SOLAR NANOANTENNA ELECTROMAGNETIC COLLECTORS FOR ENERGY PRODUCTION

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ABSTRACT

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With a rapidly growing global population and increasing trends of urbanization and industrialization, anthropogenic activities are placing a large burden on the global energy system. Today, fossil fuels such as oil, natural gas and coal power nearly all sectors of human activity. Unfortunately, fossil fuels are non-renewable and are expected to face rapid depletion over the next decades. In addition, the growing concerns over environmental impacts of greenhouse gas emissions associated with the burning of fossil fuels have pointed out the necessity of making a radical transition toward more sustainable means of energy production.

Nanoantenna solar electromagnetic collectors (NECs) are a new promising alternative technology that can potentially contribute to solving the energy challenge. NECs are small metallic structures capable of directly converting solar energy into electricity through surface plasmon resonance.

This work is a literature review of NECs for solar energy conversion. The aim of this review was to discuss the potential of NECs as a clean, sustainable alternative to fossil fuels. In addition, the possibility of using nanocellulose - a natural wood-derived polymer with remarkable properties – in the fabrication of NECs was evaluated on the basis of available literature and an interview with experts.

The high theoretical efficiency of NECs and the possibility for large-scale, low-cost fabrication methods are important advantages that can potentially make NECs a competitive alternative to photovoltaic solar cells. However, due to technical limitations, efficient energy conversion with NEC devices has not yet been demonstrated. These limitations will need to be addressed in order to make possible the design of high-performance NECs.

The analysis of material properties of nanocellulose suggest that its use in the construction of NECs may be possible. Nevertheless, experimental work will be needed in the future in order to support or reject this claim.

Key words: nanoantenna, rectenna, electromagnetic collector, infra-red radiation, nanocellulose, solar energy conversion, plasmon resonance
### KEY NOTIONS

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<th>Notion</th>
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<tr>
<td>Complex dielectric function</td>
<td>The complex dielectric function of a material describes the electrical and optical behavior of a material when an electric field such as an oscillating electromagnetic wave is applied. This function consists of two parts: the first part represents how much a material becomes polarized in response to the applied electric field, while the second part represents the absorption properties in the material.</td>
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<td>Directivity</td>
<td>A measure of how efficiently an antenna radiates in one direction. It is the ratio of the power density the antenna radiates in the direction of its strongest emission versus the power density radiated by an ideal radiator that emits radiation uniformly in all directions. A high directivity is a desirable feature in antennas.</td>
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<td>Electromagnetic radiation</td>
<td>Energy that moves through space and matter both in the form of magnetic and electric waves and in the form of a stream of particles called photons. Electromagnetic waves travel at the speed of light in a vacuum. The entire range of frequencies and wavelengths of electromagnetic radiation makes up the electromagnetic spectrum. Examples of electromagnetic radiation include radio waves, infrared, visible light, ultraviolet, x-rays and gamma rays.</td>
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<td>Electron tunneling</td>
<td>The quantum mechanical phenomenon where an electron tunnels through a potential barrier that it classically could not surmount.</td>
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<td>Impedance</td>
<td>A measure of the opposition that an electronic component, circuit or system presents to a current when a voltage is applied. Impedance is a vector quantity consisting of two independent scalar phenomena: resistance and reactance. Resistance is a measure of the extent to which a substance opposes the</td>
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movement of electrons among its atoms. Low-resistance materials are good electrical conductors, while high-resistance materials act as insulators (dielectrics). Materials with intermediate resistance are classified as semiconductors. Reactance describes the extent to which an electronic component, circuit or system stores and releases energy as the current and voltage fluctuate. Reactance is observed for (AC) alternating current but not in the case of direct current (DC). Energy may be stored in the system in the form of a magnetic field (inductive reactance) or in the form of an electric field (capacitive reactance).

Plasmonic material  A metal or metal-like material with unique optical properties. Plasmonic materials exhibit strong light absorption in the visible region of the spectrum. The origin of this absorption is associated with the collective oscillation of electrons on the surface of the material in response to the electric field caused by electromagnetic radiation. The optical properties of plasmonic materials can be modified by controlling their structure.

RC time constant  It is the product of the circuit resistance and the circuit capacitance. It is the time required to charge a capacitor, through a resistor by 63.2% between the initial and the final value, or the time required to discharge a capacitor to 36.8%.

Resonance  A phenomenon in which a system is caused to oscillate with greater amplitude at some frequencies by another vibrating system or by external forces exerted on the system. Resonance occurs when the natural frequency of a system matches the frequency of the external force.

Resonance frequency  A frequency capable of exciting a resonance maximum in a given body or system. The resonance frequency is determined by the physical parameters of the resonating object.
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1 INTRODUCTION

1.1 Objectives of the study

The objectives of this study are two-fold: (1) to discuss the potential of solar nanoantenna electromagnetic collectors (NECs), or nanoantennas, as an alternative technology for the conversion of solar infrared radiation into electricity; and (2) to assess the suitability of nanostructured cellulose as novel material in the fabrication of nanoantennas.

This study attempts to provide the reader with a clear understanding of key concepts and issues related to the production of electricity using nanoantenna devices. NECs are discussed from the perspective of energy production with the aim of determining whether or not nanoantennas can contribute to electricity production on a large scale and be competitive on the global energy market.

In addition, this study investigates the possibility of using nanocellulose, a novel and regenerative material, in the fabrication of nanoantennas by exploiting its modified material properties at the nanoscale.

1.2 Scope of the study

Chapter 3 of this study is a concise, literature-based review that explores the topic of nanoantenna electromagnetic collectors in the context of energy production and conversion. The aspects discussed hereby include a brief history of the invention of nanoantennas, a few technical notions relevant to the last part of the study, materials used in current nanoantenna structures, fabrication methods, efficiency limits and an overview of potential applications.

In chapter 4, nanoantennas are discussed in the light of economic factors such as cost of production and durability. The competitiveness of nanoantennas is also questioned and compared to other similar technologies in an attempt to understand the underlying reasons for their slow arrival on the market.
In chapter 5, the suitability of nanostructured cellulose as material in the structure of a nanoantenna is evaluated. This evaluation was performed as an interview with experts. First, a short theoretical background for nanocellulose is provided, including a few key concepts relevant to the above-stated objectives. The results and conclusions of the interview are then reported and discussed in detail.

This review does not include an extensive mathematical background for the theory of operation of nanoantennas; only essential physical properties and notions relevant to the objectives are mentioned. As nanoantennas are discussed in the context of energy production, other possible aspects (e.g. applications) not consistent with the topic were excluded.
2 CONTEXT

Since the industrial revolution, the global energy demand has been steadily increasing – at an alarming rate. Nearly all sectors of anthropogenic activities have become heavily dependent upon the use of fossil fuels. Oil, natural gas and coal are currently the main sources that are used to supply the energy necessary for human activities, accounting for over 80% of the total primary energy supply (IEA 2014a). These fuels are finite resources and will eventually be depleted. The growing global population places an additional burden on the energy production system worldwide, and a major shift towards a more sustainable energy supply is therefore necessary. In addition, the intensive use of fossil fuels has raised concerns over their impact on the environment and climate.

2.1 The energy challenge

The world’s energy system is under significant stress and faces the risk of failing to meet the energy demand of a rapidly growing global population and increasing urbanization trends. With a global population expected to reach 9 billion (United Nations 2012) and more than 60% of the population living in cities by 2040 (United Nations 2014), it is evident that this growth will have major consequences on the global energy demand.

The rise of new technological innovations and constant efforts to improve efficiency and reduce costs have contributed to the mitigation of such risks to some extent, but the security and sustainability of energy supply remain a major concern (IEA 2014b).

According to a report on the world’s energy outlook published by the International Energy Agency, global energy demand is prospected to grow by 37% by 2040 (IEA 2014b). The total primary energy supply has doubled between 1971 and 2012 with oil still being the major fuel, currently representing a share of 40% in total final consumption (IEA 2014a). The growing demand for oil in sectors of transport and petrochemicals is expected to rise oil consumption from 90 million barrels per day in 2013 to 104 million barrels per day in 2040 (IEA 2014b). However, oil resources are finite and predicted to decrease sustainably over the next few decades (Millar & Sorrell, 2014).
According to IEA in World Energy Outlook 2014, electricity is the fastest growing final form of energy. In 2012, global electricity generation exceeded 20 000 TWh, showing an increase of 270% since 1971. It is estimated that approximately 7200 gigawatts of capacity are needed to bridge the gap between current and expected demand in electricity in 2040. The ageing of currently active power plants is also an additional factor to be considered, as an estimated 40% of the current plants will be shut down by 2040. (IEA 2014a.)

