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In situ synthesis and optical limiting response of poly(*N*-vinylcarbazole) functionalized single-walled carbon nanotubes

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Abstract

A new poly(*N*-vinylcarbazole)-covalently grafted single-wall carbon nanotube (SWNT-PVK) hybrid material was synthesized by an *in situ* anionic polymerization reaction of *N*-vinylcarbazole and the negatively charged SWNTs. Incorporation of the PVK moieties onto the SWNTs' surface considerably improves the solubility and processability of SWNTs. At the same level of linear transmission, the SWNT-PVK dispersions show better optical limiting performance than the pristine SWNT dispersions, which shows this material to be a suitable candidate for viable optical limiting devices. Micro-plasma and/or micro-bubble induced nonlinear scattering is considered as the main mechanism for optical limiting.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotubes (CNTs), which exhibit a number of novel properties that make them potentially useful in many applications in electronics, optics, nanotechnology, and other fields of materials science, can be incorporated into some forms of matrix, e.g. polymer matrices, ceramics, and metals to form CNT composites [1–4]. Many efforts have currently been invested into the research of polymer/carbon nanotube composites in an attempt to allow for the fabrication of films required for the use of nanotubes in a real optical limiting application [5–8]. Optical limiting is an important application of nonlinear optics, useful for the protection of human eyes, optical elements and optical sensors from intense laser pulses. Preparing nanotube/polymer composites has in general involved mixing nanotube dispersions with solutions of the polymer and then evaporating the solvents in a controlled way [9]. The solution mixing approach is, however, limited

to polymers that freely dissolve in common solvents. An alternative method for producing a homogeneous dispersion of nanotubes is to incorporate nanotubes into thermoplastic polymers [10] at a temperature higher than the melting point of these polymers or to *in situ* polymerize suitable monomers [11] such as styrene, aniline, phenylacetylene, and others in the presence of CNTs. For these composite systems, however, a partial incompatibility of CNTs and polymer matrices leads to difficulties in achieving homogeneous dispersions and ultimately phase separation at high loadings. Distortion of the conjugation and coplanarity of the polymer backbones and an increase of the interchain distance in these systems would hinder both intra- and interchain charge-transfer processes, leading to a lower device performance. A convenient route to restrain phase separation is linking a soluble polymer or oligomer as donor and CNTs as acceptor via a covalent bond. The covalent attachment of appropriate moieties is anticipated to facilitate applications' development by improving solubility

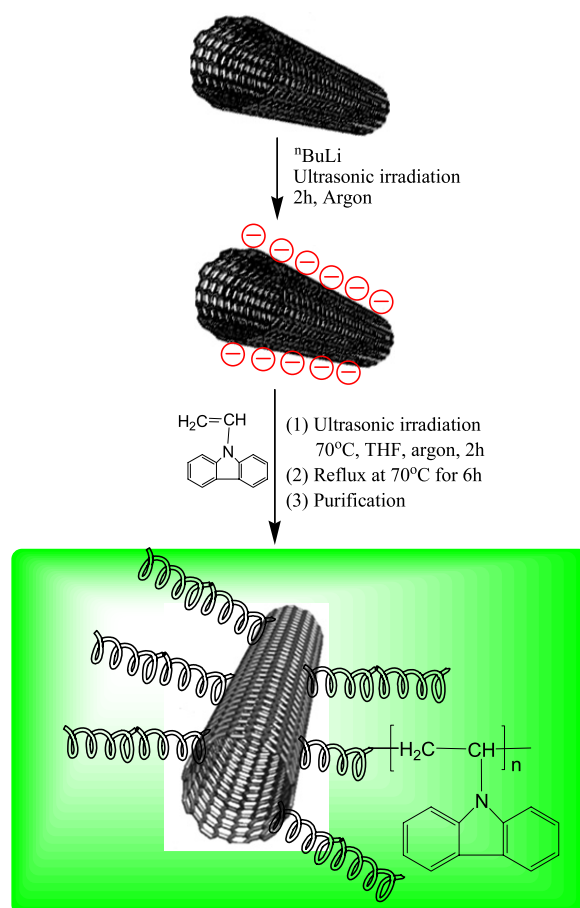
and ease of dispersion, and also providing for chemical attachment to surfaces and polymer matrices [12]. Polymer grafting can be achieved on acid-treated nanotubes [13] in which partial destruction of the tubular framework has been observed.

