

Carbon nanotube–polymer composites for photonic devices

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Abstract

We report the fabrication of high optical quality single wall carbon nanotube polyvinyl alcohol composites and their application in nanotube based photonic devices. These show a broad absorption of semiconductor tubes centred at $\sim 1.55 \mu\text{m}$, the spectral range of interest for optical communications. The films are used as mode-lockers in an erbium doped fibre laser, achieving ~ 700 fs mode-locked pulses. Raman spectroscopy shows no damage after a long time continuous laser operation.

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1. Introduction

The non-linear optical properties of single wall carbon nanotubes (SWNTs) are at the centre of an expanding area of research. SWNTs are good saturable absorbers with an ultrafast recovery time, i.e. they are pass-high filters for light, becoming transparent for sufficiently high incident power [1–3]. SWNTs have potential advantages over commonly used semiconductor saturable absorber mirrors (SESAMs) currently employed as passive mode-lockers in ultrafast lasers [4] and passive elements in lightwave systems [5]. SESAMs are multi quantum well heterostructures grown by molecular beam epitaxy followed by ion implantation to decrease recovery time [4,5]. Furthermore, their spectral range of operation is narrow [5]. On the other hand, SWNTs are cheap to manufacture self-assembling structures and easy to integrate in polymer matrixes. In contrast to other electronic applications, not having a narrow chirality selection can be an advantage, since it gives a broader operation wavelength range than SESAMs. To date, SWNTs saturable absorption properties have been exploited in amplified spontaneous emission (ASE) noise suppression [6], and in passive mode-lockers for

ultrafast lasers [6–9]. In these works SWNTs were spray-coated on quartz substrates [7], or directly grown on fibre ends or quartz substrates [8] or used in solution [9]. However, high losses in the cavity were reported, due to the residual presence of bundled and entangled nanotubes as well as catalyst particles [7,8], or the formation of bubbles when SWNTs were used in suspension [9]. These effects strongly affect the lasers properties.

The best way to overcome these disadvantages is to disperse SWNTs in a polymer matrix [6]. The use of SWNT–polymer composites in optical applications requires a homogeneous distribution of nanotubes within the polymer matrix on a scale smaller than the device operation wavelength, i.e. $1.55 \mu\text{m}$ for telecommunication applications, in order to minimize scattering losses on nanotubes bundles [6]. It has been shown that nanotubes can be unbundled in water solutions by strong ultrasonication in the presence of a surfactant [10,11]. In this case, the solution consists of individual nanotubes or small bundles surrounded by the hydrophobic surfactant [11]. SWNT water solution is suitable for composites preparation using water-soluble polymers [3]. In addition, the polymer matrix and the surfactant should be transparent to the operation wavelength, to avoid non-saturable absorption losses.

In this paper, we describe the fabrication and characterization of SWNT–PVA freestanding films and their

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application in an Erbium Doped Fibre (EDF) laser. We investigate the long-term laser operation stability in mode-locked regime and the stability of the composite during laser operation.

2. Experimental

SWNTs are grown by laser ablation as described in Ref. [12]. They are then purified with dimethylformamide from catalyst metal particles and carbon impurities [13]. Purified SWNTs are dispersed in water by a 4-h surfactant-assisted ultrasonication (Diagenode Bioruptor ultrasonicator); the surfactant used is sodium dodecylbenzenesulphonate. The concentrations are 0.05% SWNTs and 0.5% surfactant. Residual bundles are removed by filtration through a 1 μm diameter glass fibre filter. Five milliliter solution is then mixed with 2 ml of a PVA aqueous solution (200 g/l). As SWNTs may re-aggregate after they are mixed with the polymer solution, a further short ultrasonication can be necessary. Finally, the SWNT–PVA solution is dried at room temperature to obtain a $\sim 50 \mu\text{m}$ thick, 5 cm diameter freestanding film. The films are characterized by optical microscopy, multi-wavelength Raman spectroscopy (Renishaw 1000 spectrometer) and absorption spectrophotometry (Perkin Elmer Lambda 950 spectrophotometer).

A typical film size is about 20 cm^2 . In order to prepare a mode-locker a small part of the film ($\sim 2 \times 2 \text{ mm}^2$) is cut and sandwiched in an FC/PC connector, after depositing an index-matching gel onto the fibre ends. Note that, even if the cost per gram of SWNTs can appear high at present, the amount of SWNTs necessary to produce a mode-locker is negligible (at present, even without large scale process optimisation, we can potentially make ~ 500 mode-lockers with $\sim 4 \text{ mg}$ SWNTs). The connector is then placed in a fibre ring cavity. The whole system is schematised in Fig. 1. An EDF Amplifier (EDFA), which has $\sim 40 \text{ m}$ Er^{3+} -doped fibre, is used as laser active media pumped by a semiconductor laser at 980 nm. Other fibre

