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Multi-walled carbon nanotubes covalently functionalized with polyhedral oligomeric silsesquioxanes for optical limiting

Bin Zhang^a, Yu Chen^{a*}, Jun Wang^{b*}, Werner J. Blau^{b*}, Xiaodong Zhuang^a, Nan He^a

^a Key Lab for Advanced Materials, Department of Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.

^b School of Physics and the Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, University of Dublin, Dublin 2, Ireland.

Abstract

A soluble polyhedral oligomeric silsesquioxane (POSS) functionalized multi-walled carbon nanotube (MWCNT) hybrid material (MWCNT/POSS) was synthesized, in which the POSS content was estimated to be 44wt.%. This material exhibits a remarkable optical limiting performance for nanosecond laser pulses at 532 nm. Thermally-induced nonlinear scattering is the primary mechanism for the nonlinear optical response. This behaviour demonstrates that the MWCNT/POSS hybrid material is a suitable candidate for viable optical limiting devices.

1. Introduction

Nanoscale science, engineering, and technology are emerging fields where scientists and engineers are beginning to manipulate matter at the atomic and molecular scale levels to obtain materials and systems with significantly improved properties.[1] The structural, mechanical and unique electrical and optical properties of carbon nanotubes (CNTs) have stimulated extensive research activities across the world.[2, 3] The lack of solubility and

*Corresponding author. Fax: +86-21-64252485; E-mail address: chentangyu@yahoo.com (Y.Chen).

their difficult manipulation in any solvent have, however, imposed great limitations on their use. To improve the solubility of CNTs, various methods have been proposed for their functionalizations.[4-10] Chemical modification of CNTs usually include: (a) the addition of 1,3-dipoles and dienes, (b) the addition of nucleophiles, and (c) the addition of radicals. Soluble CNTs can be analyzed more thoroughly using various spectroscopic techniques, and can also be used to fabricate electronic and optoelectronic devices.

It has long been recognized that the need for passive laser protectors to protect human eyes and all optical sensors from intense laser beams is not limited to the military, but is a growing societal problem that can only escalate.[11] In the past decade, significant research effort has been invested into optical limiting materials and processes in an attempt to achieve some measure of protection from such laser beams. CNT-based functional materials exhibit a broadband optical limiting response covering the visible to infrared region.[12-18] The optical limiting responses of CNT suspensions are shown to be dominated by nonlinear scattering as a result of thermally induced solvent-bubble formation and sublimation of the nanotubes, while solubilized CNTs demonstrate optically limiting as a result of nonlinear absorption. The optical limiting responses exhibit significant solution-concentration dependency .

Here an aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS-NH₂) was directly reacted with the MWCNTs with surface-bonded acyl chloride moieties (MWCNT-COOH) to give a soluble hybrid material MWCNT/POSS (**Figure 1**). This material exhibits a remarkable optical limiting performance for nanosecond laser pulses at 532 nm. After completion of this work, a similar synthetic method for the preparation of MWCNT/POSS has been reported by Chen and his coworker.[19] In their work,

MWCNT/POSS was used to prepare the hybrids of the poly(L-lactide)(PLLA).

