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**STUDY OF OPTICAL ABSORPTION PROPERTIES OF CU-  
BASED NANOPARTICLES FOR GREEN  
PHOTOCATALYTIC AND PHOTOVOLTAIC  
APPLICATIONS BY UV-VIS SPECTROSCOPY**

VASEPÕHISTE NANOOSAKESTE OPTILISTE  
NEELDUMISOMADUSTE UURIMINE ROHELISTE  
FOTOKATALÜÜTILISTE JA FOTOGALVAANILISTE  
RAKENDUSTE JAOKS UV-VIS SPEKTROSKOOPIA ABIL

Bachelor's thesis  
Engineering

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Tartu 2023

Eesti Maaülikool		Bakalaureusetöö lühikokkuvõte	
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Pealkiri: Vasepõhiste nanoosakeste optiliste neeldumisomaduste uurimine roheliste fotokatalüütiliste ja fotogalvaaniliste rakenduste jaoks UV-Vis-spektroskoopia abil			
Lehekülgi: 42	Jooniseid: 12	Tabeleid: 3	Lisasid: 1
Osakond / Õppetool: Energiakasutuse õppetool ETIS-e teadusvaldkond ja CERC S-i kood: 4. Loodusteadused ja tehnika 4.17. Energeetikaalased uuringud T140 Energeetika Juhendaja(d): Protima Rauwel, <i>PhD</i> ; Erwan Yann Rauwel, <i>PhD</i> ; Edison Patricio Paredes Carranza, <i>MSc</i> Kaitsmiskoht ja -aasta: Tartu 2023			
<p>Päikesevalgusest juhitud fotokatalüüs ja fotogalvaanika on keskkonnasõbralikud meetodid kütuste ja elektri tootmiseks. Käesoleva lõputöö eesmärgiks on analüüsida vasepõhiste nanoosakeste optilisi omadusi, et uurida nende võimet neelata valgust päikesepektri nähtavas osas ning hinnata neid rohelise energia allika kandidaadidena. Vasepõhistel nanoosakestel on head optilised, elektroonilised ja katalüütilised omadused ning kitsas keelutsoon, mis jääb <math>\text{Cu}_2\text{O}</math> puhul vahemikku 1.4-2.5 eV ja <math>\text{Cu}_3\text{N}</math> puhul vahemikku 0.8-1.9 eV, mistõttu on need potentsiaalselt tõhusad materjalid energia tootmiseks. Mittevesilahusel põhineval sool-geel meetodil sünteesiti nelja erineva segamisajaga (20 m, 2 h, 3 h ja 5 h) vasepõhiste nanoosakeste proove. Saadud proove uuriti seejärel kasutades UV-Vis spektromeetrit. Tulemused kanti graafikule ning analüüsiti kasutades tarkvara OriginPro. Tulemustest saab järeldada, et kõik proovid neelavad valgust silmale nähtavas spektri ulatuses. Siiski, parim materjal rohelise energia tootmiseks sisaldab suures koguses <math>\text{Cu}_3\text{N}</math> nanoosakesi ning neelab valgust ka spektri lähiinfrapuna piirkonnas.</p>			
Märksõnad: Vasepõhised nanoosakesed, UV-Vis spektroskoopia, fotokatalüüs, fotogalvaanika, roheline energia			

Estonian University of Life Sciences Fr. R. Kreutzwaldi 1, Tartu 51006		Abstract of bachelor's Thesis	
Author: Aimar Puusepp		Curriculum: Engineering	
Title: Study of Optical Absorption Properties of Cu-Based Nanoparticles for Green Photocatalytic and Photovoltaic Applications by UV-Vis Spectroscopy			
Pages: 42	Figures: 12	Tables: 3	Appendixes: 1
Department / Chair: Chair of Energy Application Engineering Field of research and (CERC S) code: 4. Natural Sciences and Engineering 4.17. Energetic Research T140 Energy research Supervisors: Protima Rauwel, <i>PhD</i> ; Erwan Yann Rauwel, <i>PhD</i> ; Edison Patricio Paredes Carranza, <i>MSc</i> Place and date: Tartu 2023			
<p>Green or sunlight-driven photocatalysis and photovoltaics are environmental-friendly methods for the productions of fuels and electricity, respectively. The aim of this thesis is to use UV-Vis spectroscopy to analyze the optical properties of copper (Cu)-based nanoparticles in order to study their capability of absorbing light in the visible part of the solar spectrum and evaluate them as candidates for green energy production. Cu-based nanoparticles have good optical, electronic and catalytic properties and small band gaps of 1.4-2.5 eV for Cu<sub>2</sub>O and 0.8-1.9 eV for Cu<sub>3</sub>N, making them potentially effective materials for the production of energy. Herein, the absorption properties, band gaps and photocatalytic characteristics of four samples synthesized with different stirring time (20 min, 2 h, 3h and 5 h) using a non-aqueous sol-gel method, were investigated using UV-Vis spectroscopy. Results were plotted and analyzed using the OriginPro software. The result suggests that all the samples are sensitive to solar radiation. However, the best material for green energy production is the one containing the highest quantities of Cu<sub>3</sub>N with an absorption range extending up to the near infrared region.</p>			
Keywords: Cu-based nanoparticles, UV-Vis spectroscopy, photocatalysis, photovoltaics, green energy			

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## ACRONYMS AND ABBREVIATIONS

AU	– Arbitrary unit
Cu <sub>2</sub> O	– Copper oxide
Cu <sub>3</sub> N	– Copper nitride
eV	– Electronvolt
LED	– Light emitting diode
nm	– Nanometer
NM	– Nanomaterial
NP	–Nanoparticle
QD	– Quantum dot
SPR	– surface plasmon resonance
TiO <sub>2</sub>	– Titanium dioxide
UV	– Ultraviolet
UV-Vis	– Ultraviolet and visible light spectroscopy
ZnO	– Zinc oxide

## INTRODUCTION

The production of green and renewable energy is the need of the hour. In photocatalysis. Green energy consists of tapping the sun's potential to convert solar energy into other forms of energy i.e. fuels and electricity. Photovoltaics or solar panels are widely used for the conversion of solar energy into electricity. Similarly, photocatalysis consists of converting solar energy into fuels, such as syngas, carbon dioxide, methane, methanol and other hydrocarbons. Most popular photocatalytic nanomaterials in the market are  $\text{TiO}_2$  and  $\text{ZnO}$ . These materials are also being tested for a new generation of photovoltaics.[1] However, these nanomaterials present some drawbacks, for example, they only work under UV light radiation exposure as they present large band gaps, low adsorption capacity.[2] In addition, recent reports mention that there are already regulatory restrictions in Europe that limit the use of  $\text{TiO}_2$  nanomaterials due to their toxicity for the environment.[3] Therefore, new materials that are Earth-abundant, working under the visible light with narrow band gaps and are environmental friendly, are necessary to study.

Copper oxide ( $\text{Cu}_2\text{O}$ ) and copper nitride ( $\text{Cu}_3\text{N}$ ) nanoparticles (NP) have shown potential as effective materials for photocatalysis and photovoltaics applications. The development of these nanomaterials has led to the production of fuels such as hydrogen and hydrocarbons, while photovoltaic applications present a promising avenue towards an efficient solar energy converter through solar cell technologies.[4][5]  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$  nanoparticles present band gaps 1.4-2.5 eV for  $\text{Cu}_2\text{O}$ [6] and 0.8-1.9 eV for  $\text{Cu}_3\text{N}$ . [7] These values are a lot smaller than  $\text{TiO}_2$  and  $\text{ZnO}$ , making them theoretically more promising materials for applications like pollutants removal from water and photovoltaics. A smaller band gap allows the nanoparticles to absorb visible light more efficiently, which in turn facilitates the generation of electron-hole pairs that are then used to produce fuels via storage in chemical bonds or that can be conducted as electricity through an external load. However, photocatalysis requires a gaseous or liquid environment, as there is an exchange of the electron-holes with these gases. On the other hand, in photovoltaics, the process is carried out in open air conditions and electrons travel through a circuit without any exchange of charges with the environment.

The aim of this thesis is to use the UV-Vis spectroscopy to study the optical absorption properties of Cu based nanoparticle mixtures aimed for photocatalysis and photovoltaic applications. The nanoparticles studied in this thesis were synthesised by non-aqueous sol-gel method inside a glove box (controlled N<sub>2</sub> atmosphere), and the reagents were sealed in an autoclave for the synthesis. The nanoparticles are samples composed of different crystalline phases of Cu<sub>2</sub>O, Cu<sub>3</sub>N and Cu. The UV-Vis spectroscopy and the band gap calculations were done to evaluate the optical absorption properties of the Cu<sub>2</sub>O and the Cu<sub>3</sub>N semiconductor nanoparticles in the visible light range. These absorption properties are essential in identifying the most suitable candidate that can be used in sunlight-driven photocatalysis and photovoltaics.