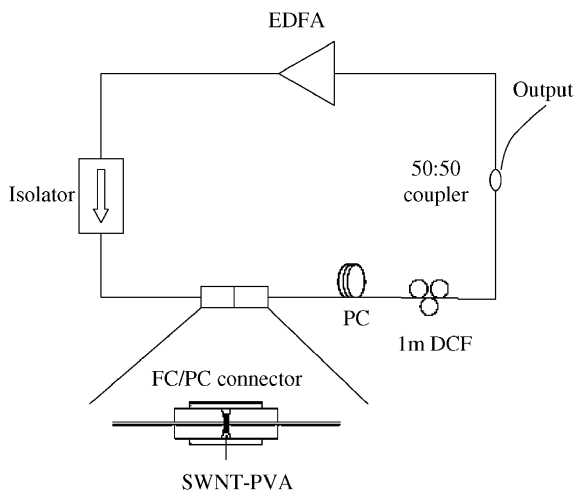


Fig. 1. Laser cavity, including EDFA, isolator, dispersion compensation fibre, polarization controller and FC/PC connector.

components are necessary to create a laser cavity containing an isolator, a fibre polarization controller (FPC), 1 m of dispersion-compensated fibre (DCF) and a 50/50 coupler. One port of the coupler is used to feed-back the cavity, while the other one is connected to an optical spectrum analyser (HP 86140A), an oscilloscope (Textronix TDS 2024) and a Second Harmonic Generation (SHG) autocorrelator (Inrad 5-14-LDA) to study the laser properties.

3. Results and discussion

The SWNT–PVA films have a homogeneous distribution of SWNTs on a sub-micrometer scale, as no bundles can be resolved by optical microscopy (Fig. 2), and, at the same time, a strong Raman signal at three different wavelengths (514, 633 and 785 nm) can be detected over the whole material, as shown in Fig. 3. From the radial breathing mode (RBM) in the Raman spectra [14,15] we can estimate a diameter distribution ranging from 1.0 to 1.3 nm. The Raman G-band is consistent with the information given by the RBM, as it shows a typical semiconducting lineshape at

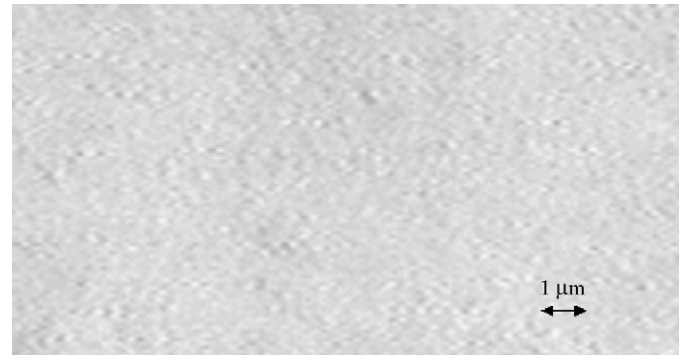


Fig. 2. Optical micrograph of a representative SWNT–PVA film.

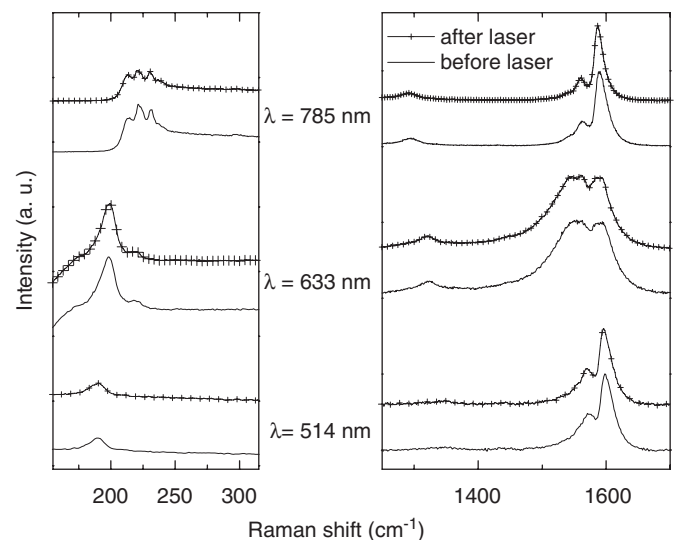


Fig. 3. Raman spectra at three different wavelengths, carried out before (solid lines) and after (solid lines +) the laser experiments.

514 and 785 nm, where semiconducting tubes are expected to be in resonance [16], and a typical metallic lineshape at 633 nm, where metallic tubes are resonantly excited [16–18].

From this diameter distribution, the optical absorption of semiconductor SWNTs is expected between 1350 and 1750 nm [16]. This is confirmed by direct UV–VIS–IR measurements (Fig. 4), which show a broad band centred at about 1550 nm. Saturable absorption is a resonant non-linear optical phenomenon, which strongly depends on optical field strength [19]. Thus the maximum of absorption band of SWNT–PVA should coincide with the wavelength of laser operation, i.e. approximately 1550 nm.

