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Theoretical performance studies of non-enzymatic glucose sensor electrode based on copper oxides thin films

Soutenu publiquement le :

Devant le jury :

Mr Khadidja BOUZIANE	**MAA (UKM Ouargla)**	**Président**
Mr Ahmed TABCHOUCHE	**MCB (UKM Ouargla)**	**Examinateur**
Mme Ouidad BAKA	**MCB (UKM Ouargla)**	**Encadreur**

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Dedication

This modest work is dedicated to:

My parents

Whom affection, love, encouragement, and prayer of day and night make me able to get such success and honor,

My brothers Mouhamed Akrem, Abdellah and Bilal and my sisters Asma and Safa,

My little lovely nieces Tasnim and Yasmine,

My dear husband SALHI Hani Whom without him I would never reach this achievement, I am truly thankful for having you in my life.

My best friend Zina BERRIM who has been a constant source of support and encouragement during the challenges of graduation,

All my friends and my family.

Abstract

Metal oxides such as copper oxides has gotten a lot of attention because it's one of the most important materials in technological advances. Also, because they are widely employed as industrial catalysts, chemical sensing devices... etc. Furthermore, there are two major types of copper oxides, namely cupric oxide (CuO) and cuprous oxide (Cu_2O), which classified as p-type semiconductors; their reported optical band gaps are 1.3 eV - 2.1 eV for CuO and 2.1 eV – 2.6 eV for Cu_2O. Because of their specific, unique properties, they could be used in nom-enzymatic glucose sensing. Various form of CuO and Cu_2O thin films as an electrode for the non-enzymatic glucose sensors were reported. From literature research, CuO thin films show that CuO nanosheet/Cu has a high sensitivity of 33950 ($\mu AmM^{-1}\ cm^{-2}$) and low detection limit of 0.33 (µM). On the other hand, Cu_2O nanometer thin-film has a high sensitivity which was equal to 23240 ($\mu A\ mM^{-1}\ cm^{-2}$) and low detection limit 1.87 (µM). Finally, a comparison between electrocatalytic parameters of the proposed sensor electrodes indicate that cupric oxide sensors exhibit better performances owing to his high sensitivity, low detection limit, and good stability.

Résumé

Les oxydes métalliques tels que les oxydes de cuivre sont attirés beaucoup d'attention car c'est l'un des matériaux les plus importants dans les technologies innovantes. Aussi, parce qu'ils sont largement utilisés comme des catalyseurs industriels, dispositifs de détection chimique... etc. Par ailleurs, il existe deux principaux types d'oxydes de cuivre, l'oxyde cuivrique (CuO) et l'oxyde cuivreux (Cu_2O), classés comme des semi-conducteurs de type p ; leurs bandes interdites sont variées entre 1,3 - 2,1 eV et 2,1 - 2,6 eV, respectivement. Différentes formes de couches minces d'oxyde de cuivre utilisées comme électrode pour la détection non-enzymatique du glucose sont rapportées dans ce travail. D'après la littérature, des nanofeuilles de CuO déposées sur Cu ont une sensibilité élevée de 33950 ($\mu AmM^{-1}\ cm^{-2}$) et une faible limite de détection de 0,33 (µM). D'autre part, les couches minces nanométriques de Cu_2O possèdent une haute sensibilité égale à 23240 (µA mM-1 cm-2) et une faible limite de détection de 1,87 (µM). Enfin et d'après la comparaison entre les paramètres électrocatalytiques des électrodes de capteur proposée, on trouve que les capteurs d'oxyde cuivrique présentent les meilleures performances en raison de sa haute sensibilité, faible limite de détection et bonne stabilité.

ملخص

حظيت أكاسيد المعادن كأكسيد النحاس باهتمام واسع في السنوات الأخيرة نظرا لأهميتها في التكنولوجيات الحديثة. كذلك، لأنها تستخدم على نطاق واسع كمحفزات صناعية، وأجهزة استشعار كيميائية ... إلخ. هناك نوعان رئيسيان من أكسيد النحاس، وهما أكسيد أحادي النحاس وأكسيد ثنائي النحاس، والتي تصنف ضمن أشباه الموصلات ويتميزان بفجوات النطاق البصري 1.3-2.1 الكترون فولت و2.1-2.6 الكترون فولط على الترتيب. نظرًا لخصائصها الفريدة والمحددة، يمكن استخدامها كأقطاب كهربائية في أجهزة الاستشعار غير الأنزيمي للجلوكوز. هناك العديد من الأشكال المختلفة الصفائح الرقيقة المصنوعة من أكسيد أحادي النحاس وأكسيد ثنائي النحاس المستعملة كقطب كهربائي لأجهزة الإستشعار غير الأنزيمي للجلوكوز و لقد تم التطرق اليها في هذا العمل. بعد البحوث والمعلومات المتحصل عليها نجد أن الصفائح الرقيقة المصنوعة من طبقة نانوية من أحادي النحاس على أكسيد النحاس تتميز بحساسية عالية قدرها 33950 ميكروآ/ م مولار* سم^2 . مع حد الاكتشاف منخفض قدره 0.33 ميكرو مولار. من ناحية أخرى الصفائح الرقيقة النانوية لأكسيد ثنائي النحاس تتميز أيضا بحساسية عالية قدرها 23240 ميكروآ/ م مولار*سم ^{2} وحد اكتشاف منخفض قدره 1.87 ميكرو مولار. وفي الأخير، بعد المقارنة بين القيم المتحصل عليها من الأقطاب الكهربائية للمستشعرات المقترحة تبين أن مستشعرات أكسيد أحادي النحاس تظهر أداءً أفضل نظرًا لحساسيتها العالية، وحدود كشفها المنخفضة، واستقرارها الجيد.

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My thanks and gratitude to our teachers who throughout the years of study have passed on their knowledge to us.

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Finally, I would also express my deep sense of gratitude to my family members and my friends for their encouragement and support throughout, which always inspired me.

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Chapitre I. Introduction on the thin films and metal oxides

Chapitre II. Glucose sensors and their Applications

Introduction

Introduction

The field of material science and engineering community's ability is conceiving to novel materials with extraordinary combination of chemical, physical and mechanical properties has changed the modern society [1]. The capacity of the discipline of material science and engineering to develop innovative materials with a combination of chemical, physical, and mechanical property has transformed modern civilization. The creation of novel materials relies heavily on the synthesis of high-quality inorganic compounds with precise size and form. We could cite the medicine catalysis, electronics and cosmetics [2].

Due to its high sensitivity and ease of use, the electrochemical glucose sensor has gotten a lot of interest. Based on the sensing material the electrochemical glucose sensors classified by: enzyme-based glucose sensors and non-enzymatic glucose sensors [3]. Enzyme-free glucose sensors have attracted a lot of interest in clinical diagnostics, the food industry, and other industries because they overcome the inherent flaws of enzyme-based biosensors [4]. And they have a many advantages such as, stability, simplicity, reproducibility, low cost, and no oxygen limitation [5].

Metal oxides are an important class of materials from both scientific and technological point of view. They found huge interesting applications in different technological fields [6] They are widely utilized as industrial catalysts, chemical sensing devices, antimicrobials, and semiconductors in medicinal applications, as well as in the creation of cosmetics and microelectronics. Among various metal oxides, Copper oxide is a semiconductor metal with unique optical, electrical and electrical properties and it has been used for various applications [7]. Cupric oxide, also known as copper II oxide, CuO, and cuprous oxide, Cu_2O, are two types of copper oxide [8].

The copper oxides thin-film electrode was used as a non-enzymatic glucose sensor because of its benefits of being nontoxic, inexpensive, readily available and mass-producible. Due to their excellent catalytic and electrochemical capabilities, they also have great sensitivity, stability and quick reaction to glucose detection [9].

The objective of this work is presenting the most important copper oxides and their applications on non-enzymatic glucose detection. In addition to an introduction and a general conclusion, this work has two separate chapters:

In the first chapter we will present a metal oxides, thin films and copper oxide thin films, their methods of elaboration and their applications in modern technologies. Then we discussed the concept of semiconductors followed by metal oxides. Finally the properties of the most important copper oxides will be presented.

In second chapter, our attention was focused on the application of copper oxides thin films in the medicinal fields like detection of non-enzymatic glucose sensors.

Finally, this manuscript was finished by a conclusion which summarizes the essential of this work.

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Chapter I:

Introduction on the thin films and metal oxides

Chapitre I. Introduction on the thin films and metal oxides

Metal oxides are essential in a variety of fields including chemistry, physics, and materials research[1]. In technological applications, the metal oxides are an important class of semiconductors, which are the basics of several applications[2], due to the industrial interest on their unique properties[3].This chapter covers the applications of metal oxide thin films and the properties of copper oxides.

I.1 Thin films

Thin film technology is simultaneously one of the oldest arts and one of the newest research studies[1]. Thin films and nanostructured coatings are essential to clean technology because they allow to do a lot with a little amount of masse[4]. They are generally used to improve the surface properties of solids. Thin films principle is a substance deposited in another substance called a substrate [1]. It can be prepared as semiconductors, resistors, conductors and insulator, all preparation types are widely used in many industrial applications[5]. A thin film may also be defined as a layer of material with a thickness ranging from one nanometer to several micrometers. Also it's well known that layer of material with one dimension is much smaller than the other[6].

I.1.1 Thin films deposition methods

Metal oxide thin films could be prepared using a variety of processes, including thermal oxidation, electrodeposition, chemical conversion, spraying, and reactive sputtering, among others [7]. This methods of preparation can be classified in two categories, physical methods and chemical methods (figure I.1) [1].

