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One-Step Coating of Silica onto Multi-Walled Carbon Nanotubes Using Polyethyleneimine for High Electrical Resistivity

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Abstract: Multi-walled carbon nanotubes (MWCNTs) were uniformly coated with silica using polyethyleneimine (PEI) as a coupling agent without subjecting the surfaces of the MWCNTs to chemical modification, such as an amine treatment or chemical oxidation. PEI was physically adsorbed onto the MWCNTs, and the silica coating process was performed through a sol-gel reaction of tetraethyl orthosilicate (TEOS) in ethanol under base catalytic conditions at room temperature. PEI was the best coupling agent for coating silica on MWCNTs among the various amphiphilic polymers and surfactant tested, which included Triton X-100, polyvinylpyrrolidone, polyethylene glycol, and sodium dodecyl sulfate. During the sol-gel process using PEI as a coupling agent, silica could be uniformly formed on MWCNTs without any structural defects. As the amount of TEOS used was increased, the thickness of coated silica layer and electrical resistivity of MWCNTs also increased (up to 5.3×10^{10} Ω sq^{-1}) owing to the high surface coverage of silica on the MWCNTs.

Keywords: multi-walled carbon nanotubes (MWCNTs), silica, sol-gel, coating, polyethyleneimine.

Introduction

Carbon nanotubes (CNTs) have attracted considerable attention because of their outstanding properties and potential usefulness in a variety of applications.[1] CNTs have many unique properties, including high mechanical strength, flexibility, electrical and thermal conductivity, low density, and chemical stability, that are regarded as advantageous qualities for several applications in the electronic industry.[1-4] However, CNTs have poor dispersion in solvents or polymers because of the strong intermolecular interactions called van der Waals force, among them, which can cause the formation of aggregations. CNTs should have good dispersion in solvent or polymer matrices to maximize the advantages of CNTs as effectual reinforcing filler.[5] Current research is primarily focused on the preparation of various types of CNT-based composite to improve the material properties and optimize the use of CNTs.[3] To enhance the poor distribution of CNTs within matrices and enable the uniform coating of inorganics or metal oxides onto CNTs, surface-modification techniques of CNTs, including amine treatment or chemical oxidation with acid, have been studied. Herein, silica was selected as a non-covalent modification material to coat CNTs.[6]

Silica (SiO_2) is an outstanding dielectric material with superb thermal properties that is capable of mitigating the disadvantages commonly encountered with CNT-based polymers.[7] By coating silica onto CNTs, their properties such as mechanical strength, thermal conductivities, and electrical resistivity can be improved.

There are many kinds of techniques to coat silica on MWCNTs.[8-15] Among these various methods, silica coating was performed using the sol-gel technique, which involves the use of a silica precursor, tetraethyl orthosilicate (TEOS) in this study. The sol-gel method is an innovative processing technique that involves the conversion from a molecular precursor state into silica material.[7,16] One of several coating methods, the sol-gel process is especially advantageous because it results in coatings with a high purity and homogeneity, and involves a processing protocol that can be implemented under mild conditions and at low temperatures.

In order to coat silica on the stable surface of CNTs, CNTs normally have to be modified through an amine treatment or chemical oxidation prior to the start of the coating process. In our study, however, instead of applying one of the aforementioned surface modifications to the multiwalled carbon nanotubes (MWCNTs), we used a seeded growth process, employing an amphiphilic polymer as a coupling agent. Various amphiphilic polymers were explored for use in the sol-gel process employed in this study, and the best coupling agent for coating the MWCNTs was determined to be polyethyleneimine (PEI). The coating mechanism consisted of the physical adsorption of amphiphilic polymer onto MWCNTs and the chemi-

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cal coating of amphiphilic polymer-assisted MWCNTs with silica following a sol-gel reaction conducted under basic conditions.[17] Specifically, ammonium hydroxide was used to catalyze the sol-gel reaction of TEOS in ethanol with the amphiphilic polymer-covered MWCNTs.

