Plasmon-enhanced Raman scattering by graphene and carbon nanotubes



Im Fachbereich Physik der Freien Universität Berlin eingereichte

Dissertation

von

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Berlin, im November 2014

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Tag der Einreichung: 11. November 2014 Tag der Aussprache: 8. Mai 2015

Abstract

The field of plasmonics studies the interaction between electromagnetic fields and free electrons in a metall, which enhance the optical near-field in the vicinity of the metal. For metallic nanostructures, the enhanced near-field is confined to a small volume called a plasmonic hotspot. Light scattering and absorption in a hotspot increases by several orders of magnitude. In this thesis I study the inelastic light scattering of graphene and carbon nanotubes subject to an enhanced near-field by Raman spectroscopy. First, I introduce and verify the concept of strained graphene as a local probe for plasmon-enhanced Raman scattering. Second, I probe the coupling of carbon nanotubes to the enhanced optical near-field in a plasmonic hotspot. To achieve the required interface, I suggest the directed dielectrophoretic deposition of nanotubes onto metallic nanostructures as a new method to couple nanotubes to plasmonic hotspots.

A graphene-covered nanodimer was probed by Raman spectroscopy. The high intensity electromagnetic near-field at the plasmonic hotspot in the dimer gap enhanced the Raman signal by a factor of thousand. The enhancement occurred for strained graphene. Strain shifts the graphene phonon frequency; vibrations at the plasmonic hotspot differ in energy from vibrations originating from other areas and acts as a local probe for enhancement. We verified the Raman enhancement by the combination of spatially resolved, polarization and excitation energy dependent measurements. As these parameters do not affect the Raman signal of graphene, we proved that the experiment probed the Raman process caused by the enhanced optical near-field.

For carbon nanotubes in the gap of a plasmonic dimer we observed Raman signal enhancements of the order $10^3 - 10^4$. Following the approach developed using graphene, we addressed the extrinsic plasmonic and the intrinsic nanotube optical response independently by varying excitation energy and polarization. We showed that (i) the Raman enhancement scales with the projection of light polarization on the tube axis and that (ii) carbon nanotube Raman features arise from fully symmetric vibrations, even in the presence of a high intensity near-field. Raman modes that require light polarizations perpendicular to the nanotube axis were impossible to observe. This settled a long standing debate in the literature on the symmetry of the experimentally observed phonon modes. The placement of the carbon nanotubes in the gap of plasmonic dimers was achieved by directed dielectrophoretic assembly, which we suggest as a new method to achieve nanotube-nanoplasmonic interfaces.

The methodologies and approaches that I developed in this thesis to couple graphene and carbon nanotubes with plasmonic structures provide a powerful and flexible tool to study the fundamentals of plasmon-enhanced Raman scattering.

List of publications

- Plasmon-enhanced Raman scattering by suspended carbon nanotubes.
 S. Heeg, N. Clark, A. Oikonomou, A. Vijayaraghavan, and S. Reich. Physica Status Solidi - Rapid Research Letters 8(9), 785-789 (2014).
- Plasmon-Enhanced Raman Scattering by Carbon Nanotubes Optically Coupled with Near-Field Cavities.
 S. Heeg, A. Oikonomou, R. Fernandez-Garcia, C. Lehmann, S.A. Maier, A. Vijayaraghavan, and S. Reich. Nano Letters 14(4), 1762-1768 (2014).
- Strained graphene as a local probe for plasmon-enhanced Raman scattering by gold nanostructures.
 S. Heeg, A. Oikonomou, R. Fernandez-Garcia, S.A. Maier, A. Vijayaraghavan, and S. Reich.
 Physica Status Solidi - Rapid Research Letters 7(12), 1067-1070 (2013).
- 4. Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene.
 S. Heeg, R. Fernandez-Garcia, A. Oikonomou, F. Schedin, R. Narula, S.A. Maier, A. Vijayaraghavan, and S. Reich. Nano Letters 13(1), 301-308 (2013).
- Raman spectra of metallic carbon nanotubes in solution and on substrates.
 B. Hatting, S. Heeg, and S. Reich.
 Physica Status Solidi (b) 250(12), 2639-2642 (2013).
- Selective interaction between nanotubes and perylene-based surfactant.
 F. Ernst, S. Heeg, T. Heek, A. Setaro, R. Haag, and S. Reich.
 Physica Status Solidi Rapid Research Letters 7(8), 546-549 (2013).

- Fermi energy shift in deposited metallic nanotubes: A Raman scattering study.
 B. Hatting, S. Heeg, K. Ataka, J. Heberle, F. Hennrich, M.M. Kappes, R. Krupke, and S. Reich.
 Physical Review B 87(16), 165442 (2013).
- Analysing the photoluminescence intensities of single-walled carbon nanotubes.
 S. Heeg, J.T. Abrahamson, M.S. Strano, and S. Reich.
 Physica Status Solidi (b) 249(12), 2473-2478 (2012).
- Selective Bundling of Zigzag Single-Walled Carbon Nanotubes.
 C. Blum, N. Sturzl, F. Hennrich, S. Lebedkin, S. Heeg, H. Dumlich, S. Reich, and M.M. Kappes.
 ACS Nano 5(4), 2847-2854 (2011).
- Assembly of carbon nanotubes and alkylated fullerenes: nanocarbon hybrid towards photovoltaic applications.
 Y. Shen, J.S. Reparaz, M.R. Wagner, A. Hoffmann, C. Thomsen, J.-O. Lee, S. Heeg, B. Hatting, S. Reich, A. Saeki, S. Seki, K. Yoshida, S. Babu, H. Möhwald, and T. Nakanishi.
 Chemical Science 2(11), 2243-2250 (2011).
- Broadened second excitonic transition of single-walled carbon nanotubes in photoluminescence excitation spectroscopy.
 S. Heeg, B. Hatting, M. Dantz, and S. Reich. Physica Status Solidi (b) 247(11-12), 2887-2890 (2010).
- Quantitative composition of a single-walled carbon nanotube sample: Raman scattering versus photoluminescence.
 S. Heeg, E. Malić, C. Casiraghi, and S. Reich.
 Physica Status Solidi (b) 246(11-12), 2740-2743 (2009).

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1 Introduction

The interaction between light and matter on the nanoscale is of key interest in science and technology. It allows exploring the fundamental physical principles and is necessary to implement nanoscale phenomena into technology. One aspect of particular interest is nanoscale optical coupling. It describes the excitation transfer by light from one object, the *source*, to another object, the *probe*. Nanoscale implies that (i) the dimensions of both objects are small enough to influence their physical properties and that (ii) the interaction occurs on length scales of the order of nanometers. According to this definition, many different combinations of physical systems and observation techniques, the *eye*, realize nanoscale optical coupling. In this thesis I describe how plasmonic nanostructures transfer optical excitations to graphene and carbon nanotubes as studied by Raman scattering. These low-dimensional carbon-based solid state systems are advantageous compared to molecules, which are traditionally used to realize nanoscale optical coupling.

Plasmonic nanostructures are tiny metallic particles that absorb light by a collective electron excitation called the localized surface plasmon resonance (LSPR) [1]. This excitation is then transferred in the immediate vicinity of the particle and creates a small volume where the electromagnetic near-field is enhanced. If two metallic particles are placed in close proximity, the light excites a collective surface plasmon resonance of dipolar nature. The gap between the two particles harbors even more intense light fields.



Figure 1.1 Thesis in a nutshell: A metallic nanostructure (*source*) transfers its optical excitation to graphene or carbon nanotubes (*probes*) by light. The interaction is monitored by Raman spectroscopy (*eye*).

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It is referred to as a plasmonic hotspot and represents the *source*. Light absorption and scattering of a *probe*, a molecule for instance, placed in a hotspot increases by orders of magnitude due to strong optical coupling.

Raman scattering, the inelastic scattering of light by vibrations, is a prime spectroscopic technique to study processes at plasmonic hotspots. It is non-destructive, yields plenty of structural information, and characterizes molecules and solid state systems. The combined effect of enhancement of Raman scattering in plasmonic hotspots due to their high intensity near-field is therefore a very powerful tool. The challenge lies in constructing and controlling an interface so that their interaction at the plasmonic hotspot can be reliably measured.

The enhancement of molecular Raman signatures was first observed on roughened metallic surfaces [2, 3], subsequently coined surface enhanced Raman scattering (SERS). The enhancement originated mainly from small gaps or pockets forming plasmonic hotspots [4, 5]. Optical coupling occurred for molecules within those pockets. The signal was overlaid by the pristine Raman signals of molecules on the surface. Progress was made by replacing the roughened surface with single nanoparticles or nanoparticle clusters with a spacing of several μ m, much larger than the spatial resolution of the optical setup of 500 nm or higher [6]. This introduced the ability to tune the localized surface plasmon resonance by the size of the nanoparticles and allowed one to monitor single plasmonic hotspots in randomly formed nanoparticle agglomerates, eventually enabling single-molecule detection [7, 8].

Progress in nanofabrication techniques such as optical lithography and particularly electron beam lithography allows to precisely tailor the size, shape, and arrangement of nanostructures. These attributes in return define the spectral position of the LSPR and the location of the plasmonic hotspot. To take into account the increased level of control provided by lithographically fabricated structures, one typically uses the term plasmon-enhanced Raman scattering (PERS). With the high degree of control afforded by modern lithographic processing, one can study the effect of the arrangement of *source* and *probe*. For a pair of closely spaced gold nanodiscs, for instance, the near-field is localized in the center of the gap between them. Even nanometers away from the center of the optical coupling, drops by several orders of magnitude [9]. For dimer structures in general, the plasmonic excitation is primarily of dipolar nature and the light in the gap is polarized along the dimer axis. The relative orientation of a molecule and its dipole to the light polarization affects the optical coupling to the plasmonic structure and must be accounted for. Despite recent progress such as the immobilization of small structures at a

hotspot [10], the exact orientation and position of a single molecular *probe* inside a single plasmonic hotspot remained impossible to control experimentally [9, 11].

In addition to the enhancement by optical near-fields commonly referred to as *electromagnetic enhancement*, there is an additional effect called *chemical enhancement* for molecules chemisorbed on plasmonic structures [12]. The metal modifies the properties of a molecule such that its optical resonance and Raman polarizability may change and can be mistaken as resulting from optical coupling. Furthermore, the role of the intrinsic molecular resonance and its relation to the external plasmonic resonance is not completely understood. There is evidence, for instance, that plasmonic enhancement of Raman scattering for single molecules occurs for an excitation at the intrinsic molecular - and not the plasmonic - resonance only [13].

Graphene, the two-dimensional crystal formed by hexagons of carbon atoms (Sec. 2.1), combines several properties that make it an almost ideal probe for plasmon-enhanced Raman scattering [14]. Graphene absorbs 2.3% of the light for wavelengths in the visible and near-infrared part of the electromagnetic spectrum [15]. The Raman cross section of graphene is intrinsically constant in this frequency domain, which coincides with the typical spectral window of surface plasmon resonances of gold and silver. Here graphene is commonly referred to as a non-resonant Raman scatterer: Changes in the Raman intensity directly probe the coupling of graphene to the plasmonic nanostructures. The interdependence between the resonances of *source* and *probe* is lifted. From a conceptional point of view, graphene possesses an additional advantage. Being a two-dimensional crystal, graphene is treated within the solid state formalism (of inelastic light scattering). It provides a vast set of physical models - e.g. a continuous electronic band structure and dispersive phonons - for the description of plasmon-enhanced Raman scattering [16, 17], which are not available for molecules.

In the following I will discuss further advantages that are associated with the use of graphene in PERS. The interface between graphene and plasmonic nanostructures is realized by placing one top of the other. This has been realized with plasmonic structures both either beneath and on top of graphene [17, 18]. The necessary fabrication and transfer techniques are well established and ensure high-quality, defect-free graphene sheets in large sizes (hundreds of μm). The two-dimensional nature of graphene guarantees the interface with the enhanced near-field for both stacking orders. The membrane is subject to coupling with both the very center of the hotspot as well as nearby areas of lower intensity. Graphene serves as a spatial integrator or detector of the near-field with the Raman signal as a read-out. The issue of orientation is also solved as the Raman signal intensity of graphene is independent of the polarization, as long as the latter is in plane

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with the graphene sheet [19]. Graphene is chemically inert, so the contact with plasmonic structure and/or the underlying substrate does not modify its electronic structure and the non-resonant character of its Raman response persists. Graphene's extended geometry, however, also comes with a drawback: Plasmon-enhanced Raman scattering at the plasmonic hotspot is always accompanied by conventional Raman scattering from the vicinity of the structure. These two contributions to the overall scattering intensity differ only in signal intensity, which may mask subtle aspects of the interaction between graphene and the plasmonic structure.

I suggested to use locally strained graphene as a new nanoscale probe for studying optical coupling by plasmon-enhanced Raman scattering of graphene [20, 21]. Graphene was placed on top of spatially isolated plasmonic structures fabricated on a flat surface. The strong adhesion of graphene to the surface of the surrounding substrate induced tensile strains in the graphene segments on and around the nanostructure. Strain shifts the graphene phonon frequency; as a result vibrations at the hotspot differ in energy from vibrations originating from other areas. In our experiments we achieved tensile strains of around 1%. The corresponding shifts of $\sim 25 \,\mathrm{cm}^{-1}$ for the G-mode and $\sim 95 \,\mathrm{cm}^{-1}$ for the 2D-mode of graphene can clearly be identified in a spectrum. For graphene on a nanodisc dimer, we observed a thousandfold enhancement of the Raman signal. Spatially resolved Raman measurements showed that the enhanced signals originated exclusively from the dimer gap, which acted as a point-like source of enhancement. Rotating the polarization of the excitation resulted in a 20-fold drop in the enhancement and in a spatial broadening of the enhanced signals. This reflected the polarization induced transition from the coupled to the uncoupled regime of the plasmonic dimer; both nanodiscs acted as two independent and spatially separated sources of much weaker enhancement as compared to the coupled case. No enhancement occurred for an excitation energy off the plasmonic resonances for both polarizations, confirming the nature of the enhancement. We extended our approach to structures of different shape and composition; all of them showed the same behavior. Enhanced Raman signals originating from graphene-covered hotspots are always identified by their frequency. This observation confirmed the universal validity of the approach I developed in this thesis. Strained graphene energetically distinguishes Raman signatures from plasmonic hotspots which cannot be spatially resolved due to the diffraction limit. The plasmonic structure that generates the hotspot simultaneously generates its own probe, while the Raman scattering cross section remains unchanged. Our probe is an unprecedented and new way to study the interaction between graphene and the plasmonic near-field, especially the fundamentals of plasmon-enhanced Raman scattering.

Single walled carbon nanotubes are the one-dimensional siblings of graphene. They

can be thought of as rolled up sheets of graphene with diameters from a few nanometers down to several Angstrom, and lengths up to centimeters [22, 23]. They are considered the prime example of a one-dimensional solid state model system. Quantum confinement along the circumference of the nanotube leads to strongly structured, resonant optical spectra that span the electromagnetic spectrum from the infrared to the ultraviolet. The shape anisotropy of nanotubes directly translates into anisotropic optical polarizability. The tubes absorb and emit light polarized parallel to their axis, while both processes are suppressed in the perpendicular case. Similar to molecules, nanotubes can be regarded as dipolar near-field *probes*. Due to their one-dimensional nature, however, the orientation of a carbon nanotube with respect to a plasmonic hotspot can be readily obtained experimentally. A nanotube placed in a hotspot such as the gap a plasmonic dimer therefore allows one to study true nanoscale optical coupling by investigating the interplay between the resonances and relative dipole orientations. The tremendous challenge is constructing the interface: A nanoscale object like a tube has to be placed inside a gap only a few tens of nanometers in width.

