Summary

Methods to generate and control light constitute a cornerstone for future technological advancement. Today, nanophotonic systems provide the means to confine, intensify, and manipulate light on very small length scales, enabling various applications such as driving catalytic reactions, harvesting sunlight in photovoltaics, or implementing novel telecommunication and computation schemes. The exploration of the optical phenomena that underly these applications, however, poses a fundamental challenge due to the diffraction limit of light. The latter constrains the spatial resolution of conventional optical microscopy and spectroscopy techniques to typically 200 nm - 300 nm in the visible spectral range. Therefore, the emergence of ever-complex and powerful nanophotonic devices relies on alternative experimental approaches to overcome this limit.

Since its advent almost 100 years ago, electron microscopy (EM) has evolved into a powerful platform to resolve structural material features at the nanometre or even atomic length scale using swift free electrons with kinetic energies of typically 5 keV - 300 keV. At the end of the last century, it has been realized that such electrons can also serve as a nanoscale source and probe of optical material excitations. This approach exploits the transient electromagnetic field of the electrons to locally polarize a specimen on time scales shorter than an optical cycle, thereby enabling the excitation of optical phenomena across the entire infra-red (IR), visible (VIS), and ultraviolet (UV) spectral range. As a result of this interaction, the electrons undergo a spontaneous energy loss that can be probed experimentally using electron energy-loss spectroscopy (EELS). Complementarily, cathodoluminescence (CL) spectroscopy can be applied to analyse the emission of radiation resulting from this process. Due to the highly localized nature of the electron-light-matter interaction, EELS and CL provide powerful spectroscopic tools to study the optical properties of nanophotonic systems fully independent of the optical diffraction limit. Vice versa, an external optical pump source that excites the optical near-field of a nanostructure can stimulate the emission and absorption of photons by the electron. The resulting modulation of the electron energy spectrum provides a direct measure of the electron-near-field interaction strength, facilitating a technique called photon-induced near-field electron microscopy (PINEM).

The study of electron-light-matter interactions using EELS, CL, and PINEM is a rapidly expanding research field. Scientists around the world are exploring the numerous opportunities that modern scanning electron microscopes (SEMs) and transmission electron microscopes (TEMs) offer to probe optical phenomena at ultra-small length and time scales, and, moreover, to manipulate, control, and harness the quantum properties of free electrons with light. These efforts are strongly correlated with recent advances in the field of nanophotonics. In particular, the emergence of nano-textured materials with artificial optical properties, called metasurfaces, offers unique potential to control the interaction of free electrons with structured optical fields. In this thesis, we make several steps to explore and demonstrate this potential. We study

the application of metasurfaces to control the generation of light by free electrons, and in turn, how this concept may be applied to manipulate the electrons themselves.

As a starting point, in Chapter 2, we investigate the fundamental correlation between the spontaneous and stimulated interaction of free electrons with light and matter. To this end, we perform spatially-resolved EELS, CL, and PINEM measurements that reveal the coupling of free electrons and photons in the optical near-field of a single chemically-synthesized gold nanostar. The latter features sharp conical protrusions with tip radii of curvature smaller than 3 nm that sustain highly-localized plasmonic resonances in the VIS to near-IR (NIR) spectral range. The CL experiments are performed in an SEM at AMOLF at an electron energy of 20 keV electron energy, while the EELS and PINEM experiments are performed in an ultra-fast TEM instrument that can be synchronized with an optical pump laser in the group of prof. Claus Ropers at the University of Göttingen at an electron energy of 200 keV. In EELS and CL, we observe the spontaneous coupling of free electrons to a number of plasmonic tip resonances in the VIS-NIR spectral range, while in PINEM we find a strong dependence of the electron-near-field interaction on the polarization of the optical pump field and its spectral overlap with these modes. By integrating the acquired EELS and CL spectra over a bandwidth of 50 meV around the tip resonance energies, we obtain spontaneous electron energy loss and photon emission probabilities in the order of 10^{-4} and 10^{-5}, respectively. In PINEM, we observe a modulation of the electron energy spectrum by up to three energy-gain and -loss sidebands at an optical pump field intensity of approximately 1 GW/cm^2 and a pump photon energy of 1.55 eV. Complemented by theory and numerical simulations, we show that all three types of measurements feature a common spatial dependence on the dipolar electric near-field distribution of a resonantly driven nanotip. Moreover, our simulations show that the interaction strength crucially depends on the electron velocity, as determined by the spatial Fourier transformation of the optical field along the electron trajectory. As a result, a maximum electron-light coupling efficiency is achieved for electrons passing by the tip apex with comparatively low kinetic energies in the range of few keV. This finding manifests a fundamental phase-matching condition for the coupling of free electrons and light that is independent of the stimulated or spontaneous nature of the interaction.

