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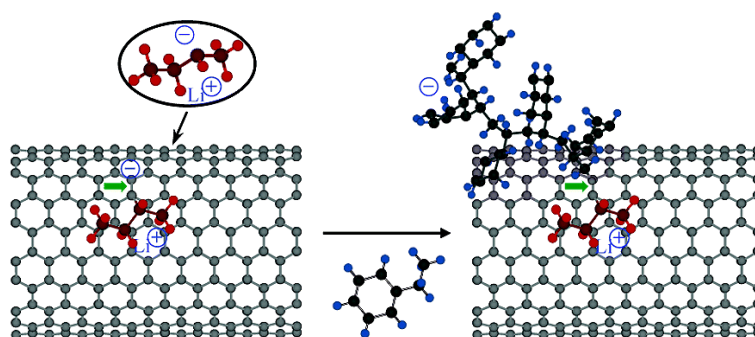
Single-Step in Situ Synthesis of Polymer-Grafted Single-Wall Nanotube Composites

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Single-Step in Situ Synthesis of Polymer-Grafted Single-Wall Nanotube Composites

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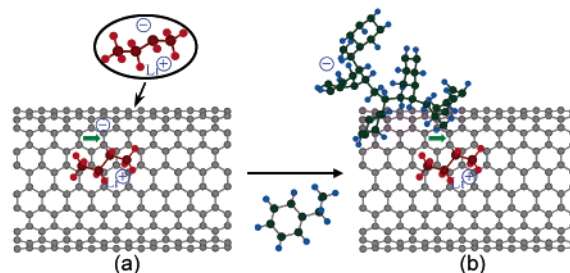Hyunsoo Chung,[§] Kilwon Cho,[‖] Chang Y. Ryu,*,[§] and Pulickel M. Ajayan*,[‡]

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Single-wall carbon nanotubes (SWNTs) have been widely touted as attractive candidates for use as fillers in composite materials due to their extremely high Young's modulus, stiffness, and flexibility.[1] Successful applications of such composite systems require well-dispersed nanotubes with good adhesion with the host matrix, which, unfortunately, is not easily realized. Processing is rendered difficult by poor solubility of SWNTs, and the exfoliation of nanotube bundles is a major challenge. Moreover, inherently weak nanotube−polymer interactions result in poor interfacial adhesion, which can lead to nanotube aggregation within the matrix. Although a variety of chemical routes have been investigated to achieve nanotube solubility,[2] most methods either shorten the nanotubes or induce excessive functionalities that disrupt the original structure of the tubes. Polymer grafting, to improve the nanotube−polymer interface, has mainly been achieved on acid-treated nanotubes,[3] which may result in partial destruction of the tubular framework.

Here, we report the development of a novel approach to in situ composite synthesis by attachment of polystyrene (PS) chains to full-length pristine SWNTs without disrupting the original structure, based on an established anionic polymerization scheme.[4] The process requires no nanotube pretreatment and works well with as-produced SWNTs. Both debundling of SWNT ropes and polymer attachment were achieved in a single step, and well-defined composites with a homogeneous dispersion of nanotubes were obtained.

SWNTs produced by the HiPCO process[5] were used without further purification, as purification procedures might introduce functionalities that hinder carbanion formation. Dried pristine SWNTs were dispersed by sonication in purified cyclohexane. *sec*-Butyllithium in slight excess of a predetermined amount (to ensure the removal of protic impurities on the SWNT surface) was added to this dispersion and sonicated in a bath for an hour. A homogeneous light yellow solution was obtained to which styrene monomer was added and polymerized at 48 °C for 2 h under sonication. Carbanions are introduced on the SWNT surface by treatment with the anionic initiator that serves to exfoliate the bundles and provide initiating sites for the polymerization of styrene (Figure 1). The negatively charged nanotubes are separated from the bundles and stay in solution due to mutual electrostatic repulsion between individual tubes, which was confirmed by long-term solution homogeneity. When styrene is added, both free *sec*-butyllithium and the nanotube carbanions initiate polymerization, resulting in an intimately mixed composite system. The polymer-

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Figure 1. Schematic (not to scale) of carbanion formation and subsequent initiation of polymerization: (a) section of SWNT sidewall showing *sec*-butyllithium addition to a double bond (green arrow indicates the bond to which it adds) and formation of anion via transfer of charge; (b) the carbanion attacks the double bond in styrene and, in turn, transfers the negative charge to the monomer. Successive addition of styrene results, and a living polymer chain is formed.

ization was terminated using degassed *n*-butanol, and the composite was recovered by precipitation with methanol. The composites were soluble in organic solvents such as dimethyl formamide, chloroform, and tetrahydrofuran.

Composites with matrix molecular weights ranging from 1600 to 100 000 g mol⁻¹ and polydispersities of ∼1.02 (determined using size exclusion chromatography (SEC)) were synthesized. The pristine SWNT loading was 0.05 wt % in all cases. To characterize the nanotube carbanions, the negative charges induced on *sec*-butyllithium-treated SWNTs were terminated with degassed *n*-butanol, yielding butylated nanotubes. PS-grafted nanotubes were recovered by subsequent workup (see Supporting Information). Control samples were made by sonicating a mixture of PS and pristine SWNTs in chloroform. For accurate comparisons, the same nanotube loading and molecular weight of PS as in the case of the PS-grafted composites were used.

