Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics Letters 378 (2003) 117–121

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

DFWM measurements of third-order susceptibility of single-wall carbon nanotubes grown without catalyst

S. Botti *, R. Ciardi, L. De Dominicis, L.S. Asilyan [1], R. Fantoni, T. Marolo [2]

ENEA, Advanced Physics Technologies Department, Via Enrico Fermi 45, 00044 Frascati, Italy

Received 5 May 2003

Abstract

Non-linear optical response of single-wall carbon nanotubes, produced without catalyst, was investigated. Third-order susceptibility Degenerate Four Wave Mixing measurements have been performed on thick film of nanotubes deposited onto quartz substrate. Results are presented as measured in the nanosecond time scale at 532 nm. The second-order hyperpolarizability γ was estimated to be as large as 1.6×10^{-29} e.s.u.

---

1. Introduction

Carbon nanotubes (CNTs) have unusual physical properties due to their peculiar structure combining one-dimensional solid state characteristics with molecular dimensions [1,2]. Though less than a decade passed since their discovery, carbon nanotubes are finding practical applications in several fields. It is well known that materials with large third-order optical non-linearities (characterized by large second-order hyperpolarizabilities γ) are required for photonic applications including all-optical switching, data processing, eye and sensor protection. However, the γ magnitudes of most materials are smaller than those needed for device construction. The existence of C=C double bonds in CNTs provides this material with delocalized π electrons around the tube walls, thus making them good candidates for non-linear optical applications. Among carbon derivatives also fullerenes should exhibit large non-linear optical responses due to the delocalization of π electrons, as much as in conjugated polymer chains, however, the effect is severely limited in the characteristic three-dimensional sphere like geometry, which leads to σ–π electrons mixing in the fullerenes molecules [3,4]. As a result, the γ value for fullerenes is several order of magnitude smaller than what required for photonic devices. On the contrary, CNTs have a one-dimensional geometry which does not limit π electrons delocalization and numerical calculations have shown that the γ magnitude can be enhanced by increasing the carbon number in the linear chain [5–7]. Should

---

* Corresponding author. Fax: +390694005607.
E-mail address: botti@frascati.enea.it (S. Botti).

[1] ENEA fellow.

[2] ENEA guest.

0009-2614/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0009-2614(03)01138-2

the carbon number be large enough, the major dynamical peaks with high γ value concentrate on a narrow frequency region near the energy gap of CNT and the highest peak magnitude is expected to become larger than 10^{-29} e.s.u. for single-wall nanotubes with more than 200 atoms (corresponding to a length of 4 nm) [8,9]. This value is appropriate for practical applications and can compete with γ magnitudes of polyenic polymers [5]. As an advantage with respect to the latter, CNTs, composed only by carbon atoms, show no residual infrared absorption, which in contrast limits polymers applications in the infrared where the telecommunication window must be matched.

Very few experimental measurements of CNTs non-linear optical response have been reported so far, therefore it is of particular interest to investigate experimentally third-order non-linearities of CNTs [10,11]. Liu et al. [10] demonstrated that carbon nanotubes have their own third optical non-linearity at 532 nm in the nanosecond time scale performing a degenerate four wave mixing (DFWM) experiment on carbon nanotubes dispersed in a solution of polypyrol and *m*-cresol with ethanol. The difficulty in obtaining a good solubility of CNTs and the strong optical DFWM background signal originating from the solvent, makes interesting to explore the possibility of directly measuring the third-order susceptibility on CNT thick films.

In order to determine the third-order susceptibility of CNTs deposited onto a quartz substrate, in this work we report the experimental results of DFWM measurements performed at 532 nm and in the nanosecond time scale. DFWM in the forward configuration was used to generate an efficient non-linear optical signal from the thick layer ($\sim$20 μm) of CNT deposited on the substrate. We verified that the substrate itself does not generate any DFWM signal, thus allowing for the determination of CNTs non-linear properties without any background subtraction.

