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Controlling exciton decay dynamics in semiconducting single-walled carbon nanotubes by surface acoustic waves

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ABSTRACT

We show that the photoluminescence intensity and decay dynamics of semiconducting single-walled carbon nanotube films can be remotely controlled by surface acoustic waves (SAW) launched on the piezoelectric substrate $LiNbO_3$. Time-resolved measurements in the picosecond regime reveal that photoluminescence quenching results from a decrease of the radiative recombination rate by up to 25% for the accessible SAW amplitudes. The SAW-induced piezoelectric field acts as a quasi-static perturbation that polarizes the luminescent exciton state reducing the oscillator strength of the radiative transition following a quadratic field dependence. Surface acoustic waves could be used for the remote and contact-free electrical control of high-speed electronic and optoelectronic nanotube-based devices.

The direct band gap of semiconducting single-walled carbon nanotubes (SWCNTs) is of unique interest for the implementation of optical and electronic devices or sensors on the same material [1–4]. On this scalable, quasi one-dimensional platform, the successful realization of voltage-controlled light emission [5] and detection [6,7] and the demonstration of quantum light emission [8] represented major advances towards this goal. A key requirement to fully exploit the application potential of SWCNT is the ability to control their optical emission and absorption properties by easily accessible external parameters. Here, electric fields applied by an external voltage have shown to be particularly suitable, which in most cases however, require time and cost-intensive elaborate nano-contacting [9,1] of the nanotubes.

In the broad field of established and novel semiconductor-based nanostructures surface acoustic waves (SAW) have proven to be an extremely versatile tool to control and probe the electronic [10–12], optical [13–18] and photonic [19,20] properties of these nanosystems over macroscopic length scales and distances at frequencies ranging from a few megahertz up to several gigahertz. This unique property is based on the almost dissipation-free propagation of these radio frequency (rf) acousto-mechanical waves on the surface of solids over distances of several millimeters at the speed of sound (c_{sound}). Thus, a SAW pulse can interact with all nanosystems within its propagation path providing a unique tool for direct massively parallel addressing and manipulation. Moreover, these SAWs can be generated all-electrically, either directly on piezoelectric substrates [21] or on arbitrary substrates using piezoelectric coupling layers [22] using interdigital transducer electrodes (IDTs) with a lithographically defined periodicity p. By applying an rf voltage to the IDT with a frequency matching the dispersion relation of a SAW $f_{rf} = f_{SAW} = c_{sound}/2p$, a SAW of wavelength $\lambda_{SAW} = 2p$ is launched. Such SAW chips are not limited to commercialized applications such as rf filtering in mobile communication devices [23,24] or SAW driven microfluidics [25], but can be directly hybridized with other types of nanosystems such as nanowires and nanotubes to study their optical [26] and electrical transport [27–29] properties.

In contrast to conventional semiconductors, for which the alternating electric fields induced by the SAW are sufficient to fully dissociate excitons, transport and inject the individual charge carriers [13,15,30,31,26], the strongly bound and short-lived excitons in SWCNT [32] are an ideal system to study the impact of a SAW representing a weak and quasi-static perturbation. Here, we show that the strong electrical fields associated with SAWs can be used to efficiently suppress or enhance the PL emission of a SWCNT film despite of the more than one order of magnitude larger exciton binding energies compared to semiconductor based systems. Furthermore, we apply time-resolved spectroscopy to directly confirm that the observed quenching of the SWCNT emission arises from a reduction of the radiative recombination rate of excitons interacting with the SAW-induced electric fields.

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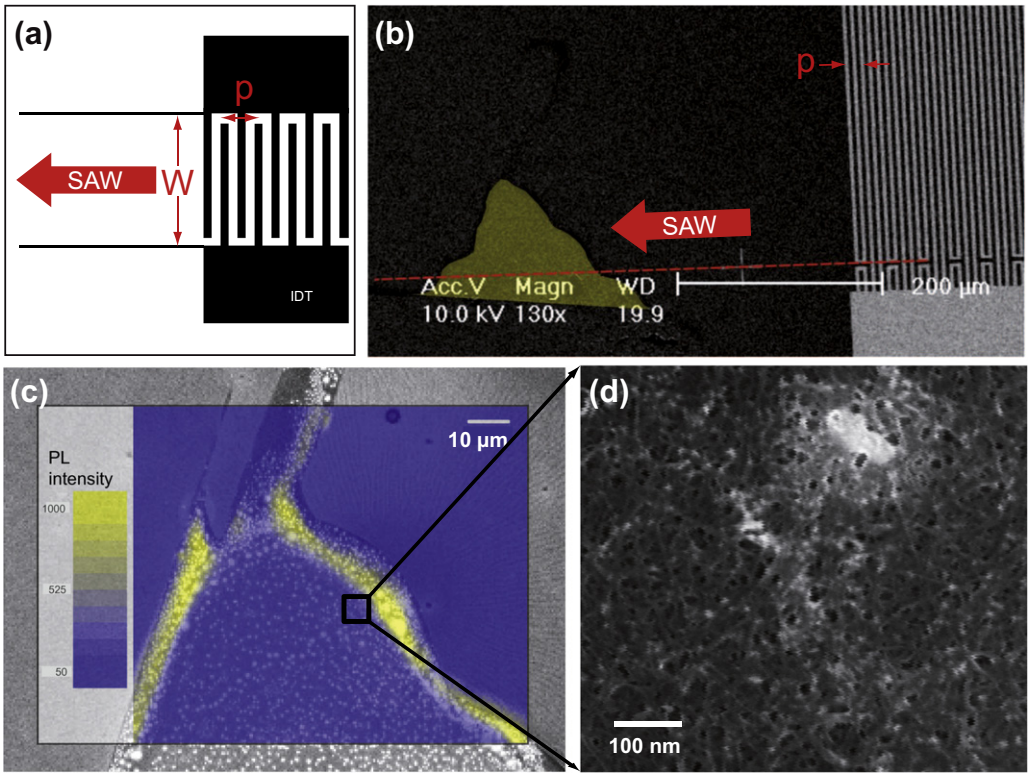

