

Carbon nanotubes for ultrafast photonics

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We report characterization by absorption and photoluminescence excitation (PLE) spectroscopy of carbon nanotube solutions, which are then used for nanotube-based composite preparation. PLE shows the presence of bundles in the solution. The composite show a saturation intensity of 5 MW/cm^2 and is used in a fibre laser to generate pulses as short as 866 fs at about 1530 nm.

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1 Introduction

Single Wall Carbon Nanotubes (SWNTs) are of great interest in photonics and optoelectronics due to their linear and non-linear optical properties. Features in the optical absorption and emission spectra are generated by excitonic transitions [1–3]. SWNTs show strong third order nonlinearities through these excitonic transitions, as they become more transparent when irradiated by high power (saturable absorption) [4–6], with fast recovery time [4, 5, 7–14]. SWNTs are thus suitable for application as saturable absorbers in passively mode-locked lasers and noise suppression filters [15–17]. SWNT-based saturable absorbers must be carefully designed to keep a balance between modulation depth, which is ruled by the SWNT concentration, and unwanted non-saturable losses, such as scattering from large bundles or entanglements and non-saturable absorption from polymer matrix, surfactants, residual catalyst particles and carbon impurities [6].

To ensure fast device operation, the relaxation time of the saturable absorber must be as short as possible [18]. The relaxation time is one order of magnitude longer in isolated SWNTs, which relax within tens of picoseconds [10–12], than in bundles, which relax within 1 ps [7, 8]. Hence, bundles are useful in SWNT-based saturable absorbers. However, their size must be smaller than the device operation wavelength to avoid non-saturable losses due to scattering [19]. It is thus crucial to find a way to detect and quantify the presence of bundles in a SWNT solution. PLE spectroscopy is a powerful tool to detect the presence of individual SWNTs [20] and bundles [21, 22] in solution.

Here, we investigate by PLE spectroscopy the presence of bundles in SWNT solutions, which are then used to prepare polymer composites. Saturable absorption properties of the composites are studied by power dependent absorption. The composites are then employed as mode-lockers in a fibre laser.

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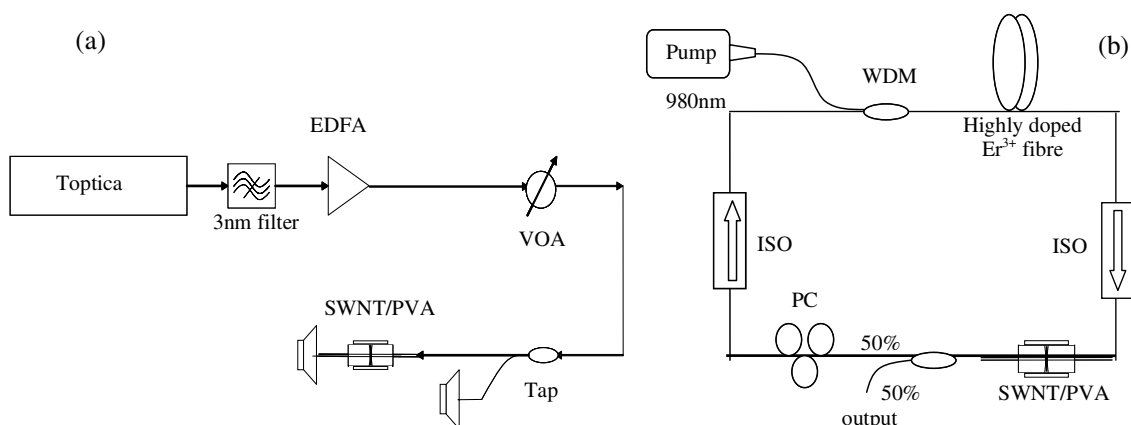


Fig. 1 a) Power dependent measurement setup; b) laser cavity.

