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Synthesis of Well-Dispersed Multiwalled Carbon Nanotubes-Polystyrene Nanocomposites via Surface Thiol-Lactam Initiated Radical Polymerization

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A fascinating nanoobject, possessing a hard core of multi-walled carbon nanotubes (MWNTs) and a relatively soft shell of brushlike polystyrene (PS) was chemically synthesized by thiol lactam initiated radical polymerization. FT-IR and X-ray photoelectron spectroscopy were employed to characterize the nanocomposites and electron microscopic methods were used to investigate the morphologies of the as-prepared hybrid nanocomposites. The MWNT-PS nanocomposites possess good dispersibility in common organic solvents. Transmission electron microscopic images of the samples provide direct evidence for the formation of a core-shell nanostructure, i.e., the MWNTs coated with the PS layer.

Keywords Hybrid nanomaterials; multi-walled carbon nanotube; polymer brush; surface functionalization; surface initiation polymerization

Introduction

Carbon nanotubes (CNTs) possessing tubular nanostructures and unique quantum and promising mechanical properties have been widely considered as attractive candidates for fabricating novel materials with desirable properties [1]. There has been intense interest on CNTs since their discovery by Iijima in 1991 because they possess unique structure, thermal stability, mechanical and electrical properties [2–4]. Many useful applications, such as field emission displays, microcircuit wiring, diodes and transistors, sensors, nanocomposites, artificial muscles and hydrogen storage have already been demonstrated [5,6]. However, since carbon nanotubes are large molecules with thousands of carbon atoms in an aromatic delocalized system they

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are practically insoluble in all solvents and are, consequently, difficult to handle. The addition of functional groups on the nanotube surface is elegant route to modify its chemical activity in order to selectively disperse the tubes in a particular medium [7]. One way to maximize the dispersion of CNTs in a solvent can be achieved by grafting polymer chains on their outer surface [8]. The functional groups attached onto the surface of the CNTs are able to react with functional monomers or polymers to form chemically bonded hybrid materials with CNTs. To date, a large variety of polymer-grafted CNTs have been synthesized and most of them exhibited superior properties such as solubility and thermal stability. Grafting macromolecules onto the convex walls of CNTs, with the aim of improving the processability and extending the applications, has been explored for several years [9]. A variety of surface initiated polymerization methods have been developed to prepare core/shell structures of various materials. Recently, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT) techniques were applied to surface-initiating graft polymerization on the convex walls of MWNTs [10,11]. Despite the improvements in these techniques, most of them have their shortcomings. For example, it is difficult to remove the metallic catalyst completely from the products and/or many reaction steps are needed to introduce functional groups to the inorganic surface for polymerization.

In this article, we report thiol-lactam initiated radical polymerization on the convex walls of MWNTs for the first time. Thiol is used as chain transfer agents in free radical polymerization to regulate the molecular weight of the resulting polymers, and synthesize the end group functional polymers and macromonomers. Zhou et al. reported that ultra thin polymer films could be obtained via a surface chain-transfer reaction [12]. However these chain transfer reactions require a radical initiator to generate the radicals, and most polymers are not bonded to the surface. Therefore, only a thin layer on the top of the inorganic surface was obtained by using this technique. On the other hand, it was reported that thiol alone could initiate polymerization via a charge transfer complex of comonomers, such as styrene/N-phenylmaliemide [13]. Recently, Hu et al. reported that the addition of N-dodecylmercaptan with ε-caprolactam in the polymerization of styrene led to the initiation of monomers, and lactam in the system played an important role by stabilizing the radical and acting as a reversible capping agent [14].

This paper reports a facile synthesis of structurally well defined multiwalled carbon nanotubes-polystyrene (MWNT-PS) nanocomposites using a two component initiation system consisting of thiol functionalized carbon nanotube (MWNT-SH) and butyrolactam (BL). This process is called thiol-lactam-initiated, radical polymerization (TLIRP).

Experimental

Materials

MWNTs with an average diameter and length of about 10–20 nm and 10 μm respectively, were provided by NANOHUB Co., Ltd. 2-mercaptoethanol, butyrolactam, methanol, toluene were purchased from Aldrich and used as received. Tetrahydrofuran (THF, Aldrich) and thionyl chloride (Duksan Pure Chemical, Korea) were freshly distilled and styrene was purified by passing the liquid through a neutral alumina column to remove the inhibitor prior to use.