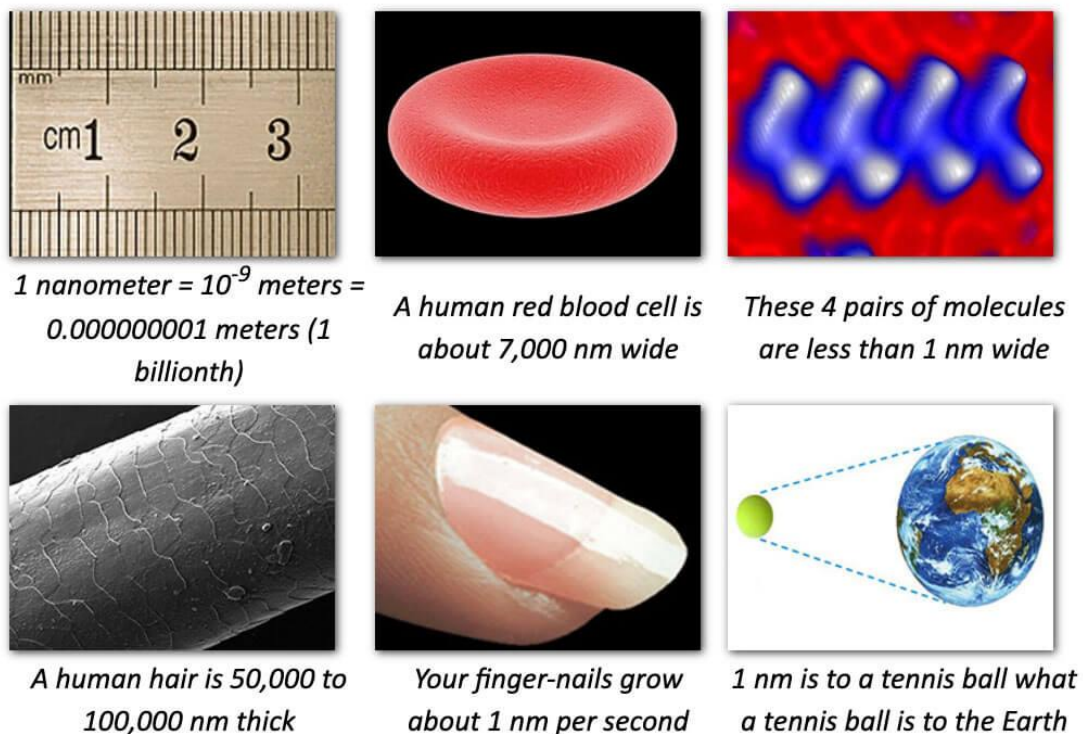
The absorption peaks of Cu<sub>2</sub>O, Cu<sub>3</sub>N and Cu nanoparticles in the visible part of the electromagnetic spectrum (400-700 nm) suggest that the nanoparticles can be used under solar radiation. The band gaps from the Tauc plot help evaluate the potential of the material as candidates for photocatalytic and photovoltaic activities under visible light exposure.

Two main parts are written in the thesis. The first part covers the theoretical background of nanotechnology, nanoparticles, UV-Vis spectroscopy, band gap calculations and Cu-based nanoparticles. The second part describes the materials and methods used in the practical part of thesis. Also, results and analysis are covered in the second part.

# 1. THEORETICAL BACKGROUND

## 1.1. Nanotechnology

Nanotechnology is the study and manipulation of materials and devices at the nanoscale. The nanoscale is 1 to 100 nanometers (nm), so it is a very precise technology (one nanometer is one millionth of a meter,  $10^{-9}$  m). At this scale (figure 1.1), the properties of materials can be significantly different than their bulk phase. Nanoscale materials behave differently than bulk materials and new applications can be developed using these nanomaterials. Nanotechnology has a broad range of applications in various fields such as agriculture, medicine, electronics, energy, and materials science. Nowadays developments in nanotechnology are very fast and new discoveries are made all the time. This new technology is used in a wide range of applications to create new and innovative products, chemicals, and materials.[8]



**Figure 1.1.** Some examples to illustrate nanoscale.[9]



One of the key techniques in nanotechnology is the ability to manipulate individual atoms and molecules to create structures and devices with specific properties. At the nanoscale, materials can have interesting biological, chemical and physical properties. For instance, some nanomaterials are found to be up to seven times stronger than their ordinary counterparts. This has led to the development of various nanomaterials such as carbon nanotubes, quantum dots, and nanoparticles.

Nanotechnology is not a new technology. Scientists have been developing nanotechnology for the last 30 years. The latest advancements in the development of electron microscopes capable of seeing atoms with a great precision have allowed scientists to work at the nanoscale with more precision. The ability to see nanomaterials and understand their structure has opened a lot of new possibilities in many different research areas like electronics, solar power and medicine.[9]

The field of medicine is one of the most promising applications of nanotechnology. Researchers are investigating the use of different nanoparticles for applications in this field. Some examples could be drug and gene delivery, probing DNA structures and tumour detection. These improvements could lead to significant changes in medical sciences and greatly improve the effectiveness of treatments for a wide range of diseases.[10]

In electronics, nanotechnology is already being used to create faster and more efficient computer chips and other electronic components. For example, carbon nanotubes are used in devices such as transistors, sensors and conductive films. Also, quantum dots are used in displays, solar cells and LEDs. By using nanomaterials and nanoscale devices, engineers can pack more computing power into smaller spaces, leading to faster, more powerful computers and other electronic devices. Today's smartphones and computers could not exist without this technology.[9]

## **1.2. Nanoparticles**

Nanoparticles (NP) are extremely small particles, typically ranging in size from 1 to 100 nanometers. NPs can be categorized based on many different characteristics like size, morphology, physical and chemical properties or shape and dimensions. Based on physical

and chemical properties, NPs are generally classified as metal, ceramics, semiconductor and polymeric. Metal NPs have well-known localized surface plasmon resonance (LSPR) characteristics, they also have unique optoelectrical properties. Metal oxide and nitride NPs are inorganic non-metallic solids. They can be found in a lot of different forms like amorphous, polycrystalline, dense, porous and hollow. Semiconductor NPs have wide bandgaps and therefore they are very important materials in areas like photocatalysis, photo optics and electronic devices. Polymeric NPs are normally organic based. These nanoparticles are used in many fields like drug delivery, imaging, and diagnostics.[11]

NPs can also be classified based on their dimensions as 0D, 1D, 2D, or 3D. Zero-dimensional (0D) NPs such as quantum dots have all three dimensions in nanoscale and all dimensions are roughly the same size. One-dimensional (1D) NPs like nanorods or nanotubes have only one dimension in the nanoscale range. 1D NP applications are nanoelectronics, nanocomposite materials and energy resources. Two-dimensional (2D) NPs like graphene have only one dimension within the nanoscale range. Three-dimensional (3D) NPs do not have any dimensions confined to the nanoscale. Nanomaterials have a high surface-area-to-volume ratio, which makes them useful for many applications like catalysis.[12]

Nanoparticles have unique properties that are different from those of their bulk counterparts. Some of the key properties of nanoparticles include enhanced mechanical properties, electronic and optical properties, magnetic properties, and thermal properties. Overall, the unique properties of nanoparticles make them useful in a wide range of applications, from medicine and electronics to energy and environmental control.

One of the most important properties of NPs is the specific surface, which is the surface to volume ratio or surface area per unit gram of the nanoparticle. NP properties and behaviour are often dependent on their high surface-area-to-volume ratio. As nanoparticles shrink, their surface area increases dramatically for the same volume of material. This means that a small number of nanoparticles can have a large surface area, which can be important for their reactivity and interactions with other materials.[11]

## **1.3. Optical properties of nanoparticles**

### **1.3.1. Optical properties**

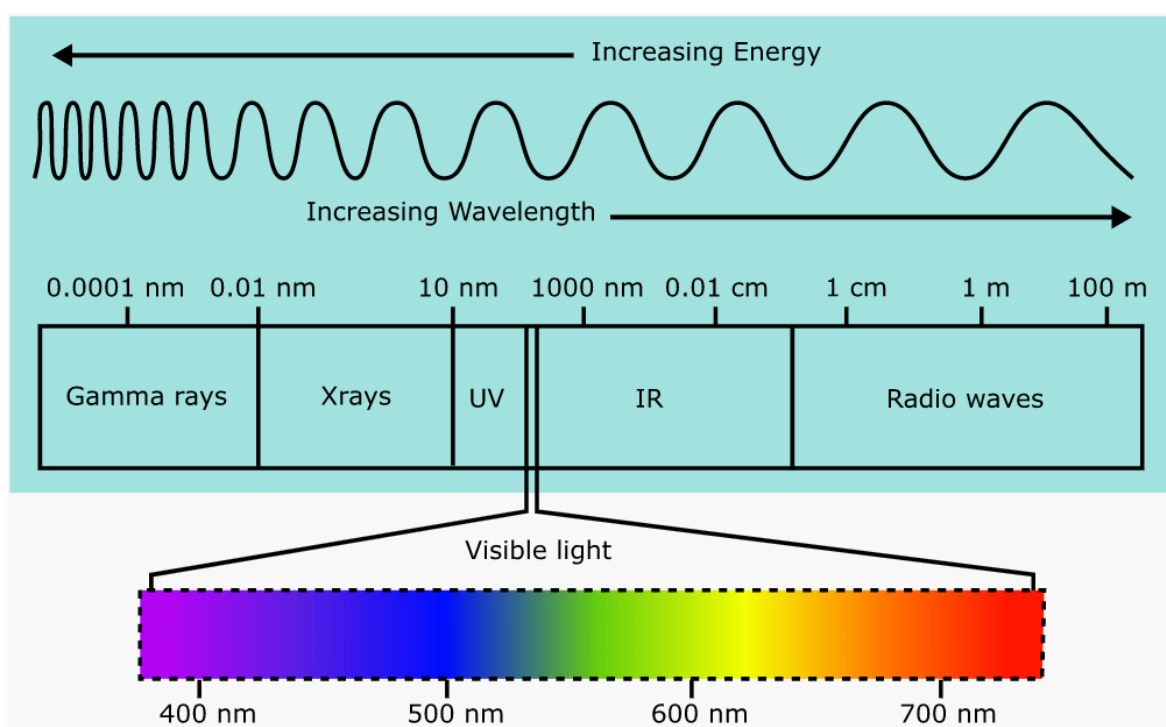
The optical properties of NPs depend on several factors, including their size, shape and composition, the small size and high surface-to-volume ratio give NPs some very unique optical properties. These optical properties are determined by the interactions of light with the nanoparticle's surface and the material it is made of. The main optical properties of nanoparticles are scattering, absorption, transmission, reflection and light emission. These properties in NPs can be significantly different than in the same bulk materials. In general, smaller nanoparticles exhibit more intense and broader absorption and scattering spectra than larger ones due to their larger specific surface area. Also, optical properties of these nanomaterials can be varied through various strategies.[13]