The CNTs were prepared with a recently settled technique which does not use metal catalyst [12,13]. The method provides a unique opportunity to measure intrinsic physical properties of CNTs, without any residual impurity otherwise derived from the chemical procedures required for complete catalyst removal.

2. Experimental

The non-linear optical properties measurements were performed using the nanosecond DFWM technique. In this method, two pulsed laser beams (pumps) with same wavelength (λ_p) and polarization state cross at an angle θ in the medium under investigation, giving rise to an optical interference pattern. If λ_p matches an allowed optical transition of some species present, the laser energy stored in the medium will modulate the molecular internal energy of the resonant species with a defined periodicity of the fringe pattern given by $\Lambda = \lambda_p / 2\sin(\frac{\theta}{2})$.

The resulting sinusoidal modulation of the complex refractive index of the medium originates in a grating able to diffract a third weak probe beam, at the same wavelength λ_p, which crosses the interaction region at the Bragg angle.

The laser radiation at 532 nm suitable to excite the non-linear optical response of the CNT was provided by the second harmonic of a Nd:YAG laser (JK2000).

The forward phase-matching geometry, shown in Fig. 1, was chosen for efficient signal DFWM generation (F-DFWM). Suitable optics were used to split from the same laser output three co-propagating beams traveling at the corners of the square before focusing by a lens ($f = 750$ mm). The F-DFWM signal emerged from the interaction region as if originating from the fourth corner of the square. After having been spatially filtered the signal was measured by means of photomultiplier tube (Hamamatsu R943-02) and visualized on the screen of a scope (Tektronik TDS 3052).

In this investigation the carbon nanotubes were prepared by annealing of carbon nanoparticles. This recently developed technique does not use metal catalyst and is able to produce single-wall nanotubes (SWNTs) with a mean diameter of 1.1 ± 0.3 nm arranged in bundles [12,13]. The non-nanotube material is constituted by residual carbon particles which are not detrimental for the χ_3

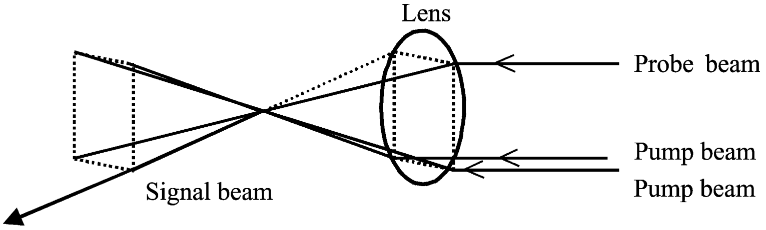

Fig. 1. Forward DFWM phase-matching scheme.

evaluation of the sample, because we verified that they do not exhibit any non-linear signal in the experimental conditions (pulse energy and duration) adopted during the measurements reported in the following. The percentage of carbon nanoparticles was evaluated by SEM and RAMAN spectroscopy and resulted to be lower than 30% [12]. The sample used in our experiment consists of 20 μm thick films of CNTs deposited by drying droplets of CNTs–ethanol suspension (1:100 by weight) onto a quartz substrate held at 200 °C. Before dropping, the suspension was sonicated for 1 h at room temperature.

The CNTs optical absorption spectra here reported were obtained by using a Perkin–Elmer λ 90 scanning spectrophotometer across a wavelength range of 200–3200 nm with a resolution of 2 nm.

3. Results and discussion

Fig. 2 shows a typical optical absorption spectrum (plotted in optical density, O.D.) of the CNT samples investigated in our experiment. Broad bands centred at 1.28 ± 0.05 and 2.2 eV, with shoulders at 1.36 ± 0.05 and 2.4 ± 0.1 eV, respectively, emerge on a background increasing at increasing photon energy. The background is ascribed to the density of states of amorphous carbon. The absorption bands, due to optical transitions of SWNTs, can be identified as interband transitions between the Van Hove singularities in the 1D electronic density of states (DOS) according to previous and current theoretical studies [14,15]. The singularities are spikes in the DOS which occur at specific energies, depending on the nanotube diameter and chirality. From band structure calculations, approximate relations were deduced between the energy E of interband transitions between DOS singularities and the nanotube diameter, suggesting that the optical absorption peaks should move to higher energy as E increases and at decreasing nanotube diameter. On the basis of the relation found [14,15], the band transition at 1.28 eV energy corresponds to the separation between the first and second pairs of Van Hove singularities in the semiconducting,