2.2 CO2 emissions and climate change

The industrial revolution led to an increase in greenhouse gas emissions of anthropogenic origin that has caused the Earth’s surface to warm by about 0.8°C since the pre-industrial era, with most of the warming occurring in the past few decades (NASA 2014). According to a report published by the International Energy Agency - Key World Energy Statistics 2014 -, over 30 gigatons of anthropologically generated CO2 were released into the atmosphere in 2012, which represents a 100% increase in CO2 emissions in just four decades. In one scenario presented in this report, CO2 levels are expected to rise by one fourth by 2035. In a second scenario based on plausible measures to limit the long-term concentration of greenhouse gases at 450 ppm CO2-equivalent (level needed to limit global average temperature rise to 2°C), the CO2 emissions have to decrease by one third by 2035. (IEA 2014a).

A rise in global temperature of 2°C and above is feared to have severe consequences on climate and the global environment, as it is predicted to cause increased floods, hurricanes, droughts, in addition to ocean acidification and rising sea levels due to melting ice caps and sea water expansion. These consequences are more than likely to have adverse effects on biodiversity, which is essential in maintaining the earth’s ecosystems in balance. (Pidcock, 2014.)
2.3 Global initiatives for tackling the energy challenge

Multiple international environmental summits and conferences are held annually to discuss issues related to limiting the environmental impact of the modern lifestyle on the environment. Some of these summits have led to the establishment of international agreements that commit their participants to taking action in energy and environmental matters.

An example of such an initiative is the European Union’s “2020 Climate and Energy Package”. Having understood the gravity of the situation, the European Union has taken the energy challenge seriously. Following agreements made at the European Council in 2007, EU leaders created a set of objectives under the Renewable Energy Directive, known as the 20-20-20 targets, in which they committed Europe to become a highly “energy-efficient, low carbon economy” by the year 2020 (European Commission 2015). The three key objectives of this agreement include a 20% reduction in EU greenhouse gas emissions from 1990 levels, an increase of the share of renewable energy to 20% in the EU’s gross final energy consumption, and a reduction of 20% in total primary energy consumption by 2020 - relative to the 2007 prospects of energy consumption in 2020. (IEA 2014c.)

Rapid progress has been observed towards achieving the energy targets, but further measures are still necessary in order to meet the expected targets by 2020 (IEA, 2014c).

2.4 Harvesting energy from the sun

The role of renewable energy sources is critical in ensuring that climate targets are met and that energy security is achieved.

Sun is the most abundant permanent source of renewable energy. The amount of solar radiation emitted by the Sun that reaches the Earth’s surface in one hour is enough to power all human activities for an entire year (Lewis & Nocera, 2006).

Solar energy is available in its direct and indirect forms: solar radiation can be harvested directly for heating purposes, but also indirectly in the form of wind, hydro, biomass and
electricity (World Energy Council 2013). The incoming solar radiation plays a major role in various climatic phenomena and can be harvested in multiple forms. For example, solar energy creates winds, waves and drives the water cycle. Radiation from the sun is also utilized by Earth’s primary energy producers – plants. Plants absorb energy from the sun and turn it into biomass through the process of photosynthesis. (Hester et al. 2003.) In fact, solar energy in all its forms (thermal, photovoltaic, wind, tidal, biomass etc.) represents the single major contributor to renewable energy sources.

The direct conversion of solar energy into electricity on a large-scale has been made possible by the emergence of photovoltaic (PV) solar cells. Photovoltaic devices are made of semiconducting materials that absorb energy from the sun to excite electrons on their surface, knocking them out of their orbit and producing an electron flow that translates into electric current. Solar cells are robust structures that require very little maintenance, and with such advantages, it is easy to understand why PV cells are an attractive technology that is rapidly expanding on the global energy market. (Mescia & Massaro, 2014).

However, photovoltaic solar cells have several limitations. Only a small part of the incoming solar radiation can be converted to electricity by semiconductors due to intrinsic material characteristics electrical properties. The remaining radiation can be absorbed by the cell but it is converted into heat. (Kotter et al. 2008.) Although important technological progress has been achieved in the field, the most efficient solar cells currently produced have showed energy conversion efficiencies of 44%, but their structure is more complex than conventional silicon-based cells and thus more expensive to produce on a commercial scale. Traditional single-junction PV cells generally have lower efficiencies in the range of 10% to 20% (Kotter et al, 2008; World Energy Council 2013). In addition, the performance of photovoltaic cells is largely dependent on weather factors and other physical conditions, which adds to the unpredictability of such devices. Power generation from photovoltaic cells fluctuates with changes in the amount of solar irradiation they receive during the day and their performance can be influenced by changes in temperature (International Energy Council 2013).
2.5 Solar nanoantenna electromagnetic collectors: A promising alternative

A relatively new technology that has yet to prove itself on the global energy market as a promising alternative to conventional solar energy conversion technologies is the nanoantenna.

Solar nanoantenna electromagnetic collectors (NECs), or nanoantennas, are devices that exploit the wave nature of light - as opposed to its particle nature, used in the design of photovoltaic solar cells (Corkish et al. 2003). NECs are small structures in the range of a few hundred nanometers to a few microns that convert the energy from electromagnetic radiation directly into current in a circuit (Mescia & Massaro, 2014, 3).

NECs are specially designed for the capture of infrared radiation (IR) of wavelengths ranging from 0.7 to 100µm, which is an abundant energy source representing approximately 50% of the total incoming solar radiation that reaches the Earth’s surface (Kotter et al, 2008; Mescia & Massaro, 2014). At these wavelengths, conventional photovoltaic cells have proven inefficient (Kotter et al. 2008). What is more, nanoantennas have been reported to demonstrate high efficiencies that outweigh those in typical photovoltaic cells by far – under certain conditions (Kotter et al. 2008).

In the following chapters, NECs are discussed in more detail. Chapter 3 aims at providing an overview of the basic theory, concepts and requirements for the design of NECs. In this chapter, selected materials and fabrication processes, efficiency limits and applications of nanoantennas are also discussed in an attempt to understand the principles of operation of these devices as well as possible limitations.
3 SOLAR NANOANTENNA ELECTROMAGNETIC COLLECTORS

Antennas are not a new technology. They are used across a wide range of frequencies in the electromagnetic spectrum and can be considered as one of the most revolutionary inventions for the modern society. Today, antennas are used for multiple telecommunication systems such as televisions, radios, cell phones, radar and satellite communication - to list a few. Conventional antennas work at radio-frequencies (RF) and either “transmit” or “receive” signals. In other words, a radio-antenna is a structure in which a free-space wave is converted into a guided wave, or vice versa. The theory and principles of RF antennas are well known and can partially be applied to nanoantennas. (Maradudin et al. 2014, 109-111.) However, due to unique material properties of metals that influence the behavior of antennas at the nanoscale, the application of traditional antenna theory in the design of optimized and efficient nanoantennas has proven difficult (Barnard, 2011).

In this chapter, the history of nanoantennas is reviewed briefly. The technical context of nanoantennas and a few design considerations are presented. In addition, information related to fabrication methods, materials, nanoantenna performance in terms of energy conversion efficiency, and an overview of current and potential applications is provided in this chapter.

3.1 Brief history of nanoantennas

Although the collection of electromagnetic radiation in the infrared region and its conversion to electricity with nanoantenna structures was suggested more than four decades ago, their arrival on commercial-scale energy markets has not yet been achieved. The concept of collecting solar energy with nanostructures that exploit the wave nature of light was first proposed by Robert Bailey in 1972. (Corkish et al. 2003, 395.)

In 1973, Bailey, along with James Fletcher, received a patent for their idea of an “electromagnetic wave energy converter” (Appendix 1). This device consisted of pairs of conical structures mutually insulated from each other and aligned in columns and rows.
with each pair electrically connected to a diode, a low-pass filter and a load. In the patent, Bailey and Fletcher also described the dimensions and spacing requirements of nanoantenna structures for improved absorption of the incident electromagnetic radiation. (Fletcher & Bailey, 1973.)

