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ORIGINAL RESEARCH

Fabrication, characterization and mode locking application of single-walled carbon nanotube/polymer composite saturable absorbers

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Abstract We present the fabrication of a high optical quality single-walled carbon nanotubes (SWNTs) polyvinyl alcohol (PVA) composite film. The composites demonstrate strong saturable absorption at ~1.5 μm, the spectral range for optical communications. By measuring the nonlinear transmission of a sub-picosecond pump pulse through the film, we were able to deduce a saturation fluence of ~13.9 μJ/cm^2 and a modulation depth ~16.9% (in absorption) at a high pulse fluence ~200 μJ/cm^2. Transient saturable absorption is investigated by measuring the transmitted autocorrelation traces at various incident power levels. Observed side-peak suppression indicates a fast recovery time on the scale of ~1 ps for our saturable absorber devices. Furthermore, we use these SWNT-PVA composite saturable absorbers as mode-lockers in an Er^{3+} fiber ring laser and achieve ~560 fs pulse generation with good jitter performance and long term stability. The laser performance is also associated with the parameters of our SWNT based saturable absorber.

Keywords Carbon nanotube · Saturable absorber · Nonlinear optical properties

Introduction

The non-linear optical properties of SWNTs are at the centre of an expanding area of research. SWNTs are good saturable absorber materials, i.e. they are pass-high filters for light, becoming transparent for sufficiently high incident power [1, 2]. This makes them ideal components for a wide range of photonic devices, such as all-optical switches, pulse compressors, noise regenerative filters, etc. Besides, SWNT based saturable absorbers possess advantages such as ultra-fast recovery time (<1 ps), wide absorption bandwidth from 1 to 2 μm and potential to integrate with micro-chip lasers due to their small footprint and simplified device preparation. All these features makes them very competitive when compared with existing passive mode locking technologies, such as semiconductor saturable absorber mirrors (SESAMs), which employ complex and costly fabrication and processing techniques, such as molecular beam epitaxy (MBE), low-temperature growth or post-growth ion-implantations [3]. Although the number of reports of SWNT mode-locked lasers is increasing and the minimum achievable pulse duration has gone below 100 fs [4], the actual performance and limitations of these devices remain unclear, due to the lack of systematic characterizations. For example, in a number of reports [5–8], only the best achievable results e.g. shortest autocorrelation traces, widest spectral widths are reported without information concerning the most important parameters of a saturable absorber device, namely modulation depth, saturation fluence, non-saturable absorption and recovery time. Also, in a laser cavity, it is important to know the actual operation scenario of such devices to fully determine the laser's operating regime. Mode area on the saturable absorber, actual modulation depths etc. are all essential information in this regard. Unfortunately, to date the majority of reports of short pulse lasers with SWNTs based mode lockers have failed to clarify the operation of their saturable absorber devices. This has greatly limited the understanding of mode-locking mechanisms associated with the reported SWNTs-based mode-locked lasers and prevented clear design guidelines for such saturable absorber devices.

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In this paper, we present the fabrication of SWNT-PVA composite saturable absorber films with strong saturable absorption at ~1.5 μm wavelength region. In addition, the nonlinear absorption of the film is characterized using a femtosecond pump pulses where we obtain a saturation fluence of ~13.9 μJ/cm^2 and a modulation depth ~16.9% (in absorption) for our composite saturable absorber. This was confirmed by complementary spectral transmission experiment using the same pulse source. Furthermore, we qualitatively characterize the recovery time of our composites by measuring the transmitted autocorrelation traces at different incident pump powers. The observed side-peak suppression indicates a fast recovery time on the scale of ~1 ps. Finally we successfully mode locked an Erbium-doped fiber laser with our SWNTs-PVA saturable absorber films. The laser delivers ~650 fs pulses at a repetition rate of 20.8 MHz and it also features excellent jitter performance as well as long term stability. The laser's performance is then associated with the device characterization of our SWNT-PVA saturable absorber.