2 Experimental

SWNTs are grown by the laser ablation (LA) technique as described in Ref. [23] without further purification. For PLE spectroscopy experiments, SWNTs are dispersed in D_2O by ultrasonication (Diagenode Nanoruptor ultrasonicator) in presence of sodium dodecylbenzenesulphonate (SDBS) as surfactant [24]. The solution is centrifuged (Beckman Coulter Ultracentrifuge) at 80 000 g for 2 hours to remove most of the bundles. PLE spectra are obtained with a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer, with InGaAs and CCD detectors and a Xenon lamp as excitation source. A 14 nm slit is used for the excitation and emission monochromators. Excitation intensity and instrument response are calibrated. Absorption measurements are performed with a Perkin Elmer Lambda 950 spectrophotometer.

In order to produce PVA composites, LA SWNTs are dispersed in H_2O and SDBS under the same conditions already described for PLE spectroscopy. The solution is then mixed with a PVA aqueous solution and dried at room temperature over a period of a few days [17].

We then perform power-dependent transmittance measurements on SWNT-PVA samples in order to test saturable absorption properties. We use a 1 ps optical pulse source centred at 1550 nm, achieved by filtering a femtosecond laser source (TOPTICA) using a 3 nm band-pass filter. The pump is amplified by an Erbium Doped Fibre Amplifier (EDFA) and a 10% tap is used to monitor the input power to the device and two power-heads are programmed to read the input/output simultaneously, Fig. 1a.

The composites are then used as a mode-lockers in a fibre ring laser. The laser setup is shown in Fig. 1b and can be summarized as follows: a 1 metre span of highly-doped Er^{3+} fibre from FibreCore acts as the gain medium (small signal gain ~ 18 dB). It is pumped by a 980 nm diode laser via a Wavelength Division Multiplexer (WDM) coupler. Two isolators are placed at both ends of the amplification section to maintain uni-directional laser operation and prevent back reflections. The SWNT mode-locker immediately follows the isolator at the signal exit of the amplification section to maximize the incident power density thus enhancing saturable absorption. A polarization controller (PC) is used to optimise the mode-locking condition. The total length of the laser cavity is estimated to be around 10 metres. Light is coupled out of the cavity through a 50:50 splitter and used to study the laser properties by optical spectrum analyzer (HP 86140A), oscilloscope (Textronix TDS 2024) and Second Harmonic Generation (SHG) autocorrelator (Inrad 5-14-LDA).

3 Results and discussion

The PLE map taken from the LA SWNT solution in D_2O is shown in Fig. 2a. Most of the features are identified as exciton–exciton resonant transitions [25]. Usually, such features exhibit a symmetrical pro-

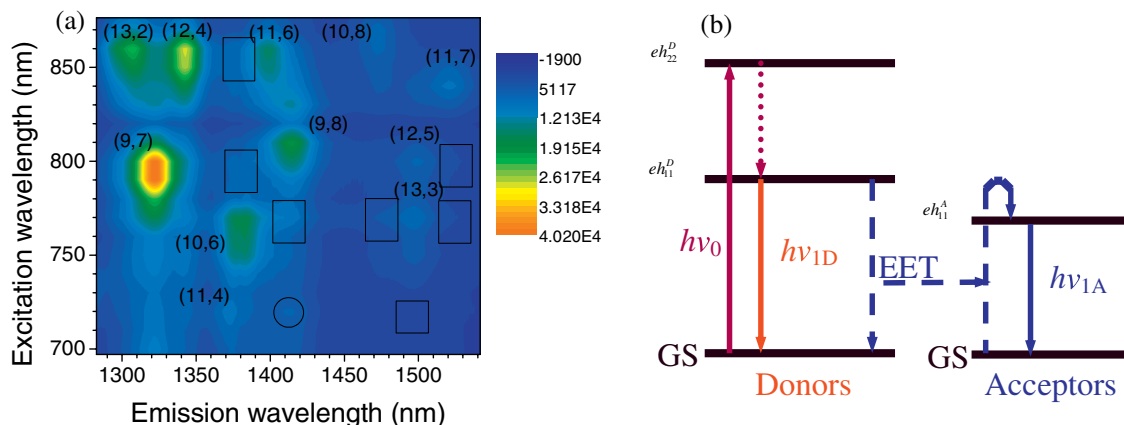


Fig. 2 (online colour at: www.pss-b.com) a) PLE map, showing exciton–exciton resonances and EET features (squares and circles); b) schematic mechanism of exciton relaxation in bundles [21].

