# NONLINEAR OPTICS AND PHOTONIC DEVICES

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## Abstract

This talk is about applications of graphene and carbon nanotubes (CNT) in the field of nonlinear optics and photonics. The first part will be concerned with exploiting the nonlinear optical behaviour of graphene and CNTs for generation of pulses in the femtosecond range called mode locking. The graphene and CNT based mode locker are passive saturable absorbers, producing pulses by only relying on the intensity dependent absorption coefficient. Using these mode lockers, recent results for the pulse length are in the range from 1 to 2.5 ps.

The second part of the talk deals with using plasmonics to enhance the optical near-field which has a possible application in Raman spectroscopy. Here we can differentiate between Surface Enhanced Raman Scattering (SERS) and Tip Enhanced Raman Scattering (TERS) where especially the latter one is well suited for observation of properties of CNTs.

## Femtosecond Pulse Generation in Fiber Lasers

A fiber laser is built up like a normal laser, except the resonator chamber is replaced by a glass fiber. If a part of the fiber gets doped with ions, e.g. $\mathrm{Er}^{3+}$, this part acts like a gain medium where population inversion leads to an amplification of the guided light by stimulated emission. A possible layout of a fiber laser is presented in fig. 1. The components are explained in the caption. A fiber laser has several advantages compared to other laser types like gas laser: By having a fiber, the laser is much more flexible in usage and design. The higher surface to volume ratio of the fiber allows a more efficient heat dissipation. And since the doped fiber can be made longer than a conventional laser resonator, a higher gain and thus more output power is possible.

To obtain femtosecond pulses, a mode locker is needed. The original idea is having a device being able to transform modes, waves at certain frequencies, propagating out of phase into modes with a fixed phase relation. If the phase difference between all modes is zero, the sum of the amplitudes of each mode will result in a large peak amplitude at a certain time. For a small time before and after, the amplitudes will interfere destructively. Depending on the number of modes this results in a large and narrow peak. This procedure is known as Kerr effect mode locking.

Another type of mode locking in fiber lasers is realised by using saturable absorption. A saturable absorber (SA) is a material with a nonlinear absorption index. The material absorbs low light intensities very strongly whereas high intensities will not be absorbed. Above a certain threshold intensity the material gets saturated and thus transparent for the incoming light. In fig. 2, the process of saturable absorption of a single pulse is presented schematically. When the pulse arrives at the SA, the light intensity rises. The first part with a very low intensity gets absorbed almost completely. The rise of the

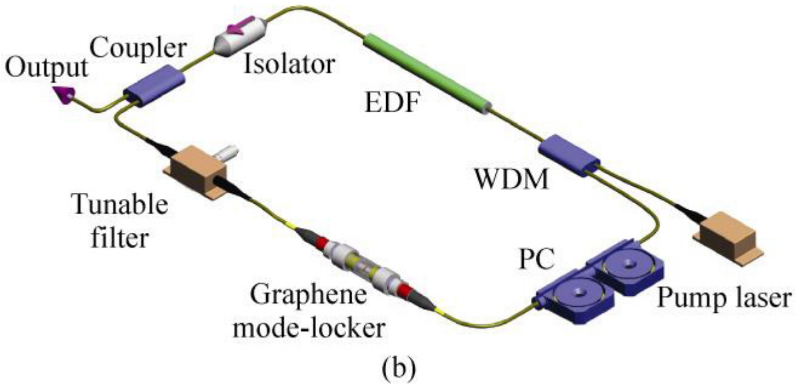

Figure 1: A possible layout of a fiber laser [1]. The pump laser is typically a diode laser. This pregenerated laser light gets coupled into the fiber by a wavelength division multiplexer (WDM). The laser gain medium in this case is the erbium doped fiber (EDM). The isolator prevents propagation of backscattered light, which would destroy the fiber. With the tuneable filter, it is possible to vary the wavelength of the laser light. Femtosecond pulses are generated in the mode locker. The polarisation controller (PC) matches the polarisation of the fiber laser light to the pulse laser light to obtain a coherent superposition of both.

