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Noncovalent Functionalization as an Alternative to Oxidative Acid Treatment of Single Wall Carbon Nanotubes with Applications for Polymer Composites

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Carbon nanotubes (CNTs) have the potential for a wide variety of applications owing to their unique physical and electronic properties.[1,2] Unfortunately, there are some limitations to these applications because single wall carbon nanotubes (SWNTs) readily form two-dimensional crystals called "bundles", which are formed mainly due to van der Waals interactions between the sidewalls of the individual tubes. This makes the SWNTs difficult to incorporate into materials and applications where individual SWNTs are needed without damaging the desirable mechanical and electronic properties of the tubes. Unmodified CNTs are very hydrophobic yet are also difficult to disperse in nonpolar organic solvents, and some organic solvents such as DMF (dimethylformamide) have actually been shown to damage the CNT structure.[3] Various methods exist to coax the CNTs into solution including oxidative acid treatment,[4,5] surfactants,[6,7] polymer wrapping,[8−10] DNA wrapping,[11] and covalent functionalization.[12] Oxidative acid treatment methods are some of the more effective means of dispersing CNTs in polar solvents, but unfortunately, these methods damage the desirable properties of the CNTs.[13−15]

We present here a method for noncovalently functionalizing SWNTs with the fluorescent molecule pyrene carboxylic acid (structure shown in Figure 1).

Pyrene carboxylic acid (PCA) attaches to the surface of SWNTs *via* physisorption, which is the result of a π−π stacking interaction between the pyrene moiety and the SWNT sidewalls, similar to the SWNT side-

ABSTRACT We have created stable dispersions of single wall carbon nanotubes (SWNTs) in water by employing a noncovalent functionalization scheme that allows carboxylic acid moieties to be attached to the SWNT surface by a π−π stacking interaction. Pyrenecarboxylic acid (PCA) is noncovalently attached to the surface of SWNTs and affords highly uniform and stable aqueous dispersions. This method was developed to provide a noncovalent alternative to the commonly used oxidative acid treatment functionalization of carbon nanotubes. This alternative strategy avoids the damage to the carbon nanotube structure inherent to oxidative acid treatments. Carbon nanotubes are commonly functionalized with oxidative acid treatment schemes to create polymer−nanotube composites and improve the adhesion between the polymer and carbon nanotubes. Composites of SWNTs and polycarbonate were prepared and tested to determine the effect of PCA on the adhesion of the SWNTs to the polymer matrix. These tests confirmed that PCA improved the SWNT−polycarbonate adhesion and improved the dispersion of the SWNTs throughout the matrix. This study demonstrates that stable dispersions of SWNTs can be achieved without substantial cutting, introduction of defects, or covalent modification, by employing a simple and effective noncovalent functionalization with PCA.

KEYWORDS: carbon nanotube · dispersion · acid treatment · noncovalent · polymer · composite · aromatic

wall interaction that leads to bundling.[16] The use of pyrene to introduce a variety of functionalities to carbon nanotubes *via* π−π stacking has been well-established by the work of various researchers.[17−21] Nakashima *et al.*[19] used trimethy-(2-oxo-2-pyren-1-yl-ethyl) ammonium bromide to disperse and solubilize SWNTs, citing earlier work by Dai *et al.*,[17] which showed an affinity between CNTs and pyrene-containing molecules. Several other pyrene-based strategies have been developed, yet none
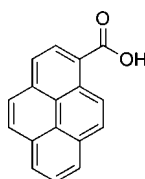
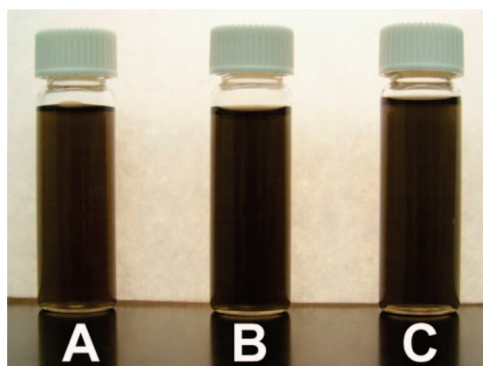**Figure 1. Structure of 1-pyrenecarboxylic acid.**