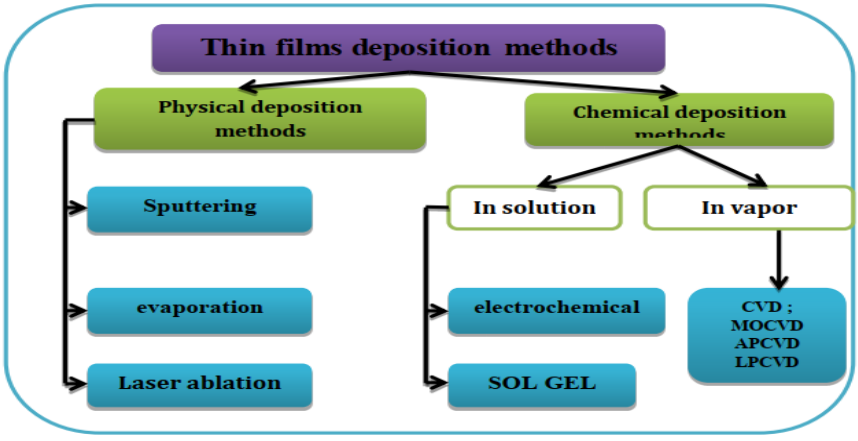

Figure I.1: *Thin films deposition methods[1].*

I.1.2 Thin films applications

In general, thin film materials has found their way into wireless communications, semiconductor devices, gas sensors, light-emitting diodes, solar cells, photoconductors, flat-panel displays, video and audio systems, computer processors, and other cutting-edge innovations[8], as shown in figure I.2.

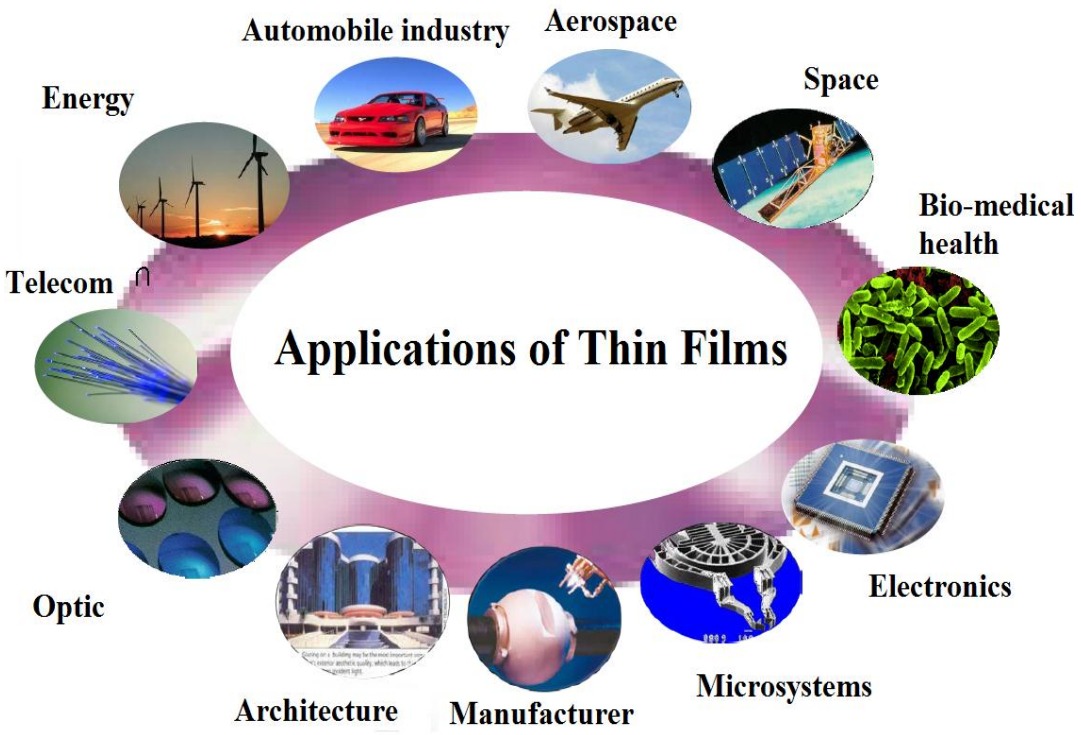

Figure I.2: *Applications of thin films*

I.2 Metal oxides

Metal elements can combine to generate a wide range of oxide compounds [2]. The consisting body of metal and oxygen called in general a metal oxide. the metal oxides can be classified according to the nature of the conduction by electrons or holes, or whether the metal oxides are simple or complex [1]. Among this oxides, we could cite ZnO, CuO, and NiO where have advantages such as low cost, easy to fabricate, also with their compact size and can detect varies types of gasses[5]. Table I.1 present some metal oxides, their position in the periodic table, band gap, and conducting nature.

Table I.1: *Some metal oxides, their position in the periodic table, band gap, and conducting nature[3].*

Name	Position of the metal in the periodic table and nature	Band gap (e/V)	Classification
WO_3	Group 6 (IV): transition metal	2.6-3.1	Semiconductor (n-type)
MnO	Group 7 (IV): transition metal	4.1	Semiconductor (n-type)
Mn_3O_4	Group 7 (IV): transition metal	2.5	Semiconductor (p-type)
MnO_2	Group 7 (IV): transition metal	β0.26 - γ 0.58-0.7	Semiconductor (n-type)
FeO	Group 8 (IV): transition metal	2.4-2.5	Semiconductor (p-type)
Fe_3O_4	Group 8 (IV): transition metal	0.1	Metallic
Fe_2O_3	Group 8 (IV): transition metal	α 2.2- γ 2.0	α =Semiconductor (n-type) γ = Semiconductor (n-type)
RuO_2	Group 8 (V): transition metal	2.2	Semiconductor (Amphoteric)
CoO	Group 9 (IV): transition metal	2.4	Semiconductor (p-type)
Co_3O_4	Group 9 (IV): transition meta	2.0-0.2	Semiconductor (p-type)
NiO	Group 10 (IV): transition metal	3.6-4.2	Semiconductor (p-type)
CuO	Group 11 (IV): transition metal	1.2-2.2	Semiconductor (p-type)
Cu_2O	Group 11 (IV): transition metal	2.1-2.2	Semiconductor (p-type)
ZnO	Group 12 (IV): poor metal	3.3-3.4	Semiconductor (p-type)
CdO	Group 12 (V): poor metal	2.2-2.9	Semiconductor (n-type)
Al_2O_3	Group 13 (III): poor metal	6.0-8.8	Semiconductor (n-type)
Ga_2O_3	Group 13 (IV): poor metal	β 4.7-4.9	Semiconductor (n-type)

The ability to detect glucose in a sensitive, quick, and convenient manner is extremely desirable for a variety of reasons, including basic biology research, bioengineering applications, and diagnosis/monitoring of diabetes and the food industry, due of the very selective bio-redox interaction between enzymes and glucose, enzyme-involved biosensors have been intensively investigated[9]. There is a major drawbacks for real usage such as, low sensitivity, complex sensor preparation procedures, and unpracticality. The industrial interest in their unique features, metal oxide thin films have been recognized for many years[3].

Metal oxide thin films was used for the detection of glucose, because they exhibit a good electrochemical properties based on their relatively, high reactivity and large specific area at the Nano scale[10]. Also they are suitable alternatives for glucose detectors as they are available, affordable, stable, easy-to-use and provide a large surface area[11].

I.3 Copper oxides

Copper (Cu) has gotten a lot of attention because it's one of the most important materials in technological advances and it's generally available[12]. Which has attracted particular interest since they are widely employed as industrial catalysts, chemical sensing devices, antimicrobials, fillers, catalysts, and semiconductors. Also useful in the development of microelectronics[13].

Copper oxide has particular importance due to its characteristics[14]. Besides, it is a semiconductor metal with unique optical, electrical and magnetic properties. Furthermore, there are two major groups of copper oxide, namely cupric oxide (CuO) and cuprous oxide (Cu_2O), which classified as p- type semiconductors; their reported optical band gaps are 1.3 eV - 2.1 eV for CuO and 2.1 eV – 2.6 eV for Cu_2O. Because of their specific unique properties, they could be used in many applications including solar cells, cathode in lithium primary cell, gas sensor, electro chromic devices and electronic device fabrication and sensor and optoelectronic industry[15].

I.3.1 Cupric oxide CuO

Copper (II) oxide (CuO) also known as cupric oxide, it has attracted particular attention because it is the simplest member of the family of copper compounds and exhibits a range of potentially useful physical properties[3].

Cupric oxide has a p-type semiconductor with a band gap ranging of 1.2 – 1.9 eV. CuO has a monoclinic crystal structure with black colour and many interesting characteristics, such as high thermal conductivity, photovoltaic properties, high stability and antimicrobial activity [16]. It can be obtained easily by heating cuprous oxide (Cu_2O) or copper in air at nearly 1273-1373 K, cupric oxide is formed as follows:

$$Cu_2O + ½\ O_2 \rightarrow 2CuO \qquad \text{(Eq.1)}$$

$$2Cu + 2\ O \rightarrow 2CuO \qquad \text{(Eq.2)}$$

I.3.1.1 Properties of CuO

CuO has gotten a lot of interest since it is the most basic member of the copper compound family and has certain beneficial features. This led to a rapid research expansion in theoretical studies, fabrication, characterization and applications of CuO based devices in the latter half of the 20th century[3]. Cupric oxide have a good properties which will be declared bellow.

Physical and chemical proprieties:

Cupric oxide is called (tenorite) in mineral form. Its chemical formula is CuO, it is a black powder insoluble in water and melting point is above 1134 °C [5]**.** Table I.2 regroups some physical and chemical properties of cupric oxide.

Table I.2: *Physical and chemical parameters of CuO[3].*

Physical and chemical properties of CuO	
Chemical names	Copper (II) oxide Cupric oxide Copper monoxide Copper oxide (CuO)
Molecular Formula	CuO
Appearance	Black powder
Solubility in water	Insoluble
Molecular Mass	79.55 g/mol
Density	ρ = 6.32 g/cm3
Relative permittivity	12
Melting point	1134°C
Boiling point	2000 °C

a) Optical properties

Thin films of CuO have a transparency between 0 and 80% in the visible region and a refractive index varies in the range of 1.5 to 3.5. Native point defects are intrinsic in semiconductors, they play an important role in the electronic properties of semiconductors. The optical properties of CuO vary according to various factors such as: grain size, substrate

temperature, thickness, doping concentration, strain strain, structural parameters, defects and disorder, as well as deposit techniques and conditions.

Under the action of a high-energy light beam or electron bombardment, copper oxide emits photons. This phenomenon corresponds to luminescence. Depending on the conditions of elaboration, different luminescence bands were observed in Figure I.3. The UV and visible luminescence are due to the near-band-edge (NBE) emission or inter band emission and to the different defect states[1].