In our previous work on the polymeric modification and functionalization of [60]fullerene [14–21], we have successfully developed two synthetic routes to bond C₆₀ covalently onto poly(*N*-vinylcarbazole) (PVK). In the first method, C₆₀ was incorporated into the side chain of PVK to give C₆₀–PVK copolymer by reacting carbanion intermediates of PVK with fullerenes [15]. After laser flash photolysis, photoinduced electron transfer between C₆₀ and inter- and intrachain carbazole units takes place. The resulting layered structure had good photoconductivity as well as an unusual temperature dependence of the ESR spectrum. The second method mainly concerns addition of the ‘living’ *n*-butyllithium-terminated poly(*N*-vinylcarbazole)lithium (PVK[−]Li⁺) chains onto C₆₀ in a heterogeneous medium [16]. Although organic groups or species can also be theoretically attached to both the internal and external surfaces of CNTs, very reactive reagents are required. Using the first method we reported, SWNTs were introduced into the side chain of PVK as a pendant group to form a ‘charm bracelet’ polymer PVK–SWNT by Wu *et al* [22] in which the main chain of PVK has to be parallel to the surface of SWNT, and consequently the bulky carbazole pendant groups arrange only in *cis*-form in the polymer structure, giving rise to a stronger steric hindrance effect and a considerable enhancement of the polymer rigidity. We tried to utilize the second method, i.e. reaction of PVK[−]Li⁺ with SWNTs, to prepare PVK-grafted SWNTs, in which a number of PVK chains are directly attached onto the surface of SWNTs, but all efforts were unsuccessful due to the bundling of SWNT ropes. Therefore it would be very important to exfoliate the bundles of SWNTs before polymerization. Viswanathan *et al* [23] introduced carbanions on the SWNT surface by treatment with the anionic initiator (^{sec}BuLi) that serves to exfoliate the bundles. The negatively charged nanotubes are separated from the bundles and stay in solution due to mutual electrostatic repulsion between individual tubes. Following this idea, we successfully *in situ* synthesized PVK-grafted SWNT (SWNT–PVK) hybrid material, as shown in scheme 1. This soluble material exhibits outstanding optical limiting response at 532 nm. In the past decade, significant research effort has been invested in optical limiting materials and processes in an attempt to achieve effective protection from the intense laser beams [5, 24].

2. Experimental section

2.1. Materials and methods

All chemicals were purchased from Aldrich and used without further purification. Organic solvents used in this study were purified, dried, and distilled under dry nitrogen. The SWNTs, with a length of 5–15 μm and a >95% purity as well, were purchased from Shenzhen Nano-Powder Engineering Inc. (China). To ensure that SWNTs are free of air and



Scheme 1. Synthesis of SWNT–PVK hybrid material.

absorbed moisture prior to functionalization, they were dried under dynamic vacuum at 200 °C for 48 h and subsequently stored under argon. *N*-vinylcarbazole (NVC, purity [GC] ≥98%, melting point: 65 °C) was recrystallized twice from methanol at 40 °C, freeze-dried, and stored *in vacuo* in the dark before use.

Infrared (IR) spectra were recorded on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. The ultraviolet–visible (UV–vis) absorption spectral measurements were carried out with a Shimadzu UV-2450 spectrophotometer. Transmission electron microscopy (TEM) images were recorded on a JEM-2100S TEM system operated at 100 kV. Molecular weights (number-average (M_n) and weight-average (M_w)) were determined with a Waters 2690 gel permeation chromatography (GPC) system using a linear polystyrene standard eluting with tetrahydrofuran.

The Z-scan technique is a well-known method to characterize the nonlinear optical (NLO) properties of materials, including nonlinear absorption, scattering, or refraction. A standard open aperture Z-scan setup was used to measure the NLO coefficients of SWNT–PVK dispersions. This measures the total transmittance through the sample as a function of incident laser intensity while the sample is gradually moved through the focus point of a lens (along the *z*-axis). The optical arrangement was the same as that used in our previous experiments in testing the nonlinear response of SWNT dispersions [25, 26]. All experiments described in

this paper were performed with 6 ns pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove higher-order modes and tightly focused using a 9 cm focal length lens. The laser was operated at the second harmonic, 532 nm, with a pulse repetition rate of 10 Hz.

