

Self-Organized Grafting of Carbon Nanotubes by End-Functionalized Polymers

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Abstract: A variety of end-functionalized polymers were grafted spontaneously onto multi-walled carbon nanotubes (MWNTs) using a solution mixing process. The end-functional groups of the polymers underwent noncovalent grafting to the defect sites at the surface of the purified MWNTs through zwitterionic interaction or hydrogen bonding. The physically grafted polymers including polystyrene (PS), poly(methyl methacrylate) (PMMA), polyethylene oxide (PEO), and polydimethylsiloxane (PDMS) provided sufficient compatibility with an organic solvent or polymer matrix, such that the nanotubes could be finely dispersed in various organic media. This approach is universally applicable to a broad range of polymer-solvent pairs, ensuring highly dispersed carbon nanotubes through simple solution mixing.

Keywords: carbon nanotubes, end-functionalized polymer, dispersion, self-organization, nanocomposites.

Introduction

Carbon nanotubes have outstanding physical and chemical properties due to their idealized one-dimensional structure consisting of sp^2 hybridized carbons.¹⁻³ The practical utilization of superior properties of individual nanotubes, however, has been limited by the bundling of nanotubes, which originates from strong tube-tube interaction.^{4,5} Various surface modification strategies relying on physical or chemical treatment have been developed to facilitate well-dispersed morphology of carbon nanotubes.⁶⁻¹¹ Stable dispersion, particularly in a volatile solvent, may provide a versatile pathway for further processing towards directed assembly into a complex architecture as well as the fabrication of films or fibers with electrical conductivity and optical transparency.

Among various surface modification methods for carbon nanotubes, noncovalent functionalization has the advantage of minimized damage to the chemical structure of the carbon nanotubes, thereby preserving their physical and chemical properties. Diverse noncovalent functionalization methods have been established utilizing amphiphiles, biopolymers, π - π stacking aromatic compounds, etc. Amphiphiles, such as lipids or block copolymers, encapsulate nanotubes to mediate dissolution in an aqueous media.¹²⁻¹⁴ Various compounds, including pyrene or porphyrin unit, interact with the sidewall of the nanotubes through π - π interaction.¹⁵⁻¹⁷ DNA or conjugated polymers are physisorbed onto the tube

surface, enhancing the compatibility with solvents.¹⁸⁻²² However, most of the currently available methods are applicable to specific solvent-dispersant pairs or require complicated and expensive chemical process.

Here we introduce a facile and robust self-organized functionalization method for carbon nanotubes utilizing end-functionalized polymers. Various polymers end-functionalized by terminal groups such as amines, hydroxyl or carboxylic acid groups are spontaneously grafted to the carbon nanotubes through a simple solution mixing process. Multi-walled carbon nanotubes (MWNTs) purified by a commonly applied process possess a limited amount of carboxylic acid groups at their surface, providing interaction sites with the end-functional groups of the polymers. Despite the limited density of grafting, the dispersion of carbon nanotubes in various organic solvents was remarkably enhanced due to the large hydrodynamic volume of the grafted polymer chain. Our approach relies on a very simple process and is universally applicable to a wide spectrum of polymer-solvent pairs. Applicability to various volatile organic solvents is potentially advantageous for further processing.

Experimental

Materials. MWNTs were purchased from Iljin Nanotec, Inc.. Benzene and dimethylformamide (DMF) were purchased from Merck. Methyl ethyl ketone (MEK) was purchased from Aldrich. Octadecylamine (ODA) was purchased from Sigma. Monodisperse amine terminated PS (PS-NH₂), carboxylic acid terminated PS (PS-COOH), and PS having the

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same M_w of 3,000 g/mol, and hydroxy terminated PMMA (PMMA-OH) having M_w of 6,000 g/mol were purchased from Polymer Source, Inc.. PS-COOH with M_w of 50,000 g/mol and amine terminated PEO (PEO-NH₂) with M_w of 2,000 g/mol were purchased from Scientific Polymer Products, Inc.. PS with M_w of 50,000 g/mol and benzene were purchased from Polysciences, Inc.. Amine terminated PDMS (PDMS-NH₂) was purchased from Aldrich. All materials except MWNTs were used without further purification. The purification of MWNTs was carried out by sonicating MWNTs in the mixture of sulfuric acid and nitric acid (volume ratio of 3:1) for 10 h. The temperature of acid solution was maintained about 60-70 °C. Upon sonication, metal catalysts were removed and a limited amount of carboxyl functional groups were formed at the edges and sidewalls of the MWNTs. Amorphous carbon and residual acid solutions were removed by subsequent heat treatment at 400 °C that continued for 40 min under atmospheric conditions.

