Sub-100 fs two-color pump-probe spectroscopy of Single Wall Carbon Nanotubes with a 100 MHz Er-fiber laser system

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Abstract: An extremely compact and versatile near-infrared two-color femtosecond pump-probe spectroscopy apparatus based on an amplified Er-fiber laser system is presented and applied to the characterization of the relaxation dynamics of single-wall carbon nanotubes with fundamental absorption in the 2 μm spectral region. By implementing a fast-scan technique, dynamics as long as 3 ps are acquired in 5 s with a relative sensitivity of 10^{-4} and a temporal resolution below 100 fs at 2 μm.

OCIS codes: (300.6340) Spectroscopy; (120.6200) Instrumentation, measurement, and metrology; (320.7150) Ultrafast optics; (140.4050) Laser and laser optics.

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1. Introduction

Two color pump-probe experiments with femtosecond light pulses are a key tool for studying ultrafast dynamics of a great variety of materials and systems, and provide unique information of elementary photophysical processes occurring in atoms, molecules, and solids [1-3]. The most widely used configurations are based on amplified Ti:sapphire systems delivering very high energy pulses with kHz repetition rate. Due to the high pulse energy, the efficiency of nonlinear processes such as optical parametric amplification is strongly enhanced, and broadly and independently tunable pump and probe pulses can be easily synthesized [4]. This gives Ti:sapphire systems extremely high versatility and temporal resolution [5]. On the other hand, due to the limited repetition rate, quite long measurements with low modulation frequency and lock-in detection are required, resulting in sensitivity not exceeding 1 part per 10^4. At the expense of tuning capabilities and temporal resolution, sensitivities as high as 1 part per 10^6 can be achieved combining the use of an optical parametric oscillator (OPO), which operates at hundreds MHz repetition rate [6], with high-speed acusto-optical modulators. Both approaches, however, suffer from high system complexity and cost.

In this paper we present a novel system for pump-probe experiments in the near-infrared region at 100 MHz repetition rate, based on a compact and cost-effective Er-fiber laser. The system uses a fast-scan technique, allowing us to acquire 3-ps long dynamics with sub-100-fs temporal resolution, with sensitivity as high as 1 part per 10^4, for measurements averaged over a 5-s acquisition time. A detailed description of the system performances is provided, and an application to the characterization of single-wall carbon nanotubes (SWCNTs) is discussed. A 370 fs relaxation time around 2 μm is found, which is promising in view of exploiting such materials as fast saturable absorbers for passively mode-locked Tm and Ho lasers [7].

2. Experimental apparatus

The pump-probe apparatus is driven by a mode-locked Er-doped fiber laser (Toptica FFS) with two optically amplified branches delivering ~65 fs pulses centered at 1.55 μm with 100 MHz rep-rate and 250 mW average output power. One of the branches is coupled to a

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highly nonlinear fiber generating an octave-spanning supercontinuum (SC) from 1 to 2.3 µm. In our configuration, the first branch is used to excite the sample, while the SC output is spectrally filtered by an f-f spectral shaper to provide a single probe pulse with a narrower band, tunable from 1.6 to 2.3 µm. As shown in Fig. 1, the spectral shaper is composed by a SF10 prism used with Brewster incidence and at minimum deviation, a folding spherical concave mirror with a 1 m radius of curvature, a flat mirror placed in the Fourier plane, and a variable slit placed in front of the mirror. Adjustments of the horizontal position and of the width of the slit allow, respectively, tuning and tailoring of the probe spectrum. It is worth noting that the SF10 prism is chosen since it introduces negligible group-velocity dispersion in the 1.8-2.2 µm spectral range used in experiments reported in this paper. In the pump probe experiments the optical delay is periodically varied, in a fast scan configuration [8], by a retro-reflector mounted on an electro-mechanical shaker placed in the probe-arm. By driving the shaker with a triangular wave function at 26 Hz, the optical delay can be varied up to ~3 ps. If longer dynamics are to be studied, the system can be operated in a more conventional slow-scan configuration with pump intensity modulation, lock-in detection, and step-by-step change of the optical delay through a PC-controlled motor stage placed on the probe arm [9]. Pump and probe beams are independently focused on the sample down to spot sizes of 75 and 32 µm, respectively. For the pump beam we use a BK7 lens with a focal length of 250 mm while for the probe beam we adopt a 100 mm lens in CaF_2 to minimize dispersion-induced probe broadening. The probe optical power is measured with an extended InGaAs detector placed at the output of a PC-controlled monochromator allowing for wavelength resolved acquisition of the pump-probe dynamics. In the fast-scan mode, a digital oscilloscope triggered by the shaker modulation signal allows the pump-probe trace to be visualized, averaged and recorded with extremely fast acquisition times.