Device fabrication

To date, SWNT based mode-lockers have taken one of the following forms: SWNT solution [9], SWNT layers grown or spray-coated over optical parts [5, 6], or SWNT-polymer composites [7]. Among these methods, dispersing SWNTs in a polymer matrix seems to be the most promising one since it allows for homogeneous dispersion of nanotubes within the polymer matrix on a scale smaller than the device operation wavelength to minimize scattering losses. In this study, we fabricated free-standing SWNT-PVA composite films with peak absorption at ~1.5 μm and subsequently use it to form a fiber compatible mode locker device for pulse generation in an Er^{3+}-doped fiber laser. SWNTs are grown by laser ablation as described in Ref. [10]. They are then purified with dimethylformamide from catalyst metal particles and carbon impurities [11]. 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 mm 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 ~50 μm thick, 5 cm diameter freestanding film. A typical film size is about 20 cm^2. Figure 1 shows the optical absorbance of the composite film. The absorption peak clearly resides at ~1.5 μm. This near resonance growth is very important for achieving maximum modulation depth. Figure 2 shows an optical micrograph of an representative SWNT-PVA film, illustrating the homogeneousness with the current fabrication. In order to prepare a mode locker, a small part of the film (~2×2 mm^2) is cut and sandwiched in an FC/PC fiber connector, after depositing index-matching gel onto the fiber 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 the moment, even without large scale process optimization, we can potentially make ~500 mode-lockers with ~ 4 mg SWNTs).

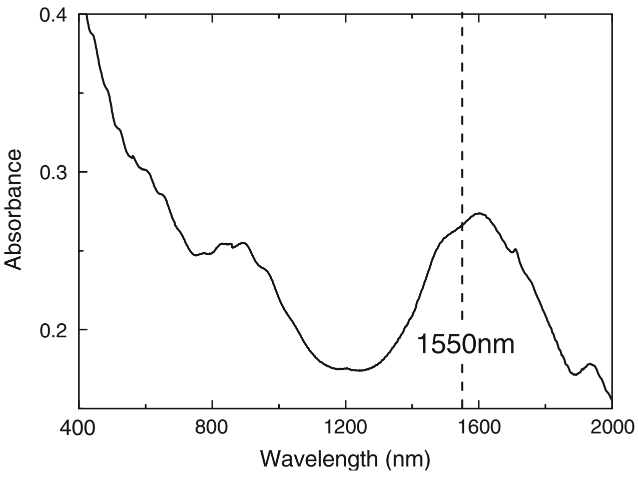

Fig. 1 Optical absorbance of SWNT-PVA film

Characterization of SWNT-PVA mode locker

The saturable absorption of the mode locker device is characterized using 650 fs pump pulses (C-band) from a

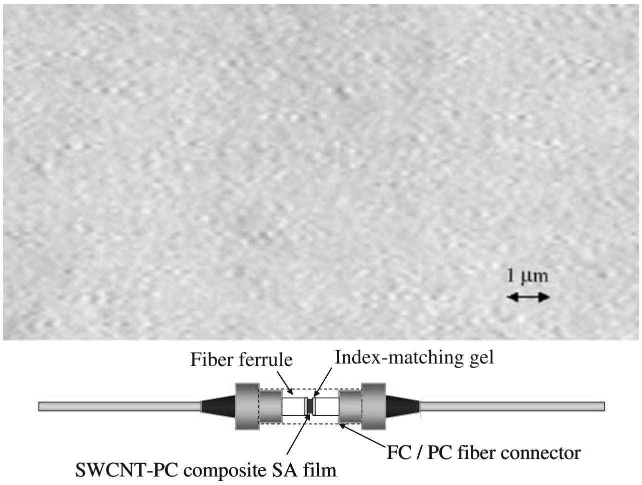

Fig. 2 **a** Optical micrograph of a representative SWNT-PVA film; **b** schematic of the SWNT-PVA mode locker device

commercial femtosecond fiber laser (Toptica Photonics, AG) operating at 77 MHz. A simple two-level saturable absorber model was used to fit the experimental data [12].

