PVK-Modified Single-Walled Carbon Nanotubes with Effective Photoinduced Electron Transfer

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SWNTs are among the most attractive one-dimensional materials in the scientific world. Recently, considerable work has been done to modify SWNTs in order to bring these fascinating carbon structures into the fold of (macro)molecular chemistry and to endow SWNTs with ultimate new characteristics.[1] The polymer wrapping of SWNTs has been proved to be an effective supramolecular approach to modify SWNTs.[2] Certain polymers could also be bound to the SWNT surface covalently through the defect sites introduced by oxidation.[3] These polymer−SWNT materials offered new opportunities for the application of SWNTs in many fields such as optoelectronics[4] and sensors.[5] In this paper, we report our strategy of covalent polymer functionalization of the side wall of SWNTs. We find that a novel dyad material of PVK-functionalized SWNTs can exhibit large optical limiting effects due to the photoinduced electron-transfer interaction.

To date, the covalent functionalization of the side wall of SWNTs has been achieved by several research groups. Their methods include direct fluorination and subsequent nucleophilic substitution,[6] addition of carbenes,[7,8] radicals,[7−9] and nitrenes,[7] electrochemical or thermochemical reduction of aryl diazonium in solvent[10] or solvent-free conditions,[11] [1,3]dipolar cycloaddition of azomethine ylides,[12] electrophilic addition,[13] and mechano-chemical addition.[14] Our functionalization methodology reported in this communication is based on the nucleophilic reaction of polymeric carbanions generated from organometallic reagents such as sodium hydride or butyllithium. This methodology was proved to be effective in the functionalization of [60]fullerenes and/or [70]fullerenes.[15−17] Various forms of SWNTs from Carbon Nanotechnologies Inc. at Rice, including the purified pyrolytic grown HiPco SWNTs and buckypaper SWNTs, could be incorporated into polymers through this method. In our experiments, PVK-modified SWNTs (PVK−SWNT) and polybutadiene (PB)-modified SWNTs (PB−SWNT) were obtained (Supporting Information).

The PVK−SWNT has reasonable solubility in chloroform, THF, toluene, and *o*-dichlorobenzene. The UV−vis−NIR absorption spectrum is shown in Figure 1a together with that of pristine SWNTs. The featureless absorption of PVK−SWNT is an indication of the successful functionalization of SWNTs, in which the introduction of sp^3-hybridized carbon atoms disrupts the extended π-network of the bare sp^2-hybridized nanotubes.[6c,10] The Raman spectrum of PVK−SWNT (Figure 1b, dash line) displays an intensive peak at 1595 cm^{-1} together with some other peaks derived from PVK. Compared with that of pristine SWNTs (Figure 1b, solid line), the D line of 1280 cm^{-1} of PVK−SWNT is increased obviously. This is an expected result of introduction of covalently bound moieties to the carbon nanotube framework, wherein some of the sp^2 carbons have been converted to sp^3 hybridization.[10] In the meantime, the existence of a RBM Raman line of the PVK−SWNT sample in the low-frequency range strongly suggests the remaining of the tubular structure of the sample.[14] The UV−vis−NIR and Raman spectra of PB−SWNT also give similar results (Supporting Information).

To determine the SWNT contents in the samples,[18] thermogravimetric analysis (TGA) experiments were conducted with a heating rate of 10 °C/min in the presence of nitrogen. Shown in Figure 1c is the mass loss for both pristine PVK and the PVK−SWNT. Clearly, the PVK backbones in the PVK−SWNT sample are completely decomposed at 400−500 °C with no mass loss for SWNT up to ∼700 °C.[19] As a result, ∼5 mass % incorporation of SWNT was obtained. Similarly, the TGA experiment of PB−SWNT sample gives a ∼8 mass % incorporation of SWNT (Supporting Information). The scanning electron microscopy (SEM) image of PVK−SWNT is also shown in Figure 1d, in which certain amounts of SWNTs can be seen clearly.

The optical limiting performance of the samples was investigated at 532 nm with linearly polarized 10 ns pulses generated from a Q-switched Nd:YAG laser at 532 nm. C_{60} was employed as a standard. For comparison, the concentration of all samples was adjusted to be 60% linear transmittance at 532 nm. The nonlinear transmission of both PVK−SWNT and PB−SWNT occurs at ∼0.02 J/cm^2, almost the same as C_{60}. However, along with the increase of the input fluence up to 1 J/cm^2, PVK−SWNT shows much better optical limiting performance than PB−SWNT and even better than C_{60} (Figure 2).