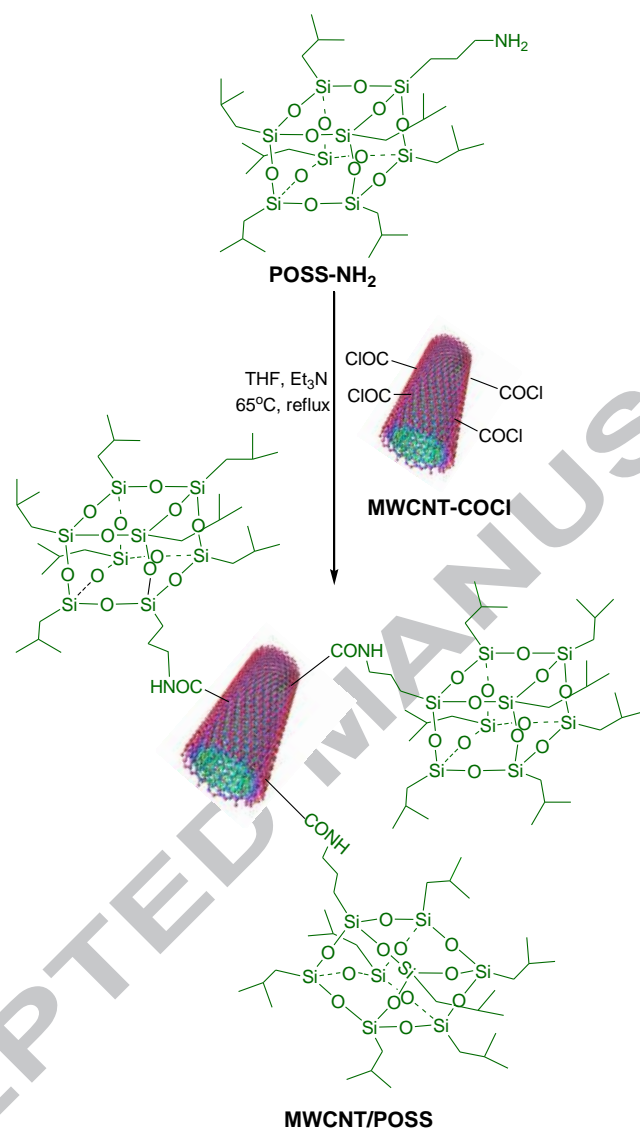


Figure 1. Preparation of the POSS-covalently functionalized MWCNTs.

2. Experimental

2.1 General

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 MWCNTs, with a diameter of 10~20 nm, a length of 5~15 μm and a >95% purity as well, were purchased from Tsinghua Nano-Powder Engineering Centre (Beijing, China).

POSS-NH₂ was purchased from Hybrid Plastics Company. The operations for synthesis prior to the termination reaction were carried out under purified argon.

Infrared (IR) spectra were recorded on a Nicolet Nagma-IR 550 spectrophotometer using KBr pellets. Raman spectra were taken at room temperature with a MicroRaman System RM3000 spectrometer and an argon ion laser operating at a wavelength of 514.5 nm as the excitation source. The Ultraviolet /Visible (UV/Vis) absorption spectral measurements were carried out with a Shimadzu UV-2450 spectrophotometer. Thermal properties of the samples were measured using a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) in flowing (100 mL min⁻¹) N₂. Transmission electron microscopy (TEM) images were recorded on a JEM-2100S TEM system operated at 100 kV.

All the Z-scan experiments were performed using 6 ns pulses from a Q-switched Nd:YAG laser. The beam was spatially filtered to remove higher-order modes, and tightly focused with a 9 cm focal length lens. The laser was operated at its second harmonic, 532 nm, with a pulse repetition rate of 10 Hz. Simultaneously, a focusing lens setup was arranged at ~30° to the direct incident beam to monitor the scattered light from dispersions. All samples were tested in 0.1 cm quartz cells.

2.2 Preparation of MWCNT-COCl

5.0 g of crude MWCNTs were marinated in 38% HCl for one day, filtered and washed with deionization water until neutral. A mixture of MWCNTs, HNO₃ (30 ml, 60%) and H₂SO₄ (90 ml, 98%) was sonicated at 40°C for 30 min. first, and then was refluxed 2h. After termination of reaction, it was allowed to cool down to room temperature. The mixture was diluted with a large amount of deionized water, followed by a vacuum-filtering through a

Nylon film ($\phi 0.45\mu\text{m}$). The obtained solid, in which polar carboxyl groups were introduced into the convex surface of MWCNTs, was washed with water until the aqueous layer reached neutral, and then was vacuum-dried at 60°C for 3h. The COOH-containing MWCNTs (500 mg) were reacted with a large excess of SOCl_2 containing a catalytic amount of *N,N*-dimethylformamide under reflux for 24h. After centrifugation, the remaining solid was washed with anhydrous tetrahydrofuran (THF) to remove the residual thionyl chloride.