Experimental

Materials. MWCNTs were purchased from Nanocyl (Belgium). The MWCNTs had a diameter of 9.5 nm, length of 1.5 μm, and purity of 95%. Triton X-100 was obtained from Daejung Chemicals & Metals Co., Ltd. (S. Korea) and polyvinylpyrrolidone (PVP, Mw: 40,000 g mol^{-1}) from Junsei Chemical Co., Ltd. (Japan). Sodium dodecyl sulfate (SDS, ≥99%), polyethylene glycol (PEG, Mw: 4,400 g mol^{-1}), and polyethyleneimine (PEI, Mw: 800 g mol^{-1}) were supplied by Sigma-Aldrich (USA). Tetraethyl orthosilicate (TEOS, ≥95%) was obtained from Junsei Chemical Co., Ltd. (Japan), ammonium hydroxide (25-30 wt% NH_3 in water) from Duksan Chemicals Co., Ltd. (S. Korea) and ethanol from OCI Co., Ltd. (S. Korea).

Silica-Coating on MWCNTs. Silica-coated MWCNTs were prepared by the following procedures. 2 g of MWCNTs was dispersed in 100 mL of ethanol using a bath type sonicator for 1 h. After dispersion, the amphiphilic polymer was poured into the solution and vigorously stirred for 6 h. It is noted that the amount of PEI among the amphiphilic polymers was 200 wt% to MWCNTs. Following stirring, ammonium hydroxide was injected in the mixture to serve as a catalyst for the sol-gel process. Then TEOS was added and the reaction vessel was stirred vigorously at the room temperature for 24 h. After synthesis, the resulting material was filtered with ethanol to remove any unreacted amphiphilic polymer and silica particles and then dried at 60 °C in a vacuum oven. Finally, silica-coated MWCNTs were obtained and characterized. During the sol-gel process, various amphiphilic polymers and surfactant were used for the coating of silica onto the MWCNTs, including Triton X-100, PVP, PEG, PEI, and SDS. In addition, the amount of TEOS used (500, 1000, 1500, 2000, 2500 wt% to MWCNTs) was changed to optimize the amount of silica coated on the MWCNTs.

Characterization. Field-emission transmission electron microscopy (FE-TEM, JEOL JEM-2100F) and scanning electron microscopy (SEM, Hitachi S-4300) were used to observe the morphologies of the silica-coated MWCNTs. Thermogravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851) was used for evaluating the amounts of silica coated on the MWCNTs. X-ray diffraction (XRD) analysis (Rigaku D/MAX 200 V/PC) was used to determine the structures of the silica-coated MWCNTs. Thin film powders were prepared for the measurements of surface resistivities using two resistivity meters: (1) a high resistivity meter (Mitsubishi Chemical, Hiresta-UP) based on constant-voltage processing with a concentric ring probe and measurement range of 10^4 to 10^{13} Ω and (2) a low resistivity meter (Mitsubishi Chemical, Loresta-GP) based on constant current processing with a linear four-point probe and measurement range of 10^{-3} to 10^7 Ω.

Results and Discussion

Figures 1 and 2 show the morphologies of the silica-coated MWCNTs that were synthesized using several amphiphilic polymers and surfactant for optimizing the one-step coating process. Triton X-100, PVP, PEG, and SDS were used as the coupling agents. These micrographs present that silica did not grow on the surface of MWCNTs which are synthesized by using above amphiphilic polymers and surfactant. The absence