I proposed and implemented an assembly and characterization scheme to realize optical coupling between carbon nanotubes and plasmonic hotspots [24, 25]. Nanotubes were deposited by dielectrophoresis [26, 27] on top of prefabricated plasmonic antennas on a single device level. The strongest optical coupling was observed for nanotubes placed in the gap of a dimer, where the near-field in the gap enhanced the Raman signatures by a factor 10^3 . I was able to show that carbon nanotubes perpetuate their highly anisotropic polarization dependence even in the presence of this high intensity near-field. The interaction between the near-field and the CNT depends on the relative orientation of light polarization and tube axis. Carbon nanotubes at different orientations relative to the near-field polarization exhibit varying degrees of optical coupling as seen by PERS. The nanoplasmonic-nanotube interface developed in this thesis allows to individually address the resonant optical response of dimer and carbon nanotube and their interplay by the choice of excitation energy and polarization. Furthermore, all the building blocks are tunable. The resonance of the plasmonic nanostructure can be tuned by its shape and size. Dielectrophoresis, on the other hand, allows one to deposit carbon nanotube material with preselected optical transition energies [28, 29].

Coupling nanotubes to plasmonic structures will provide insight into the physics of highly correlated electron systems. The optical transitions of CNTs are dominated by excitons with strong binding energies ($\sim 1 \text{ eV}$) [30, 31]. Depending on the microscopic structure, nanotubes may be either of metallic or semiconducting type. In particular the latter were successfully implemented as nanoscale photodetectors and photovoltaic

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devices [32, 33]. The assembly scheme developed in this thesis holds great promise to boost the performance of these devices by integrating them with plasmonic structures.

Such strategies are also sought after for graphene, which is regarded as a prime material for photodetectors. Particularly beneficial are its fast response time and broad frequency range operation [34–36]. The responsivity of graphene based photodetectors, however, is limited by the absorption of graphene. The absorption (2.3%) is very strong for a monolayer structure but too low for photo detection. A promising strategy to increase the absorption in graphene is interfacing it with plasmonic structures [34, 37]. Processes relevant for photocurrent generation, e.g. the controversially discussed doping of graphene by hot electrons [18, 38, 39] from the metal, may be probed by strained graphene.

The body of this thesis begins with an introduction to the structural and optical properties of graphene (Sec. 2.1), carbon nanotubes (Sec. 2.2), and plasmonic nanostructures (Sec. 2.2). I will then briefly introduce the basics of Raman scattering (Sec. 3.1), focussing on the excitation energy dependence of Raman scattering in solid state systems. The phonons and Raman response of graphene is presented in Sec. 3.2. Similar to their structural and optical properties, the Raman scattering response of carbon nanotubes, presented in Sec. 3.3, is closely related to graphene. The chapter ends with a brief discussion of plasmon-enhanced Raman scattering. My contribution to the publications forming this thesis is provided in Sec. 4, followed by Sec. 5 that connects the publications. Concluding remarks and an outlook of ongoing and future projects round up this thesis in Sec. 6.

2 Nanostructures

2.1. Graphene

Since its discovery by *Geim and Novoselov* [40], graphene has attracted enormous interest both for its fundamental physics and its potential for applications [41–43]. It is a model system for two-dimensional materials and its ballistic transport [44] at room temperature makes graphene a prime material for transistors and interconnects. This property, in combination with its constant and frequency independent optical absorption, motivates the use of graphene in optoelectronic applications such as broadband, ultra fast photodetectors [45].

Graphene is a flat sheet of carbon. The atoms are arranged in a hexagonal structure as shown in Fig. 2.1(a). Each carbon atom forms a covalent sp^2 bond with its three nearest neighbors. The orbital of the fourth valence electron is oriented perpendicular to the graphene plane and forms bands of delocalized electrons. These (π -)bands are responsible for the electronic and optical properties of graphene.

The lattice vectors a_1 and a_2 form the unit cell of graphene shown in Fig. 2.1(b). The



Figure 2.1. (a) Transmission electron microscope image of graphene's hexagonal structure. (b) Crystallographic structure of graphene with the lattice vectors a_1 and a_2 , which span the unit cell. Atoms belonging to different sublattices are marked with different colors. (c) Brillouin zone of graphene with the high-symmetry points Γ , K, M and K' and high symmetry lines (blue). The scale bar in (a) is 0.5 Å and the picture is taken from [46].

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unit cell contains two carbon atoms which are separated by $a_{cc} = 1.422$ Å. Typically, the crystallographic structure of graphene is described by assigning the atoms in the unit cell to two superimposed sublattices [47] indicated by colors in Fig. 2.1(b). The Brillouin zone of graphene is of hexagonal shape as shown in Fig. 2.1(c), with the Γ point at the zone center. The high symmetry points K and K' are located at the corners of the Brillouin zone, and the M-point in-between them.

2.1.1. Bandstructure and optical properties

A simple nearest neighbor tight-binding approximation [47, 48] adequately describes the band structures of graphene and the results in the dispersion relation

$$E^{\pm}(k_x, k_y) = \pm \gamma_0 \sqrt{1 + 4\cos\frac{\sqrt{3k_x a}}{2}\cos\frac{k_y a}{2} + 4\cos^2\frac{k_y a}{2}}, \qquad (2.1)$$

for the $(\pi^*$ -)conduction band and $(\pi$ -)valence band of graphene, where γ_0 denotes the nearest neighbor overlap integral and $a = |\mathbf{a_1}| = |\mathbf{a_2}| = \sqrt{3}a_{cc} = 0.246$ nm. The band structure of graphene calculated from Eqn. (2.1) is shown in Fig. 2.2(a). Valence and conduction band meet at three K and three K' points which are connected by red lines in Fig. 2.2(a). K and K' are inequivalent as they cannot be transformed into each other by a reciprocal lattice vector. These crossing points are called Dirac or charge neutrality points; for pristine and undoped graphene, the valence band is completely filled with electrons and the conduction band is completely empty. The Fermi energy is located exactly at the Dirac points. As a consequence, graphene is commonly described as a semimetal with a continuous but vanishing electronic density of states at the charge neutrality points.

The band structure described above gives rise to most of the peculiar properties of graphene. For energies close the Fermi energy, the electronic dispersion relation is approximately linear as indicated in Fig. 2.2(b). The electrons behave like massless Fermions and follow the Dirac-equation. Close to K(K'), they are composed of contributions from both sublattices, which is typically implemented by two component wave functions in the form of spinors and referred to as pseudo spin or chirality. This parameter interconnects electrons and holes of opposite momentum as they belong to the same sublattice [41].

Despite being only one atom thick, graphene absorbs 2.3% of light. The absorption is constant over a large range of photon energies from the near infrared to the visible as indicated in Fig. 2.2(c). This behavior originates from the two-dimensional nature and the gapless electronic spectrum of graphene and is independent of any material



Figure 2.2. (a) Bandstructure of graphene calculated from Eqn. (2.1). The high symmetry points Γ , K, K' and M are indicated as dots. The Dirac points are connected by red lines, which correspond to the Fermi energy of undoped graphene. In the vicinity of the K(K') points as in (b), the electron dispersion is approximately linear. The red arrows in (b) indicated constant light absorption for a wide range of frequencies. (c) Experimental white light transmission of a suspended graphene layer measured by *Nair et al.* [15].

parameters [15]. It can be discussed qualitatively in a straight forward manner, which I will briefly outline following Reference [49].

According to *Fermi's Golden rule* the absorption probability P of a photon with frequency ω and field \boldsymbol{E} per unit time is

$$P = \frac{2\pi}{\hbar} |M|^2 N(\epsilon) \tag{2.2}$$

where M is the matrix element for the interaction between light and Dirac fermions and $N(\epsilon)$ is the electronic density of states at the final state with $\epsilon = \hbar \omega/2$, see Fig. 2.2(b). In the vicinity of K(K') - here the term vicinity refers to photon energies well within the

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visible spectrum - N is a linear function of ϵ can be expressed in terms of ω as

$$N(\hbar\omega/2) = \frac{\omega}{\pi\hbar v_F^2}.$$
(2.3)

with the Fermi velocity of graphene v_F . The square of the matrix element M is given as

$$|M|^2 = \frac{e^2 v_F^2}{8\,\omega^2} |\mathbf{E}|^2,\tag{2.4}$$

where e is the charge of the electron. Inserting Eqns. (2.3) and (2.4) in Eqn. (2.2) yields the absorption probability per unit time

$$P = \frac{2\pi}{\hbar} \frac{e^2 v_F^2}{8\omega^2} |\boldsymbol{E}|^2 \frac{\omega}{\pi \hbar v_F^2} = \frac{e^2}{4\hbar\omega} |\boldsymbol{E}|^2.$$
(2.5)

It is remarkable to note that P is independent of the only quantity related the material, the Fermi velocity v_F . The absorption coefficient η is given by the ratio of the absorbed energy $W_a = P\hbar\omega$ and the incident photon flux $W_i = c |\mathbf{E}|^2/(4\pi)$ as

$$\eta = \frac{W_a}{W_i} = \frac{\pi e^2}{\hbar c} \approx 2.3\% \quad , \tag{2.6}$$

which is universal. The most intuitive description and summary of Eq. (2.6) is probably that both the electron-photon coupling matrix elements and the density of states cancel out upon calculation the absorption probability.

2.2. Carbon nanotubes

Carbon nanotubes are hollow cylinders of rolled up graphene or few-layer graphene sheets. They were first discovered in the form of multi-walled tubes by *Iijima* [50], and shortly after in their single-walled form [51, 52]. With diameters on the order of one to few nanometers and lengths up to centimeters [23], single-walled carbon nanotubes are described as quasi one-dimensional solid state systems [22]. Quantum confinement effects along the circumference govern the nanotube's properties; every way of rolling up a graphene sheet into a carbon nanotube implements a unique microscopic structure with a unique set of electronic and optical properties. Nanotubes of comparable diameters may be metallic or semiconducting with varying band gap energies. Combined with ballistic electron transport at room temperature [53, 54], high conductivity [55], and mechanical stability [56], nanotubes represent a versatile material for a broad range of applications. I will introduce the basic properties of carbon nanotubes, followed by a more detailed focus on their optical properties relevant for my work presented in this thesis.

The chiral vector c uniquely specifies the microscopic structure of a carbon nanotube. It is expressed as a linear combination of the two graphene lattice vectors a_1 and a_2 as

$$\boldsymbol{c} = n_1 \boldsymbol{a_1} + n_2 \boldsymbol{a_2}, \tag{2.7}$$

where n_1 and n_2 take integer values only and $n_1 \ge n_2$. Rolling up the graphene sheet along c as shown in Fig. 2.3 (a-c) forms the corresponding nanotube. A particular nanotube type is then specified by the pair (n_1, n_2) and is referred to as the tube's chirality. Carbon nanotubes whose chiral vectors are parallel the two distinct graphene



Figure 2.3. (a) The linear combination of the graphene lattice vectors a_1 and a_2 form the circumference $c = 10 a_1 + 10 a_2$ of a (10,10) nanotube. The circumference and the minimum translational period (not shown) define the graphene rectangle which is rolled up in (b) to form the nanotube in (c). The helix around a chiral (8,4), a zigzag (10,0), and a armchair (6,6) tube is shown in (d). From Ref. [57].

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edges are either called armchair (n, n) or zigzag (n, 0) tubes. All other nanotubes are called chiral nanotubes. Examples of the three types are shown in Fig. 2.3 (d), where the helix of each the nanotubes is shown in grey. The chiral vector defines the diameter d of a carbon nanotube as

$$d = \frac{|\mathbf{c}|}{\pi} = \frac{\sqrt{3} a_{cc}}{\pi} \sqrt{n_1^2 + n_1 n_2 + n_2^2},$$
(2.8)

and its chiral angle Θ between c and the zigzag direction as

$$\Theta = \arccos\left(\frac{\boldsymbol{c} \cdot \boldsymbol{a_1}}{|\boldsymbol{c}| \cdot |\boldsymbol{a_1}|}\right) = \arccos\left(\frac{n_1 + n_2/2}{\sqrt{n_1^2 + n_1 n_2 + n_2^2}}\right).$$
(2.9)

Both the diameter and the chiral angle provide a very useful and intuitive way to illustrate the electronic properties of nanotubes and their dependence on the chirality, as I will discuss in the following.

2.2.1. Band structure

Within the zone-folding approach, a nanotube is regarded as an infinitely long cylinder. The electronic wave functions along the tube axis are Bloch functions as in threedimensional solids and contribute a continuous component k_z to the reciprocal vector \boldsymbol{k} . Along the circumference of the nanotube, however, the electronic wave functions are quantized fulfilling

$$\boldsymbol{c} \cdot \boldsymbol{k} = 2\pi m, \quad \text{with } m \in \mathbb{N}.$$
 (2.10)

As a result, the allowed electronic wave vectors of carbon nanotubes are quantized with respect to the circumference of the tube and continuous along the axis. We can directly obtain the electronic structure of a nanotube by mapping the allowed states of carbon nanotubes on the electronic band structure of graphene. Within the reciprocal lattice vector space of graphene, the Brillouin zone of nanotubes consists of parallel lines as shown in Fig. 2.4(a) and (b). The separation of the lines depends via |c| inversely on the diameter of the nanotube. The orientation of the lines corresponds to the chiral angle. If the K(K') points of graphene are among the allowed electronic states such as in Fig. 2.4(a), a nanotube is metallic; otherwise it is semiconducting as in Fig. 2.4(b). In terms of chirality, a nanotube is metallic [58, 59] if

$$(n_1 - n_2) \mod 3 = 0, \tag{2.11}$$

and semiconducting otherwise. Within the zone-folding approximation, the electronic energies of graphene along the lines of the allowed wave vectors build up the electronic



Figure 2.4. Energy contours of graphene overlaid with the allowed electronic states of a metallic (a) and semiconducting (b) carbon nanotube. Each line corresponds to a different quasi angular momentum m. (c) Band structure of the (10,10) nanotubes calculated *ab-initio* assigned with the corresponding m. Panels (a) and (b) are taken from [60]. Panel (c) is adapted from Ref. [48].

band structure of nanotubes. As an example, the band structure of a metallic (10, 10) tube is depicted in Fig. 2.4(b). Each conduction and valence subband of the tube belongs to a different quantum number m, also called quasi-angular momentum. Every nanotube chirality corresponds to a unique set of subbands.

2.2.2. Optical properties

Due to their one-dimensional nature, carbon nanotubes are optically anisotropic. The interaction with light polarized perpendicular to the tube axis is strongly suppressed by depolarization [61–64], also referred to as the *antenna effect*. Nanotubes predominantly absorb and emit light polarized along the their axis, which requires $\Delta m = 0$ [65]. Optical transitions in CNTs therefore occur only between states which are associated with subbands of equal quasi-angular momentum.

The energetic separation of the band maxima and minima of the same m in Fig. 2.4(c), in the following labeled E_{ii} , are systematically connected to the microscopic structure of the corresponding nanotube. Typically, they are plotted versus the nanotube diameter in a so called *Kataura* plot [66], which is shown in Fig. 2.5(a). The E_{ii} follow a general 1/d behavior which is easily understood within the zone-folding picture. The smaller the diameter of the nanotubes, the further away from the K(K') points the electronic bands are located. In the energy range relevant for optical transitions, the equi-energy contours of the Dirac cones are not radially symmetric any more, see Fig. 2.4 (a,b) around

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Figure 2.5. (a) Kataura plot of the optical transition energies plotted versus the diameter for semiconducting (closed dots) and metallic (open dots) carbon nanotubes. (b) Optical absorption in the excitonic picture occurs at the exciton wavevector $Q \approx 0$. The excitonic states eh_{ii} are commonly labelled as E_{ii} as it the case in (a). Panels (a) and (b) are adapted from Refs. [57] and [68], respectively.

the K and K' points. They are influenced by the trigonal symmetry of the underlying graphene Brillouin zone, also referred trigonal warping [67]. Therefore, the E_{ii} of a carbon nanotube systematically deviate from the 1/d behavior depending on the chiral angle as shown in Fig. 2.5(a).

The optical excitations in carbon nanotubes arise from excitons [30, 31]. Owing to their reduced dimensionality and inefficient dielectric screening, the exciton binding energy E_b in nanotubes is huge (~ 1 eV in vacuum, ~ 0.4 eV for surfactant coated tubes [57]), compared to bulk semiconductors (few meV). As a result, excitons are present at room temperature ($k_bT \approx 25 \text{ meV} \ll E_b$), and the oscillator strength of the optical transitions in CNTs is transferred entirely from band-to-band to excitonic transitions. Light absorption is described as the transition of an exciton from its ground state to the excited states eh_{11}, eh_{22} , shown in Fig. 2.5(b). The labeling indicates the connection to E_{11}, E_{22} as introduced before. The systematic dependencies of the optical transitions on diameter and chiral angle as given in the *Kataura* plot in Fig. 2.5(a) remain valid for excitons.