Since then, intensive research in the field of nanoantennas has taken place and multiple patents for electromagnetic energy converter devices have been issued. In 1984, Alvin Marks was the first to patent a device that explicitly stated the use of sub-micron antennas for the direct conversion of solar energy to electricity. Marks’ device brought structural improvements to Bailey’s invention and showed a substantially higher performance. (Corkish et al. 2003, 395; Nazarov et al. 2014, 243; Sadashivappa & Sharvari, 2015, 1.) Following his first invention, Marks also patented multiple other devices with varying structures and materials intended for the collection and conversion of electromagnetic energy (Corkish et al. 2003, 395-396).

In 1996, Guang H. Lin reported the first experimental evidence of a nanostructure with antenna-like properties. His device consisted of an array of parallel dipole antennas on a silicon substrate. The device was reported to absorb electromagnetic radiation at a resonant frequency dependent on the frequency of the incident wavelength and the antenna dimensions. In addition, his invention allowed for the rectification of light in the visible range, which is a critical aspect for the conversion of solar energy into electricity. (Corkish et al. 2003, 395-396; Nazarov et al. 2014, 243; Sadashivappa & Sharvari, 2015, 1-2.)

Following a request from the National Renewable Energy Laboratory (USA), ITN Energy Systems Inc. conducted a relatively thorough study with the aim of demonstrating the feasibility of high-efficiency optical frequency technology (nanoantennas) at a single wavelength. Although ITN Energy Systems Inc. succeeded at achieving over 50% energy conversion efficiency with nanoantenna-rectifier structures operating in the microwave range at a 10 GHz frequency, a very low efficiency was observed (less than 1%) at 10μm wavelengths (30THz). (Corkish & Green, 2002, 1-2; Corkish et al. 2003, 395-396; Nazarov et al. 2014, 243-244; Sadashivappa & Sharvari, 2015, 1-2.)

More recently, a large variety of nanoantenna structures has been investigated by a number of research groups worldwide in an attempt to overcome scientific and engineering challenges faced in the design of efficient nanoantennas. Examples of nanoantennas are presented in section 3.2.6.
3.2 Technical context and design considerations

In this section, the basic theory for the operation of nanoantennas is presented. A few design and material considerations that influence the performance of nanoantenna electromagnetic collectors are reviewed. In addition, the theoretical energy conversion efficiency is also discussed.

3.2.1 Simplified theory of operation

Although the first nanoantenna models were initially inspired by their analogous macroscopic antennas operating in the RF domain, the principles by which they operate differ significantly.

Due to their cyclic nature, electromagnetic waves induce time-varying electric fields in metals that exert a force on the gas of electrons inside the material, causing the charge carriers to oscillate in a collective movement. This phenomenon is known as surface plasmon. Specific optical frequencies can cause the nanoantenna to resonate at the same frequency as the incoming wavelength, enabling the absorption of the incoming radiation. (Barnard, 2011.) At these frequencies, the resonance produces a displacement of charges inside the metal, causing the oscillating electrons (i.e. surface plasmon) to freely move across the nanoantenna. The flow of electrons across the nanoantenna produces an alternating current that has the same frequency as the resonance. (Kotter et al. 2008.) However, because the nanoantenna itself does not provide a way to convert the collected current into DC current, the structure needs to be complemented with a rectifying element (Mescia & Massaro, 2014). The whole structure is commonly referred to as a rectenna.
Picture 1 below represents a typical rectenna block diagram.

![Block diagram of a rectenna](image)

PICTURE 1. Block diagram of a rectenna (Mescia & Massaro, 2014, 3).

The components of a rectenna generally consist of a nanoantenna that collects the incoming infrared radiation, a diode to rectify high-frequency AC current into DC current, and a load for the storage or use of the converted current. In addition, the low-pass filters provide impedance-matching between the different components to ensure a higher performance of the structure (Mescia & Massaro, 2014, 2-3).

### 3.2.2 Wave propagation and complex dielectric function

When the dimensions of a nanostructure are significantly smaller than the incident wavelength, it can be considered that the entire structure experiences a uniform electric field at any instant in time due to the high coherence of the incoming electromagnetic radiation. In this case, the resonance effects can be determined by solving for the electrostatic potential (corresponding to the operating voltage) for a structure of a given geometry and dielectric constant embedded within a uniform electric field. However, when the dimensions of a nanoantenna become comparable to the resonance wavelength, the optical phase can vary across the structure and retardation effects in wave propagation become non-negligible. (Barnard, 2011, 2-3.) At optical frequencies, the conductivity of metals changes dramatically. At these frequencies, metals no longer behave as perfect conductors and thus are unable to respond to the time-varying electric field immediately. (Novotny, 2009, 5.) In this case, the dielectric properties of metals become frequency-dependent. This property affects wave propagation within the material. (Barnard, 2011, 2-4; Moddel & Grover, 2013, 235-239; Mescia & Massaro, 2014, 2-3.) The interaction of nanoantennas with the electromagnetic field in this regime is determined by a complex
dielectric function, which can be described using the Lorentz-Drude model (Mescia & Massaro, 2014, 2-3):

\[
\varepsilon_r(\omega) = \varepsilon_r^f(\omega) + \varepsilon_r^b(\omega)
\]

where

\(\omega\) is the frequency of the incident electromagnetic wave
\(\varepsilon_r(\omega)\) is the frequency-dependent dielectric function
\(\varepsilon_r^f(\omega)\) is the part describing the contribution of free electrons to the relative dielectric constant.
\(\varepsilon_r^b(\omega)\) is the part describing the contribution of bound electrons to the relative dielectric constant.

\(\varepsilon_r^f(\omega)\) describes the degree of polarization in the material due to the electric field induced by an electromagnetic wave, while \(\varepsilon_r^b(\omega)\) reflects the extent of absorption that occurs in the material due to non-ideal conduction properties (dissipative losses).

The contribution of free-electron effects to the dielectric function can be described by the Drude model:

\[
\varepsilon_r^f(\omega) = 1 - \frac{\Omega_p^2}{\omega^2 - (\omega - i\Gamma_0)^2} \tag{2}
\]

On the other hand, the contribution of bound electrons to the dielectric function can be described by a model similar to the Lorentz result for insulators:

\[
\varepsilon_r^b(\omega) = \sum_{j=1}^{k} \frac{f_j\omega_p^2}{(\omega_j^2 - \omega^2) + i\omega \Gamma_j} \tag{3}
\]

where

\(\omega_p\) is the plasma frequency
\(k\) is the number of oscillators with frequency \(\omega_j\), strength \(f_j\) and lifetime \(1/\Gamma_j\)
\(\Omega_p\) is the plasma frequency of the free-electron transitions with oscillator strength \(f_0\) and damping constant \(\Gamma_0\)
Because the resonant length of the antenna does not scale linearly with the incident frequency, the effective wavelength $\lambda_{\text{eff}}$ at which the nanoantenna is induced in resonance mode can be calculated as follows:

$$\lambda_{\text{eff}} = n_1 + n_2 \frac{\lambda}{\lambda_p}$$

where

- $\lambda$ is the wavelength of the incident electromagnetic radiation
- $\lambda_p$ is the plasma wavelength of the metal
- $n_1$ and $n_2$ are constant values depending on the geometry and dielectric parameters of the nanoantenna.

### 3.2.3 Non-resonant field enhancement

Non-resonant effects can also be used to improve field (light) enhancement properties in a nanoantenna structure. One way to do so is the introduction of a small gap in the metal structure, known as a feedgap. The improvement of field concentration in this case can be attributed to the build-up of charges of opposite signs across the metal-dielectric interface by forcing charge carriers into a very small space.

Picture 2 is a simulation of the near-field enhancement that occurs in a gold optical nanoantenna structure designed with a feedgap. The simulation shows a large near-field enhancement in the feedgap region, indicating that the nanoantenna is efficiently concentrating the electric field within the gap.

![Picture 2](image)

PICTURE 2. Simulation of electric field distribution and near-field enhancement in the feedgap of a gold nanoantenna (Barnard, 2011, 3).
Another similar approach that can be used to enhance field concentration is taking advantage of the lightning rod effect (Barnard, 2011, 5). In an electrically charged object, the electric fields are the strongest in its sharpest features. For instance, in a lightning rod, the strongest electric fields are found at the sharp tip of the rod. (UT Austin, undated.) The lightning effect has a similar influence on charges to that of the feedgap. In a nanoantenna, a sharp metal termination alters field continuity in the metal, forcing electrons into a small space (Barnard, 2011, 5).

