1

Introduction

1.1 Light

Light is all around us. It provides us with energy and information. From light bulbs or screens in our daily life to the complete history of planet earth that is powered by sunlight, we cannot think of a life without light. Our most dominant sense is our vision,[1] with which we obtain information about the world around us via light hitting our eyes. Information on the internet is swiftly spread around the world in the form of light signals in glass fibers. The sunlight hitting the earth in a single day contains twenty times more energy than what humankind consumes in a year.[2] This light keeps us warm, makes plants grow, and just a tiny fraction of all that light is used to generate electricity with solar cells.

Having control over light - being able to detect, collect, generate and guide light - is extremely important for all kinds of technologies. From large-scale solar cells to bright and efficient light-emitting diodes (LEDs), from glass fiber cables across the ocean to tiny on-chip circuits that communicate with light, all require control over generating, absorbing, or sensing light in/from a specific direction, at a specific wavelength. With solar cells we usually want to absorb as much light as possible, to convert it to electricity. Although not always: sometimes, for aesthetic reasons or double functionality we might want to absorb only specific colors, or only part of the light. For lighting and screens, we want efficient light emission of a specific (mix of) color(s). The light only has to go into a specific direction: towards the viewer. In information technology, light signals can be used to process information. On-chip light circuits require microscopic light emitters and detectors, and light signals that travel in a specific direction with accurate emission and detection

1.2 Nanophotonics

For achieving such control over light emission and absorption, we can find a wide range of tools for light manipulation in the field of nanophotonics, where one studies the interaction of light with nanometer-sized objects. Since these objects are on the order of, or smaller than the wavelength of light, they ‘see’ the light differently than macroscopic objects. While large objects experience light as a continuum, nano-scale structures can interact with individual photons and feel the fluctuating electric and magnetic fields of light. Next

to the material properties, the size and shape of a nano-scale object become very important for how it interacts with light. This allows, for example, to have very strong interaction for only a specific color, when the corresponding wavelength exactly matches the size of the structure. This is called a resonance. For light-emitting materials, the color, rate, and efficiency at which they emit light can be influenced by the shape and size, as well as the direction of light emission.

Nanophotonics can be split up into two categories: plasmonics and dielectrics. In plasmonics, metals are used. The free electrons in a metal, which are also responsible for the electrical conductivity, react to the electric field of light. When light shines on a metal nanoparticle, the electrons can start to collectively move with the electric field, called a plasmon resonance. This gives a very strong interaction between the light and the particle, resulting in strong light scattering for particles much smaller than the wavelength of light. However, some energy is always dissipated as heat in the metal. This parasitic absorption makes plasmonics inherently lossy. On the other hand, there are dielectric materials, i.e. insulators. Here the electrons are not free to move, but in an electric field they can still get displaced a bit from the nuclei. The material becomes polarized, and the polarizability is an important parameter for the optical response. When the material is transparent, i.e. non-absorbing, at the wavelength of interest, dielectric nanostructures can be (almost) free from parasitic absorption. Dielectric structures need to be larger than plasmonics, on the order of the wavelength or larger. Light can be trapped inside a transparent dielectric and bounce back and forth in a cavity, or travel along the length in a waveguide. When the light goes from one material to another, with a different refractive index, it changes direction, an effect used on the used on macroscopic scale in lenses and prisms. When periodic structures or small holes are used, interference of light from different locations on the structure can give diffraction patterns. By combining resonances, wave guiding, diffractive and refractive effects, dielectrics provide a large range of tools to manipulate light absorption, emission, and scattering. In this thesis, we study nanophotonics of dielectrics, because the parasitic absorption in plasmonics is detrimental to the envisioned applications in solar cells.