Some metal nanoparticles like gold and silver display surface plasmon resonance. This allows free electrons in these materials to naturally resonate at a frequency depending on the NPs size and shape. The plasmon resonance results in a strong absorption and scattering of light at specific wavelengths, which can be modified by changing the size, shape and composition of the NPs. [13] In addition to plasmon resonance, metal nanoparticles can also exhibit surface plasmon resonance (SPR), which is the resonance of the surface electrons with the electromagnetic field of the incident light. This property is particularly useful for applications such as sensing and photothermal therapy.[14]

Other NPs, like semiconductor materials also known as quantum dots (QD) depend strongly on their size when emitting light. Smaller NPs have larger band gaps. This size-dependent behaviour arises due to quantum confinement effects that arise when the particle size is comparable to the wavelength of the electronic excitations. QDs are widely used in different technologies in many fields of science and engineering like medical imaging, solar cells, LEDs television etc. [13]

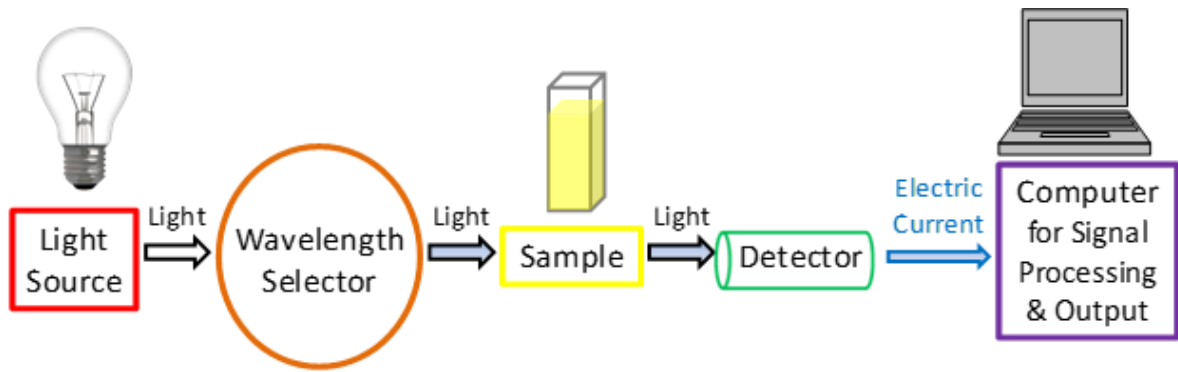
### 1.3.2. UV/Vis spectroscopy

UV-Vis spectroscopy is a technique used to analyze the absorption of light in the ultraviolet-visible region of the electromagnetic spectrum. This technique is widely used in chemistry, biochemistry, and materials science to study the electronic structure of molecules, including their bonding and electronic transitions. UV/Vis spectroscopy is a technique that measures absorption of light by samples in ultraviolet (UV) ca 180-400 nm and in visible (Vis) ca 400-780 nm range in electromagnetic spectrum (figure 1.2).[15]



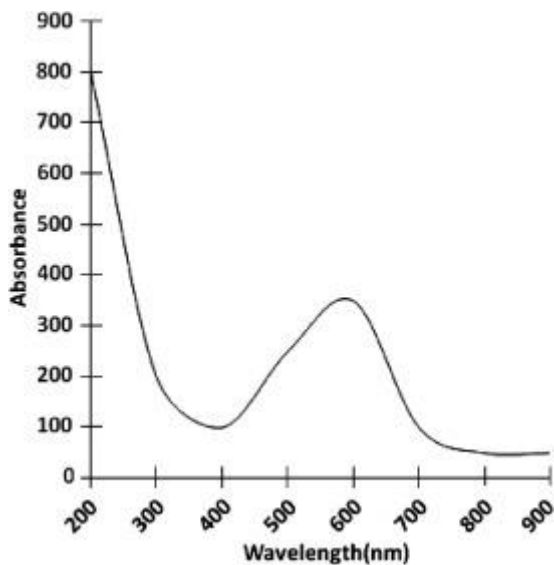
**Figure 1.2.** Electromagnetic spectrum.[15]

The working principle of UV-Vis spectroscopy (figure 1.3) is that a beam of light is passed through the sample, and the amount of light absorbed by the sample is measured as a function of wavelength. The resulting spectrum is then compared to a blank sample. This comparison provides information about the electronic transitions that occur in the sample. Energy difference determines which wavelengths of light will be absorbed by the sample, and therefore provides information about the sample's electronic structure.[16]



**Figure 1.3.** A simplified working principle of UV-Vis spectrophotometer.[16]

Information gained from the UV-Vis spectroscopy is usually presented as a graph of an absorption spectrum (figure 1.4). Wavelength is presented on the horizontal x axis and absorbance in the vertical y axis. The peak in the graph means that less light of that wavelength is able to pass through the sample and reach the detector. Light in this wavelength is being absorbed by the sample. [16]



**Figure 1.4.** An example of copper nanoparticles absorption graph taken with UV/Vis spectrophotometer. Adapted with permission from[17]

The absorbance measured with UV-Vis spectrophotometer is equal to the logarithm of a fraction involving the intensity of light before passing through the sample ( $I_0$ ) divided by the intensity of light after passing through the sample ( $I$ ) which result is the transmittance ( $T$ ), and it shows, how much light passes through the sample.

$$A = \log_{10} \left( \frac{I_0}{I} \right)$$

A - absorbance in arbitrary units (AU);

$I_0$  - intensity of light before passing through the sample;

I - intensity of light after passing through the sample.[16]

Furthermore, Beer-Lambert law states that the amount of light absorbed by the sample is directly proportional to samples length and concentration.[18]

$$A = \epsilon lc$$

A - absorbance in arbitrary units (AU);

$\epsilon$  - the molar absorptivity coefficient constant;

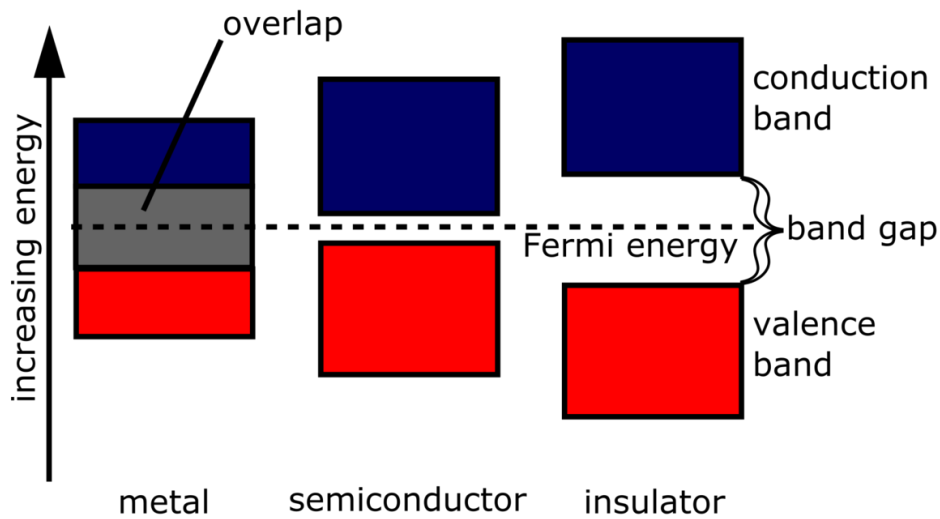
l – length of the sample cell (cm);

c - concentration of the sample.

### **1.3.3. Band gap**

In physics, the band gap refers to the energy range that exists between the valence band of electrons and the conduction band in a material. This energy range represents a zone where electrons cannot exist. The size of the band gap (figure 1.5) defines its electrical properties. Materials with no band gap, such as metals, have a large number of available electrons in the conduction band and can easily conduct electricity. However, materials with a large band gap have a small number of available electrons in the conduction band and are poor conductors of electricity. Materials are considered insulators when their band gap is higher than 4 eV.