The confirmation of the saturable absorption properties of our SWNT–PVA composite comes from the EDF laser operation. This shows continuous wave (cw) lasing regime without the nanotube composite as well as when a pure PVA film is placed in the connector. This appears as a narrow peak in Fig. 5a (solid line). Only when the SWNT–PVA composite is in the cavity, we observe generation of stable mode-locked pulses. These have a 5 MHz fundamental repetition rate and an average output power up to 9 dBm (8 mW). The output pulse spectrum (Fig. 5a) shows a main band centred at ~ 1563 nm, with two side features at ~ 1552 and ~ 1570 nm. The sharp intensity decrease on the long-wavelength side of the band is due to the limitation of our EDF amplifier (Fig. 5a EDFA curve). The two spectral features at ~ 1552 and 1570 nm are caused by the dispersion and non-linear processes in the fibre under high power pumping conditions [20]. To measure the pulse width, we utilize the SHG autocorrelation technique [21]. The autocorrelation trace is well fitted by a Gaussian function with FWHM = 995 fs (Fig. 5b). The real pulse width is then obtained by multiplying the autocorrelation trace FWHM by the de-correlation factor, which is 0.707 for Gaussian pulses [21]. This gives a pulse width of 703 fs. The minor pedestal observed in the autocorrelation data can be assigned to intracavity noise, caused by insertion losses in the FC/PC connector when the SWNT–PVA film

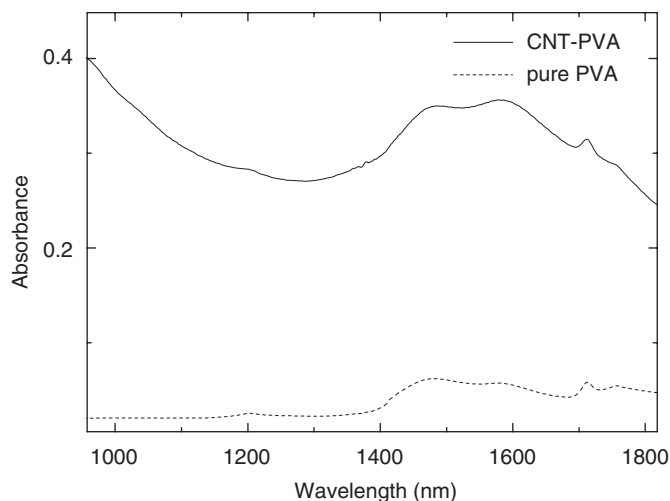


Fig. 4. Optical absorption spectrum of the SWNT–PVA composite (solid line) and of a pure PVA film (dashed line).

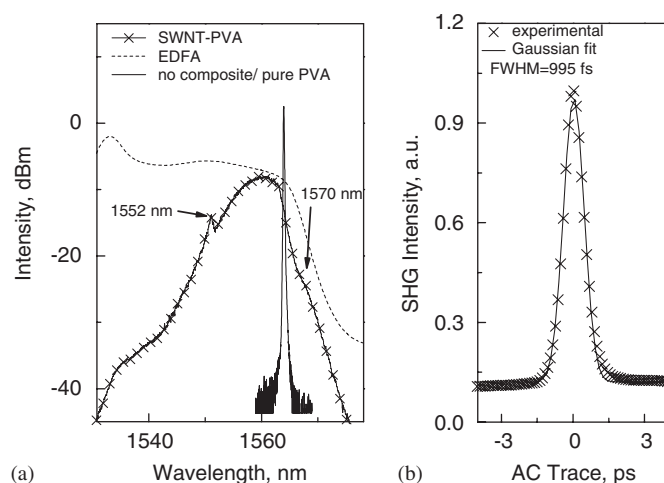


Fig. 5. (a) Laser optical output spectrum from SWNT–PVA composite (solid line x), EDFA (dashed line) and only PVA (solid line); (b) autocorrelation trace from SWNT–PVA composite.

is introduced, non-saturable absorption induced by the film itself and dispersion and non-linear effects in the fibre.

Raman measurements are taken on the SWNT–PVA saturable absorbers before and after their use in the laser ring cavity (Fig. 3). The spectra remain unchanged after a 600 h continuous operation, showing that no damage occurs on our CNT-based mode-lockers.

Previous approaches, where the CNT layer was either spray coated on glass substrates [7] or directly grown [8], did not achieve the same high quality optical films, due to the presence of nanotubes bundles, carbon impurities and catalyst particles, which are a source of non-saturable losses, such as scattering and surface reflection. Furthermore, in these works additional optics was used for precise alignment in the lightwave system, which induced further significant insertion losses. On the other hand, our results show great promise for the utilization of SWNT–polymer composites, which only require well-established and cheap wet chemistry production process, allowing a very homogeneous SWNT dispersion in the PVA matrix. The main limitation for the utilization of our SWNT–PVA composites comes from intrinsic non-saturable losses of the PVA in the telecommunication wavelength range (Fig. 4). Furthermore, its water solubility might affect the long-term device operation due to moisture. Further work is thus necessary to develop SWNT composites, utilising polymer matrixes transparent in the telecommunication window, and with higher stability against environmental conditions (such as polyimide, polycarbonate and polyacrylates).

4. Conclusion

We fabricated a homogeneous SWNT–PVA composite material, which is used as passive mode-locker in an EDF laser, generating 703 fs light pulses. We demonstrated

long-time stable operation in mode-locking regime with high output power.

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