Fabrication of Carbon nanotube–poly-methyl-methacrylate composites for nonlinear photonic devices

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Abstract: Carbon nanotubes (CNT) are an attractive material for photonic applications due to their nonlinear optical properties, such as the nonlinear saturable absorption and high third order nonlinearity. However their utilization has been hindered by the lack of flexibility on the device design which rises from the current methods of Carbon nanotube deposition within the optical system. A suitable approach to solve this problem is to embed the CNTs in an optical material from which complex devices such as optical waveguides or optical fibers can be fabricated. Here, we propose a novel method to fabricate Carbon nanotube-doped poly-methyl-methacrylate (PMMA) composites in which the Carbon nanotubes are dispersed in the methyl-methacrylate (MMA) monomer solution prior to and during the polarization process. This method allows the bundle separation and dispersion of the CNT in a liquid state without the need for solvents, hence simplifying the method and facilitating the fabrication of volume CNT-PMMA. Volume fabrication makes this technique suitable for the fabrication of CNT-doped polymer fibers. In this paper, we also analyzed the merits of adding dopants such as diphenyl sulfide (DPS) and benzyl benzoate (BEN) to the CNT-PMMA composite and we observed that DPS plays the role of CNT dispersion stabilizer that can improve the device performance. The CNT-PMMA composite was employed to implement passive mode-locked laser.

OCIS codes: (160.5470) Polymers; (140.4050) Mode-locked lasers; (190.4400) Nonlinear Optics, Materials

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1. Introduction

Carbon nanotubes (CNT) are structures from the fullerene family which are created when a carbon honeycomb sheet rolls in itself to form a cylinder. Due to their outstanding physical properties, they have become a major topic of research in areas as diverse as material science, chemistry, electronics and recently in photonics [1]. CNTs exhibit exceptional nonlinear optical properties which include nonlinear saturable absorption, ultrafast recovery time, high third-order optical nonlinearity, and broad bandwidth operation thus CNTs are rapidly becoming a key component in various photonic devices such as saturable absorbers used for noise suppression and as the intensity dependent component in passive mode-locked lasers [2]. Preceding technologies employed semiconductor-based saturable absorbers (SESAM) [3] and fiber Kerr-based non-linear devices [4]. The fabrication of SESAM is expensive, requiring clean room facilities, specific fabrication for each operational wavelength as well as additional procedures to reduce the devices recovery time. Nonlinear fiber devices require long lengths of the nonlinear fiber jeopardizing the device stability and lowering the repetition rate. CNT-based saturable absorbers (SA) have demonstrated major advantages, in terms of cost, simplicity of fabrication, flexibility in the operational wavelength as well as the previously mention recovery time, hence CNT-based SA are starting to replace SESAM in multiple applications.

The first demonstrations of CNT-based photonic devices were fabricated by spray-coating a substrate with CNTs suspended in a solvent [2] or by directly synthesizing a CNT film on a substrate [5]. Those reports confirm the feasibility and great potential of this novel technology, yet those fabrication techniques suffered stringent limitations since the CNT-based devices could only be formed as thin films, and this limits the interaction length between the propagating light and the CNT and hinders the efficient exploitation of their nonlinear properties. In addition, these devices suffer degradation owing to the permanent contact with the external environment. In order to fully utilize the nonlinear optical properties of CNT, these shortcomings must be addressed. Current research efforts are aimed at finding an optimum host material in which to disperse and embed the individual CNTs. Polymers have been identified as such suitable host material since they are transparent at optical communications wavelengths and have a structural composition that allows uniform dispersion of the CNTs. There have been several reports of composites consisting of CNT

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embedded in polymers such as polyvinylalcohol [6], polyamide [7], or carboxymethyl cellulose (CMC) [7, 8]. Those devices were used as saturable absorbers in various passively mode-locked laser configurations. However, in all those reports the CNT-polymer composite devices were also limited to thin-films, thus they also experience the limitations stated above. Recently, two significant advances towards the efficient exploitation of CNT-based photonics have been reported. First, CNT–polymer composites with a thickness of more than 1 mm were fabricated using poly-methyl-methacrylate (PMMA) and polystyrene (PS) by evaporating organic solvents chlorobenzene or tetrahydrofuran (THF) slowly from a CNT–polymer mixed solution. These devices can be optically polished, thus boosting their applicability in photonic applications [9]. Soon after, a CNT-doped waveguide using thin-film fabrication techniques and photolithography was implemented for the first time [10].