Semiconductors are materials where the band gap is between the insulator and conductor, usually between 0.6 and 1.5 eV. They can be made to conduct electricity under certain conditions, such as when they are exposed to light or heat, for example. This property makes semiconductors useful in a lot of different applications like electronics, solar panels and LEDs.[19]



**Figure 1.5.** Different sizes of band gaps for conductors, semiconductors and insulators.[19]

In nanotechnology, the concept of band gap is important because the properties of materials change when they are scaled down to nanoscale. Any change in the nanoscale has a direct impact on the characteristics of the band gap. As the size of a material decreases, its bandgap energy can increase or decrease, depending on the material and the specific nanoscale structure.[20]

The bandgap energy of a material can be determined using UV-Vis spectroscopy. The UV-Vis spectrum of a material shows the absorption or transmission of light as a function of its wavelength. The bandgap energy can be calculated using this formula:[18]

$$E = \frac{hc}{\lambda}$$

E - energy of band gap (eV);

h - Planck's constant (  $6,626 \cdot 10^{-34} \text{ Js}$ );

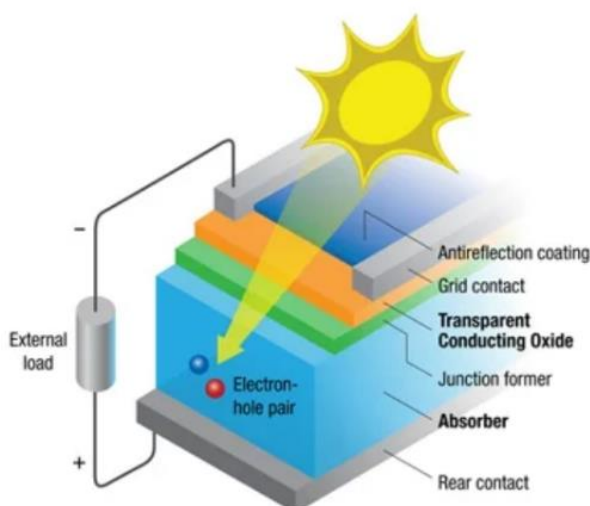
c - speed of light in a vacuum (  $2,998 \cdot 10^8 \frac{\text{m}}{\text{s}}$ );

$\lambda$  - wavelength (m).

### 1.3.4. Applications of nanoparticles

Nowadays there are some applications in which the optical properties of the NPs are important. One of these applications is in the field of semiconductor nanomaterials. Some of the major applications of semiconductor nanomaterials are in electronics, solar panels, energy storage and energy productions like photocatalysis etc. [21]

One of the main applications for NPs nowadays is enhancing the work of solar panels. A solar panel has many layers of photovoltaic cells (figure 1.6), NPs have the potential to enhance the performance of each layer.[22]

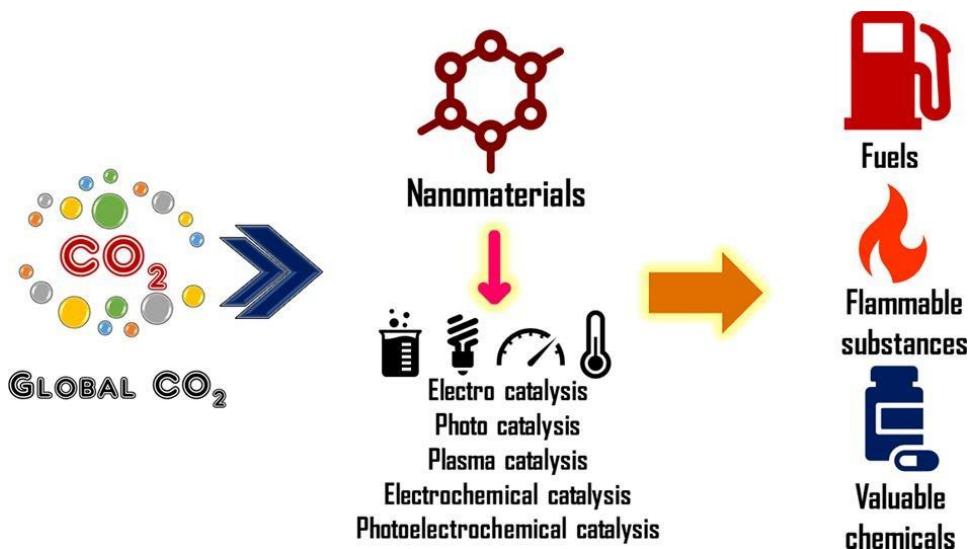


**Figure 1.6.** Schematic of a photovoltaic cell.[22]

Another large application field for NPs is photocatalysis. In this field NPs have many different uses like CO<sub>2</sub> reduction. Nanomaterials such as TiO<sub>2</sub>, ZnO, and Cu<sub>2</sub>O have been used in photocatalytic CO<sub>2</sub> reduction to produce new chemicals and fuels. In some cases these nanomaterials can efficiently reduce CO<sub>2</sub> to produce chemicals such as methanol and ethanol, which can be used as alternative fuels (figure 1.7).[23] Converting solar energy into chemical energy to create so-called “solar fuels” is a promising method to solve the environment and energy problems in future. This transformation can be used to create fuels like hydrogen, methane and methanol. Hydrogen (H<sub>2</sub>) is carbon-neutral, abundant and renewable. It can be used in many different applications like transport, power generation and heating. H<sub>2</sub> also has high calorific value per mass. These properties make H<sub>2</sub> one of the most



promising alternatives for fossil fuels. One of the ways to convert solar energy to H<sub>2</sub> is via the photocatalytic process, where semiconductor materials like TiO<sub>2</sub> or Cu<sub>2</sub>O are used to convert solar energy to hydrogen.[24]



**Figure 1.7.** Possible applications for CO<sub>2</sub> reduction with nanomaterials. Adapted with permission from[23]

## 1.4. Cu-based nanoparticles

### 1.4.1. Copper

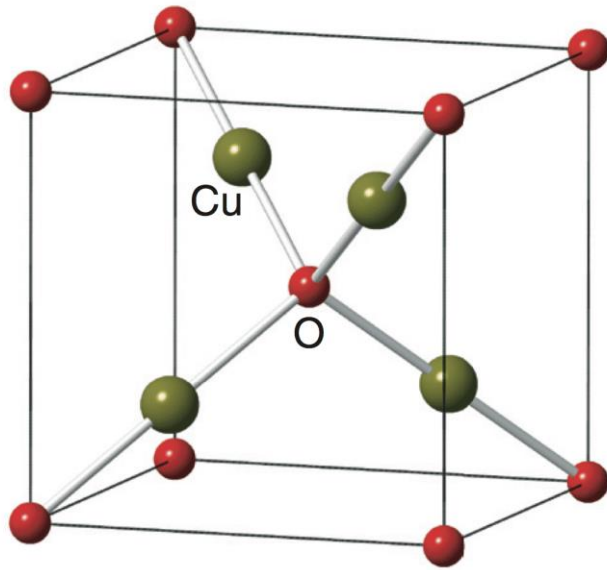
Copper is a chemical element, its symbol is Cu and atomic number 29. It is a soft metal that is widely used in electrical wiring, plumbing, roofing, and other applications. Copper is a reddish-orange colour when it is in its pure form. Copper is relatively abundant in the Earth's crust. Its deposits are found in many parts of the world, with the largest producers being Chile, Peru, China, the United States, and Australia. Copper is usually mined from large open-pit mines or underground mines. The total amount of copper in the Earth's crust is difficult to estimate precisely, but some estimates suggest that there may be as much as 2.5 trillion metric tons of copper in the crust. However, much of this copper is not easily accessible or economically viable to extract.

Copper is an excellent conductor of electricity and is second only to silver in electrical conductivity. It is widely used in electrical wiring, motors and transformers because of its high conductivity. Copper is also a good thermal conductor, which makes it useful in applications where heat needs to be quickly transferred. Copper has several alloys that are used in various applications. For example, brass is an alloy of copper and zinc that is used in musical instruments, decorative objects, and plumbing fixtures. Bronze is an alloy of copper and tin that is used in sculptures, coins and other decorative objects.

Copper forms a wide range of compounds with different oxidation states including Copper(I) oxide ( $\text{Cu}_2\text{O}$ ) and Copper (I) nitride ( $\text{Cu}_3\text{N}$ ).  $\text{Cu}_2\text{O}$ , also known as cuprous oxide, is a red or brownish-red crystal that occurs in nature as minerals. It is a semiconductor material and is widely used in solar cell production, catalysis, and electronics.  $\text{Cu}_2\text{O}$  is also used as a pigment, particularly in ceramics and glassware. It is insoluble in water and is stable in air.  $\text{Cu}_3\text{N}$  is a dark blue or black solid that is a rare copper compound. It is a semiconductor that has potential use in electronics and optoelectronics, such as in solar cells and light-emitting devices.[25]

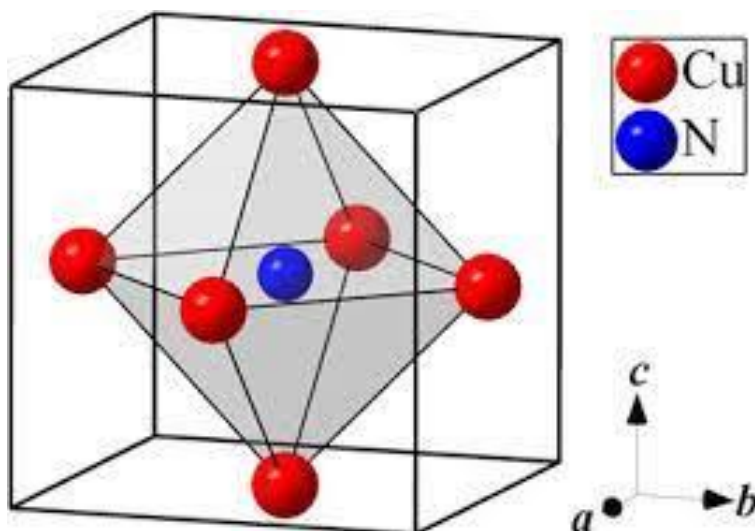
#### **1.4.2. $\text{Cu}_2\text{O}$ and $\text{Cu}_3\text{N}$ nanoparticles**

Cuprous oxide,  $\text{Cu}_2\text{O}$ , is a chemical compound composed of copper and oxygen atoms, it has a reddish-brown colour.  $\text{Cu}_2\text{O}$  is a compound with a relatively simple crystal structure (figure 1.8) that consists of copper ions ( $\text{Cu}^+$ ) and oxide ions ( $\text{O}^{2-}$ ). The simple cubic structure and narrow band gap around 2.17 eV makes it an attractive material for research and development for many different fields of application like energy conversion, sensor devices and environmental purification. There are different methods to synthesize  $\text{Cu}_2\text{O}$ , some examples are thermal synthesis, sol-gel method, and electrodeposition.[6]  $\text{Cu}_2\text{O}$  is a p-type oxide semiconductor.[26]



**Figure 1.8.**  $\text{Cu}_2\text{O}$  crystal structure.[27]

Copper nitride,  $\text{Cu}_3\text{N}$ , is a chemical compound composed of copper and nitrogen atoms. It is a blue-black powder with a crystal structure (figure 1.9) that consists of copper ions ( $\text{Cu}^+$ ) and nitrogen ions ( $\text{N}^{3-}$ ). It has a hexagonal layered crystal structure and a band gap of 1.7 eV.



