

Carbon Nanotube Polycarbonate Composites for Ultrafast Lasers**

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Single-wall carbon nanotubes (SWNTs) are at the center of nanotechnology research. Their nonlinear optical behavior makes them promising for applications in ultrafast photonics.^[1–8] SWNTs are indeed good saturable absorbers, i.e., they are transparent to high-intensity light, with ultrafast recovery time.^[1–3] Saturable absorbers must always keep a delicate balance between the modulation depth and nonsaturable losses,^[9] while ensuring a short recovery time.^[10] The use of SWNTs dispersed in a composite material has so far proven to be one of the most successful approaches to their application as saturable absorbers.^[4–8,11] In fact, the modulation depth, which is proportional to the SWNT concentration,^[3,5] can be controlled by tuning the SWNT concentration within the material, while the nonsaturable losses due to scattering from SWNT bundles can be minimized by making the bundles smaller than the device operation wavelength.^[3,6] The latter can be achieved when SWNTs are dispersed in a solvent. The presence of bundles is, however, useful to minimize the recovery time.^[12–14] The use of a polymer matrix offers the best compromise in terms of bundle-size control and ease of device integration.^[4–8] This can be optimized at the SWNT dispersion stage, and probed by photoluminescence (PL) spectroscopy, which allows for the detection of isolated SWNTs^[15,16] as well as small bundles.^[17]

The ideal host polymer for SWNTs to be used as saturable absorbers must be highly transparent in the wavelength range of interest, reducing propagation losses^[18] and ensuring minimum refractive index mismatch with SWNTs to avoid scattering.^[19] The host should also be thermally and environmentally stable, as thermal damage or moisture adsorption can adversely affect its transparency.^[18] However, polyvinyl-alcohol (PVA), the polymer most widely used so far^[3–8] for this application, does not meet these requirements,

presenting high loss in the telecommunications wavelength range (~ 1550 nm), as discussed below. Moreover, it has a low glass-transition temperature ($T_g \sim 85^\circ\text{C}$), decomposes in air just above 200°C ,^[20,21] and absorbs large amounts of moisture due to the high concentration of $-\text{OH}$ groups along its chain.^[21] Cellulose derivatives have also been used as polymer matrices for SWNTs,^[11] though their hydrophilic character^[21] may affect their transparency on a long-term basis due to moisture absorption. A set of new, stable, transparent polymers is thus needed for a significant step forward in the field. We believe that polycarbonate, poly(methyl methacrylate), or polyimides are an ideal choice, because of their high transparency and environmental, thermal, and chemical stabilities.^[18,21]

Despite its wide use in photonics, for example for optical waveguides,^[18] polycarbonate (PC) has so far been used as polymer matrix for SWNTs only for mechanical applications.^[22–25] Here, we use PC as a new optical polymer matrix, in which SWNTs can be dispersed homogeneously. PC is far more stable than PVA, with $T_g \sim 150^\circ\text{C}$ ^[21] and air degradation only above 400°C .^[26] Also, the presence of aromatic rings in its backbone makes PC hydrophobic, limiting moisture absorption.^[21] Our PC–SWNT composites showed strong modulation depth, and were employed as mode lockers in a fiber laser, in which they generated ~ 200 fs pulses at 1560 nm, amongst the shortest reported for SWNT-based saturable absorbers.

Conjugated polymers, such as poly(phenylene vinylene) (PPV) derivatives, were proven effective to disperse bundles^[27,28] as well as individual SWNTs^[29] in common organic solvents such as chloroform^[27,28] or tetrahydrofuran (THF),^[29] due to π – π stacking of the aromatic rings of the polymer on the SWNT sidewalls through van der Waals interactions.^[27–29]

The choice of SWNTs is crucial, as saturable absorption is a resonant effect^[30,31] and SWNT optical absorption depends on their diameter.^[32] We use SWNTs grown by laser ablation,^[33] with diameter range 1.0–1.3 nm. This ensures broad absorption around 1550 nm.^[32] We disperse our SWNTs by ultrasonic treatment using regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) as dispersant in 1,2-dichlorobenzene (DCB). Figure 1a shows the absorption spectrum of SWNTs from the SWNT–P3HT–DCB solution used to prepare our composites. The absorption spectrum from a SWNT–D₂O solution with sodium dodecylbenzenesulphonate (SDBS) is also shown for comparison. The DCB solution and the reference D₂O solution show absorptions in the range 1400–1700 nm. While the D₂O solution has very narrow features, the same features, though still observed, are much broader and blue-shifted in the DCB