Metal cones and wedges are good examples of structures that can be utilized in the design of efficient field-enhancing nanoantennas. These shapes have been showed to increase field concentration gradually within the nanoantenna as the electron wave propagates towards the narrow end of the structure (Barnard, 2011, 5).

3.2.4 Construction and materials

For the purpose of energy conversion, the nanoantenna needs to be coupled to a rectifying element and connected to an electric circuit, as shown in picture 1. A review of the main constituents of rectennas and materials used in their construction are discussed in this section.

When radiation reaches the rectenna, it is first collected by the nanoantenna element. One possible configuration for an array of nanoantenna elements consists of three main parts: a metal antenna layer, a dielectric standoff layer where the spacing creates an optical resonance cavity, and a ground-plane. The ground-plane is used to reflect radiation back toward the antenna and the standoff layer acts as a transmission line in which resonance effects are enhanced. (Kotter et al. 2010.)
The materials used in the construction of nanoantennas are commonly metals (e.g. silver and gold) for the antenna layer, and a transparent dielectric material for the standoff substrate, such as plastic polymers or glass (Kotter et al. 2010).

The alternating current generated in the nanoantenna is then collected and rectified into direct current by the rectifying element. At GHz frequencies, Schottky diodes can be used for rectification, but the transit time of charges in the semiconductor p-n junction limits their efficiency at THz and optical frequencies. Above 12THz, Metal-Insulator-Metal (MIM) diodes are commonly used for this purpose. The transport mechanism of charge carriers (i.e. electrons) is based on the electron tunneling between two metallic sheets separated by a very thin oxide layer whose thickness is a few nanometers – generally less than 3 nm in thickness. For an efficient MIM diode, the barrier height between metals typically needs to be less than 0.5 eV. The tunneling time is on the order of femtoseconds, which is an advantageous property because the high frequencies of THz and optical radiation require high-speed rectification. (Moddel & Grover, 2013, 8-27; Zhu et al. 2013, 5.) Examples of material combinations used for diode rectifiers include Ni/NiO/Ni, Nb/Nb2O5/Pt, Nb/TiO2/Pt, Cu/TiO2/Pt, Nb/MgO/Pt and Nb/Al2O3/Nb (Moddel & Grover, 2013, 225, 328).
Because the output obtained from a single nanoantenna element is not sufficient to drive the rectifier and extract power, nanoantennas are combined and arranged into arrays to increase their signal. The total field captured by the array corresponds to the vector addition of the fields captured by separate nanoantennas, assuming that the fields of individual elements interact in a constructive way. (Moddel & Grover, 2013, 246-247.)

Picture 4 below shows an example of a square-spiral nanoantenna array constructed on a dielectric substrate.

PICTURE 4. Array of square-spiral nanoantennas (Kotter et al. 2010, 3).
3.2.5 Design requirements

In order to construct an efficient rectenna structure for energy conversion, several key aspects related to the electric behavior, the choice of materials and the geometry of both the antenna and the diode have to be addressed.

First, the nanoantenna is required to be able to efficiently capture all polarizations of light. For this purpose, a wide acceptance angle is essential. Nanoantennas should also be able to efficiently concentrate the incoming radiation and guide it to the desired direction. Ideally, the material used in the construction of the nanoantenna should exhibit no losses during the collection of electromagnetic radiation, but this is hardly achievable due to the finite conductivity of metals at THz frequencies. (Moddel & Grover, 2013, 14; Zhu et al. 2013, 8.)

For the rectifying diode, the design considerations that need to be considered are more challenging than in the case of the nanoantenna, as several circuit-related aspects have to be addressed simultaneously. In addition to the small size required for its successful incorporation in a rectenna structure, the diode should have a small turn-on voltage and demonstrate high-speed rectification (Mescia & Massaro, 2014, 6). The most critical aspects that influence its performance are diode resistance, capacitance and reverse-bias leakage. The impedance of the diode must also match that of the nanoantenna for efficient power transfer. In addition, the RC time constant must be much smaller than the time constant corresponding to THz frequencies (in the order of femtoseconds) to ensure efficient rectification. Finally, it is essential for the diode to have a small to negligible reverse-bias leakage and a low forward resistance to enable the movement of charge carriers in one direction. Concerning the choice of materials, electrical stability under high current density is crucial. (Moddel & Grover, 2013, 8-10, 89-109.)

The overall performance of nanoantenna arrays is influenced by several factors, such as the geometrical configuration of the array, the spacing between individual nanoantenna elements, the excitation amplitude and phase of the elements, and the relative pattern of the individual element (Moddel & Grover, 2013, 246-247).
3.2.6 Common nanoantenna designs

So far, research in nanoantennas has primarily focused on structures made of metallic materials (e.g. gold or silver) that can support plasmonic resonance. A large variety of antenna geometries has been researched for multiple potential applications. The main types of nanoantennas are presented in Picture 5.

![Picture 5. Main types of plasmonic nanoantennas (Krasnok et al. 2014, 145)](image)

Different types of plasmonic antennas may have different properties and hence serve different purposes. For instance, dipole nanoantennas have a high coefficient of electric field localization and bowtie nanoantennas have a broadband absorption spectrum. On the other hand, the high directivity obtained with Yagi-Uda optical antennas can be useful in many applications in wireless communication or on an optical chip. (Krasnok et al. 2014, 145-146.)

More complex structures have also been designed for the research of optimal nanoantenna dimensions and geometry. For example, some of these structures include square-spiral nanoantennas, log-periodic and Archimedean-spiral antennas (Kotter et al. 2010; Briones et al. 2013).
Picture 6 shows the shape of these three types of nanoantenna patterns.

![Nanoantenna patterns](image)

**PICTURE 6.** Optical antennas. (a) log-periodic antenna, (b) square-spiral antenna and (c) Archimedean-spiral antenna (Briones et al, 2013, 4).

Spiral-shaped optical antennas have been the subject of multiple studies in the field of solar energy conversion due to their notable properties. This type of nanoantennas generally have a broad bandwidth and can concentrate light efficiently. They also demonstrate a high directivity that can be further improved by increasing the number of arms. In addition, they are good resonators and are therefore expected to capture a large electric field at resonance. (Mescia & Massaro, 2014, 4; Kotter et al. 2010.)

In addition to plasmonic nanoantennas, it has recently been suggested that optical antennas constructed with all-dielectric materials could be good competitors to their metallic counterparts due to unique features not found in plasmonic nanoantennas (Krasnok, 2014, 143-167).

Dielectric materials in the construction of optical antennas have several advantages over their metallic counterparts for two main reasons: first, dielectric materials exhibit very low dissipative losses at optical frequencies, indicating that only a minimal part of the electromagnetic wave is turned into heat instead of current – dissipative losses are up to two orders of magnitude smaller for silicon when compared with gold or silver nanoparticles (Maksymov et al. 2012,4-5). Second, dielectric materials generally have a very high permittivity, which supports both electric and magnetic resonance modes in the material and thus improves radiation efficiency and antenna directivity, expanding the range of applications for nanoantenna structures. (Krasnok et al. 2012; Maksymov et al. 2012, 4-5; Krasnok et al. 2014, 143-167.)
A recent study (Krasnok et al. 2012) used silicon nanoparticles to demonstrate the performance of all-dielectric nanoantennas. The designed antenna, an all-dielectric Yagi-Uda nanoantenna, consisted of four directors and one reflector particle made of silicon. In this type of structure, the optimal performance is obtained when the director nanoparticles sustain a magnetic resonance and the reflector nanoparticle sustains an electric resonance. For this reason, the radii of the director and reflector nanoparticles were carefully chosen to achieve the maximal constructive interference in the forward direction, suppressing radiation in the opposite direction. Picture 7 shows a 3D representation of the antenna.