**Figure 1.9.**  $\text{Cu}_3\text{N}$  crystal structure. Adapted with permission from[28]

There are lot of ways to synthesis  $\text{Cu}_3\text{N}$ , like solid–gas state synthesis, solvothermal, sol-gel, non-thermal plasma, electrospinning, electrodeposition, atomic layer deposition, chemical vapor deposition and laser ablation method. However, the synthesis of  $\text{Cu}_3\text{N}$  is quite difficult if compared to other metal oxides, sulphides and oxynitrides. Metal nitride nanostructures also oxidize in ambient conditions, making them even more unstable.  $\text{Cu}_2\text{O}$  is still a valuable compound because of its catalytic activity, electrical conductivity and magnetic properties, and is used in many areas like optical storage devices and memory chips. [7]

## **2. MATERIALS AND METHODS**

### **2.1. Nanomaterials and chemicals**

The Cu-based nanoparticles used in this thesis were synthesized by Mr. Patricio Paredes using a non-aqueous sol-gel method inside a glovebox (controlled N<sub>2</sub> atmosphere) and the reagents were sealed in an autoclave for the synthesis.[29] The sol-gel method is a technique for the synthesis of various materials, including ceramics, glasses, and metal oxides. It is a chemical process that involves the conversion of a liquid "sol" into a solid "gel" network by the process of gelation. The main steps of this process are hydrolysis, condensation, aging, drying and calcination.[30]

In this experiment non-aqueous sol-gel method is used. The main difference between the non-aqueous sol-gel method and the regular sol-gel method is the solvent used in the process. In the regular sol-gel method, the solvent is typically water-based, while in the non-aqueous sol-gel method, the solvent used is not water-based.[31]

The solvent used to disperse the nanoparticles for the UV-Vis measurements was 2-propanol (purchased from Honeywell). The chemical is of analytical grade, and it was used as received without further purification.

### **2.2. Sample preparation**

In this work, four samples of Cu-based nanoparticles were studied for optical absorption properties by UV-Vis spectroscopy. The samples were synthesized with different stirring times inside the glovebox. The sample parameters are detailed in table below (table 2.1). Each sample has weight of 2 mg each and is dispersed in 15 ml of isopropanol. Samples used for UV-Vis measurements should have low concentrations such as 133 mg/l. The absorption may change when the sample concentration is too high or a not suitable solvent is used. It is important to use non-interacting solvents to reduce the error in the absorbance values.[32]

**Table 2.1.** Nanoparticle samples.

	<b>Name</b>	<b>Stirring time</b>
<b>Sample 1</b>	<b>Cu-20m</b>	<b>20 min</b>
<b>Sample 2</b>	<b>Cu-2h</b>	<b>2 h</b>
<b>Sample 3</b>	<b>Cu-3h</b>	<b>3 h</b>
<b>Sample 4</b>	<b>Cu-5h</b>	<b>5 h</b>

The preparation of the copper-based samples for UV-Vis spectroscopy were carried out as follows:

1. The weight of each sample was 2 mg.
2. Sonication process was carried out for 2 min. It is important because it helps to disperse homogeneously the nanoparticles in the solution, which can improve the precision of measurements.
3. Isopropanol was used as the blank sample.

### **2.3. UV-Vis spectroscopy measurements**

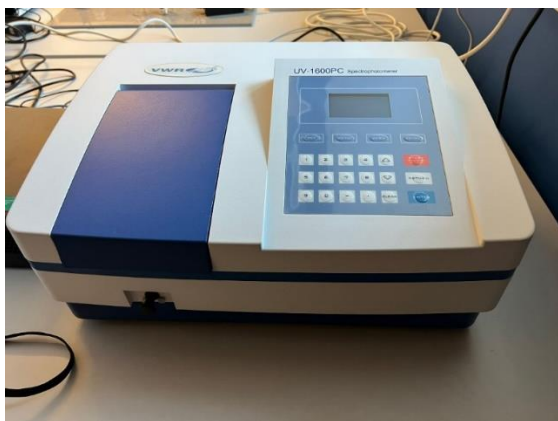
The optical absorbance of the nanoparticles was measured using a VWR UV-VIS spectrometer (UV-1600PC, USA) in 350–1100 nm region (figure 2.1). Some specifications about spectrometer used in experiment are in the table below (table 2.2).

**Table 2.2.** Specifications of VWR UV-VIS spectrometer UV-1600PC.[33]

Measuring modes	Photometry, quantitation, kinetics
Optical design	Single beam
Wavelength accuracy	±0,5 nm
Wavelength range	190 - 1100 nm
Memory	200 results and 200 standard curves

The range of measurement of the spectrophotometer is from 190 to 1100 nm. Four samples were measured simultaneously, one of which was the blank sample. When the samples were in the machine the signal output of the instrument in under dark conditions was measured. This was the dark current step, which is an important process in UV-Vis spectroscopy

because it helps to account for any electronic noise or background signal present in the instrument, which can affect the accuracy of measurements. Three measurements were made with each sample to prove that the machine functions properly and the measurements are correct.



**Figure 2.1.** VWR UV-VIS spectrometer UV-1600PC.

## **2.4. Band gaps calculations**

The band gap energy of the nanomaterials was calculated using the Tauc plot method. The Tauc plot is a graphical method used to determine the optical band gap of a material from its absorption spectrum. The plot is based on the Tauc equation, which describes the relationship between the absorption coefficient of a material and its energy band gap.

The Tauc plot is a graph of:

$$(\alpha \cdot h \cdot \nu)^n = (h \cdot \nu - E_g)$$

$\alpha$  - the absorption coefficient,

$h$  - Planck's constant,

$\nu$  - the frequency of light,

$E_g$  - the energy band gap,

$n$  - the constant that depend on the material's properties.

The X-axis in a Tauc plot represents the photon energy ( $h\nu$ ) in electron volts (eV). The Y axis of the Tauc plot represents the square of the absorption coefficient,  $(\alpha h\nu)^2$ , which is a dimensionless quantity. The square of the absorption coefficient is used because it is proportional to the absorption coefficient and allows the Tauc plot to be more easily interpreted.

Therefore, the bandgap of the nanoparticles were determined by extrapolating the linear region of the Tauc plot to the X-axis. The intercept of the linear region with the X-axis corresponds to the bandgap energy of the material. However, this procedure requires the extrapolation of the flat part of the Tauc plot which can be quite subjective and can therefore result in errors.[34]

The position and intensity of the absorption peaks in the UV-Vis spectrum provide important information about the electronic structure and optical properties of the material. For example, the position of the absorption peaks can be used to determine the bandgap of a semiconductor material, which is the minimum energy required to excite an electron from the valence band to the conduction band. The intensity of the absorption peaks can be used to estimate the concentration of absorbing species in a sample.

In the UV-Vis spectrum, the absorption peaks correspond to the wavelengths of light that are absorbed by the material. The location of the absorption peaks depends on the electronic structure of the material, including the energy levels of the valence and conduction bands and the nature of the electronic transitions that occur.[35]

