

Attachment of Metal Oxide Nanoparticles on Carbon Nanotubes with Different Oxidation Levels

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Abstract. An efficient surface modification technique for fabricating tin dioxide/carbon composite nanotubes has been developed. This technique combines with implantation of acidic groups, interaction between surface oxides and metal ions or hydration molecules, and thermal. To functionalize multi-layered carbon nanotubes (CNTs), gaseous oxidation at 300°C was used to build functional oxygen groups including carboxyl, carbonyl and hydroxyl group, on ends or sidewalls of CNTs. X-ray photoelectron spectroscopy clearly indicated that the atomic ratio of attached tin-oxide on the oxidized CNTs gradually increases with the oxidation level, i.e., surface O/C atomic ratio. This evidence reflected that the surface oxides act as an adsorption center that strongly interacts with metal ions or hydration molecules in aqueous phase.

Introduction

Recently, self-assembly (SA) approach has received considerable attraction because of its variety of applications for fabrication of complex supramolecular or material nanoarchitectures [1-3]. Pioneer studies have devoted to investigating in enhancing the functionality of carbon nanotubes (CNTs) via SA techniques [2]. Generally, their techniques utilize strong interaction between functional groups and the sidewall of carbon nanomaterials. To achieve the functionality, surface acidity treatment on CNT is an essential step before SA surface modification. Implantation of oxygen groups onto CNT surface is one of frequently used methods that can modify surface acidity or hydrophilicity. Pervious studies also pointed out surface oxide groups, carboxyl and hydroxyl groups, can strongly interact with the other functional groups such as thiol- or amino- groups [4]. They have successfully formed these functionalized DNA-, alloy-, and metal-attached CNTs.

In this work, we propose an efficient SA method to fabricate metal oxide/carbon composite nanotubes. The method consists of implantation of acidic groups, ionic interaction and heat treatment. It is generally recognized that multi-layered CNTs with “clean” and “exposure” surfaces composed of numerous defects on sidewalls of nanotubes. Gaseous oxygen treatment can oxidize the surface of nanotubes, forming surface oxides on sidewalls and both ends of CNTs. By oxidizing the nanotubes for various periods, different oxidation levels of the treated nanotubes can be easily prepared. This procedure is able to introduce carboxyl, carbonyl, and hydroxyl groups grown at any defects in the sidewalls of nanotubes. These oxygen groups show an affinity to couple with metal ions in aqueous phase via the interaction of ionic exchange or surface polarity [5]. During the SA process, each functional group can serve as an active site, capable of specifically adsorbing with metal ions in aqueous solution. Then a heat treatment is performed to solidify the treated nanotubes, thus, fabricating the composite nanotubes. The method can be simply used to functionalize diverse metal or alloy/CNT composites.

Experimental

Several oxidation treatments such as gas oxidation, chemical-wet impregnation, plasma modification, have been applied to improve surface acidity of carbons. Among the approaches, nitric oxidization

has been frequently used to maximize the number of surface carboxylic acid groups onto single-walled CNTs [6]. This work used gaseous oxidation at 300°C under an air gas flow to build up surface oxide groups because advantages of the oxidation method are environmental friendly (without chemical use), convenient (without complicated process and equipment), and keeping completely surface morphology of nanotubes. By varying oxidation time, different oxidized levels of the nanotube surfaces could be acquired. X-ray photoelectron spectroscopy (XPS, VG ESCA210) with a MgK α radiation (B.E.= 1253.6 eV) was applied to examine the O/C atomic ratio and chemical environment of the oxidized CNTs.

To functionalize the oxidized CNTs with SnO₂ nanoparticles, a SA interaction followed by a direct heating was adopted. The typical procedure for the functionalization of the composite nanofibers can be described as follows: 0.5 g CNTs was mixed with 0.5 M tin (VI) chloride (Merck, reagent-grade) and stirred under Ar atmosphere at 30°C for 6 hr. This wet process enables Sn⁴⁺ ions to interact with each surface acidic group. Then the one-by-one interaction can facilitate a SA layer along a length of the CNTs. After that, the ionic-adsorbed CNTs were separated from the Sn-salt solution by using a filtration apparatus. The direct heating process was performed at 450 °C under an Ar atmosphere, thus, giving a nanostructured composite nanofiber. The as-grown CNTs were characterized by field-emission scanning electron microscope (FE-SEM, LEO 1530) and high-resolution transmission electron microscope (HR-TEM, JEOL 2010).