Figure 2. Digital photograph of three CNT dispersions after several days. (A) SWNT after 3 h reflux in concentrated 3:1 mixture of sulfuric and nitric acid dispersed in water. (B) PCA modified SWNT dispersed in water and (C) dispersed in tetrahydrofuran.

have attempted utilize 1-pyrenecarboxylic acid, one of the simplest possible pyrene-containing molecules. This previous work has served as the inspiration and basis for the current study. Considering the extensive use of carboxylic acid functionalized CNTs in the literature, use of PCA with CNTs is an obvious combination of these widely used methods. By employing a facile physisorption-based modification of the SWNT surface, it is possible to obtain several favorable results of oxidative acid treatment without any substantial damage to the SWNT structure. It should be noted that there are a few major differences between oxidative acid treatments and this PCA method. This PCA functionalization method will not purify the SWNT material and will also not cause substantial cutting or tip opening of the SWNTs, which can be viewed as desirable outcomes of standard oxidative acid treatments. Figure 2 shows three samples of CNT dispersions, which demonstrate that this method can still generate similar dispersions to oxidative acid treatment despite these differences.
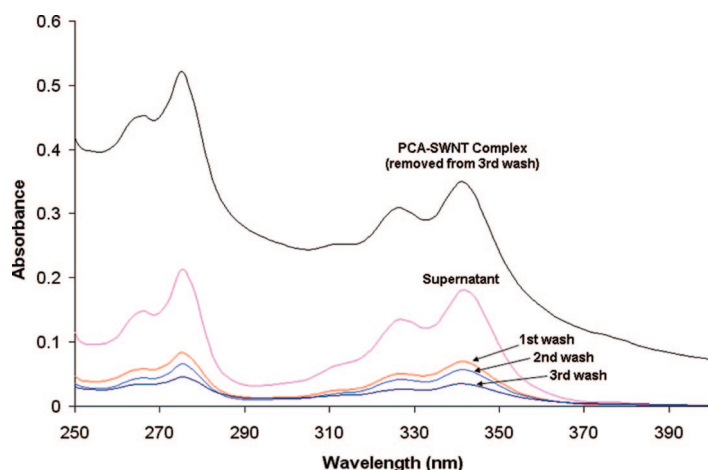

Figure 3. Spectroscopic monitoring of unbound PCA removal. The upper curve is the profile of washed PCA−SWNT complex dispersed in water that was removed after the third wash, demonstrating SWNT bound PCA strongly absorbing.

RESULTS AND DISCUSSION

PCA is highly soluble in methanol but has a very low solubility in water. Once PCA has physisorbed to the SWNT surface, the resultant PCA−SWNT complex becomes more soluble in polar solvents due to the introduction of polar carboxylic acid groups on the surface. This is why the addition of a lower amount of concentrated PCA/methanol solution to a larger quantity of deionized water will drive the PCA out of solution onto the SWNT surface and increase the solvent polarity. Any remaining unbound PCA is removed from the solution by several washing and centrifugation cycles using water, which also reduces the amount of methanol present to a trace. The final solution of PCA−SWNT is a nearly opaque black suspension and remains stable for weeks or longer with minimal precipitation formed. In the case where water-based solutions are not suitable, solvent transfer from water to tetrahydrofuran (THF) can be achieved by repeatedly adding THF, then centrifuging the sample and decanting the supernatant.

Removal of unbound PCA is monitored using a Perkin-Elmer Lambda 900 UV−vis spectroscope at room temperature. PCA is a member of a large class of pyrene-based fluorophores and exhibits strong absorbance peaks which allow for easy identification of even trace amounts. The data shown in Figure 3 are from the washing and centrifugation cycles after physisorption has occurred during mixing.

