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2009 Nanotechnology 20 285702

(http://iopscience.iop.org/0957-4484/20/28/285702)

Nanotechnology **20** (2009) 285702 (7pp) doi:10.1088/0957-4484/20/28/285702

The synthesis of high coercivity cobalt-in-carbon nanotube hybrid structures and their optical limiting properties

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Received 8 April 2009, in final form 15 May 2009
Published 24 June 2009
Online at stacks.iop.org/Nano/20/285702

Abstract

Magnetic heterostructures with carbon nanotubes having multiple functionalities are fascinating materials which can be manipulated by means of an external magnetic field. In this paper we report our investigations on the synthesis and optical limiting properties of pristine cobalt nanotubes and high coercivity cobalt-in-carbon nanotubes (a new nanosystem where carbon nanotubes are filled with cobalt nanotubes). A general mobility assisted growth mechanism for the formation of one-dimensional nanostructures inside nanopores is verified in the case of carbon nanotubes. The open-aperture z-scan technique is employed for the optical limiting measurements in which nanosecond laser pulses at 532 nm have been used for optical excitation. Compared to the benchmark pristine carbon nanotubes these materials show an enhanced nonlinear optical absorption, and the nonlinear optical parameters calculated from the data show that these materials are efficient optical limiters. To the best of our knowledge this is the first report where the optical limiting properties of metal nanotubes are compared to those of carbon nanotubes.

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

1. Introduction

The design and controlled growth of one-dimensional nanostructures constitute an area of high impact in the field of nanoscience and nanotechnology [1]. The landmark paper by Iijima [2] on carbon nanotubes (CNTs) sparked the interest of the scientific community to nanotube based materials, largely because of their application potential in functional nanodevices and sensors [3]. Several techniques were reported for the synthesis of metal nanotubes thereafter. These include chemical routes such as the chemical reduction of metallic complexes, and chemical vapor infiltration within porous templates such as AAO and polymer nanochannels after modifying their walls chemically [4–7]. This often resulted in impure wires and tubes which were not ideally suited for many applications [8, 9]. Electrodeposition over a nanoporous membrane is an alternative to these chemical routes and other sophisticated routes such as molecular beam epitaxy or pulse laser deposition. Moreover it is a simple, low cost and elegant technique for the preparation of one-dimensional structures with high purity.

Nanocomposites consisting of CNTs and magnetic materials have been attracting the interest of many researchers, and a considerable amount of research is under way in this

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area, especially on the synthesis and characterization [10, 11]. Numerous attempts were made earlier to fill CNTs with metallic elements or compounds, which achieved only limited success [12]. The application potential of these metal encapsulated composites extends to various fields like spin polarized transportation, magnetoresistive random access memories, nanoelectronic devices and radar absorbers [13].

An understanding of the growth mechanism will help in the design of various heterogeneous structures and hybrid multifunctional nanostructures, and a mechanism for the formation of one-dimensional nanostructures such as nanowires and nanotubes was proposed, based on mobility assisted growth [8]. In our earlier works [8, 14], we fabricated cobalt nanotubes (Co NTs), thick walled Co NTs, cobalt nanowires (Co NWs) and nickel nanowires (Ni NWs) using template assisted electrodeposition on nanoporous alumina, by employing different precursors. A detailed growth mechanism was discussed in these works and the veracity of the model was tested using various precursors. The role of the hydration layer and the mobility of the cations was well established. In the present paper, an extension of these studies for the fabrication of cobalt nanotubes using acetate precursors is carried out on carbon nanotubes instead of AAO with a view to testing the mobility assisted growth of nanostructures inside nanoporous templates. Moreover, controlled growth of magnetic nanostructures over CNTs has additional leverage for the fabrication of large scale functional nanostructures with multiple functionalities [15].