2.3 Preparation of MWCNT/POSS hybrid material

To a suspension of MWCNT-COCl (50 mg) in anhydrous THF (30 ml) was added POSS-NH₂ (500 mg) and Et₃N (1 ml) under purified argon. The reaction mixture was sonicated 1h at 40°C first, and then refluxed at 60°C for 2 days. After cooling to room temperature, the dark solution was vacuum-filtered through a Nylon film ($\phi 0.22\mu\text{m}$). The solid product obtained was washed with distilled water to remove inorganic salts formed during the reaction first, and then washed with THF to remove any possible unreacted POSS molecules. 72.0 mg of the target material after vacuum-dryness at 50°C for 24h was obtained.

3. Results and Discussion

A typical POSS molecule, represented by the formula ($\text{R}_8\text{Si}_8\text{O}_{12}$), consists of a rigid and cubic silica core with a 0.53-nm side length. Its core is surrounded by eight organic corner groups, which endow the POSS molecule with higher reactivity and solubility in organic solvents.[20-22] Incorporation of the POSS molecules onto a CNT surface can considerably improve the solubility and processability of CNT, as shown in **Figure 2**. The solubility of the MWCNT/POSS is mainly dependent on the percentage of POSS grafted onto CNT.

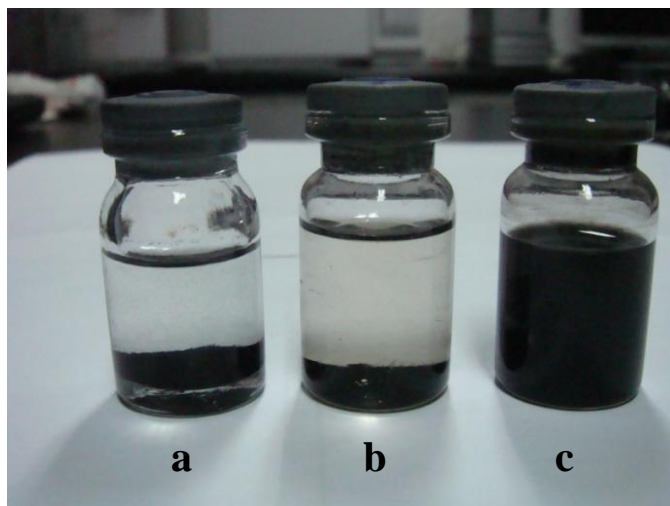


Figure 2. Comparison of solubility of the samples in THF: (a) MWCNTs, (b) MWCNT-COOH, and (c) MWCNT/POSS(with 44wt% POSS). A black dispersion shown in (c) is stable for at least one month.

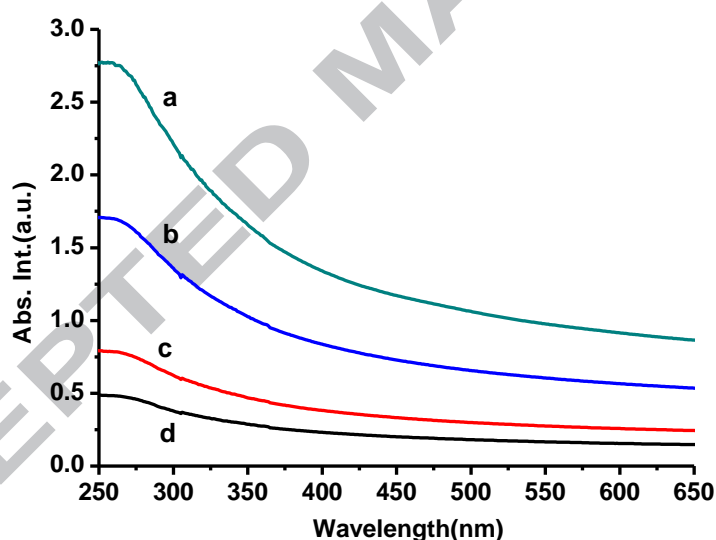


Figure 3. UV/Vis absorption spectra of MWCNT/POSS in different concentrations: (a) 10 mg/L, (b) 5 mg/L, (c) 2 mg/L, and (d) 1 mg/L in THF.

After functionalization with POSS, the resultant material exhibited a typical electronic absorption spectrum of solubilized carbon nanotube [23] (**Figure 3**), in which the absorbance decreases gradually from UV to the visible region. In contrast to the MWCNT/POSS, the POSS-NH₂ has a flat profile of low absorbance over the ultraviolet-visible region leading to its clear appearance.