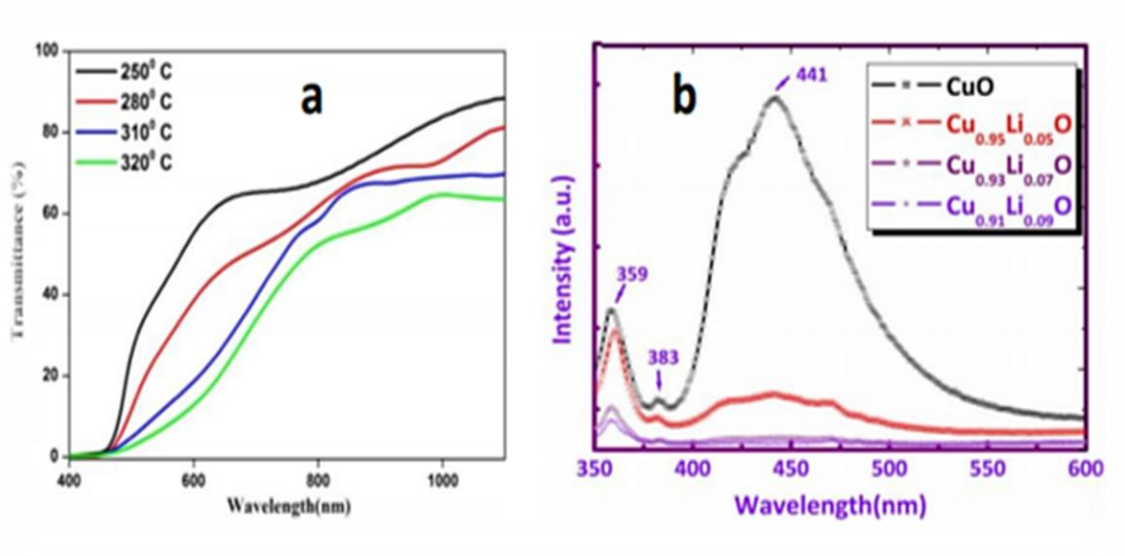

Figure I.3: *Transmittance (a) and photoluminescence (b) of CuO thin films[1]*

The optical properties are a crucial parameter for thin films. The importance of CuO optical proprieties originated from it is useful applications as an absorber layer in solar cells. This application requires the fulfillment of a high absorption in the visible range of solar spectrum[3].

The optical properties are also altered by the preparation conditions. In Figure I.4 we have reported transmission spectra of CuO thin films deposited by spray pyrolysis, sputtering, SILAR and Sol-gel method. The existence of an interference fringe in the transmission spectra of films made by the sputtering process is notable; nevertheless, this fringe is rarely seen in the transmission spectra of CuO films. The existence of this interference fringe is a signature of surface smoothness of the deposited films. From the transmission spectra represented in Figure I.4, We can see that the films made with the spray technique do not have this fringe. In compared to films deposited by the sputtering approach, this shows that the elaborated films have a rough surface [3].

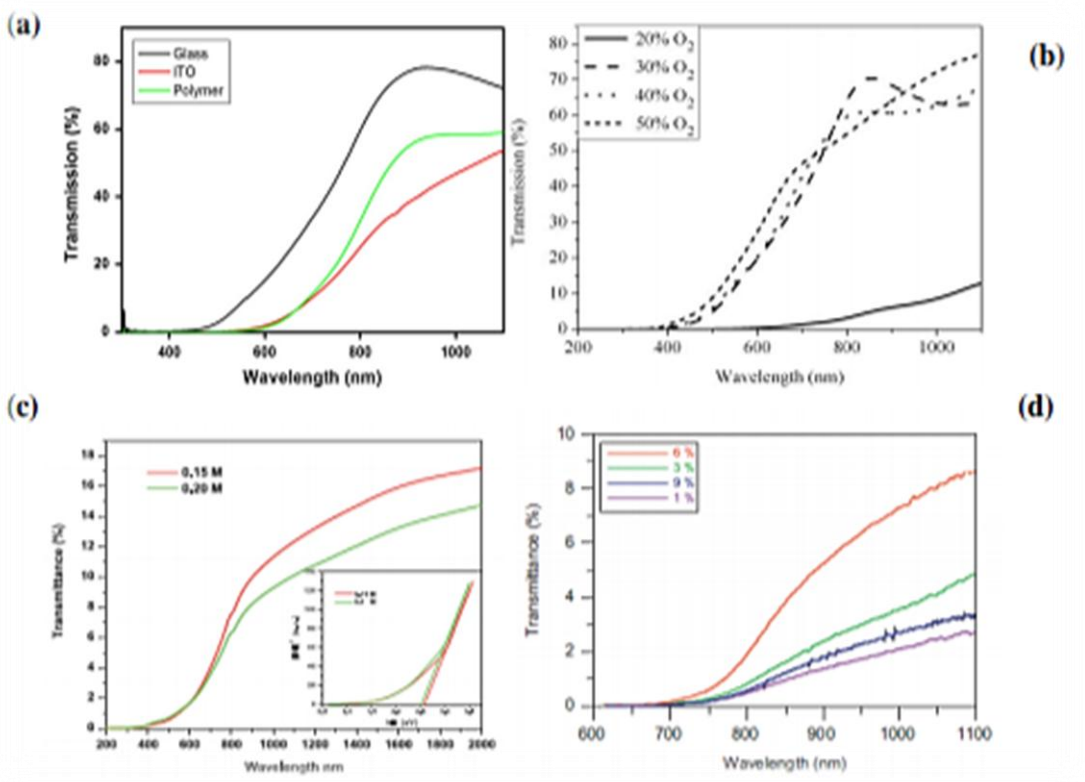

Figure I.4: *Transmittance spectra reported in CuO thin films prepared by different techniques: (a) sol- gel, (b) sputtering, (c) spray pyrolysis, (d) SILAR method [3]*

b) Electrical properties

CuO is a p-type semiconductor with smallest band gap of 1.2 – 1.9 eV. The figure I.5 shows the electronic structure of CuO in the monoclinic structure. CuO generally shows low conductivity. Large variations in the resistivity values have been reported as well as a strong dependence of the resistivity according to the method of elaboration, which have been attributed to either non-stoichiometry or grain boundary conduction[1].

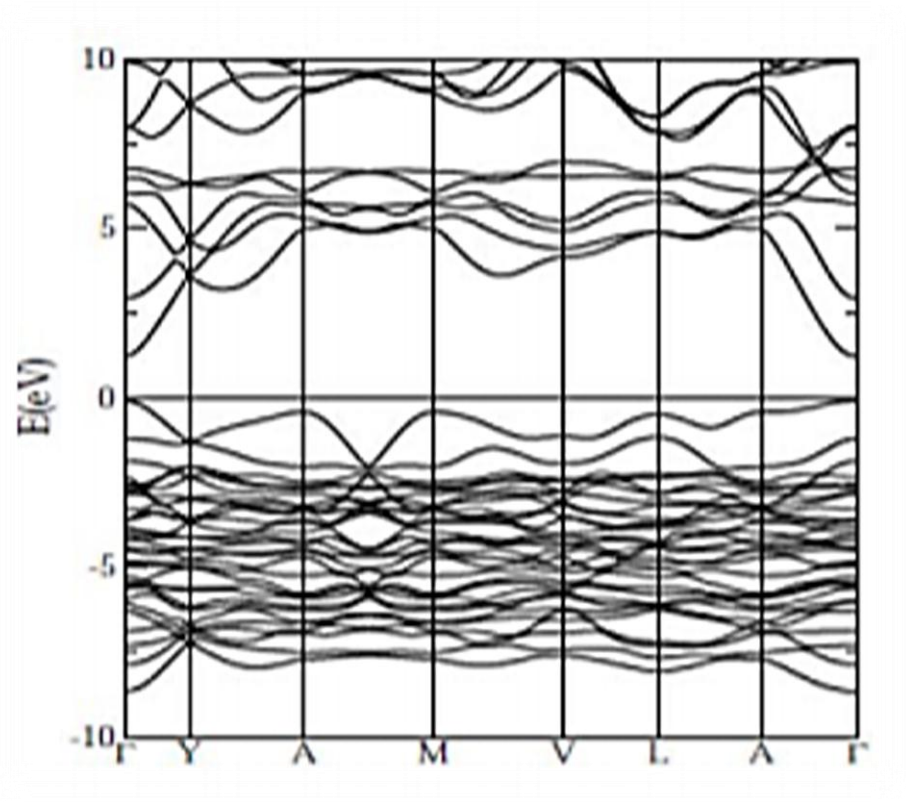

Figure I.5: *Band structure of CuO calculated using the Density Function Theory DFT+U[1]*

c) Structural properties

Deposition conditions and method are strongly affecting the thin film growth. Based on findings of previous studies, the main parameter must be controlled in order to achieve a high quality film is deposition temperature. The effect of deposition temperature, annealing temperature, and substrate temperature on present phase and (hkl) orientation of CuO thin films by several of deposition techniques is shown in Table I. 3[5].

The experimental conditions must be carefully chosen in order to obtain the desired structural properties. For example: some authors agreed that the increase in the substrate temperature improves the films crystallinity and yields to the change from amorphous to polycrystalline structure[3].

Table I.3: *Structural properties of CuO thin film deposited by different method[5]*

Deposition method	Parameter	Present phase	(hkl) orientation
Thermal decomposition	Temperature 400^0C 500^0C	CuO CuO	(002) (111) (002) (111)
Thermal oxidation	Annealing Temperature 150^0C 200^0C 250^0C 275^0C-1000^0C	Cu,Cu_2O Cu_2O Cu_2O, CuO CuO	(111) (200) (111) (200) (111) (111)
Spray pyrolysis	Substrate temperature 250^0C 350^0C 450^0C	Cu_2O,CuO Cu_2O,CuO,Cu_2O,CuO Cu_2O,CuO	(111) (200) (111)(200) (200) (020) (111) (200)
Spin coating	Annealing temperature 300^0-400^0C 500^0C-700^0C	CuO CuO	(002) (111) (112) (110)(002) (111)(200) (112)(221)(004)(023)

A unit cell of CuO consists of Cu^{2+} ions which are coordinated by four O^{2-} ions. Monoclinic crystal structure of cupric oxide (CuO) is shown in figure I.5[5].

d) Crystallography proprieties of CuO

CuO is distinguished from the transition metal monoxides 3d by its monoclinic structure. It is a black ionic solid having as fusion temperature 1134°C. In this structure, copper is at the center of square planes defined by oxygen anions [5]. The monoclinic structure is shown in Figure I.6.