Creating bulk CNT-polymer compounds is important since it provides a platform to fabricate complex photonic structures such as CNT-doped fibers, and such structures would allow the efficient exploitation of the nonlinear saturable absorption and third order nonlinearity of CNTs. CNTs can be used for all-optical switching due to their high third order nonlinearity, however longer interactions and efficient CNT-light interaction are required in order to achieve this [11]. In this paper, we propose an alternative method to produce bulk CNT-embedded PMMA with a tangible improvement in the dispersibility of the CNTs and with added flexibility on device design. In contrast to previous reports, the CNTs are added in a solution of methyl-methacrylate (MMA) monomer with a polymerization initiator. CNTs are mixed and dispersed by ultrasonication in methyl-methacrylate (MMA) monomer prior to and during the polymerization process, thus it does not require the use of solvents. The CNTs are dispersed in a low viscosity liquid (MMA) rather than a dissolved polymer, hence CNT bundle separation is facilitated. After the thermally-aided polymerization we obtain a bulk state of evenly dispersed CNT-doped PMMA. By employing this method, we were able to fabricate samples of any desired dimensions by adjusting the amount of monomer used with excellent reproducibility.

In this paper, we investigate the merits of CNT-PMMA composites as saturable absorbers with and without the addition of dopants diphenyl sulfide (DPS) and benzyl benzoate (BEN). We demonstrate that the addition of the dopant DPS further improves the quality of the CNT dispersion. DPS plays an important role as a CNT dispersion stabilizer in PMMA, which could be attributed to the similar chemical structure of DPS and CNT. The added dopant, DPS, has higher refractive index than PMMA, and thus it has been utilized as a dopant of the core of graded-index polymer optical fiber [12]. With the method we are here proposing, we foresee the fabrication of CNT-doped polymer optical fibers (CNT-doped POF).

Finally, we experimentally demonstrate the functionality of the resulting CNT-polymer composite by implementing a CNT-polymer saturable absorber mode-locker in a passively mode-locked ring-cavity fiber laser. A 1mm slab is cut and optically polished from the CNT-polymer composite. Demonstrating the feasibility of fabricating bulk CNT-polymer composites is important since it provides the foundations for fabricating more complex structures such as CNT-doped fibers and waveguides. This method provides the platform to build complex photonic devices such as CNT-doped polymer optical fibers and waveguides, opening a new route to utilize efficiently the nonlinear optical properties of carbon nanotubes.

2. Fabrication and CNT-polymer properties

CNTs tend to agglomerate together forming bundles of tens to hundreds of individual carbon nanotubes, the dispersion of such bundles is a key factor to fabricate efficient devices. The dispersion of the bundles is generally carried out by subjecting the CNTs to an ultrasonic bath in the presence of a solvent. In previous approaches to fabricate CNT-doped polymers the CNTs have been dispersed in a solution of polymer. As a result, the process of solvent evaporation was inevitable, and this limited the composite dimensions. Furthermore, the dispersion takes place in a rather viscous solution complicating the breaking up of bundles and efficient dispersion of the CNT. The defining difference of our method is that CNTs are

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dispersed in the host monomer prior and during its polymerization reaction, thus improving and simplifying the process.

In our technique, a specified amount of commercial CNTs, made by the High-Pressure CO Conversion (HiPCO) method is added in DPS or BEN (liquid state), and the mixture is exposed to ultrasonication for 1 hour in order to separate the CNT-bundles into individual CNTs. Then, methyl-methacrylate (MMA) monomer and a polymerization initiator are added to the mixture while it is heated at 60^{o}C for about 3 hours. Ultrasonication is carried out throughout the process of polymerization. Finally, we obtain a rod-like CNT-doped PMMA composite of several millimeters. From the rod, disk-like samples are cut out, and both surfaces are hand-polished to have the desired thickness. In Fig. 1 images of 1mm disks cut from the CNT-PMMA rod samples are shown. The concentration of CNT, equal for all three samples, is 50ppm (parts per million) and the concentration of the dopant was 15 % by weight (one sample contained dopant DPS, one contained BEN and one did not contain any dopant). The concentration of CNTs is equal in all three samples.