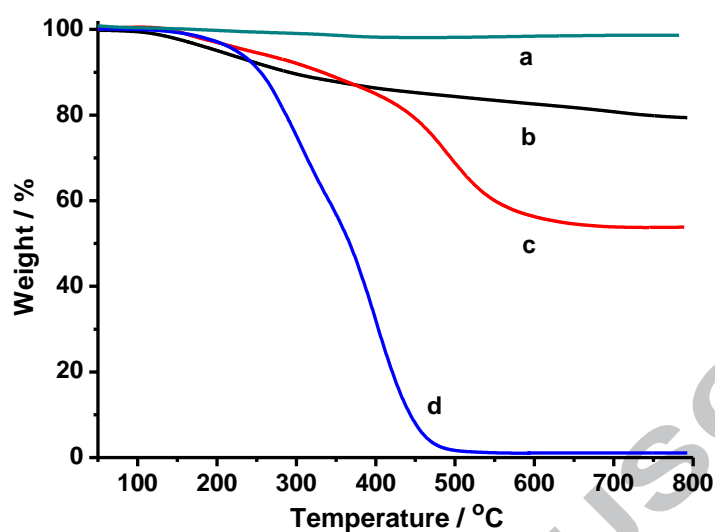


Figure 4. TGA profiles of (a) MWCNTs , (b) MWCNT-COOH, (c) MWCNT/POSS and (d) POSS-NH₂ in flowing (100 mL.min⁻¹) N₂.

The thermal properties of the samples were investigated by thermogravimetric analysis (TGA) in nitrogen atmosphere (**Figure 4**). There are about 4% weight loss of the pristine CNTs after heating to 230⁰C due to the possible organic and inorganic impurities (including possible organic solvents) trapped in the MWCNTs. The decomposed MWCNT residues seems to be very stable over a wide temperature range of 240-750⁰C. In contrast, the acid-functionalized MWCNTs (*i.e.*, MWCNT-COOH) are less thermally stable perhaps due to the defects on the nanotube surface caused by the acid etching. The TGA curve of MWCNT-COOH exhibited a rapid mass loss of 15% between 100 and 400⁰C, followed by a very slow weight loss of 5% up to 750⁰C at which the amount of the MWCNT residue is about 80% . By comparing the amount of the residues these two samples left at 750⁰C, the wt% of oxygen-containing groups at MWCNT defect sites was estimated roughly to be about 16%. Before 550⁰C the POSS-NH₂ has completely decomposed, and the residue that remain is less than 2% at 700⁰C. For MWCNT/POSS, the weight loss of 46% was observed at 700⁰C.

By assuming that before 800°C the POSS residues remaining in MWCNT/POSS have the same wt% as that of the POSS-NH₂ complex, and the wt% of oxygen-containing groups at MWCNT defect sites is close to zero at 700°C, the wt% of MWCNTs in the resulting product is found to be about 56%. In other words, the actual amount of POSS grafted onto the surface of MWCNTs is about 44%.

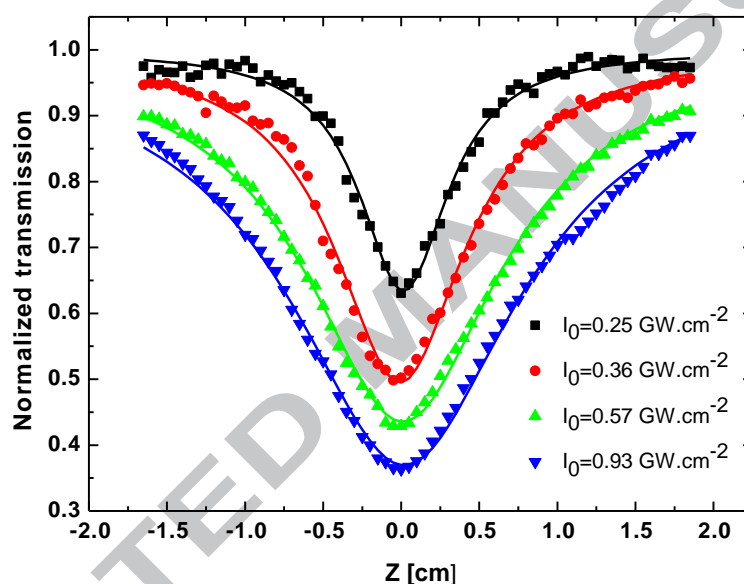


Figure 5. Typical open aperture Z-scan curves of MWCNT/POSS with the concentration of 0.5 mg/mL in chloroform. The solid lines are the numerical fittings.