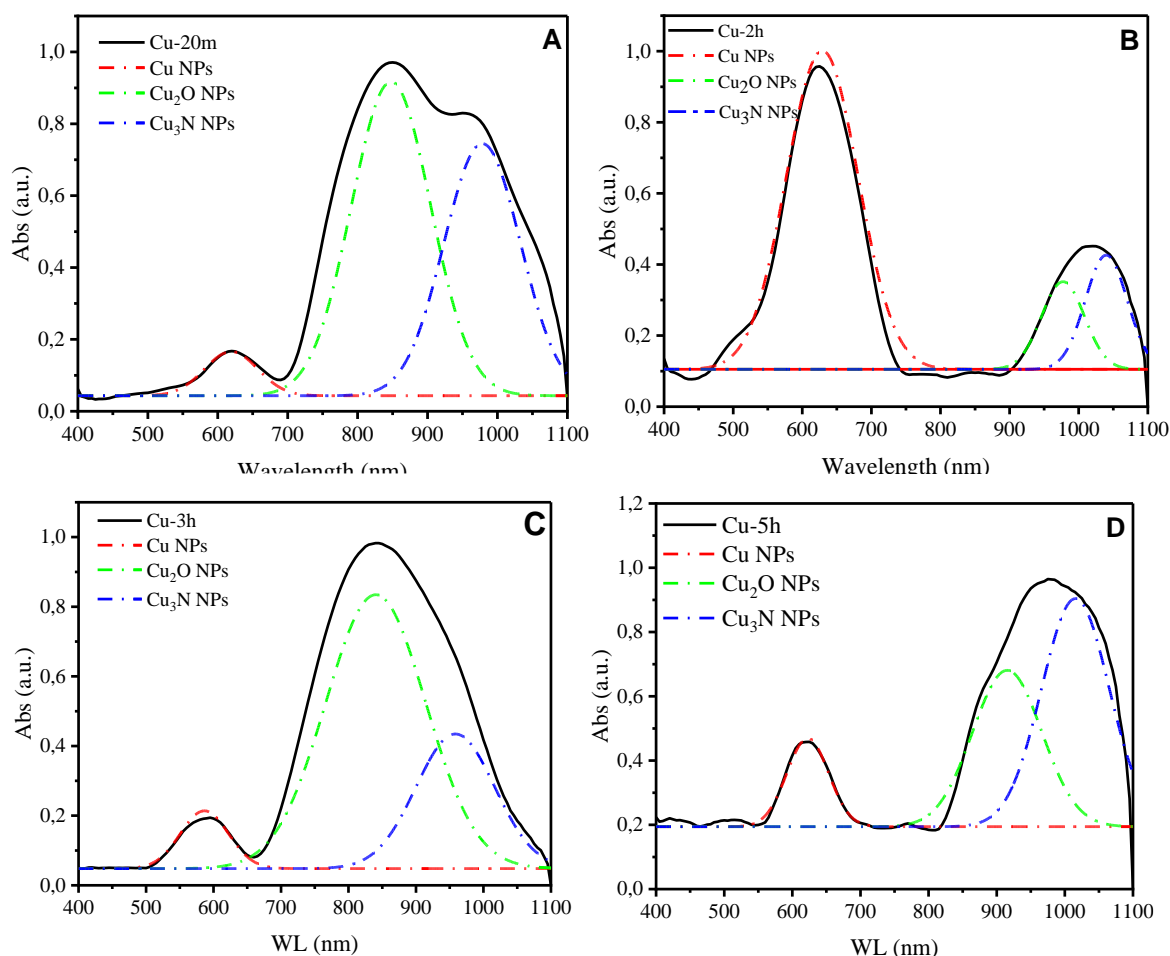


## **3. RESULTS AND DISCUSSION**

### **3.1. UV-Vis spectra**

The absorption properties of the copper-based nanoparticles prepared for this work were measured using UV-Vis spectroscopy. Three measurements were made with each sample. Then, data with the best quality and least noise was selected for this study. The chosen data were normalized and then plotted using the OriginPro software. The graphical results of the absorption peaks are presented in the image below (figure 3.1). Furthermore, for further study the peak deconvolution analysis was performed to every spectrum, in order to compare the differences between each compound.

The deconvolution of the absorption peaks in UV-Vis spectroscopy is important because it allows us to indicate and analyze individual peaks. In this experiment, samples consisted of three different copper phases that contained overlapping peaks. These peaks may be difficult to distinguish and interpret if not deconvoluted, because they have similar absorption range. Thus, deconvolution method was done to separate the overlapping peaks and provide information about the individual peaks of  $\text{Cu}_2\text{O}$ ,  $\text{Cu}_3\text{N}$  and Cu nanoparticles. This can allow a more accurate analysis of the sample.



**Figure 3.1.** Absorption peaks of Cu based nanoparticles. Figure A is the sample with 20 m stirring time, B is the sample with 2 h stirring time, C is the sample with 3 h stirring time and D is the sample with 5 h stirring time.

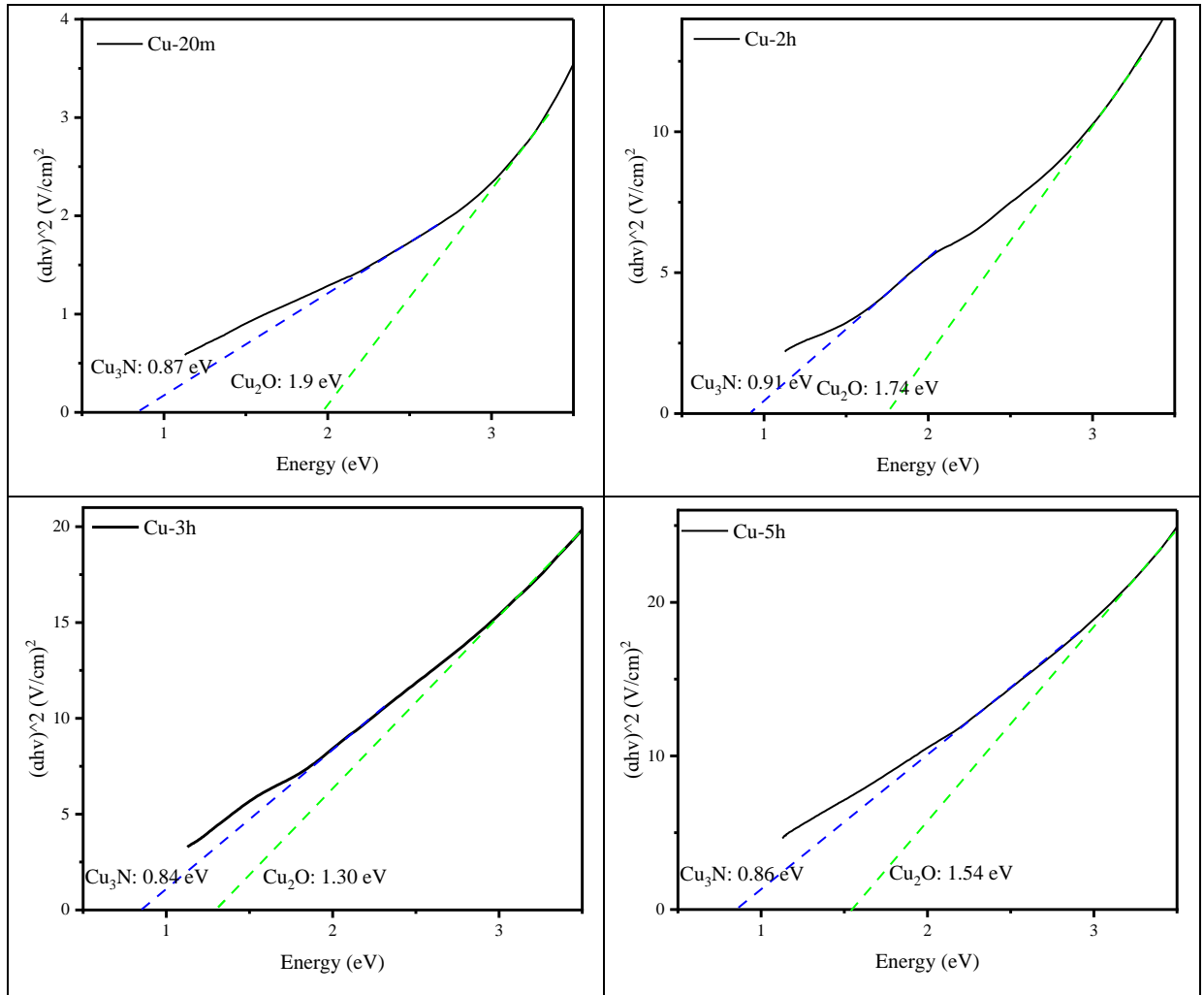
The UV-Vis absorption results of the Cu-based nanoparticles mixture are shown in Figure 3.1. For all samples (Figure 3.1. A-D) the characteristic surface plasmonic peak of the Cu metal nanoparticles is located in the reported range from 590 to 620 nm. Localized surface plasmon peak of Cu is an optical phenomenon that arises when light is incident on a metal nanoparticle that is smaller than the wavelength of incident light. This produces a strong interaction between the incident electric field and the free conduction electrons of the metal nanoparticles.[36] This peak helps to absorb light at the visible range for each compound because of the light interaction with a material (metal or semiconductor) that has free electrons. This effect can increase the absorption of light and generate electrons with high energy. Additionally, this may in turn lead to increased electron-hole pair generation, which is the primary process in photocatalysis.[37]

The characteristic absorption peaks of the  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$  phases were also found and discussed below. In Cu-20m sample (Figure 3.1. A) the absorption peak for  $\text{Cu}_2\text{O}$  is located at 847 nm and the absorption peak for  $\text{Cu}_3\text{N}$  is at 981 nm. For the sample Cu-2h (Figure 3.1. B) the absorption peak for  $\text{Cu}_2\text{O}$  is at 974 nm and the absorption peak for  $\text{Cu}_3\text{N}$  is at 1040 nm. For the sample Cu-3h (Figure 3.1. C) the absorption peak for  $\text{Cu}_2\text{O}$  is at 842 nm and the absorption peak for  $\text{Cu}_3\text{N}$  is at 961 nm. Finally for the Cu-5h (Figure 3.1. D) the absorption peak for  $\text{Cu}_2\text{O}$  is at 913 nm and the absorption peak for  $\text{Cu}_3\text{N}$  is at 1019 nm. These peaks are consistent with the results from literature.[38][39][40] However the shift in the peaks can be explained by many factors like the change of the particles size, sample concentration and specially the synthesis conditions.[41]

### 3.2. Band gaps

The band gap of the Cu-based nanoparticles synthesized inside a glove box at different stirring times was calculated using the Tauc plot method according to the formula explained before in 2.4 section. After plotting, the linear line considering the flat area was drawn and the band gap values for  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$  semiconductors were determined. The band gaps are the line intercept of the X-axis. The results are of the figure below (figure 3.2) and summarized in the table (table 3.1).