It was reported that both SWNT and MWNT suspensions were good optical limiters with a nonlinear light scattering mechanism,[20−22] while solubilized carbon

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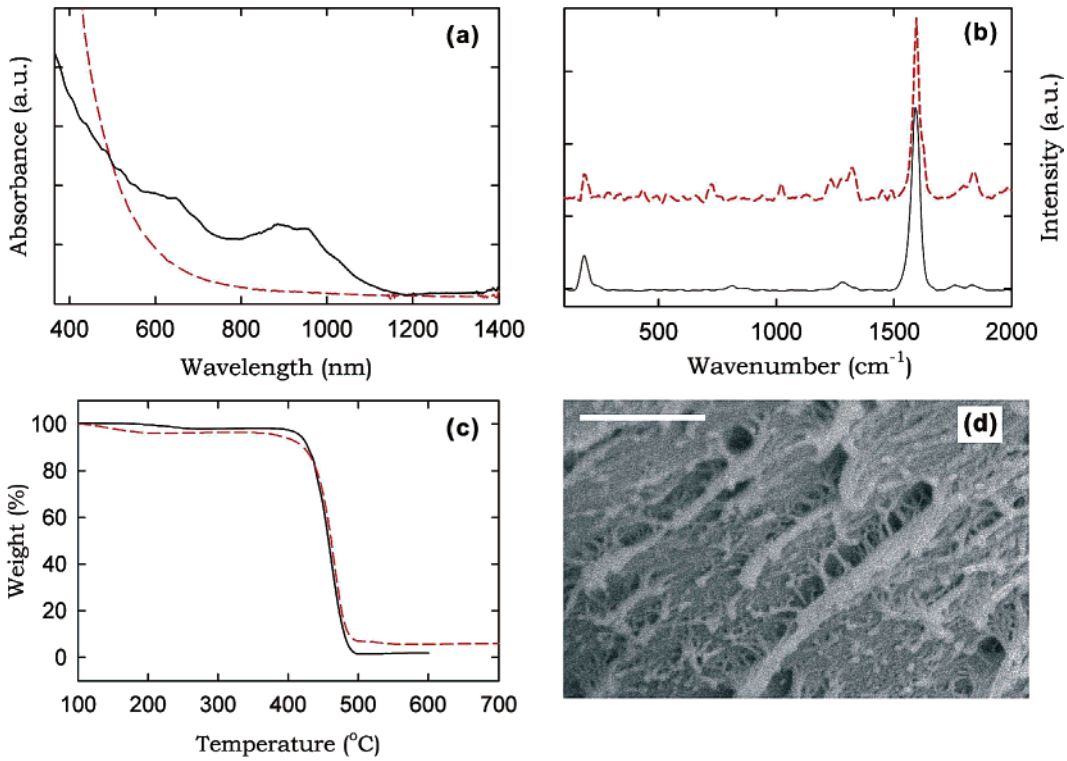

Figure 1. (a) UV−vis−NIR absorption spectra of pristine SWNTs (solid line) in DMF and PVK−SWNT (dash line) in chloroform. (b) Raman spectra of pristine SWNTs (solid line) and the PVK−SWNT (dash line). (c) TGA weight loss data of PVK (solid line) and PVK−SWNT (dash line). Experiments were carried out in nitrogen. Scanning rate: 10 °C min^{-1}. (d) SEM image of PVK−SWNT. Scale bar: 500 nm.

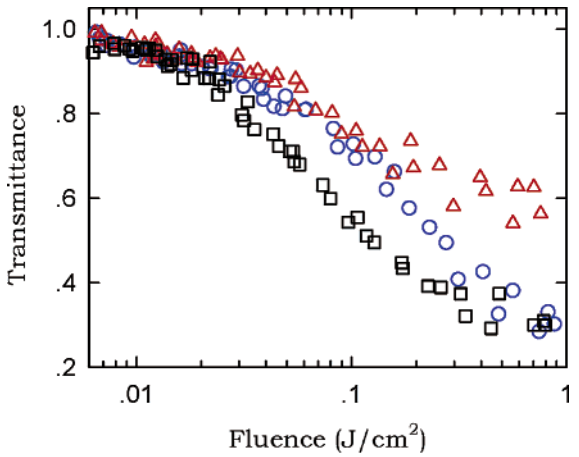

Figure 2. Optical limiting responses to 10 ns, 532 nm optical pulses, of PVK−SWNT (square) in chloroform, PB−SWNT (triangle) in *o*-dichlorobenzene, and C_{60} (circle) in toluene.