Z-scan technique is widely used to study the intensity-dependent NLO processes, including nonlinear absorption, scattering and refraction.[24-27] Typical open aperture Z-scan results for a 0.5 mg/mL MWCNT/POSS dispersion were depicted in **Figure 5**, where the normalized transmission was plotted as a function of sample position z at different on-focus intensities. For all Z-scans, they showed a reduction in the transmission about the focus of the lens, a typical optical limiting characteristic. The depth of reduction varies as the on-focus intensity. The minimal normalized transmittance reaches 65% at the on-focus intensity of 0.25

GW/cm² (1.50 J/cm²), which further decreases to 36% as the intensity increases to 0.93 GW/cm² (5.58 J/cm²). Effective NLO coefficients were deduced from the Z-scan data by fitting theory reported previously.[28] No NLO response was detected in the POSS solution. The linear and NLO coefficients are summarized in Table 1.

Table 1. Summary of the linear and nonlinear optical properties for MWCNT/POSS and POSS in chloroform.

Samples	Conc. [mg/mL]	T [%]	Abs [cm ⁻¹]	β_{eff} [cm GW ⁻¹]	$\text{Im} \{\chi_{\text{eff}}^{(3)}\}$ [$\times 10^{-11}$ esu]
MWCNT/POSS	0.5	40.9	8.94	90.4 \pm 8.6	3.18 \pm 0.30
POSS	0.5	100.0	0	0	0

Figure 6 illustrates the normalized transmission and scattered light as functions of incident energy density. The MWCNT/POSS dispersions exhibit strong scattering signal at higher intensities, followed by the decreasing of transmission. POSS is a non-optically active material, and acts as a solubility promoter in the MWCNT/POSS hybrid material. Therefore the observed nonlinear optical response is logically from the contribution of MWCNT itself. In this case, the nonlinear scattering is the main mechanism for the optical limiting response. For other CNTs containing simple solubilizing reagents,[12] however, the optical limiting mechanism of these materials is quite complicated if the grafted solubilizing reagents are optically active. Besides nonlinear scattering contribution to the optical limiting, there may also be other contributions e.g. nonlinear absorption, electronic absorption and others to the optical limiting.[12] In the nonlinear scattering process, the photon energy from intense laser pulses is absorbed effectively by the nanotubes, resulting in the vaporization and ionization of

nanotubes to form microplasmas. The rapidly expanded microplasmas can strongly scatter the incident light, giving rise to an abrupt decrease of the transmitted energy. On the other hand, the heat energy can be transferred from the nanotubes to the surrounding liquid to generate microbubbles, which is another origin of scattering centers.[28-29] The observed significant NLO responses demonstrate that the MWCNT/POSS hybrid material is a suitable candidate for viable optical limiting devices.