Specifically, in sample Cu-20m the band gap for  $\text{Cu}_2\text{O}$  is 1.80 eV and for  $\text{Cu}_3\text{N}$  is 0.87 eV. For the sample Cu-2h the band gap for  $\text{Cu}_2\text{O}$  is 1.74 eV and for  $\text{Cu}_3\text{N}$  is 0.91 eV. In sample Cu-3h the band gap for  $\text{Cu}_2\text{O}$  is 1.30 eV and for  $\text{Cu}_3\text{N}$  is 0.84 eV. Lastly, for Cu-5h sample the band gap for  $\text{Cu}_2\text{O}$  is 1.54 eV and for  $\text{Cu}_3\text{N}$  is 0.86 eV. The band gap values calculated using Tauc plot method (figure 3.2) are generally consistent with the findings from literature. Reports say that the band gap for  $\text{Cu}_2\text{O}$  are located in the range from 1.8–2.5 eV[39] and for  $\text{Cu}_3\text{N}$  in the range around of 0.2 eV–2 eV for visible light absorption [42]. However, two samples (Cu-3h and Cu-5h) have  $\text{Cu}_2\text{O}$  band gap lower than reported. This effect can be explained by the change in stirring time which can influence nanoparticle size that in turn can change the band gap.[43]. In addition, the lower band gap of the  $\text{Cu}_2\text{O}$  could be affected by the presence of  $\text{Cu}_3\text{N}$  nanoparticles in the composition. Probably, there is an overlap of the band gap between  $\text{Cu}_3\text{N}$  and  $\text{Cu}_2\text{O}$  during the calculations.



**Figure 3.2.** Band gap values of the samples using Tauc plot method.

### 3.3. Evaluating the potential for photocatalytic and photovoltaic properties

In photovoltaic process solar energy is converted directly into electricity using photovoltaic cells typically made of semiconductor material. Photovoltaic cells absorb photons from sunlight and generate an electric current through the photovoltaic effect.[44] Photoenergy can be also used to produce solar fuels such as hydrocarbons or hydrogen through a process called photocatalysis. Fuel production through photovoltaics is still in the early stages of development, and these approaches are being explored as part of efforts to achieve sustainable and carbon-neutral energy systems.[45]

Photocatalysis is a chemical process in which light energy is used to initiate or enhance a chemical reaction. In photocatalysis, is consider as a catalyst material which absorbs light energy and uses it to initiate or enhance a chemical reaction. The most common example of photocatalysis is the use of sunlight to split water molecules into oxygen and hydrogen. Photocatalyst is a material (semiconductor) that absorbs light to create electron-hole pairs. Semiconductors can work as photocatalysts even in room temperatures when under illumination. When a photocatalyst gets enough energy (specific wavelength), the electron is absorbed from valence band and excited to the conduction band. That means, a hole is created in valence band and electron-hole pairs are created. Photocatalysis can be used for many different applications like storage of energy, air purification or wastewater treatment.[46] A good photocatalyst for these applications is semiconductor material with a narrow band gap allowing easy creation of electron-hole pairs. It should have high absorbance in the visible light spectrum for solar driven photocatalysis with an optimum concentration of nanoparticles in the solution.[47]

According to the Beer-Lambert law, the amount of light absorbed by the sample is directly proportional to the concentration and the type of the absorbing material present in the solution. Moreover, the intensity of the absorption peak also qualitatively indicates the concentration of the nanoparticles present in the sample. Therefore, the intensity of the absorption peaks will depend on the amount of Cu, Cu<sub>2</sub>O and Cu<sub>3</sub>N nanoparticles, because it is related to the ability to absorb light. The wavelength where the absorption peak is located shows the range in the solar spectrum where absorption properties are enhanced. In semiconductor materials the band gaps indicate how easy it is for electrons to do the transition from the valence band to the conduction band.[47] The smaller the gap, the easier it is to transit. All these measured properties are presented in the table below (table 3.1).

Intensities of the absorption peaks were normalized in the scale of 0 to 1 and considered as our reference to study the photocatalytic characteristics based on the variation in peak intensities of the absorption spectra of Cu, Cu<sub>2</sub>O and Cu<sub>3</sub>N nanoparticles. The results are detailed in Table 3.1. Specifically, sample Cu-20m the intensity of the plasmonic peak of Cu metal is 0.2, for Cu<sub>2</sub>O peak is 1 and for the Cu<sub>3</sub>N is 0.8. In sample Cu-2h the intensity of the surface plasmonic peak of the Cu metal is 1, for the Cu<sub>2</sub>O peak is 0.1 and for Cu<sub>3</sub>N is 0.5. In sample Cu-3h the intensity of Cu metal plasmonic peak is 0.2, for Cu<sub>2</sub>O peak is 1 and for the Cu<sub>3</sub>N is 0.7. Finally, for Cu-5h sample the intensity of Cu metal plasmonic peak is 0.5, for the Cu<sub>2</sub>O peak is 0.7 and for Cu<sub>3</sub>N is 1.

**Table 3.1.** Measured properties of the Cu-based nanoparticles.

Sample	Wavelength of the absorption peak (nm)			Intensity of the absorption peaks (normalized scale)			Band gaps (eV)	
	Cu	Cu <sub>2</sub> O	Cu <sub>3</sub> N	Cu	Cu <sub>2</sub> O	Cu <sub>3</sub> N	Cu <sub>2</sub> O	Cu <sub>3</sub> N
<b>Cu-20m</b>	620	847	981	0.16	1	0.82	1.91	0.87
<b>Cu-2h</b>	622	974	1040	1	0.32	0.44	1.74	0.91
<b>Cu-3h</b>	595	842	961	0.19	1	0.64	1.30	0.84
<b>Cu-5h</b>	619	913	1019	0.45	0.67	1	1.54	0.86

Based on the previous information from the absorption spectra, the intensity and band gaps, it can be concluded that the best photocatalyst for wastewater treatment is Cu-3h sample. This conclusion is supported mainly by the small band gap of Cu-3h sample. The band gaps for Cu-3h sample are 1.30 eV for Cu<sub>2</sub>O and 0.84 eV for Cu<sub>3</sub>N. These values are very small and allow easy creation of electron-hole pairs necessary for chemical reactions to start in photocatalytic processes under visible light. Furthermore, the sample has a high absorption peak in both Cu<sub>2</sub>O at 842 nm and for Cu<sub>3</sub>N at 961 nm. That means that the material can absorb a large amount of visible light, which increases the photocatalytic activity needed for oxidation-reduction reactions. Also, the peaks indicate that the Cu-3h sample has relatively high amount of Cu<sub>2</sub>O and Cu<sub>3</sub>N nanoparticles. The plasmonic peak is also present at 595 nm, which helps to absorb light in the visible spectrum.

Although the Cu-20m sample presents good characteristics as a photocatalyst using visible light, the band gap of the Cu<sub>2</sub>O could present a small deficiency in the photocatalytic activity in comparison with Cu-3h sample. However, the intensity of the absorption peaks and the absorption range of Cu<sub>2</sub>O and Cu<sub>3</sub>N in the electromagnetic spectrum for Cu-20m provide good photocatalytic properties. On the other hand, the Cu-5h sample presents optimal band gap for photocatalysis in visible light, however the absorption ranges of Cu<sub>2</sub>O and Cu<sub>3</sub>N suggest a disadvantage in the photocatalysis process in visible light. Finally, the Cu-2h sample could not be as effective for photocatalysis processes for several reasons. First, the fact that the peak with the highest intensity corresponds to the plasmonic peak of the Cu

metal surface. Therefore, the sample has more properties of a metal than a semiconductor. Second, the ranges and intensity in the absorption in visible light of  $\text{Cu}_2\text{O}$  and  $\text{Cu}_3\text{N}$  suggest a disadvantage in the characteristics as a photocatalyst.

## CONCLUSION

The objective of this study was to study different samples of copper-based nanoparticles using UV-Vis spectroscopy and to identify candidates with suitable photovoltaic and photocatalytic capabilities based on their absorption range. In principle, materials with absorption ranges of 500nm to 900nm with a maximum absorption at 550 nm would be ideal candidates for this application. The maximum absorption of 550 nm corresponds to the maximum of the solar emission spectrum. The most suitable sample was the Cu-3h that had an absorption peak at 595 nm, corresponding to the absorption of Cu-nanoparticles. A total of four samples synthesized using different stirring times (20 minutes, 2 hours, 3 hours and 5 hours) were examined. They all had suitable absorption ranges for green photocatalysis and photovoltaic applications. Samples were synthesized using a non-aqueous sol-gel method and then studied using a UV-Vis spectrophotometer, results were collected and studied using OriginPro software. Three different phases were identified in the samples: Cu, Cu<sub>2</sub>O and Cu<sub>3</sub>N. Main parameters considered in results were band gap values, wavelengths and intensities of absorption peaks. Band gaps were plotted and calculated using the Tauc plot method in OriginPro. For wavelengths and intensities of absorption peaks, data collected from the UV-Vis spectrometer were normalized and plotted using OriginPro software.

According to the results, the best sample is the one synthesized with 3 hours stirring time. It exhibits high absorption peaks in both Cu<sub>2</sub>O and Cu<sub>3</sub>N phase, most Cu<sub>2</sub>O and Cu<sub>3</sub>N crystal structure in overall quantity of the sample and low band gap values. The plasmonic peak of copper is also present at 550 nm, which helps to absorb light.