Results and Discussion

To investigate the surface oxides onto the CNTs, XPS technique is used to examine the oxidation levels for all CNTs. Note that each sample has been designated by using the nomenclature of carbon nanotube (CN) followed by the oxidization time (in units of min). The XPS spectra of the oxidized CNTs are shown in Fig. 1(a), illustrating that O 1s peak intensity gradually increases with the gaseous oxidation time. Quantitative analysis is carried out to evaluate the surface C and O atomic concentration determined from their scan spectra that have binding energies of ca. 284.6 and 533.5 eV, respectively. As listed in Table 1, owing to surface-cleaning treatment at 900°C, the original CNT exhibits a clean surface, i.e., without any oxygen existence. The O 1s/C 1s atomic ratio shows an increase with the oxidation time, i.e., an increase from 0.01 to 2.77 after gaseous oxidation. This can be attributed to the fact that oxygen is chemically bonded with the ends or defects of carbon networks during the oxidation process.

Table 1. Surface atomic ratio and distribution of functional oxygen groups of the oxidized carbon nanotubes determined from deconvolution of XP C1s spectra.

Sample No.	O 1s/C 1s	Functional Oxygen Group Distribution		
		C–O (%)	C=O (%)	O–C=O (%)
CN0	0.01	0	0	0
CN5	0.82	45	29	26
CN30	1.30	48	27	25
CN60	1.48	45	31	24
CN300	2.77	43	38	19

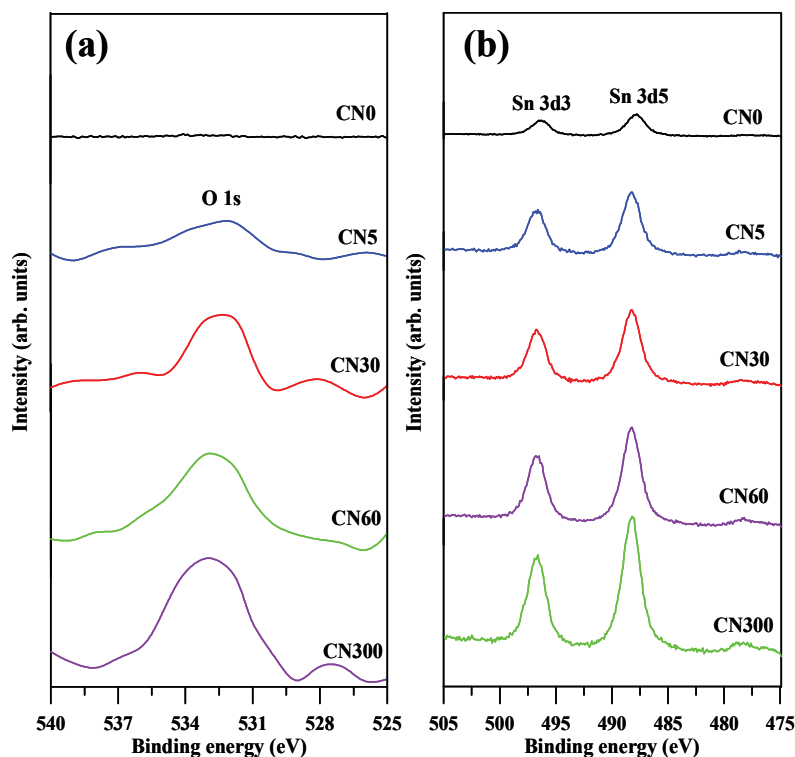


Figure 1. (a) XP spectra of O 1s peak for the oxidized CNTs, and (b) XP spectra of Sn 3d5 peak for the self-assembly composite nanotubes with different oxidation levels.

The broad C1s peak ranged from 280 to 292 eV in the XP spectra may comprise of peaks contributed by several carbon-based functional groups that have different binding energies. These binding energy peaks have been identified as C or C–H at 284.6 eV, C–O at 286.7 eV, C=O at 288.4 eV and O–C=O at 289.7 eV. The C 1s peak of CNTs can be deconvoluted using a peak synthesis procedure in which Gaussian peak shape is assumed to fit each component with a fixed binding energy and an average full-width half maximum value of 1.5 eV. The distribution of oxygen containing groups of each CNTs is thus determined from deconvolution of XP C1s spectra, and the results are also given in Table 1. We can observe that both the percentages of C–O and O–C=O slightly decrease with the oxidation level, and the increase in oxygen content upon oxidation is mainly contributed by the formation of C=O group.