Acid-Base Titration to Measure the Concentration of -COOH in MWNTs. MWNTs (10 mg) were dispersed in an aqueous solution of NaHCO₃ (0.05 M, 20 mL) and stirred for three days. The solids were removed by vigorous centrifuging, and the resultant clear solution was diluted with 90 mL of deionized water. A part of the solution (20 mL) was mixed with an aqueous HCl solution (0.05 M, 4 mL) and boiled for 30 min to remove CO₂. Finally, titration was performed with NaOH (0.05 M) until the resulting solution became neutral. Backward titration was also performed to confirm the results.^{23,24}

Self-Organized Grafting Process and FT-IR Characterization of MWNT-Polymer Interaction. The purified MWNTs were dispersed in an organic solvent through a simple sonication process. Purified MWNTs (0.1 mg), polymers (20 mg) and a solvent (1 g) were sealed in a vial and sonicated for 5 h. The samples for IR measurement were prepared by sonicating MWNTs and end-functionalized polymers (1:1 weight ratio) in benzene and subsequent film casting. The Fourier transform-infrared spectra (FT-IR) of prepared samples were recorded on Bruker IFS66V/S & HYPERION 3000 in ATR (attenuated total reflection) mode. The number of scans was 512, and the scanning resolution was 2 cm⁻¹.

Preparation and Characterization of PS/MWNT Nanocomposite Films. The purified MWNTs (10 wt%) were dispersed in the benzene solution of PS (5 wt%) by sonication. PS (M_w of 50,000 g/mol) and the mixture of PS-NH₂ (M_w of 3,000 g/mol) and PS (M_w of 50,000 g/mol) with a weight ratio of 1:9 were applied as matrices. Polymers and MWNTs were added in benzene and sonicated for fine dispersion. The prepared dispersion was spin-coated on a glass substrate to prepare a nanocomposite film. The morphologies of carbon nanotubes in the prepared nanocomposites were examined by HITACHI S4800 scanning electron microscope (SEM) and Philips F20 transmission electron

microscope (TEM). The sample for SEM was prepared by etching away the polymer matrix at the surface of a nanocomposite film by reactive ion etching (RIE). The condition of RIE was 50 W, 0.06 torr of O₂, and 15 s. A specimen for TEM analysis was prepared using ultramicrotome, Power-Tome X of Boeckeler Instruments, Inc. The nanocomposite films were molded in epoxy and then cut into very thin slices with a thickness of around 50 nm. The slices floating on the water surface were recovered on carbon coated copper grids and observed by TEM.

Results and Discussion

The MWNTs used in this work were purified by a routinely applied process based on acid treatment followed by heat treatment.²⁵ The acid titration method was applied to quantify the amount of functional groups, and the results are summarized in Table I.^{23,24} The content of the functional group did not significantly increase during purification.

The self-organized grafting of MWNTs with end-functionalized polymers was manifested by a model experiment presented in Figure 1. The dark phase at the bottom of each vial corresponds to the aqueous dispersion of MWNTs temporarily stabilized by sonication. The organic phase located over the aqueous phase, corresponds to a pure benzene or benzene solution of ODA or benzene solution of PS or benzene solution of PS-NH₂. Note that the vial having pure benzene or benzene solution of PS as organic phases showed concave menisci at the interface, while the vials containing amine terminated compounds showed convex menisci due to the segregation of an amine functional group to the interface. Figure 1(b) shows the same vials after stirring for 24 h. No significant change has been observed in the three vials located in the left side. However, the vial with PS-NH₂ exhibited inversion of color between the two phases, indicating that MWNTs had moved from an aqueous phase into organic phase. Neither ODA with a short alkyl chain nor PS without an end-functional group showed remarkable interaction with nanotubes. Only PS-NH₂ interacted with MWNTs strongly enough to disperse them in benzene. Interestingly, the color inversion did not occur when the stirring was performed at an elevated temperature of 80 °C. This signifies that the interaction between PS-NH₂ and carbon nanotubes is relying on noncovalent interaction rather than direct