![Picture 7. All-dielectric Yagi-Uda nanoantenna, consisting of the reflector (sphere 1 on the left) and four directors (spheres 2-5). (Maksymov et al. 2012)](image)

The results of the study suggest a very good directivity and an almost negligible backscattering across the nanoantenna structure. In addition, when the spacing between nanoparticles was decreased, the radiation efficiency of the all-dielectric nanoantenna was found to be insensitive to the separation distance, while the radiation efficiency of a plasmonic antenna of similar design and dimensions was greatly affected by the decrease in distance between particles. This is due to increased metal losses caused by proximity of adjacent metallic nanoparticles. However, the overall performance of both the dielectric nanoantenna and its metallic counterpart did not show a significant difference. This result can be attributed to the fact that silicon nanoparticles, although exhibiting small dissipative losses, absorb the electromagnetic energy by their whole volume, while absorption only occurs at the surface of metallic particles, resulting in no substantial difference in the performance of the two types of nanoantennas investigated in this study. (Krasnok, et al., 2012; Maksymov et al, 2012, 4-5.)
Many other dielectric materials such as germanium, aluminum arsenide and aluminum antimonide also exhibit high permittivity and low dissipative losses, making them potentially suitable materials for the design of all-dielectric nanoantennas (Krasnok et al. 2012).

### 3.2.7 Efficiency limits

The energy conversion efficiency of a rectenna structure is essentially dependent on the combined efficiencies of its two main components, the nanoantenna and the rectifying element (Sadashivappa & Sharvari, 2015, 6). The nanoantenna efficiency reflects its capacity to concentrate radiation and guide it to the desired direction. The efficiency of the rectifying element is related to its ability to rectify the generated AC current into DC current.

However, numerous loss mechanisms exist for each stage of the energy conversion process. The efficiency of the nanoantenna itself depends on the combined efficiencies of several factors such as the ability to couple the incident electromagnetic radiation and dissipative losses within nanoantenna structure. Other factors such as impedance matching to the rectifying element and the coupling efficiency of the rectifier to the load also influence efficiency. Therefore, the overall efficiency $\eta$ for a rectenna can be described as the product of the efficiencies of each step in the energy conversion process. It is expressed as follows: (Moddel & Grover, 2013, 15, 31-32.)

$$\eta = \eta_a \eta_s \eta_c \eta_j$$

where

$\eta_a$ is the efficiency of coupling the incident electromagnetic radiation to the antenna. It is dependent on the radiation pattern of the nanoantenna and its bandwidth.

$\eta_s$ is the efficiency with which the collected energy is transmitted to the rectifier (diode).
\( \eta_c \) is the coupling efficiency between the antenna and the diode. This requires impedance matching for efficient power transfer. Series resistance losses in the diode also need to be considered.

\( \eta_j \) is the efficiency with which power received by the diode is rectified.

Bailey first suggested that the maximum solar energy conversion efficiency for nanoantennas could, in theory, be close to 100%. However, progress in research has proven that the efficiency of nanoantennas is subject to more restrictive limitations (Corkish et al. undated).

It has been suggested that the ultimate energy conversion efficiency limit for a rectenna with an ideal rectifying element is only limited by the Landsberg limit of 93.3%, which is a strictly thermodynamic radiation conversion limit. For a non-frequency-selective collector with ideal concentrating properties, the nanoantenna is expected to behave like a solar thermal collector with the corresponding Landsberg efficiency limit of 85.4%. For a nanoantenna with infinite selectivity (infinite number of frequency-selective filters), the limit is estimated to be 86.8%. (Zhu et al. 2013, 8-10; Corkish et al., undated, 6-7.)

However, this limit is still questioned, and more realistic analyses taking the coherence of sunlight\(^1\) into account have pointed out that the Trivich-Flinn efficiency limit applicable to photovoltaic solar conversion may also be valid for nanoantennas (Moddel & Grover, 2013, 17; Zhu et al. 2013; Corkish et al. undated, 6-7). This is attributed to the broadband efficiency limit: in order to obtain 100% quantum efficiency (one electron excited per one photon), the operating voltage of the rectenna has to be equal to the photon energy of the incoming electromagnetic radiation. This condition can be met for monochromatic sources. However, for broadband illumination such as solar radiation, because a rectenna can only function at a single operating voltage, only photons at the operating voltage can be optimally used. Photons with lower energy are not collected, and higher energy photons are only absorbed partially, which prevents the efficient collection of radiation over the entire range of the solar spectrum. For this reason, the broadband rectenna efficiency limit is 44% for the solar spectrum. In traditional single-junction solar cells, the same efficiency limit is obtained because the solar cell operates at a single bandgap energy. Therefore, an analogy between these two types of solar energy

\(^{1}\)Sunlight is coherent only over a limited area. A coherence of 90% for a broadband solar spectrum can be obtained over a circle of radius no larger than 19\(\mu m\) (Moddel & Grover, 2013, 5). The incident electromagnetic radiation must be at least partially coherent to ensure that the components from nanoantenna arrays combine in a constructive manner (Corkish, et al., 2003, 398).
converters can be drawn, since the operating voltage in a rectenna limits the efficiency similarly to the way bandgap limits the efficiency in conventional solar cells. (Moddel & Grover, 2013, 47-68; Zhu et al. 2013, 9-10.)

However, to this date, the power conversion efficiencies obtained experimentally remain extremely low. This is mainly attributed to the challenges faced in the design of rectennas, i.e. the choice of materials, the poor AC-to-DC rectification at THz frequencies and the impedance mismatch between the nanoantenna element and the diode used for rectification. In a numerical simulation conducted by Briones et al. (2013), the power conversion efficiencies obtained at infrared wavelengths for three types of broadband antennas coupled with MIM or Esaki diodes were in the order of $10^{-9}$ to $10^{-6}$. These results were associated with the poor performance of diodes at high frequencies, but also to the impedance mismatch between rectenna components.

3.3 Methods of fabrication

The recent advances in self-assembly methods and ultra-high resolution lithography have enabled the development of precise patterning techniques at the nanoscale level. These methods of fabrication can be classified as either top-down or bottom-up techniques, depending on the approach. In bottom-up techniques, smaller components are assembled into more complex structures using interactions between nanoparticles to create the desired geometry, while top-down techniques rely on conventional microfabrication methods where externally controlled tools are used to generate the desired patterns. Because of the minimal size of individual nanoantenna elements, the amount of current that can be extracted is barely measurable. Thus, the ability to produce periodic arrays of nanoantennas on large areas of substrate material is a desirable feature in the fabrication process. Some of these fabrication methods can potentially support the fast and inexpensive large-scale production of nanoantennas. (Maradudin et al., 2014, 129-130; Mescia & Massaro, 2014, 7-8; Yao & Liu, 2014, 197-201.)

Because nanoantennas require accurate control of geometry and dimensions, fabrication techniques like Electron Beam Lithography (EBL), X-ray lithography, Focused Ion-Beam (FIB) milling or other similar ultra-high resolution techniques are generally used
for their high precision (Kotter et al. 2010, 5). EBL and FIB milling are fabrication methods that can generate large arrays of precisely patterned, nearly identical nanostructures with defined orientation, dimensions and distances. However, these methods are slow and expensive. Therefore, they do not support the production of nanoantenna structures on a commercial scale. (Kotter et al. 2010, 5-7; Mescia & Massaro, 2014, 7.) In parallel, other low-cost alternative methods such as nanoimprint lithography (NIL) and roll-to-roll processing have recently been suggested and are currently being investigated. The major advantage of NIL and roll-to-roll processing in comparison to other processes is that they offer the possibility for rapid, high-capacity and low-cost production of large areas of nanoantenna arrays.

In 2008, Kotter et al. (2008) demonstrated, for the first time, the feasibility of large-scale manufacture of functional nanoantenna devices on flexible substrate using a roll-to-roll fabrication process referred to as nanoforming. In their experiment, they created a flexible substrate covered by millions of nanoantennas on its surface. Picture 8 is a picture of the nanoantenna sheet fabricated by Kotter et al. at the Idaho National Laboratory.

![Flexible nanoantenna sheet](Kotter., et al., 2010).

This fabrication method is a multi-step process in which the relief pattern of a master template is first fabricated by using conventional e-beam lithography or another similar technique. Because of the fragility of the original template, second and third generation templates are created. These templates, or “tools”, are durable, inexpensive and highly accurate, thus suitable for repeated mass-replication of the desired pattern onto polymer substrates. In this demonstration, the polymer substrate chosen for this purpose was polyethylene due to its transparency in the IR region. Picture 9 represents the pattern replication process (see picture 9a), and the schematic of antenna and ground plane
processes (picture 9b). In the pattern replication process, a template is used to imprint the desired pattern into a polymer substrate. The latter process describes the steps followed to obtain the complete nanoantenna structure (Kotter et al. 2010, 5-7).