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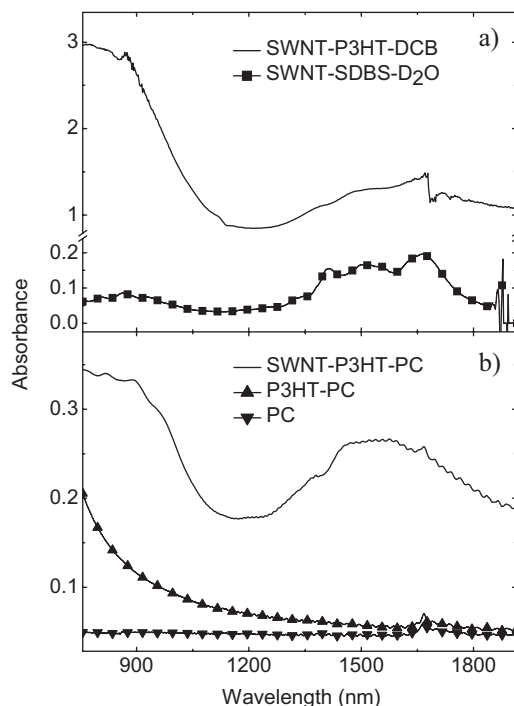


Figure 1. a) Absorption spectra from SWNT-P3HT-DCB solution (line) and SWNT-D₂O solution (line + squares). The oscillations at ~1680 nm for DCB and at >1860 nm for D₂O are due to solvent absorption. b) Absorption spectra from SWNT-P3HT-PC composite (line), P3HT-PC (line + up triangles) and PC (line + down triangles).

solution, and almost merge in a unique, broad band covering the whole range. This indicates that SWNTs are present in the DCB solution as large bundles, as absorption broadens with bundling.^[34,35] This is further confirmed by the absence of PL in our DCB solutions. These show a significant absorbance increase in the region below 1100 nm, most likely due to π - π interactions between P3HT and SWNTs,^[29] as pure P3HT in DCB does not absorb above 600 nm.

Absorbance of a solute in a solvent is proportional to its concentration through the Lambert-Beer law.^[36] The only absorbance values of SWNTs dispersed by a conjugated polymer previously reported are ~0.1 at 600–800 nm^[27] and ~0.2 at 1100–1500 nm.^[29] Our solution showed an absorbance of ~1.5 at 1400–1700 nm. While we cannot compare our absorbance value with that reported in ref. [27] due to the different wavelength range, we can with ref. [29]. We thus estimate a SWNT concentration seven to eight times higher in our solution than in ref. [29]. This is likely to arise from the presence of large bundles, in contrast to the isolated SWNTs reported in ref. [29], due to different dispersion procedures.

Despite the high concentration of bundles, our processing technique ensures that these were sub-micrometer sized, key to avoiding scattering losses when operating at 1550 nm.^[37] This was confirmed by optical microscopy (Fig. 2), showing only a few residual aggregates, with most bundles below the optical resolution limit. These residual aggregates either remain in

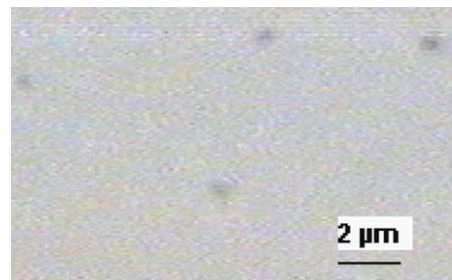


Figure 2. Optical image of the SWNT-P3HT-PC composite.

solution after ultracentrifugation or are formed during solvent evaporation.

