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Introduction

"There are two ways of spreading light:
to be the candle or the mirror that reflects it."
— Edith Wharton, 1902

Light is a diverse phenomenon that surrounds us in many different forms. Harnessing and controlling this phenomenon is becoming more and more relevant to satisfy the ever-growing demand for technological progress in our society. Over most of human history, light has only been accessible to us in the form of sunlight or as a fire. It took until the 19th century that the advent of the first incandescent light bulbs laid the foundation for our modern use of light. By exploiting the flow of current through a thin conductive wire, electrical power is converted into black-body radiation, most of which is released as heat and a small fraction of which is perceived as visible light. Over the decades, this approach has been complemented by numerous methods to generate light with much greater power conversion efficiencies and in a much more controlled fashion. Important examples include fluorescent light tubes that harness optical transitions in gas atoms, or light-emitting diodes that rely on the radiative recombination of electrical charges in a semiconductor [1]. In the early 1960s, another technological revolution was unleashed by the advent of the laser – an amplifier for light [2–6]. The laser relies on a reflective cavity that contains a gain medium, such as fluorescent gas or a semiconductor to compress and intensify light in a small volume [7]. Today, this invention is indispensable to virtually any application that requires a powerful light source in research and technology.

Fundamentally, light can be described both as an electromagnetic wave [10] and as a stream of particles that carry a discrete amount of energy and momentum, called photons [11]. In its role as a wave, the light comprises electric and magnetic field components which carry a frequency, wavelength, amplitude, polarization, and phase. As shown in Fig. 1.1, light is not just limited to what is perceived by the human eye.

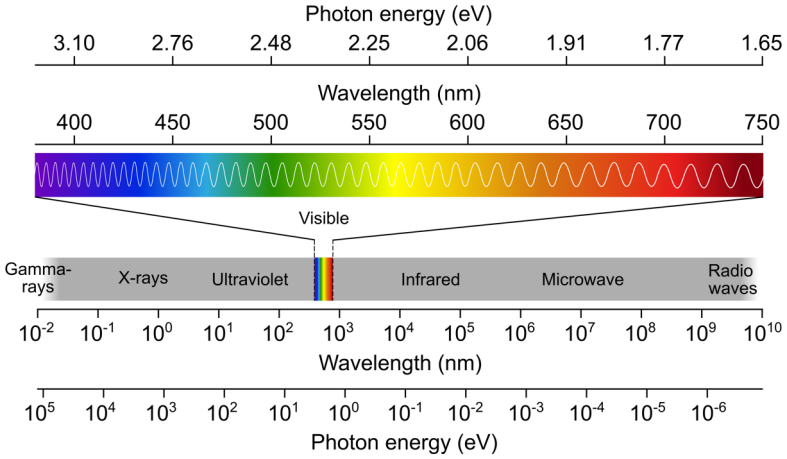

Figure 1.1: The electromagnetic spectrum. There are no hard boundaries between the different categories of radiation, but rather continuous transitions. Figure created on basis of refs. [8, 9].

Instead, light can assume many different forms, including radio waves that are used to broadcast information over large distances, microwave radiation that is used for telecommunication, infra-red (IR) radiation that transmits heat, ultraviolet (UV) radiation that enables the fabrication of computer chips, X-radiation that is applied for medical imaging, and highly-energetic gamma radiation that results from the decay of atomic nuclei. The wavelength and photon energy of light stand in inverse relation to one another. For example, the visible (VIS) spectrum extends in wavelength from approximately 380 nm (violet) to 750 nm (red), while the corresponding photon energies range from 3.26 eV to 1.65 eV electron-volts (eV). In this thesis, we focus on radiation in the IR-VIS-UV spectral range, hereinafter referred to as the optical regime.

The response of a material to a certain kind of radiation is determined by its dielectric properties. As light propagates through matter, its wavelength is compressed by the refractive index of the medium. This gives rise to refraction of light as it encounters the interface between two media [12]. In addition, impurities and defects in a material can generate optical transitions that lead to the absorption or emission of light. And furthermore, structured materials can scatter or guide light, thereby controlling its propagation, re-directing or even shaping the light [12]. Experimentally, such phenomena can be studied using spectroscopic and interferometric tools that probe the effect of a material on the spectral composition, the intensity, the phase and the polarization of light [13]. The spatial resolution at which such experiments can be performed is typically constrained by the optical diffraction limit, given by approximately half the wavelength of the light in the embedding medium. This is also known as the Abbe limit which defines the maximum spatial resolution of an optical microscope [14]. However, many interesting phenomena take place at much smaller length scales [15]. Specifically, in the proximity of tiny nanoparticles, the intensity of light can be enhanced on very small length scales, giving rise to the formation of localized optical near-fields [12, 16].