Synthesis of MWNT-COOH

For the chemical oxidation and surface functionalization of carbon nanotubes, 1 g of MWNTs were mixed with the solution of conc. HNO_3 and H_2SO_4 in 1:3 ratio and the mixture was ultra sonicated for around 10 hrs. The acid-oxidized MWNTs were washed with deionized water, separated by centrifuging, and further vacuum filtered thoroughly using a filter paper until the pH of the filtrate became neutral. The solid was then dried under vacuum for 24 hrs at 40°C to yield 0.9 g (~90%) of the carboxylic-acid-functionalized MWNT (MWNT-COOH). These acid treatments may shorten the length of the MWNT and introduce carboxylic acid groups [10].

Synthesis of MWNT-SH

The oxidized MWNTs were converted to the acid-chloride-functionalized MWNTs (MWNT-COCl) by treating them with thionyl chloride ($SOCl_2$). Dried MWNT-COOH (0.8 g) reacted with $SOCl_2$(20 mL) at 65°C under nitrogen atmosphere for 24 hrs. After the reaction was completed, the unreacted $SOCl_2$ was evaporated with a rotary evaporator. Subsequently, it was dried under vacuum at room temperature for 24 hrs to give acid chloride-functionalized MWNTs (MWNT-COCl). Because of its high reactivity (i.e., low stability), –COCl is hydrolyzed readily into carboxylate ions in air. Consequently the MWNT-COCl samples were kept away from air. The prepared MWNT-COCl reacted with 2-mercaptoethanol (20 mL) at 120°C for 48 hrs under nitrogen atmosphere. Then the resulting reaction mixture was dissolved in excess THF and vacuum filtered to yield thiol functionalized MWNTs (MWNT-SH), which was subsequently dried overnight under vacuum.

Synthesis of MWNT-PS by TLIRP

A typical procedure for synthesizing MWNT-PS nanocomposite by thiol-lactam initiated radical polymerization technique is as follows: 0.05 g of MWNT-SH and 5.0 g of toluene was mixed well using sonicator for well dispersion. Then the reaction mixture was transferred to a 50 mL round bottom flask equipped with a reflux condenser. 2.5 g of butyrolactam (BL) and 5.0 g of styrene (column separated) was added into the reaction mixture with stirring and nitrogen gas passing at room temperature for 1 h. Then the flask was immersed in the reaction chamber (oil bath) at 100°C immediately and kept stirring for 24 hrs. At the end of the reaction the viscosity increased dramatically. The resulting solid was precipitated into 100 mL of methanol. The PS-coated MWNT sample (MWNT-PS) was washed with THF and vacuum filtered using sintered glass filter and dried overnight under vacuum.

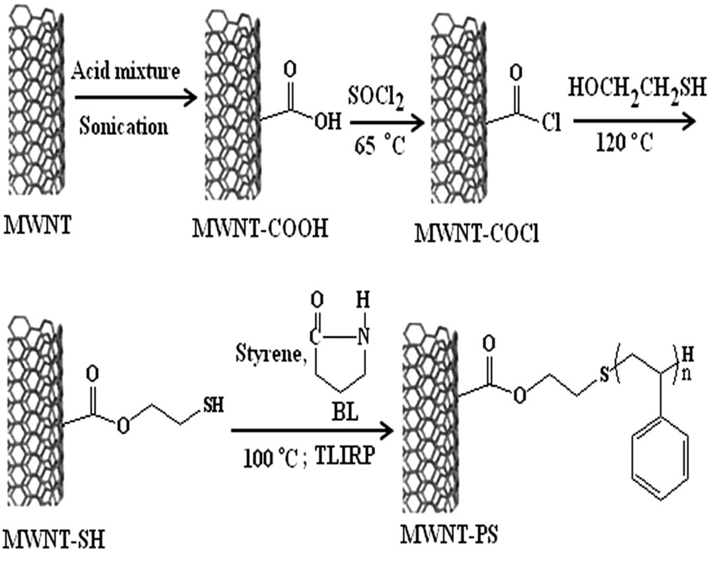
Measurements

Fourier-transformed infrared spectrophotometry (FT-IR) was employed to characterize the change in the surface functionalities of MWNTs using a BOMEM Hartman & Braun FT-IR spectrometer. The X-ray photoelectron spectroscopy (XPS) data was obtained on a MultiLab ESCA 2000 electron spectrometer (THERMO VG Scientific) using 300 W AlKα radiations. Transmission electron microscopic (TEM) images were recorded using a Hitachi H-7500 instrument to observe the nanoscale structures of the MWNT-PS hybrids. The samples were dispersed in toluene by ultrasonication, and finally it was dropped onto carbon-coated Cu grids for TEM observation. The morphology and elemental analysis of the polymer –CNT hybrids were carried out by using scanning electron microscopy (SEM) with a, Hitachi S-2700 model microscope.