All samples were prepared by dissolving the compound in organic solvent with a concentration of 1.0 g l^{-1} , followed by gentle agitation for ~ 30 min in a low-power (60 W) sonic bath to ensure complete and uniform dispersal. The final dispersions were introduced into 1.0 cm quartz cells for Z-scan measurements. Linear extinction coefficients, α_0 , as defined by $T = \exp(-\alpha_0 L)$ were measured at 532 nm for the SWNT–PVK dispersions, where T defines the ratio of transmitted to incident laser light and $L = 1.0$ cm is the sample thickness. The α_0 of the 1.0 g l^{-1} dispersions is 0.34 cm^{-1} , which corresponds to a linear transmission T of 71.4%.

2.2. Synthesis of SWNT–PVK

The operation for synthesis was carried out under highly purified dry argon by use of standard schlenk tubes. To a suspension of SWNTs (200 mg) in anhydrous tetrahydrofuran (THF) (30 ml), which was pre-sonicated 30 min at room temperature, was rapidly added 2 ml of n-butyllithium (1.6 M solution in hexane). After ultrasonic irradiation for 90 min, 200 mg of *N*-vinylcarbazole in THF (20 ml) was added into the above system, followed by sonicating 4 h at 70 °C. After termination of the ultrasonic irradiation, the reaction mixture was continued to reflux for 10 h, and then allowed to cool to room temperature. To this system was added 1 ml of acidified MeOH solution under stirring to terminate the negative charges of the reaction mixture. After evaporation of the solvent and washing with distilled water several times, the collected crude product was extracted with chloroform (150 ml) for three days in a Soxhlet apparatus to remove ungrafted poly(*N*-vinylcarbazole) and some possible small molecules. The residual solid in the thimble was re-dissolved in THF, sonicated 1 h, and then laid at room temperature for 40 min. The filtrate was evaporated to dryness to give 178 mg of brownish yellow solid.

3. Results and discussion

It is known that C_{60} can react with lithium alkyl and Grignard reagents to give alkylated metal fullerenes [27]. Similarly, CNTs can also be attacked by nucleophiles. As an example, a novel approach on the usage of sec-butyllithium-treated SWNTs as initiators of anionic polymerization for *in situ* synthesis of polystyrene-grafted SWNTs was reported by Viswanathan *et al* [23]. This method 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. Furthermore, MWNTs can also be effectively functionalized using n-butyllithium and then chemically bonded to halogenated species [28]. n-butyllithium

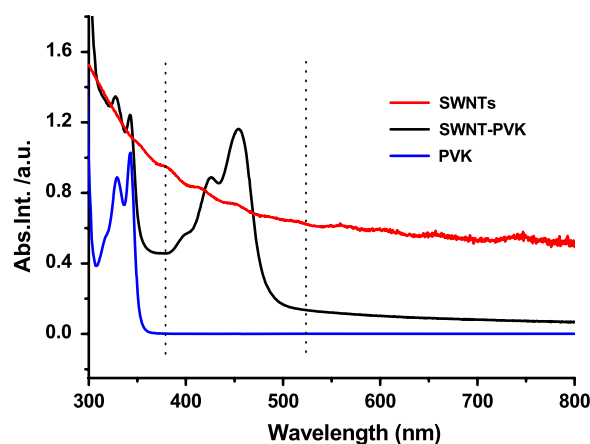


Figure 1. UV-vis absorption spectra for the samples in THF.

preferentially attacks the more reactive sidewall defects, tips, and other nonhexagonal regions. Upon treatment with n-butyllithium, the negatively charged nanotubes are separated from the bundles and stay in solution as a result of mutual electrostatic repulsion between individual tubes [23]. Using the SWNT carbanions as the anionic initiator, SWNT–PVK was successfully obtained. By GPC analysis against a linear polystyrene standard it was found that the PVK covalently grafted onto SWNTs, which can be removed from the nanotube surface in the presence of 3-chloroperoxybenzoic acid, has M_n of 7.30×10^3 , and a polydispersity of 1.2. Incorporation of the PVK moieties onto SWNTs considerably improved the solubility and processability of SWNTs.

As shown in figure 1, the pure PVK is essentially transparent at wavelengths longer than 350 nm [6, 15, 29, 30], while the SWNT–PVK has a new structure in the absorption spectrum in which the peaks centered at 398, 426, and 453 nm can be logically ascribed to charge-transfer (CT) peaks due to the possible inter- and intramolecular charge transfer in the system [15].

Because of the electron-withdrawing property of SWNTs, and the overwhelming contributions of multiple PVK chains in the SWNT–PVK structure, which may lead to a great encapsulation to SWNTs, the observed IR spectrum of SWNT–PVK (figure 2) is in general similar to that of PVK, but slightly shifted to the lower wavenumbers, followed by the enhanced intensities of some bands at 1035, 1087, 1355, and 1633 cm^{-1} .

