Figure 2 shows the microscopic images of Metal-MWNT nanocomposites. GNPs stabilized by PVP were well distributed in the MWNT networks, whereas GNPs and SNPs stabilized by PSS and SDS were aggregated in the MWNT networks and their sizes became large. This result could be supported by the TEM images in figure 2(d) and (h), in which GNPs stabilized by PVP were well distributed in the sidewalls of MWNTs without any aggregation. On the other hand, SNP analogues distributed in the MWNT networks were aggregated and their sizes were too large to decorate the sidewalls of MWNTs.
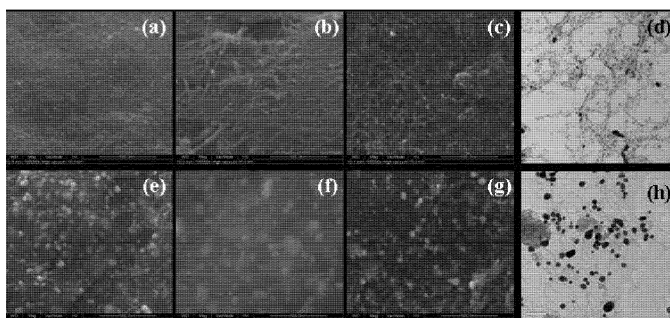

Figure 2. *SEM images of metal-MWNT nanocomposites. (a) Au(PVP)-MWNT, (b) Au(PSS)-MWNT, (c) Au(SDS)-MWNT, (e) Ag(PVP)-MWNT, (f) Ag(PSS)-MWNT, (g) Ag(SDS)-MWNT. (d) and (h) are the TEM images of nanocomposites (a) and (e), respectively.*

As compared to Au-MWNT nanocomposites, the sizes of silvers were larger than golds in their nanocomposites. These SEM images showed that the size and distribution of nanoparticles in the MWNT networks were also dependent on the surfactants used for nanoparticle preparation. When PSS and SDS were used to prepare

nanoparticles, the resultant nanoparticles have got together and form globules. This figures show that the inter-particle agglomeration of GNPs has been reduced only in GNPs stabilized by PVP.

The characteristic sharp peaks corresponding to the (111), (200), (220), and (311) facets of gold and silver NPs were found by XRD measurements on these nanocomposites as shown in figure 3. The peaks demonstrated that the as-prepared nanoparticles were pure crystalline with a face-centered cubic structure (Lee et al, .2007).
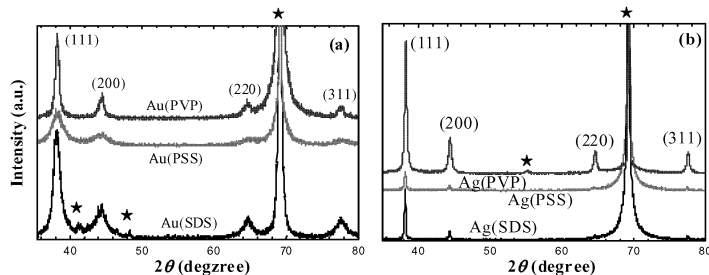

Figure 3. XRD patterns of (a) Au-MWNT and (b) Ag-MWNT nanocomposites. The description on each pattern represents that gold or silver nanoparticles included in the nanocomposite are stabilized by PVP, PSS and SDS, respectively. Stars in these figures were assigned to Si peaks (~70 °) or impurity peaks.
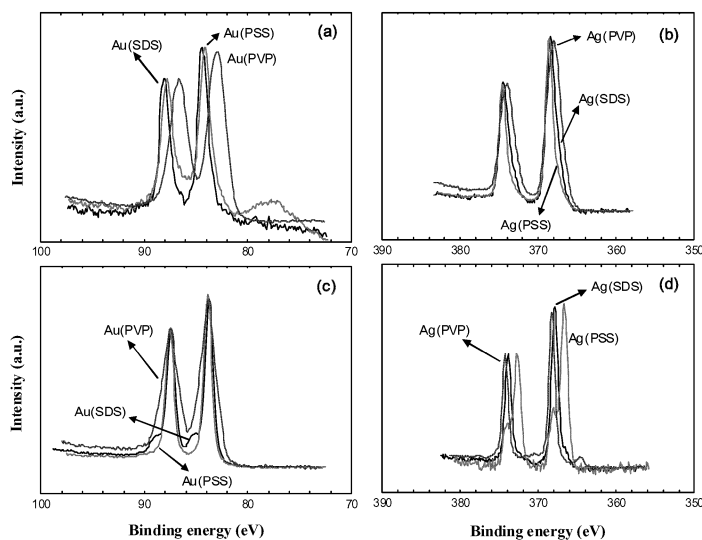

Figure 4. XPS spectra of (a) gold nanoparticles, (b) silver nanoparticles, (c) Au-MWNTs and (d) Ag-MWNT nanocomposites. Each description in parenthesis represents the surfactants (PVP, PSS and SDS) used for stabilizers of gold or silver nanoparticles.

XPS data provide the important evidence for the formation of metal-MWNTs nanocomposites. The inter-particular interaction between nanoparticles and MWNTs during the formation of nanocomposite causes the redistribution of electron densities

and changes the binding energy states of nanoparticles. Our previous results (Rabbani et al., in press) supported this interpretation.

As shown in figure 4, binding energies of nanoparticles were dependent on the species of surfactants; (Au $4f_{5/2}$ and $4f_{7/2}$) 86.7 eV and 83.3 eV for Au(PVP), 87.8 eV and 84.1 eV for Au(PSS), 88.1 eV and 84.4 eV for Au(SDS), (Ag $3d_{5/2}$ and $3d_{7/2}$) 374.0 eV and 368.0 eV for Ag(PVP), 374.6 eV and 368.6 eV for Ag(PSS), 374.5 eV and 368.5 eV for Ag(SDS). The higher shift of binding energy might be caused by the electrical repulsion between the surface electrons of nanoparticles and negatively-charged surfactants covering the nanoparticles. In both gold and silver nanoparticles, PSS and SDS with anionic character shifted the binding energies of the gold and silver nanoparticles to the higher positions than PVP. As nanocomposites were formed from nanopartices (Au or Ag) and MWNTs, the electron densities accumulated by negatively-charged surfactants were re-distributed into the nanoparticles and the surfaces of MWNTs. The binding energies of nanoparticles covered by PVP shifted toward the higher positions by the formation of nanocomposites, whereas others covered by PSS and SDS shifted toward the lower positions. Although the reason was not understood yet, the higher binding energy might be caused by the difference of the electron redistribution of PVP unlike PSS and SDS.

4. Summary

A series of metal nanoparticles and their composites were prepared by the intrinsic electrostatic interaction of counter-charged stabilizers for nanoparticles and MWNTs and compared each other. Nanoparticles stabilized by PVP, PSS and SDS were negatively charged in an aqueous solution. On the other hand, PDDA stabilized MWNTs have positively charged outer surface. UV/Vis spectra showed the characteristic absorption bands related to the surface plasmon of gold and silver nanoparticle in aqueous solution. The absorption bands of GNPs were slightly broadened, depending on stabilizer used in preparing nanoparticles. TEM images and XPS analysis demonstrated that the preparation of metal/MWNT nanocompsite was considerably dependent on the surfactants, and the size and the shape of the nanoparticles. Among a series of nanoparticles only Au(PVP) formed nanocomposite with MWNTs as other species were aggregated and hence forms large sized NPs.

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