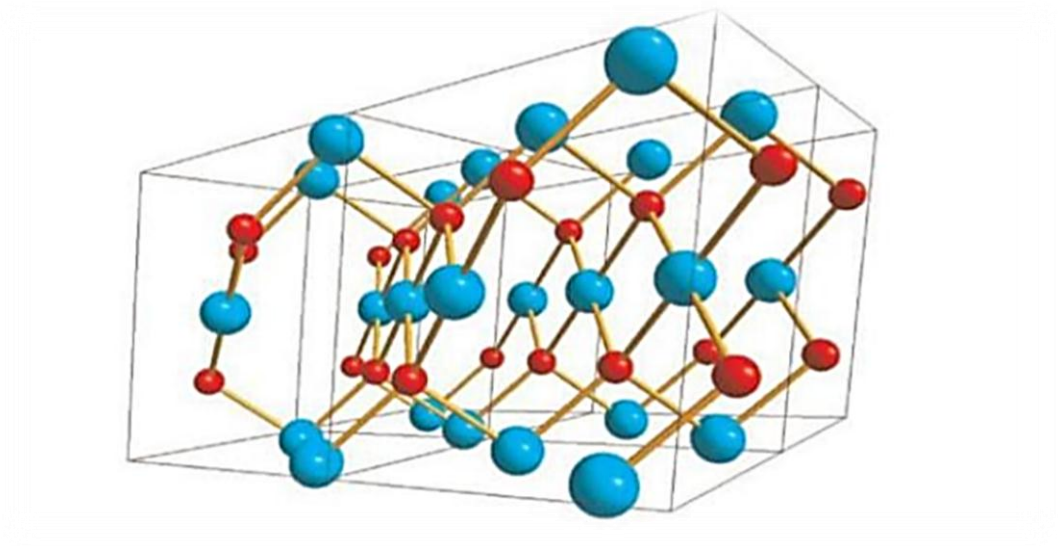

Figure I.6: *Monoclinic Structure of CuO [3]*

Cupric oxide has tenorite crystal structure. Tenorite crystallizes in the C2/c space group with lattices parameters defined in Table I.4 [1].

Table I.4: *Crystallographic parameters of cupric oxide according to Wells (1984) and Åsbrink and Norrby (1970)[9][11]*

Crystallography properties of CuO	
CuO structure	monoclinic
Space group	C2/c
Lattice parameters	a = 4.6837 Å b = 3.4226 Å c = 5.1288 Å β = 99.548° α ,γ = 90°
Cell volume	81.08 Å3
Cell content	4 [CuO]
Shortest distances **dCu-O** **dO-O** **dCu-Cu**	1.96Å 2.62Å 2.90Å

e) Films morphology

Films surface morphology is an interesting characteristics that is required for film application as gas sensor or any applications requiring high specific exchange surface or light scattering. CuO thin films morphology is generally examined by SEM (Scanning Electronic Microscopy) and AFM (Atomic Force Microscopy) observation. It is reported that CuO morphology is close related to the deposition technique and conditions[3].

The morphology of CuO is depending on deposition method and conditions. Figure I.7 shows the SEM image of CuO deposited by various method and conditions[5]. This diversity in morphology is due to the difference in deposition process involved in each technique [9].

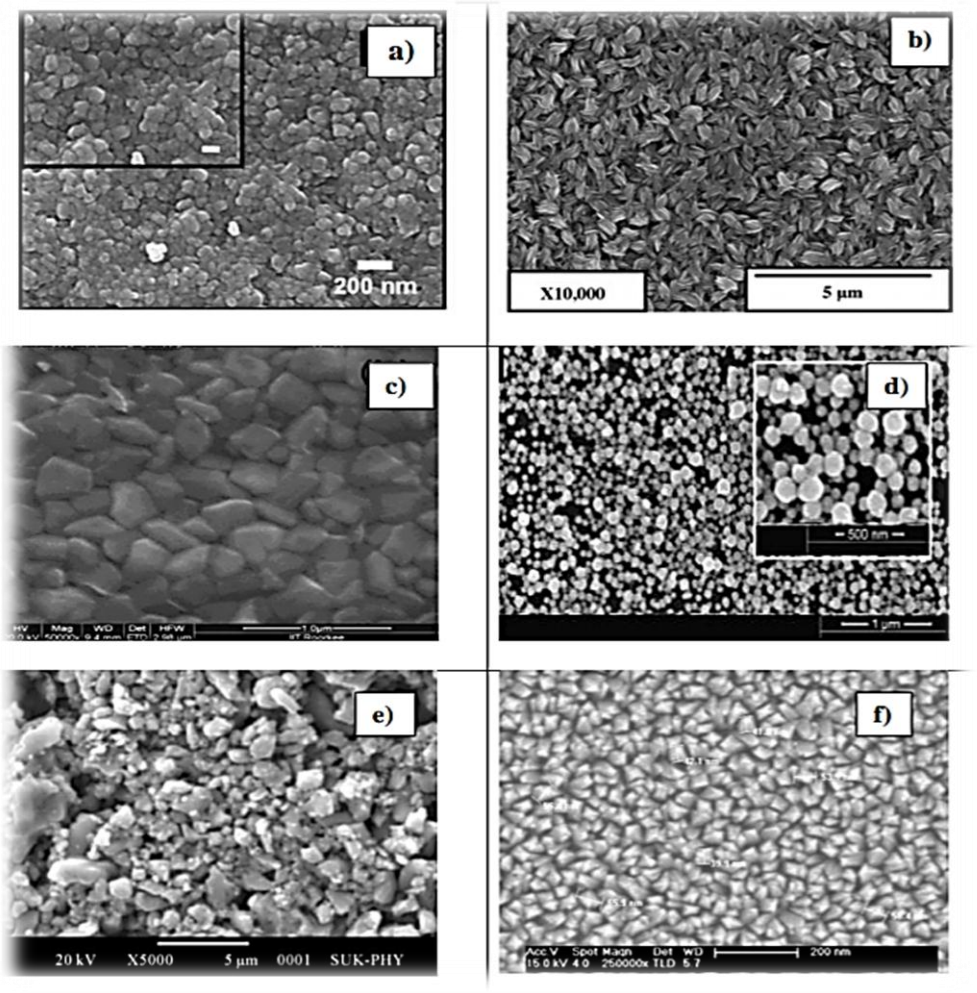

Figure I.7: *SEM image of CuO deposited by a) spray pyrolysis technique, b) chemical bath deposition (CBD), c) ultrasonic spray pyrolysis, d) CVD, e) spin coating, f) DC magnetron sputtring [5]*

For CuO thin films prepared by the CVD, the substrate temperature and flow rates are the most important parameter that will affect the morphology of thin film. The film morphology

highly dependent on substrate temperature. Increasing substrate temperature, the particles become larger and form a continuous film. Furthermore, when AFM was used to further investigate the film morphology, the deposition rate and thickness is increased as the increasing substrate temperature[5].

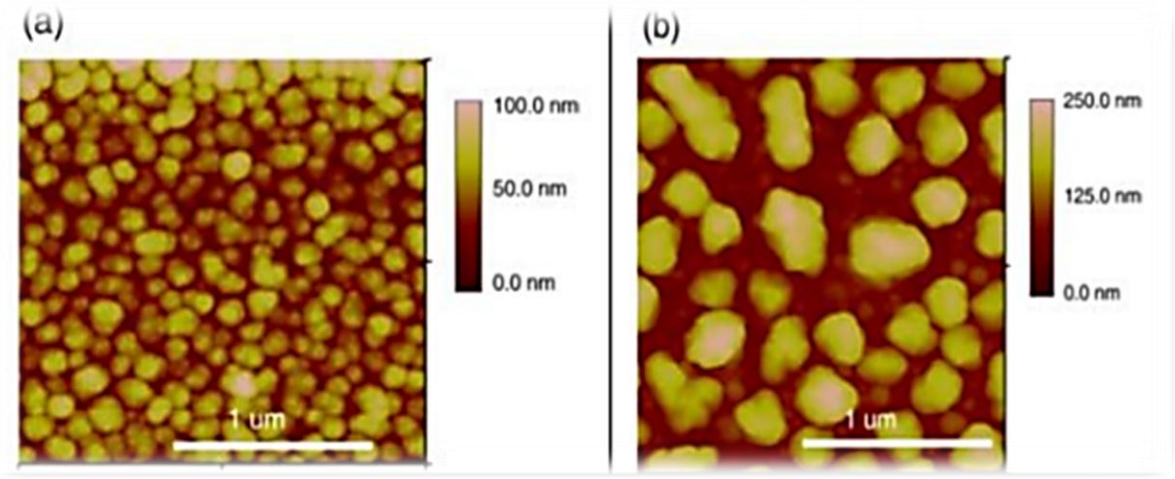

Figure I.8: *AFM of thin copper oxide films deposited by FACVD (a) deposition at 200 °C, (b) deposition at 400 °C [5].*

I.3.1.2 Applications of cupric oxide:

CuO has gotten a lot of interest since it's the simplest copper compound and has a lot of potentially useful physical features including superconductivity at high temperatures, electron correlation effects, and spin dynamics. CuO, being a major p type semiconductor, offers a wide range of uses, including gas sensors, solar energy conversion and field emission emitters catalysis batteries high temperature superconductors [12].