The successful fabrication and use of photonic devices depends upon the availability of good nonlinear optical materials. Over the years various materials such as inorganics, organics, organometallics and semiconductors have been studied for their nonlinear optical properties [16–21]. Recently, interest in the field of photonic devices has surged due to the advent of nanoparticles and nanostructures. Nanotubes and nanowires are attractive in this regard, as they possess a unique one-dimensional physical geometry [22, 23]. These one-dimensional nanomaterials are found to have a characteristic behavior in the optical as well as in the electrical regimes, arising from their peculiar geometry [24, 25]. For instance, a number of authors have reported optical nonlinearities in carbon nanotubes [22, 23, 26–31]. The expertise gained in the bulk production of carbon nanotubes [32] attracted the attention of the scientific community for fabricating nanotubes and nanowires of various other inorganic materials, which are also found to possess many features similar to those of the CNTs. Nanotubes in general have high thermal and chemical stability, along with high electrical conductivity and a fast optical nonlinearity. Carbon nanotubes can be suitably functionalized to serve as versatile one-dimensional nanostructures for various optical limiting applications. This is abundantly evident from the vast literature available on this topic of research. Wang and Blau highlighted the optical limiting properties of various hybrid nanostructures and CNT based composites in a recent review article [33]. Mechanisms such as nonlinear scattering, two-photon or three-photon absorption, and reverse saturable absorption phenomena including free carrier and excited state absorption are thought to be responsible for optical limiting. Moreover, the possibility of the simultaneous occurrence of different mechanisms in the same system giving rise to strong optical limiting properties cannot be ruled out.

Electrodeposited metal nanowires are increasingly becoming popular, and they are a hot topic of research due to their application potential in ultrahigh density magnetic recording, ultrafast optical switching, and microwave devices. Metal nanotubes are another interesting system of current research where they can find enormous applications in hybrid nanostructures for possible energy storage devices, cell separation and diagnosis [34]. In the recent past, strong optical limiting has been observed in metal nanowires synthesized from cobalt, manganese, silver, gold and nickel [35, 36], and their optical limiting was compared to those of single-walled and multiwalled carbon nanotubes (SWCNT and MWCNT respectively).

In the present investigation we synthesized a novel hybrid nanosystem called the cobalt-in-carbon nanotube, where cobalt nanotubes are grown coaxially inside multiwalled carbon nanotubes using electrodeposition, and the general mobility assisted growth mechanism suggested for the growth of metal nanowires/tubes inside alumina pores is verified in the case of carbon nanotubes. The nonlinear optical limiting properties of carbon nanotubes, cobalt nanotubes and cobalt-in-carbon nanotubes are compared. All samples are synthesized and measured in the nanotube form, and to the best of our knowledge this is the first report where optical limiting properties of metal nanotubes are compared to those of carbon nanotubes. Such a comparison is more appropriate, as these tubular structures will induce a similar kind of geometrical field distortion in the incident electromagnetic radiation.

2. Experimental details

2.1. Sample preparation

MWCNTs were synthesized by template assisted chemical vapor deposition (CVD) over a nanoporous alumina template (99.9% pure, Whatman). Acetylene was used as the precursor for pyrolysis and argon as the carrier gas. The partial pressure of the gas mixture was 150 Torr. The temperature for pyrolysis was optimized at 650 °C for the formation of good quality nanotubes. The flow rates of acetylene (10 sccm) and argon (70 sccm) were also optimized during the CVD process to obtain MWCNTs with maximum inner diameter. The resultant nanotubes were plasma etched for removing the amorphous carbon content using a radio frequency (RF) plasma unit (Harrick PDC-32G, plasma power 18 W) and then used for further characterization. Cobalt nanotubes (Co NTs) were prepared by template assisted electrodeposition of cobalt ions over the nanochannels of alumina. The electrodeposition was carried out on the nanopores, using a standard three-electrode potentiostat system (Princeton EG&G 273 A). 0.2 M cobalt acetate was used as the precursor for electrodeposition. Initially, a layer of Ag (about 200 nm thickness) was thermally evaporated onto one side of the alumina template, which acted as the working electrode for electrodeposition. Ag/AgCl was the reference electrode and platinum served as the