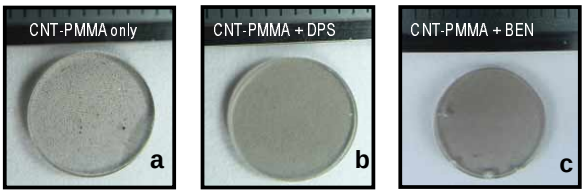

Fig. 1. Cut and polished disk samples of (a) undoped CNT-PMMA, (b) DPS-doped CNT-PMMA and (c) BEN-doped CNT-PMMA. Black-colored spots in (a) indicate areas with CNT agglomeration, such areas are not visible in (b) and (c) indicating that the addition of dopants DPS and BEN facilitates CNT dispersion.

It is worth noting the presence of black-colored spots owing to the agglomeration of CNTs in the sample without dopant Fig. 1(a), whereas the sample with BEN (Fig. 1(c)) and in particular DPS (Fig. 1(b)) looks visually homogeneous. We attribute the improved dispersibility of CNT in the dopant containing samples to the interaction between the benzene rings in DPS molecules and the six-member rings on CNT. Thus, DPS plays a role as a dispersion stabilizer of the CNTs.

In addition to the visual comparison in Fig. 1, Raman spectra of the three samples were measured and are shown in Fig. 2. Raman spectroscopy is a particularly powerful tool to investigate the presence and characteristics of CNTs in a sample [13].

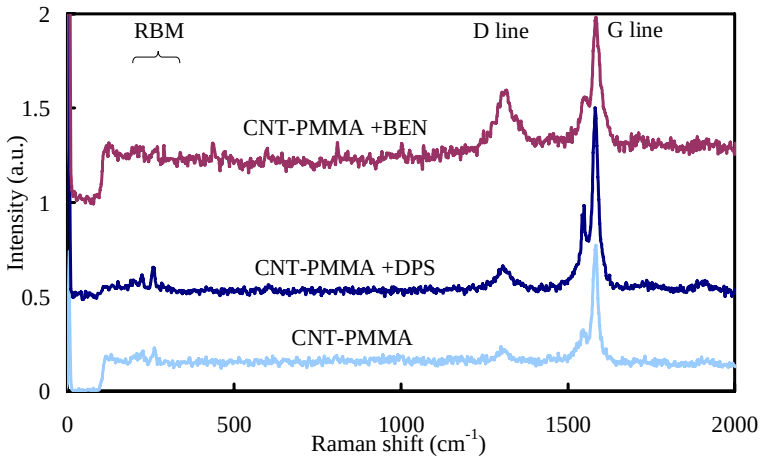

Fig. 2. Raman Spectra of the three samples; undoped CNT-PMMA, DPS-doped CNT-PMMA and BEN-doped CNT-PMMA.

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Several peaks associated to the Carbon family can be distinguished. In Fig. 2 we can observe the G band at a Raman shift of 1587cm^{-1} and the D Bands at 1333cm^{-1}, both these features are features of the graphite. The presence of CNTs is unequivocally demonstrated by the presence of radial breathing modes (RBM) with Raman shifts from 200cm^{-1} to 290cm^{-1} as well as the splitting of the G band. The most relevant observation from Fig. 2 is the different intensities observed in the RBM for the three samples. The RBM are stronger for the sample doped with DPS than for the undoped CNT-PMMA component. On the other hand, the RBM appear to be suppressed by the presence of BEN in the polymer matrix.

In Fig. 3, we investigate the absorption properties of the three samples. The absorption spectra was measured by a spectrometer. Polymer samples without CNT were used to normalize the measured values, hence the features observed in Fig. 3 refer solely to the presence of CNTs. Absorption peaks from HiPCO CNT sprayed onto a glass plate are shown in the inset of Fig. 3, for comparison with the polymer samples. Absorption peaks raise from the inter Van Hove transitions between the different semiconductor and metal transitions and can be clearly identified in the spectrometer measurements of the spray sample [1, 2]. The characteristics of the absorption peaks are dependent on the single wall CNT diameter and diameter distribution. This curve shows discrete saturable absorption in the 1550 nm region, ensuring its applicability as nonlinear saturable absorber.