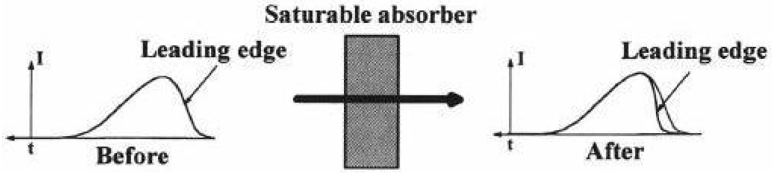

Figure 2: Schematical representation of the operation of a saturable absorber [2]. The leading edge of the incoming pulse is diminished while the peak is not, as the SA is already saturated. For slow SA, the trailing edge won't be absorbed since the relaxation time is longer than the peak duration.

intensity leads to a fast saturation of the SA involving absorption of the leading edge. This results in a very steep leading edge of the pulse. The peak won't get absorbed since the SA needs time to relax for further absorption. If the relaxation process needs longer time than the length of the pulse, the trailing edge will stay the same, whereas for fast SA this edge will also be absorbed partially which results in almost symmetric peaks. For a proper pulsed operation in a ring laser, the gain should be settled in between the maximum and minimum SA intensity loss to prevent small disturbances from being amplified and to have amplification at all, respectively. Intensity fluctuations of the pumped continuous wave laser light will be either amplified to single pulses or suppressed after multiple round trips in the fiber.

Compared to expensive semiconductor SA, graphene and CNT SA are a competitive alternative, as will be explained shortly. The saturation process in CNTs happens due to their semiconducting behaviour by having bandgaps. After production, all kinds of CNTs with different chirality and diameter will be present, thus different bandgaps are obtained. If light of an arbitrary energy shines onto the SA containing CNTs, it will be in resonance with one set of tubes so electrons are excited from the valence into the conduction band. They will remain there during their lifetime. All possible states will be filled according to the density of states above the bandgap and thus they will block excitation of further electrons, called Pauli Blocking. The SA gets saturated and light will go through the material. The lifetime of the electrons in the excited states defines the relaxation time of the SA which predominantly determines the length of the pulses. The variety of bandgaps

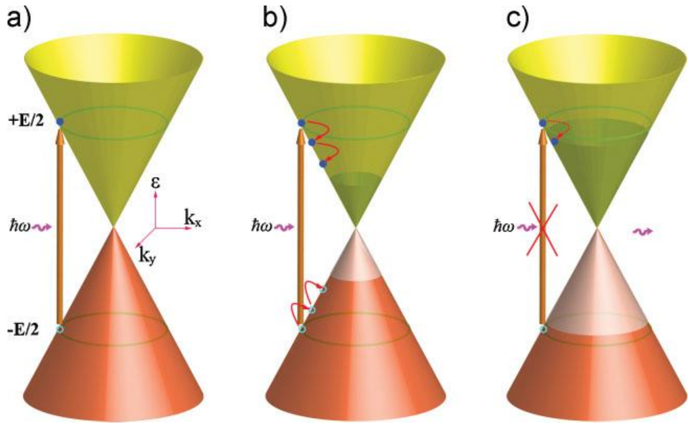

Figure 3: Excitation and saturation process at the K-point of the graphene bandstructure [3]. a) Incoming light creates excited electrons in the conduction band. b) Electrons relax within the conduction band due to pair-carrier and electron-phonon collisions and thus fill up all available states from the bottom of this band. c) All possible states for excitations are filled so further incoming light cannot cause transitions anymore (Pauli blocking), the SA is saturated.

ensures that there is always a resonance frequency for every incoming light so the CNT based SA is applicable for a wide range of wavelengths, for example the telecommunication band at 1.5 $\mu$m

In the case of graphene, instead of having different bandgaps, the dirac cone with zero-bandgap at the K-point exists. The advantage here is that every kind of incoming light creates an excitation. The saturation process is sketched in fig. 3. The incoming light excites electrons over the zero-bandgap. These electrons will relax nonradiatively due to carrier-carrier and electron-phonon scattering processes on timescales of 100 fs, filling up all states in the conduction band from the dirac point onwards. Since all states are filled, further incidence of light cannot create more excitations. The light goes through the material without getting absorbed anymore due to Pauli blocking. The electrons in the vicinity of the dirac point can perform interband relaxation into the valence band by phonon emission, which defines the relaxation time of the saturable absorber. Since there are only a few states near the dirac point, this process takes much longer, on the timescale of 1 ps.

The group of Z. Sun et al. ([1],[4]) constructed a fiber laser with a graphene as well as a CNT based mode locker. They were able to produce pulses of a width of 1 ps with the graphene SA and around 2.5 ps with the CNT SA. These pulses were also tuneable in a wavelength range of 35 nm around 1.5 $\mu$m, where the limitation of the wavelength tuning was only set by the tuneable filter, but not by the SA.