$$\alpha = \alpha_{\mathrm{ns}} + \alpha_0/(1 + I/I_{\mathrm{sat}}) \tag{1}$$

where α_0 is the linear limit of the saturable absorption component, α_{ns} is the non-saturable absorption component and I_{sat} is the saturation fluence [12]. The fitting has revealed a saturable absorption of 16.9% and a saturation fluence of ~13.9 µJ/cm^2 (~18.9 MW/cm^2). This corresponds to a 6% modulation in transmission (as shown in Fig. 3 inset) Repeated measurements after 2 h irradiation at high fluence (~200 µJ/cm^2) show no significant degradation of the composite, indicating good thermal stability of the SWNT-PVA composites. The relatively large non-saturable absorption of 82.5% is assigned to both the non-saturated absorbance of the film and the linear divergence loss at the fibre mode coupler, due to the film thickness of ~50 µm. This non-saturable loss can be optimized by reducing the thickness of the composite film.

In addition to the nonlinear power transmission measurements, we carried out a complementary spectral transmission experiment on the SWNT-PVA mode locker devices. An optical spectrum analyzer (OSA) was used to determine the spectral transmission by subtracting the transmitted spectra from the incident ones. To minimize effects contributed from fiber nonlinearities, the output pigtail fiber (~10 cm) was directly connecting to the input port of the OSA. The pump pulse is the same as was used in the power transmission measurement and we limit the power to ~3 dBm to make sure the input pump pulses maintain its spectral shape over the power range investigated. Figure 4 shows the spectral loss curves at different power levels. The decrease of losses with increasing incident power is as a result of the saturable absorption of the material. By averaging the spectral loss value over the 10 nm span from 1,545 to 1,555 nm, we can obtain the deduced device loss curve. Figure 5 presents the loss curve together with the inferred nonlinear transmission trace from which a modulation depth of 6% (in transmission) was obtained. This indeed corresponds very well with the result we have obtained with the nonlinear power transmission measurements.

The last parameter needed to be characterized is the saturable absorber recovery time. Conventionally, this is done using the pump-and-probe experiment [13], where a pump pulse is used to excite the material under test and a second pulse (normally much weaker in power and is controlled by a variable delay line) is used to probe the carrier dynamics within the excited material. But this method involves complex experimental apparatus and for our fiber-pigtailed mode locker device, it is not readily compatible with the pump-and-probe setup. In this study, we use a much simplified approach to qualitatively estimate