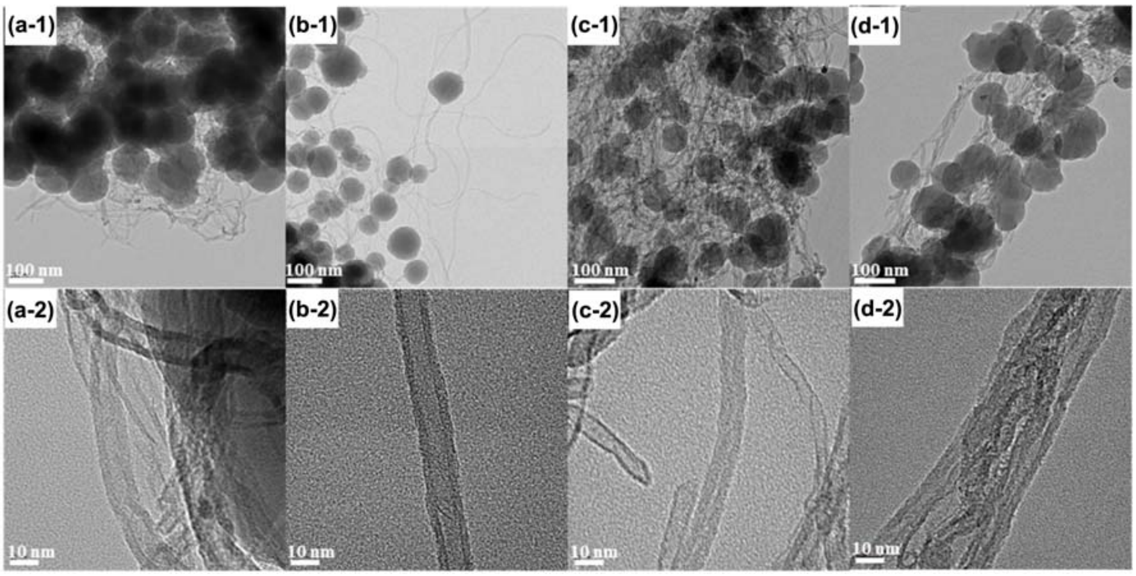


Figure 1. FE-TEM micrographs of silica coated MWCNTs synthesized at 1000 wt% TEOS and different amphiphilic polymers (a-1,2) Triton X-100, (b-1,2) PVP, (c-1,2) PEG, and (d-1,2) SDS.

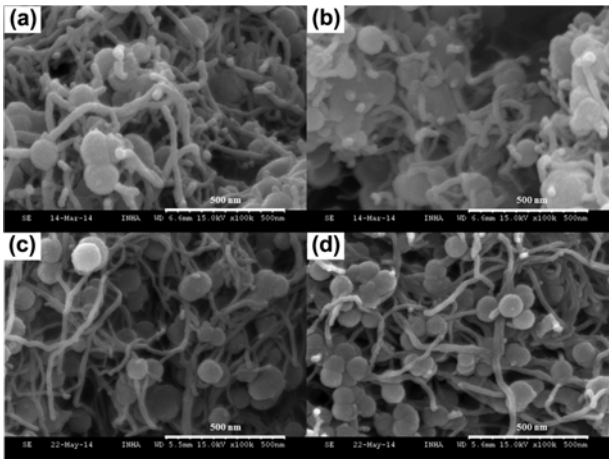
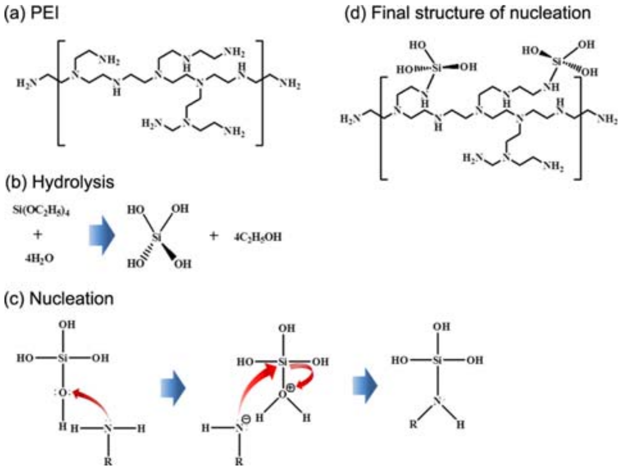