The advantages of graphene and CNT mode lockers compared to conventional ones are their low production costs, their broadband tuneability, a better efficiency since the lower saturation intensity allows for lower pump power at the same laser gain, and fast relaxation times makes generation of ultrashort pulses possible. CNTs compared to graphene SA have the disadvantage of producing additional losses due to tubes not being in resonance having nonsaturable absorption.

## Enhanced Raman Scattering on Graphene and CNTs

Characterization and selection of CNTs is very important for their possible future applications. Tip enhanced Raman scattering is a new, efficient method of characterizing single

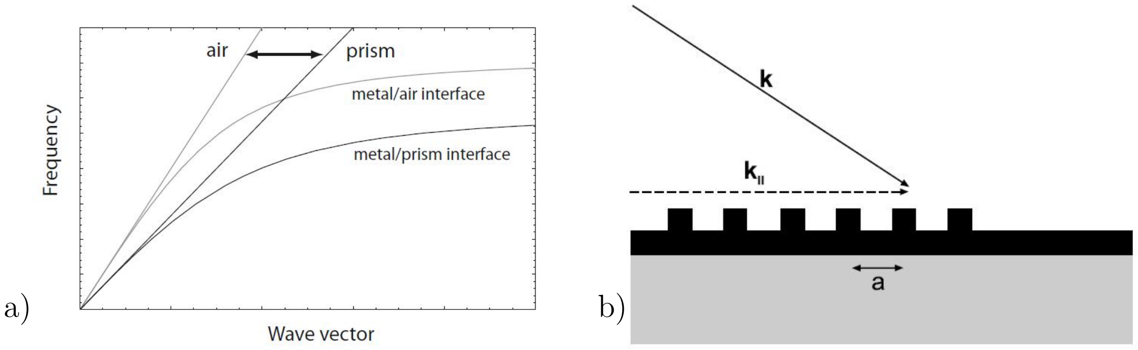

Figure 4: a) Dispersion relation of light and SPP in different media. The dispersion relations for the same propagation medium only cross at $k = 0$ forbids excitation of SPPs. At an interface of metal, air and prism coupling is allowed. b) Excitation of SPPs are also possible using gratings, where a phase matching condition imposes restrictions upon the wave vector of the incoming light. [5]

CNTs by enhancing the measured Raman signal through plasmons.

Plasmonics in general deals with oscillations of the electron cloud in metals excited either by incident particles or electromagnetic waves. One can differentiate between different types of plasmons: the volume plasmon, the surface plasmon polariton (SPP) and the localized surface plasmon polariton as a special case of the SPP.

The volume plasmon is a longitudinal oscillation of the electron cloud in a bulk metal. Its longitudinal character prevents it from being excited by light, which is solely transversal in free space. So these plasmons are not applicable to spectroscopy, like Raman scattering.

The second kind of plasmons, SPPs, are propagating waves of the electrons confined to the surface between a dielectric and metallic material. The generated electric field extends about 20 nm inside the metal and several hundreds of nm outside. SPPs cannot be excited by the incidence of normal light. The first requirement, as mentioned before, is a metal-dielectric interface with the incoming light frequency being lower than the metal plasma frequency $\omega_P$, so that the dielectric constant changes sign. Secondly, the light has to be polarized perpendicular to the surface to have the electric wave oscillation across the interface. Thirdly, energy and momentum conservation demands a crossing of the dispersion relations of the SPP and light. Since at a normal metal-air interface the only crossing point is at $k = 0$, one needs different methods like an interface between a prism, air and metal. There, a crossing at finite $k$ is possible (compare fig. 4 a) ). Excitation of SPPs can also be realized by etching a grating onto the surface of the metal, as it is shown in fig. 4 b). Here, a certain phase matching condition has to be met. Rough surfaces can also be seen as gratings so excitations are allowed there as well without a coupling medium.

If the metal is decreased in size to nanometer scale, excited SPPs cannot propagate freely but are rather reflected from the boundary of the nanoparticle (NP) and thus create standing waves inside. These excitations are called localized SPPs. The small size does not impose any conditions on the incoming light anymore, so localized SPPs can be excited by any kind of light. In a classical picture, the electron cloud in the NP oscillates with the frequency of the driving electromagnetic field. Due to the confinement in the small volume, polarisation charges are created at the edges of the NP, acting like a restoring force. In the simple view of a driven harmonic oscillator, the amplitude of the electric field caused by the electron cloud will be greatly amplified at a certain resonance frequency. Light incidence at this frequency leads to an enhancement of the absorption, the scattering