Table I. Carboxylic Acid Concentrations in Pristine and Purified MWNTs

Sample	-COOH Content ^a	
	Forward Titration	Backward Titration
Pristine MWNTs	3.7 %	2.5 %
Purified MWNTs	4.0 %	5.9 %

^aMeasured by acid-base titration.^{23,24} -COOH content indicates the ratio of carbon in carboxylic acid groups to total carbons in MWNTs.

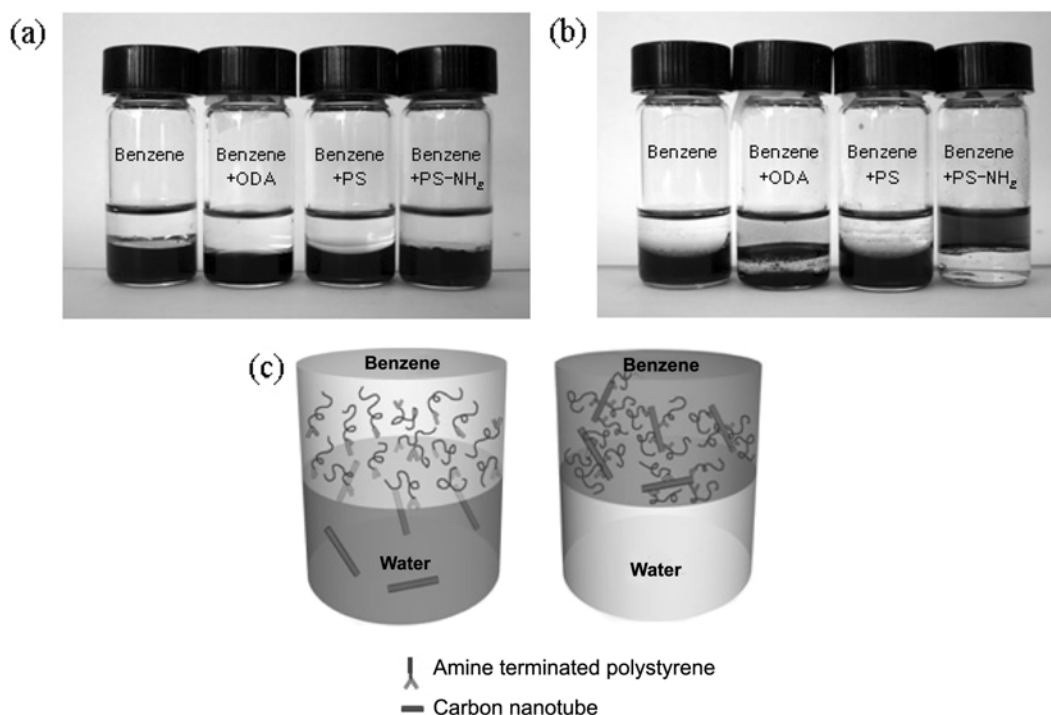


Figure 1. Photographs and a schematic for transferring MWNTs from water phase to benzene phase by self-organized functionalization by end-functionalized polymers. In (a) and (b), the lower phases are aqueous dispersion of as-purified MWNTs, and the upper phases are pure benzene, benzene solutions of ODA, benzene solution of PS, and benzene solution of PS-NH₂. (a) Before and (b) after stirring the samples for 24 h. (c) Schematic of transferring MWNTs in the PS-NH₂ sample.

covalent bonding.