1.3 Need for improvement

With the tremendous challenges of the energy transition, existing technologies need to be further optimized and new technologies must be developed. To supply the world with renewable energy, solar, together with wind, is expected to be the major player. To reach the target of less than 1.5° global warming, electricity generation from solar energy has to increase by a factor of 50 in 2050, as shown in figure 1.1.[3] To realize this, solar energy technologies need to be developed further in many aspects.[4] Efficiency improvements are needed to meet the demand and reduce costs, material consumption, and land area use. New photovoltaic (PV) materials must come to market, and semi-transparent and flexible devices must be developed for the increasing range of specific applications. Also on the energy-saving side, large improvements are needed. LEDs must become more efficient to satisfy the growing demand for lighting and displays. Traditional electronics or mechanics might get replaced by more energy-efficient systems from the emerging field of smart materials. For example, by mimicking the human brain with artificial synapses based on optical networks,[5] energy-efficient hardware can be developed for already widely used artificial intelligence algorithms.[6]

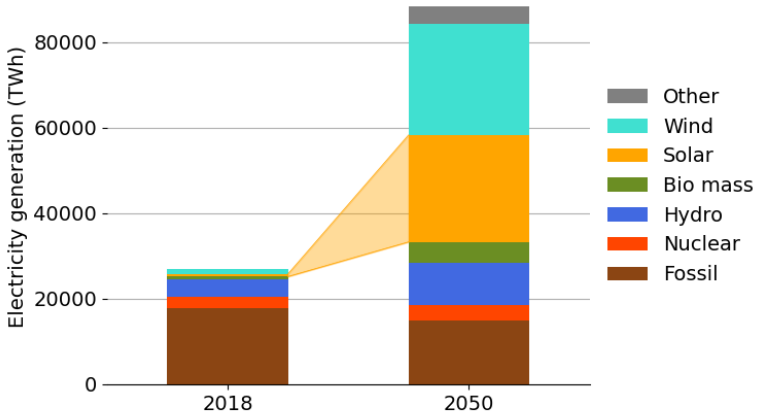

Figure 1.1: Electricity generation in 2018 and needed electricity generation in 2050 by source to reach the 1.5° global warming scenario. Electricity generation from solar power has to increase by a factor of forty from about 600 TWh in 2018 to 25000 TWh in 2050.[3]

1.4 Solar cells

Currently, over 90% of all solar energy generation relies on silicon PV cells.[7] Although tremendous improvements have been made over the past decades in terms of efficiency and costs, silicon solar cells are reaching their limits. Given the intrinsic material properties of silicon, efficiencies above 29% simply cannot be achieved. To keep up with the decrease in price per kWh installed capacity necessary for further growth of the PV market, new techniques must be developed. Nanophotonics provides many tools for further optimization.[8] It has been widely studied for improving solar cell performance, where traditionally the focus has been on improving light absorption, important for maximizing the current generated by the solar cell.[9] The voltage of a cell was more considered a material property, determined by the bandgap and the quality of the material. This has led to record solar cells having their short circuit current (J_{sc}) close to the theoretical limit, while the open-circuit voltage (V_{oc}) was lagging behind.[10] However, by accurately managing the light going into and out of the solar cell with nanophotonic engineering, V_{oc} can also be increased. The mechanisms behind this will be discussed in detail in chapter 2. Also, new solar cell materials must come to market, to fill niche applications where silicon is not applicable, like flexible solar cells, or to join forces with silicon solar cells in tandem configurations. In a tandem solar cell, two materials are combined, that absorb different parts of the solar spectrum: one for the high energy blue and green light and one for the lower energy orange and red light. For both tandem and flexible solar cells, halide perovskite materials are promising candidates, which will be discussed in the next section.

1.4.1 LUMINESCENT SOLAR CONCENTRATORS

Luminescent solar concentrators (LSCs) are an interesting alternative to planar PV panels. LSCs rely on a transparent slab of material impregnated with fluorescent particles. These particles, called luminophores, absorb incident sunlight and re-emit it as fluorescence. Due to total internal reflection on the surfaces of the slab, light is guided towards the edges. Here it is collected with PV cells that are much smaller than the total collection area. This technique has several advantages. First of all the large collection area can be made of an inexpensive polymer or glass, and much less PV cell material is needed. Highly efficient but expensive PV materials like gallium-arsenide become affordable for the small PV cells on the edges. Furthermore, it allows for semi-transparent and colored devices, which suit building-integrated PV. So far efficiency of LSCs has been low, due to the additional loss pathways in the process towards generating electricity. First of all, efficient luminophores are needed, that re-emit close to 100% of the light that they absorb. Subsequently, the light has to travel through the waveguide towards the PV cells. Photons that are emitted towards the waveguide surface at angles smaller than the angle of total internal reflection will escape from the waveguide. Photons that are guided by the waveguide, can be scattered or re-absorbed by the luminophores, which again gives a chance of escaping from the waveguide or decaying non-radiatively in the luminophore. Nanophotonic structures can play an important role in overcoming these limitations and optimizing the waveguide efficiency of LSCs. Since they can be used to accurately control absorption and emission properties as a funtion of wavelength and angle, emission into the waveguide can be improved and re-absorption can be reduced, while maintaining high sunlight absorption. Together with recent improvements in luminophore efficiency, nanophotonic techniques for directional light emission open new possibilities for high-efficiency LSCs.