The open aperture Z-scans for the SWNT–PVK dispersions at different incident intensities are depicted in figure 3. All open aperture Z-scans performed in this study exhibited a reduction in the transmission. The depth of reduction changes along with the variation of the on-focus intensity. The minimum transmission T_{\min} , i.e. the normalized transmission, at the focus of the incident beam is decreased as the intensity is increased. The nonlinear extinction coefficients, including nonlinear absorption and/or nonlinear scattering, β_{eff} , were deduced from the Z-scan data by curve fitting theory based on an intensity dependent extinction coefficient [31]. The incident laser pulsed energy used in the Z-scan measurement was altered from 0.12 to 0.35 mJ. The corresponding on-focus beam intensity varied from 0.54 to 1.27 GW cm^{-2} .

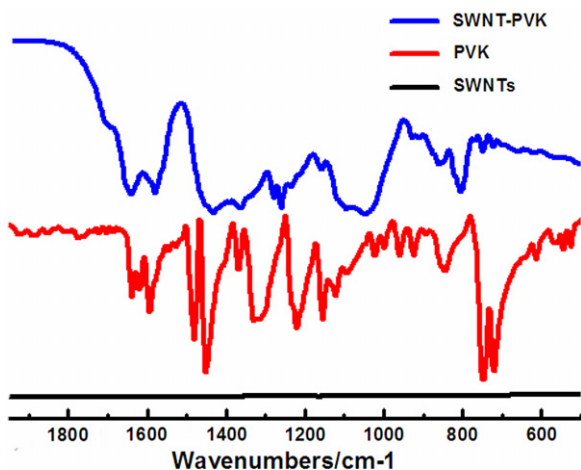


Figure 2. IR spectra of SWNTs, PVK, and SWNT-PVK.

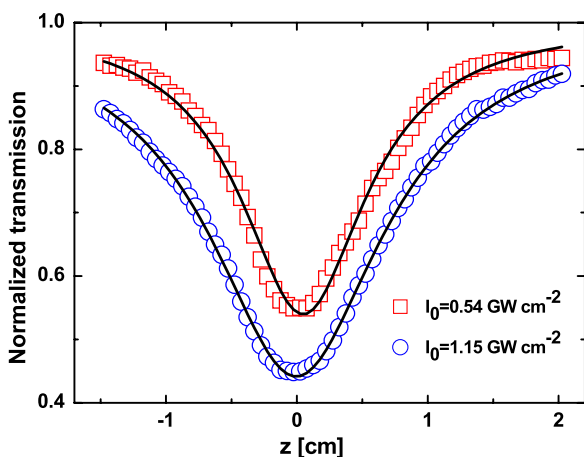


Figure 3. Z-scan data for the SWNT-PVK dispersions at different on-focus intensities. The solid lines are the theoretical fit curves.

The variation of β_{eff} with the on-focus intensity is illustrated in figure 4. It is seen that the nonlinear coefficients β_{eff} decrease as the intensity is increased. For example, the β_{eff} is 4.72 cm GW^{-1} at 0.64 GW cm^{-2} , which decreases to 3.39 cm GW^{-1} at 1.15 GW cm^{-2} .

Figure 5, in which the normalized transmission was plotted as a function of input energy density (J cm^{-2}), presents the optical limiting behavior of the SWNT-PVK dispersions. Because the optical limiting curves were directly converted from the Z-scan data, there is no error included in the optical limiting results. In an effort to evaluate the ability of the optical limiting of SWNT-PVK dispersions, we carried out the Z-scan measurements for pristine SWNT dispersions, for comparison purposes. The SWNT dispersions were prepared in *N,N'*-dimethylformamide (DMF) using the preparation procedure reported previously [32]. The SWNT-PVK dispersions exhibit better optical limiting performance than the pristine SWNT dispersions. The linear and nonlinear coefficients of the SWNT-PVK, SWNTs, and C_{60} are summarized in table 1. It should be pointed out that the nonlinear optical response of the nanotube dispersions arises from the generation of