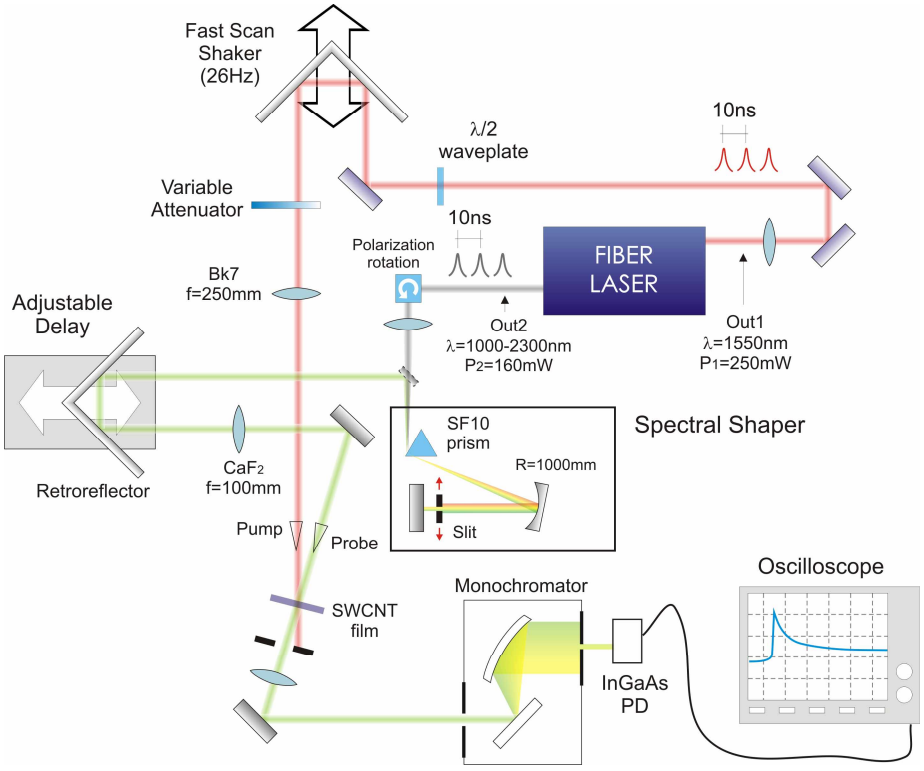

Fig. 1. Near-infrared two-color pump-probe set-up

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3. System performance

The two main features of a system exploiting a SC light for high temporal resolution pump-probe experiments are, in the spectral domain, the filtering and tuning ability, and, in the temporal domain, the possibility of synthesizing a single short pulse (secondary probe pulses could indeed induce parasitic excitation of the sample).