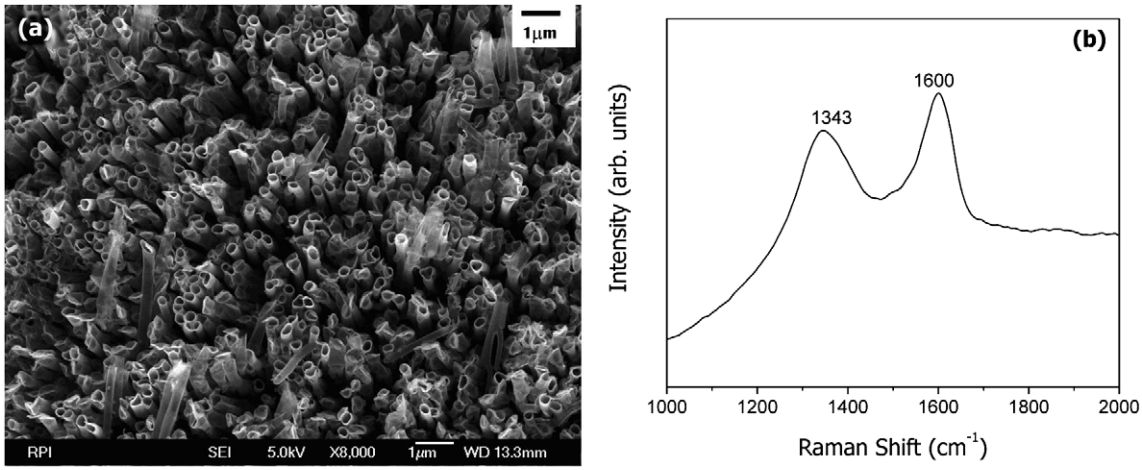

Figure 1. (a) FESEM image of MWCNTs, (b) micro-Raman results for the MWCNTs.

counter electrode. In order to synthesize cobalt-in-carbon nanotube structures, the MWCNTs were prepared by the CVD pyrolysis of acetylene as explained above, and were then filled with cobalt ('cobalt-in-carbon' nanotubes) by the method of electrodeposition using cobalt acetate as the precursor. Cobalt and carbon nanotubes are found to form into a coaxial structure.

2.2. The z-scan measurement

We made the z-scan [37] measurements using a frequency doubled Q-switched Nd:YAG laser (Quanta Ray, Spectra Physics) having a nominal pulse width of 7 ns at 532 nm wavelength. The laser was focused using a plano-convex lens of 20 cm focal length, and the focal spot radius (ω_0) was 18 μm. The laser pulse energy was 25 μJ. The peak optical intensity seen by the sample at the beam focus is of the order of 10^{12} W m^{-2}. The nanotube samples were dissolved in a mixture of toluene and ethanol (in the ratio 2:1) and then sonicated for 10 min for uniform dispersion. They were then taken in a 1 mm glass cuvette which was mounted on a stepper motor controlled linear translation stage. All samples were prepared at low concentrations such that their linear transmission was 83% at 532 nm, when taken in the 1 mm path length cuvette. The sample was translated in the z direction in small steps, and the transmitted energy was measured for each position z using a pyroelectric laser energy detector (Laser Probe Inc.). The experiment was automated such that laser pulses could be generated on demand. The interval between two successive laser pulses was always kept sufficiently large (typically more than 1 s) to enable the complete thermal relaxation of the sample before the arrival of the following pulse.

3. Results and discussion

The high aspect ratio (∼330) multiwall carbon nanotubes (MWCNTs) were prepared and were characterized by field emission scanning electron microscopy (JSM-6335 FESEM) as shown in figure 1(a). Results of micro-Raman studies at an excitation wavelength of 514 nm are shown in figure 1(b).

The characteristic peaks of graphitization, order G (E_{2g} mode in the graphite structure of carbon, 1600 cm^{-1}) and disorder D (1343 cm^{-1}), can be seen [38]. Considering the extent of graphitization as a yardstick for the quality of CNTs, the relatively higher sharp peak of G (the intensity ratio of G to D is ∼1.2) indicates the formation of moderate quality nanotubes. Figure 2 shows the FESEM and energy dispersive spectrum (EDS) of crystalline cobalt nanotubes. The FESEM image was taken after the removal of the alumina template by 3 M NaOH solution.