XPS technique is also used to investigate the tin-oxide/carbon composite nanotubes. Basically, XPS can detect atomic concentration at ~ 10 nm in depth that is beneficial for the surface measurement of the composite nanotubes. The spectra of Sn 3d5 peak for all samples are shown in Fig. 1(b). We observe that the peak heights of Sn 3d5 show an increase with oxidation level. As shown in Fig. 1(b), we find that Sn ratio onto CNTs is an increasing function of oxidation level. This result can be presumably due to the possibility that surface oxide groups promote a strong interaction between Sn ions and oxidized surface of nanotubes, thus leading to a greater amount of metal ions adsorbed onto the CNT surface. This can be inferred by that the presence of surface oxides enhances surface hydrophilicity, facilitating surface affinity to polar molecules such as metal ions and hydration molecules. Although original CNT still has 2.3% of tin concentration, this can ascribed to *nonspecific adsorption behavior* of the porous CNTs, thus depositing a trace amount of tin oxides on the inner or outer tubes.

Figs. 2(a) and 2(b) clearly shows FE-SEM and HR-TEM images of the virgin CNTs, respectively.

We find that each nanotube has an average diameter of 50 nm and a wall thickness of 5 nm. After the SA surface modification, we can observe that SnO₂ nanoparticles with a mean diameter of 5 nm

are attached along the length of nanotube, as shown in Figs. 2(c) and 2(d). *The images clearly show that tin-oxide nanoparticles cover the whole nanotube, and higher density of nanoparticles dispersed onto the nanotube can be fabricated at higher oxidation level.*

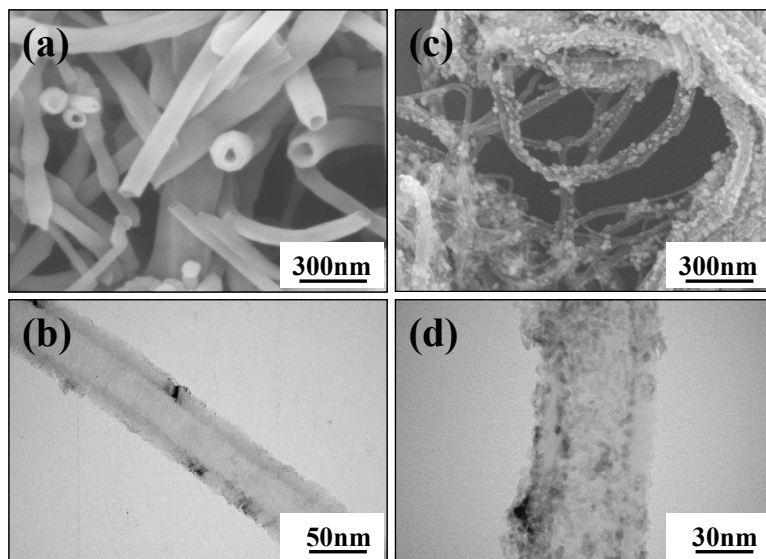


Figure 2. FE-SEM images of (a) original CNTs and (c) SnO₂/CNT composites. TEM images of (b) original CNTs and (d) SnO₂/CNT composites.

Summary

In summary, the metal-oxide/carbon composite nanotubes can be successfully fabricated through an efficient surface modification technique, which consists of implantation of functional oxygen groups, interaction between surface oxides and metal ions, followed by a thermal treatment. Different oxidation levels of carbon nanotubes could be prepared by varying different oxidation periods in gaseous phase. XPS investigation showed that O/C atomic ratio gradually increased with the oxidation time, and the types of oxygen groups were mainly carboxyl, carbonyl and hydroxyl groups. The SnO₂ nanoparticles with a mean diameter of 5 nm were found to cover the nanotubes. Based on the surface modification, these composite nanotubes can be used in a variety of applications including high-sensitivity gas sensor, catalysts for use of micro-fuel cell and photoelectronic device.

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References

- [1] Y. Lu, H. Fan, A. Stump, T. L. Ward, T. Rieker, and C. J. Brinker: Nature Vol. 398 (1999), p. 223.
- [2] J. Zhu, M. Yudasaka, M. Zhang, D. Kasuya, and S. Iijima: Nano Lett. Vol. 3 (2003), p. 1239.
- [3] O. Ikkala, and G. T. Brinke: Science Vol. 295 (2002), p. 2407.
- [4] M. Sano, A. Kamino, J. Okamura, and S. Shinkai: Nano Lett. Vol. 2 (2002), p. 531.
- [5] C.-T. Hsieh, and H. Teng: Carbon Vol. 40 (2001), p. 667.
- [6] H. Hu, B. Zhao, M. A. Hamon, K. Kamaras, M. E. Itkis, and R. C. Haddon, J. Am. Chem. Soc. Vol. 125 (2003), p. 14893.