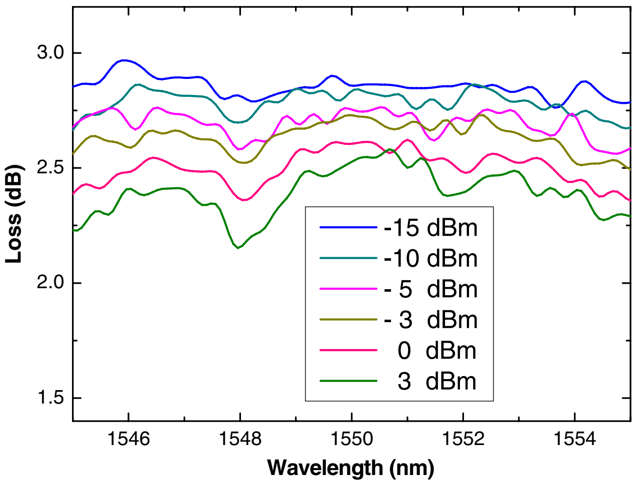

Fig. 4 Spectral transmission measurements

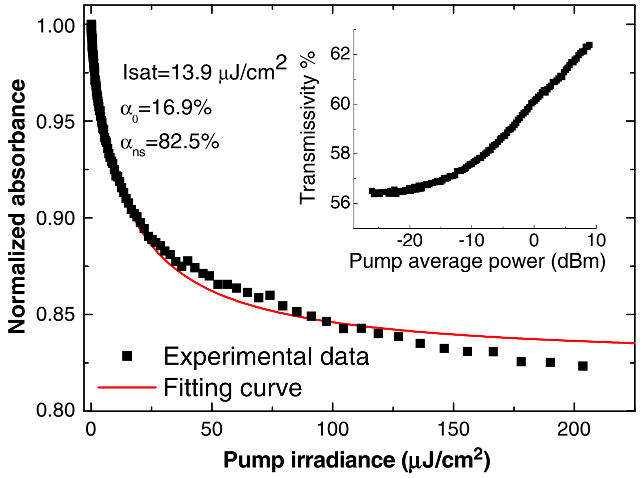

Fig. 3 Nonlinear absorption measurement (*inset*: nonlinear transmission curve)

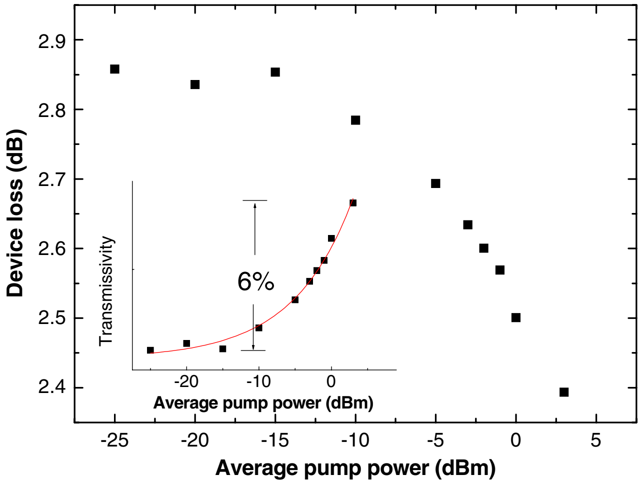

Fig. 5 Deduced device loss curve from spectral transmission measurement. *Inset*: a modulation depth of 6% (in transmission)