Next, in Chapter 3, we exploit the phase-matching condition for free-electron-light coupling to demonstrate spectral and angular control over the generation of Smith-Purcell radiation (SPR) by free electrons that excite a metasurface under grazing incidence. The project is performed in collaboration with the groups of prof. Ido Kaminer at Technion and prof. Ady Arie at Tel Aviv University. As a specific example, we implement metalenses based on chirped nano gratings that generate SPR with a converging (concave) or diverging (convex) wavefront in the VIS-NIR spectral range. Using focused ion beam milling, the structures are fabricated onto a silicon wafer with a thin gold layer, ranging in pitch from 163 nm to 228 nm over a total length of 20 μm. The orientation of the grating chirp determines the concave or convex curvature of the emission wavefronts. For reference, we also implement a periodic nano grating with a constant pitch of 189 nm, generating conventional SPR that is emitted in the form of plane waves. To characterize the different grating geometries, we apply hyperspectral angle-resolved CL detection in the SEM, revealing their far-field radiation patterns

across a broad spectral range. Remarkably, we achieve a coherent electron-sample interaction range over more than 100 metagrating periods. As a result, SPR that is excited at a nominal design wavelength of 580 nm is distributed over effective numerical apertures of 0.48 ± 0.05 and 0.45 ± 0.05, for the converging and the diverging metalenses, respectively. 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. Building up on the metalens concept, we further present numerical simulations of a split-ring resonator (SRR) metasurface that provides simultaneous focusing and polarization control over SPR by exploiting the optical bi-anisotropy of the SRR meta-atoms.

Considering the close correlation between the emission and absorption of photons by free electrons as demonstrated in Chapter 2, it becomes clear that the concept of shaping free-electron radiation by metasurfaces (Chapter 3) can be also inverted to structure optical fields that manipulate the electron wave function. In either configuration, interfacing the metasurface with suitable optics for the extraction or injection of radiation, respectively, is a critical challenge. In Chapter 4, we address this challenge by demonstrating the coupling of free electrons and light via the SP effect in a circular metagrating that is fabricated onto the input facet of a metal-coated multi-mode optical fibre. The structure extends over a total diameter of 100 µm with a constant radial pitch of 200 nm. Resorting to the same hyperspectral angle-resolved CL detection approach as in Chapter 3, we experimentally resolve the dispersion of SPR that is emitted into both free space and the fibre core, for variable electron energies in the range of 5 keV to 30 keV. In free space, we observe emission of first-, second-, and third-order SPR in the UV to NIR spectral range that follows the theoretically expected angular dispersion relation. At an electron energy of 30 keV, we measure photon emission probabilities of first- and second-order SPR of $4.7 \cdot 10^{-4}$ and $5.0 \cdot 10^{-5}$, respectively (spectral bandwidth ~0.2 eV). SPR that is generated inside the fibre and that escapes through the cladding layer shows a modified angular dispersion that is determined by the refractive index of the fibre core and its refraction at the fibre-vacuum interface. Furthermore, first-order SPR that is detected by a fibre-coupled spectrometer reveals the coherent excitation of guided optical modes, which are spectrally filtered according to the finite numerical aperture of the fibre. Along with the coherent excitation of SPR, we also detect a broadband distribution of incoherent CL that is generated by electrons penetrating the input facet of the fibre, and scattering inelastically. We distinguish the excitation of non-bridging oxygen hole centres (NBOHCs) and oxygen deficient centres (ODCs) with mean photon emission energies of 1.95 eV and 2.80 eV, respectively. In addition, we find that incoherent CL generated within the ODC spectral range couples to a Rayleigh anomaly of the metagrating, giving rise to a Fano resonance that overlaps with the dispersion of second-order SPR at 20-keV electron energy. This phenomenon demonstrates the great potential of metasurfaces to combine the SP effect with resonant electromagnetic excitations that are supported by the metasurface such as lattice resonances.