Surprisingly, the excitonic transitions are blue-shifted compared to band-to-band transitions. Intuitively one would expect a redshift due to the excitonic binding energy. This is due to electron-electron interactions, which overcompensate the redshift caused by electron-hole interactions [69]. The transition occurs at eh_{ii} for the exciton wavevector $Q \approx 0$, which combines electrons and holes of opposite momentum.

The excitonic nature of the optical transitions in CNTs has several important consequences; they affect the radiative lifetimes and make the tubes' optical transitions susceptible to changes in the environment [57, 70]. The description of resonant Raman scattering in carbon nanotubes changes as well, as described in Sec. 3.1. In some cases, however, treating the optical transitions of carbon nanotubes within the band-to-band picture is sufficient.

2.3. Plasmonic nanostructures

A plasmon is a collective oscillation of free electrons in the bulk of a metal. It can be thought of as a spatial oscillation of the electrons against the ion cores. The frequency of the plasmon is given by

$$\omega_{\rm p} = \sqrt{\frac{ne^2}{\epsilon_0 m}},\tag{2.12}$$

with the electron density n, the charge e and mass m of the electron, and the vacuum permittivity ϵ_0 . At the surface of a metal light may excite surface plasmons¹, which can be regarded as propagating surface charge fluctuations, Fig. 2.6(a). For tiny metallic particles of sub-wavelength dimensions, schematically depicted in Fig. 2.6(b), these charge fluctuations are localized and termed localized surface plasmon resonances (LSPR). They give rise to strong optical responses of resonant nature, which stretch from the infrared to the visible region of the electromagnetic spectrum. In the following I introduce the basic principles of LSPRs and how they give rise to near-field enhancement. Coupling between neighboring particles will be discussed for two closely spaced gold nanodiscs as they represent the primary plasmonic nanostructure investigated in this thesis.

2.3.1. Localized surface plasmon resonances

The complex dielectric function $\epsilon(\omega)$ of a metal describes its response to light of frequency ω and is given by

$$\epsilon(\omega) = \epsilon_{\infty}(\omega) - \frac{\omega_p}{\omega^2 + i\gamma\omega},\tag{2.13}$$

where γ is the electron collision frequency in the bulk. The second term of Eq. (2.13) corresponds to the free electron response of the metal as described by the Drude model. For higher frequencies, inter band transitions from the valence to the conduction band contribute to the optical response and are taken into account by ϵ_{∞} .

¹The excitation of a propagating surface plasmon requires phase matching, e.g. by using a prism in the *Kretschmann* configuration, see e.g. Ref. [1].

2. Nanostructures



Figure 2.6. (a) Propagating surface plasmon at a metallic surface. (b) Metallic nanosphere (right) exhibits a localized surface plasmon resonance; this collective excitation of electrons gives rise to a strong near-field at the particles surface. (c) Real part of the dielectric functions of of gold (yellow) and sliver (grey) with the corresponding imaginary parts shown in (d). (e) Scattering spectra of silver particles of different shapes, which are shown as insets. The figures in (a,b) are taken from Ref. [71], and (c,d) are taken from Ref. [72] with the original data in (b,c) from Johnson and Christi [73]. Panel (e) is taken from Ref. [74].

For small metallic particles with dimensions of the order of 100 nm and below, localized surface plasmons are predominantly of dipolar nature and higher orders may be neglected. The resonance condition depends on the volume V of the particle, its dielectric function as in Eqn. (2.13), the dielectric function of the surrounding medium ϵ_{sm} and the shape of the particle incorporated in the form factor κ . It is typically given as the dipolar polarizability

$$\alpha(\omega) = (1+\kappa)\epsilon_0 V \frac{\epsilon(\omega) - \epsilon_{sm}(\omega)}{\epsilon(\omega) + \kappa \epsilon_{sm}(\omega)},$$
(2.14)

with $\kappa = 2$ for a sphere. The localized surface plasmon resonance between the excitation of the surface electrons and incoming light occurs for $\operatorname{Re}[\epsilon(\omega)] = -\kappa \epsilon_{sm}(\omega)$ - assuming that the imaginary part of ϵ slowly varies with ω . The optical properties of the nanoparticle such as the near-field, absorption and scattering are dominated by this resonance. At the surface of the nanoparticle, for instance, the near-field \boldsymbol{E} is given by a superposition of the incoming field E_0 and the dipole field originating from the metallic particle as [75, 76]

$$\boldsymbol{E} = \boldsymbol{E}_{\boldsymbol{0}} + \frac{\kappa \epsilon_m}{\epsilon + \kappa \epsilon_{sm}} \boldsymbol{E}_{\boldsymbol{0}}, \qquad (2.15)$$

where the second term scales with r^{-3} from the particles centre at r = 0. Upon resonant excitation, the near-field intensity $|\mathbf{E}|^2$ is greatly enhanced and gives rise to increased Raman scattering, as described in Sec. 3.4. Similarly, the absorption and the scattering of the particle are resonantly enhanced. They approximately scale with the polarizability as $|\alpha|^2$ (absorption) and Im[α] (scattering). Measuring the absorption and/or scattering of nanostructures is therefore a common way to determine the frequency of the LSPR.

It is instructive to display the effect of the variables that influence the spectral position of the LSPR. Figure 2.6 (c) and (d) show the real and imaginary part of the dielectric function of gold and silver, respectively. The resonances of a spherical particle in air $(\kappa = 2, \epsilon_{sm} = 1)$, for instance, would largely differ for gold ($\geq 500 \text{ nm}$) and silver ($\leq 400 \text{ nm}$). Silver particles of similar dimensions but different shape, may exhibit very different resonances as evidenced in their scattering behavior shown in Fig. 2.6(e). Nanostructures of highly anisotropic shape - e.g. lengthy nanorods - have different form factors and hence result in different LSPR modes along the corresponding axes.

2.3.2. Coupled plasmonic dimers

When two particles are brought into close proximity, they interact via their near-field. The electric field experienced by one particle is the sum of the incident field and the near-field of the other particle. As a result, their localized surface plasmon resonances become coupled and the near-field enhancement is maximal in the gap between them. The coupling can be elegantly treated by analogy to electronic orbitals in molecules [1, 77, 78]: the modes of the isolated particle hybridize to form coupled modes. This is schematically shown in Fig. 2.7(a), where the direction and phase of the charge oscillations are indicated. The mode with the maximum distance for charges of opposite sign is lowest in energy, even lower than for isolated nanodiscs. This mode has a relatively large dipole moment and interacts strongly with light; it requires the polarization of the excitation to be parallel to the axis of the dimer and is referred as bright-, cavity-, or dimer mode. The other modes of higher energy interact with light either not at all or only weakly (e.g. the in-phase charge oscillation, second from top). The latter is energetically very close to the LSPR of an isolated nanodisc. It requires the polarization of the excitation to be perpendicular to the dimer axis, and is referred to as isolated- or uncoupled mode. Figure 2.7(b) and (c) show the absorption of nanodisc dimers with decreasing gap sizes [79] for light polarizations parallel and perpendicular to the dimer, respectively. While the energy of the cavity mode in 2.7(b) decreases with the gap size, the resonance the isolated mode remains almost entirely unaffected.

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Figure 2.7. (a) Hybrid plasmon modes for two close by nanodiscs plotted against the energy of the excitation. Only for in-phase charge oscillations the modes may couple to light. (b,c) Absorption of nanodisc dimers with varying gap size for the cavity mode (b) and the isolated mode. The caption OD refers to optical density, as the measurement of the absorption was taken in transmission. Panel (a) is taken from Ref. [78], and panels (b) and (c) are adapted from Ref. [79].

3 Raman scattering

Raman spectroscopy is a non-destructive characterization technique of major importance, which provides an insight into fundamental properties of physical systems. In this chapter, I briefly introduce the basics of Raman scattering in solid state systems. I will focus on resonant Raman scattering in solid state systems, which is particularly important for understanding Raman scattering in graphene and carbon nanotubes. Subsequently, the Raman signatures of graphene and carbon nanotubes will be introduced. The section will be rounded up by introducing plasmon-enhanced Raman scattering, including a brief review on recent works that study PERS on graphene and tubes.

3.1. Basic concepts

Within the microscopic theory in solids, first order Raman scattering can be broken down into three steps [68, 80]. An incoming photon with the frequency ω_1 is absorbed by exciting an electron-hole pair. The electron hole pair inelastically scatters by emitting (Stokes process) or annihilating (Anti-Stokes process) a phonon with the frequency ω_{ph} . It finally recombines radiatively by emitting a photon of the frequency ω_2 . The Feynman diagram corresponding to the Stokes process is shown in Fig. 3.1, where any (time) order



Figure 3.1 Incoming photon with wave vector $\mathbf{k_1}$ and frequency ω_1 excites an electron-hole pair, which scatters inelastically whilst emitting a phonon of wave vector \mathbf{q} and frequency ω_{ph} . The electron-hole pair recombines radiatively by emitting a photon with wave vector $\mathbf{k_2}$ and frequency ω_2 . After Refs. [22, 80].

3. Raman scattering

is possible. In the Raman process the overall energy and momentum is conserved

$$\boldsymbol{k_1} = \boldsymbol{k_2} \pm \boldsymbol{q} \tag{3.1}$$

$$\hbar\omega_1 = \hbar\omega_2 \pm \hbar\omega_{ph}, \qquad (3.2)$$

where \pm refers to the Stokes and Anti-Stokes process and k_1, k_2 and q denote the wave vectors of the absorbed photon, the emitted photon and the phonon, respectively. While electrons and holes mediate the scattering process, the initial and final state of the electronic system are the same. For first-order one-phonon Raman scattering, only Γ -point phonons with $q \approx 0$ adhere momentum conservation, compare Eq. (3.1).

From the point of view of formal quantum electrodynamics, the Raman scattering amplitude is equivalent to the matrix element $K_{2f,10}$ of the process shown in Fig. 3.1. The electron-photon interaction is given by the electron-radiation Hamiltonian H_{eR} and the electron-phonon coupling is given by the electron-phonon Hamiltonian H_{ePh} , compare Fig. 3.1. The corresponding transition matrix elements contribute to $K_{2f,10}$ and the scattering amplitude of a first order Stokes process is then given as [80]

$$K_{2f,10} = \sum_{a,b} \frac{\langle \omega_2, f, i | H_{eR} | 0, f, b \rangle \langle 0, f, b, | H_{ePh} | 0, 0, a \rangle \langle 0, 0, a | H_{eR} | \omega_1, 0, i \rangle}{(\hbar \omega_1 - E^e_{ai} - i\gamma)(\underbrace{\hbar \omega_1 - \hbar \omega_{ph}}_{=\hbar \omega_2} - E^e_{bi} - i\gamma)},$$
(3.3)

where $|\omega_1, 0, i\rangle$ denotes the photonic state of an incoming photon of energy $\hbar\omega_1$, ground state of the phonon (no phonon), and the initial state *i* of the electronic system. In the state $|\omega_2, f, i\rangle$ after the scattering process, the photonic state is defined by the emitted photon of the energy $\hbar\omega$, the final phononic state *f*, and the final electronic state, which is the same as the initial state *i*. The sum runs over all intermediate electronic states *a* and *b*, and E_{ai}^e is the energy difference between the states *a* and *i* (same for *b*). The Raman scattering amplitude is kept finite by introducing the lifetime γ of the corresponding electronic state. The Raman scattering cross section or intensity is

$$I \sim |K_{2f,10}|^2$$
. (3.4)

Without going into the details of calculating the Raman scattering amplitude, its structure is very helpful to elucidate the concepts necessary to understand the resonant nature of Raman scattering in carbon nanotubes and graphene. If both a and b are virtual states as indicated by the dashed lines in Fig. 3.2(a), the scattering process is called non-resonant. Such a process typically yields a low Raman intensity, which remains constant upon

3.1. Basic concepts



Figure 3.2. Simplified sketch of (a) non resonant and single resonant Raman scattering with (b) incoming resonance or (c) outgoing resonance. (d) Double resonant Raman scattering. The solid lines represent the real states of the system. Virtual states are indicated by dashed lines. Arrows indicate the phonon (green) as well incoming and scattered photons (red). All sketches refer to the Stokes-process only.

changing $\hbar\omega_1$. A typical example for excitation energies in the visible and infrared spectral region is diamond (band gap ~ 5.5 eV). Single-resonant Raman scattering occurs if one the intermediate states is an eigenstate of the system. The corresponding term in the denominator of Eqn. 3.1 becomes small and enhances the Raman intensity. If the incoming photon matches an optical transition as in Fig. 3.2(b), the scattering process is called incoming resonance. An outgoing resonance occurs if the scattered photon matches the energy of the transition as depicted in Fig. 3.2(c). The energetic difference between the two processes is given by the energy of the phonon in the scattering process. Double resonant Raman scattering occurs if both the intermediate states are eigenstates of the system as shown in 3.2(d). Such a situation is rarely observed in a scattering process that involves only one phonon, but may be achieved by applying e.g. uniaxial stress to tune the electronic eigenstates accordingly [81].

It is very instructive to have closer look at the calculation of the $K_{2f,10}$ for some specific cases, as discussed in detail by *Thomsen et al.* [57] and in Refs. [82]. For a one-dimensional system with one pair of parabolic bands and the optical transition energy E_{ii} , the energy differences between initial and the intermediates states take the form

$$E_{ai}^{e}(k) = E_{bi}^{e}(k) = E_{ii} + \frac{\hbar^2 k^2}{2\mu},$$
(3.5)

where k is the wave vector of the electron and the reduced effective electron mass μ , that incorporates the masses of electron m_e and hole m_h as $1/\mu = 1/m_e + 1/m_h$. The sum in

3. Raman scattering

Eq. 3.1 converts into an integral over k and leads to

$$I \sim \left|K_{2f,10}\right|^2 \propto \left|\frac{1}{i\hbar\omega_{ph}}\left(\frac{1}{\sqrt{\hbar\omega_1 - E_{ii} - i\gamma}} - \frac{1}{\sqrt{\hbar\omega_1 - \hbar\omega_{ph} - E_{ii} - i\gamma}}\right)\right|^2.$$
 (3.6)

The Raman intensity after evaluating the absolute value in Eq. (3.6), yields two symmetric maxima at the energies of both the incoming and the outgoing resonance.

The matrix element $K_{2f,10}$ and the way it is evaluated changes if we consider only one discrete electronic state, instead of a continuum of states as before. An example is excitons in carbon nanotubes, Sec. 2.2. Only one state eh_{ii} with the exciton momentum $Q \approx 0$ is involved and $E_{ai}^e(k) = E_{bi}^e(k) = eh_{ii}$. If no other excitonic state close in energy is available for the Raman process, the sum over all electronic states a and b is no longer required and the corresponding Raman cross section is then

$$I \sim |K_{2f,10}|^2 \propto \left| \frac{1}{\hbar\omega_{ph}} \left(\frac{1}{\hbar\omega_1 - E_{ii} - i\gamma} - \frac{1}{\hbar\omega_1 - \hbar\omega_{ph} - E_{ii} - i\gamma} \right) \right|^2.$$
(3.7)

Compared to the band-to-band case, the Raman intensity arising from an excitonic transition also yields two symmetric but somewhat sharper maxima for incoming and outgoing resonance, respectively. The form of Eqn. (3.7) is also interesting from a more general point of view. It allows an intuitive connection to the general optical properties of the system I discussed above.