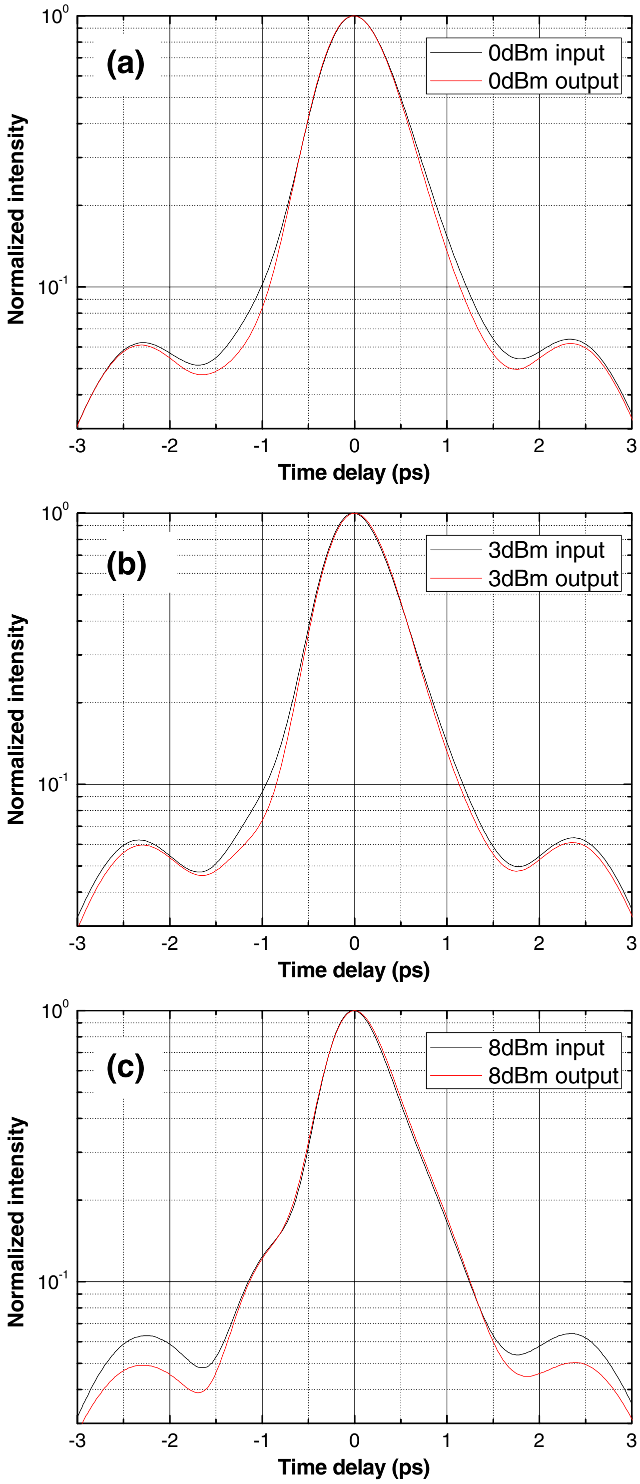

Fig. 6 **a**–**c** Transmitted autocorrelation traces of the pump pulses at different incident power

the recovery time of our device. We do this by measuring the transmitted pump pulse autocorrelation traces at different incident power levels. By comparing the peak-to-shoulder suppression ratio, we can qualitatively estimate the scale of recovery time for our SWNT mode locker. It should be noted that, this method doesn't provide us with an accurate account of the carrier dynamics as provided by pump-and-probe measurement; it is intended only for a proof-of-principle experiment. Moreover, this pulse reshaping capabilities of the SWNT-PVA saturable absorbers are potentially useful for 2R or 3R regeneration applications for optical communication systems. Figure 6 shows the results for the measurement. It can be seen that at higher pump powers, the side peaks associated with the autocorrelation main peak got reduced in intensity. In time domain, the distance between the main peak and side peak is about 2.5 ps, this means that the loss should have largely recovered within this time range. Also from the results, there is no visible change in the pulse duration. This may indicate that the input pulse has FWHM duration similar to that of the recovery time of the absorbers.

Laser results and discussion

Figure 7 illustrates the laser setup. One-meter piece of highly-doped Er^{3+} fibre (EDF) acts as the gain medium. It is pumped by a 976 nm laser diode (LD) via a wavelength division multiplexer (WDM). Two isolators (ISO) are placed at both ends of the Er^{3+} fibre to maintain unidirectional laser operation. The SWNT-PVA mode-locker is placed after the isolator at the output of the amplification section to enhance saturable absorption, and light is then coupled out of the cavity via a 50/50 splitter. A polarization controller (PC) is used to optimize the mode-locking condition. The total length of the laser cavity *L* is estimated to be 9.66 m.

At low pump powers, the laser operates in an unstable Q-switched state. When pump power reaches 40 mW,