Among other uses, these near-fields permit metallic nanoparticles to stimulate and amplify photo-catalytic reactions [17–20]. In photovoltaics, the scattering of light by nanoscale structures can be harnessed to enhance light trapping in a solar cell [21–23]. And in integrated photonics, nanostructured materials can be used to manipulate and control the flow of light [24–27]. There is a long list of applications which rely on the spatial confinement of light at deep-subwavelength length scales [15], raising the question: how can such localized optical phenomena be studied experimentally?

1.1 The interplay of free electrons and light

With the advent of electron microscopy in 1931 it has become possible to resolve structural material features fully independent of the optical diffraction limit [29]. This is achieved by exploiting high-energy electrons (typically 5 - 300 keV) that undergo elastic and inelastic collisions with the constituent atoms of a material [30]. Interestingly, over the past two decades, it has been shown that electron microscopy also provides a powerful platform to probe optical phenomena at the nanometer length scale by exploiting the coupling of the transient electric field of the electrons to polarisable charges in a specimen [31–33]. This coupling is fundamentally different from the

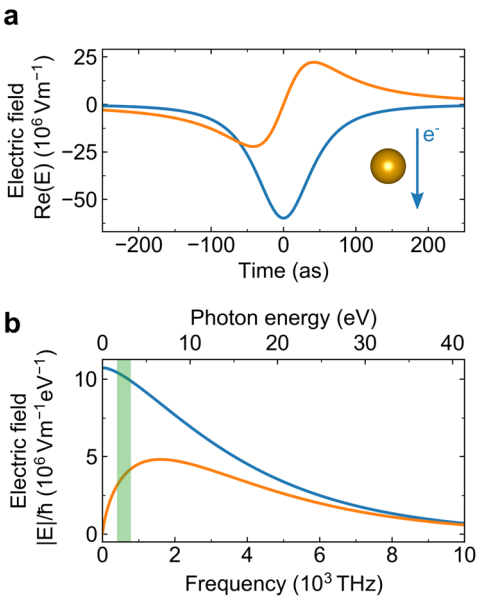

Figure 1.2: a Electric field of a swift free electron that acts on a gold nanosphere at a distance of 5 nm to the electron trajectory. The electron has a kinetic energy of 20 keV, corresponding to a velocity of approximately 27 % of the speed of light in vacuum. The blue and the orange curves represent the real parts of the radial and the longitudinal electric field components, respectively. **b** Spectral representation of the radial (blue curve) and longitudinal (orange curve) electron electric field components in **a**. The data are expressed in terms of the electromagnetic wave frequencies (bottom axis) and corresponding photon energies (top axis). Figure created on basis of ref. [28].

excitation of a material with light as it is highly localized in both space and time. As a consequence, the electron can drive optical phenomena on very small length and time scales, and over a very broad spectral range [28]. To illustrate this correlation, Fig. 1.2a shows the time evolution of the electric field that a swift free electron exerts on a gold nanosphere as it passes by in close proximity. The blue and the orange curves represent the radial and the longitudinal electric field components, respectively. As can be seen, the field undergoes a single cycle with a duration of less than a femtosecond. As further shown in Fig. 1.2b, this ultra-short electromagnetic pulse can be decomposed into a broad spectrum of electromagnetic waves with photon energies from zero to several tens of electron-volts, thus extending over the entire IR-VIS-UV spectral range.

As an electron polarises a material and couples to an optical excitation, it undergoes a spontaneous energy loss which can be probed experimentally using electron energy-loss spectroscopy (EELS) [34–37]. EELS is a common technique that was originally implemented in transmission electron microscopes (TEMs) to study bulk excitations by electrons upon inelastic scattering in a thin specimen [38, 39]. The advent of electron spectrometers, based on magnetic prisms that disperse electrons with an energy resolution much better than 1 eV, opened up an entirely new world of using EELS to study optical material properties [37, 40]. Nowadays, state-of-the-art EELS systems that are integrated in TEMs with a mono-chromated electron source provide an energy resolution down to a few tens of meV [41, 42], even enabling the observation of low-energy phononic excitations in the crystal lattice of a specimen [43–50].