PICTURE 9. (a) Schematic of pattern replication process. (b) Schematic of antenna and ground plane process (Kotter et al. 2010).

Another approach that has been suggested for the precise fabrication of nanoantenna structures is the self-assembly method. This approach relies on wet chemical synthesis techniques that are driven by interactions between nanoparticles to synthesize the desired antenna geometries. This fabrication technique promises low-cost, high efficiency and precision in the fabrication of complex structures, and could therefore be one alternative to conventional lithography (Yao & Liu, 2014).
3.4 Applications

The diversity of possible nanoantenna designs has strongly encouraged researchers to develop new exciting applications in the field of energy conversion. In this section, a few examples of applications in this context are discussed.

3.4.1 Improving efficiency of thin film solar cells

Recent studies have demonstrated the potential advantage of using plasmonic nanoantennas for the improvement of thin film solar cell performance. Nanoantennas could potentially enhance light absorption in the active layer (where charge carriers are generated) of a solar cell, thus improving its efficiency in a substantial manner. In theory, a thick active layer is a desirable feature in solar cells because the thickness directly correlates with light absorption. However, in low-cost, commercial thin film solar cells, the efficiency is generally limited by poor charge carrier diffusion lengths within the active layer due to the weak electric properties of materials (e.g. amorphous silicon). In other words, if the active layer is thick enough to absorb all the incident radiation, the charge carriers are not efficiently collected due to the short diffusion length. (Barnard, 2011, 62-65.) This is especially true for electromagnetic radiation of wavelengths between 600nm and 1100 nm (Maksymov et al. 2012, 12-13).

Adding a nanoantenna layer in a thin film PV cell can improve efficiency due to the ability of the antenna to concentrate light into its near-field, resulting in a higher concentration of charge carriers. In addition, nanoantennas have an important scattering property that enables the reflection of light into the active layers of the PV cell where absorption occurs. (Barnard, 2011, 62-65.)
Picture 10 below describes the relationship between the layer thickness and carrier absorption efficiency for a thick layer PV cell, a thin layer PV cell, and a plasmonic PV cell with optimized dimensions.

![Graphical representation of light absorption vs. carrier collection relationship](image)

**PICTURE 10.** Graphical representation of the light absorption vs. carrier collection relationship in terms of active layer thickness (Barnard, 2011, 63).

In a theoretical simulation of absorption enhancement, Barnard found that the absorption of light in a plasmonic PV cell with optimized nanoantenna and layer thickness dimensions could yield in a 43% improvement of light absorption in the plasmonic PV cell design.

### 3.4.2 Other applications in the context of energy production

In addition to improving the energy conversion efficiency of thin-film solar cells, the large-scale commercialization of nanoantenna technology would offer a diversity of applications in the field of energy conversion.

By combining nanoantennas with appropriate rectifying elements, these structures could be integrated into consumer electronic devices (e.g. smart phones, computers, etc.) and allow for the continual charging of their batteries. In addition, nanoantennas could be designed to recycle residual heat from consumer electronic devices and reconvert it into...
electricity. Larger nanoantenna platforms could be used as coating for the roofs of buildings and the energy produced could be consumed on-site or fed to the power grid. (Kotter et al. 2008, 6.)

Nanoantennas could also play a significant role in improving the effectiveness of passive energy management systems, since their integration into building insulation and window coatings for example, would enable the collection of waste heat and its conversion into electricity (Kotter et al. 2010, 7-8). In this context, the use of nanoantennas can also be advantageous in large-scale industrial processes where big quantities of waste heat are generated (Maradudin et al. 2014, 130-131).

Moreover, nanoantennas could be fabricated onto double-sided panels that could absorb infrared radiation during the day, but also during the night. One side of the panel would consist of broad-band nanoantenna arrays that would absorb a broad spectrum of wavelengths during the day, while the other side of the panel would contain nanoantennas specially designed to absorb electromagnetic radiation in the narrow frequency range of radiation re-emitted by Earth’s surface. (Kotter et al. 2008, 6; Kotter et al. 2010, 7-8.)
ADVANTAGES AND CHALLENGES OF NANOANTENNAS

To this day, the efficiency of solar energy conversion with nanoantenna devices remains very low (less than 1%), and no rectenna solar cells have been successfully constructed yet (Moddel & Grover, 2013, 19). The role of nanoantennas in solar energy conversion could, nonetheless, be significant in the years to come. Rectenna solar cells have several advantages over conventional photovoltaic solar cells, but significant challenges that limit their performance and viability as an alternative energy conversion mechanism remain. In this section, the most important advantages and challenges, as well as recent progress in the field are discussed.

4.1 Advantages and challenges

Rectenna solar cells have the potential to be competitive to conventional solar cells due to several advantageous characteristics. First, if technical limitations are overcome, the ultimate energy conversion efficiency is at least as high as that of a photovoltaic solar cell – possibly higher. The efficiency of rectennas can be improved by incorporating several sizes of nanoantennas in the same structure in order to obtain a better coverage of the solar spectrum. This is a similar approach to multi-junction solar cells in raising the energy conversion efficiency, but the procedure is relatively simple and less expensive because it can be achieved by only controlling the operating voltage and the size of nanoantennas. In addition, the materials required for the fabrication of rectennas are available, and in thin form, they are economical. Moreover, the fabrication of nanoantennas can be less expensive than the fabrication of photovoltaic solar cells because the materials do not need to be epitaxial. (Moddel & Grover, 2013, 19-20.) With the development of new low-cost fabrication methods, rectennas can potentially be a commercially viable alternative to photovoltaic solar cells and suitable for large-scale production.

However, before rectennas can become part of the global energy scene, several challenges critical to their performance have to be tackled. For the nanoantenna, these challenges are
essentially related to the choice of materials and antenna geometry. The behavior of individual nanoantennas is also affected when placed in an array, where the spacing between elements is critical to their absorption properties. One additional aspect to consider is that real-world nanostructures generally have optical properties that are less ideal when compared to their corresponding bulk materials, and are therefore not performing as well as predicted. This difference can be attributed to problems during fabrication, size effects, poor surface passivation, polycrystallinity and the presence of chemical impurities in the nanoantenna material. (Barnard, 2011, 25.) For diodes, the most critical challenge is to achieve efficient rectification at THz frequencies. Although MIM diodes show promising features, there is room for innovations in this context. Designing optimal rectenna components necessitates the simultaneous satisfaction of all nanoantenna and diode requirements.

4.2 Recent progress and future prospects

Currently, many of the challenges faced in the design of highly performing rectennas are being investigated, resulting in continual progress in the understanding of light-matter interaction at optical frequencies. New low-cost nanoantenna fabrication methods have been suggested and are currently being optimized (Kotter et al 2010; Moddel et al. 2013, 337-370).

For instance, Kotter et al. (2010) designed a spiral-square nanoantenna that exhibits high directivity and good angular reception characteristics. As a result, the antenna has a wider angle of incidence exposure in comparison to conventional photovoltaic devices, since all the incoming solar radiation that falls within the radiation beam of the nanoantenna is collected. The optimization of energy collection exploiting this characteristic is an important advantage for practical applications as it may reduce the need for additional solar tracking mechanisms in nanoantenna electromagnetic collector structures (Kotter et al, 2010, 2; Maksymov et al. 2012, 6; Moddel & Grover, 2013, 234-235).

Concerning diodes, many new promising alternatives are being researched. Examples include Metal-Insulator-Insulator-Metal (MIIM) diodes, travelling-wave diodes, sharp-tip diodes and geometric diodes. Geometric diodes (see pic. 11 below), for instance, are
designed so that the asymmetry of the physical shape of the device causes charge carriers to move more easily in the forward direction than in the opposite direction due to the funneling effect of the arrowhead-shaped constriction area. This type of diode presents advantages over MIM diodes in terms of capacitance and resistance, enabling ultrafast rectification. (Moddel & Grover, 2013, 10-14; Zhu et al. 2013, 6-8.)

5 CASE STUDY – Preliminary evaluation of the suitability of nanostructured cellulose as candidate material for the fabrication of nanoantennas

This chapter is an attempt to evaluate the possibility of using nanocellulose in the structure of nanoantennas for the purpose of energy conversion. Little research has been done in this context, thus the results of this case study are essentially based on an interview with experts in the field of nanocellulose, and a general comparison between relevant material properties of cellulose and material requirements for the fabrication of nanoantenna structures.