file [25]. However, many exciton–exciton features in this PLE map are not symmetrical and have broad/elongated patterns, as shown by open squares in Fig. 2a. This suggests that some PLE features associated with Exciton Energy Transfer (EET) lie close to exciton–exciton transitions [21]. There is also a PLE feature at ($\lambda_{\text{ex}} = 718 \text{ nm}$, $\lambda_{\text{em}} = 1413 \text{ nm}$), indicated in the map by an open circle, which has not been observed before and does not belong to any known exciton–exciton resonance [25]. A careful analysis of the map shows that these features match emission energies of tubes with smaller eh_{11} transitions and excitation energies of tubes with higher eh_{11} transitions. For example, the (718 nm, 1413 nm) peak matches excitation energy of the (11,4) tube and emission energy of the (9,8) tube. Such new features arise from exciton energy transfer in nanotube bundles [21], as schematised in Fig. 2b: a photon is absorbed by tube 1 promoting a transition to eh_{22} , then the system relaxes nonradiatively to eh_{11} . Now the system has two possible alternatives: either emitting a photon of energy $h\nu_{1D}$ and relaxing to the ground state, or acting as donor transferring the energy to tube 2, which can now relax to the ground state emitting a photon of energy $h\nu_{1A} < h\nu_{1D}$ [21]. The (718 nm, 1413 nm) peak can thus be interpreted as (11,4) tube acting as donor and (9,8) as acceptor. All EET features are summarised in Table 1. Other EET features might be hidden by the strong exciton–exciton resonances.

The absorption spectrum of the LA-D₂O solution is shown in Fig. 3 (line + squares). We observe a band arising from the eh_{11} excitonic transitions of SWNTs extending from $\sim 1350 \text{ nm}$ to $\sim 1750 \text{ nm}$. This is made up of multiple features, due to the presence of isolated nanotubes [20] along with bundles. The equivalent LA-H₂O solution is used to prepare SWNT-PVA composites. These composites have bundles smaller than $\sim 1 \mu\text{m}$, as the material is homogeneous under optical microscopy [17], thus keeping the optimum compromise between avoiding scattering losses [19] and minimising the carrier relaxation time [7, 8, 10–12]. The absorption spectrum of the composite is shown in Fig. 3 (solid line). We observe

Table 1 Summary of EET features.

$(\lambda_{\text{ex}}, \lambda_{\text{em}})$	donor	acceptor
(795, 1380)	(9,7)	(10,6), (11,4)
(769, 1413)	(10,6)	(9,8)
(718, 1413)	(11,4)	(9,8)
(845, 1476)	(12,4)	(10,8)
(769, 1476)	(10,6)	(10,8)
(798, 1526)	(9,7), (12,5)	(11,7)
(769, 1526)	(10,6), (13,3)	(11,7)

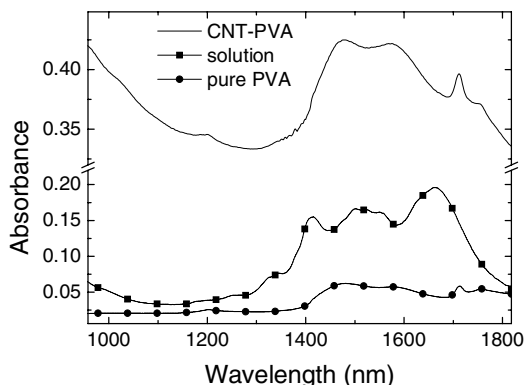


Fig. 3 Absorption spectra of LA-D₂O starting solution (line + squares), CNT-PVA composite (line) and pure PVA (line + circles).

a broad peak centred at ~1570 nm, which is ~50 nm red-shifted from the solution due to the different environment [26, 27]. The broad feature at 1480 nm and the sharp one at 1710 nm come from the PVA matrix, as shown in Fig. 3.