To investigate the noncovalent interaction, Infrared (IR) spectroscopic analyses were performed. In Figure 2, the IR curves of pure PS-NH₂ and PS-NH₂ grafted MWNTs are compared. The grafting was performed by dissolving both MWNTs and PS-NH₂ in benzene (mass ratio 1:1) and the subsequent solution casting of films upon an inert substrate. The slight shift of C=C stretching peaks located around 1492 and 1451 cm⁻¹ is due to the π - π interaction between the phenyl ring of PS and the side wall of MWNTs.²⁶ Most significantly, the peak for the N-H bending of pure PS-NH₂ observed at 1600 cm⁻¹ was red-shifted to 1516 cm⁻¹ upon grafting to MWNT surface. It indicates a very strong noncovalent interaction between the terminal amine group and carboxylic groups on the nanotube surface.²⁷ A small peak at 1580 cm⁻¹ results from the deprotonation of the carboxyl groups on the surface of the MWNTs.²⁸ The schematic for interaction between a polymer and the MWNTs is depicted in Figure 2(c). The PS-NH₂ is physically grafted at the end and side walls of the MWNTs through zwitterionic interaction with carboxylic acid groups generated upon the purification of MWNTs. The grafting density is low due to the limited amount of carboxylic acid at the surface of the purified MWNTs. However, large hydrodynamic volume of the grafted polymer chains provides sufficient compatibility to

the organic solvent to promote the dispersion of the MWNTs.

Since our approach relies on noncovalent interaction of common functional groups, it can be extensively applied to various end-functionalized polymers. Figure 3 demonstrates the enhancement of the MWNTs dispersion in various organic solvents in the presence of various end-functionalized polymers. The backbones and end-functional groups of the applied polymers had diverse chemical structures. The concentrations of polymer and MWNTs were fixed at 2 and 0.01 wt% for all samples. Figure 3(a) represents the dispersion of MWNTs in benzene in the presence of various organic end-functionalized polymers such as PS-NH₂, PS-COOH, PMMA-OH or PEO-NH₂. The number average molecular weights of all used polymers were 3,000 g/mol, except PMMA-OH, whose molecular weight was 6,000 g/mol. As shown in the vial located in the left side, purified MWNTs could not be dispersed in pure benzene. However, when end-functionalized polymers were added, the dispersibility of MWNTs was greatly improved by the self-organized grafting of end-functionalized polymers. We note that the interaction between carboxylic acid or hydroxyl terminated polymer and MWNTs occurred through hydrogen bonding.

Figure 3(b) shows the enhancement of nanotubes dispersibility using an end-functionalized inorganic polymer. When