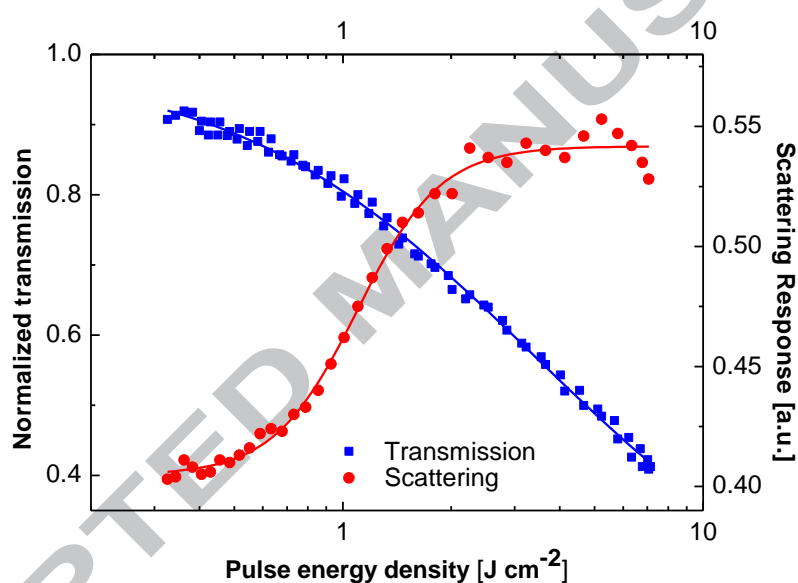


Figure 6. Plots of normalized transmission and scattering response against incident pulse energy density for MWCNT/POSS in chloroform. The solid lines are intended as a visual guide.

4 . Conclusions

An aminopropylisobutyl polyhedral oligomeric silsesquioxane (POSS-NH₂) was directly reacted with the MWCNTs with surface-bonded acyl chloride moieties (MWCNT-COOH) to give a new soluble hybrid material MWCNT/POSS. This material exhibits a remarkable optical limiting performance for nanosecond laser pulses at 532 nm. Thermally-induced nonlinear scattering is the primary mechanism for the nonlinear optical response. After

functionalization with the highly soluble POSS, the processability of MWCNTs is significantly improved too.

Acknowledgements

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References

- [1] Guldi DM, Rahman GMA, Jux N, Balbinot D, Tagmatarchis N, Prato M. Multiwalled CNTs in donor-acceptor nanohybrids - towards long-lived electron transfer products. *Chemical Communications*. 2005(15):2038-40.
- [2] Lambin P, Fonseca A, Vigneron JP, Nagy JB, Lucas AA. Structural and electronic properties of bent CNTs. *Chemical Physics Letters*. 1995;245(1):85-9.
- [3] Mintmire JW, White CT. Electronic structure simulations of CNTs. *Synthetic Metals*. 1996;77(1-3):231-4.
- [4] Aziz MA, Park S, Jon S, Yang H. Amperometric immunosensing using an indium tin oxide electrode modified with multi-walled CNT and poly(ethylene glycol)-silane copolymer. *Chemical Communications*. 2007(25):2610-2.
- [5] Kovtyukhova NI, Mallouk TE, Pan L, Dickey EC. Individual single-walled nanotubes and hydrogels made by oxidative exfoliation of CNT ropes. *Journal of the American Chemical Society*. 2003;125(32):9761-9.
- [6] Salzman CG, Llewellyn SA, Tobias G, Ward MAH, Huh Y, Green MLH. The role of

- carboxylated carbonaceous fragments in the functionalization and spectroscopy of a single-walled carbon-nanotube material. *Advanced Materials*. 2007;19(6):883-7.
- [7] Shaffer MSP, Koziol K. Polystyrene grafted multi-walled CNTs. *Chemical Communications*. 2002(18):2074-5.
- [8] Sun YP, Fu KF, Lin Y, Huang WJ. Functionalized CNTs: Properties and applications. *Accounts of Chemical Research*. 2002;35(12):1096-104.
- [9] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of CNTs. *Chemical Reviews*. 2006;106(3):1105-36.
- [10] Viswanathan G, Chakrapani N, Yang HC, Wei BQ, Chung HS, Cho KW, et al. Single-step in situ synthesis of polymer-grafted single-wall nanotube hybrids. *Journal of the American Chemical Society*. 2003;125(31):9258-9.
- [11] Spangler CW. Recent development in the design of organic materials for optical power limiting. *Journal of Materials Chemistry* 1999; 9:2013-20
- [12] Chen Y, Lin Y, Liu Y, Doyle J, He N, Zhuang XD, et al. CNT-based functional materials for optical limiting. *Journal of Nanoscience and Nanotechnology*. 2007;7(4-5):1268-83.
- [13] Wang J, Chen Y, Blau WJ. Carbon nanotubes and nanotube composites for nonlinear optical devices. *Journal of Materials Chemistry* 2009; 19(40): 7425-43.
- [14] Chen Y, Sai Muthukumar V, Wang Y, Li C, Sivarama Krishnan S, Siva Sankara Sai S, Venkataramanah K, Mitra S. Microwave-assisted solid-state grafting of multi-walled carbon nanotubes on polyurethane for the synthesis of a composite with optical limiting properties. *Journal of Materials Chemistry* 2009; 19(36): 6568-72.
- [15] Narayanan TN, Sandeep CS, Shaijumon MM, Ajayan PM, Philip R, Anantharaman MR,