It should be pointed out that, although the absorption from LA SWNTs extends up to 1700 nm (Fig. 3), no feature can be observed in the map above 1550 nm due to the limited sensitivity of our detector above this wavelength. However, this range is enough for us to assess the presence of bundles in the solution.

To maximise saturable absorption [28] the operation wavelength should match the absorption peak. Given the broad feature at ~1550 nm, this is the wavelength of our experiments.

Power dependent absorption measurements for these composites are shown in Fig. 4a. At 1550 nm, a decrease of 4% in absorbance is recorded. By fitting the experimental data with the equation [28, 29]:

$$\alpha = \frac{\alpha_0}{1 + I/I_s} + \alpha_{NS}, \quad (1)$$

where α_0 is the linear limit of the saturable absorption component, α_{NS} is the nonsaturable absorption component and I_s the saturation intensity, we derive a saturation intensity of ~5 MW/cm² and a non-saturable component of ~96%.

The SWNT-PVA composite is finally used in our ring cavity laser, allowing the generation of stable mode-locked pulses with ~14 MHz repetition rate. Figure 4b shows the optical output spectrum, with a single symmetrical peak centred at 1532 nm. The output power is ~0.1 mW. The autocorrelation trace is shown in Fig. 4c. The curve is fitted by a Gaussian function with FWHM 1.22 ps. The pulse width is derived multiplying the FWHM by the decorrelation factor, which is 0.707 for Gaussian pulses [29].

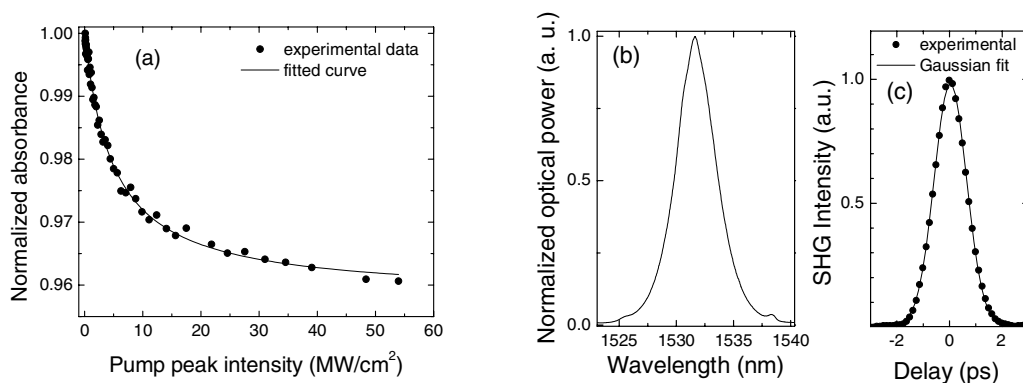


Fig. 4 a) Power dependent measurements; b) laser output optical spectrum; c) autocorrelation trace.

This gives a pulse width of 866 fs. The time bandwidth product (TBP) is an estimation of the pulse quality inside the cavity and is obtained by multiplying the pulse duration, in seconds, by the optical spectrum width, in Hertz [30]. In our case, the pulse is Fourier transform limited, as $TBP \approx 0.43$, very close to the theoretical value of 0.44 for gaussian pulses [30]. This means that the pulse is as short as allowed by the spectral width, and dispersion and chirping in the cavity are reduced to the minimum.

4 Conclusions

We demonstrate the possibility to use PLE spectroscopy to assess the presence of bundles in SWNT solutions, in order to optimise the conditions for polymer composite preparation. The composites show strong saturable absorption and generate stable femtosecond mode-locked pulses in a fibre laser cavity.

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