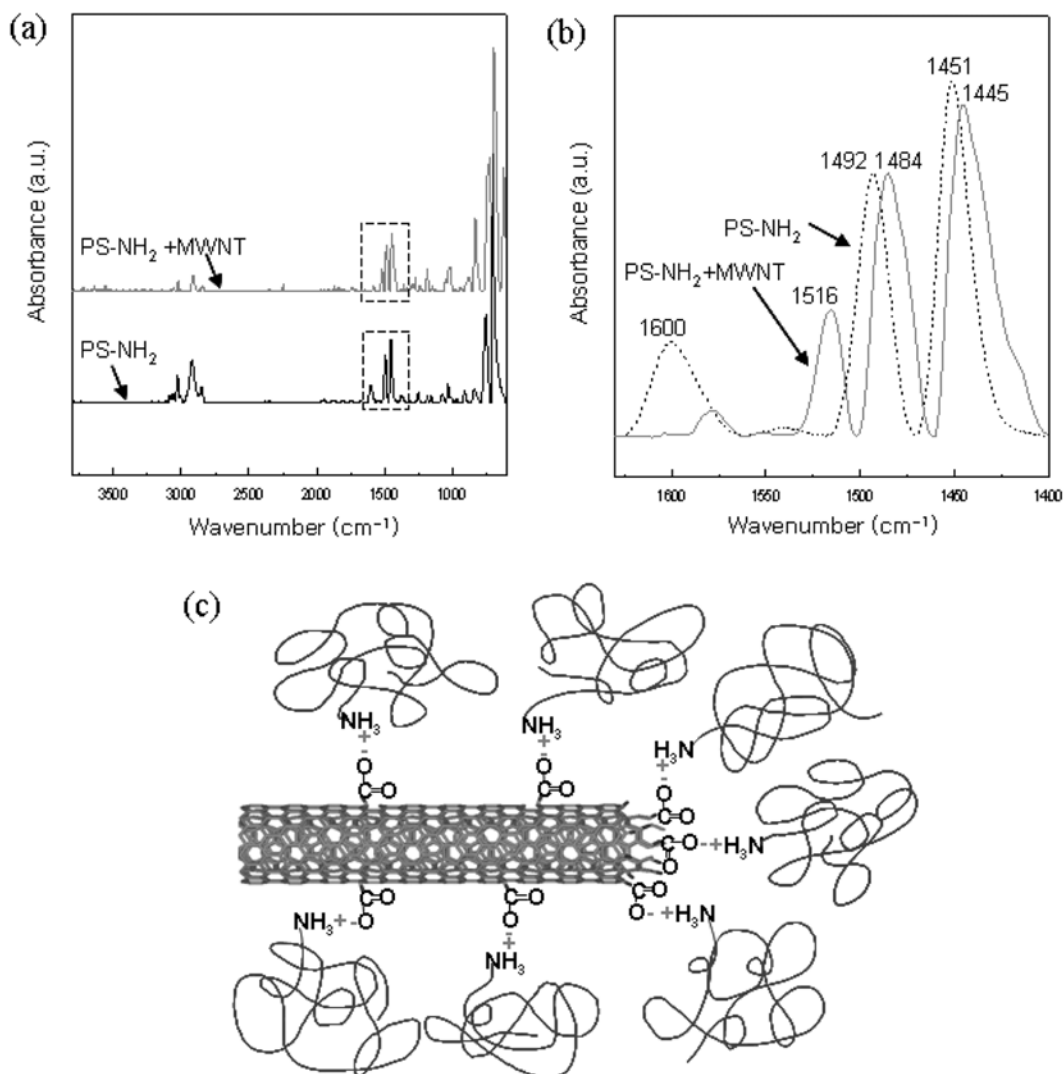


Figure 2. FT-IR spectra of pure PS-NH₂ and PS-NH₂ functionalized MWNT. (a) Overview of the FT-IR spectra, and (b) overlapped N-H bending peaks of PS-NH₂ (dot line), and PS-NH₂ functionalized MWNT (solid line). (c) A schematic model describing the zwitterionic interaction between the amine groups of PS-NH₂ and the carboxyl groups of MWNTs.

PDMS-NH₂ was added, the dispersibility of MWNTs in MEK was greatly promoted. The dispersion showed better transparency in the presence of PDMS-NH₂ due to a finer dispersion of nanotubes (no large aggregate of MWNTs was observed in the vial). Figure 3(c) shows the dispersion of MWNTs in DMF. DMF is well-known as an effective dispersing solvent for carbon nanotubes. Nonetheless, the dispersibility could be further enhanced by applying end-functionalized polymer. We note that in our approach, the dispersibility of nanotubes was generally enhanced as the strength of interaction between a pair of functional groups increased (NH₂ > COOH > OH) and the polarity of solvent decreased. A polar solvent may screen the functionalities of functional groups.

PS/MWNTs composite films were prepared utilizing self-

organized grafting process and their morphology was characterized to verify the nanoscale dispersion of MWNTs. The films were simply prepared by spin-casting from a benzene solution containing both MWNT and matrix polymer. The composition of the polymer and MWNTs were adjusted for a MWNT content of 5 or 10 wt% in the finally fabricated films (film thickness: 120 nm). The dispersion of MWNTs in the PS matrix depended remarkably on the presence of an end-functionalized polymer. As shown in Figure 4(a), the MWNTs were hardly dispersed and aggregated in the film without any end-functionalized polymer (M_w of 50,000 g/mol). Large aggregates of MWNTs easily discernable by naked eyes were inhomogeneously distributed over the whole film. The optical uniformity of the film could be greatly improved by adding a small amount of end-func-