Figure 2. SEM micrographs of silica coated MWCNTs synthesized at 1000 wt% TEOS and different amphiphilic polymers (a) Triton X-100, (b) PVP, (c) PEG, and (d) SDS.

of silica growth on the MWCNTs was apparent in high-magnification FE-TEM images, and this morphological study indicates that the silica coating reactions using these coupling agents were not effectual. Adsorption of amphiphilic polymers or surfactants on MWCNTs surfaces results in steric repulsion. With Triton X-100, PVP, PEG, and SDS, such repulsive forces did not exceed van der Waals forces of attraction, thereby not improving the dispersion of nanotubes. Therefore, these coupling agents failed to help coat silica onto the surfaces of the MWCNTs.

The chemical structure of PEI and the mechanism of silica coating in the case of the PEI-adsorbed MWCNTs are described in Scheme I. Structurally, PEI contains a number of primary, secondary amine groups, as represented in Scheme I(a). In Scheme I(b) and (c), we depict the role of PEI as a coupling agent. TEOS, a silica precursor, undergoes hydrolysis with water and changes into silicic acid. The silicic acid reacts with the amine groups of the PEI that is physically adsorbed onto MWCNTs; the hydroxyl group of silicic acid becomes leaving group, and a Si-N chemical bond is generated from the heterogeneous nucleation of silica on PEI. This mechanism could be explained through the acid dissociation constant (pK_a). The acid dissociation constant (pK_a) for primary amines in PEI is 4.5 (for secondary amines, it is 6.7) at pH 4.[18] In addition, PEI displays a degree of deprotonation of 0% at pH 4, in contrast to approximately 55% at pH 5 and 80% at pH 7.4.[18,19] This indicates that the pH affects the protonation of the amine groups of the PEI. Therefore, we performed the sol-gel reaction under basic catalytic conditions using ammonium hydroxide, and the amine groups of PEI were successfully deprotonated during the silica coating process.



Scheme I. Chemical structures and mechanism of silica coating with PEI: (a) PEI structure, (b) hydrolysis of TEOS with water, (c) nucleation of silica on PEI, and (d) final structure of nucleation of silica on PEI.

The TEM and SEM micrographs in Figures 3 and 4 demonstrate that the growth of silica on the MWCNTs occurred effectively when PEI was used as a coupling agent. These results might be caused because PEI-absorbed MWCNTs had repulsive forces more than van der Waals forces, thereby enhancing the dispersion of nanotubes in silica sol. Also, it is due to strong interactions between basically modified MWCNTs and acidic TEOS, and OH-N bonding formed by PEI and TEOS, which may be stronger than OH-O bonding formed by other amphiphilic polymers and TEOS. The degree of silica coating on the PEI-adsorbed MWCNTs was determined by the amount of silica precursor, TEOS, used. Greater the amount of TEOS available for the sol-gel reaction, the greater was the amount of silica coated onto the PEI-adsorbed MWCNTs. The silica was not coated uniformly onto the MWCNTs until the amount of TEOS was over 1500 wt% with respect to the weight of the MWCNTs being coated. In addition, from the selective area diffraction pattern (SADP) of the silica-coated MWCNTs shown in Figure 3(e-1), we were able to verify that the silica coated uniformly on the MWCNTs was amorphous because of no any dots or lines for crystal.

The variation in the average diameter of the silica-coated MWCNTs with different amounts of TEOS is presented in Figure 5. The average diameter was measured by selecting approximately 50 linear lines, from one point to the opposite point across the MWCNTs, in the TEM micrographs (Figure 3). The greater the amount of TEOS used, the longer was diameter of silica-coated MWCNTs, as shown in Figure 5. The trend of average diameter of silica-coated MWCNTs linearly increases as the amount of TEOS used. When 2500 wt% of TEOS was used, the average diameter of the silica-coated MWCNTs was approximately 80 nm and the average thickness of silica layer covering the MWCNTs was approximately 35 nm. The average thickness of silica layer was calculated by subtracting the average diameter of the uncoated MWCNTs (~9.5 nm) from the average diameter of the silica-coated MWCNTs and dividing the result by 2.