Aside from the characteristic energy loss that an optical excitation leaves as a fingerprint on the electron, the decay of the induced polarization can give rise to the emission of far-field radiation, called cathodoluminescence (CL) [31, 51, 52]. The emitted light carries detailed information which can be retrieved using angle-, polarization- and time-resolved optical spectroscopy [53–62]. Historically, CL analysis has been mainly performed in scanning electron microscopes (SEM), where light is collected using a parabolic mirror. Lately, similar optics have been also introduced in TEM instruments, providing the benefit of a spatial resolutions down to the atomic scale [60, 62]. However, as compared to SEMs, TEMs typically feature very small specimen chambers with dimensions of a few mm which introduces substantial practical constraints.

Another exciting development in the field of electron microscopy is the recent advent of ultra-fast TEM (UTEM) [63–65]. In this approach, laser pulses are used to generate electron pulses as short as several hundred femtoseconds by photo-excitation of the electron cathode, enabling time-resolved spectroscopic measurements. This concept has laid the foundation for photon-induced near-field electron microscopy (PINEM) in which part of the pump laser light is used to optically excite a specimen [66]. Thereby, the laser induces an intense optical near field which is traversed by the electron pulse. As a consequence, the electrons can undergo energy-gain and -loss transitions by stimulated emission and absorption photons [66–70], which can be probed using a magnetic spectrometer as in EELS. The modulation of the electron energy spectrum provides a direct measure of the electron-light interaction strength [67–71]. In recent years, this correlation has been exploited to probe laser-induced optical near-field distributions in various photonic systems, such as carbon nanotubes [66], metallic nanostructures [70, 72–78], photonic crystal cavities [79], and much more [80–84].

The PINEM technique not only yields insights into the distribution of optical fields at the nanoscale. Just like light, electrons exhibit both a particle and a wave-like character [85–87]. According to the laws of quantum mechanics, one can only define a probability for an electron to be at a certain point in space for a given instance in time, as described by the electron wave function [88]. The emission and absorption of photons affects the energy and momentum distribution of the electron, which in turn results in a modulation of its wave function [68–70]. This phenomenon enables the realization of numerous fascinating phenomena as demonstrated in several recent experimental and theoretical publications [70, 71, 79, 81, 89–101]. For example, after its interaction with an optical field, the electron can split up into ultra-short electron wave packets, facilitating ultra-fast optical spectroscopic measurements at attosecond time scales [78, 80, 90, 91]. Furthermore, the electron wave function can be tailored in the plane transverse to its direction of propagation [92, 93], which may enable aberration corrections in an electron microscope [95]. And finally, the electron can be exploited as an information carrier for quantum applications in which light is used to imprint information onto the electron wave function [96, 98, 99].

The fundamental mechanisms that govern the exchange of energy between free electrons and light in EELS, CL, and PINEM are intimately linked [71, 76, 102]. While a photon in free space cannot exchange energy with an electron due to a violation of momentum conservation, the localization of photons in an optical near field introduces a momentum uncertainty that facilitates the interaction [69, 103]. From a wave-like perspective, this means that the optical field is composed of a distribution of evanescent field components which cannot propagate through space, but decay exponentially away from the material boundary [12]. These field components, called Fourier waves, feature wavelengths which are effectively shorter than that of light in free space. Figuratively speaking, this permits the electron to “surf” on a light wave which maintains a constant phase throughout the interaction, a condition known as electron-light phase matching [69, 104]. In the presence of an optical pump field as in PINEM, such a phase-matched interaction renders a net acceleration or deceleration which in turn causes the electron to undergo energy-gain or loss transitions in integer units of the photon energy. In EELS and CL, only an energy loss is possible, however, the electron-light coupling mechanism is fundamentally the same as in PINEM.

Photonic systems allow optical fields to be shaped such that phase-matching between free electrons and light can be optimized. This has been exploited in several recent experiments to enhance the PINEM effect, using a glass prism [82], microcavities [81, 83], and other dielectric structures [84, 99, 105, 106]. Vice versa, phase-matched interactions can also lead to strongly enhanced CL emission. One such example is the Smith-Purcell (SP) effect [107], in which a single electron polarizes a periodic system along a grazing trajectory, thereby inducing multiple radiative excitations that interfere in the far field. Due to the phase-lag between these excitations, the emitted light features a unique angular dispersion which depends on the pitch of the system and the electron velocity.

These fascinating new developments inspire further thoughts on how optical fields can be structured to manipulate their interaction with free electrons. A very powerful approach to tailor the fundamental properties of light relies on texturing the surface

of a material with a pattern of nanoscale structures, known as metasurfaces [108–113]. So far, a wide range of metasurface geometries have been demonstrated that can shape light fields in many different ways, enabling ultra-thin optical elements for imaging and focusing [114–118], polarization control [119, 120], analog image processing[121, 122] and optical computing [123, 124], non-linear frequency conversion [125–129], holography [130, 131], and many applications more [108–113]. In addition, recent advances have been made to design electrically, thermally and optically tunable metasurfaces that provide dynamic control over light [132]. These various capabilities render optical metasurfaces an ideal platform to prepare complex optical fields that efficiently couple to free electrons. In particular, the combination of phase-matched interactions with the resonant enhancement of light in nanostructures opens up a new dimension of control. The use of optical metasurfaces to harness, manipulate and control free-electron-light-matter interactions is an ambitious goal that requires many steps of exploration, several of which are addressed in this thesis.