The EDS quantifies the presence of cobalt in cobalt nanotubes. Figure 3 depicts the FESEM (top view) and micro-Raman results for cobalt-in-carbon nanotubes.

The bright open ended FESEM images indicate the formation coaxial structure. Micro-Raman studies on cobalt-in-carbon nanotubes show that the relative intensity of D peaks is higher than that of G peaks. This indicates the presence of defects due to the introduction of cobalt into pristine CNTs [12]. The formation of coaxial structures is further verified using TEM imaging and elemental mapping. Figure 4(a) depicts the TEM image (lateral view) of a cobalt-in-carbon nanotube. The elemental mapping is carried out on this image and is shown in figure 4(b).

The formation of the coaxial structure is evident from the uniform mixing of the colors green (carbon) and red (cobalt). Figure 5 shows the room temperature $M(H)$ behavior of the Co-in-MWCNT for field parallel to the nanotube. The magnetization measurements were carried out using a SQUID magnetometer (MPMS-5S XL Quantum Design).

The very high value of the coercivity (H_c ∼ 550 Oe) indicates that the easy axis of magnetization is parallel to the tube axis and is arising out of the very high shape anisotropy due to the very high aspect ratio of these tubular structures (aspect ratio: ∼330) [6, 39]. Since the coercivity value for bulk cobalt is only 10 Oe, the very high value obtained here can arise only from the uniaxial shape anisotropy, in the nanowire or nanotube form of cobalt. The FESEM image shows the open ends of the nanostructure, which confirm the nanotube structure of the prepared sample. This further verifies the general mobility assisted growth mechanism that we discussed

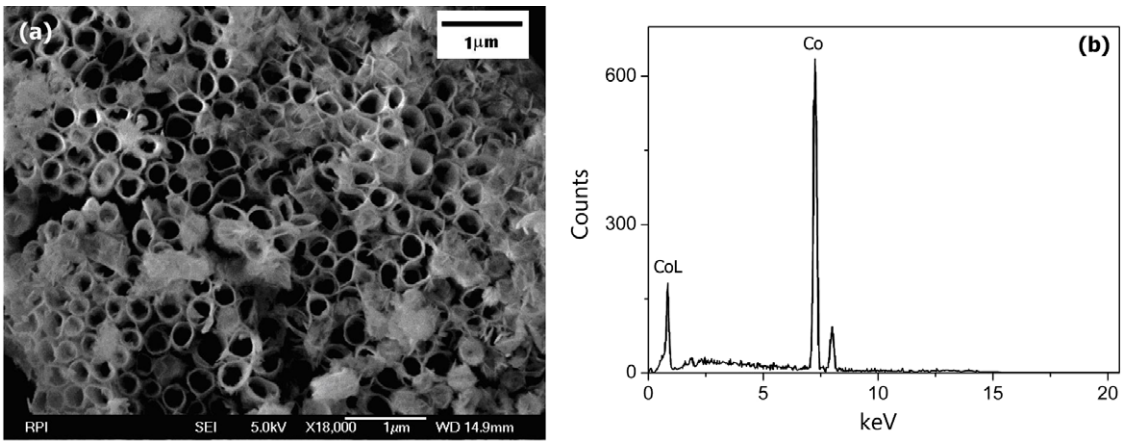

Figure 2. (a) FESEM image of cobalt nanotubes, (b) EDS of cobalt nanotubes.