- The synthesis of high coercivity cobalt-in-carbon nanotube hybrid structures and their optical limiting properties. *Nanotechnology* 2009; 20(28): 285702/1-285702/7.
- [16]Zhang L, Allen SD, Woelfle C, Zhang F. Influence of polymer structures on optical power limiting performance of single-walled carbon nanotubes. *Journal of Physical Chemistry C* 2009; 113(31): 13979-84.
- [17]He N, Chen Y, Bai JR, Wang J, Blau WJ, Zhu JH. Preparation and optical limiting properties of multi-walled carbon nanotubes with π -conjugated metal-free phthalocyanine moieties. *Journal of Physical Chemistry C* 2009; 113(30): 13029-35.
- [18]Hasi WLJ, Lu ZW, Fu ML, Lu HH, Gong S, Lin DY, He WM. Investigation of optical limiting based on the combination of stimulated Brillouin scattering and carbon nanotube/HT-270 suspension. *Laser and Particle Beams* 2009; 27(3): 533-6.
- [19]Chen GX, Shimizu H. Multiwalled CNTs grafted with polyhedral oligomeric silsesquioxane and its dispersion in poly(L-lactide) matrix. *Polymer* 2008;49(4):943-51.
- [20]Drazkowski DB, Lee A, Haddad TS, Cookson DJ. Chemical substituent effects on morphological transitions in styrene-butadiene-styrene triblock copolymer grafted with polyhedral oligomeric silsesquioxanes. *Macromolecules*. 2006;39(5):1854-63.
- [21]Liu YL, Tseng MC, Fangchiang MH. Polymerization and hybrids properties of multifunctional methylmethacrylate POSS. *Journal of Polymer Science Part A:Polymer Chemistry*. 2008;46(15):5157-66.
- [22]Kolel-Veetil MK, Dominguez DD, Keller TM. Dendritic networks containing polyhedral oligomeric silsesquioxane (POSS) and carborane clusters. *Journal of Polymer Science Part A: Polymer Chemistry*. 2008;46(7):2581-7.

- [23]Wu HX, Tong R, Qiu XQ, Yang HF, Lin YH, Cai RF, Qian SX. Functionalization of multiwalled carbon nanotubes with polystyrene under atom transfer radical polymerization conditions, *Carbon* 2007; 45:152-9.
- [24]Chen Y, Barthel M, Seiler M, Subramanian LR, Bertagnolli H, Hanack M. An axially bridged indium phthalocyanine dimer with an in-in bond. *Angewandte Chemie-International Edition*. 2002;41(17):3239-42.
- [25]Chen Y, Dini D, Hanack M, Fujitsuka M, Ito O. Excited state properties of monomeric and dimeric axially bridged indium phthalocyanines upon UV-Vis laser irradiation. *Chemical Communications*. 2004(3):340-1.
- [26]Chen Y, Fujitsuka M, O'Flaherty SM, Hanack M, Ito O, Blau WJ. Strong optical limiting of soluble axially substituted gallium and indium phthalocyanines. *Advanced Materials*. 2003;15(11):899-902.
- [27]Chen Y, Hanack M, Araki Y, Ito O. Axially modified gallium phthalocyanines and naphthalocyanines for optical limiting. *Chemical Society Reviews*. 2005;34(6):517-29.
- [28]Wang J, Blau WJ. Solvent effect on optical limiting properties of single-walled CNT dispersions. *Journal of Physical Chemistry C*. 2008;112(7):2298-303.
- [29]Wang J, Blau WJ. Nonlinear optical and optical limiting properties of individual single-walled CNTs. *Applied Physics B-Lasers and Optics*. 2008;91(3-4):521-4.