1.2 Outline of this thesis

As a starting point, in **Chapter 2**, we experimentally study the fundamental correlation between the electron-light-matter interactions that govern EELS, CL and PINEM at the nanometer length scale. While their correlations have been theoretically explored in the past, there has been no experimental observation of all three electron-light interaction mechanisms on the same physical system so far. Here, we study the EELS, CL and PINEM responses of a chemically-synthesized gold nanostar with sharp conical protrusions that sustain highly localized optical near-field distributions in the VIS-NIR spectral range. The CL experiments were done in the SEM-CL instrument at AMOLF while the EELS and PINEM experiments were performed in a UTEM in the group of prof. Claus Ropers at the University of Göttingen. We show how all three techniques rely on the same fundamental phase-matching condition for the coupling between free electrons and light, and demonstrate how this affects the measured spatial near-field distributions of the nanotips.

In **Chapter 3**, we exploit the phase-matching condition for the coupling of electrons and light to design a metasurface that shapes the wavefront of Smith Purcell radiation (SPR), in collaboration with the groups of prof. Ido Kaminer at Technion and prof. Ady Arie at Tel Aviv University in Isreal. Specifically, we implement metalenses based on chirped nano gratings that generate converging or diverging SPR in the VIS-NIR spectral range. To characterize our samples, we apply hyperspectral angle-resolved CL detection in the SEM, revealing the far-field radiation patterns of our metalenses across a broad spectral range. Our measurements are complemented by numerical simulations and analytical theory that display the correlation between the experimental data and the effects of focusing and defocusing, as well as the underlying electron-near-field coupling mechanism.

The insights from Chapter 2 demonstrate the close correlation of photon emission and absorption by free electrons. This inspires the idea that the metasurface concept as explored in Chapter 3 could be also translated to PINEM experiments, in which an external optical pump field is being shaped to manipulate the electron itself. Vice-versa,

PINEM experiments correlated with CL analysis can provide a deeper fundamental understanding of the electron-light-matter interaction. However, so far, PINEM is primarily performed in TEMs which are equipped with suitable electron spectrometers, while CL is mostly implemented in SEMs which offer large specimen chambers with ample room for the integration of light collection optics. An implementation of both techniques, also in combination with EELS on a single platform is of great interest, however, has not been realized so far. In the next two chapters, we demonstrate how these three techniques can be brought closer together in the SEM.

In **Chapter 4**, we adapt the SP effect to demonstrate the coherent coupling of free-electrons and guided optical modes in a circular metallo-dielectric metagrating that is fabricated onto the input facet of a multi-mode optical fibre. Again, resorting to hyperspectral angle-resolved CL detection as in Chapter 3, we are able to resolve and distinguish the dispersion of SP radiation that is emitted into both free space and the fiber core, for a wide range of electron energies. Light detected by an external spectrometer reveals the coherent excitation of guided modes which are found to be spectrally filtered according to the finite numerical aperture of the fibre, and the characteristic dispersion of the SP effect in the fiber core. The concept of an optical-fibre integrated metasurface offers great potential to manipulate an optical pump field that is injected through the fiber, rendering a versatile platform to synthesize complex electron wave packets in the SEM.

Finally, in **Chapter 5** we explore the technical implementation of electron spectroscopy in the SEM, a prerequisite for PINEM, on the basis of an electrostatic retarding field energy analyzer (RFA) that was originally developed in the group of prof. P. Kruit at the Technical University of Delft. We introduce and characterize a modified version of the RFA that enables the acquisition of electron spectra over an energy range from 4 keV to 11 keV, at a resolution better than 1 eV and under pulsed electron beam conditions as typically employed in PINEM.

Overall, this thesis presents fundamental insights into the coupling of free electrons, light, and matter at the nanometer length scale. It shows how the use of optical metasurfaces opens up a powerful new direction to master this interaction at will, and how combined CL and PINEM experiments could be implemented on a single platform. These insights form the basis to generate novel forms of light, to resolve the dynamics of optical phenomena on ultra-small length and time scales, and to further harness and explore the electron wave nature through its interaction with light and matter.