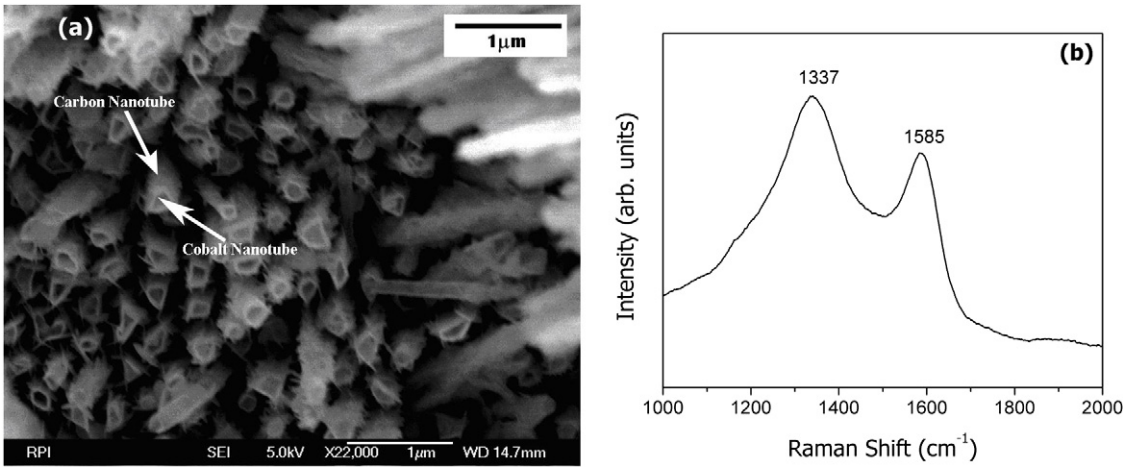

Figure 3. (a) FESEM for the cobalt-in-carbon nanotube, (b) micro-Raman results for the cobalt-in-carbon nanotube.

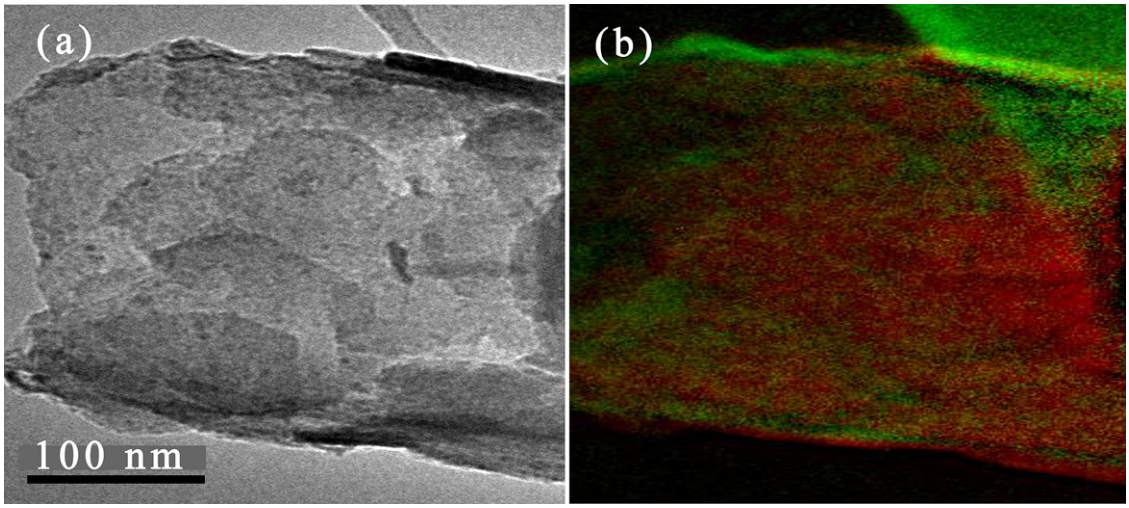

Figure 4. (a) TEM image of a cobalt-in-carbon nanotube, (b) elemental mapping of a cobalt-in-carbon nanotube (the red color indicates cobalt and the green color indicates carbon).

in detail in our earlier reports [8, 12], i.e., the hydration layer in the cation and mobility of the cation determine the resultant morphology of one-dimensional nanostructures after electrodeposition.

We observed strong optical limiting signals from the present carbon nanotube, cobalt nanotube and the cobalt-in-carbon nanotube samples. In the case of carbon nanotube samples, optical limiting is reported to have contributions from