Figure 6(a) represents the loss in weight of the silica-coated

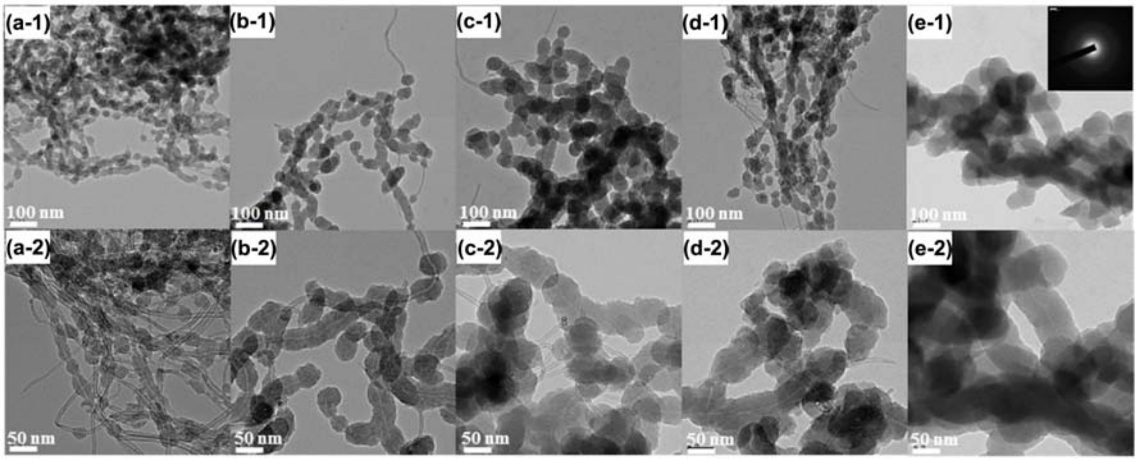


Figure 3. FE-TEM micrographs of silica coated MWCNTs prepared at 200 wt% PEI and different amounts of TEOS (a-1,2) 500, (b-1,2) 1000, (c-1,2) 1500, (d-1,2) 2000, and (e-1,2) 2500 wt%.