Finally, in Chapter 5, we explore the implementation of a suitable electron energy spectrometer to perform PINEM experiments in the SEM. In combination with the wide range of spectroscopic CL detection capabilities offered by our SEM-CL instrument,

such experiments could provide new fundamental insights into the quantum nature of the electron-light-matter interaction. Notably, SEMs offer the benefit of providing access to non-relativistic electron energies at which the electron-light coupling can be substantially enhanced as shown in Chapter 2. Furthermore, these instruments offer large specimen chambers which provide ample room for the integration of experimental infrastructure. So far, however, electron spectrometers that fulfil the demands on resolution and sensitivity to probe the interaction of free electrons and light have been mainly implemented in TEMs that operate at relativistic electron energies of several tens to hundreds of keV. Here, we demonstrate an electrostatic retarding field analyzer (RFA) that can be integrated into an SEM to perform high-resolution spectroscopic measurements at non-relativistic electron energies. We first use an RFA that was originally developed in the group of prof. Pieter Kruit at the Technical University of Delft to study the continuous-beam emission of our SEM-CL instrument at an electron energy of 5 keV. The measurements reveal electron energy spectra with a full-width-at-half-maximum (FWHM) of (0.88 ± 0.01) eV at a beam current of 5 pA and (2.98 ± 0.02) eV at a beam current of 8.7 nA. Furthermore, we perform numerical simulations that suggest an upper limit on the energy resolution of the RFA of 0.1 eV. We then introduce a modified version of the RFA that is prepared for operation over an extended range of electron energies and under pulsed electron beam conditions as typically employed in PINEM. These conditions are emulated using an electrostatic beam blanker that enables the generation of electron pulses with a variable number of electrons and a duration down to several hundred picoseconds. The RFA is equipped with a direct-electron counter based on a Timepix 3 CMOS chip that provides nearly single-electron sensitivity from an electron energy of 10 keV onwards. At an electron pulse rate of 200 kHz and in a regime of less than one electron per pulse, we resolve electron spectra at electron energies between 4 keV and 11 keV. The FWHM of these spectra ranges from (0.69 ± 0.11) eV to (1.23 ± 0.03) eV. Above 11 keV we observe the onset of electrical breakdown, while below 4 keV the sensitivity of the electron counter becomes insufficient. Present limitations of the RFA are identified regarding acquisition speed, alignment sensitivity, and rate capability, all of which can be improved by further technical modifications.

Altogether, this thesis demonstrates the great potential of optical metasurfaces to harness and control the interplay of free electrons, light, and matter at the nanometer length scale. We demonstrate the fundamental correlation of spontaneous and stimulated electron-photon interactions that permits the use of complementary nanophotonic systems to both generate light and manipulate the electron wave function. We show how near-field effects in a metasurface provide control over the spectral and angular distribution of free-electron radiation, and we demonstrate how guided optical modes in an optical fibre can be coupled to free electrons using a metagrating that is patterned onto the fibre end-facet. Finally, we show how an optical modulation of non-relativistic free electrons in the SEM could be probed experimentally using an electrostatic retarding field analyser. The insights from this thesis may enable the design of complex light sources that can operate over an ultra-broad spectral range, may inspire novel spectroscopic tools to resolve the dynamics of optical phenomena on ultra-small length and time scales, and, ultimately, may contribute to a deeper fundamental understanding of the electron-light-matter interaction.