As shown for instance in Refs. [68, 82], the two complex arguments within the absolute value above - expressed in terms of real and imaginary part - represent the complex dielectric function $\epsilon(\omega) = \epsilon_r(\omega) + i\epsilon_i(\omega)$ and thereby provide a connection to fundamental material properties like reflection and absorption. The Raman scattering cross section in Eqn. (3.7) can expressed as

$$I \propto \left(\frac{1}{\hbar\omega_{ph}}\right)^2 |\epsilon(\omega_1) - \epsilon(\omega_2)|^2 \quad \text{or}$$
(3.8)

$$\propto \left| \frac{\epsilon(\omega_1) - \epsilon(\omega_2)}{\hbar\omega_1 - \hbar\omega_2} \right|^2 \quad \text{and} \tag{3.9}$$

$$\propto \left|\frac{\partial\epsilon}{\partial E}\right|^2 \quad \text{for} \quad |\hbar\omega_1 - \hbar\omega_2| \ll \hbar\omega_1,$$
 (3.10)

and depends on the difference of ϵ for excitation and emission. For small phonon energies, the Raman scattering cross section I is proportional to the square of the derivative of the dielectric function with respect to the excitation energy E. If the real part of ϵ is a very slowly varying function of E, the Raman scattering cross section is proportional to the derivate of the absorption α with respect to the energy as $|\partial \alpha/\partial E|^2$ via $\alpha \propto \epsilon_i$. The results of Eqns. (3.8) - (3.10) can also be obtained from the macroscopic theory of Raman scattering, e.g. in Ref. [68].

If one is interested in the Raman selection rules only - that is if the matrix element in Eqn. 3.1 is zero or not - it is useful to express the Raman intensity via contracting the Raman tensor \mathcal{R} as

$$I \sim |\mathbf{e}_s \cdot \mathcal{R} \cdot \mathbf{e}_i|^2 \,, \tag{3.11}$$

where \mathbf{e}_i and \mathbf{e}_s are the polarization of the incident and scattered light, respectively. The form of \mathcal{R} is connected to the symmetry or representation of a particular vibration. Polarization dependent Raman measurements on unoriented samples, for instance on carbon nanotube ensembles [22], allow one to determine wether a specific component of \mathcal{R} is zero, thereby revealing the symmetry of the corresponding Raman active vibration.

3.2. Graphene

The Raman spectrum of graphene carries a lot of information. Raman scattering has therefore developed into a versatile and important tool to characterize graphene and its derivatives. Comprehensive reviews and a large body of literature therein discuss every aspect in great detail [83–85]. In this section I will briefly introduce the dominating Raman active vibrations in graphene and how they are related to graphene's peculiar electronic properties.

With the unit cell containing two atoms, graphene has three optical and three acoustic phonon branches [19]. The calculated phonon dispersion along the high symmetry axes is shown in Fig. 3.3(a), with the corresponding acronyms explained in the figure caption. The dominant Raman-active vibrations in graphene arise from the transversal optical (TO) and longitudinal optical (LO) phonon branches. At the Γ -point, they form the double degenerate E_{2g} phonon mode. Due to the occurrence of a Kohn anomaly ¹, the electron-phonon coupling of this mode is particularly strong at Γ . A second Kohn anomaly occurs for the TO-phonons of A_{1g} symmetry close to K(K'). The phonons from both Kohn anomalies play a major role in the Raman signatures of graphene.

A typical Raman spectrum of graphene consists of distinct peaks and is shown in

¹The partial dielectric screening of vibrations can rapidly change in metals and lead to an unusual phonon dispersion - the Kohn anomaly - and strong electron-phonon coupling. It may occur if a phonon wavevector **q** and two electronic states $\mathbf{k_1}$, $\mathbf{k_2}$ on the Fermi surface fulfill $\mathbf{k_1} = \mathbf{k_2} + \mathbf{q}$. In graphene the Fermi surface is point-like at K(K'). Kohn anomalies occur for $\mathbf{q} = 0$ (E_{2g} mode at Γ) and $\mathbf{q} \approx K$ (A_{1g} -TO mode around K).



Figure 3.3. (a) Calculated phonon dispersion of graphene with three acoustic (A) and three optical (O) branches. Only the in-plane longitudinal (L) and transverse (T) optical phonons are Raman active. The ZO is the optical out-of-plane mode. The ZA mode is an out-of-plane acoustic mode, the TA mode is an in-plane acoustic mode, and the LA branch is the longitudinal acoustic mode. (b) Raman spectrum of graphene on SiO₂ at $\lambda = 638$ nm excitation with the dominant D, G, 2D and 2D' Raman modes of graphene. Panel (a) is taken from [86], courtesy of P. May.

Fig. 3.3(b) for a laser excitation of 1.94 eV. The most prominent, most informative and most (controversially) discussed peaks are found in the range between 1250 cm^{-1} and 3400 cm^{-1} . Similarly, they play an important role in the Raman signature of graphene-related allotropes like graphene nanoribbons, carbon nanotubes, and graphite. The Raman scattering process involves one phonon for the *G*- and *D*-mode and two phonons for the 2D and 2D' modes.

The G(raphite)-peak at around 1582 cm^{-1} corresponds to the doubly degenerate E_{2g} optical phonon modes from the Γ -point. It is a vibration in the plane of the sp^2 bonds and the only first-order Raman active phonon with $\mathbf{q} = 0$. Due to its high frequency, the G-mode is a very sensitive probe for external perturbations such as doping [87, 88] or strain [89, 90]. Given the linear electronic dispersion of graphene, one would intuitively expect the G-mode to arise from a single resonant Raman process with ingoing and outgoing resonances as introduced in Sec. 3.1, with the corresponding process shown in Fig. 3.4(a). This is not the case, however, because the contributions from transitions at different electronic k-states to the Raman scattering amplitude, Eq. 3.1, interfere destructively [91]. This can be directly seen from calculating the corresponding matrix element $K_{2f,10}$, which I will outline in the following.

For the linear bands of graphene with the Fermi velocity v_F , the intermediate electronic

3.2. Graphene



Figure 3.4. (a) Scattering process for the *G*-mode with $q \approx 0$ and the Fermi velocity v_F . (b) After the resonant absorption of the photon, the electron is scattered from *K* to *K'* (and vice versa) by the *D*-mode phonon. A defect elastically scatters back the electron, followed by the photon emission (red). The process may occur for different time orders and hole scattering (weak lines). (c) 2*D* mode: A second phonon replaces the defect. For hole scattering (weak lines), additional resonances may occur. (d) 2*D'* mode: the scattering occurs within one cone.

states involved in the Raman process are given as $E_{ai}^e = E_{bi}^e = 2|k|v_F$. In one dimension, the sum over all intermediate states in the matrix element $K_{2f,10}$, see Eq. 3.1, can be converted to an integral over k [92]. The Raman intensity given in Eqn. (3.4) is then

$$\begin{split} I \sim |K_{2f,10}|^2 \propto & \left| \int_0^\infty \frac{1}{(\hbar\omega_1 - 2kv_F - i\gamma)(\hbar\omega_1 - 2kv_F - \hbar\omega_{ph} - i\gamma)} \right|^2 \\ \propto & \left| \frac{1}{2v_F \hbar\omega_{ph}} ln \left(\frac{\hbar\omega_1 - \hbar\omega_{ph} - i\gamma}{\hbar\omega_1 - i\gamma} \right) \right|^2, \end{split}$$

where the logarithm varies slowly with $\hbar\omega_1$ but no resonances occur ($\hbar\omega_1 \gg 0 \text{ eV}$). The *G*-mode is therefore of non-resonant nature, in contrast to the simplified picture shown in Fig. 3.4(a). Due to strong electron-phonon coupling via the Kohn-anomaly, on the other hand, it has an intrinsically high Raman intensity, even compared to carbon-based volume scatterers such as diamond.

The *D*-mode stems from the TO-branch close to K and is a double-resonant, one-phonon second order Raman scattering process [83, 92, 93]. Due to $\mathbf{q} \approx \mathbf{K} \neq 0$, it is forbidden as it does not conserve momentum in the overall Raman process. A defect in the graphene lattice, however, actives the *D*(efect)-mode by providing the necessary momentum via elastic scattering. The particular phonon energy is then selected by fulfilling the resonance condition for double-resonant Raman scattering, as schematized in Fig. 3.4(b). The scattering occurs between different valleys and for electrons, holes, or both (dominant contribution) in any given time order. The *D*-mode is dispersive with the excitation energy, which allows one to probe its phonon dispersion in any available excitation window. It shows very strong electron-phonon coupling due to the Kohn anomaly near *K*.

3. Raman scattering

The 2D mode is a second order two-phonon Raman process. Similar to the D-mode, it originates from scattering by phonons from the TO phonon branch. The 2D-mode arises from a double resonant Raman process between K and K', shown in Fig. 3.4(c). Instead of a defect in the case of the D-mode, the second phonon provides the necessary momentum such that the process is allowed. Both 2D mode phonons arise from the vicinity of the K-point, and due to the Kohn anomaly their electron-phonon coupling is strong. In combination with the double resonant character of the scattering process, the 2D-mode shows a much higher intensity than the G-mode. This is surprising, as the G-mode involves only one phonon in the scattering process [94, 95]. The matrix elements for two phonon scattering are typically much smaller than the matrix elements for one phonon scattering. The intensity ratio shown in Fig. 3.3(b) typically serves as a fingerprint to identify graphene, e.g. in comparison to bi- or multilayer graphene.

The 2D' mode arises from two LO phonons near the Γ -point, where the dispersion of this phonon branch overbends. The process is double resonant like the 2D-mode, but in contrast to the latter the scattering occurs within the same Dirac cone as shown in Fig. 3.4(d).

3.3. Carbon nanotubes

Similar to graphene, the Raman spectrum of carbon nanotubes carries a wealth of structural information [22, 57, 83, 96]. It allows, for instance, to determine the diameter of a carbon nanotube, its metallicity, wether it is defective or not, and under the right circumstances even the chirality of a particular isolated nanotube. In the following I will briefly introduce the dominant Raman active modes in CNTs and comment on the resonant nature of their Raman response.

Figure 3.5 shows the Raman spectrum of carbon nanotubes deposited on a SiO₂ substrate. In addition to the modes between 1250 cm^{-1} and 3400 cm^{-1} as for graphene, important Raman modes for carbon nanotubes occur also in range between 100 cm^{-1} and 400 cm^{-1} . The curvature of the carbon nanotube wall lifts the degeneracy of the *G*-peak present in graphene. The high energy spectrum of nanotubes consist of TO and LO phonons², generally referred to as G^- and G^+ , just below 1600 cm^{-1} . The corresponding shape and relative intensity distribution in Fig. 3.5 is typical for semiconducting carbon nanotubes. In metallic nanotubes, the G^+ or LO-mode is broadened and downshifted; similar to graphene, these tubes have allowed electronic states belonging to bands that cross at the K(K') points. They provide an additional phonon decay channel by the

²In achiral nanotubes, only one of the vibrations is allowed by selection rules.



Figure 3.5. Raman spectrum of predominantly semiconducting carbon nanotubes for $\lambda = 638$ nm. The inset shows the mostly radial, in-phase nature of the radial breathing mode. The inset is taken from Ref. [70].

excitation of an electron-hole pair around K. The frequency downshift of the LO-phonon is caused by the Kohn-anomaly at the Γ -point. The vibrations cause the periodic opening of a small band-gap, which in return lowers the electronic contribution to the phonon energy [97, 98].

The radial breathing mode (RBM) in the low energy part of the spectrum in Fig. 3.5 is a typical feature in the Raman spectrum of carbon nanotubes. All atoms move radially in-phase, and the frequency ω_{RBM} is in a good approximation connected to nanotube diameter by $\omega_{RBM} = c_1/d + c_2$, with several sets of parameters (c_1, c_2) available in the literature [99–101].

Both the radial breathing mode and the G-mode arise from single-resonant Raman scattering, see Sec. 3.1. The Raman intensity observed in an experiment depends strongly on the particular combination of tube and excitation energy. Figure 3.6(a) plots the



Figure 3.6. (a) Resonant Raman profiles of the RBMs for several carbon nanotube chiralities. The data was acquired from an ensemble of nanotube in solution. (b) Resonant Raman profile of the G-peak intensity for a solution highly enriched with (10,5) nanotubes. Panels (a) and (b) are adapted from Refs. [70] and [103], respectively.

integrated RBM intensity against the excitation energy for several nanotube chiralities. The resonance window for these four tubes is similar and amounts to about 20 meV. Due to the small phonon energy range of 15 - 45 meV, incoming and outgoing resonance overlap and cannot be separated. The *G*-mode, on the other hand, has a much broader resonance window. Its comparably large energy of ~ 200 meV allows one to separate incoming and outgoing resonance as shown in Fig. 3.6(b) for the (10, 5) tube.

In a typical experiment on few or even one nanotube it is therefore much more likely to observe a G-mode but no radial breathing mode. A RBM verifies the presence of a particular tube chirality. It is not sufficient, however, to rule out the contribution of other CNTs to the G-peak that may be out of resonance with their RBMs. This fact is sometimes neglected in literature, e.g. in Ref. [102]. In analogy to graphene, the dispersive D-mode in nanotubes is activated by a defect and arises from a double resonant Raman process. The 2D-mode is double resonant, independent of the defect density and requires two phonons for momentum conservation.
3.4. Plasmon-enhanced Raman scattering

Plasmon-enhanced Raman scattering (PERS) describes the enhancement of Raman signal by localized surface plasmons that arise from well defined metal nanostructures. The process is mediated by the enhanced electromagnetic near-field produced by the structure. In this thesis, more specifically, PERS describes the enhancement of Raman signals of graphene and carbon nanotubes at hotspots in the gap of isolated plasmonic dimers. The process itself is considered to consist of three separate steps:

- Enhanced absorption If the incident radiation of frequency ω_1 described by the field $E_0(\omega_1)$ matches the resonance of a localized surface plasmon $\hbar\omega_{LSPR}$, the near-field at the corresponding hotspot is strongly enhanced. The absorption of an object at the hotspot increases by the factor $f_{abs} = |E(\omega_1)|/|E_0(\omega_1)|^2$.
- Raman scattering The Raman scattering process occurs as described in Sec. 3.1. The Raman intensity I_R scales linear with f_{abs} . This assumes that the Raman tensor remains unchanged, which is not necessarily the case for chemical enhancement.
- Enhanced emission If the scattered field $E(\omega_2)$ matches the resonance of a localized surface plasmon, it couples to the plasmonic structure and the emitted light is enhanced in the far field. The intensity of the Raman scattered light increases by the factor $f_{em} = |\mathbf{E}(\omega_2)|/|\mathbf{E}_0(\omega_2)|^2$.

The idea behind enhanced emission is that the radiative dipole representing the Raman scattered light is directly affected by the nearby metallic structures. They directly enhance the energy extracted from the emitting dipole [104]. The magnitude of both enhanced absorption and emission depend on the exact position of the Raman scatterer within the hotspot and its orientation (if applicable, e.g. for molecules and carbon nanotubes).

It is instructive to discuss different scenarios for the processes describes above. For small phonon energies, and both the incident and the scattered light falling within the spectral width of the localized surface plasmon resonance. The Raman enhancement I_{PERS} scales with the fourth power of the electric field amplitude as

$$I_{PERS} = f_{abs} \times f_{em} \times I_R = \frac{|\boldsymbol{E}(\omega)|^4}{|\boldsymbol{E}_0(\omega)|^4} \times I_R, \qquad (3.12)$$

with $\omega \approx \omega_{LSPR} \approx \omega_1 \approx \omega_2$. For larger phonon energies, e.g. the 2D-mode of graphene, this is not necessarily the case. Enhanced absorption and emission are two separate scenarios, which can be independently addressed by the choice of excitation energy relative

3. Raman scattering

to the LSPR. It is worth noting that the enhancement of both absorption and emission is treated in the classical framework, whereas Raman scattering is described in the quantum mechanical picture. In the following I will briefly discuss several works related to PERS of graphene and carbon nanotubes, which are representative for the state of the art in the field.