1.5 PEROVSKITES

Perovskites can be easily called the new wonder material of the twenty-first century. Although this material family was discovered already in 1839 and studied extensively for its superconducting properties, it has experienced an incredible revival since the discovery of a 2% efficient perovskite solar cell in 2006.[11] Initially, the name perovskite referred to a calcium titanium oxide mineral with the chemical formula $CaTiO_3$, but nowadays the name is used to describe the family of materials that consist of corner-sharing octahedra, usually with the generic chemical formula ABX_3. This structure is shown in figure 1.2a. Corner-sharing BX_6 octahedra form the core of the structure and largely determine the optical and electronic properties. The A-site cations in between balance the charge and proivde the necessary crystal stability. Perovskites with many different cations and anions have been made, resulting in a wide range of material properties. In addition, different cations and anions can be mixed within a perovskite crystal, allowing for fine-tuning the properties. A well-known example is the possibility of bandgap tuning through mixing of different halide anions. By gradually moving from pure chloride, via mixed states with bromide, to pure iodide, emission from cesium lead halide perovskite quantum dots can cover the full visible spectrum, shown in figure 1.2b.[12] Perovskites can be easily processed, for example from solution, which gives it the prospect for mass production at low costs.[13] Since the first perovskite solar cell in 2006, a tremendous increase in efficiency has been achieved, to 25.5% in 2020, with which it can now compete with silicon. Also other applications

have been successfully demonstrated, ranging from sensors to batteries and from LEDs to memory devices.

The main limiting factors that are still hampering large-scale application of perovskite devices are stability and toxicity. A perovskite is basically a salt, which easily dissolves in water. For solar cell devices, the high sensitivity to water, and even to humidity in the air, is detrimental. The best performing perovskite solar cells contain lead atoms, which makes dissolving in water and leaking into the environment a serious health threat. In addition, perovskites are known to show a lot of imperfections in the crystal lattice, of missing atoms or atoms at the wrong position. One of the special properties of perovskties is that optical and electronic properties do not suffer a lot from such defects. This is contrary to many other materials, like silicon, where an almost perfect crystal is needed for optimal functioning. On the other hand, these defects make the perovskite properties subject to change. Under influence of light, pressure or electric fields, ions can move around, called ion migration, which changes the optoelectrical properties. While this kind of behavior in some cases can be used, for example in sensors, where sensitivity to external stimuli is desirable, it often limits stable functioning devices. While a lot of research has been dedicated to making perovskites more stable, we show in this thesis how the dynamic nature can be used to our advantage.

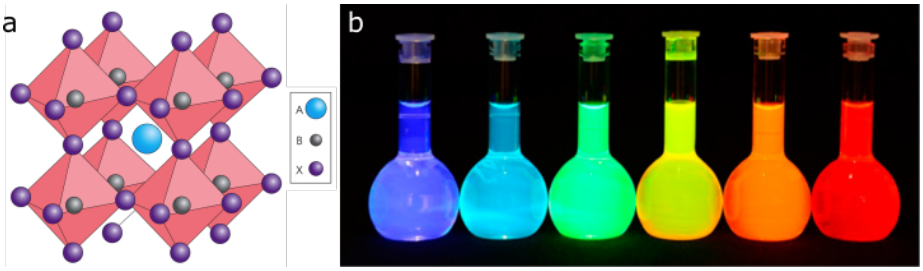

Figure 1.2: a) The atomic structure of perovskite crystal. It consists of two cations (A and B) in the center and on the corners of the cube, respectively, and anions C on the faces of the cube. Each cation and anion can also be a mixture of different elements or molecules, which provides an incredible range of properties that can be accurately tuned by the chemical composition of the perovskite.Figure taken from;[14] b) Cesium Lead halide ($CsPbX_3$, X= Cl, Br, I) nanocrystals can emit light at all visible wavelengths by varying the halide composition. Figure taken from[12]