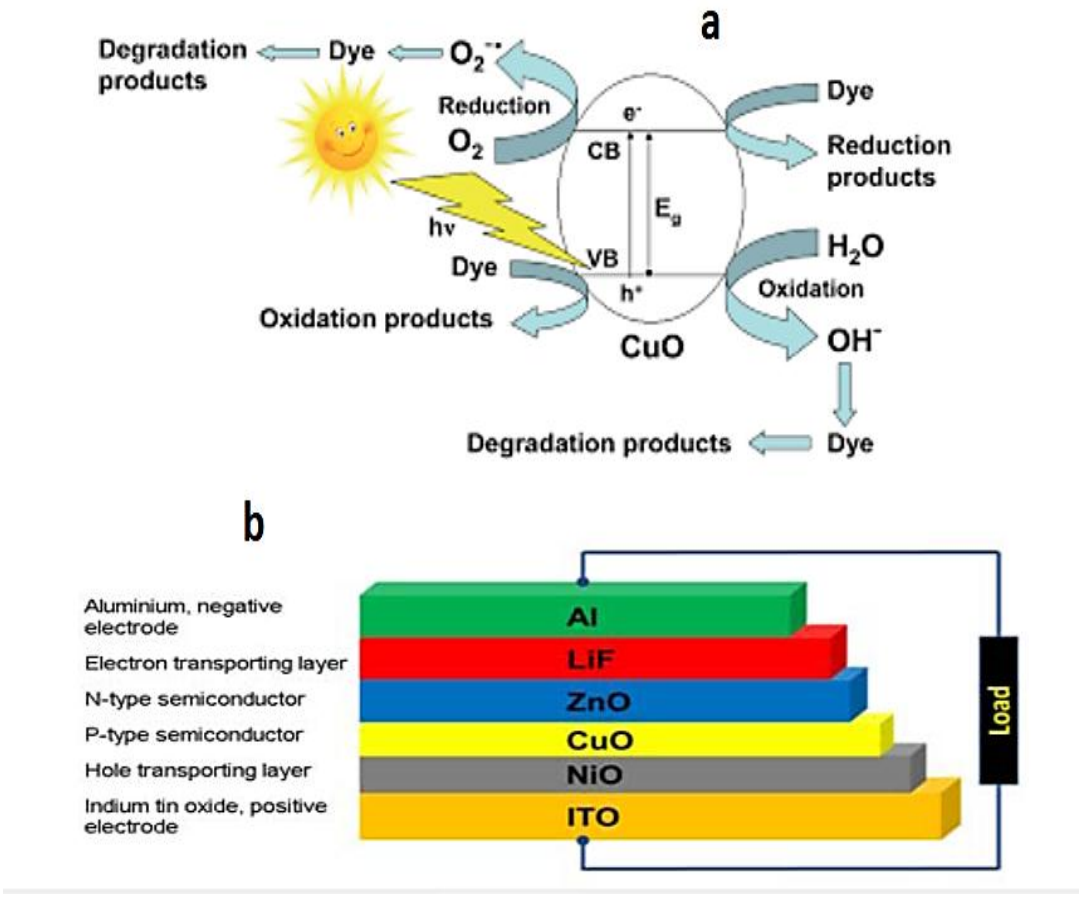

Figure I.9: *Applications of CuO, photocatalysis, solar cell[1].*

I.3.2 Cuprous oxide Cu_2O

Cuprous oxide is known by the term "cuprite." Cu_2O is derived from the Latin word cuprum, which means copper. It was once referred to as "ruby copper" by miners. Cuprite is a key copper resource that is still mined in numerous locations across the world. Because there is only one oxygen atom for every two copper atoms, all copper ores except native copper cuprite offer the highest yield of copper per molecule. As a natural specimen, cuprite offers outstanding examples of fully formed cubic crystal formations. The cube octahedron dodecahedron, as well as combinations of these shapes, are crystal habits. Cuprite's color ranges from red to a deep red that may look almost black in dark crystals. Other types, such as chalcotrichite, create long needle-like crystals with a bright red and a unique brilliance, making them attractive display cabinet specimens[17]. Also it is the most fascinating phase of copper oxides because of its high optical absorption coefficient in the visible region and relatively excellent electrical characteristics[7].

I.3.2.1 Properties of Cu_2O

Copper (I) Oxide an inorganic compound which have a good properties and constitute important advantages and render Cu_2O as the most interesting phase of copper oxides[7]. Cuprous have a numerous properties such non-toxic, high optical absorption and good electrical properties.

a) Physical and chemical proprieties

Copper (I) Oxide has the chemical formula Cu_2O, also classified as an inorganic substance with a cubic structure and a p-type semiconductor. It has a band gap of 2.0 eV and is brownish-red in color[7]. Some physicochemical properties of cuprous oxide are regrouped in Table I.5.

Table I.5: *Physical and chemical properties of Cu_2O [1]*

Physical and chemical properties of Cu_2O	
Chemical names	Copper (I) oxide Cuprous oxide Cuprite Cuprum
Molecular formula	Cu_2O
Appearance	Brownish-red powder
Density	6.10g/cm3
Molar mass	143.092g/mol
Fusion point	1235˚C

b) Optical properties

The optical properties of the cuprous oxide nano-films with different thicknesses (50, 65, and 75nm) were studied by recording the absorbance spectra at the range of wavelength between 190- 1100nm. It is possible also to determine the optical properties such as transmittance, absorption coefficient (α), refractive index (n), optical energy gap (Eg), dielectric constant (real (εr) and imaginary(εi)).

Light absorption characteristics of the Cu_2O nanofilms were obtained by ultraviolet-visible (UV–Vis) spectroscopy. Figure I.10 shows the absorption spectra of the fabricated films

for different thicknesses (50nm, 65nm and 75nm). The absorption spectra of the fabricated Cu_2O nanofilms on glass substrate show a maximum absorption in the range (190-300 nm). The absorbance increased with the increasing of film thickness. The increasing of the absorbance with the thickness leads to the increasing the atoms that make more collisions between the atoms and the incident photons[18].

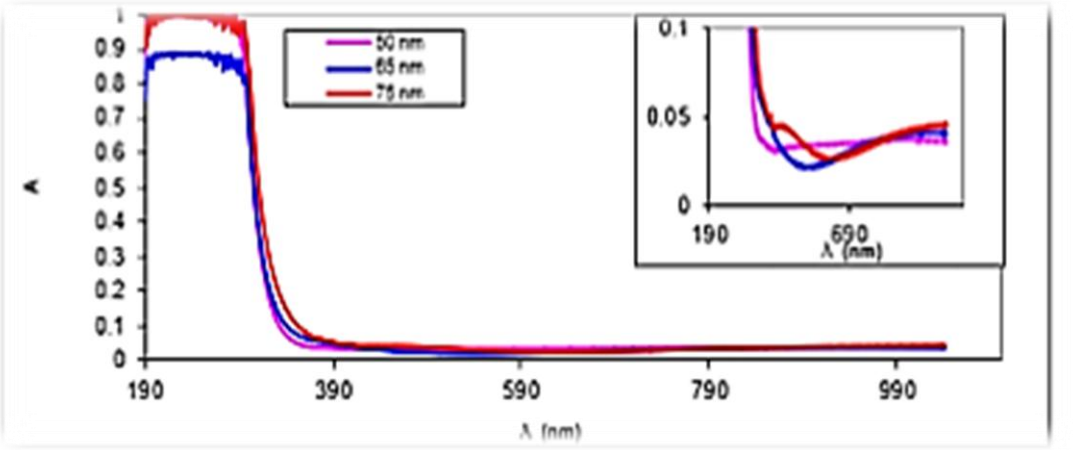

Figure I.10: *The absorbance variation as a function of wavelength for the Cu_2O thin films prepared by solar cell application[18].*

c) Electrical properties

This oxide as solid or thin films is a p-type semiconductor with a direct band gap 2 eV. This mode of conduction has been attributed to the presence, at room temperature, of copper vacancies[1].

In addition to the original interest to Cu_2O as a low-cost material for solar cells, a new potential application area of cuprite (as a photocatalist for hydrogen production from water). Also cuprite shows a long-term stability and a surprisingly high quantum efficiency for the photocathodic reduction of oxygen. As a p type photoelectrode in an electrochemical photovoltaic cell, Cu_2O might be a promising material, not for direct photoelectrochemical water splitting but in combination with an appropriate redox system [11].

d) Structural properties

A very important issue to be addressed first is how well these self-consistent electronic structure calculations, based on density functional theory (DFT), can reproduce the experimentally observed electronic structure of this compound[17].

Because of its remarkable exciton spectra, the electron energy bands of Cu_2O have been successfully exploited. Cuprite has a lengthy sequence of exciton transitions that starts with a forbidden line. From a theoretical standpoint, there are a few other elements of cuprite's electrical structure that are interesting. For instance, non-cubic symmetry of the local coordination of Cu cations in this compound causes a non-vanishing electric field gradient on the Cu nuclei, quite uncommon a situation for cubic structures. Cuprite's crystal structure combines excellent overall symmetry with poor local coordination[17].

e) Crystallography properties

The cuprous oxide has a crystalline cubic structure with a lattice parameter of 4.2696 Å. The crystal structure corresponds to the space group $Pn\bar{3}m$, which incorporate a full octahedral symmetry. The crystalline cubic structure is shown in Figure I.11 [19].

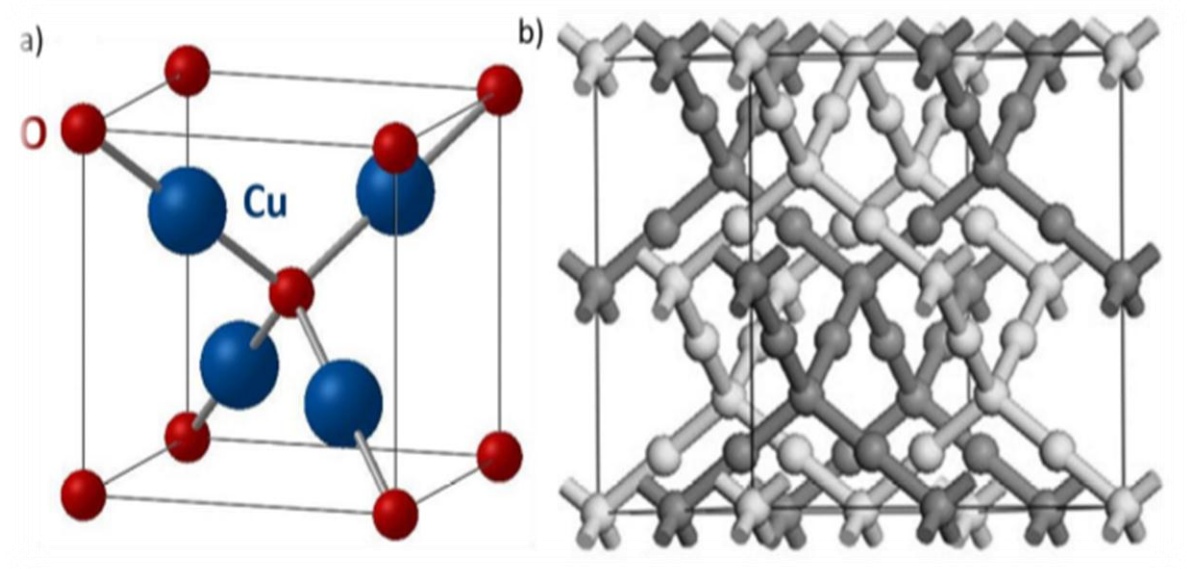

Figure I.11: *Crystallographic structure of Cu_2O with oxygen atoms as the origin of the bcc cell. Oxygen represented in red and Copper in blue. (b) Cu_2O atomic structure. The two interpenetrating Cu–O–Cu networks[19].*

The oxygen atoms are tetrahedrally coordinated by the copper, while the copper ones are linearly coordinated by the oxygen ones. The distance between Cu-O is 1.85 Å, O-O is 3.68 Å and Cu-Cu is 3.02 Å. This structure creates an oxide with a density of 6.10 $g.cm^{-3}$, and a molar mass of 143.09 $g.mol^{-1}$[19].