The persons that were interviewed for this purpose are professors from the department of paper, textile and chemical engineering of Tampere University of applied Sciences (TAMK), Mr Arto Nikkilä and Mrs Päivi Viitaharju.

5.1 General introduction to nanocellulose

Cellulose is the most abundant polymer found in nature and accounts for approximately 40% of the available lignocellulosic biomass (Nair et al. 2014). It is an organic compound with the formula \((\text{C}_6\text{H}_{10}\text{O}_5)_n\), consisting of a linear chain of several hundreds to thousands of glucose units linked to each other by glycosidic bonds (Karhe, 2012).

Picture 12 below represents the chemical structure of cellulose.

![Chemical structure of cellulose](image)

Nanocellulose commonly refers to a material derived from cellulose wood fibers, in which the particles have one or more dimensions in the range of 1 to 100 nanometers (Kangas, 2014, 9).

The idea of producing nanostructured cellulose is not new. The first patents for the production of microfibrillated cellulose (MFC) date back to the beginning of the 1980s. At that time, the production process was energy-intensive and resulted in prices of nanocellulose too high to be considered for commercial-scale production. However, with the decreasing demand for paper production, wood industries have started to show interest in investigating new possibilities and applications for wood-derived materials. The recent progress in processing techniques of cellulose has significantly reduced the need for high energy inputs and made possible the production of nanocellulose on a larger scale. As a result, the research of nanocellulose has intensified and many new applications are currently being developed. (Kangas, 2014.)

Nanocellulose has attracted a lot of attention, and for a good reason. On top of being a widely available, environment-friendly, renewable material, nanocellulose has shown unique material properties not found in its bulk counterpart. These novel material properties offer the possibility for extremely diverse applications. The most important properties include mechanical properties such as high tensile strength, stiffness, light weight and flexibility, and highly tunable chemical properties through surface functionalization. In addition, nanocellulose can be made transparent and electrically conductive. (Dufresne, 2013; Kangas, 2014; Nikkilä & Viitaharju, 2015.) This diversity of properties support equally versatile applications: nanocellulose can be used in composites and construction materials, packaging, paint pigments and inks, electronic devices, flexible solar panels, thin films, biomedical applications and even food products – to cite a few. (Kangas, 2012, 2014; Ragauskas, undated)

5.2 Nanocellulose research in Finland

Wood and paper industries continue to play an important role in the Finnish economy. The challenges faced by these industries during the past decades have also created the opportunity for forestry companies to look for new directions in the development of
innovative value-added products. In this context, nanocellulose is an ideal material. Today, Finnish paper companies have become global leaders in the research and commercialization of nanocellulose. (Forsström, 2012.)

For instance, UPM-Kymmene Ltd is currently developing new applications for micro- and nanofibrillated cellulose together with its industrial partners. The company intends to create the pre-conditions needed for the industrial-scale production of products for paper and packaging applications, concrete and paint industries. Another good pioneering example is Stora Enso. The company has constructed a pre-commercial plant for the production of microfibrillated cellulose and is currently testing its use for packaging applications, fibre-based paper and board products as well as barrier materials. The long-term objectives of Stora Enso involve the development of completely new products for the replacement of fossil-based products materials such as plastics and certain chemicals. (Forsström, 2012; Kangas, 2014.)

In addition to the research done by companies, the properties and applications of nanocellulose are also being studied in universities and research laboratories in pilot-scale projects (Kangas, 2014).

In 2008, the Finnish Centre for Nanocellulosic Technologies was established for the cross-disciplinary research of nanocellulose. This center was a common initiative of Aalto University School of Science and Technology, VTT (the Finnish Technical Research Centre) and UPM. The objectives of this partnership involved the creation of projects that investigate different aspects of production, technology, physical and chemical modification, and characterization in order to produce new innovative products that can respond to market demand. In 2013, the partnership contract ended as the objectives were completed. Today, the partners are involved in multiple publicly funded projects. (Kangas, 2014; Koskinen et al. undated.)

5.3 Types of nanocellulose and methods of production

Nanocellulose can be obtained from various raw materials. The most commonly used sources of raw materials include trees and other lignocellulosic plants due to their availability, but their use is limited by challenges related to the extraction of nanocellulose
from the plant. For this reason, other biomass sources that contain low levels of lignin are often preferred. In addition, nanocellulose can be obtained from agricultural crops and wastes such as cotton, linen, hemp and sugar cane. One further possibility for the production of nanocellulose is by bacterial processing of glucose. (Kangas, 2014, 8.)

Nanocellulose can be classified into three types according to its production process, morphology and particle size: nanofibrillated cellulose (NFC), nanocrystalline cellulose (NCC) and bacterial cellulose (BC). Over the years, many production techniques that rely on mechanical, chemical and enzymatic processes have been developed for the production of different types of nanocellulose.

Nanofibrillated cellulose is typically obtained by using various mechanical treatments. These treatments generally consist of high-pressure homogenization and/or grinding. However, because this type of treatment is usually energy-intensive, other pre-treatment methods have been used to reduce energy consumption. Examples of such methods include mechanical cutting, acid hydrolysis and enzymatic pretreatment. (Dufresne, 2013, 2; Kangas, 2014, 15-19.). The width of nanofibrillated cellulose fibers is in the range of 20 to 40 nanometers and they can be several micrometers in length. Mechanically produced nanofibrillated cellulose exhibits highly branched fibers and high flexibility. For this reason, they are used in applications like composite materials, thin film coating and porous materials. (Kangas, 2014, 8-14.) Picture 13 shows the structural appearance of nanofibrillated cellulose under a scanning electron microscope (SEM).

Nanocrystalline cellulose, on the other hand, is obtained by applying chemical treatments. This is commonly done by using a controlled strong acid hydrolysis treatment where
chemical bonds between cellulosic fibers are broken under the action of acid. Different strong acids have been used to hydrolyze cellulose, but hydrochloric and sulfuric acids are the most widely used. (Dufresne, 2013, 2.) The particle size obtained is generally in the order of 2 to 20 nanometers for width and 100 to 600 nanometers in length. Nanocrystalline cellulose also exhibits high levels of crystallinity (62-90%), which is the reason behind its high rigidity. In addition, high thermal stability has been reported. This type of nanocellulose can potentially be used for strengthening nanocomposites, thin-film applications, electronic displays and packaging, as well as in applications that require materials to be stable at high temperatures. (Kangas, 2014, 8-14.) Picture 14 shows the structural appearance of nanocrystalline cellulose under an atomic force microscope.


The preparation of bacterial cellulose requires a completely different approach, since it is produced by a bottom-up polymerization process in which nanocellulose is synthesized from glucose molecules by bacteria (e.g. acetobacter xylinum). The fiber width obtained is typically within the range of 20 to 100 nanometers. These fibers are in turn composed of nanofibrils of widths ranging from 2 to 4 nanometers. Bacterial cellulose has properties that vary from plant cellulose. It exhibits high levels of and biocompatibility, and due to its large specific surface area, it is extremely hydrophilic. Bacterial nanocellulose is also generally characterized by its high mechanical strength and flexibility. As a result of these properties, this type of nanocellulose is suitable for biomedical applications. (Kangas, 2014, 8-14.)
The structural appearance of bacterial cellulose is presented in picture 15 below.

![Picture 15. Structural appearance of bacterial nanocellulose using SEM (Kangas, 2014, 14).](image)

5.4 Relevant material properties and applications

As mentioned earlier in this chapter, nanocellulose has a large diversity of interesting material properties that support its use in various areas of application. In this section, a few properties relevant to this study are discussed, together with other advantages of nanocellulose.

Many research groups have been able to successfully demonstrate unique mechanical, chemical, optical and electrical properties of nanocellulose. From the nanoantenna design point of view, the following properties can be considered advantageous: flexibility, transparency, conductivity, thermal stability, mechanical strength and plasmon resonance.

Non-treated nanocellulose is naturally a dielectric material (Kangas, 2014, 36), but its electric properties can be altered. Hamedi et al. (2014) have demonstrated a successful, low-cost method for making a highly conductive, flexible and semitransparent nanocomposite material. The material studied was a bicomponent composed of nanofibrillated cellulose and single-wall carbon nanotubes (NFC:SWNT) produced by using a self-assembly method. The maximum conductivities reported exceeded 200 S/cm.
and maximum current densities of 1400 A/cm² were achieved. The high conductivities were attained without significant degradation of the mechanical properties of the material.