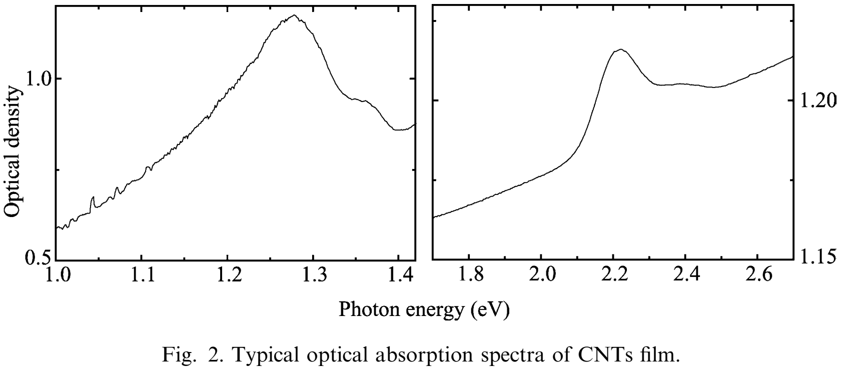

Fig. 2. Typical optical absorption spectra of CNTs film.

chiral nanotubes with a diameter of about 1.1 nm, while the transition at higher energy belongs to metallic nanotubes. Therefore, as expected, our sample is a mixture of nanotubes with different chirality; the non-negligible absorption occurring at the exciting laser wavelength (532 nm), is suitable to excite non-linear optical response.

The magnitude of the tensor component $\chi^{(3)}_{1111}$ of our CNT sample was measured by setting the two pump beams and the probe beam in the same polarization state. For a quantitative determination of $\chi^{(3)}_{1111}$ the experimental apparatus must be calibrated in advance, by measuring the DFWM signal intensity of a reference sample with a well-known $\chi^{(3)}_{1111\mathrm{ref}}$.

The cubic susceptibility of the sample is then obtained by using the relation

$$\chi^{(3)}_{1111} = \frac{l_{\mathrm{ref}}}{l}\left(\frac{n}{n_{\mathrm{ref}}}\right)^2 \frac{\alpha l}{(1-\mathrm{e}^{-\alpha l})\mathrm{e}^{-\alpha l/2}}\left(\frac{I}{I_{\mathrm{ref}}}\right)^{1/2}\chi^{(3)}_{1111\mathrm{ref}}, \tag{1}$$

where l, n, α and I are the interaction length, the index of refraction, the absorption coefficient and the DFWM signal intensity, respectively.

As reference sample a solution of Rhodamine 6G diluted in methanol (concentration 10^{-6} M) was utilized. The corresponding value of $\chi^{(3)}_{\mathrm{ref}}$ was 4.5×10^{-13} e.s.u. [16] and in our experimental conditions $l_{\mathrm{ref}} = 1$ mm and $n_{\mathrm{ref}} = 1.33$ for nanosecond pulses. For the carbon nanotubes sample used in the measurements data in Eq. (1) were: $l = 20$ μm, $n = 2$ and $\alpha = 0.54\times10^3$ cm^{-1}. No detectable DFWM signal was observed from CNTs at pump beam intensity lower than 0.5 mJ, while in the range between 0.5 and 1 mJ the poor signal to noise ratio (S/N) did not allow any quantitative determination. A good S/N was achieved in the excitation energy range between 1.1 and 1.8 mJ, where a cubic dependence of the DFWM signal as a function of the laser intensity was recorded (Fig. 3). In agreement with Liu et al. [10], the cubic dependence indicates that a one-photon process is responsible for the third-order optical non-linearity on the nanosecond time scale at 532 nm. At pump beam intensities larger than 2 mJ a decrease of the DFWM signal and a corresponding increase of the optical noise is observed. Most probably, due to the local heating, nanotubes are peeled off from the substrate. In our experimental condition a pump beams energy of 2 mJ of energy corresponds to a fluence of 2.8 J/cm^2 (assuming a spot size of 300 μm in the focal point), a value which cannot lead directly to the vaporization of carbon nanotubes via laser ablation with microplasma formation [17].