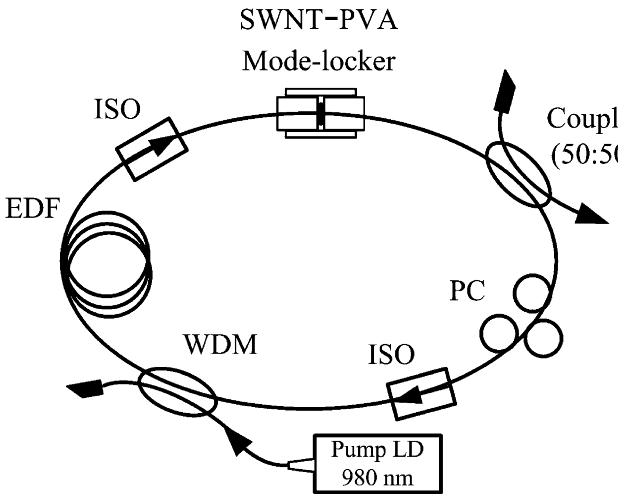

Fig. 7 Laser schematic (*PC* polarization controller, *ISO* isolator, *EDF* erbium-doped fiber, *LD* laser diode, *WDM* wavelength division multiplexer)

single pulse mode-locking self-starts, producing a stable pulse train at a repetition rate of 20.8 MHz. This self-starting behaviour has been observed before for SWNT doped polymers [4] and was contributed to the relatively long-lived recovery time associated with isolated SWNT. This is also believed to be assisted by the low saturation fluence of our mode locker devices. As pump power further increases beyond 60 mW, the laser starts operating in a double-pulse mode, due to soliton energy quantization phenomenon. However, stable mode-locking can be achieved as soon as the pump power is brought back below 60 mW. Figure 8 shows the output AC traces and optical spectra recorded (after 2 m of fibre pigtail) at different pump powers. It is found that the output pulse duration decreases with increasing pump power and the minimum value of ~640 fs is obtained at a pump power of 58.2 mW. We also detect a growing low-intensity background (continuum) as the cavity power increases. This indicates the increased strength of the dispersive waves when the soliton pulse adapts itself to the increased gain inside the laser cavity and may account for the destabilization of the soliton pulses [14]. The ~30 dB peak to background ratio is limited by the dynamical range of our autocorrelator and the relatively low input power. From Fig. 8b, asymmetric spectral broadening is observed and this is caused by the sharp decrease of gain profile of the Er^{3+} fibre beyond 1,560 nm. Five pairs of sidebands are also visible on both sides of the central wavelengths. When the pump power reaches 58.2 mW, fine structures appear between spectral peaks (Fig. 3b) and subsequent increase of pumping destroys the mode-locking. The time bandwidth product corresponding to the shortest pulse width is 0.52, larger than the transform-limited prediction 0.315 for Sech^2 temporal profiles. Fibre lead cutback measurements taken at 58.2 mW pump power (not shown for brevity) reveals an initial output pulse width about 560 fs. This gives a time bandwidth product of 0.42 at the output of the laser, which is still slightly chirped. Using the method given in [15], the average dispersion value of the cavity is estimated to be $\overline{\beta}_2 = -27.4\ \mathrm{ps}^2/\mathrm{km}$, yielding a residual cavity dispersion of around 0.265 ps^2. This is believed to have limited the minimum pulse duration achievable with the current laser cavity through the relationship $\tau_{\min} \approx \sqrt{L|\beta_{2-\mathrm{ave}}|}$, where $\tau_{\min}$ is the minimum pulse duration, L is the length of the laser cavity and $\beta_{2\text{-ave}}$ is the average cavity dispersion value [15]. An optimized cavity dispersion management may further reduce the output pulse width through the mechanism of soliton mode-locking.