Results and Discussion

Surface Functionalization of MWNTs

Scheme 1 illustrates the surface functionalization of MWNTs and the synthesis of MWNT-PS core-shell nanocomposites by thiol-lactam initiated radical polymerization. The resulting MWNT-SH particles were used as initiators for TLIRP where BL was used as a radical generating agent for polymerization. At the initial stage of polymerization, BL induces hydrogen transfer from MWNT-SH and produces free radicals, MWNT-S$^\bullet$ and BL-H$^\bullet$. Radical polymerization then proceeds via radical addition with unstable MWNT-S$^\bullet$ [12]. BL-H$^\bullet$ may act as a capping agent for the growing polymer chain, which terminates the polymerization process and leads to the control of the polymerization. Figure 1 shows the FT-IR results of the MWNTs obtained at different surface functionalization steps. The spectra of pristine MWNTs (Fig. 1a) had no obvious vibration peaks. The presence of carboxylic groups of MWNT-COOH after the oxidation step was confirmed with a C=O band stretching (Fig. 1b) that appeared at around 1740 cm^{-1}, whereas, the band at 1360 cm^{-1} and several low intensity peaks could be attributed to the C–O stretching vibrations of the –COOH groups. The FT-IR spectrum of MWNT-SH (Fig. 1c) shows an absorption band at 1421, which assigned to the stretching vibration of $-CH_2$ groups. Peaks at 1181 and 1140 cm^{-1} correspond to the asymmetrical and symmetrical stretching vibrations of C–O–C. The spectra of MWNT-PS modified by thiol-lactam initiated radical polymerization shows the characteristic vibration peaks



Scheme 1. Reaction scheme for the synthesis of MWNT-PS nanocomposites by TLIRP.

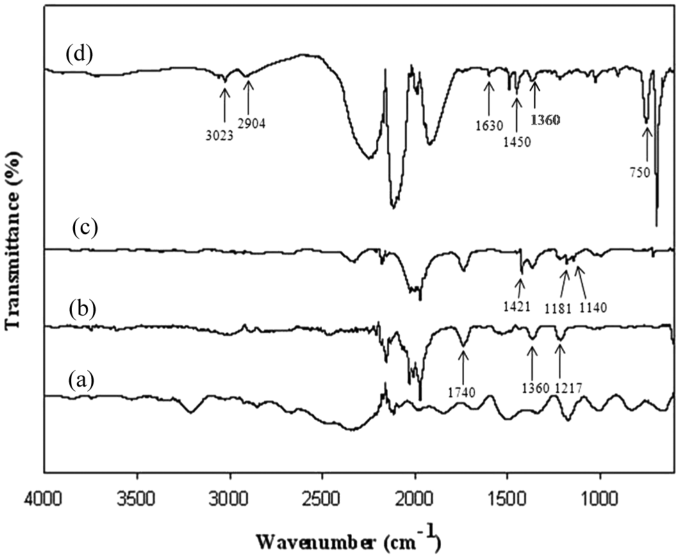


Figure 1. FT-IR spectra of (a) pristine MWNTs, (b) MWNT-COOH, (c) MWNT-SH, and (d) MWNT-PS.

of PS (Fig. 1d).The absorption bands assigned to C–H stretch (3023 cm^{-1}) from the aromatic rings. The peak at 2904 cm^{-1} is asymmetrical stretching vibration of $-CH_2$. The peak of 1450 and 1360 cm^{-1} are assigned to the flexural vibrations of $-CH_2$. Furthermore, additional bands at 750 cm^{-1} characteristic of the out of plane C–H vibration, and 1630 cm^{-1} characteristic of C=C ring stretching vibrations were present. The presence of these vibration peaks indicates that PS attached onto the surface of MWNTs. Butyrolactam has generally N–H stretching vibration at around 3350 cm^{-1} and N–H bending at 1610 cm^{-1}, which are absent in the Figure 1d. It means that there are no N-compounds in the nanocomposites. XPS spectrum of MWNT-SH was applied to directly show the existence of –SH group. Figure 2 shows the XPS spectrum of MWNTs samples. The peaks at 285, 532 and 164 eV are attributed to C, O and S respectively. The binding energy of S_{2p} at 164 eV in the XPS spectrum demonstrates the existence of –SH groups on the surface of MWNTs.