The original supernatant shows strong absorbance peaks due to the presence of unbound PCA, which is reduced in consecutive washing/centrifugation cycles. The amount of unbound PCA is substantially reduced in the supernatant of the final wash. Less than 0.5 mL of water containing the PCA−SWNT precipitate in the final wash is removed from the bottom of the centrifuge tube and added to 20 mL of deionized water, which is then bath sonicated for several minutes. This dispersion is then further diluted with approximately 30 mL of deionized water until the signal is not saturated and examined in the UV−vis spectrophotometer. It can be seen in Figure 3 that the dispersed SWNTs removed after the third washing have PCA bound on their surfaces, which results in a strong absorbance profile. It should be noted that the background seen around the 300 and 380 nm regions is due in part to the optical opacity of carbon nanotubes, and the original supernatant contained some dispersed SWNTs not removed by the initial centrifugation. The PCA−SWNT signal represents a sample with a substantial quantity of dispersed SWNTs, which lower the optical transparency and therefore the increased background is observed. It was later determined with fluorescence spectroscopy that this absorbance does indeed lead to a fluorescence emission and is not quenched by the presence of SWNTs (Figure 4).

We determined the amount of PCA that interacts with the SWNTs by monitoring the unbound PCA in the supernatant with varying amounts of SWNTs added. It was found that 10.0 mg of SWNT was sufficient to remove 1.65 mg of PCA from solution, leaving just a trace signal, which can be seen in Figure 5.

To estimate the coverage of the SWNTs by PCA, calculations were done using information from nanotube modeling software (Nanotube Modeler 1.4.0, JCrystalSoft). This modeling software was used to obtain the approximate surface area per mass for SWNTs typical to the samples used in this work. For the case where 10.0 mg of SWNTs is combined completely with 1.65 mg of PCA, a theoretical coverage of 1 molecule of PCA to every 1.25 nm for a (10,0) SWNT with a diameter of 0.78 nm and 1 molecule of PCA to every 0.8 nm for a (16,0) SWNT with a diameter of 1.24 nm was found. The majority of the SWNTs used are within the range of these diameters, which yields an average value of about 1 PCA molecule per 1 nm of SWNT length as a theoretical estimate of coverage. SWNTs deposited from solution are frequently observed bundled, so it may be possible that the coverage is higher than this estimate if these SWNT bundles exist in the dispersed solution, as well. Alternatively, when considering the possibility of PCA stacking on top of each other, the coverage of SWNTs would be reduced. Therefore 1 molecule of PCA per 1 nm SWNT should be considered the approximate estimate of coverage, which is supported by similar results in modeling studies of pyrene−SWNT interactions.[22] These modeling studies have also suggested that the PCA can possibly assume a stacked configuration specifically at defect sites, and this would lower the coverage per unit area. The SWNTs used in the current work are relatively free of defects as determined by Raman spectroscopy, and therefore, minimal amounts of PCA stacking should occur. This estimate assumes pristine SWNTs existing as individual tubes and not in bundles; however, the bundling of SWNTs in solution and the defect-site stacking of pyrenes are both unknown variables which can have a direct impact on this coverage estimate.

Confocal fluorescence microscopy showed that a liquid droplet of PCA−SWNT in water is dispersed uniformly, showing an even fluorescence throughout the droplet on a glass coverslip. However, upon drying, the PCA and SWNT segregate and fluorescent PCA crystals can be seen forming (see Supporting Information). This segregation upon drying occurs for aqueous solutions and solutions of PCA−SWNT in THF. On the basis of these observations, it can be assumed that obtaining a dry powder of the PCA−SWNT complex can only be achieved by a strategy which addresses the aggregation behavior of the components. It has been shown that some polymers can prevent the aggregation of PCA through hydrogen bonding. Su *et al.*
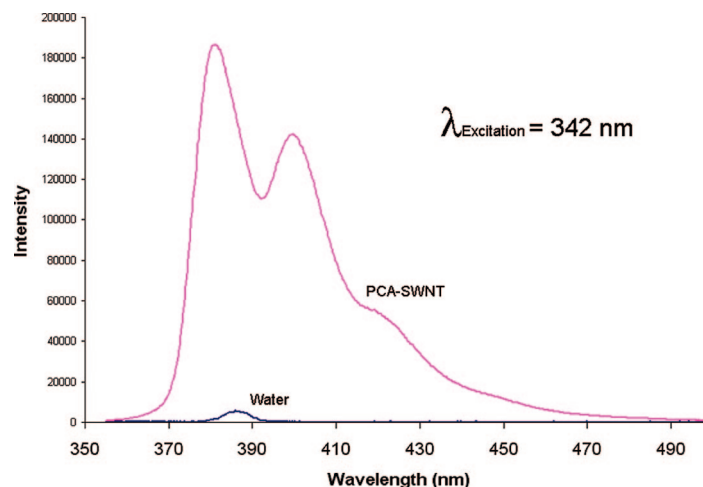