Other studies have shown that nanofibrillated cellulose can be exploited in printed electronic circuits as supportive substrate or used to create flexible solar panels. In addition, nanocomposites containing nanocellulose have been found to tolerate high temperatures (up to 270 °C for short exposure time and up to 230 °C for an exposure time exceeding 12 hours) without the alteration of material properties. (Kangas, 2014, 35.)

Moreover, the transparency of nanocellulose can be tuned by controlling the size of particles. In general, the smaller the particle size, the more transparent the material. This property can be used to fabricate thin films and coatings. (Kangas, 2014; Nikkilä & Viitaharju, 2015.)

Campbell et al. (2014) demonstrated the possibility of making self-assembled crystalline nanocellulose films by shear alignment into highly ordered crystalline structures. In this study, the crystalline structure of nanocellulose was used to produce hybrid films decorated with gold-nanorods, which showed strong, polarization-sensitive surface plasmon resonance.

Nikkilä and Viitaharju (2015) pointed out that in addition to the above mentioned properties, nanocellulose presents several other advantages: it is a widely available, nontoxic, renewable and biodegradable material that can be produced sustainably at a relatively low cost. In addition, it has been suggested that nanocellulose has the potential to substitute fossil-fuel based materials such as plastic polymers and other chemicals. Furthermore, the sensitivity of nanocellulose to weather elements such as moisture and UV radiation can be controlled efficiently, making the design of highly durable structures possible. (Kalia, et al., 2011; Nikkilä & Viitaharju, 2015.)

5.5 Evaluation of applicability and future research needs

In order to be incorporated in the structure of solar electromagnetic nanoantenna collectors, nanocellulose has to satisfy several requirements depending on the component considered (see chapter 3). In the case of plasmonic nanoantennas, the material used is generally a metal or metal-like material that can support surface plasmon resonance.
Although the plasmonic material no longer behaves as a perfect conductor at the nanoscale, its conductivity is still high, in the order of $10^5$ to $10^7$ Sm$^{-1}$ (Moddel & Grover, 2013, 236).

The material properties discussed in section 5.4 suggest that it may be possible to use nanocellulose in the fabrication of nanoantenna electromagnetic collectors. The high conductivities that can be obtained for nanocellulose composites could be exploited in making nanoantenna elements if they can be shown to support surface plasmon resonance and field enhancement properties. In this context, the possibility of designing nanocellulose-based materials that can incorporate metallic nanoparticles or more complex structures is an exciting discovery, because it offers a new opportunity for designing nanoantenna structures.

The dielectric nature and the tunable transparency, together with the high mechanical strength and thermal stability of nanocellulose, could potentially be exploited in the fabrication of a transparent optical resonance cavity substrate that acts as a mechanical support for the nanoantenna array, suppressing the need for plastic polymers or glass. In a similar fashion, the flexibility of nanocellulose could be utilized in creating flexible nanoantenna substrates for wearable consumer electronics applications for example. However, it has to be possible to create a material that exhibits many desirable properties simultaneously. Because the thickness of the optical cavity layer is a critical factor for the performance of a nanoantenna, high control over substrate thickness is required. One additional challenge to consider in this context is the compatibility of organic and inorganic materials, i.e. surface adhesion properties. For a functional nanoantenna, it is necessary to have a steady structure in which the nanoantenna element is incorporated into the substrate in a stable manner.

From a process point of view, the fabrication of nanoantennas is complex and requires high-resolution patterning techniques because the size and geometry of nanoantennas are essential parameters for performance. Nanocellulose has to demonstrate the possibility for highly controllable fabrication processes and shape tuning.

For applications like rectenna solar cells, nanocellulose has to be made durable and insensitive to weather factors such as moisture, UV radiation and rain. This can be done by surface modification techniques where hydrophobicity is increased. For UV weathering, the degradation of nanocellulose-based materials can be prevented by adding a wavelength-selective protective coating on the structure.
At a first glance, the comparison between nanocellulose properties and nanoantenna requirements suggests that nanocellulose could be used in the fabrication of nanoantennas. Nikkilä and Viitaharju (2015) believe that the properties of nanocellulose can be tuned to obtain materials with exceptional properties, fit for the construction of nanoantennas. Due to the limited available research on this specific topic, the suitability of nanocellulose is still unclear and will have to be studied experimentally.

Another influential aspect to consider is the cost of fabrication. According to Nikkilä & Viitaharju (2015), although nanocellulose can be obtained at a relatively low cost, its functionalization and modification of properties can rapidly raise the price of production. In addition, the availability and extractability of cellulose in the raw material also influence the cost. Therefore, the viability of nanocellulose as material for the fabrication of nanoantennas strongly depend of the extent to which its properties are modified and which material it is intended to substitute.
6 CONCLUSIONS

Although nanoantennas have not yet been demonstrated to successfully convert energy from electromagnetic radiation into electricity at efficiencies that would make them commercially attractive, large progress has taken place since their invention more than four decades ago.

Currently, the performance of nanoantennas is limited by factors like metal losses, bandwidth, directivity, impedance match between components and AC-to-DC rectification. If the technical challenges faced in the design of efficient nanoantenna converters are addressed, these devices have the potential to become a competitive alternative to photovoltaic solar cells.

The materials used in nanoantennas are relatively low-cost and the fabrication processes can be inexpensive if nanoimprint and roll-to-roll techniques are used. In addition, nanoantenna collectors support a wide range of applications. They can potentially be integrated onto flexible consumer electronic devices to charge their batteries continuously, or used as coating for buildings and windows for passive energy management.

With a maximum theoretical efficiency of 44% if not higher, nanoantennas could become important contributors to the global energy production in the near future. In that sense, nanoantenna converters also have the potential to encourage the transition from fossil fuels to a more sustainable energy production.

Nanocellulose is a novel material with impressive properties and a very large number of possible applications. This natural polymer has many interesting material properties that are consistent with some of the material requirements for the design of nanoantennas. This suggests that using nanocellulose as a support substrate, protective layer or in the fabrication of the nanoantenna itself is not out of the question. However, more experimental work will be needed in the future in order to support or reject this claim.
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APPENDICES

Appendix 1. Illustrations of the electromagnetic wave energy converter proposed by Fletcher and Bailey, 1973.

Fig. 1 is a representative view schematically illustrating the principles of the invention.

Fig. 2 is a perspective diagram illustrating an embodiment of the invention particularly adapted for converting solar energy into electric power.

Fig. 3 is a side sectional view of the embodiment illustrated in Fig. 2.
Appendix 2. Interview questions for Arto Nikkilä and Päivi Viitaharju

ASSESSING THE POTENTIAL OF NANOCELLULOSE FOR THE DESIGN OF NANOANTENNAS
Date: 29 April 2015

GENERAL QUESTIONS

1. How significant is the research of nanocellulose in Finland?
2. Why is nanocellulose seen as a promising novel material?
3. What are the most important areas of research for nanocellulose?
4. What are the advantages of nanocellulose?
5. What are the challenges faced with nanocellulose? (cost of fabrication, material properties, etc.)
6. How do you see the future prospects for nanocellulose and its derived compounds?

PREPARATION METHODS

7. What are the most common types and preparation methods of nanocellulose?
8. Can nanocellulose be given a crystalline structure? If so, what is the estimated cost of production compared to other common methods?
9. Is the surface modification of nanocellulose possible? (e.g. coating with metallic particles)

MATERIAL PROPERTIES

10. What are the most interesting material properties of nanocellulose?
11. What could you say about the following properties concerning nanocellulose: electrical conductivity, optical properties, flexibility, transparency, thermal stability, hydrophobicity, surface adhesion, magnetic properties?
12. Does the origin of the bulk material (e.g. pine vs. algae) influence material properties of nanocellulose?
13. How durable is nanocellulose? (lifespan, resistance to weather)

DISCUSSION

14. Given the material properties and your current knowledge about nanoantenna structures (rectennas), can you think of any possible application for nanocellulose in the design of nanoantennas?
15. Can you think of reasons for the non-viability of this idea? (E.g. challenges, wrong material properties, cost etc.)