Morphology of MWNT-PS Nanocomposite

The structure and morphology of core-shell MWNT-PS nanocomposites were characterized using SEM and TEM analysis. Figure 3 shows the SEM images of thiol functionalized MWNTs and PS grafted nanotubes. As can be seen from Figure 3a after oxidation process, the MWNTs tend to become open ended tubes to some extent because of the end cap cutting [15]. No difference in the morphology of the nanotubes was observed after the thiol group functionalization. However, after the radical polymerization, the thickness of MWNTs was increased from around 10 nm to 15 nm with an increase in external surface roughness while retaining the tubular morphology of individual nanotubes. TEM image provide a direct description for the sample. The TEM images of the tubular morphologies of the crude and

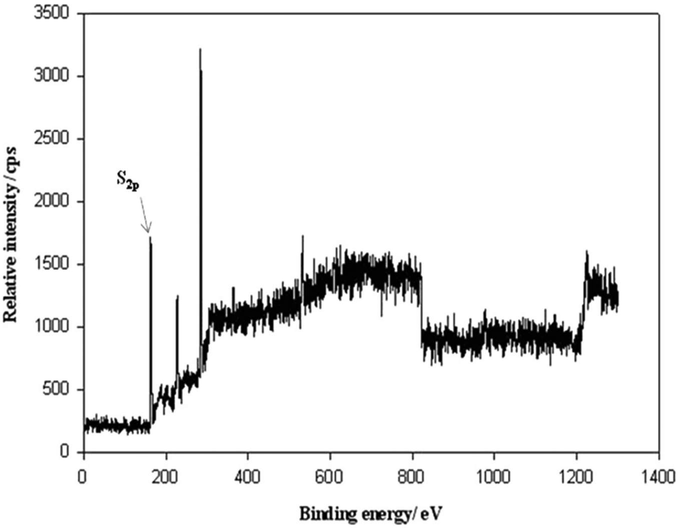


Figure 2. XPS spectrum of MWNT-SH.

functionalized MWNTs are shown in the Figure 4. The average diameters of the crude nanotubes are about 10–20 nm and the average length of the MWNTs are about 8–10 micrometers. In the TEM images of crude MWNTs (Fig. 4a), many jointed tubes mass together seriously. However, it can be seen from Figure 4b after the thiol-lactam initiated radical polymerization on the surface of MWNTs, the carbon nanotubes dispersed well in common organic solvent, which results from the good solubility of the MWNT-PS nanocomposites in solvent. For the samples of MWNT-PS core-shell nanocomposite (Fig. 4c) it was found that the tubes were clothed with a polymer layer. These images reveal that the surface functionalized nanotubes of the MWNTs were encapsulated by PS polymer chain with a thickness of around 12 nm. In other words, clearly visible MWNTs core with PS polymer brushes on the outer surface of nanotubes was observed by TEM.

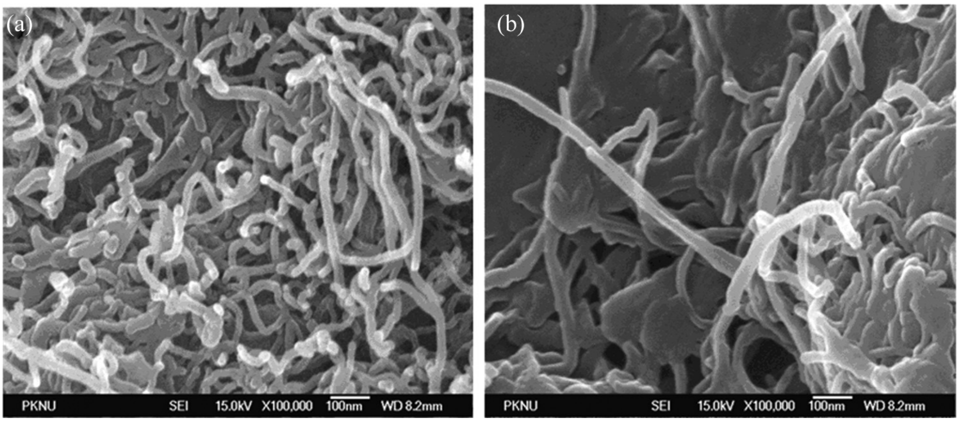


Figure 3. SEM images of (a) thiol functionalized MWNTs and (b) MWNT-PS.