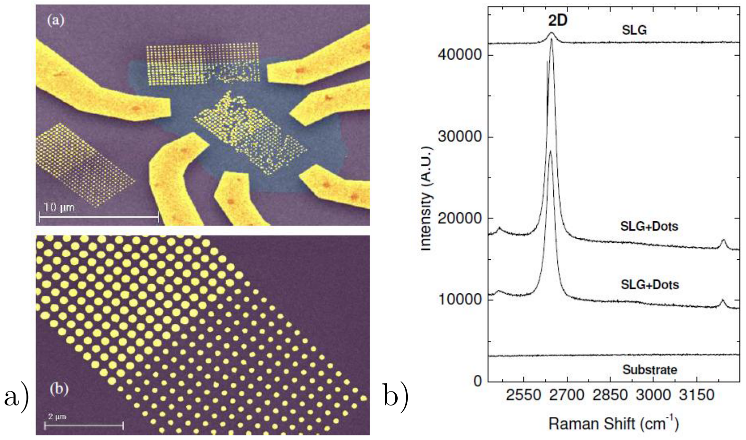

Figure 5: a) Arrangement of NPs (yellow) on SiO (purple) and a SLG sample (blue). b) Raman signal in the vicinity of the 2D peak. A huge enhancement of the signal with NPs compared to normal graphene can be seen. [6]

cross section and the electric near field outside of the particle. Light amplification around NPs also happens due to the lightning rod effect. If the shape of the NP is not spherical anymore, the field lines will concentrate at sharp edges leading to stronger electric fields.

Arranging an ensemble of NPs onto a surface results in an interaction of the near field of the particles so incoming light will be amplified further. An application of this effect is Raman scattering where the signal collected from the sample is usually weak, which is called surface enhanced Raman scattering (SERS). A placement of NPs onto the sample leads to a higher intensity in the near field of the particles and thus more phonons can be excited. This signal, which is already amplified, will be further enhanced through exciting additional SPPs in the NPs. The total enhancement is $I_{SERS} \propto I^4_{Raman}$ for the intensity and $10^{14}$ for the Raman cross section. In fig. 5 a single layer graphene (SLG) sample is measured with SERS. In b) one can clearly observe a great increase of the measured intensity compared to a Raman measurement without NPs.
Another approach to using localized SPPs for Raman spectroscopy is called tip enhanced Raman cattering (TERS). An AFM-Tip is brought close to the sample and a laser is focused on the tip apex, coming from a perpendicular direction. The laser will excite

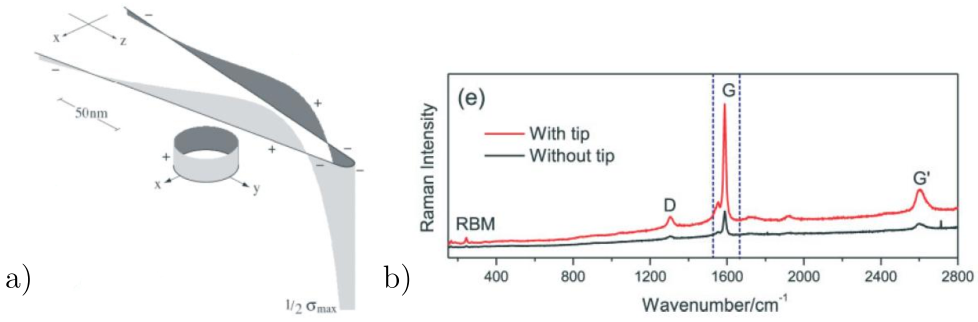

Figure 6: a) Simulation of the charge density depending on the position at the surface of the tip. A large electron concentration at the tip apex is visible. The graph is rotationally symmetric. b) Measured Raman spectrum with (red) and without (black) TERS. The whole spectrum is enhanced due to localized SPPs in the tip. [7]

localized SPPs and thus create a large electron concentration at the apex (compare fig. 6). The electrical near field around the tip apex is, as in SERS, used to excite phonons in the sample. The large field strength leads to an amplified Raman signal. Since this effect only takes place at a spot determined by the evanescent field around the tip apex, which is roughly 100 nm, this method provides a high spatial resolution. The tip rasters the sample and gives a TERS signal at each spot. As a consequence, an overall averaging process of the signal of the whole sample does not appear, as is the case with normal Raman spectroscopy. The latter even allows measurement of Raman spectra from single molecules. Indeed, this method is suited for characterization of CNTs. All crucial properties of nanotubes can be obtained with Raman spectroscopy. In fig. 6 b) the comparison of a normal Raman spectrum with a TERS spectrum of CNTs is shown. An enhancement of all peaks can be seen, even the very weak signal from the radial breathing mode.

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