Figure 1b compares the absorption spectra from a SWNT-P3HT-PC composite, P3HT-PC, and pure PC. All composites are 40 μm thick. The SWNT-P3HT-PC spectrum shows high absorption around 1550 nm, i.e., the wavelength used for telecommunication devices. This is essential as saturable absorption is a strongly resonant phenomenon.^[30,31] Spectra from P3HT-PC and pure PC show very low absorption in the same region, confirming that the band around 1550 nm comes from the SWNTs. Our pure PC film is indeed highly transparent in this region, with a transmission loss at 1550 nm of 0.26 dB, almost half of that of a PVA film with the same thickness, for which the loss is 0.48 dB.

The saturable absorption properties of our composites are characterized by power-dependent measurements at 1550 nm, Figure 3. Data were fitted using the equation^[31]

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

where α_0 is the linear limit of the saturable absorption, α_{NS} is the nonsaturable absorption component, and I_s is the saturation intensity, defined as the intensity required to reduce the saturable component to half of its original value. Our

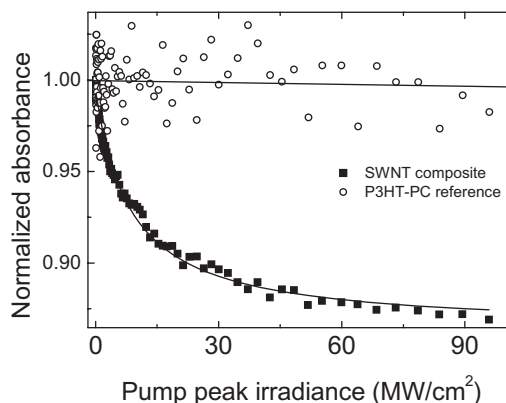


Figure 3. Power-dependent absorption measurements of SWNT-P3HT-PC (squares) and P3HT-PC reference (open circles).

SWNT-PC composite shows 13% saturable and 87% nonsaturable absorption, as per Figure 3. The saturation intensity is 7 MW cm^{-2} . The saturable component arises entirely from SWNTs, as the P3HT-PC reference did not display nonlinear absorption at high laser intensities (Fig. 3). The nonsaturable component has two main contributions. The first is the fiber-to-fiber spacing (see Experimental section), due to the thickness of the SWNT-polymer composite. The second is the absorption background (Fig. 1b). This is mainly due to residual carbonaceous impurities still present after centrifugation, as the starting nanotube material is used without further purification (see Experimental section). Other minor sources of nonsaturable absorption are scattering from residual aggregates (Fig. 2) and the absorption tail of P3HT (Fig. 1b).

The composite is finally used as passive mode-locker in a fiber laser. Mode-locking self-starts in the cavity at a minimum pump power of 17.5 mW from a fiber-coupled diode laser. Below this threshold, continuous wave (CW) operation is observed. We record output powers of up to 0.9 mW (Fig. 4). Stable single-pulse operation is obtained from 17.5 to 26 mW pump power. Figure 5a shows the output optical spectrum, recorded at 26 mW pump power, the upper limit for stable mode-locking operation. It is centered at 1560 nm, with 13 nm full-width at half-maximum (FWHM), and shows typical soliton sidebands, arising from intracavity periodical perturbations.^[38,39] Their positions are symmetric with respect to the peak wavelength, while their amplitudes are not equal as expected because of the asymmetry of the net gain spectrum.^[40] Second-harmonic-generation autocorrelation (SHG) is used to measure the pulse width. The autocorrelation (AC) trace for our composite is shown in Figure 5b. The experimental data are fitted by a sech^2 model, as predicted for soliton pulses^[9], and show a FWHM of 297 fs, which, divided by 1.54, the decorrelation factor for sech^2 pulses, gives a pulse width of 193 fs, amongst the shortest reported for SWNTs in fiber lasers.^[4-6,8,11] The time-bandwidth product (TBP) is the product of the spectral width (in Hz) and the pulse duration (in seconds), and is an estimation of the pulse

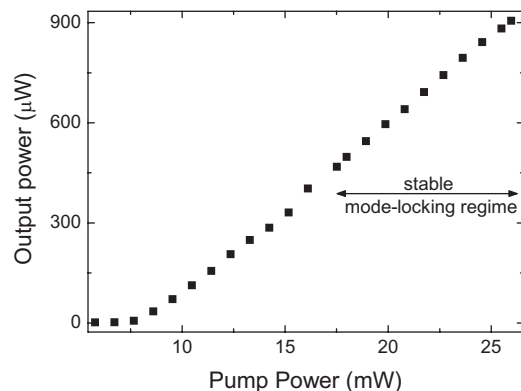


Figure 4. Output power as a function of pump power. Mode-locking is self-started above 26 mW pump power.