The SC light delivered by the laser source covers more than an octave of spectrum and exhibits, as shown by the spectra reported in Fig. 2(a)-(d), two well distinct peaks at opposite positions with respect to the central wavelength at 1550 nm. Their wavelength can be easily tuned by acting on the chirp of the pulse entering the nonlinear fiber: for negligible chirp the spectrum covers the broadest range, from ~1 to ~2.3 μm (a), while, for increasing chirp, narrower spectra with modified peak positions are obtained (see evolution from (b) to (d)). By means of the spectral shaper described in Section 2, the main peaks can be extracted, and, in the long wavelength region adopted in the experiments, very clean tunable spectra as those reported in Fig. 3(a) can be obtained. The width of these spectra supports approximately 32 fs long pulses with an average power of about 20 mW. In the time domain the pulses associated with the spectra reported in Fig. 3(a) are nearly transform-limited as a result of soliton-like propagation in the non-linear fiber. The experimentally measured pulse-width is about 40 fs, as retrieved from autocorrelation measurement reported in Fig. 3(b). It is worth noting that, in the short wavelength region, the SC pulses are no longer transform-limited, and an SF10 prims compressor module is required for combing spectral shaping with dispersion compensation [10]. The overall temporal resolution of the pump-probe set-up amounts to ~76 fs, which results from the convolution of the 40 fs probe pulses with 65 fs pump pulses. In the case the pump is provided by the short wavelength SC peaks, the temporal resolution can be further reduced to 56 fs.

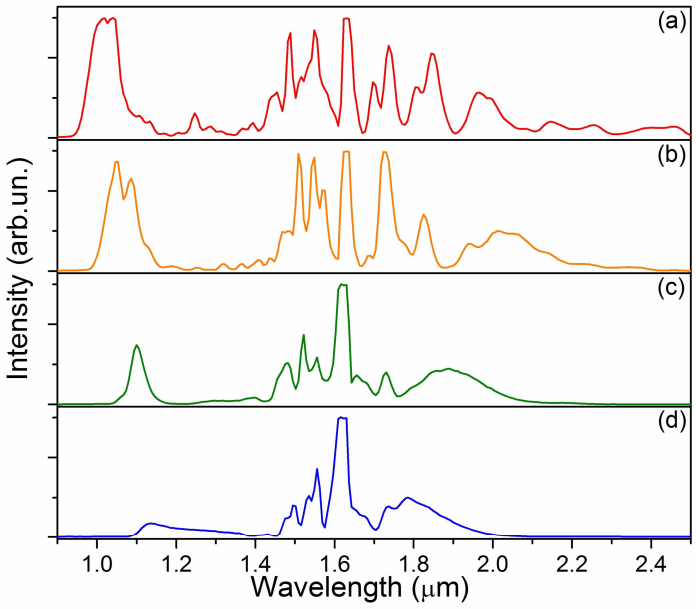

Fig. 2. From (a) to (d): SC spectra for increasing chirp of the pulses coupled into the highly nonlinear fiber.

The acquisition of the relaxation dynamics of the sample is performed, as described in section 2, in a fast-scan mode. For samples giving large differential signals, this configuration allows one to achieve high signal-to-noise ratio (SNR) in combination with fast acquisition times, without artifacts due to periodic heating induced by pump intensity modulation [11]. The transmission *T* of the probe beam through the sample is recorded on the oscilloscope as a

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function of time. When both pump and probe beams are present, a small differential signal ΔT is superimposed to the large T background: this signal is periodic with a frequency of 26 Hz. By means of a band-pass electrical filter from 8 Hz to 1 kHz the ΔT signal is extracted by filtering out the CW background together with the laser high frequency noise (this does not

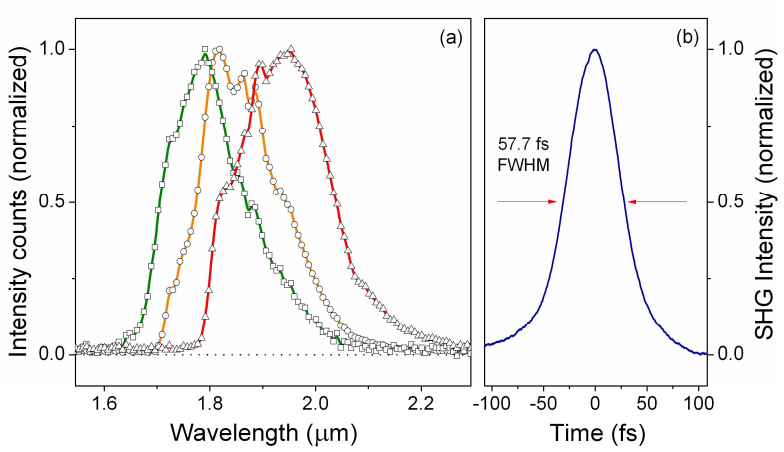

Fig. 3. (a): SC spectra at the output of the spectral shaper. (b): intensity autocorrelation trace of the pulses with spectrum centered at 1.95 μm.