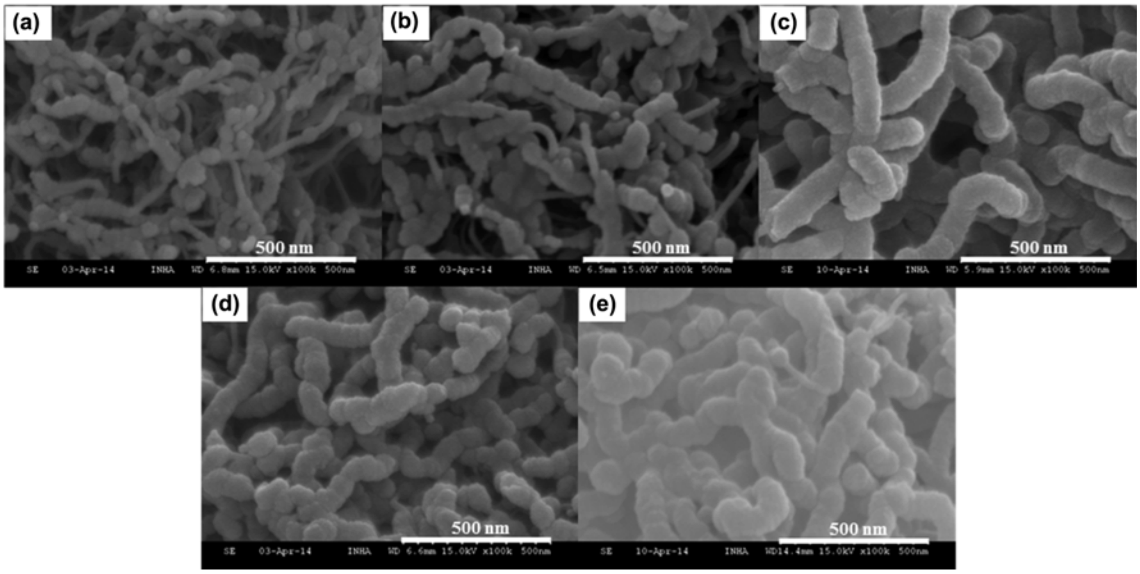


Figure 4. SEM micrographs of silica coated MWCNTs prepared at 200 wt% PEI and different amounts of TEOS (a) 500, (b) 1000, (c) 1500, (d) 2000, and (e) 2500 wt%.

MWCNTs prepared with different amounts of TEOS, obtained by TGA at a heating rate of 10 ºC min^{-1}; the samples were heated from ambient temperature to 750 ºC in air. For the raw MWCNTs, there is the decrease in weight by evaporation of water at the temperature below 200 ºC. The decomposition takes place at temperatures ranging from 350 to 700 ºC; the disordered and amorphous carbons at 350-500 ºC, and the perfect MWCNTs structure at ~700 ºC. Upon increasing the temperature, the silica-coated MWCNTs first undergoes loss of moisture, then the weight loss between 200 and 350 ºC is attributed to the decomposition behavior of PEI, followed by the degradation of MWCNTs. The oxidization of the raw MWCNTs begins at lower temperature than that of silica-coated MWCNTs because of thermal stability improvement through silica coating onto MWCNTs. The decrease in weight is indicative of how much silica is coated on the MWCNTs. We observed that the amount of silica on the MWCNTs increased as the amount of TEOS used was increased, as shown in Figure 6(b). These are calculated by subtracting the residues of raw MWCNTs from that of silica-coated MWCNTs at 750 ºC. The reason why the raw MWCNTs have the TGA residues, 5 wt%, at high temperature is because their purity is just 95%. Since the TGA residues of the raw MWCNTs and PEI-absorbed MWCNTs were almost identical at 750 ºC, the amount of silica on the MWCNTs was calculated based on the residues of the raw MWCNTs. This trend extrapolated from the TGA results of the raw and silica-coated MWCNTs is in keeping with the extent of silica coverage observed in the TEM and SEM photomicrographs (Figures 3 and 4).

Figure 7 displays the XRD patterns of the raw MWCNTs,

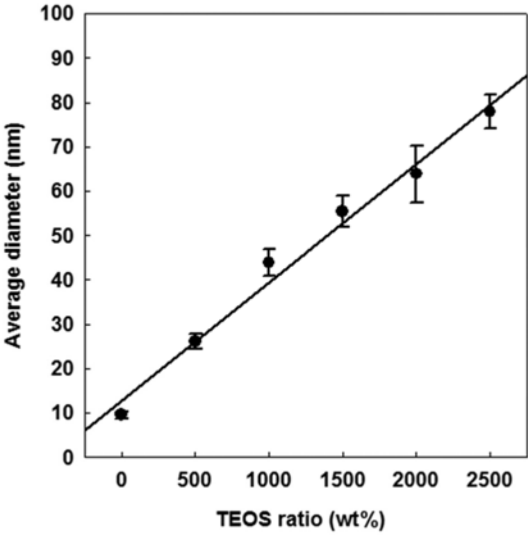


Figure 5. Average diameter of silica coated MWCNTs as a function of TEOS contents.