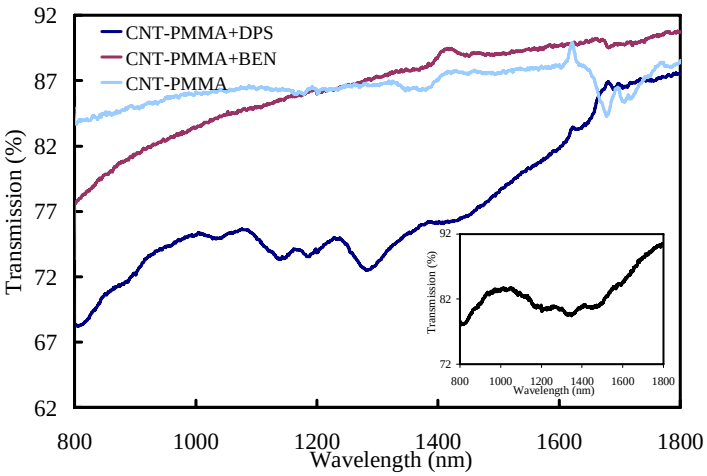

Fig. 3. Raman Spectra of the three samples, CNT-PMMA composite, DPS-doped CNT-PMMA and BEN-doped CNT-PMMA with the addition of dopant BEN. (Inset) Absorption spectra of a Silica plate sprayed with HiPCO CNTs. (Note: The discontinuity observed at approximately 800nm is caused by a change of grating in the spectrometer).

Pronounce absorption peaks are observed in the DPS-doped samples, by comparing this absorption spectra with the spectra from the sprayed sample, we can conclude that the absorption characteristics of the CNT are not affected by been embedded in the DPS-PMMA polymer. On the other hand, we observed a significant less pronounced absorption peaks in the undoped CNT-PMMA and BEN-doped CNT-PMMA samples. We can attribute the lower absorption observed in the PMMA samples to less effective dispersion of the CNT, this was also confirmed by visual inspection (Fig. 1). The addition of BEN induces a suppression of the absorption peaks, yet the sample was visually homogeneous, similar effects have been previously reported after chemical doping so this results suggest that the addition of BEN leads to chemical doping of the CNT leading to a reduction of available electrons in the valence band for the Van-Hove transitions [14]. The combine results from the Raman and spectrometer measurements as well as the direct visual inspection of the samples indicate that with the addition of DPS the sample presents improved CNT dispersion and saturable absorption compared to the undoped CNT-PMMA composites, while adding the dopant BEN

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improves the dispersion of the CNT in the polymer matrix but suppresses the saturable absorption properties of the CNT.

3. Optics results

The majority of the photonic devices incorporating CNTs are based on its nonlinear saturable absorption. Nonlinear saturable absorbers are materials with an intensity-dependent optical absorption; hence they are widely used as noise suppressors. This intensity dependence is also employed to discriminate in favor of pulse formation in passively mode-locked lasers by saturable absorption [15]. In this case, the saturable absorption leads to strong absorption of the cw light propagating through the cavity while the high intensity pulses propagate through a media were absorption is saturated. In this paper, we implement a passively modelocked lasers based on the saturable absorption properties of a 1mm-slab CNT-PMMA slab with the addition of dopant DPS. As it was shown earlier in the paper, the addition of DPS during fabrication leads to an improvement of the dispersion of CNTs.

We investigate the performance of the CNT-doped Polymer sample as a saturable absorber, a sample with 1mm thickness, a CNT concentration 50ppm and 15% by weight concentration of the DPS dopant was introduced in the fiber laser ring outlined in Fig. 4(a). An erbium-doped fiber amplifier (EDFA) is used as the laser gain medium. The light is launched in and out of the 1 mm-thick sample by two optical systems consisting of two fiber-collimating lenses with a focal length of 1.8mm, hence the propagating light is focused in the polymer sample, the combine losses from coupling the light in and out of the fiber was approximately 2.5dBm. The sample was slightly angled and angle connectors were used; this was necessary to suppress deleterious back reflections which may prevent mode-locking from taking place. Additionally an optical isolator is used to ensure unidirectional operation within the laser cavity. 10% of the intracavity lasing light is coupled out as laser output while the remaining 90% is launched back into the cavity as feedback. Cavity dispersion was optimized by adding a 6-m long SMF fiber. The laser operation exhibited some polarization dependence hence a polarization controller (PC) was inserted in the cavity.