3.4.1. PERS of graphene

Graphene is a newcomer in the field of surface- and plasmon-enhanced Raman scattering. In a seminal work in 2010, *Schedin et al.* made use of graphene as a prototype twodimensional test material for the first time [17]. Dense arrays of gold nanodiscs were fabricated on top of mechanically exfoliated graphene, Fig. 3.7(a), claiming enhancement of the order of 35. Using several laser lines with different excitation wavelengths, the authors probed different regimes of PERS and concluded that the enhanced signal follows the fourth power of local field amplitude as discussed in the previous section. The same group realized much higher enhancement of up to a factor of 1000 for graphene deposited on top of plasmonic dimer arrays [105], see Fig 3.7(b). *Fang et al.* sandwiched complex plasmonic structures between two layers of graphene, and observed Raman enhancement from the visible to the near infrared region [18]. These studies demonstrated the feasibility of graphene as a two-dimensional probe for plasmon-enhanced Raman scattering over a broad range of wavelengths. Additionally, they showed that graphene can be interfaced with plasmonic structures in any desired stacking order. It is difficult to compare the



Figure 3.7. (a) Arrays of Au plasmonic nanodiscs fabricated on top of mechanically exfoliated graphene (blue). (b) Schematics of graphene placed on top of closely spaced plasmonic dimers. (c) Scanning electron microscopy image of graphene-oligomer-graphene sandwich. The nanostructures are fabricated on top of the bottom graphene layer, followed by the deposition of the top graphene layer. The images in (a), (b), and (c) are adapted from Refs. [17, 18, 105], respectively.

reported enhancement factors amongst each other: All measurements were performed on ensembles of nanostructures and the number of plasmonic hotspots per unit area was not factored in.

3.4.2. PERS of carbon nanotubes

Plasmon-enhanced Raman scattering by carbon nanotubes in a controlled manner as defined in the introduction and at the beginning of this section has not been realized prior to the works presented in this thesis. The interface of CNTs and enhanced near-field intensities was realized in various ways, mostly by tip-enhanced Raman spectroscopy (TERS). Here, the end of a metal coated tip, e.g. that of an atomic force microscope, is illuminated and acts as the active plasmonic element [106–109].

Besides TERS, the interface of tubes and plasmonic particles was realized by *Chu et al.*, who grew nanoparticles on aligned tubes by electroless deposition [110]. Defects in the atomic structure of the nanotubes served as seed locations for growth, which led to a dense but random Au nanoparticle decoration of the CNT surface as shown in Fig. 3.8(a). Raman spectra of CNTs with different grades of nanoparticle coverage are presented in Fig. 3.8(b). The authors concluded that compared to pristine nanotubes (1), decoration with few isolated nanoparticle (2), and clusters (3) subsequently increased Raman intensity by plasmonic enhancement. In a similar study, *Assmus et al.* investigated the effect of an isolated Au nanoparticle dimer, Fig. 3.8(c), which led to a 30-fold enhancement of the Raman signal of a carbon nanotube [111, 112].

An alternative approach to realize PERS by carbon nanotubes was suggested by *Takase* et al. [102], who dispersed carbon nanotubes on top of gold nanopyramids. The authors claimed that the tubes would fall in nanometer sized gaps between the pyramids upon deposition, as schematized in Fig. 3.8(d), and deduced a near-field induced breakdown of optical selection rules. It requires a vivid imagination, however, to see how the SEM image provided within the same panel confirms the suggested arrangement.

3. Raman scattering



Figure 3.8. (a) AFM image of CNTs decorated with gold nanoparticles. (b) Raman spectra of tubes in (a). Compared to pristine tubes (1), the Raman intensity increases for few nanoparticles (2), and is maximal for nanoparticles clusters (3). The isolated CNT in (c) shows the highest enhancement where it is interfaced with a nanoparticle dimer, see inset. (d) Schematic and scanning electron microscope picture of a nanotube apparently placed in-between two gold nanopyramids. Panels (a) and (b) are adapted from Refs. [110], and panels (c) and (d) are adapted from References [111] and [102], respectively.

4 Papers forming this thesis

1. Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene.

S. Heeg, R. Fernandez-Garcia, A. Oikonomou, F. Schedin, R. Narula, S.A. Maier, A. Vijayaraghavan, and S. Reich.

Nano Letters 13(1), 301-308 (2013).

I performed the AFM and Raman measurements, interpreted the data and wrote the manuscript. All authors discussed the data and commented on the manuscript. The project was conceived by A. Vijayaraghavan, S. Reich, and me. R. Fernandez-Garcia and S.A. Maier performed the numerical simulations and dark-field measurements. A. Oikonomou and Fred Schedin fabricated the nanostructures. A. Oikonomou performed SEM characterization, and produced and transfered graphene on top of the structures.

2. Strained graphene as a local probe for plasmon-enhanced Raman scattering by gold nanostructures.

S. Heeg, A. Oikonomou, R. Fernandez-Garcia, S.A. Maier, A. Vijayaraghavan, and S. Reich.

Physica Status Solidi - Rapid Research Letters 7(12), 1067-1070 (2013).

I performed the AFM and Raman measurements, interpreted the data and wrote the manuscript. All authors commented on the manuscript. The project was conceived by me together with S. Reich. A. Oikonomou fabricated the nanostructures and produced and transfered graphene on top of the structures.

 Plasmon-Enhanced Raman Scattering by Carbon Nanotubes Optically Coupled with Near-Field Cavities.
 S. Heeg, A. Oikonomou, R. Fernandez-Garcia, C. Lehmann, S.A. Maier, A. Vijayaraghavan, and S. Reich.
 Nano Letters 14(4), 1762-1768 (2014).

4. Papers forming this thesis

I performed the AFM and Raman measurements, interpreted the data and wrote the manuscript. S. Reich and I conceived the study. A. Vijayaraghavan in I designed and planned the dielectrophoretic deposition on top of plasmonic structures. A. Oikonomou fabricated the nanostructures, deposited the nanotubes and performed SEM characterization. R. Fernandez-Garcia and S.A. performed the numerical simulations. R. Fernandez-Garcia and I performed dark-field measurements. C. Lehmann and I performed conductive-AFM measurements. All authors commented on the manuscript.

 Plasmon-enhanced Raman scattering by suspended carbon nanotubes.
 S. Heeg, N. Clark, A. Oikonomou, A. Vijayaraghavan, and S. Reich. Physica Status Solidi - Rapid Research Letters 8(9), 785-789 (2014).

A. Oikonomou fabricated the nanostructures and deposited the nanotubes. I performed AFM and Raman measurements, interpreted the data and wrote the manuscript. N. Clark and A. Vijayaraghavan assisted in the interpretation of AFM data. All authors commented on the manuscript. I conceived the experiment together with S. Reich.

5 Connection of the papers

In this thesis I aimed to devise, realize and characterize an interface between graphene and plasmonic structures that allows to address the fundamentals of plasmon-enhanced Raman scattering. Graphene is the ideal material to study these fundamentals. The Raman cross section is constant and independent of the wavelength and the polarization of incident and scattered light. This suitability has been utilized to study PERS or plasmon enhanced sensing in several recent works as discussed in more detail in Sec. 3.4.1.

We chose Au nanodimers as the plasmonic core unit. The plasmonic excitations of the nanodimers are well understood and can be treated approximately analytically and numerically. Further advantages are the reproducible fabrication and the possibility to combine experimental techniques (Raman scattering, dark field spectroscopy, atomic force and electron microscopy). The localized surface plasmon resonance of a dimer has pronounced wavelength and polarization dependencies, and the enhanced near-field resides predominantly in the dimer gap. We reasoned that these properties would also govern the response of the coupled system as seen in plasmon-enhanced Raman scattering. The combination of graphene and a plasmonic dimer should therefore allow one to address the very fundamental aspect of light-matter interaction by PERS.

Dimers consisting of two closely spaced Au nanodiscs (diameter 100 nm, gap 30 nm, height 45 nm) were fabricated on a flat SiO₂ surface and covered with mechanically exfoliated graphene, Fig. 5.1(a). The distance between two dimers was so large such that each dimer acts as an isolated plasmonic structures without the collective resonances. Signal enhancement would only arise from one dimer at the time. We decided to stack graphene on top of the dimers and not the other way around for two primary reasons: it allows to probe the interaction at the nanodisc surfaces and it does not restrict processing steps during dimer fabrication, which may otherwise damage the graphene membrane.

The configuration of the graphene layer placed on top of the dimer is schematically depicted in Fig. 5.1(a). Graphene is suspended across the dimer gap and between the nanodisc edges and the substrate. The corresponding three-dimensional height image

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Figure 5.1. (a) Schematic view of graphene covered plasmonic dimer. (b) 3D Topography of graphene covered dimer as seen by AFM. (c) PERS spectrum of strained graphene on top of the dimers (red) and reference (black). Adapted from Ref. [20].

obtained by AFM given in Fig. 5.1(b). Further away from the dimer, the graphene adheres to the surface of the substrate. This adhesion has two important effects: First, it pulls the suspended graphene in the gap of the dimer, the location of the strongly enhanced near-field. Second, it elongates the graphene, thereby inducing strain in suspended parts of the membrane, reaching maximum strain at the gap.

The combination of the two effects is evident from Fig. 5.1(c), where I compare the plasmon-enhanced Raman spectrum upon resonant excitation of the plasmonic dimer (red) to a reference spectrum (black). The signal enhancement arises exclusively for graphene under strain. The strain softens the vibrational frequency of the phonons. Graphene phonons at the plasmonic hotspot differ in energy from other areas and act as a local probe. This probe is naturally placed in the vicinity of the hotspot, as it is produced by the nanostructure itself. The Raman spectrum upon enhancement in Fig. 5.1(c) contains a twofold set of information; one from the surrounding area and one spectrally redshifted set of peaks arising from the hotspot. The absence of a downshifted D-peak confirms the structural integrity of the graphene membrane. Both the G- and 2D' - peaks allow the estimation of the strain at the plasmonic hotspot [89, 113]. The 2D peak is suitable to quantify the experimentally observed enhancement due to its high intrinsic intensity as well as a comparably large strain-induced shift rate.

The high energy of the 2D peak ($\approx 320 \text{ meV}$) allows one to investigate the regimes of both plasmon-enhanced absorption and emission separately as discussed in Sec. 3.4.1. The enhancement displayed in Fig. 5.1(c) represents enhanced absorption, in agreement with simulations and experimental dark field spectra of our dimer structures. Surprisingly we did not observe enhanced emission for excitation energies for which the 2D-peak overlaps with the plasmonic resonance of the dimer structure. While this does not affect any of the results in this thesis, the lack of enhanced emission is of high interest and subject of ongoing studies, which I will briefly comment on in Sec. 6.

We verified the nature of the enhancement by a combination of spatially resolved, polarization and excitation energy dependent measurements. As the intrinsic Raman intensity of graphene remains unaffected, any changes in intensity are related to the plasmonic enhancement of Raman scattering by the dimer structure. Fig. 5.2 shows a line scan across the dimer structure with the polarization of the excitation set along the dimer axis. It shows that the enhancement arises from a small area in the gap region, which harbors a strongly enhanced light field, Sec. 2.3. Away from this area, the observed Raman intensities dropped immediately. From simulations of the spatial distribution of the near-field intensity we estimated the area of the enhancement. Factoring in this localization we were able to confirm an overall PERS enhancement of the order of 10^3 .

We lifted the localization of the enhancement by choosing the polarization of the excitation (and emission) perpendicular to the dimer axis. In this regime the nanodiscs are not coupled, the overall near-field enhancement drops, and the gap in-between them is free of any enhancing near-field. The discs act as two independent, spatially separated sources of plasmonic particles, which was reflected by a broadened spatial profile of the Raman intensity. The overall enhancement dropped by a factor of 20 compared to the coupled case, which is qualitatively expected as discussed in Sec. 2.3. Rotating the



Figure 5.2. Line scan across the dimer with the increased intensity arising exclusively for downshifted vibrational frequencies from a small area. Taken from the Supporting Information of Ref. [20].

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polarization of the excitation is hence equivalent to switching "on" and "off" the enhanced near-field in the plasmonic cavity formed by the nanodisc dimer.

The final piece of evidence supporting our approach was the Raman response of the graphene-covered dimer upon excitation away from the dimer resonance. No enhancement occurred, and no effect of the polarization on the spatial distribution of the measured Raman signals was observed. This confirmed that the previously observed polarization dependence and spatial distribution of the enhanced Raman signals arose exclusively from the plasmonic response of the dimer structure. The proof of principle results introducing the use of strained graphene to probe plasmonic enhancement from Au nanodimers and the apparent lack of enhanced emission was published in the first of the papers comprising this thesis, Heeg *et al.*, Nano Letters 13(1), 301-308 (2013).

The next logical step was to extend these pioneering results to establish the use of strained graphene as a probe for plasmon-enhanced Raman scattering. To achieve this, we investigated three alternative plasmonic nanoantenna designs as schematized in Fig. 5.3(a). Each of them represents a different class of plasmonic structure. Triple nanodiscs host enhanced near-fields in the two gaps in-between them and can be regarded as an example for complex plasmonic structures with more than one hotspot. The double rods form a dimer whose gap has a high aspect-ratio and sharp edges. The single nanodisc, finally, represents a gapless plasmonic structure and, in a broader sense, isolated nanoparticles of arbitrary shape.



Figure 5.3. (a) Schematic of top view of plasmonic structures, whose height profiles after graphene transfer are shown in (b). (c) PERS spectra ($\lambda_L = 638 \text{ nm}$) of the 2D-peak of the structures shown in (a) and (b), as well as reference spectra (black). Adapted from Ref. [21].

For all three structures the morphology after graphene-coating, see line scans crossing the gaps in Fig. 5.3(b), is on par with the previously investigated nanodisc dimer: the graphene membrane is pulled into the gap(s) by adhesion and is suspended between the edges and the substrate. The Raman spectra in the presence of plasmonic enhancement are shown in Fig. 5.3(c). For the two coupled structures in particular, the enhanced intensity arises exclusively from softened vibrations. This confirms the general applicability of strained graphene as a probe for PERS.

It is interesting to note that the vibrational softening at the hotspots is practically the same for the triple dots and the double rods. Intuitively, one would expect the strain configuration - and hence the frequency of our probe - to differ with the geometry, size and arrangement of the nanoantennas. This is not the case here. Most likely, the strain at the hotspots - and also the topography - represents the equilibrium between the energy stored in adhesion to the substrate and in strain.

The overall enhancement of the Raman signal including hotspot localization amounts to around 100 for all three structures, around an order of magnitude lower that for the nanodisc dimer. We attribute the difference to a generally lower near-field enhancement and/or reduced spectral overlap of the excitation with the plasmonic resonance. The comparably low intensities, on the other hand, indicate the low detection threshold enabled by our approach. Due to the spectral shift of the enhanced Raman signals from the hotspot, even enhancement factors that are five to ten times smaller than the ones displayed in Fig. 5.3(c) are detectable. The outlined extension and generalization of strained graphene as a probe for plasmon-enhanced Raman scattering by plasmonic nanostructures was published in the second paper of this thesis, S. Heeg *et al.*, Physica Status Solidi - Rapid Research Letters 7(12), 1067-1070 (2013).

The second part of this thesis demonstrates an interface between carbon nanotubes and plasmonic nanostructures. Such a system realizes true nanoscale optical coupling a one-dimensional and a zero-dimensional system. To achieve this we made use of our graphene-based characterization scheme in several ways, both in a quantitative and qualitative manner. The most obvious connection is the choice of plasmonic unit. We used the same type of dimer structure, which had shown thousandfold cavity-induced enhancement for graphene. The challenge relied in devising and implementing a method to place a carbon nanotube in the dimer gap.

Together with the Nano-functional Materials group based in Manchester, I identified the dielectrophoretic deposition (DEP) as the promising candidate to interface carbon nanotubes with gapped plasmonic structures. This method assembles CNTs from solution precisely between two sharp metal electrodes, Fig. 5.4(a), between which an alternating

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Figure 5.4. (a) An alternating current (AC) applied between two electrodes assembles carbon nanotubes from solution such that they form an interface with plasmonic nanostructures. (b) AFM image of a small bundle of carbon nanotubes placed in the plasmonic cavity of a nanodisc dimer. (c) Raman spectrum of the small nanotube bundle shown in (b). The polarization of the excitation switches on (red) and off (blue) the cavity. Panels (b) and (c) are taken from Ref. [24].

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current is applied [26, 114]. Nanotubes are deposited as well as oriented predominantly along the axis connecting the electrodes. Ideally, this process is self-limiting. As soon as a nanotube establish a conductive pathway between the electrodes, further tubes are repelled from the region [115]. Typically the deposition occurs simultaneously at hundreds of locations.