allow, however, to get rid of the low-frequency noise of detectors and laser). Thanks to remarkably good intensity-noise properties of the laser system, a satisfactory sensitivity as high as 1 part per 10^4 is experimentally obtained after 5 s averaging, which is sufficient to retrieve almost in real-time very clean pump-probe traces from SWCNTs. The pump-probe measurements are preceded by a preliminary determination of the linearity of the time scale, which is related to the uniformity of the scan velocity. This is achieved by monitoring the temporal shift of the pump-probe traces induced by PC-controlled variations of the optical delay in the probe arm. A calibration curve is determined, and used for software correction of the temporal scale. In order to evaluate how much the sensitivity of the system can be

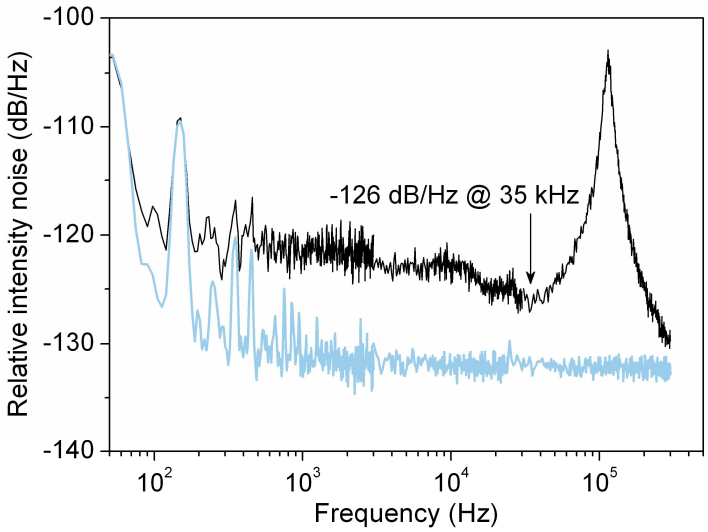

Fig. 4. Electrical power spectrum of the laser intensity noise as measured with a fast extended InGaAs detector (black line) together with the measured noise floor (light blue line).

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improved by adopting a slow-scan configuration, the relative intensity noise (RIN) performance of the laser source was measured by means of a fast InGaAs detector and of an electrical spectrum analyzer. The corresponding spectrum, reported as a black line in Fig. 4 together with the noise floor (light blue line), shows a prominent peak centered around 110 kHz, due to laser relaxation oscillations, and a minimum of about -126 dB/Hz around 35 kHz. With such a modulation frequency, achievable with a mechanical chopper, and a lock-in detection with 0.5 s integration time, pump-probe experiments with relative sensitivity as high as 10^{-6} can be foreseen. Such a sensitivity is expected to derive from the reduction by a factor of 10 of the intensity noise (from -115 dB/Hz to -125 dB/Hz) and by a factor of about 100 of the measurement bandwidth (from 1 kHz to less than 10 Hz), resulting in an overall SNR improvement by about two orders of magnitude. By using an acousto-optic-modulator (AOM) at frequencies higher than 200 kHz, even better SNR could be achieved, but at the price of a reduced temporal resolution, due to pulse-broadening in the modulator.

4. Pump probe dynamics of SWCNTs

The carrier dynamics of SWCNTs has been extensively studied over the past years, employing time resolved spectroscopy [12-20]. Excitonic states play a key role in the radiative and nonradiative process within semiconducting SWCNTs [16-18]. Typically, time resolved spectroscopy reveals a multicomponent relaxation dynamics, with a fast component about 1 ps or less and a slow component, which lasts from tens of ps to 100 ns. The long life component is associated with the radiative transition responsible for the IR photoluminescence [15]. The fast component is usually associated to nonradiative processes such as carrier thermalisation [12], intersubband relaxation from the higher exciton manifold states [18], relaxation within exciton levels [21], exciton energy transfer within nanotube bundles [22], exciton-exciton annihilation [16], and Auger recombination [23]. In large SWCNT bundles, charge transfer of the photoexcited carriers from semiconducting to metallic tubes was also suggested [14]. Despite much progress in the study of excitons in SWCNTs, the nature of the relaxation dynamic is not fully understood, and further efforts would be useful for the optimisation of this material for various photonics applications [24, 25].