Figure 4. Fluorescence of PCA−SWNT in water using a Spex Fluorolog-Tau3 spectrofluorometer equipped with a Peltier cooling unit to maintain sample temperature.

showed that polymethyl methacrylate (PMMA) was able to prevent aggregation of PCA when creating PMMA composites in THF or toluene.[23] This suggests that under certain conditions PCA−SWNT can be incorporated into a host matrix without segregation of the components.

Possible damage to the SWNTs caused by the bath sonication steps was evaluated *via* Raman spectroscopy. SWNTs were analyzed before and after being bath sonicated with 20 mL of water for 40 min in a glass vial. These results were compared to SWNTs that were sonicated in concentrated nitric acid with a wand-type sonicator and to another SWNT sample which was subjected to a 3 h acid reflux (3:1 mixture of 5 M sulfuric and nitric acids). These are both typical treatments required for covalent functionalization. The wand-sonicated sample was prepared in a method consistent with the work of Kaempgen *et al.*, which showed
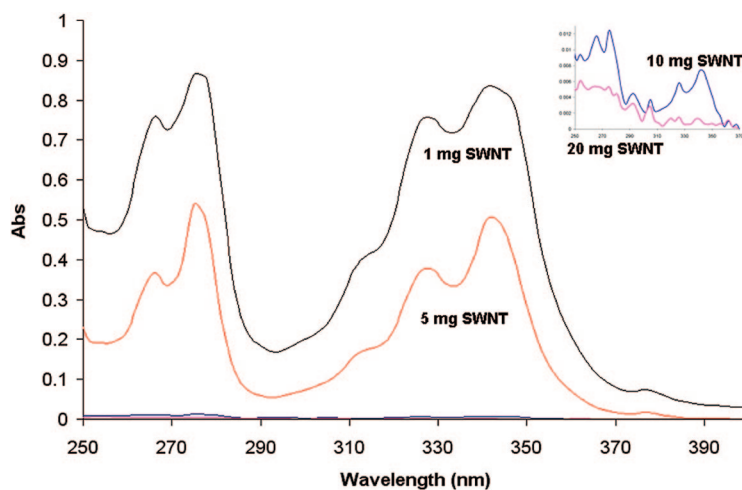

Figure 5. UV−vis spectroscopy determination of PCA/SWNT ratio. The mass of SWNT added to a solution of 1.65 mg of PCA is increased until the PCA is completely removed from solution. The inset shows that 10 mg is sufficient to remove all but a trace of the PCA, and this corresponds to 0.165:1 weight ratio of PCA to SWNTs.
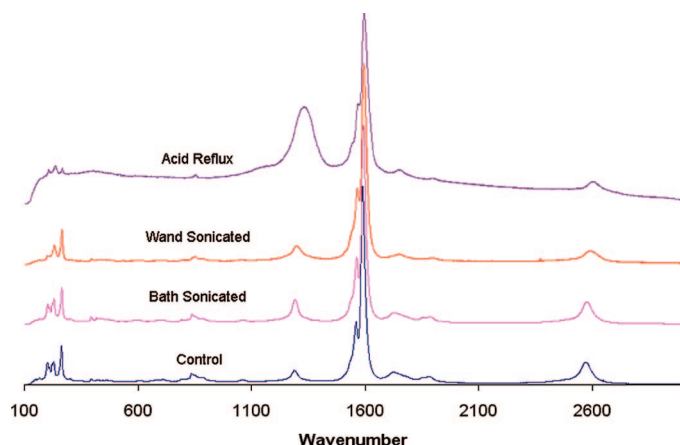
Figure 6. Extended scan with Raman spectrometer using a 785 nm diode laser. The *x*-axis is given in wavenumbers (reciprocal centimeters) and is plotted against an arbitrary intensity, with the G-band peak at approximately 1600 cm^{-1} normalized to 1.