Our key idea was to place plasmonic nanostructures between the electrodes, exactly where DEP deposits the nanotubes. The orientation of the structures was chosen according to the desired type of interface. Placing nanodisc dimers in perpendicular orientation between the electrodes allowed assembling tubes inside the dimer gaps as shown in Fig. 5.4(b), reflecting unprecedented accuracy and control over the interface. We confirmed the optical coupling of the dimer resonance and the nanotube by plasmon-enhanced Raman scattering, Figure 5.4(c), following the characterization scheme developed using graphene. For the excitation polarized along the dimer axis (red), the strongly enhanced nearfield in the cavity increased the Raman response of the CNT, namely the *G*-peak and *D*-peak as discussed in Sec. 3.3, by a factor of 30 as compared to the perpendicular polarization(blue). We confirmed the cavity-induced nature of the enhancement by spatially resolved measurement and by choosing an excitation energy away from the dimer resonance. Here we relied on the scheme developed for graphene coupled to dimers.

The polarization behavior is remarkable as it is inverted compared to a nanotube's



Figure 5.5 *G*-mode Raman spectra of a small nanotube bundle placed inside the dimer gap acquired under different experimental conditions. The cavity is only switched on for the matching combination of polarization and excitation (red). The *G*-mode shape is independent of excitation wavelength and polarization and arises from fully symmetric vibrations only. From Ref. [24].

intrinsic response, Sec. 2.2, for which light absorption and scattering polarized perpendicular to the tube axis are strongly suppressed. A careful analysis of the *G*-peak shape, shown in Fig. 5.5, confirmed that this suppression perpetuates to a high degree even in the presence of the high-intensity light fields in the dimer gap: Additional Raman modes associated with light polarizations perpendicular to the tube axis¹ did not appear. The observation of these Raman modes was claimed in the early 2000s [116, 117]. Other studies, e.g. polarization dependent measurements on isolated nanotubes, reported their suppression [118]. Subsequently, the topic was controversially discussed in the nanotube Raman community. More recently, there has been a consensus these that Raman are suppressed by depolarization in conventional Raman scattering. It was hypothesized, however, that they may appear in near-field measurements, e.g. tip-enhanced Raman scattering [109]. Our study confirmed that vibrations associated with light polarizations perpendicular to nanotube axis are impossible to observe. We provided the final piece of evidence to settle the discussion which has been going on the literature for over a decade.

The key to understanding the nature of the enhancement was a close investigation of the relative orientation of the nanotube within the cavity. Fig. 5.4(b) shows that the tube was not oriented strictly perpendicular to the dimer axis but rather at an angle of 75° , allowing the partial interaction of CNT and light inside the cavity. Compared to this nanotube, others oriented at almost 90° showed a 20-fold drop in Raman enhancement.

¹I provided a detailed discussion of these modes and the associated selection rules in the Supporting information of Ref. [24].

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We concluded that the experimentally observed Raman signals of CNTs in plasmonic cavities predominantly arise from projection of the enhanced near-field polarization on the tube axis.

This has several important consequences: First, it allowed us to factor in the depolarization effect (×8) in the overall enhancement. In combination with signal localization (×9) as seen in spatially resolved measurements this led to an overall enhancement $\geq 10^3$, in agreement with the values obtained for graphene coupled to dimers. Secondly, it generally allows one to address the intrinsic optical response of the cavity and the tube individually by the choice of polarization. In our case this coincided with an energetic separation between the resonances of the dimer plasmon and the nanotube.

The true strength of DEP as implemented here lies in its flexibility. Beyond placing tubes in nanometer sized gaps, we suspended them across dimers formed by rods or over a single nanodisc. The exact shape and composition of the nanoantennas did not influence the nanotubes deposition. This will allow tuning the optical response of the plasmonic hotspot in the future, by choice of the appropriate shape, size, geometry and material of the plasmonic antenna. The optical resonances of the nanotubes, on the other hand, can be tuned by the appropriate choice of starting material, e.g. chirality enriched suspensions. The concept of using dielectrophoretic deposition (DEP) of carbon nanotubes for the assembly of nanoplasmonic-nanotube systems by directing the tubes onto Au plasmonic antennas was published in S. Heeg *et al.*, Nano Letters 14(4), 1762-1768 (2014).

In the last paper forming the body of this thesis, S. Heeg *et al.*, Physica Status Solidi - Rapid Research Letters $\mathbf{8}(9)$, 785-789 (2014), I showed that the orientation of a tube inside the cavity can be as effective for generating Raman enhancement as placing the tube precisely at the plasmonic hotspot. This confirmed the polarization dependence which we observed earlier. To the best of my knowledge, this study represents the first report on plasmon-enhanced Raman scattering by suspended carbon nanotubes.

A small tube bundle was partially suspended in the cavity, Fig. 5.6 (a). Despite the lack of spatial overlap with the near-fields of highest intensity in the very center of the gap, the CNT showed considerable cavity induced enhancement, Fig. 5.6 (b). The unusual location, on the other hand, realized a relatively good alignment (45°) of the nanotube axis with the polarization of the cavity near-fields, much higher than for the tubes crossing the gap perpendicularly, which I discussed previously [24]. For this angle, the enhancement factor due to polarization projection was four, much lower than for tubes crossing the cavity. Nevertheless the overall enhancement was on the order 10^3 . Together with the spectral overlap of the tube resonance and the excitation energy, this provided a strong indicator that the enhancement factors in Ref. [24] represent a lower boundary and are in fact up



Figure 5.6. (a) Schematic of small CNT bundle partially suspended inside a plasmonic dimer cavity. (b) Plasmon-enhanced (red) and pristine (blue) Raman spectra of the tube segments in the cavity shown in (a). From Ref. [25].

to an order of magnitude higher.

The tube segments subject to enhancement did not show any signs of mechanical stress or any kind of static or dynamic doping. This is important if one is interested in investigating the interaction of nanotubes and plasmonic structures by plasmonenhanced emissive processes such as electro- or photoluminescence. Such measurements are preferentially performed on suspended carbon nanotubes, as the interaction with the substrate often quenches the luminescence. Suspending the tubes using the plasmonic antennas themselves, on the other hand, requires direct physical contact with the metal structures. The absence of doping for the suspended tube shows that such quenching is unlikely to occur using our assembly scheme. It makes CNTs suspended in plasmonic cavities a viable experimental configuration.

6 Summary and outlook

In this thesis, I have realized the optical coupling of graphene and carbon nanotubes to metallic nanostructures in new and unprecedented ways. For both of theses lowdimensional systems, I verified by plasmon-enhanced Raman scattering their interaction with the high intensity electromagnetic near-field at plasmonic hotspots. Strained graphene locally probes the near-field of gapped plasmonic nanoantennas by serving as a twodimensional detector with an intrinsically constant Raman response. Dimer cavities generate Raman signal enhancements up to 10^3 and induce the strain probe in the graphene membrane. Carbon nanotubes inside comparable cavities show the same or even larger enhancement while preserving their highly anisotropic optical response. The nanotube-dimer interface on a single device level was achieved by directed dielectrophoretic deposition.

The strength of both systems lies in the high degree of control over the interface in the experiments. The optical responses of both the plasmonic elements and graphene/CNTs are well know and are preserved upon combination. The focus on isolated plasmonic structures made it possible to characterize the topography of the interface to a high degree. The combination of both aspects enabled me to describe the optical coupling of plasmonic dimers to graphene and tubes in great detail. The unique combination of methods realized in creating the nanoscale coupled systems presented here form the basis for a range of ongoing and future studies that I will describe and comment on in the following.

The most interesting observation from a fundamental point of view is certainly the apparent lack of plasmon-enhanced emission of Raman scattered light for graphene. In the course of this thesis, all experiments conducted on various plasmonic structures interfaced with graphene lacked enhancement for 532 nm excitation. For clarity, I compare in Fig. 6.1(a) the energies of the excitation and Raman lines for the regimes of enhanced absorption (red) and emission (green), together with the dark field spectrum of the gold dimer discussed by us in Ref. [20]. If plasmon-enhanced emission were present, the coupled



Figure 6.1. (a) Dark field spectrum of gapped plasmonic dimer plotted together with the laser excitation and graphene Raman emission wavelengths for the regimes of enhanced absorption (red) and emission (green). (b) *G*-peak Raman spectrum (red) of highly strained graphene on top of plasmonic dimer. The shift of 80 cm^{-1} compared to the reference (black) corresponds to a tensile strain of ~ 2.8%. Panel (a) is adapted from Ref. [20]. The data in (b) is unpublished.

and uncoupled resonances of all antennas (single discs, dimers, trimers, with different sizes and geometries) must be shaped such that they show up to thousandfold enhancement at 638 nm but no measurable interaction with light occurs for 616 nm, the emission wavelength of the 2D-mode for 532 nm excitation. This scenario seems unrealistic for the width of the plasmon resonance observed by dark field spectroscopy, Fig. 6.1(a), more so if we take into account the low detection threshold provided by strained graphene as a probe. Beyond very weak or entirely absent plasmon-enhanced emission, our observations are in principle compatible with very narrow plasmonic resonances, much sharper than the dark-field spectrum in Fig. 6.1(a) suggests. This would lead to scenarios where the G- and 2D-mode emission wavelengths probe different energetic regimes of enhanced emission independently.

An explanation for above behavior is currently developed in the Reich group at FU Berlin. From the theory side, the interference between classical and quantum mechanical Raman scattering channels may provide a suitable explanation for the apparent lack of enhanced emission for graphene coupled to plasmonic structures. Experimentally, further insight is gained by measuring resonant Raman profiles of individual graphene covered dimers. Here the excitation is swept over a large energy range such that all regimes of enhancement are covered. These measurements are challenging, as the sensitivity is low compared to spectrometers optimized for one or few excitation wavelengths. They represent, on the other hand, the first application of strained graphene as a probe for PERS; enhanced Raman peaks are clearly and unequivocally identified by their energy.

Graphene is most prominent member of a growing family of two-dimensional materials with a variety of properties [119, 120]. Monolayer transition-metal dichalcogenides, for instance, are semiconductors with direct band gaps ranging from the visible to the infrared, while hexagonal boron-nitride is a two dimensional wide band gap (>5 eV) semiconductor. Like graphene, these materials can be exfoliated mechanically and transferred onto other substrates, which makes them candidates for interfacing them with plasmonic structures. PERS may then be studied for materials with e.g. electronic transitions energetically close to the plasmonic resonance. Similar to graphene, some these of two-dimensional systems have Raman active phonons which are independent of the polarization of incident and scattered light. The characterization schemes for PERS on graphene developed in this thesis can thus be partially or entirely applied.

Beyond probing enhanced near-fields, strain in graphene is of scientific interest [121], as it allows one to mechanically alter the properties of graphene. Inhomogeneous strain, for instance, may result in internal magnetic fields of up to 10 Tesla in the graphene membrane [122]. As shown in this thesis, plasmonic nanostructures can induce local inhomogeneous strain in graphene, and simultaneously provide the means of local detection by PERS. Such local optical probing by Raman spectroscopy is typically not available for alternative methods used to create nonuniform strain [123]. By enhancing the adhesion to the substrate through surface treatment, we surpassed the previously measured strain values (< 1%). The highest tensile strain observed so far for graphene on plasmonic dimers is 2.8%, with the corresponding G-peak spectrum shown in Fig. 6.1(b).

Carbon nanotubes offer a great flexibility for optical coupling. Selected nanotube chiralities exhibit different energetic orders and distances of the plasmonic and the nanotube excitonic resonance. The required suspensions of monochiral tubes are available in high quality and have been successfully deposited by dielectrophoresis [28, 29]. Studying single nanotubes of specific chirality will help for understanding the nature of plasmon-enhanced Raman scattering. One particular question is to what extent — or if at all — an energetic overlap between the resonances of tube and dimer is required for the plasmonic enhancement of Raman signals. This is related to the small nanotube bundle I studied in Ref. [24]. Within the sensitivity of the experiment, it lacked an intrinsic response for the excitation matching the plasmonic resonance. Without knowing the exact chiralities of all tubes forming the bundle, however, the possibility of non-resonant Raman scattering in

6. Summary and outlook



Figure 6.2. A nanotube bundle crossing a nanodisc (left) is moved into the dimer gap (right) by the tip of an atomic force microscope. Only after moving the nanotube, plasmon-enhanced Raman signals occur. The data is not published.

carbon nanotubes cannot investigated. Efforts to deposit isolated nanotubes of predefined chirality in plasmonic dimers are currently undertaken.

To further study and confirm the position and polarization dependence of PERS by nanotubes, we conduct efforts to alter the position and the orientation of nanotubes in hotspots after DEP. An example of such nanoscale manipulation is shown in Fig. 6.2. The AFM picture in (a) shows a nanotube bundle crossing one nanodisc of a plasmonic dimer. A gentle push by the tip of the AFM moved the bundle into the gap and changed the relative orientation of its segments, Fig. 6.2 (b). Cavity-induced Raman enhancement occurred only after the bundle was moved in the hotspot.

Beyond Raman scattering, the assembly scheme developed in this thesis provides the means to study the interaction between nanotubes and plasmonic structures by alternative techniques. Time resolved spectroscopy of plasmonic enhancement, for instance, will find the time scales of the interaction between the metal plasmon and the nanotube's excitons. More intriguing, however, are electrical measurement performed on a CNT placed in plasmonic dimers as depicted in Fig. 6.3(a). The electrodes used for dielectrophoresis serve as source and drain contacts, and a gate voltage is applied via the silicon substrate. Plasmon-enhanced photocurrent generation electrically probes the light absorption and charge carrier generation by near-fields at the dimer gap. Similar to our PERS experiment, the polarization of the excitation will switch on and off the plasmonic cavity and provides an ideal built-in reference.

Dielectrophoretic deposition of carbon nanotubes is a highly scalable process, and integration densities of several million devices per square centimeter have been achieved [115]. So far we have used this scalability to assemble, identify and investigate optimal interfaces.



Figure 6.3. (a) DEP assembles a nanotube for plasmon-enhanced photocurrent detection. The enhanced near-field in the dimer cavity increases light absorption. The resulting photoexcited charge carriers (blue arrows) are extracted by the electrodes used for dielectrophoresis. (b) Schematic of plasmon-enhanced photodetector where multiple tubes harvest charge photoexcited carriers from generated by an assembly of plasmonic hotspots.

Only about 2-3% of the devices were suitable for PERS studies. Here I define suitable to refer only to devices with nanotubes placed in the dimer gap without additional tubes in the immediate vicinity. Other tubes hamper optical characterization at the level of depth conducted in this thesis. A photodetector based on our nanotube-nanoplasmonic interfaces is not bound to such restrictions. It will consist of multiple carbon nanotubes interfaced with extended plasmonic nanostructures which contain several hotspots, Fig. 6.3(b). The enhanced near-fields in each hotspot increase the nanotubes' light absorption. The photoexcited charge carriers are collected at the electrodes.

In a device as sketched in Fig. 6.3(b) a sufficient number of tubes will be subject to the enhanced near-field. The nanotube and electrode material will be optimized for charge carrier extraction, e.g. using paladium electrodes to minimize the contact resistance with the nanotube. It is important to note that all constituent parts of a nanotube-nanoplasmonic photodetector and its assembly can be scaled up to wafer size. This is particular relevant for the fabrication of the plasmonic nanostructures, which coercively requires electron-beam lithography. This technology is on its way to become increasingly available at scales and operation speeds necessary of technological exploitation [124].

In conclusion, this discussion of research projects that are currently underway demonstrate that coupling plasmonic nanostructures to graphene and carbon nanotubes, as accomplished in this thesis, is only the founding ground work. Many steps in different directions are to follow. The interfaces created and described will help to clarify the fundamentals of plasmon-enhanced Raman scattering. Beyond PERS, they will allow us to address fundamental and complex interactions between plasmons and low dimensional solid state systems. A scalable route to plasmon-enhanced photodetection and its transition to technology is opened.

Appendix

A Experimental methods

A.1. Raman spectrometers

The Raman measurements published in the papers that form this thesis were taken on either a *Horiba Jobin Yvon XplorA* or a *Witec Alpha 300*. Both systems are single-grating Raman spectrometers. In the following, I will briefly describe the basic setup of these spectrometers shown in Fig. A.1, which can be divided into a microscopic unit and a spectrometer unit. I point out the specifics of each instrument where applicable.