The Cu_2O structure has another relevant characteristic, its dichotomy. There are two identical and interpenetrating networks of Cu and O atoms inside the crystal, which do not have direct chemical bond between them. Both network have an anti-SiO_2 structure that are stable due to Van-der-Waals forces 3. This is visible in the Figure I.11 b. by the two different tones of grey in each network[19].

Table I.6: *Crystallographic parameters of cuprous oxide according to Wells (1984) and Åsbrink and Norrby (1970)[11].*

Crystallography properties of Cu_2O	
Cu2O structure	Cubic
Space group	$Pn\bar{3}m$
Lattice parameters	a = 4.27 Å
Shortest distances	
dCu-O	1.84Å
dO-O	3.68 Å
dCu-Cu	3.02Å

f) Films morphology

The AFM images of pure cuprous oxide (Cu_2O) thin films prepared by solar cell application show a uniform granular surface morphology. The root mean square (RMS) increased from0.38 nm of Cu_2O thin films to 1.83 nm with the increasing of film thickness from 50nm to 75nm, which is in accordance with the findings of researches of Dehimi et al. The average grain diameter was investigated from the plane view images, which indicates a decreasing from 289.3nm to 251.7nm as the thickness increased from 50 to 75nm of the fabricated Cu_2O films[18].

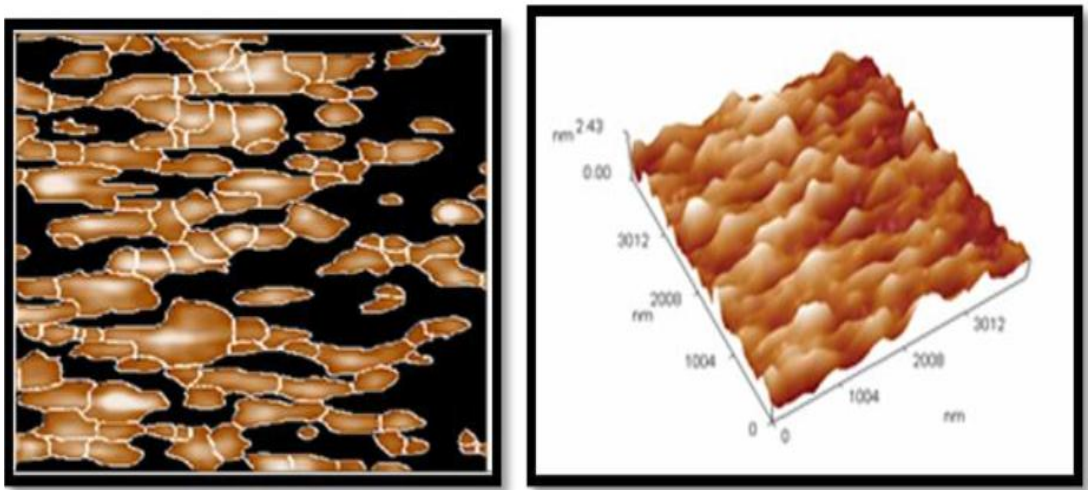

Figure I.12: *The AFM images of cuprous oxide films with the thickness 50 nm, a-3D, b-distribution granular[18].*

I.3.2.2 Applications of cuprous oxide:

Cuprous oxide (Cu_2O) is a classical material that has been recently actively studied as an earth abundant, low cost, and non-toxic, p-type semiconductor for various applications such as gas sensors, resistive switching memory devices, thin film transistors and in photoelectrochemical devices[20].

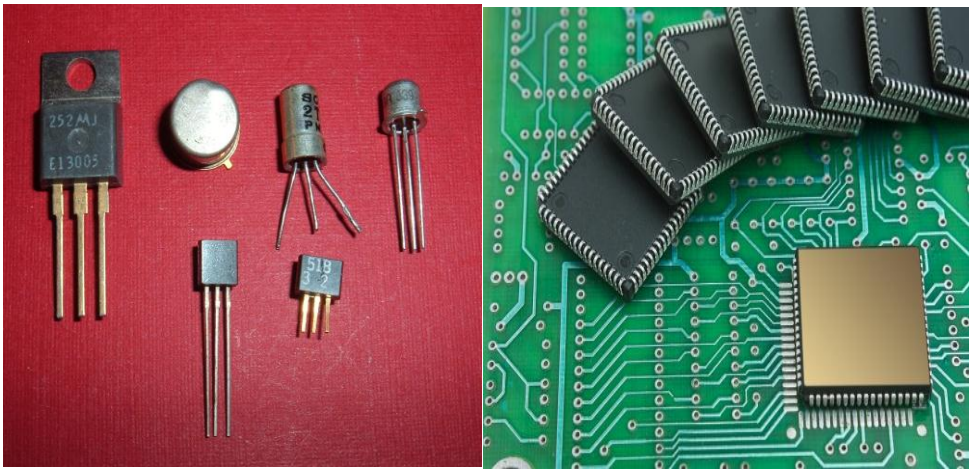

Figure I.13: *Applications of Cu_2O, transistors, switching memory.*

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Chapter II:

Glucose sensors and their Applications

Chapter. II. Glucose sensors and their Applications

In this chapter, we will provide several notions concerning glucose sensors as well as a historical overview of their development. Furthermore, an application of both copper oxides will be discussed, followed by a comparison of previous studies on both copper oxide glucose detection.

II.1 Glucose sensors

The detection of glucose is crucial and has been extensively researched; yet, because glucose lacks chromophoric and fluorophoric ligands, it is difficult to detect using traditional photometric techniques. Electrochemical detection is becoming more common due to the ease of instrumentation and operation. Many laboratories have engaged in efforts to develop new electrode materials that exhibit unique electrocatalytic activity for the determination of glucose [1].

Glucose also known as grape sugar, blood sugar, or corn sugar, serves as a source of energy for a living cell and a metabolic intermediate. It is one of the main products of photosynthesis and is responsible for cellular respiration in both prokaryotes and eukaryotes. Only D−glucose (dextrose) is biologically active while L−glucose cannot be metabolized by cells in the biochemical process [2]. Glucose is a carbohydrate that is required for the production of proteins, glycogens, and lipids in important catabolic processes such as oxidative phosphorylation and glycolysis. Glucose is absorbed through the intestines, and, converted by the liver into a more stable form of glycogen, regulated by the hormone insulin [3].

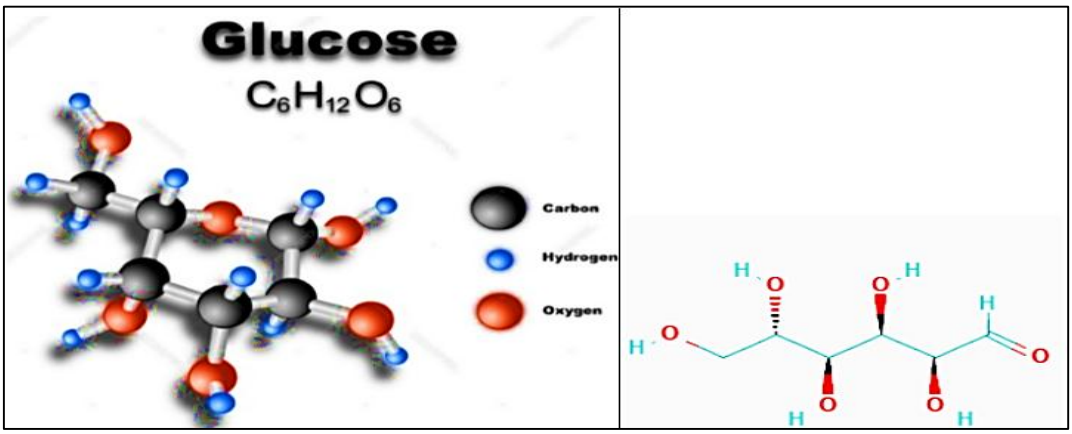

Figure II.1: *Structures of glucose*.

Low blood glucose concentrations can induce seizures, loss of consciousness, and death in most tissues and organs, including the brain. Long-term elevations in blood glucose

concentrations, on the other hand, can cause blindness, renal failure, vascular disease, and neuropathy, hence blood glucose levels must be kept below strict limits. The process of maintaining blood glucose at a steady-state level is called glucose homeostasis. This is accomplished by the finely hormone regulation of peripheral glucose uptake, heaptic glucose production and glucose uptake during carbohydrate ingestion. This is accomplished by optimizing a number of parameters, including the amount of carbohydrate ingestion and intestinal absorption the rate at which glucose is used by peripheral tissues and which glucose is lost by the kidney. To avoid postprandial hyperglycemia (uncontrolled rises in blood glucose levels after meals) and fasting hypoglycemia (low blood glucose levels during fasting periods), the body can modulate levels through a number of cellular processes. Hormones, cytokines, and fuel substrates all communicate important mechanisms that are perceived by cellular systems [4].

A sensor could be defined as a device that receives a signal or stimulus and responds to the stimulus in the form of an electrical signal. The output signals correspond to some forms of electrical signal, such as current or voltage. The sensor is a device that receives different kinds of signal i.e. physical, chemical or biological signal and converts them into an electric signal. Sensors are grouped into many categories depending on the input signal and conversion mechanism material used in sensor properties such as cost accuracy and range [5].