It is known that[6] negative charges can be introduced on C_{60} and these carbanions can further be used as anionic initiators. The small diameters of HiPCO SWNTs offer high reactivities for carbanion addition reactions on sidewalls because of their high curvatures. Evidence for the formation of carbanions and subsequent attachment of PS chains was obtained using Raman spectroscopy (Figure 2a). Apart from the two characteristic Raman active modes in SWNTs (E_{2g} and ω_{RBM}), a third mode (D-band), indicative of disorder or sp^3 character within the nanotube framework, is found at ca. 1320 cm⁻¹. In our case, the intensity relative to the E_{2g} mode of this disorder-induced peak is indicative of the extent of covalent modification of the nanotube surface. Both butylated and PS-grafted SWNTs show an increase in relative intensity of the D-band when compared to pristine SWNTs. This increase is not due to sonication, as control samples sonicated in cyclohexane for 3 h exhibited no change in the disorder mode. Analysis of the radial breathing mode
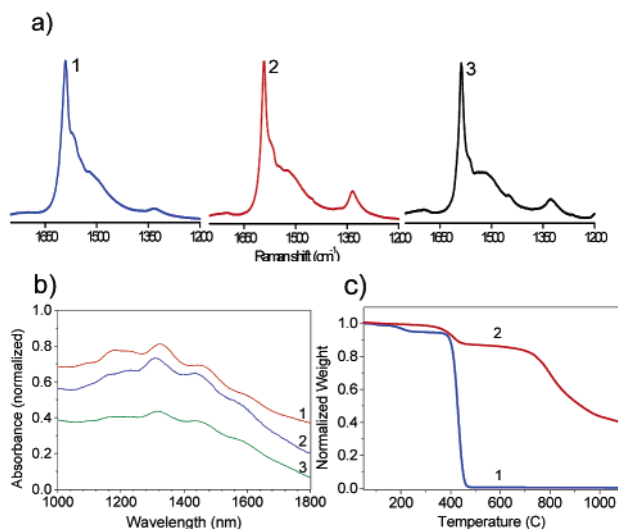
Figure 2. (a) Raman scattering spectra (514.4 nm) of (1) pristine SWNTs, (2) butylated SWNTs, and (3) PS-grafted SWNTs; (b) NIR absorption spectra of (1) pristine SWNTs, (2) butylated SWNTs, and (3) PS-grafted SWNTs; and (c) TGA traces (in N_2, 15 °C min^{-1}) of (1) pure PS and (2) PS-grafted SWNTs.

Figure 3. Tapping mode AFM image of a PS-grafted SWNT/PS film: (a) topography and (b) AFM height profile of an individual nanotube of diameter ∼0.8 nm.

frequencies was inconclusive due to the presence of characteristic C−X bending modes of PS in the same region, and no useful information could be obtained.

Excessive chemical modification of the nanotube surface can lead to degradation of the nanotube mechanical strength[7] and also result in loss of electronic structure. The ideal scenario for successful applications of SWNTs in composite materials would be to bring about the necessary modification to promote better adhesion with the matrix while maintaining the basic integrity of the SWNT structure. Absorption behavior in the NIR region (Figure 2b) is not greatly affected by covalent modification, although peaks corresponding to the van Hove singularities in the nanotube DOS are slightly shifted to lower wavelengths due to alteration of the π system. It has been reported[8] that nanotube electronic structure can be retained at low functionalization levels. Also, in the UV/visible range (see Supporting Information), there is no complete loss of structure as is seen in heavily functionalized nanotubes.[2,3] These results are suggestive of a low addition density of polystyrene chains, which was confirmed by both the Raman data (Figure 2a) and also the thermogravimetric analysis (TGA) of the PS-grafted nanotubes recovered from the composite (Figure 2c). The PS content in grafted SWNTs is ∼10 wt %, which is demonstrative of the low degree of functionalization.

Changes in intrinsic polymer properties brought about by the addition of SWNTs are indicative of nanotube−matrix interactions. Increases in glass transition temperatures (T_g) of composite systems containing SWNTs have been predicted by classical molecular dynamic simulations.[9] While simple mixing of SWNTs and PS (control) leads to little change in the T_g of the PS matrix, a very low nanotube loading of only 0.05 wt % in the PS-grafted composites increased the T_g of the matrix by up to 15 °C (see Supporting Information). This is quite remarkable considering the low degree of functionalization and nanotube loading. Similar behavior was exhibited for the entire range of matrix molecular weights synthesized. The magnitude of the change, however, decreased for higher molecular weights (see Supporting Information). The T_g increase is attributed to the decrease in mobility of the chains as a result of intimate interactions with PS attached to the nanotube surface. In effect, the attachment of polymer chains to the nanotube surface promotes better matrix−SWNT adhesion.
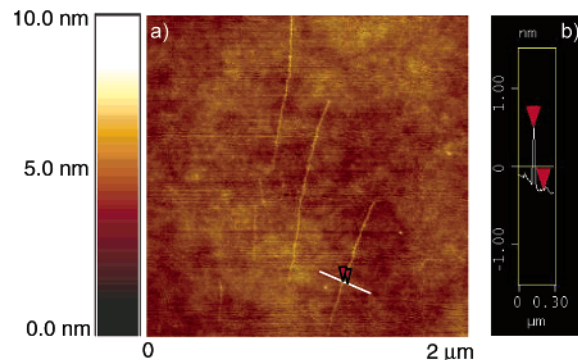
A tapping mode AFM image of a composite thin film reveals a good dispersion of the polystyrene-grafted SWNTs, and essentially only individual tubes are seen (Figure 3). In addition, the original length of the SWNTs (∼1 μm) seems unaltered, proving that the grafting process does not lead to structural degradation of the nanotube framework.

In conclusion, the method for grafting PS chains to SWNTs outlined in this study is a simple, scalable process that results in SWNT bundle exfoliation and polymer grafting in a single step, while retaining structural integrity of the nanotube framework. The carbanions on the SWNT surface help keep the nanotubes separate in solution and lead to the development of homogeneous composites with well-dispersed nanotubes.

Supporting Information Available: Experimental details and methods, UV/visible spectra, and DSC curves (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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