The excitation laser (dotted arrows in Fig. A.1) is coupled into the central beam path of the microscope unit upon reflection from a beam splitter. The intensity of the laser is regulated either by an internal set of interchangeable filters of varying optical density (Xplora) or by adjusting the intensity with an external step less aperture (*Alpha 300*). The light is then guided through an objective which focusses the laser on the sample. The size of the focal spot depends on the numerical aperture (NA) in combination with the



Figure A.1. Schematics of single-grating Raman spectrometer. Adapted from Ref. [125].

A. Experimental methods

wavelength of the excitation. For the measurements in this thesis, I mostly used $100 \times$ objectives with NA= 0.95. While the diffraction limit in principle allows beam diameters similar to or smaller than the wavelength of the excitation, realistic experimental setups achieve spots diameters around $1 \,\mu$ m. The sample itself is placed on a piezoelectric stage with three axes. Lateral movement allows spatial mapping and height adjustment enables the fine tuning of the focus via the stage.

The Raman scattered light is collected by the same objective used for focussing the laser, realizing a backscattering configuration. It is then guided back on the central optical beam bath, together with Rayleigh scattered and reflected laser light (black arrow). A swing-away beam splitter enables imaging of the laser spot and the sample on a camera such that the desired area can be selected for measurements. Edge filters prevent light at the wavelength of the laser from entering the body of the spectrometer, Only light of lower energy such as photoluminescence and Raman signals are transmitted. Every laser wavelength requires a specific edge filter. The filters are changed either manually together with other optical components (*Alpha 300*) or a motorized filter drawer (*Xplora*). A $\lambda/2$ -plate combined with an analyzer allows to measure the polarization dependence of the Raman intensity. An adjustable pinhole can realize confocality, which restricts the spatial depth of the scattering volume. For low-dimensional system like carbon nanotubes and graphene, this is typically not necessary.

After the pinhole, the Raman scattered light enters the spectrometer trough the entrance slit. It is then focussed on an grating which disperses the light onto a silicon-based charge coupled device (CCD), where the Raman spectrum is recorded. The focal length of the spectrometer - corresponding to the distance between grating and CCD in Fig. A.1 - defines the resolution of the spectrometer, together with the total number of grooves of the grating and the width of the entrance slit. The *Alpha 300* has two and the *Xplora* has four gratings, which range from 600 to 2400 grooves/mm. For the latter and 532 nm excitation, and resolution of around 2 cm^{-1} can be achieved.

For the Alpha 300, the setup between the edge filter and the dispersive grating deviates from Fig. A.1. Instead of a direct optical beam path, the microscope and spectrometer units are connected by an optical fiber. The fiber acts as a pinhole and as the entrance slit of the spectrometer. The choice of spectrometer for a particular measurement is given by the strengths of each of them: The Xplora allows higher resolution and is optimized for high sensitivity. It is particularly suited for point measurements or small maps. The Alpha 300, on the other hand, is optimized for large area mapping. It allows very fast acquisition times in the millisecond range and the software brings superior tools for data handling and parameter extraction.

A.2. Atomic force microscope

An atomic force microscope (AFM) measures the topography of a sample by dragging a sharp tip over the surface of the sample. The tip itself is mounted on a cantilever, Fig. A.2. Several operational modes are possible. In contact mode, the tip touches the sample during a scan. Changes in the morphology of the sample deflect the tip and hence the cantilever. The cantilever moves up or down to compensate for the deflection of the tip. This movement is recorded and represents the topography of the sample. In non-contact or tapping mode, the tip does not touch the sample but oscillates at a certain distance away from the surface at kilohertz frequencies. It is deflected from the sample by van-der-Waals forces.

The horizontal and vertical changes of the tip position are measured indirectly by the cantilever that is equipped with a reflective coating. A low-power laser is aligned onto the cantilever such and reflected into a photodetector. Upon deflection, the reflection of the cantilever moves across the detector and is translated into the movement of the tip. Typically, the sample itself is mounted on a piezo stage for lateral movement, and the cantilever is equipped with a piezo drive to change its relative height position.

All but one measurement in this thesis were conducted in non-contact mode using a $Park \ XE150$. It has a good height resolution and allows to identify carbon nanotubes as well as graphene. The lateral resolution represent the folding of the tip shape and the



XYZ piezo stage

Figure A.2. Schematics of an atomic force microscope.

A. Experimental methods

topography. For this reason, carbon nanotubes measured in tapping mode may shows widths of up to fifty nanometers. I avoided using contact mode in all Experiments, to avoid moving nanotubes or even rapturing the graphene membrane.

B German abstract

B.1. Kurzfassung

Das physikalische Gebiet der Plasmonik beschreibt Wechselwirkungsprozesse zwischen elektromagnetischen Feldern und freien Elektronen in Metallen. Die optischen Nahfelder in der unmittelbaren Umgebung der Metalle weisen hohe Intensitäten auf. Metallische Nanostrukturen führen zu plasmonischen Hotspots, in denen hohe Feldstärken auf kleinste Volumen konzentriert sind. Die Absorption und Streuung von Licht steigt dort immens an. In der vorliegenden Arbeit untersuche ich mittels Ramanspektroskopie die inelastische Streuung von Licht an Graphen und Kohlenstoffnanoröhren unter dem Einfluss plasmonisch verstärkter Nahfelder. Zunächst führe ich das Konzept verspannten Graphens als Sonde zur Messung plasmonisch verstärkter Ramanstreuung ein. Im Anschluss untersuche ich die Wechselwirkung von Kohlenstoffnanoröhren mit plasmonischen Nahfeldern mittels Ramanstreuung. Die Kopplung von Nanoröhren mit Bereichen hoher Nahfeldintensität erreiche ich durch gezieltes dielelektrophoretisches Abscheiden der Nanoröhren auf plasmonische Strukturen.

Ein plasmonischer Dimer wurde mit Graphen belegt und per Ramanstreuung charakterisiert. Die hohe Nahfeldintensität in der Dimerkavität verstärkte das Graphensignal tausendfach. Die verstärkten Signale stammen ausschliesslich von verspanntem Graphen. Verspannung verschiebt die Vibrationsfrequenzen im Graphen; die Verspannung im Graphen entspricht somit einer lokalen Sonde für die plasmonisch verstärkten Nahfelder. Diese Sonde befindet sich automatisch am richtigen Ort, da sie von der Nanostruktur selbst erzeugt wird. Wir verifizierten die Verstärkung durch ortsaufgelöste Ramanmessungen mit unterschiedlichen Anregungsenergien und -polarisationen. Unsere Methode delektiert die direkte Wechselwirkung von Graphen mit verstärkten Nahfeldern misst: Das intrinsische Ramansignal von Graphen hängt weder von der Polarization noch von der Wellenlänte des einbestrahlten Lichtes ab.

Für in der Kavität plasmonischer Dimere platzierte Kohlenstoffnanoröhren konnten

B. German abstract

wir Verstärkungen der Ramansignale in der Grössenordnung 10³ bis 10⁴ beobachten. Es gelang es uns, die intrinsischen Resonanzen der Nanoröhren und die externen Resonanzen der Dimere durch die Wahl von Anregungspolarisation und -energie getrennt zu detektieren. Dies zeigte unter anderem, dass plasmonenverstärkte Ramanstreuung an Kohlenstoffnanoröhren mit der Projektion der Nahfeldpolarisation auf die Achse der Nanoröhre skaliert. Desweiteren konnten wir zeigen, das selbst unter Einfluss starker Nahfelder ausschliesslich vollsymmtrische Phononen zum Ramanspektrum von Kohlenstoffnanoröhren beitragen: Ramanmoden, die für ihre Anregung Lichtpolarisationen rechtwinklig zur Achse der Nanoröhre benötigen, können nicht beobachtet werden. Dies klärt eine langjährigen wissenschaftliche Debatte über die Symmetrie der Phononen in Nanoröhren. Das zielgerichtete Ablegen von Kohlenstoffnanoröhren in die Kavitäten metallischer Dimere gelang uns per dielektrophoretischer Abscheidung der Nanoröhren auf die Nanostrukturen. Dieses von uns entwickelte Verfahren stellt in einer verallgemeinerten Form eine neuartige Methode zur Verknüpfung von Kohlenstoffnanoröhren mit plasmonische Systeme dar.

Die in dieser Doktorarbeit entwickelten experimentellen und konzeptionellen Methodiken zur Kopplung von Graphen und Kohlenstoffnanoröhren an plasmonische Strukturen werden es in der Zukunft ermöglichen, die fundamentalen Grundlagen plasmonisch-verstärkter Ramanstreuung zu ergründen.

C | Papers as published

For copyright reasons, the four publications comprising this cummulative thesis are not included in the online version. The publications are listed below together with their digital object identifiers.

- Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene.
 S. Heeg, R. Fernandez-Garcia, A. Oikonomou, F. Schedin, R. Narula, S.A. Maier, A. Vijayaraghavan, and S. Reich. Nano Letters 13(1), 301-308 (2013). http://dx.doi.org/10.1021/nl3041542
- 2. Strained graphene as a local probe for plasmon-enhanced Raman scattering by gold nanostructures.

S. Heeg, A. Oikonomou, R. Fernandez-Garcia, S.A. Maier, A. Vijayaraghavan, and S. Reich.

Physica Status Solidi - Rapid Research Letters 7(12), 1067-1070 (2013). http://dx.doi.org/10.1002/pssr.201308145

- Plasmon-Enhanced Raman Scattering by Carbon Nanotubes Optically Coupled with Near-Field Cavities.
 S. Heeg, A. Oikonomou, R. Fernandez-Garcia, C. Lehmann, S.A. Maier, A. Vijayaraghavan, and S. Reich.
 Nano Letters 14(4), 1762-1768 (2014).
 http://dx.doi.org/10.1021/n1404229w
- Plasmon-enhanced Raman scattering by suspended carbon nanotubes.
 S. Heeg, N. Clark, A. Oikonomou, A. Vijayaraghavan, and S. Reich. Physica Status Solidi - Rapid Research Letters 8(9), 785-789 (2014). http://dx.doi.org/10.1002/pssr.201409253

Acknowledgements

Throughout my years at Freie Universität Berlin, I received help, support and assistance by many people. I want to use this opportunity to thank...

... my supervisor, Stephanie Reich, for her guidance, encouragement and support in the course this thesis. I owe her my scientific education, and learned from her how to approach things in a much wider context. I was fortunate to be given the freedom to explore what I wanted to pursue, but also to receive support during the "dark times", when nothing worked out at all. She was always available for countless discussions and chats, which often evolved from the one, very brief question I originally brought along.

... the members of AG Reich for all the good work and all the good fun, in particular Benjamin Hatting, André Boden, Pascal Blümmel, Heiko Dumlich, Friedericke Ernst, Izabela Firkowska, Mareeni Gläske, Philip Klar, Patryk Kusch, Christian Lehmann, Gudrun May-Nasseri, Antonio Setaro.

... the Manchester *NanoFunc* crew, for making and providing all these wonderful samples which I never stopp(ed) burning. Thanks to Aravind Vijayaraghavan, Nick Clark and Antonios Oikonomou, with whom I form the successful *Wurst-Feta* conglomerate.

... Roberto Fernandez-Garcia and Stefan Maier from Imperial College London, who introduced me to the world of plasmonics.

... all the other members of the *NanoSpec* project for the scientific discussions and the fun times during all our meetings. Thanks Talia Jeshua, Aaron Lewis, Kirsten Strain, and Eleanor Campbell.

... all the other people from the scientific community that helped me during this PhD in

C. Papers as published

the form of bouncing around ideas and thoughts (with or without a drink) or by providing samples of all forms.

... Janina Maultzsch for being my co-supervisor.

... my friends and my family for the continous support that made the whole thing here possible. Thank you!

Eidesstattliche Erklärung

Hiermit versichere ich, daß ich alle verwendeten Hilfsmittel und Hilfen angegeben und die vorliegende Arbeit auf dieser Grundlage selbstständig verfasst habe. Diese Arbeit ist nicht schon einmal in einem früheren Promotionsverfahren eingereicht worden.

Sebastian Heeg
- S. A. Maier. Plasmonics: Fundamentals and Applications. Springer, Berlin, Germany (2007).
- [2] M. Fleischmann et al. Raman spectra of pyridine adsorbed at a silver electrode. Journal of Photochemistry and Photobiology A: Chemistry, 26(2): 163–166 (1974).
- [3] D. L. Jeanmaire et al. Surface raman spectroelectrochemistry. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 84(1): 1–20 (1977).
- [4] P. K. Aravind *et al.* The interaction between electromagnetic resonances and its role in spectroscopic studies of molecules adsorbed on colloidal particles or metal spheres. *Surface Science*, **110**(1): 189–204 (1981).
- [5] M. Moskovits. Surface-enhanced Raman spectroscopy: a brief retrospective. Journal of Raman Spectroscopy, 36(6-7): 485–496 (2005).
- [6] J. A. Creighton *et al.* Plasma resonance enhancement of Raman scattering by pyridine adsorbed on silver or gold sol particles of size comparable to the excitation wavelength. *Journal of the Chemical Society, Faraday Transactions 2*, **75**: 790 (1979).
- [7] K. Kneipp et al. Single molecule detection using surface-enhanced Raman scattering (SERS). Physical Review Letters, 78(9): 1667–1670 (1997).
- [8] S. Nie *et al.* Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering. *Science*, 275(5303): 1102–1106 (1997).
- [9] P. G. Etchegoin *et al.* A perspective on single molecule SERS: current status and future challenges. *Physical Chemistry Chemical Physics*, **10**(40): 6079–6089 (2008).
- [10] C. M. Galloway *et al.* Plasmon-Assisted Delivery of Single Nano-Objects in an Optical Hot Spot. *Nano Letters*, **13**(9): 4299–4304 (2013).

- [11] L. Novotny et al. Antennas for light. Nature Photonics, 5(2): 83–90 (2011).
- M. Moskovits. Surface-enhanced spectroscopy. Reviews of Modern Physics, 57: 783–826 (1985).
- [13] J. A. Dieringer *et al.* Surface-Enhanced Raman Excitation Spectroscopy of a Single Rhodamine 6G Molecule. *Journal of the American Chemical Society*, 131(2): 849–854 (2009).
- [14] A. N. Grigorenko et al. Graphene plasmonics. Nature Photonics, 6(11): 749–758 (2012).
- [15] R. R. Nair *et al.* Fine structure constant defines visual transparency of graphene. *Science*, **320**(5881): 1308 (2008).
- [16] R. V. Maximiano *et al.* Mechanism of near-field Raman enhancement in twodimensional systems. *Physical Review B*, 85(23): 235434 (2012).
- [17] F. Schedin *et al.* Surface-Enhanced Raman Spectroscopy of Graphene. ACS Nano, 4(10): 5617–5626 (2010).
- [18] Z. Fang *et al.* Graphene-Antenna Sandwich Photodetector. *Nano Letters*, **12**(7): 3808–3813 (2012).
- [19] S. Reich et al. Raman spectroscopy of graphite. Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 362(1824): 2271–2288 (2004).
- [20] S. Heeg *et al.* Polarized Plasmonic Enhancement by Au Nanostructures Probed through Raman Scattering of Suspended Graphene. *Nano Letters*, **13**(1): 301–308 (2013).
- [21] S. Heeg et al. Strained graphene as a local probe for plasmon-enhanced Raman scattering by gold nanostructures. *Physica Status Solidi-Rapid Research Letters*, 7(12): 1067–1070 (2013).
- [22] S. Reich et al. Carbon Nanotubes: An Introduction to the Basic Concepts and Physical Properties. Wiley-VCH, Weinheim, Germany (2004).
- [23] L. X. Zheng *et al.* Ultralong single-wall carbon nanotubes. *Nature Materials*, 3(10): 673–676 (2004).