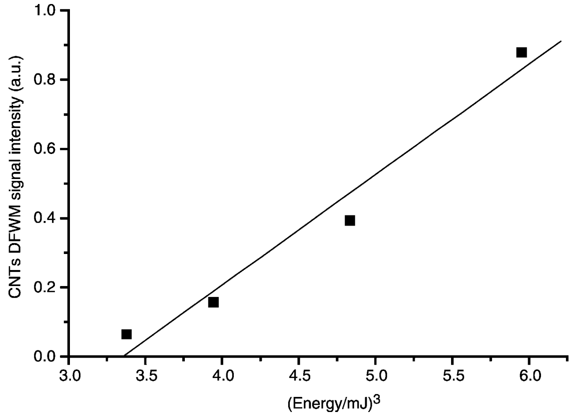

Fig. 3. Dependence of the CNTs DFWM signal on the cube of the pump beam energy. The good linear fit (standard deviation = 4%) indicates the one-photon nature of the excitation involved.

The $\chi^{(3)}_{1111}$ of the CNT sample was measured with a pump beam fluence of 2 J/cm^2 and a value of 5×10^{-3} was found for the (I/I_{ref}) ratio. By using Eq. (1) the component $\chi^{(3)}_{1111}$ of the CNT sample was calculated and the value of 1.2×10^{-11} e.s.u. was obtained.

A possible contribution to the nanosecond non-linear response of carbon nanotubes could be due to higher absorption of excited states with respect to the ground state in a reverse saturable absorption type mechanism. The high absorption cross-section of excited states can be understood in terms of the increased transition probability through dipole allowed transitions and of the large number of final states available. The association of nanosecond non-linear response of CNTs with an excited-state population can be further confirmed by the following discussion. At 532 nm in the nanosecond time scale the ratio $\chi^{(3)}_{1122}/\chi^{(3)}_{1111}$ was measured, after the insertion of a $\lambda/2$ retardation plate polarized the probe beam orthogonally with respect to the two pump beams. A value of

0.11 was found for the $\chi^{(3)}_{1122}/\chi^{(3)}_{1111}$ ratio which indicates a violation of the Kleinmann symmetry condition $\chi^{(3)}_{1122}/\chi^{(3)}_{1111} = 1/3$ for strictly non-resonant electronic processes [18].

We could not derive the magnitude of second-order hyperpolarizability γ for each CNTs because, in our synthesis process, they have a wide distribution of lengths (2 ± 1 μm) and diameters. In this respect, we estimated only the average contribution from each carbon atom in the nanotube using the following relation [12]:

$$\gamma_c = \frac{\chi^{(3)}}{N\rho L}, \tag{2}$$

where N and ρ are, respectively, the number density of carbon atoms and the CNT purity, while L is the local field correction given by

$$L = \left(\frac{2 + n^2}{3}\right)^4. \tag{3}$$

By assuming a CNT number density of 10^{14} cm^{-3} it turns that $N = 8 \pm 4 \times 10^{21}$ cm^{-3}. If $L = 3.16$ and $\rho = 0.7$, as in our sample, the magnitude of γ_c for each atom in CNTs is then calculated to be $(9 \pm 5) \times 10^{-34}$ e.s.u. For C_{60}, whose γ was determined to be $(7.5 \pm 2)10^{-34}$ e.s.u. [3,4,19] the contribution for atom to the third-order non-linearity is about 1.2×10^{-35} e.s.u. Therefore, the contribution of one carbon atom in the carbon nanotubes is one order of magnitude larger than that in C_{60}.