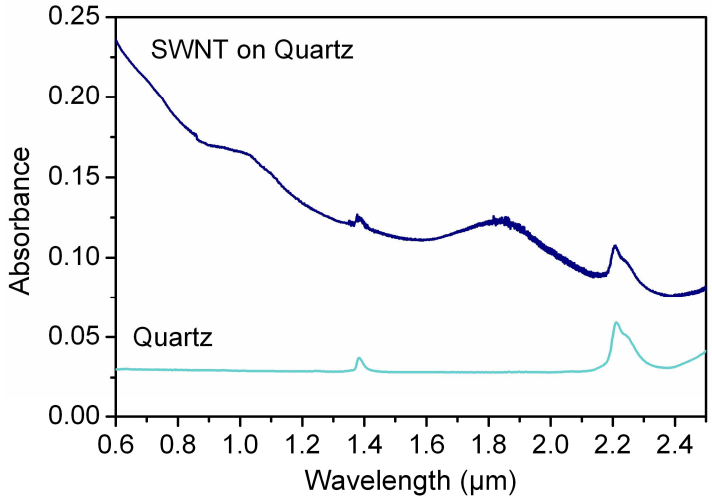

Fig. 5. Optical absorption of SWCNTs.

We test the pump-probe configuration by studying the temporal dynamics of SWCNTs designed to provide fast saturable absorption around 1.8-2 μm, which is a particularly interesting region for mode-locking of broadband active media such as Tm and Ho-doped fibres. We use commercially available SWCNTs (CarboLex Inc, USA) grown by arc discharge. 1 mg of SWCNTs is dispersed in 20 ml of dimethylformamide (DMF) by 1 hour

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strong ultrasonication. The suspension is then centrifuged for 30 minutes at 2800 RPM to remove big aggregates. Finally, the supernatant solution is spray-coated onto a quartz substrate. The optical absorption measured with a Perkin Elmer Lambda 950 spectrometer is shown in Fig. 5. A broad band with a maximum at 1850 nm corresponds to absorption of semiconducting SWCNTs with diameters between 1.3 and 1.6 nm, as also confirmed by Raman spectroscopy. Figure 5 also shows the background spectrum coming from the quartz substrate.

The fast scan technique allows us to perform particularly rapid measurements. For every wavelength selected by the monochromator, a 2.5 ps temporal dynamic is recorded and averaged 128 times by the oscilloscope in a 5 s time window. By changing the monochromator wavelength in steps of 20 nm, a full transient spectrum ranging from 1.8 to 2.2 μm is acquired in less than 3 min, which is roughly the time required for taking one scan at fixed wavelength in a slow scan configuration.

The $\Delta T/T$ signal, which is proportional to the electronic population excited on upper energy levels by the pump pulse [1], is plotted in Fig. 6(a) on a bi-dimensional chart as a function of probe wavelength and pump-probe time delay: horizontal cuts of the chart give insight into the time evolution of the absorption spectrum, while vertical cuts provide the relaxation dynamics for given wavelengths. In particular, Fig. 6(b) reports the transient spectra as acquired at a 0, 300 and 2000 fs delay (dotted horizontal lines in section a)), while Fig. 6(c) reports the temporal evolution of the population at a 2 μm wavelength (dotted vertical line in (a)), for different pump power levels.