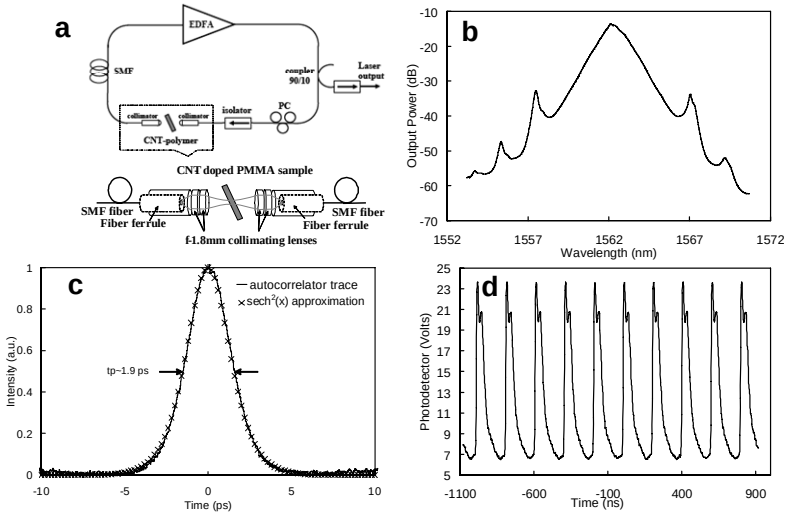

Fig. 4. (a). Experimental set up. A CNT-doped polymer slab with 1mm thickness is inserted into a ring cavity fiber laser. (b) Optical spectrum of the laser output the soliton-like spectra centered at 1562 nm with a FWHM of 1.4 nm. (c) Autocorrelator trace and secant hyperbolic ($sech^2$) approximation indicating a pulse duration of 1.9ps. (d) Photo-detector measurement show a pulse train with 190 ns pulse interval corresponding to a repetition rate of 5.3 MHz.

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The output of the passively mode-locked fiber laser was analyzed; Fig. 4(b) shows the optical spectrum of the laser output. A soliton-like spectra centered at 1562 nm confirms the passive mode-locking. The spectral bandwidth at full-width half-maximum (FWHM) was 1.4 nm. The autocorrelator trace is shown in Fig. 4(c), to estimate the pulse duration we assume a secant hyperbolic pulse shape ($sech^2$), typical of passively mode-locked laser systems, thus these measurements yields a pulse duration of 1.9 ps. The closely fitted $sech^2$ approximation is also depicted in Fig. 4(c). The FWHM of spectral bandwidth and pulse trace yield a time-bandwidth product of 0.327 indicating that the laser operation is close to transform limited $sech^2$ pulses. The pulse duration of 1.9ps is one order of magnitude longer than a previous report of a similar composite [9]. We attribute the longer pulse duration here reported to the lower saturable absorption of the composite, which is a direct result of employing one tenth of CNT concentration and the fact that the S_1 absorption band is centered at 1450 nm, which leads to lower nonlinear saturable absorption at the output laser central wavelength of 1562 nm.

Photo-detector measurements in Fig. 4(d) shows a pulse train with a 190 ns interval between pulses which corresponds to a repetition rate of 5.3 MHz also confirmed by rf measurements, the cavity length is 28.5m. In Fig. 4(d) soliton energy quantization can also be recognized. This phenomenon is well documented and particularly common in fiber laser configurations. It is caused by a peak-power limiting effect of the laser cavity and gain competition, leading ultimately to the formation of multiple solitons within the laser cavity [16]. The above results demonstrate the efficient operation of the saturable devices fabricated by our method in a passive mode-locked laser system. Passive modelocking was also achieved by the undoped CNT-PMMA sample; however the performance in terms of pulse duration and laser stability of the DPS-doped CNT-PMMA sample was superior. Attempts to achieve passive modelocking with the BEN-doped CNT-PMMA samples were unsuccessful.

4. Conclusion

In this paper, we present a novel technique to embed CNT into a PMMA matrix and implement a passively mode-locked fiber laser making use of the resulting composite. In the method that we propose, CNT bundles are separated and dispersed prior to, and during the polymerization process; hence CNT dispersion takes place in a liquid state without the need for solvents. This approach, simplifies the embedding of CNTs in the polymer matrix, and more importantly permits fabrication in volume. Fabrication of complex structures such as CNT-doped polymer fibers or waveguides is obtainable with the approach we are presenting. In this paper, the effect of adding dopants DPS and BEN was investigated. The results indicate that DPS plays the role of CNT dispersion stabilizer and thus a significant improvement in the CNT-PMMA composite optical properties was observed. Finally, we implemented a passively mode-locked ring cavity fiber laser utilizing the nonlinear saturable absorption properties of such CNT-PMMA slab. This method is suitable for the fabrication of CNT-doped waveguide and fiber structures opening a route to further exploit the nonlinear optical properties of CNT for photonic applications.

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