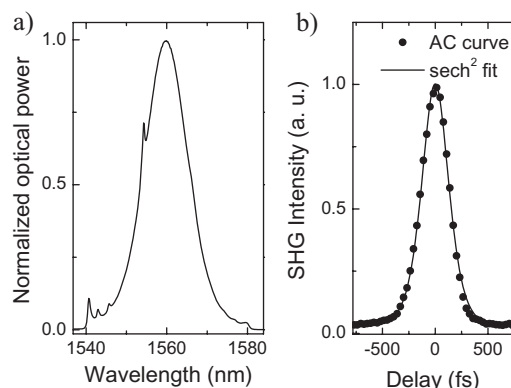


Figure 5. a) Output pulse spectrum, centered at 1560 nm, with soliton sidebands. b) AC trace and sech^2 fitting curve, showing 193 fs pulse width.

quality,^[41] as it should be as close as possible to the minimum theoretical value calculated for a particular type of pulse. For our composites, the spectral bandwidth is $\sim 1.6 \times 10^{12} \text{ Hz}$ (13 nm), giving a TBP of 0.31, matching the theoretical value of 0.314 for Fourier transform limited sech^2 pulses.^[41] This means that the pulse is as short as allowed by the spectral width.

In summary, we demonstrated polycarbonate as a new photonic polymer host, where SWNTs were homogeneously dispersed on a sub-micrometer scale. The polymer is almost two times more transparent than PVA and is greatly superior in thermal and environmental stability, resulting in very high-quality composites. They present a strong saturable absorption at 1550 nm, and generate 193 fs pulses in our laser cavity. These results could enable the wide use of polycarbonate for optical applications using SWNTs in the near-IR range.

Experimental

SWNTs were grown by laser ablation [33] and used without further purification. SWNTs (2.5 mg) were dispersed in 1,2-dichlorobenzene (DCB) (10 ml) by 3 h ultrasonication (Bioruptor ultrasonicator, Diagenode), in presence of regioregular P3HT (3 mg). Both solvent and chemicals were purchased from Sigma-Aldrich. The solution was filtered through a $1 \mu\text{m}$ retention filter (Millipore) and then centrifuged (Beckman-Coulter ultracentrifuge) at $300\,000 g$ for 3 h to remove residual bundles and heavy catalyst particles. Pellets of PC, a copolymer of bisphenol A and bisphenol TMC, purchased from Apec, were added to the solution and dissolved by further ultrasonication. The resulting SWNT-P3HT-PC solution was finally dried at room temperature under vacuum for 24 h. SWNT concentration and film thickness were controlled by tuning the amount of solution and polymer used in the drying mixture. For the results shown in this work, 3 mL of solution and 120 mg of PC were used. The material was characterized by optical microscopy (Leica Microscope) and Vis-IR spectroscopy (Perkin Elmer Lambda 950).

A $\sim 2 \text{ mm}^2$ SWNT-PC composite was packaged by sandwiching the film in the fiber-pigtailed FC/PC connector, with index-matching gel on both fiber ends.

Power-dependent absorption measurements were carried out in the following setup: the connector was coupled to a $\sim 650 \text{ fs}$ optical-pulse source, centered at 1550 nm. This was achieved by filtering a femtosecond fiber laser (TOPTICA) using a 3 nm band-pass filter.

The laser beam was amplified by an erbium-doped fiber amplifier (EDFA) and a 10% tap was used to monitor the input power to the connector, containing our composite. Two power-heads were programmed to read the input/output simultaneously.

The same connector was then used as part of our laser cavity. The laser was in a ring configuration, using erbium-doped fiber (EDF) as the gain medium. The EDF was pumped by a fiber-coupled diode laser at 976 nm via a wavelength-division multiplexer (WDM). Unidirectional operation was ensured by insertion of an optical isolator (ISO). A fused coupler with 20/80 ratio was used as output coupler. Output pulses were collected from the 20% port, whereas the 80% port was used to feed pulses back into the cavity. The total length of the laser cavity was around 5.5 m.

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