that brief sonication can actually improve SWNT conductivity, possible through a p-doping mechanism caused by partial oxidation.[24] The results of the Raman work can be seen in Figure 6, which shows the extended scans of all the samples with a 785 nm laser, which give data on the relative level of defects, but not quantitative data on the number of defect sites.

The D-band, which is seen at about 1350 cm^{-1}, increased after sonication and increased dramatically after acid refluxing. This corresponds to an increasing level of disordered carbon bonding consistent with defects in the graphitic lattice of the SWNTs.[25] It can be seen that the spectrum of the bath-sonicated sample most closely matches the spectrum of the as-received control sample, including the radial breathing mode from 100 too 300 cm^{-1} and the D′-band near 2600 cm^{-1}. After only 3 h of the acid refluxing, the sample has been substantially altered, with a large amount of disordered carbon bonding. The areas of the peaks of the D-band and G-band for each sample have been compared in Figure 7 to show the approximate level of defects between the samples relative to the control SWNT material.

A closer examination of the D-band (see Supporting Information) shows that the bath-sonicated sample does have a greater increase in peak intensity, but the

Sample	D-Band	G-Band	Ratio
Control	2.2	7.6	0.289
Bath Sonicated	2.4	6.8	0.353
Wand Sonicated	1.4	3.9	0.359
Acid Refluxed	4.5	3.0	1.500

Figure 7. Raman data for several samples of SWNTs. The integrated areas under the D-band and G-band are listed along with the ratio of D-band/G-band, which gives an estimate of the relative level of defects present in the corresponding sample material, showing the two sonication methods are very similar, and the acid reflux has a much higher level of defects.

wand-sonicated sample has a greater shift and also has a broadening of the peak relative to the control. It can therefore be assumed that, while the concentration of defect sites is comparable between the two sonicated samples, the types of defects may vary, but nevertheless, the bath sonication will not have a noticeably negative effect on the conductivity of the SWNTs. It is possible that the small number of defect sites created by the bath sonication may actually increase the SWNTs' conductivity, similar to the results of short periods of wand sonication in nitric acid.[24]

There are many potential benefits of the PCA−SWNT system, and one of the most important is the ability to replace existing oxidative acid treatment strategies which can shorten and introduce structural/electrical defects to SWNTs. One of the most common uses of such acid-treated CNTs is to incorporate them into a polymer matrix as reinforcing filler, which can increase the tensile strength of the material. We conducted studies on polycarbonate to determine the improvement in tensile properties upon addition of PCA−SWNT and to compare that to the effect of unmodified SWNTs. CNTs are known to show a shift in Raman wavenumber as a function of their mechanical strain.[26] In the case of a carbon nanotube−polymer composite material, the nanotubes are strained by the matrix material when the matrix is subjected to load. Using this fact, we can test the load transfer effectiveness between a matrix polymer and carbon nanotubes by monitoring the D′ (disorder peak at ∼2600 cm^{-1} for SWNT) nanotube Raman peak within a polymer matrix as a function of the composite strain. For a more effective load transfer (either by improved interfacial interaction between the nanotubes and the matrix or better dispersion of the SWNT−smaller bundles), the slope of the Raman shift as a function of composite strain will be steeper than for a weaker interface.

The results of the Raman acquisitions are shown in Figure 8. It can be clearly observed that the slope of the Raman shift is greater in the PCA functionalized sample, indicating a more effective loading of the SWNT with functionalization than in the control sample. Furthermore, at approximately 0.3% strain, the control sample's slope begins to plateau and become more unstable.