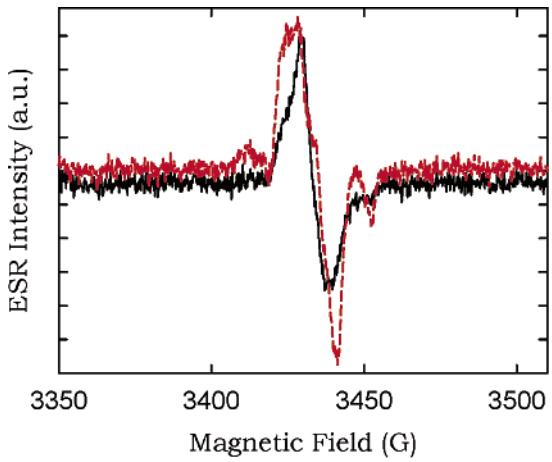

Figure 3. ESR spectra of PVK−SWNT without (solid line) and with (dash line) UV light illumination.

nanotubes shown relatively weak optical limiting performance with a proposed nonlinear absorption mechanism.[23,24]As for our experiments, the optical limiting performance is apparently not due to nonlinear light scattering. Considering that both PVK and PB do not absorb light at the wavelength investigated, and the absorption of light should be due to the SWNTs, our optical limiting results strongly suggest the nonlinear absorption mechanism.

The fluorescence of PVK was quenched by the attachment of SWNTs, which implies there is photoinduced electron transfer from PVK to the SWNT moieties.[25] Definitive evidence of electron transfer was observed in the ESR experiments (Figure 3). No ESR signal was observed for both pure PVK and PB samples without and with UV light illumination. The ESR spectrum of pristine SWNTs only shows a huge ferromagnetic resonance signal and is not affected under illumination.[26] However, the ESR spectrum of PB−SWNT (Supporting Information) displays a strong and symmetric signal at $g \approx 2.003$ (where g is the electron g factor) with $\Delta H_{pp} \approx 2.7$ G (where ΔH_{pp} is the peak-to-peak line width). The g value is larger than that of vacuum-annealed SWNTs ($g = 2.001 \pm 0.001$)[27] but similar to that of Haddon's solubilized SWNTs ($g = 2.003 \pm 0.001$).[26] Under UV light illumination, no change of this signal was observed. The ESR spectrum of PVK−SWNT, however, reveals a relatively wide and unsymmetric line shape with a g value of 2.004 and ΔH_{pp} of 7.1 G. When the sample was illuminated with light, two additional photoinduced spin signals could be resolved at $g \approx 1.997$ with $\Delta H_{pp} \approx 14$ G and at $g \approx 2.009$ with $\Delta H_{pp} \approx 20$ G, while the signal at $g = 2.004$ remained

unchanged. As the ESR spectra of PB−SWNT and pristine PVK did not change under the same illumination, the two new signals in the ESR spectrum of PVK−SWNT should be due to the photoinduced interaction between PVK and SWNTs. According to Safoula's report,[28] the *g* value of 2.009 is assigned to the $(PVK)^+$ and the other *g* value of 1.997 should be assigned to the $(SWNT)^-$. Thus, the new spin signals under illumination indicate that there is photoinduced electron transfer from PVK to SWNTs. This photoinduced electron transfer could produce a charge-separated excited state and result in a large optical limiting effect, just as the semiconducting polymer/methanofullerene system reported before.[29]

In summary, we have synthesized PVK- and PB-modified SWNTs through nucleophilic reaction. The photoinduced electron transfer is observed in the PVK−SWNT system and results in large optical limiting effects. This novel material together with other potential SWNT-based dyad materials are promising candidates in the applications ranging from nanotube-based electronics to polymer-based electronics, such as photovoltaic devices.

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Supporting Information Available: UV−vis−NIR spectra of SWNTs and PB−SWNT, Raman spectra of SWNTs and PB−SWNTs, TGA curves of PB and PB−SWNT, SEM image, and ESR spectrum of PB−SWNT. This material is available free of charge via the Internet at http://pubs.acs.org.

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