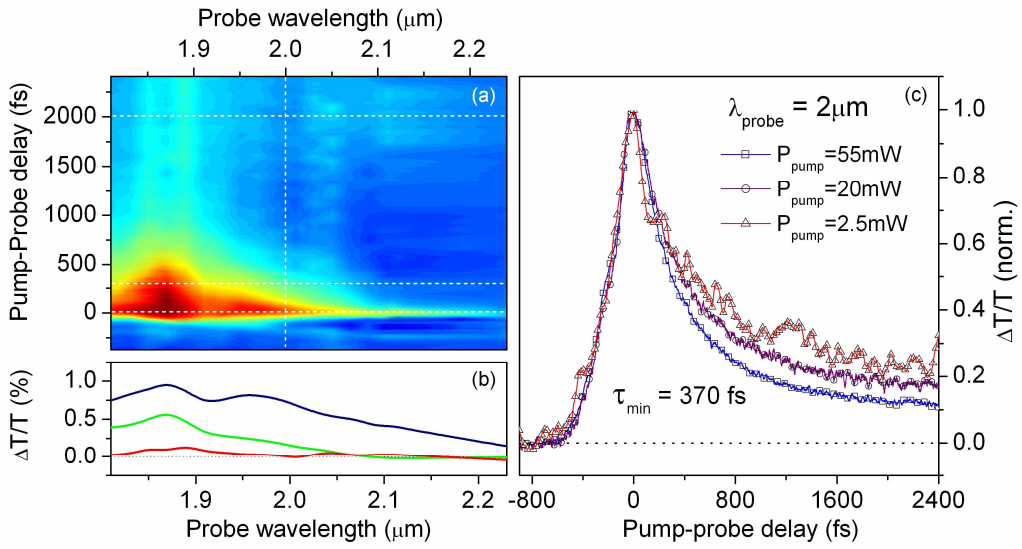

Fig. 6. (a) $\Delta T/T$ signal of the SWCNT plotted on a bidimensional chart as a function of time delay and probe wavelength. (b) Transient spectrum at different delays: zero (blue curve), 300 fs (green curve) and 2000 fs (red curve). (c) Pump probe traces (normalized) for increasing pump power.

The measured signal is positive over the entire range of explored wavelengths and delays, and can be assigned to the photo-bleaching of the nanotubes absorption band centered at ~1.9 μm. The time evolution of the signal corresponds therefore to the population recovery from the excited states to the ground state. The temporal dynamics is composed by a combination of a fast and a slow decay, the latter one being characterized by a time constant larger than the 3 ps time window allowed by the fast-scan configuration. The fast time constant remains below 800 fs in the whole probe wavelength range, in agreement with previous measurements on smaller diameter HiPco and laser ablation SWCNTs deposed [13,

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19, 20]. When moving from shorter to longer probe wavelengths, an appreciable decrease of the fast constant down to 520 fs is observed, together with a less pronounced long-lived tail. It is worth noting that, due to a significant amount of metallic tubes in the investigated SWCNT bundles, the fast component of the transient dynamics can be connected with tunneling of photoexcited carriers from semiconducting to metallic SWCNTs [19]. An interesting feature that is more evident for longer wavelengths (above 2 μm) is the dependence of the fast time constant on the pump power. The temporal dynamics in Fig. 6(c) indicate in fact a decrease of the recovery time from 520 fs to 370 fs upon increasing the average pump power from 2.5 to 55 mW, which could be caused by exciton-exciton annihilation or Auger recombination [16, 23]. This behavior is quite promising in view of exploiting SWCNTs as fast saturable absorbers in high intensity laser optical cavities[25,13,26]. In particular, the observed relaxation times should enable the generation of sub-ps pulses in the mode-locking regime.

5. Conclusions

A new system for ultrafast spectroscopy based on an amplified Er-doped fiber laser is presented and characterized. The system provides a cost effective solution for pump-probe experiments with temporal resolution below 100 fs, spectral tunability from 1 to 2.3 μm and high sensitivity both with fast and slow scan configurations. It has been successfully applied to the pump-probe characterization of large diameter SWCNTs, with a photo-bleaching band centered around 1.9 μm and a relaxation time as low as 370 fs, promising for the realization of fast saturable absorbers in the longest wavelengths near-IR region.

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