Looking to Figure 9, where dispersion states of the PCA modified and control samples are shown, it can be seen that there is an improved dispersion in the functionalized sample. This observation, coupled with an increase in the interfacial bond strength, is likely the mechanisms for the increased loading effectiveness observed in the PCA functionalization by the Raman strain shift analysis. With reduced bundle size, there is greater interfacial volume between matrix and nanotube causing an increased slope for the Raman shift with strain. Likewise, a stronger interfacial bond due to the func-

tionalization causes an increase in loading effectiveness and hence an increase in slope.

SWNTs modified with PCA exhibit many of the desirable properties of SWNTs subjected to standard oxidative acid treatment, while avoiding covalent modification of the SWNTs and the associated drawbacks. Oxidative acid treatment with nitric acid has been shown to reduce the conductivity of SWNTs after only a short period of time. Kaempgen et al.[24] found that 3 min of sonication in nitric acid can actually increase the conductivity of SWNTs, possibly due to p-doping by the oxygen atoms, but further exposure will reduce the conductivity of the SWNTs due to the introduction of scattering centers as the result of increasing disorder in the graphitic lattice. The time required to substantially solubilize SWNTs with oxidative acids is much longer than 3 min, ranging from several hours up to 1 day. Damage to the mechanical structure of SWNTs also occurs during oxidative acid treatment, and this damage can lead to cutting[14] and ultimately yield shorter SWNTs in suspension. Additionally, SWNTs that have a damaged lattice structure as a result of oxidative acid treatment are more likely to fail under tension and in so have a reduced capability of providing enhancement of tensile strength to the host matrix.

In summary, the work presented here is a facile noncovalent method for the production of soluble SWNTs as an alternative to oxidative acid treatment and other covalent modification strategies. This method allows for SWNTs to maintain their desirable attributes such as electrical conductivity, high aspect ratio, and chemical stability while overcoming the undesirable attributes of insolubility and lack of adhesion to the host matrix when used as a reinforcing additive. Currently, there exists a multitude of functionalization schemes for CNTs, but very few offer a clear alternative to oxidative acid treatment. This method not only provides such an alternative but also additionally has the benefit of fluorescence of the

SWNT-PC Composite Raman Strain Shift

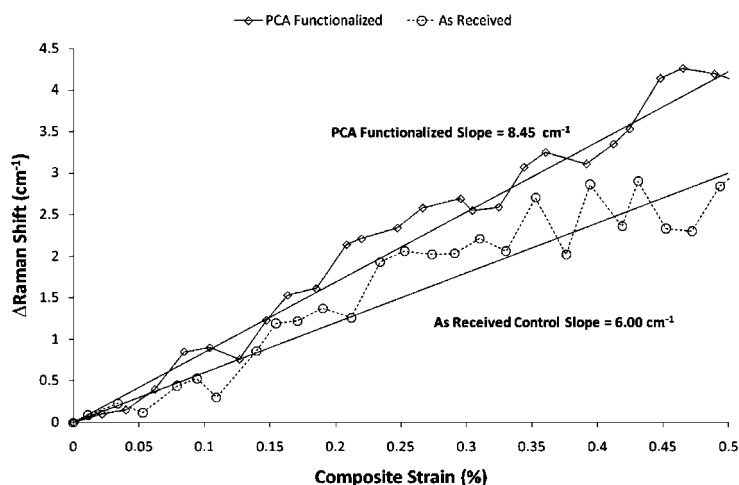— PCA Functionalized · · ⊙ · · As Received

Figure 8. Raman shift for treated and untreated composite samples. There is a noticeable increase in slope for the treated sample, indicating increased effectiveness of load transfer. Debonding also occurs earlier in the untreated case as evidenced by the slope plateau.
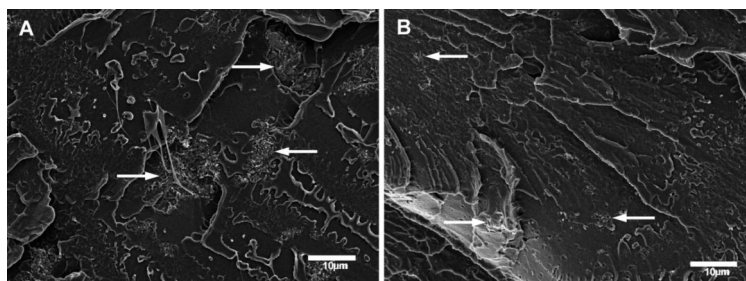