- [24] S. Heeg et al. Plasmon-Enhanced Raman Scattering by Carbon Nanotubes Optically Coupled with Near-Field Cavities. Nano Letters, 14(4): 1762–1768 (2014).
- [25] S. Heeg et al. Plasmon-enhanced Raman scattering by suspended carbon nanotubes. Physica Status Solidi-Rapid Research Letters, 8(9): 785–789 (2013).
- [26] R. Krupke *et al.* Simultaneous Deposition of Metallic Bundles of Single-walled Carbon Nanotubes Using Ac-dielectrophoresis. *Nano Letters*, 3(8): 1019–1023 (2003).
- [27] A. Vijayaraghavan *et al.* Dielectrophoretic Assembly of High-Density Arrays of Individual Graphene Devices for Rapid Screening. ACS Nano, 3(7): 1729–1734 (2009).
- [28] A. Vijayaraghavan *et al.* Toward Single-Chirality Carbon Nanotube Device Arrays. ACS Nano, 4(5): 2748–2754 (2010).
- [29] A. Vijayaraghavan. Applications of chirality-sorted individual single-wall carbon nanotube devices. Journal of Materials Chemistry, 22(15): 7083 (2012).
- [30] F. Wang et al. The optical resonances in carbon nanotubes arise from excitons. Science, 308(5723): 838–841 (2005).
- [31] J. Maultzsch et al. Exciton binding energies in carbon nanotubes from two-photon photoluminescence. *Physical Review B*, 72(24): 241402 (2005).
- [32] P. Avouris *et al.* Carbon-nanotube photonics and optoelectronics. *Nature Photonics*, 2(6): 341–350 (2008).
- [33] N. M. Gabor *et al.* Extremely Efficient Multiple Electron-Hole Pair Generation in Carbon Nanotube Photodiodes. *Science*, **325**(5946): 1367–1371 (2009).
- [34] X. Gan *et al.* Chip-integrated ultrafast graphene photodetector with high responsivity. *Nature Photonics*, 7(11): 883–887 (2013).
- [35] Z. Sun *et al.* Graphene and graphene-like two-dimensional materials in photodetection: mechanisms and methodology. ACS Nano, 8(5): 4133–4156 (2014).
- [36] N. M. Gabor *et al.* Hot Carrier-Assisted Intrinsic Photoresponse in Graphene. *Science*, **334**(6056): 648–652 (2011).
- [37] T. J. Echtermeyer *et al.* Strong plasmonic enhancement of photovoltage in graphene. *Nature Communications*, 2: 458 (2011).

- [38] Z. Fang *et al.* Plasmon-Induced Doping of Graphene. ACS Nano, 6(11): 10222–10228 (2012).
- [39] T. Hosseini *et al.* On plasmon-induced photocurrent and doping of metal-patterned graphene. *Applied Physics Letters*, **105**(4): 043104 (2014).
- [40] K. S. Novoselov *et al.* Electric field effect in atomically thin carbon films. *Science*, 306(5696): 666–669 (2004).
- [41] A. K. Geim *et al.* The rise of graphene. *Nature Materials*, **6**(3): 183–191 (2007).
- [42] A. H. Castro Neto et al. The electronic properties of graphene. Reviews of Modern Physics, 81(1): 109–162 (2009).
- [43] F. Bonaccorso *et al.* Graphene photonics and optoelectronics. *Nature Photonics*, 4(9): 611–622 (2010).
- [44] X. Du et al. Approaching ballistic transport in suspended graphene. Nature Nanotechnology, 3(8): 491–495 (2008).
- [45] F. Xia et al. Ultrafast graphene photodetector. Nature Nanotechnology, 4(12): 839–843 (2009).
- [46] J. C. Meyer *et al.* Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes. *Nano Letters*, 8(11): 3582–3586 (2008).
- [47] P. Wallace. The Band Theory of Graphite. Physical Review, 71(9): 622–634 (1947).
- [48] S. Reich *et al.* Tight-binding description of graphene. *Physical Review B*, **66**(3): 035412 (2002).
- [49] M. I. Katsnelson *et al. Graphene*. Carbon in Two Dimensions. Cambridge University Press, Cambridge, UK (2012).
- [50] S. Iijima. Helical microtubules of graphitic carbon. Nature, 354(6348): 56–58 (1991).
- [51] S. Iijima et al. Single-shell carbon nanotubes of 1-nm diameter. Nature, 363(6430): 603–605 (1993).
- [52] D. S. Bethune *et al.* Cobalt-catalysed growth of carbon nanotubes with singleatomic-layer walls. *Nature*, **363**(6430): 605–607 (1993).

- [53] S. J. Tans *et al.* Room-temperature transistor based on a single carbon nanotube. *Nature*, **393**(6680): 49–52 (1998).
- [54] A. Javey *et al.* Ballistic carbon nanotube field-effect transistors. *Nature*, **424**(6949):
 654–657 (2003).
- [55] E. Pop *et al.* Thermal conductance of an individual single-wall carbon nanotube above room temperature. *Nano Letters*, **6**(1): 96–100 (2006).
- [56] M. Treacy *et al.* Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature*, **381**: 678–680 (1996).
- [57] C. Thomsen *et al.* Raman scattering in carbon nanotubes. In *Light Scatteriung in Solids IX*, edited by M. Cardona and R. Merlin, Springer Verlag, Berlin, Germany, vol. 108 of *Topics in Applied Physics* (2007).
- [58] N. Hamada et al. Phys. Rev. Lett. 68, 1579 (1992): New one-dimensional conductors: Graphitic microtubules. *Physical Review Letters*,68(10): 1579–1581 (1992).
- [59] R. Saito et al. Electronic structure of graphene tubules based on C60. Physical Review B, 46(3): 1804–1811 (1992).
- [60] T. Ando. The electronic properties of graphene and carbon nanotubes. NPG Asia Materials, 1(1): 17–21 (2009).
- [61] H. Ajiki et al. Aharonov-Bohm effect in carbon nanotubes. Physica B: Condensed Matter, 201: 349–352 (1994).
- [62] L. X. Benedict *et al.* Static polarizabilities of single-wall carbon nanotubes. *Physical Review B*, **52**(11): 8541 (1995).
- [63] S. Tasaki *et al.* pi-band contribution to the optical properties of carbon nanotubes: Effects of chirality. *Physical Review B*, 57(15): 9301–9318 (1998).
- [64] L. C. Qin *et al.* Materials science The smallest carbon nanotube. *Nature*, 408(6808): 50–50 (2000).
- [65] M. Damnjanović. Standard components of polar and axial vectors for quasi onedimensional systems. *Physics Letters A*, 94(8): 337–339 (1983).
- [66] H. Kataura *et al.* Optical properties of single-wall carbon nanotubes. Synthetic Metals, **103**(1-3): 2555–2558 (1999).

- [67] R. Saito *et al.* Trigonal warping effect of carbon nanotubes. *Physical Review B*, 61(4): 2981–2990 (2000).
- [68] P. Y. Yu et al. Fundamentals of semiconductors. Springer Verlag, Berlin, Germany (2005).
- [69] C. D. Spataru *et al.* Quasiparticle and excitonic effects in the optical response of nanotubes and nanoribbons. *Carbon nanotubes*, **111**: 195–227 (2008).
- [70] J. Maultzsch *et al.* Radial breathing mode of single-walled carbon nanotubes: Optical transition energies and chiral-index assignment. *Physical Review B*, **72**(20): 205438 (2005).
- [71] K. A. Willets et al. Localized Surface Plasmon Resonance Spectroscopy and Sensing. Annual Review of Physical Chemistry, 58(1): 267–297 (2007).
- [72] K. M. Mayer *et al.* Localized surface plasmon resonance sensors. *Chemical Reviews*, 111(6): 3828–3857 (2011).
- [73] P. B. Johnson *et al.* Optical Constants of the Noble Metals. *Physical Review B*, 6(12): 4370–4379 (1972).
- [74] J. J. Mock *et al.* Shape effects in plasmon resonance of individual colloidal silver nanoparticles. *Journal of Chemical Physics*, **116**(15): 6755–6759 (2002).
- [75] U. Kreibig et al. Optical Properties of Metal Clusters. Springer (2010).
- [76] P. K. Jain *et al.* Plasmonic coupling in noble metal nanostructures. *Chemical Physics Letters*, 487(4-6): 153–164 (2010).
- [77] E. Prodan *et al.* A hybridization model for the plasmon response of complex nanostructures. *Science*, **302**(5644): 419–422 (2003).
- [78] V. Giannini *et al.* Controlling Light Localization and Light-Matter Interactions with Nanoplasmonics. *Small*, 6(22): 2498–2507 (2010).
- [79] P. K. Jain *et al.* On the universal scaling behavior of the distance decay of plasmon coupling in metal nanoparticle pairs: a plasmon ruler equation. *Nano Letters*, 7(7): 2080–2088 (2007).
- [80] R. M. Martin Resonant Raman scattering. In Light Scatteriung in Solids I, edited by M. Cardona, Springer Verlag, Berlin, Germany, vol. 8 of Topics in Applied Physics (1983).

- [81] F. Cerdeira *et al.* Stress-induced doubly resonant Raman scattering in GaAs. *Physical Review Letters*, 57(25): 3209–3212 (1986).
- [82] R. M. Martin. Resonance Raman-Scattering Near Critical-Points. *Physical Review B*, 10(6): 2620–2631 (1974).
- [83] A. Jorio et al. Raman Spectroscopy in Graphene Related Systems. Wiley-VCH, Berlin, Germany (2011).
- [84] R. Saito *et al.* Raman spectroscopy of graphene and carbon nanotubes. Advances in Physics, **60**(3): 413–550 (2011).
- [85] A. C. Ferrari *et al.* Raman spectroscopy as a versatile tool forstudying the properties of graphene. *Nature Nanotechnology*, 8(4): 235–246 (2013).
- [86] P. May. Electronic and vibrational properties of low-dimensional carbon systems. Ph.D. thesis, Technische Universität Berlin, Berlin, Germany (2012).
- [87] S. Pisana *et al.* Breakdown of the adiabatic Born-Oppenheimer approximation in graphene. *Nature Materials*, 6(3): 198–201 (2007).
- [88] A. Das et al. Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. Nature Nanotechnology, 3(4): 210–215 (2008).
- [89] T. M. G. Mohiuddin *et al.* Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gruneisen parameters, and sample orientation. *Physical Review B*, **79**(20) (2009).
- [90] M. Huang et al. Phonon softening and crystallographic orientation of strained graphene studied by Raman spectroscopy. Proceedings of the National Academy of Sciences of the United States of America, 106(18): 7304–7308 (2009).
- [91] C.-F. Chen *et al.* Controlling inelastic light scattering quantum pathways in graphene. *Nature*, 471(7340): 617–620 (2011).
- [92] C. Thomsen *et al.* Double resonant Raman scattering in graphite. *Physical Review Letters*, 85(24): 5214–5217 (2000).
- [93] P. Venezuela *et al.* Theory of double-resonant Raman spectra in graphene: Intensity and line shape of defect-induced and two-phonon bands. *Physical Review B*, 84(3): 035433 (2011).

- [94] A. C. Ferrari et al. Raman spectrum of graphene and graphene layers. Physical Review Letters, 97(18): 187401 (2006).
- [95] D. Graf *et al.* Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene. *Nano Letters*, 7(2): 238–242 (2007).
- [96] C. Thomsen et al. Resonant Raman spectroscopy of nanotubes. Philosophical Transactions of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences, 362(1824): 2337–2359 (2004).
- [97] J. C. Tsang et al. Doping and phonon renormalization in carbon nanotubes. Nature Nanotechnology, 2(11): 725–730 (2007).
- [98] B. Hatting et al. Fermi energy shift in deposited metallic nanotubes: A Raman scattering study. Physical Review B, 87(16): 165442 (2013).
- [99] C. Fantini *et al.* Optical transition energies for carbon nanotubes from resonant Raman spectroscopy: Environment and temperature effects. *Physical Review Letters*, 93(14): 147406 (2004).
- [100] H. Telg et al. Chirality distribution and transition energies of carbon nanotubes. Physical Review Letters, 93(17): 177401 (2004).
- [101] J. C. Meyer *et al.* Raman modes of index-identified freestanding single-walled carbon nanotubes. *Physical Review Letters*, 95(21): 217401 (2005).
- [102] M. Takase *et al.* Selection-rule breakdown in plasmon-induced electronic excitation of an isolated single-walled carbon nanotube. *Nature Photonics*, 7(7): 550–554 (2013).
- [103] J. G. Duque *et al.* Violation of the Condon Approximation in Semiconducting Carbon Nanotubes. ACS Nano, 5(6): 5233–5241 (2011).
- [104] E. Le Ru et al. Principles of Surface-Enhanced Raman Spectroscopy. and related plasmonic effects. Elsevier (2008).
- [105] V. G. Kravets *et al.* Surface Hydrogenation and Optics of a Graphene Sheet Transferred onto a Plasmonic Nanoarray. *The Journal of Physical Chemistry C*, 116(6): 3882–3887 (2012).
- [106] A. Hartschuh et al. High-Resolution Near-Field Raman Microscopy of Single-Walled Carbon Nanotubes. Physical Review Letters, 90(9): 095503 (2003).

- [107] A. Hartschuh. Simultaneous Fluorescence and Raman Scattering from Single Carbon Nanotubes. Science, 301(5638): 1354–1356 (2003).
- [108] C. Georgi *et al.* Probing Exciton Localization in Single-Walled Carbon Nanotubes Using High-Resolution Near-Field Microscopy. ACS Nano, 4(10): 5914–5920 (2010).
- [109] L. G. Cançado *et al.* Mechanism of near-field Raman enhancement in onedimensional systems. *Physical Review Letters*, **103**(18): 186101 (2009).
- [110] H. Chu et al. Decoration of Gold Nanoparticles on Surface-Grown Single-Walled Carbon Nanotubes for Detection of Every Nanotube by Surface-Enhanced Raman Spectroscopy. Journal of the American Chemical Society, 131(40): 14310–14316 (2009).
- [111] T. Assmus *et al.* Raman properties of gold nanoparticle-decorated individual carbon nanotubes. *Applied Physics Letters*, **90**(17): 173109 (2007).
- [112] M. Scolari *et al.* Surface Enhanced Raman Scattering of Carbon Nanotubes Decorated by Individual Fluorescent Gold Particles. *The Journal of Physical Chemistry* C, **112**(2): 391–396 (2008).
- [113] J. Zabel *et al.* Raman Spectroscopy of Graphene and Bilayer under Biaxial Strain: Bubbles and Balloons. *Nano Letters*, **12**(2): 617–621 (2012).
- [114] R. Krupke et al. Surface conductance induced dielectrophoresis of semiconducting single-walled carbon nanotubes. Nano Letters, 4(8): 1395–1399 (2004).
- [115] A. Vijayaraghavan *et al.* Ultra-Large-Scale Directed Assembly of Single-Walled Carbon Nanotube Devices. *Nano Letters*, 7(6): 1556–1560 (2007).
- [116] A. Jorio et al. Polarized raman study of single-wall semiconducting carbon nanotubes. *Physical Review Letters*, 85(12): 2617–2620 (2000).
- [117] A. Jorio *et al.* Resonance Raman spectra of carbon nanotubes by cross-polarized light. *Physical Review Letters*, **90**(10): 107403 (2003).
- [118] G. Duesberg et al. Polarized Raman spectroscopy on isolated single-wall carbon nanotubes. Physical Review Letters, 85(25): 5436–5439 (2000).
- [119] K. S. Novoselov et al. Two-dimensional atomic crystals. Proceedings of the National Academy of Sciences, 102(30): 10451–10453 (2005).

- [120] A. K. Geim *et al.* Van der Waals heterostructures. *Nature*, **499**(7459): 419–425 (2013).
- [121] M. A. Bissett *et al.* Effect of Domain Boundaries on the Raman Spectra of Mechanically Strained Graphene. ACS Nano, 6(11): 10229–10238 (2012).
- [122] F. Guinea *et al.* Energy gaps and a zero-field quantum Hall effect in graphene by strain engineering. *Nature Physics*, 6(1): 30–33 (2009).
- [123] M. A. Bissett *et al.* Strain engineering the properties of graphene and other twodimensional crystals. *Physical Chemistry Chemical Physics*, **16**(23): 11124–11138 (2014).
- [124] E. B. Kley et al. Enhanced e-beam pattern writing for nano-optics based on character projection. In Proceedings of the 28th European Mask and Lithography Conference (EMLC 2012), edited by U. F. W. Behringer and W. Maurer (2012).
- [125] S. Heeg. Quantitative composition of a single-walled carbon nanotube sample. Diplomathesis, Freie Universität Berlin, Berlin, Germany (2008).