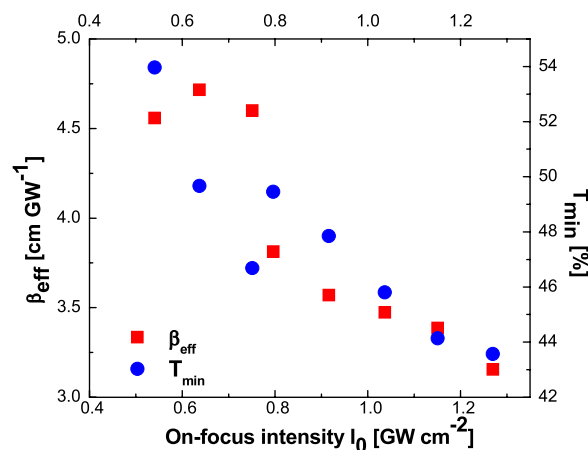


Figure 4. Nonlinear extinction coefficient and T_{min} as functions of on-focus intensity for the 1.0 g l^{-1} SWNT-PVK dispersions.

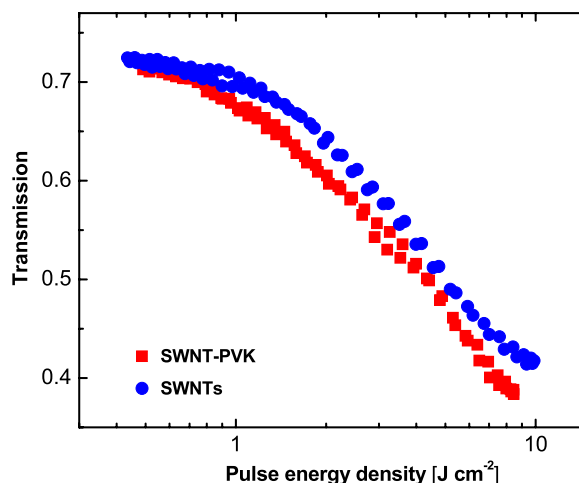


Figure 5. Optical limiting behavior for the SWNT-PVK and SWNT dispersions at the same level of linear transmission.

carbon plasmas and/or gas bubbles, while that of C_{60} arises from reverse saturable absorption. The pure PVK reference exhibited no nonlinear optical and optical limiting responses of its own.

The mechanism leading to the optical limiting effect in carbon nanotubes and nanotube composites has been studied extensively [5, 33, 34]. The nonlinear scattering, which originates from the heat-induced micro-plasmas and/or micro-bubbles, is regarded as the principal mechanism for optical limiting. Thus, we believe the pronounced optical limiting response of the SWNT-PVK dispersions is mainly attributed to the nonlinear scattering. As the solvent properties are very important for optical limiting of carbon nanotube dispersions [35], the enhanced optical limiting performance of SWNT-PVK dispersions is mainly due to the lower thermodynamic parameters, such as surface tension, viscosity, and boiling point of THF in comparison with DMF. In nanotube dispersions, the induced scattering centers, micro-plasmas, and micro-bubbles will expand much faster in the solvents of lower thermodynamic parameters, resulting in more effective light scattering and hence optical limiting [35, 36].

Table 1. Linear and nonlinear coefficients for the SWNT–PVK and SWNT dispersions. α_0 : linear extinction coefficients; β_{eff} : nonlinear extinction coefficient; $\text{Im}\{\chi^{(3)}\}$: the imaginary third-order susceptibility.

Sample	Solvent	Conc. (g l ⁻¹)	T (%)	α_0 (cm ⁻¹)	β_{eff} (cm GW ⁻¹)	$\text{Im}\{\chi^{(3)}\}$ (esu $\times 10^{-12}$)
SWNT–PVK	THF	1.0	71.4	0.34	3.91 \pm 0.54	1.30 \pm 0.18
SWNTs	DMF	~0.008	73.4	0.31	3.19 \pm 0.32	1.10 \pm 0.11
C ₆₀	Toluene	0.11	81.9	0.20	3.28 \pm 0.51	1.24 \pm 0.19

With the help of the PVK layer, the PVK–SWNTs can be dispersed homogeneously into the solvents with lower thermodynamic parameters, which will largely improve the optical limiting performance of the nanotube dispersions. In contrast, the pristine SWNTs can only be dispersed very well into the organic solvents with suitable but larger thermodynamic parameters, such as DMF, NMP, DMA, etc [32].

4. Conclusion

The *in situ* synthesized SWNT–PVK possesses excellent solubility in a range of common solvents. When dispersed in THF, the SWNT–PVK dispersions exhibit outstanding nonlinear optical and optical limiting properties for ns laser pulses at 532 nm. At the same level of linear transmission, the SWNT–PVK dispersions show better optical limiting performance than the pristine SWNT dispersions.

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