Figure 9. FE-SEM images of fracture surfaces of (A) control SWNT and (B) PCA−SWNT in a polycarbonate host matrix. Arrows indicate locations of several SWNT agglomerates, with those in sample B being substantially smaller throughout.

PCA−SWNT complex in solution in the visible spectrum. The solutions afforded by this method are stable over long time periods and can be applied to a variety of systems. This functionalization scheme is a valuable addition to existing CNT functionalization schemes, showing that alternatives to existing methods will enable greater versatility of CNT processing.

METHODS

Purified SWNTs (Undiym Inc.) are added to deionized water in an 8 dram glass vial and are sonicated with a Branson 5510 bath sonicator for several minutes at room temperature to allow for the formation of a temporary suspension. A stock solution of PCA is created by adding 1 mg of PCA to every 3 mL of methanol and briefly sonicated in a small bath sonicator to fully dissolve, yielding a 1.35 mM solution. The PCA dissolved in methanol is then added to the SWNTs in water (1:2 ratio, PCA in methanol/SWNTs in water) at room temperature and subjected to further bath sonication for approximately 30 min. The resultant PCA−SWNT complex is washed with deionized water and centrifuged repeatedly to remove methanol.

UV−vis spectroscopy used to obtain the data in Figures 3 and 5 was conducted with a Perkin-Elmer Lambda 900 UV−vis spectrophotometer (samples observed at room temperature). The samples seen in Figure 3 were prepared us-

ing the method described and then were consecutively washed by centrifugation, decantation, addition of fresh DI water, sonication, and further centrifugation. This cycle was repeated for three washing cycles, and then the precipitated PCA−SWNT material was removed from the final wash cycle and sonicated before analysis in the UV−vis spectrophotometer. The samples studied in Figure 5 were also made by the method described above, but with a constant (1.65 mg) amount of PCA and a variable amount of SWNTs. Once the PCA and SWNTs had been allowed to react through sonication, the samples were subjected to centrifugation without any washing, and then the supernatant was directly observed in the UV−vis spectrophotometer to determine the relative quantity of unbound PCA present. The data presented in Figure 4 were obtained by observing a diluted stable aqueous dispersion of PCA−SWNT with a Spex Fluorolog-Tau3 spectrofluorometer equipped with a Peltier cooling unit to main-

tain sample temperature (20 °C), and water was used as a control to show the background absorbance.

The PCA−SWNT was incorporated into a matrix polymer to examine its potential to incorporate SWNTs in a host matrix. To optimize the Raman signal from the nanotubes, a transparent matrix polymer, polycarbonate (GE Lexan 124), was used. To produce the composite, both the nanotubes and polycarbonate were put into solution with tetrahydrofuran (THF) as the solvent. This solution of polymer and nanotubes was then precipitated in methanol and collected by vacuum filtration. This composite material was then dried in a vacuum oven at 60 °C for several hours. The loosely bound composite was then compounded by compression molding into tensile testing dog bone shaped samples. These tensile samples were then placed into an *in situ* mechanical testing jig configured for Raman spectrum and strain acquisition. The schematics for the experimental setup of the Renishaw Ramascope S3000 can be found in the Supporting Information. The laser used for all Raman experiments was a 785 nm diode laser with line focus 5 μm $\times$ 15 μm at 100X magnification. The laser intensity was reduced to less than 3 mW *via* neutral density filters to avoid sample melting and local heating. The strain was applied in 0.025% increments from 0 to 0.5% strain and measured using a foil strain gage fixed to the underside of the tensile sample. Static Raman spectra were collected for 15 s after each strain increment.

Supporting Information Available: Additional figures. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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