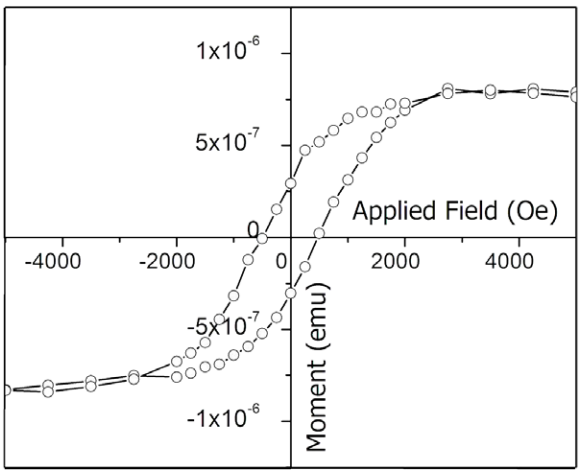

Figure 5. The room temperature $M(H)$ behavior of the cobalt-in-carbon nanotubes for field parallel to the nanotube.

two-photon absorption (2PA) and nonlinear scattering [30]. In metal nanoparticle systems contributions from interband transitions and free carrier absorption have been noticed, and the net nonlinearity sometimes appears in the form of an 'effective' three-photon absorption (3PA) phenomenon [40]. In a pure 2PA process two photons will be simultaneously absorbed while in a pure 3PA process three photons will be simultaneously absorbed, and both of these are instantaneous nonlinear optical phenomena. Compared to those for the usual one-photon absorption process, the cross sections for these phenomena are generally low, but they become significant when the samples are irradiated with intense laser pulses of picoseconds or shorter duration. With nanosecond pulse excitation, accumulative nonlinear optical phenomena like excited state absorption and free carrier absorption become more prominent. Depending on the material system under study, the excitation wavelength and the applied laser fluence, a combination of the instantaneous and accumulative nonlinear effects may take place. These, however, will appear like pure 2PA or pure 3PA ones in a simple transmission measurement like the z-scan. These combined nonlinearities can hence be termed as 'effective 2PA' and 'effective 3PA' processes to distinguish them from pure 2PA and 3PA processes. Time-resolved pump–probe experiments are required to distinguish between instantaneous and accumulative nonlinearities, and the conventional z-scan can throw light only on the order and magnitude of the nonlinearity.

We found that the fluence versus transmittance curve for the carbon nanotube samples (derived from the z-scan results) fits well to an effective 2PA process (figure 6(a)), whereas the corresponding results for the metal nanotube samples fit well to an effective 3PA process (figure 6(b)).

For the cobalt-in-carbon nanotube samples the data set does not fit well either to an effective 2PA or an effective 3PA process: rather, it fits to an intermediate order of nonlinearity (figure 7).

For calculating these fits numerically we used the generalized z-scan equations given by Gu *et al* [41]. The normalized transmittance of the sample from an open-aperture z-scan, for an $(n+1)$-photon absorption process, is given by

$$T_{n+1}(x) = \frac{\int_0^\infty 2\pi I(L,x) r \, \mathrm{d}r}{\exp(-\alpha_0 L) \int_0^\infty 2\pi I(r,x) r \, \mathrm{d}r} \qquad (1)$$

where $I(L,x)$ is the transmitted intensity, and $I(r,x)$ is the intensity of the focused Gaussian laser beam traveling along the $+z$ direction. $z = 0$ is the beam focus, and $x = z/z_0$ is the relative position of the sample with respect to the focus (z_0 is the diffraction length, also known as the Rayleigh range). α_0 is the linear absorption coefficient and L is the sample length. The numerical fits presented in figures 6(a), (b) and 7 were calculated using the above equation. The samples obviously behave as optical limiters. The calculated 2PA coefficient (β_1) is 1.7×10^{-10} m W^{-1} for the MWCNT samples, while the 3PA coefficient (β_2) is 3×10^{-22} m^3 W^{-2} for the cobalt nanotubes. Cobalt-in-carbon nanotubes show a mixed behavior, and the calculated β_1 is 2×10^{-10} m W^{-1} and β_2 is 8×10^{-23} m^3 W^{-2}. The origin of the observed nonlinear