We can find sensors everywhere, and the whole world is full of sensors and their applications. There are many types of sensors available around us, in our offices, gardens, shopping malls, homes, cars, toys etc. Starting with applications like turning on the lights, fans, and television, through automated temperature adjustment by air conditioning, fire alarms, and detecting obstacles when driving, these sensors make our lives so much easier and more comfortable. A sensor is a device which receives signals as well as responding to a signal or stimulus. The stimulus signals can be defied by the measure, property, or state which is sensed. A sensor may alternatively be described as a translator that translates nonelectrical values to electrical values. A sensor's output signal might be in the form of voltage, current, or charge. A sensor has many forms of input properties and electrical output properties [5].

Table II.1: *Sensors based on their detection properties [5].*

Types	Properties
Thermal sensor	Temperature, heat, flow of heat… etc
Electrical sensor	Resistance, current, voltage, inductance,
Magnetic sensor	Magnetic flux density, magnetic moment, etc
Optical sensor	Intensity of light, wavelength,. Etc
Chemical sensor	Composition, pH, concentration, …etc
Pressure sensor	Pressure, force… etc
Vibration sensor	Displacement, acceleration, velocity, etc
Rain/moisture sensor	Water, moisture, etc
Tilt sensors	Angle of inclination, etc
Speed sensor	Velocity, distance etc

Sensors are divided into two categories. Sensors that are both passive and active. A passive sensor does not require any additional energy and produces an electric signal in response to specific conditions. The sensor transfers input energy to output signal energy in this way. Photographic, thermal, electric field, chemical, infrared, and seismic sensors are examples of passive sensors. In order to generate output signals, active sensors require external sources of energy known as excitation signals. Due to their own qualities that may be adjusted in reaction to an external stimulus and then converted into electric signals, active sensors are also known as parametric sensors. Active sensors are used in meteorology and the monitoring of the earth's surface and atmosphere, among other things [5].

Clark & Lyons were the first to present the notion of a glucose sensor in 1962. Depending on the number of applications under consideration, glucose sensors may be divided into three categories:

a) The enzyme-based needle type electrochemical glucose sensors are the first and by far the biggest group. The detection concept of these sensors is based on the monitoring of

glucose oxidation catalyzed by enymes. Glucose sensors with amperometric or potentiometric working principles, such as hydrogen peroxide electrodes, oxygen electrodes, mediators, and potentiometric electrodes, fall within this group.

b) Glucose sensors based on direct electro oxidation of glucose on noble metal electrodes are classified as electrocatalytic glucose sensors.
c) Glucose sensors based on a variety of detection or glucose extraction techniques make up the third group. Affinity-based glucose sensors, coated wire glucose electrodes, reverse iontophoresis-based glucose sensors, and microdialysis-based glucose sensors are all included in this category [6].

II.1.1 History of glucose sensors

Efforts to measure glucose in urine stretch back to the mid-1800s, laying the groundwork for contemporary diabetic therapy. The most significant advancement in the commercialization of urine glucose testing occurred in 1908, when Benedict invented a copper reagent for urine glucose, which was used for more than 50 years with several variations. The cumbersome heating approach was made more convenient in 1945 with the release of Clinitest (Ames, Elkhart, IN), which included a redesigned copper reagent tablet. The level of glycosuria was related to the color of the heated solution after glucose was oxidized. Ames created the first blood glucose test strip, the Dextrostix, in 1965, utilizing glucose oxidase. A huge drop of blood was deposited on the strip and wiped away after 60 seconds. For a semi-quantitative measurement of blood glucose, the resulting color was compared to a chart on the bottle. This early strip was intended for use in doctors' offices rather than at home. The first glucose meter, the Dextrostix, was used in the 1970s, but its precision and accuracy were poor. By the mid-1970s, the idea of patients utilizing blood glucose data at home was being considered, and by 1980, the Dextrometer was introduced; this meter combined the Dextrostix with a digital display[7].

Anton Clemens submitted the first patent in the United States in 1971 for a blood glucose monitor for use at the point of treatment in diabetic patients. The Ames reflectance meter was a gadget that measured the color change of enzyme-based reagent strips automatically. Previously, blood glucose was calculated by eye reading the color shift on a chart. The Ames Reflectance Meter was replaced by the Ames Eyetone, which became widely used but was limited to clinical settings such as doctors' offices and hospital wards[8].

Meters and strips that required less blood became more affordable during the 1980s. Self-monitoring of blood glucose (SMBG) has become the standard of care, particularly for type 1 diabetic patients. This advancement, together with A1C testing and insulin pump therapy, enabled the Diabetes Control and Complications Trial, which offers a clear response to the longtime dispute concerning the association between glucose control and diabetes complications.

Following the initial studies, there was an increase in interest in home blood-glucose monitoring, and in 1986 the American Diabetes Association, the Food and Drug Administration, and the National Institutes of Health issued a joint statement recommending self-monitoring of blood glucose for the following uses:

- Pregnancy complicated by diabetes mellitus.
- Individuals with a propensity for severe ketosis or hypoglycaemia.
- Individuals prone to hypoglycaemia who may not experience the usual warning symptoms.
- Individuals on intensive treatment programs, especially those using portable insulin infusion devices and multiple daily injections.
- Individuals with abnormal renal glucose thresholds [8].

SMBG technology advanced during the late 1980s, 1990s, and early 2000s. Blood removal was reduced, fewer volumes of blood were required, electrochemical strips were produced, larger hematocrit ranges were allowed, and new enzymatic assays were employed. Lancets have also gotten better. By 2010, SMBG was virtually painless and recommended for all patients receiving insulin and most who were not [7].

Medtronic (Northridge, CA) debuted the Guardian REAL-Time CGM system in 2004, which may alert patients to potentially severe hyperglycemia or hypoglycemia, and the same firm delivered the first combined pump and sensor in 2006. Dexcom (San Diego, CA) released its first real-time CGM, the STS, the same year (Short-Term Sensor). Abbott (Alameda, CA) developed the FreeStyle Navigator in the United States in 2008. For insulin decisions to be made, all of the original CGM systems required blood glucose confirmation. [7].

II.1.2 Types of glucose sensors

Electrochemical sensors are generally divided into two categories both enzymatic and non-enzymatic glucose sensors.

II.1.2.1 Enzymatic glucose sensors

The most common method for determining blood glucose levels is to utilize enzyme-based sensing. Because of their great specificity and sensitivity, enzymes like glucose oxidase GOx and glucose dehydrogenase detect glucose and deliver the real glucose concentration. Unfortunately, due to inherent nature of enzymes, biosensors are unstable, and their function is affected by a variety of environmental conditions such as humidity, pH, oxygen concentration, hazardous compounds, and temperature. Furthermore, immobilization of the enzyme on the solid electrode necessitates a sophisticated technique involving adsorption cross linking entrapment, and electropolymerization, which may reduce the activity of the glucose oxidase (GOx). Because the sensitivity of these glucose sensors is largely determined by the activity of the immobilized enzymes, repeatability remains a key quality control concern[2].

a) Working principle of enzymatic glucose sensors

The enzymatic electrode, which typically consists of the substrate electrode, matrix material, glucose oxidase and Nafion ion exchange membrane, is the most important component of these types of glucose sensors. Most current research on glucose sensors has focused on improving their reaction to glucose, i.e., more electrons should be created on the enzymatic electrode and subsequently captured effectively by the substrate electrode. On the one hand, the yield of electrons is limited by the quantity of GOx adsorption on the matrix material, which is controlled by the matrix material's surface area. On the other hand, the transfer rate of these electrons relies on the conductivity of the matrix material. As a result, it's important to look for the best matrix material for immobilizing glucose oxidase (GOx) in order to improve the performance of enzymatic glucose sensors[9].

Glucose oxidase produces an oxidative current, which is monitored by electrochemical glucose biosensors. Free glucose is catalyzed by gox gox produces gluconic acid and hydrogen peroxide (H_2O_2). H_2O_2 produced by GOx deprotonates to produce free protons, dissolved oxygen and 2 electrons under anexternal oxidative potential. The electrical signal that is detected is proportional to the glucose concentration[10].

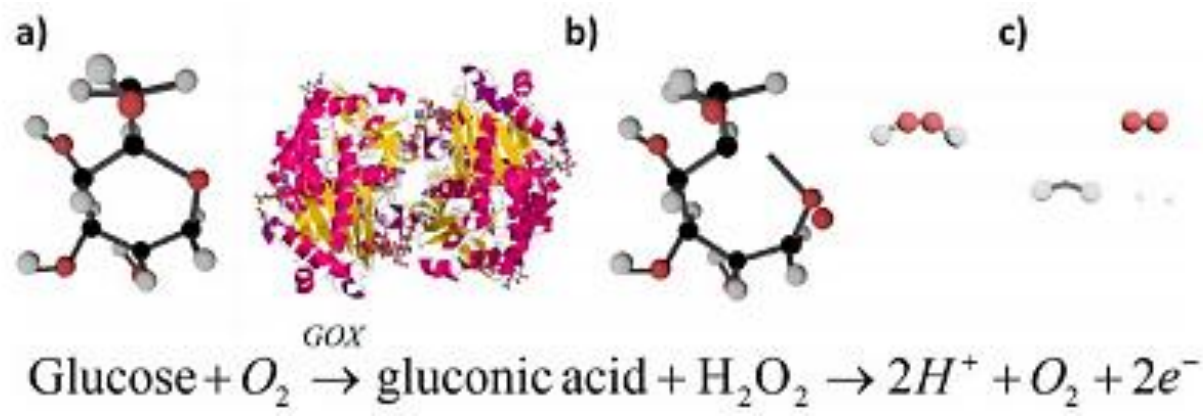

Figure II.2: *Basic working principle for glucose biosensors, a) Glucose binds in the enzymatic binding pocket of glucose oxidase, b) An applied potential catalyzes the oxidation of glucose to gluconic acid and hydrogen peroxide, c) Hydrogen peroxide dissociates to O_2, 2 H^+, and 2 free electrons; electrons are measured using electrochemical or optical techniques [10].*

Convection and/or diffusion move glucose towards the enzymatic layer when the electrode is submerged in the test environment. And after that, glucose diffuses within the enzyme layer, accompanied by the enzymatic transformation of glucose into the reaction products hydrogen peroxide and gluconic acid, which migrate in all directions, including backwards to the sample environment. Meanwhile oxygen, used in the enzymatic reaction, migrates towards the reaction side. At the transducer interface, hydrogen peroxide or oxygen is transformed into an electrical signal, depending on the transducer technology utilized[6].