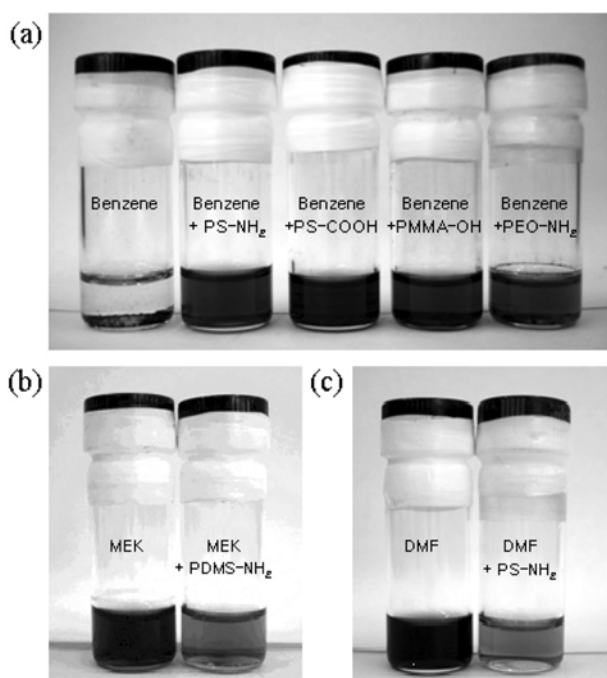


Figure 3. MWNT dispersions in organic solvents with various end-functionalized polymers. (a) MWNT dispersions in pure benzene or benzene in the presence of PS-NH₂, PS-COOH, PMMA-OH, and PEO-NH₂. (b) MWNT dispersions in MEK without and with PDMS-NH₂. (c) MWNT dispersions in DMF without and with PS-NH₂.

tionalized polymer. Figure 4(b) shows a photograph of PS/MWNTs nanocomposite film including 10 wt% of PS-NH₂. No optically visible aggregate was observed. To identify the dispersion of the MWNTs in a nanoscopic scale, the nanocomposite films were treated by RIE and the morphology of exposed MWNTs was observed by FE-TEM. Despite the high content of MWNTs of 5 wt%, the MWNTs were individually separated and uniformly dispersed in a polymer matrix forming percolated network morphology (Figure 4(c)). The SEM morphology manifests that the finely dispersed morphology of MWNTs in an organic solvent was well-preserved upon further processing for film preparation. TEM observation was also performed for the thin sliced samples prepared by ultramicrotomy and presented in the Figure 4(d). The highly magnified TEM images shows that MWNTs consisting of a number of carbon layers were well-dispersed in the polymer blends matrix.

Conclusions

Various end-functionalized polymers were spontaneously grafted to purified MWNTs through simple solution mixing process. The physical grafting of the end-functionalized polymer provided the compatibility with organic solvents and polymers such that the functionalized MWNTs were

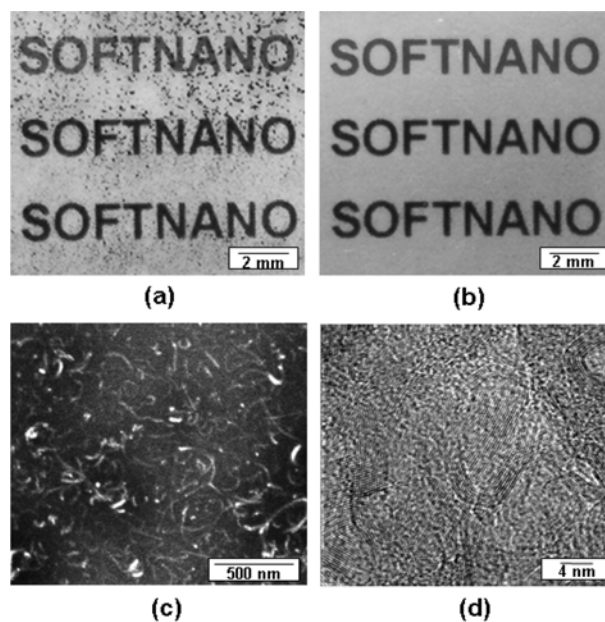


Figure 4. Optical micrographs of nanocomposite films including 10 wt% of MWNTs in the matrix of (a) PS and (b) the mixture of PS-NH₂ and PS with a weight ratio of 1:9, respectively. The films deposited on a glass plate were placed over paper where letters were printed in various colors. (c) SEM image of a nanocomposite surface etched by RIE including MWNTs of 5 wt%. (d) TEM image of an ultrathin section of nanocomposite film including MWNTs of 10 wt%.

finely dispersed in organic solvents and polymer matrices. Further processing into nanocomposite films through spin-casting led to finely dispersed morphology of carbon nanotubes up to a high content above 10 wt%. The application of our self-organized grafting method is anticipated not only for composites, but also for diverse purposes as well, including assembly, patterning, and fabrication of film or fiber.

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