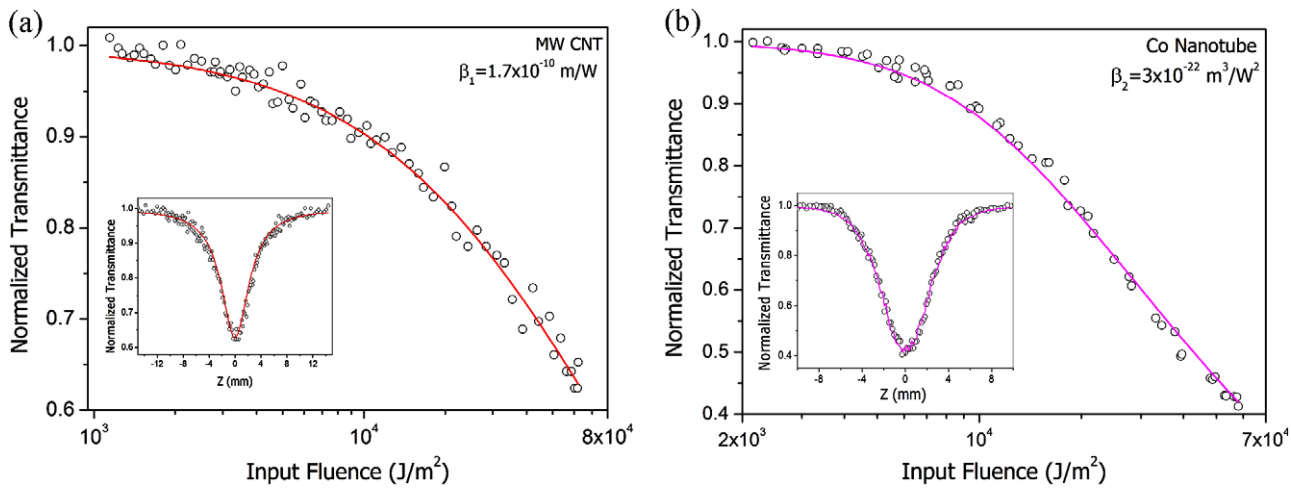

Figure 6. Nonlinear transmission in samples under 532 nm, 7 ns laser irradiation. The insets give the open-aperture z-scan curves. Hollow circles are experimental data points and the solid line is a numerical fit to the data for an effective 2PA and 3PA processes: (a) for MWCNTs (2PA process), (b) for Co nanotubes (3PA process).

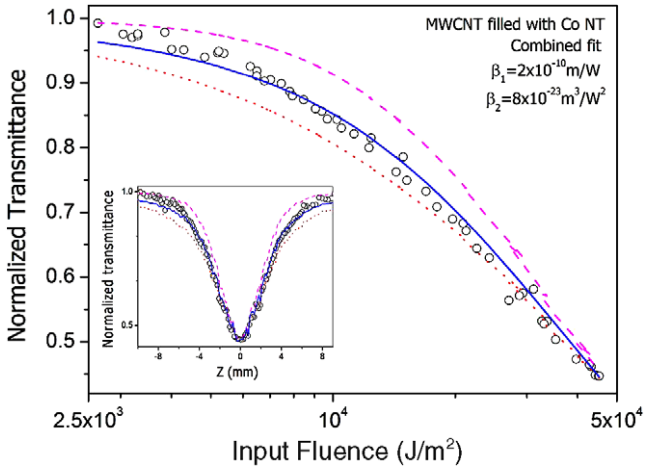

Figure 7. Nonlinear transmission of cobalt-in-carbon nanotubes under 532 nm, 7 ns laser irradiation. The inset shows the open-aperture z-scan curve. Hollow circles are experimental data. The dotted curve is the best 2PA fit, and the dashed curve is the best 3PA fit. The solid curve shows the best fit to the data, obtained by assuming the simultaneous occurrence of effective 2PA and effective 3PA phenomena.