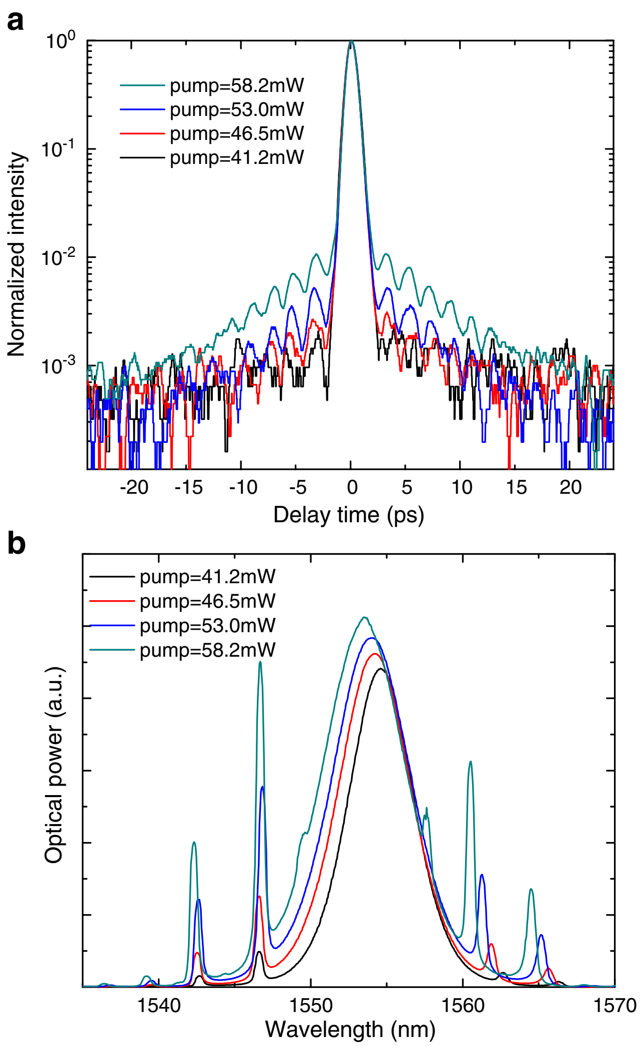

Fig. 8 **a** Output autocorrelation traces. **b** Output spectra at four different pumping levels. Traces from *bottom* to *top* correspond to increasing pump power of 41.2; 46.5; 53; 58.2 mW respectively

The average power incident onto our SWNT-PVA film is between 5–7.5 dBm, corresponding to a peak intensity of 450–780 $\mathrm{MW/cm^2}$. This is more than twenty times the saturation intensity of our device (~18.9 $\mathrm{MW/cm^2}$), indicating a full saturation regime. The intra-cavity power may be optimized by further reducing the non-saturable losses of the mode-locker. But this is not a major limitation for our current laser. Stability test has shown that the laser can operate continuously for days without loosing mode-locking. This

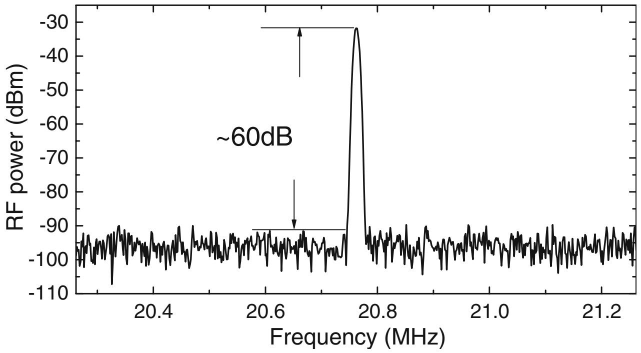

Fig. 9 RF power spectrum of laser output

might be contributed to the good thermal properties of our composite film. Jitter performance of the laser is also quite desirable with Fig. 9 showing the RF spectrum of the first harmonic of the laser output, a 60 dB peak to background ratio is observed (at a resolution bandwidth of 9 kHz and the peak is located at 20.762 MHz), which corresponds to our fundamental cavity frequency.

Conclusion

We fabricated a homogeneous SWNT-PVA composite saturable absorber, which features a low saturation fluence ~13.9 μJ/cm^2 and a large modulation depth ~16.9% (in absorption). Spectral and transient saturable absorption measurements are carried out in addition to the nonlinear power transmission experiment. We further use the composite as mode locker in an EDF laser, generating 650 fs light pulses. We demonstrate long-time stable operation of the SWNT mode-locked laser with good jitter performance. The laser's performance is associated with the characterization of our saturable absorber.

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