With the value of γ_c for the carbon atoms, we can calculate the magnitude of γ_{CNT} for a single-wall nanotube with length 1 μm and diameter 1.1 nm, $\gamma_{CNT} \approx 1.6 \times 10^{-29}$ e.s.u. This is an appropriate value for photonic devices which can compete with those of polyenic polymers for non-linear optical applications. However, this value is four orders of magnitude smaller than theoretical prediction [12] which gives $\gamma_{CNT} \approx 10^{-25}$ e.s.u. for a single-wall nanotube with length 1 μm. It is worth noticing that such disagreement was observed also by Wang et al. [12] for γ values of single-wall nanotubes with length 160 nm from data taken at 820 nm wavelength. Further investigations are required to understand the inadequacy of current theories in modeling results of experiments performed at different wavelengths.

4. Conclusion

We have demonstrated that single-walled nanotubes synthesized without catalyst with a non-conventional laser assisted procedure have their own third-order non-linear optical response at 532 nm. At this wavelength, the nanosecond third-order susceptibility is partially ascribed to a reverse saturable absorption mechanism. We have estimated a γ_{CNT} value of 1.6×10^{-29} e.s.u. that, although not as large as expected from theoretical calculations, is still suitable for non-linear optical applications.

References

[1] S. Iijima, Nature (London) 354 (1991) 56.

[2] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.

[3] S.R. Flom, R.G.S. Pong, F.J. Bartoli, Z.H. Kafafi, Phys. Rev. B 46 (2002) 15998.

[4] D. Neher, G.I. Stegeman, F.A. Tinker, N. Peyghambarian, Opt. Lett. 17 (1992).

[5] R. Xie, J. Jiang, J. Appl. Phys. 83 (1998) 3001.

[6] R. Xie, J. Jiang, Chem. Phys. Lett. 280 (1997) 66.

[7] R. Xie, J. Jiang, Appl. Phys. Lett. 71 (1997) 1029.

[8] V. Margulis, T. Sizikova, Physica B 245 (1998) 173.

[9] X. Wan, J. Dong, D. Xing, Phys. Rev. B 58 (1998) 6756.

[10] X. Liu, J. Si, B. Chang, G. Xu, Q. Yang, Z. Pan, S. Xie, P. Ye, J. Fan, M. Wan, Appl. Phys. Lett. 74 (1999) 164.

[11] S. Botti, R. Ciardi, M.L. Terranova, S. Piccirillo, V. Sessa, M. Rossi, M. Vittori-Antisari, Appl. Phys. Lett. 80 (2002) 1441.

[12] F. Wang, W. Huang, H. Yang, Q. Gong, Z. Shi, X. Zhou, D. Qiang, Z. Gu, Chem. Phys. Lett. 320 (2000) 411.

[13] S. Botti, R. Ciardi, M.L. Terranova, S. Piccirillo, V. Sessa, M. Rossi, Chem. Phys. Lett. 355 (2002) 395.

[14] T. Pichler, M. Knupfer, M.S. Golden, J. Fink, A. Rinzler, R.E. Smalley, Phys. Rev. Lett. 80 (1998) 4729.

[15] M.S. Dresselhaus, in: L.P. Biro et al. (Eds.), Carbon Filaments and Nanotubes: Common Origin Differing Applications, vol. 11, Kluwer Academic Publishers, Dordrecht, 2001.

[16] A. Costela, J.M. Figuera, F. Florido, Opt. Commun. 100 (1993) 536.

[17] P. Chen, X. Wu, X. Sun, J. Liu, W. Ji, K.L. Tan, Phys. Rev. Lett. 82 (1999) 2548.

[18] M.D. Levenson, S.S. Kano, Introduction to Nonlinear Laser Spectroscopy, Academic Press, London, 1988.

[19] J.S. Meth, H. Vanherzeele, Y. Wang, Chem. Phys. Lett. 197 (1992) 26.