the silica-coated MWCNTs using different amounts of TEOS, and pure silica. The typical diffraction peak assigned to the (002) plane of the raw MWCNTs is observed at 2θ=26.4°, as presented in Figure 7(a). As can be seen from Figure 7(b)-(f), the XRD patterns of the silica-coated MWCNTs were shifted to smaller angles and were slightly broader. This peak shift and broadening indicates that these patterns are affected by the peaks of amorphous silica. A silica-related peak was centered at 2θ=23°; this location is indicative of the amorphous nature of the silica nanoparticles. Further, this means that amorphous silica was uniformly coated on the MWCNTs, and it is also in keeping with the results seen in Figure 3(e-1). Kim *et al.* reported that MWCNTs could be coated with silica after being chemically modified by grafting hydroxyl groups on the surface.[20] They had found that the original peak related to the raw MWCNTs was absent in the XRD patterns of the silica-coated MWCNTs. This result occurs because the plane of the MWCNTs is altered by the generation of hydroxyl groups on the surface of MWCNTs. However, since we did not chemically modify the MWCNTs in this study, the peak related to the raw MWCNTs was still present after the sol-gel reaction for coating silica.

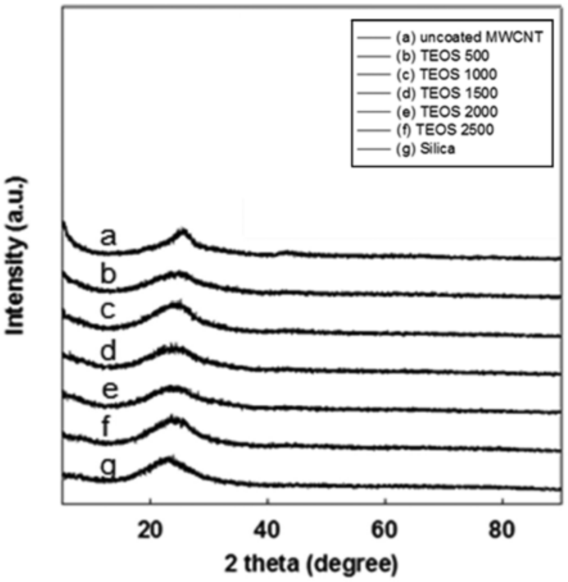


Figure 7. X-Ray diffraction (XRD) patterns of (a) raw MWCNTs, (b-f) silica coated MWCNTs at different amounts of TEOS, and (g) pure silica.

Figure 8 shows the changes in the surface resistivity of the silica-coated MWCNTs upon varying the amount of TEOS used. The surface resistivity directly indicates the degree of silica coverage on the surface of the MWCNTs. The electrical