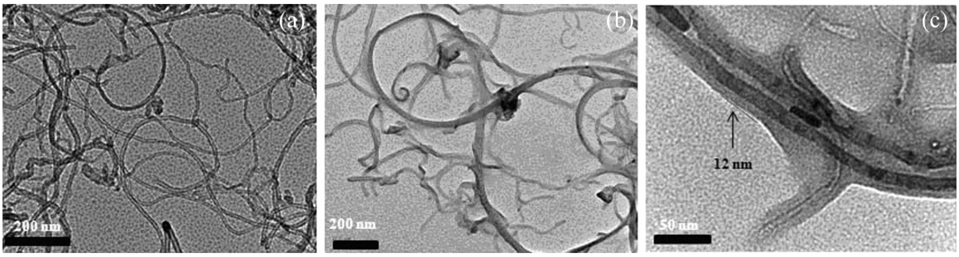


Figure 4. TEM image of the (a) pristine MWNTs and (b) MWNT-PS at lower magnification and (c) at higher magnification.

Dispersion Stability of MWNT-PS

The obvious variation in solubility and dispersibility for functionalized MWNT samples during the synthesis process still indicated the covalent linkage between various functional groups and MWNTs. To compare the suspension stability of the MWNTs obtained, toluene solutions (1.0 wt%) with different MWNTs were prepared. Figure 5 shows the dispersed states of the MWNT samples after 5 hrs. Comparison of these photographs indicate that the suspension stability of the pristine, oxidized MWNTs and thiol functionalized MWNTs were poor (Figs. 5a–c) and sedimentation takes place only after several minutes. On the other hand MWNT-PS presented the best stability (Fig. 5d). Even after 5 hrs there is no sedimentation in the toluene solution. The evolution of the solubility of the MWNT-contained samples verified that every step of the modification was successful, and the carboxyl groups, thiol groups and PS chains did covalently link to the convex walls of MWNTs. From the above results, it is concluded that polystyrene has been successfully grafted onto the surface of MWNTs.

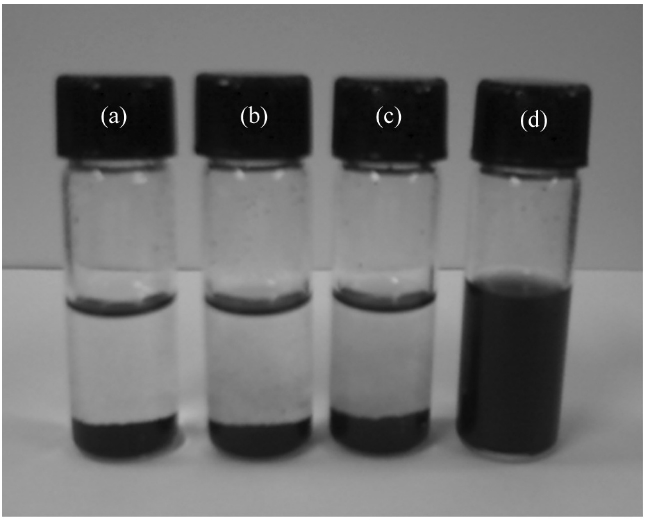


Figure 5. Dispersibility of the MWNTs dispersed in toluene (weight ratio 1.0%); (a) pristine MWNTs, (b) oxidized MWNTs, (c) MWNT-SH and (d) MWNT-PS.

Conclusions

In summary, the surface functionalization of MWNTs with PS via thiol-lactam initiated radical polymerization was investigated. After the thiol groups were introduced onto the convex walls of MWNTs, styrene polymerized successfully on the surface of MWNTs via TLIRP method, forming a core-shell nanocomposite. The related covalent functionalization has been confirmed by FT-IR, XPS, SEM and TEM characterization. The as prepared MWNT-PS had good dispersibility in common organic solvents. It is believed that this methodology can be used in the synthesis of other polymer coated carbon nanotubes with increasing complexity and functionality in the polymeric shells.

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