Fig. 1. (a) Schematic of the experimenal configuration used for the remote control of exciton decay in SWCNT. The samples are based on the piezoelectric substrate $LiNbO_3$. Interdigital transducers (IDT) with varying periodicities p were fabricated on the surface by standard optical lithography in order to launch surface acoustic waves. Drop-casting a SWCNT solution resulted in carbon nanotube films after drying. (b) Large area SEM image illustrating the IDT and the propagation direction of the SAW. (c) Magnified view of the area shaded yellow in (b). The corresponding PL intensity image is super-imposed onto the SEM image. The PL intensity is strongest in regions with very high SWCNT coverage. (d) Magnified view of the area marked by the square in (c) featuring a dense SWCNT network that has been used for the following measurements.

For our experiments we fabricated hybrid SWCNT-SAW devices consisting of a strongly piezoelectric lithium niobate ($LiNbO_3$) chip and a thin film of SWCNT (Fig. 1). On the $LiNbO_3$ substrate a set of different IDTs are fabricated which allow for SAW generation. Details on the IDT design and fabrication can be found in the Supporting information of this paper. For the experiments presented in this manuscript we used the IDT marked in the micrograph operating at a frequency of $f_{SAW} = 121$ MHz. An aqueous solution of CoMoCAT-SWCNTs wrapped by single-stranded DNA was dripped onto the chip surface in the propagation path of the SAW. This material contains mainly thin diameter nanotubes dominated by the species (6,4) and (6,5) [33–35]. A scheme illustrating the experimental configuration is shown in Fig. 1(a) together with a series of SEM images of the sample with increasing magnification (Fig. 1(b–d)). The magnified view of the area marked by the black square in Fig. 1(c) shown in (d) reveals a dense but rather uniform coverage of the surface with SWCNTs. The PL intensity measured for this sample is superimposed on the SEM image in Fig. 1(c). Strong PL is observed for high SWCNT coverage. The PL data presented in this paper were recorded in the area shown in Fig. 1(d). PL detection on $LiNbO_3$ substrates is hindered by the high refractive index of the material resulting in dominant radiation into the substrate. Thus, detection of single nanotube PL is not feasible with standard glass microscope objectives.

Nanotube PL was studied using a confocal raster scanning microscope with laser excitation at 565 nm or 800 nm. The PL signal was detected by an avalanche photo diode (APD) after passing spectral filters to select nanotube PL. A narrow bandpass filter transmitting at $\lambda = 980$ nm ± 10 nm was used to select the PL emitted from (6,5)-nanotubes, whereas light from both (6,5)- and (6,4)-nanotubes was detected using a 863 nm long pass filter. PL spectra were recorded by a spectrometer coupled to a CCD camera. Time-traces recorded in the second to microsecond regime allowed for the direct investigation of the influence of the SAW on the PL. High laser intensities were found to lead to an exponential decrease of the PL intensity due to photo-oxidation [36]. The PL time-traces recorded while varying the SAW amplitude were recorded at the lowest possible excitation intensities and corrected for residual PL bleaching by subtracting a single exponential decay contribution. Blinking events, presumably related to oxygen adsorption from air, were occasionally observed on the time-scale of seconds [36]. Repeated PL intensity measurements were carried out to distinguish SAW-induced effects. The decay dynamics of excitons in the picosecond range was observed using time-correlated single photon (TCSPC). Pulsed laser excitation at 800 nm was provided by a Ti:Sa-oscillator with a pulse duration of about 150 fs and a repetition rate of 76 MHz. Exciton lifetimes were determined by fitting the measured PL transients using exponential decay functions convoluted with the independently determined instrument response function [37]. In all experiments SAWs were generated using a conventional rf signal generator with a maximum output power of 200 mW.

In Fig. 2(a) a typical PL spectrum of the sample is shown featuring two emission bands centered at 890 nm and 990 nm identified as (6,4) and (6,5) nanotube emission, respectively. After the rf signal is switched on at $f_{rf} = 121$ MHz (excitation power $P = 200$ mW) the PL intensity is reduced uniformly by about 30% by the generated SAW. To unambiguously prove that this effect indeed arises from the SAW we keep the applied rf power constant and scan the applied frequency through the resonance of the IDT. In the normalized PL intensity $\Delta I = I^{SAW}(f)/I^0$ presented in Fig. 2(b) we observe a pronounced minimum at the design frequency of the IDT