1.6 Motivation and outline

In this thesis we investigate how dielectric nanophotonic structures can be used to create directional light emission. Through a combination of theoretical analysis and experimental verification we investigate several directional emitting dielectric systems. Simulations show the potential impact of such emitters on device performance: the effect of directional nanophotonic structures on performance in realistic operating conditions for planar and tandem solar cells, the effect of controlled halide segregation on perovskite solar cell performance and the effect of directional emitters on LSC efficiency. A newly built experimental setup is used to measure directivity with higher accuracy than before, in which a record directivity from all-dielectric nanostructures is measured and the dynamics

of a self-optimizing system are tracked.

In **Chapter 2** we give a general introduction of how nanophotonic engineering can be used to reach high efficiency solar cells. The detailed balance method is introduced, which gives an upper limit to solar cell efficiency, which can be used to benchmark solar cell performance. We explain the importance of controlling the light emission for reaching high open circuit voltages, and analyze the potential effect of two nanophotonic applications on solar cell performance in real world operating conditions.

In **Chapter 3** we give experimental evidence of a new record in directional emission from an all-dielectric nanostructured microlens. This record value was achieved by making three improvements compared to previous work. First, a well-localized emitter at the center of the lens was fabricated with direct electron beam patterning of quantum dot emitters. Second, the fabricated lens structure was optimized to accurately match the designed shape. Finally, with a dedicated measurement setup the full directivity into all angles could be measured, by combining a Fourier microscope with an integrating sphere. In conventional measurement schemes only the partial directivity within the numerical aperture of the objective can be determined.

In **Chapter 4** we show how this same microlens can be used for a self-optimizing system, where we use the dynamic nature of mixed halide perovskite films to make a responsive and adaptive system. It shows some of the basic requirements for material learning and memory and can be seen as a case study for a wide range of potential applications where the dynamic and adaptive nature of perovskites is used as a feature. Here we use ligh-induced phase segregation of halide ions in a mixed halide perovskite film to form an emitter in the hotspot of the microlens. The concept of reciprocity states that an emitter in the hotspot of an incoming plane wave, will give directional emission into the direction of the incoming light. This makes the system self-aligned and robust against small distortions in the lens, resulting in higher directivity compared to that of the same lens in Chapter 3.

In **Chapter 5** we investigate how the self-aligned photo-induced phase segregation concept can be applied to perovskite solar cells to make a self-tracking solar concentrator system with absorption of diffuse sunlight. While phase segregation of halide ions in mixed halide perovskites in many cases reduces performance, we show that it can lead to effective concentration and thereby higher efficiency when it happens in a controlled manner. Instead of the nanophotonic microlenses, we use simple glass microspheres, that focus the incoming sunlight, induce local phase segregation and redirect the emission. Simulations predict large potential increases in solar cell performance. Simple large scale monolayer self-assembly of spheres, resulting in increased absorption and directional emission was shown experimentally. The simple fabrication of sphere monolayers gives the prospect for large scale application.

Chapter 6 discusses the potential of directional light emission for Luminescent Solar Concentrators. Thorough Monte Carlo ray-tracing simulations reveal the importance of directivity and the potential for high efficiency LSCs. While intensive research on luminophores with high photoluminescent quantum yield has led to almost perfect emitters, there has been less attention for directional emitters, while both factors are equally important for final performance.

In the final chapter, **Chapter 7**, a more detailed analysis of the concept of forward emitting structures, as introduced in chapter 6, is performed. The Monte Carlo ray-tracing

model is expanded to also include the effects of anisotropic absorption, and the additional benefits of forward emitting structures are revealed.