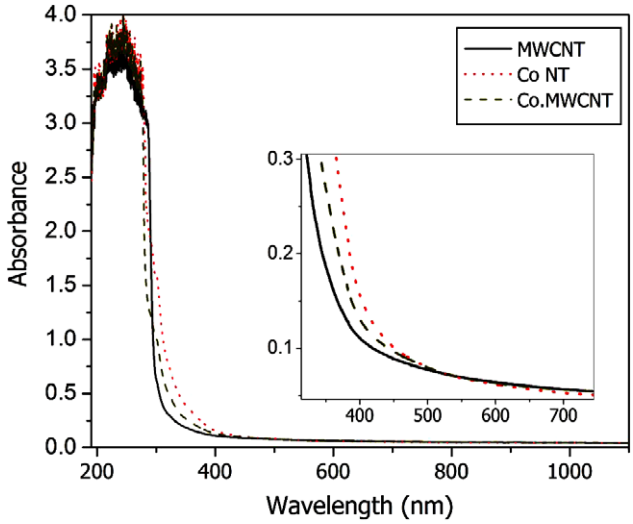

Figure 8. UV–visible absorption spectra of the MWCNT, cobalt nanotube and the cobalt nanotube filled MWCNT samples.

absorption can be explained from the absorption spectra of the samples given in figure 8.

Figure 8 shows the UV–visible absorption spectra of the samples dispersed in a mixture of toluene:ethanol (in 2:1 ratio), measured in a 1 mm quartz cuvette, using a Perkin-Elmer Lambda 35 spectrophotometer. The solvent absorption is not subtracted from the spectra. From the inset we see that there is some absorption at 532 nm, complementing the linear transmission of 83% of the samples. The absorption is much stronger at the two-photon wavelength of 266 nm. Obviously this absorption spectrum allows one-photon, two-photon, and two-step absorptions to take place at 532 nm (since the spectrophotometer has a lower wavelength limit of 190 nm we could not measure the absorption at the three-photon wavelength of 177 nm). As the samples are metallic in nature, there is a high probability of additional photon absorption from the terminal level reached by the two-photon and two-step transitions. It may also be noted that the photoelectric work function of Co is 5 eV, and this energy will be given and exceeded by three 532 nm photons (3×2.33 eV $=$ 6.99 eV). The nature of the absorption spectra thus explains the observation of effective 2PA, effective 3PA, and the intermediary type nonlinear absorption exhibited by the samples.

In general, the optical limiting mechanism in MWCNTs can be expected to have a contribution from induced thermal scattering (also known as nonlinear scattering) as well, due to the similarities in optical limiting with the well known carbon black suspensions [42]. The general model for the fluence based limiting in carbon nanotubes due to nonlinear scattering can be summarized as follows: the thermal energy from laser absorption is transferred to the surrounding solvent medium, resulting in the formation of microplasmas at lower fluence levels. An increase in the fluence results in the desorption of oxygen and amorphous carbon, and increasing the fluence further leads to localized heating and eventually the ionization of MWCNTs, forming rapidly expanding microsized plasmas [23]. Since more heat is transferred to the solvents at this stage, more microbubbles are also created. These microbubbles and the microplasmas formed at the focal regions will strongly scatter the input radiation from its normal transmission path, thereby resulting in a nonlinear decrease in the measured transmitted light. However, the highly transparent samples absorb only a small fraction of the input light and hence induced thermal scattering has to be minimal in the present case.

4. Conclusions

In conclusion, we have synthesized carbon, cobalt, and high coercivity cobalt-in-carbon nanotubes, and investigated their optical limiting properties. The general mobility assisted growth mechanism for the formation of one-dimensional structures during electrodeposition is verified for other nanopores such as carbon nanotubes. In comparison to the benchmark carbon nanotubes, cobalt and cobalt-in-carbon nanotubes are found to show a higher nonlinear absorption. To our knowledge this is the first report where the optical limiting properties of a metal nanotube are compared to those of carbon nanotubes. The cobalt-in-carbon nanotubes exhibit an interesting transmission behavior, where effective two-photon and effective three-photon absorption nonlinearities are present simultaneously. The nonlinear parameters numerically calculated from these measurements show that these materials are efficient optical limiters. In addition to potential applications in safety devices for sensitive optical detectors and human eyes, this type of multifunctional material can find use in various other fields also, such as high power supercapacitor electrodes, sensors, and catalysis.

Acknowledgments

TNN acknowledges the financial support received from Interconnect Focus Center at Rensselaer Polytechnic Institute,

Troy, New York, USA. TNN also thanks Kerala State Council for Science, Technology and Environment (D.O. No. 004/FSHIP/05/KSCSTE), Kerala, India, for financial support in the form of a research fellowship.

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