The results of this thesis have shown that copper-based nanoparticles have the potential to be good nanomaterials for photocatalysis and photovoltaics. Of course, future research needs to be done in this field and photocurrent generation along with electrochemical properties need further evaluation to test their potential as photovoltaics and fuel producing photocatalysts, respectively.



# ÜLDKOKKUVÕTE

## **Vasepõhiste nanoosakeste optiliste neeldumisomaduste uurimine roheliste fotokatalüütiliste ja fotogalvaaniliste rakenduste jaoks UV-Vis-spektroskoopia abil**

Päikesevalgusest juhitud fotokatalüüs ja fotogalvaanika on uued ja keskkonnasõbralikud meetodid kütuste ja elektri tootmiseks ning orgaaniliste saasteainete veest eemaldamiseks. Antud bakalaureusetöö raames uuriti erinevate vasepõhiste nanomaterjalide omadusi, et välja selgitada, milline nendest sobiks kõige paremini keskkonnasõbralike lahenduste jaoks.

Praegu enim kasutatavad fotokatalüütilised nanomaterjalid on titaandioksiid ( $\text{TiO}_2$ ) ja tsinkoksiid ( $\text{ZnO}$ ). Nendel nanomaterjalidel esineb aga mõningaid puuduseid: nad rakenduvad ainult UV-kiirguse spektris, neil on lai keelutsoon ning madalad optilised omadused. Seetõttu on suur vajadus uute materjalide järele, mida selles valdkonnas kasutada. Need materjalid peaksid rakenduma nähtava valguse spektris, olema kitsa keelutsooniga, keskkonnasõbralikud ning kergesti kättesaadavad. Vaskoksiid ( $\text{Cu}_2\text{O}$ ) ja vasknitriid ( $\text{Cu}_3\text{N}$ ) on näidanud potentsiaali tõhusate nanomaterjalidena. Neil on head optilised, elektroonilised ja katalüütilised omadused ning kitsas keelutsoon, mis jääb  $\text{Cu}_2\text{O}$  puhul vahemikku 1,4-2,5 eV ja  $\text{Cu}_3\text{N}$  puhul vahemikku 0,8-1,9 eV.

Käesoleva lõputöö eesmärgiks on analüüsida UV-Vis spektroskoopia abil vasepõhiste nanoosakeste optilisi omadusi, et uurida nende võimet neelata valgust päikesespektri nähtavas osas ning hinnata neid rohelise energia allika kandidaatidena. Selles töös uuritud nanomaterjalid sünteesiti EMÜ tehnikamajas mittevesilahusel põhineval sool-geel meetodil. Uuritud nanomaterjalide koostises esines kolm erinevat kristallstruktuuri: Cu,  $\text{Cu}_2\text{O}$  ja  $\text{Cu}_3\text{N}$ . Kokku sünteesiti nelja erineva segamisajaga vasepõhiste nanomaterjalide proovid: 20 minutit (Cu-20m), 2 tundi (Cu-2h), 3 tundi (Cu-3h) ja 5 tundi (Cu-5h). Saadud proovide optilisi neeldumisomadusi uuriti seejärel lainepikkustel 350-1100 nm, kasutades UV-Vis spektromeetrit. Iga prooviga tehti kolm mõõtmist. Seejärel valiti mõõtmiste hulgast uuringu jaoks väiksema taustamüra ning parima kvaliteediga andmed. Tulemused kanti graafikule ning analüüsiti kasutades tarkvara OriginPro.

Saadud tulemusi uuriti kahel üksteist täiendaval moel. Esiteks normaliseeriti kõigist neljast proovist saadud andmed ja seejärel loodi nendest OriginPro tarkvara abil graafik, mille X-teljel on lainepikkus (nm) ning teisel teljel optiliste neeldumispikiide kõrgused normaliseeritud skaalal (joonis 3.1). Teiseks analüüsiti UV-Vis spektroskoopia teel saadud tulemusi kasutades Tauci graafikuid (joonis 3.2). See on graafiline meetod, mida kasutatakse materjali keelutsooni laiuse määramiseks. Tauci graafiku X-teljel on footoni energia ( $h\nu$ ) elektronvoltides (eV) ning graafiku Y-teljel on neeldumistegur  $(\alpha h\nu)^2$ , mis on ühikuta suurus.

Optiliste neeldumisomaduste uurimise tulemused näitavad, et proovi Cu-20m plasmooniline tipp asub lainepikkusel 620 nm, Cu<sub>2</sub>O faasi tipp asub lainepikkusel 850 nm ning Cu<sub>3</sub>N faasil 1000 nm. Plasmoonilise tipu kõrgus on 0,2, Cu<sub>2</sub>O faasi tipu kõrgus on 1 ning Cu<sub>3</sub>N tipu kõrgus on 0,8. Proovi Cu-2h plasmooniline tipp asub lainepikkusel 620 nm, Cu<sub>2</sub>O faasi tipp asub lainepikkusel 850 nm ning Cu<sub>3</sub>N faasil 1000 nm. Plasmoonilise tipu kõrgus on 1, Cu<sub>2</sub>O faasi tippu kõrgus on 0,1 ning Cu<sub>3</sub>N tipu kõrgus on 0,5. Proovi Cu-3h plasmooniline tipp asub lainepikkusel 550 nm, Cu<sub>2</sub>O faasi tipp asub lainepikkusel 820 nm ning Cu<sub>3</sub>N faasil 1000 nm. Plasmoonilise tipu kõrgus on 0,2, Cu<sub>2</sub>O faasi tippu kõrgus on 1 ning Cu<sub>3</sub>N tipu kõrgus on 0,7. Proovi Cu-2h plasmooniline tipp asub lainepikkusel 620 nm, Cu<sub>2</sub>O faasi tipp asub lainepikkusel 900 nm ning Cu<sub>3</sub>N faasil 1000 nm. Plasmoonilise tipu kõrgus on 0,5, Cu<sub>2</sub>O faasi tipu kõrgus on 0,17 ning Cu<sub>3</sub>N tipu kõrgus on 1.

Optiliste neeldumispikiide graafilised tulemused näitavad, et kõikides erineva segamisajaga proovides on esindatud kõik kristallstruktuurid: Cu, Cu<sub>2</sub>O ja Cu<sub>3</sub>N. Kõikide proovide puhul asub Cu faasi neeldumise tipp umbes 620 nm juures, ainult proovil Cu-3h asub see umbes 550 nm juures. Seda nihet saab seletada nanoosakeste suuruse, kontsentratsiooni või temperatuuri muutumisega. Cu<sub>2</sub>O faasi neeldumise tipp asub umbes 850 nm juures, välja arvatud proovil Cu-5h, kus tipp on umbes 900 nm juures. Kõik Cu<sub>3</sub>N faasi neeldumise tipud on infrapunavalguse spektris, umbes 1000 nm juures.

Tauci graafikutelt on näha, et keelutsooni väärtused on proovi Cu-20m puhul 1,8 eV Cu<sub>2</sub>O faasil ning 0,87 eV Cu<sub>3</sub>N faasil. Proovi Cu-2h puhul on keelutsooni väärtused 1,74 eV Cu<sub>2</sub>O faasil ning 0,91 eV Cu<sub>3</sub>N faasil. Proovi Cu-3h puhul on keelutsooni väärtused 1,3 eV Cu<sub>2</sub>O faasil ning 0,84 eV Cu<sub>3</sub>N faasil ning Proovi Cu-5h keelutsooni väärtused on 1,54 eV Cu<sub>2</sub>O faasil ning 0,86 eV Cu<sub>3</sub>N faasil.

Tulemuste analüüsist saab järeldada, et parim proov fotokatalüütiliste ning fotogalvaaniliste rakenduste jaoks on Cu-3h, sellel on kõige intensiivsemad optilised neeldumisomadused Cu<sub>2</sub>O ja Cu<sub>3</sub>N faasis. Plasmooniline tipp on 550 nm juures, mis aitab kaasa valguse neeldumisele nähtava valguse spektris. Samuti on nanoosakeste keelutsooni väärtused (1,3 eV Cu<sub>2</sub>O; 0,84 eV Cu<sub>3</sub>N) väga madalad.

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## **APENDIXES**

# LIHTLITSENTS

## **Lisa 1. Lihtlitsents lõputöö salvestamiseks ja üldsusele kättesaadavaks tegemiseks ning juhendaja(te) kinnitus lõputöö kaitsmisele lubamise kohta**

Mina Aimar Puusepp, sünniaeg 20.03.1988

1. annan Eesti Maaülikoolile tasuta loa (lihtlitsentsi) enda loodud lõputöö  
“Study of optical absorption properties of Cu-based nanoparticles for green photocatalytic and photovoltaic applications by UV-Vis spectroscopy”  
mille juhendaja (d) on Protima Rauwel, Erwan Rauwel ja Edison Patricio Paredes Carranza

- 1.1. salvestamiseks säilitamise eesmärgil,
- 1.2. digiarhiivi DSpace lisamiseks ja
- 1.3. veebikeskkonnas üldsusele kättesaadavaks tegemiseks

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Lõputöö autor

Aimar Puusepp

*/Allkirjastatud digitaalselt/*

Tartu 06.06.2023

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## **Juhendaja(te) kinnitus lõputöö kaitsmisele lubamise kohta**

Luban lõputöö kaitsmisele.

Prof. Protima Rauwel, *PhD*;

Prof. Erwan Yann Rauwel, *PhD*;

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06.06.2023