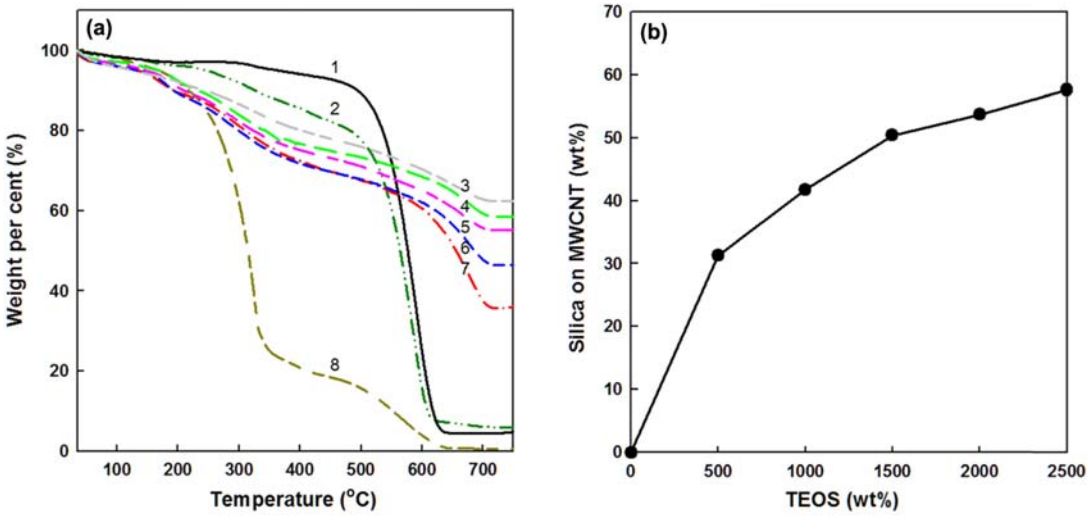


Figure 6. (a) TGA weight loss curves of (1) the raw MWCNTs, (2) PEI-absorbed MWCNTs, (3-7) silica-coated MWCNTs prepared at different amounts of TEOS (500, 1000, 1500, 2000, 2500 wt%, respectively) and (8) PEI, and (b) the amount of silica on MWCNTs.

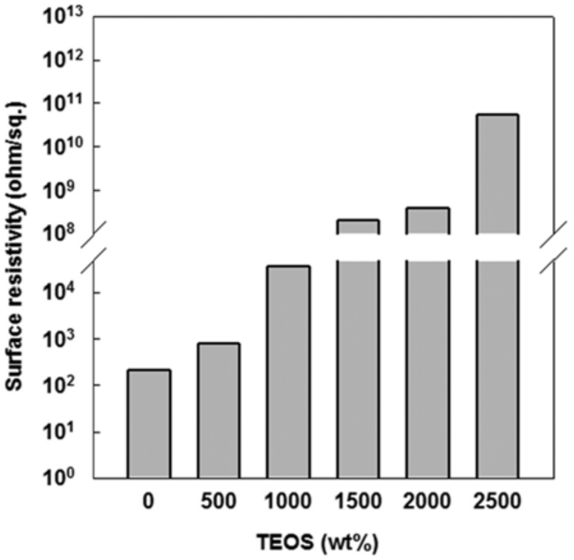


Figure 8. Surface resistivity of silica coated MWCNTs at different amounts of TEOS.

resistivity was linearly increased with the amount of silica coated on MWCNTs. The surface resistivity of the raw MWCNTs was 2.065×10^2 Ω sq^{-1} and this results suggest the raw MWCNTs have outstanding electrical conducting properties. On the other hand, that of the silica-coated MWCNTs using 2500 wt% TEOS was 5.3×10^{10} Ω sq^{-1}, which indicates electrical resistance properties of the MWCNTs are improved up to a level of that of semiconductor. In other words, this suggests that a uniform silica coating was formed on the PEI-adsorbed MWCNTs and that its presence improved the electrical insulating properties of the MWCNTs. Choi *et al.* have addressed this issue on the basis of the increase in the surface resistivity of silica-coated graphite.[21] In their study, the surface resistivity of silica-coated graphite when PVP was used as a coupling agent was over 10^{12} Ω sq^{-1}, indicating that silica-coated graphite is a perfect electrical insulator.[21] The resistivity of the silica-coated MWCNTs investigated in our study is lower than that obtained in the above study of graphite, even though both studies employed the sol-gel technique. This difference arises because the silica sol-gel coating process is more difficult for use with MWCNTs than with graphite, because MWCNTs have a higher aspect ratio, stronger agglomeration, and fewer edge sites as compared to graphite. Through the silica coating process, the electrical resistivity of MWCNTs having poor electrical insulating properties finally reaches a level of semiconducting materials.

Conclusions

In summary, a uniform amorphous silica coating was formed on MWCNTs with the assistance of PEI under basic conditions without having to modify the MWCNTs chemically. The presence of PEI on the MWCNTs facilitated the process of coating them with a uniform silica layer. PEI is physically adsorbed onto the MWCNTs, and the silica sol-gel reaction proceeds to completion, during which the hydrolysis of TEOS and nucleation of silica onto PEI occur. The thickness of the silica layer formed on the MWCNTs depended on the amount of precursor used, with the amount of silica on the MWCNTs increasing with an increase in the quantity of TEOS added. Finally, the electrical resistivity of the MWCNTs also improved after the formation of the silica coating under the mild processing conditions used.

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