II.1.2.2 Non-enzymatic glucose sensors

This type of sensor has a high sensitivity since it uses direct electrocatalytic oxidation of glucose at an electrode surface, long-term stability, resistance to temperature effects, low reaction times, and repeatable manufacture. To produce non-enzymatic glucose sensors, a variety of materials have been employed, such as noble metals (Au, Pt, etc.) , transition-metals, metal alloys, conducting polymer, graphene and metal oxides[11].

b) Working principle of non-enzymatic glucose sensors

Most enzyme-free glucose sensor electrocatalysts have a catalytic effect that is connected to the metal center of the material. There are now two widely recognized theories that can explain the catalytic process of glucose on the electrode surface. The adsorption of active chemicals by electrode materials is used in several electrocatalytic processes. Pletcher originally developed a chemical adsorption model for glucose oxidation, in which metal atoms' d-orbitals attach to glucose molecules. The catalytic process is shown in the following figure:

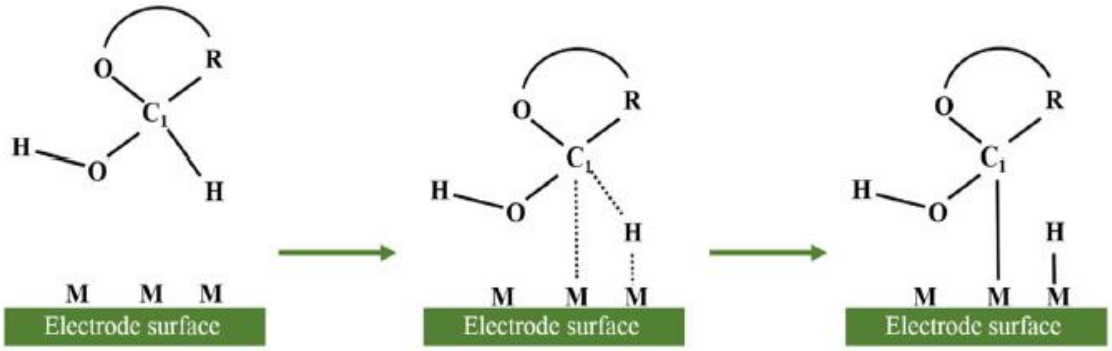

Figure II.3: *An illustration of the chemisorption model in glucose oxidation. M: metal atom; C1: hemiacetalic carbon atom; R: other parts of the glucose molecule[12].*

Under the effect of the electrode, the link between the c1 atom of glucose and the hemiacetalic hydrogen atom breaks. This dehydrogenation happens at the same time as the chemical adsorption of glucose, which is a crucial step in controlling the reaction rate. The adsorbate will be oxidized to glucono lactone and then transformed to gluconic acid on the electrode surface. Given that the adsorbent will occupy the catalytic center of the electrode material, modifying the nanostructure and morphology of the catalyst to enhance the active site of the material can enhance the rate of glucose oxidation (Figure II.4).

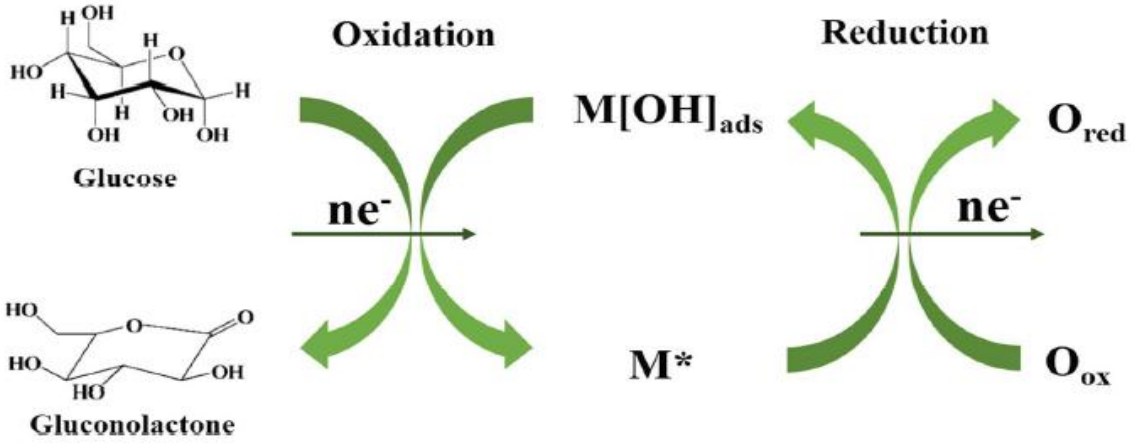

Figure II.4: *The schematic diagram of incipient hydrous oxide adatom mediator (IHOAM) model. M* is the reductive metal adsorption site. M[OH] ads stands for oxidative adsorbed hydroxide radical, which plays an important role in promoting glucose oxidation[12].*

The metal oxides on the electrode will be oxidized by the anod's bias. The formed oxides with higher oxidation numbers have a strong oxidizing ability to produce surface bound OH_{ads} radicals, which play a vital role in the process of glucose catalysis. To enhance the creation of OH_{ads}, the electro oxidation of glucose is often carried out in alkaline solution, which can also assure the durability of metal oxide based electrodes[12].

II.2 Applications of copper oxides thin films on non-enzymatic glucose sensors

The introduction of nanotechnology has provided more possibilities for the preparation of highly efficient catalytic materials. Among the synthesized electrocatalysts, metal oxides have been used as a substrate or catalyst for glucose oxidation reaction in non-enzymatic glucose sensor development [12]. In particular, copper thin films with different shapes have been widely studied due to their unusual properties and potential applications.

II.2.1 Applications of Cupric oxide CuO

In 2009, S. Cherevko et al. was formed porous CuO electrodes (figure II.5.B, D) from the electrodeposition of Cu on Pt/Ti/Si substrate and subsequent annealing in air (figure II.5.A, C). The sensing performances of the porous CuO electrodes were evaluated as a glucose sensor in 0.1M NaOH solution. The porous CuO film showing a high sensitivity of 2.9 mA cm^{-2} mM^{-1}, and a low detection limit of 0.14 M. Due to the high efficiency of the electrode morphology, the highest sensitivity among non-enzymatic sensors based on Cu or CuO was achieved as presented in figure II.5.E[13].

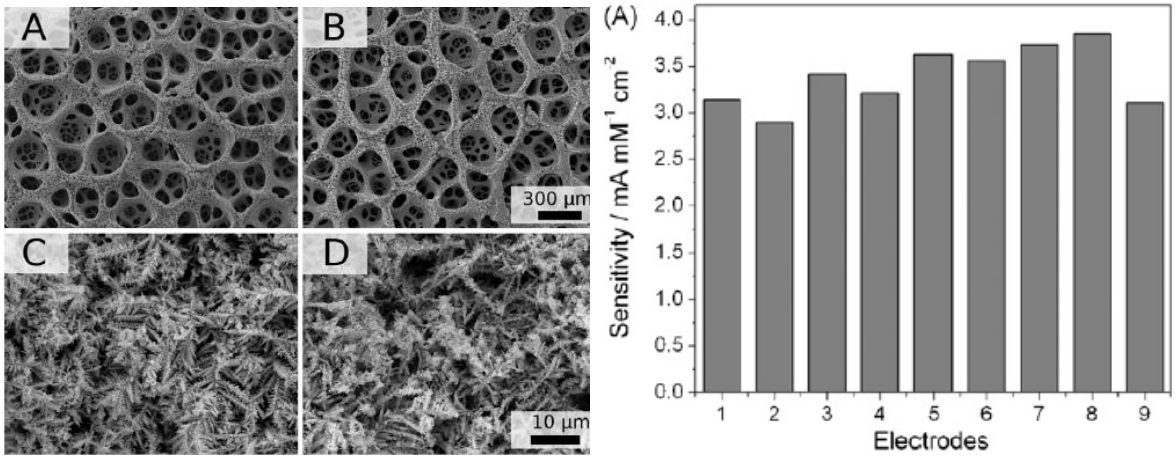

Figure II.5: *A, C) FE-SEM images of as-deposited porous Cu film, B, D) CuO structures obtained after heating porous copper and E) Sensitivity values measured on nine different porous CuO electrodes in glucose concentration range 0.5–2.5mM[13].*

In 2010, X. Wang et al. synthesized for the first time CuO flowers and nanorods on graphane electrode by the composite-hydroxide and the composite-molten-salt method, respectively. The as-prepared samples have been used to construct non-enzymatic glucose sensors. The results of this study show that CuO flowers and nanorods have exhibited highly enhanced electrocatalysis towards glucose oxidation compared with that of a bare graphite electrode (figure II.6.C)[14].

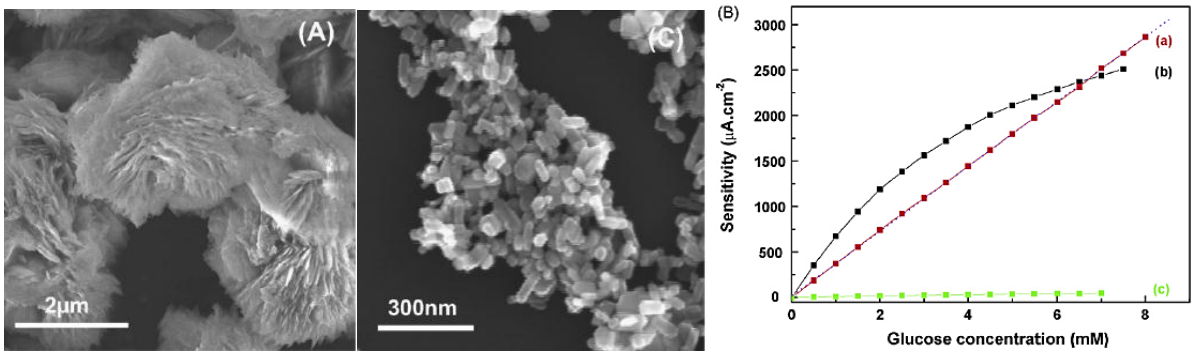

Figure II.6: *A and B) FE-SEM image of CuO synthesized by the CHM method and the CMS method, respectively. C) The corresponding calibrate sensitivity plot (B) of the CuO nanorods/G electrode (a), CuO flowers/G electrode (b) and G electrode (c)[14].*

Though the electrode based on the CuO flowers has higher sensitivity than that of the CuO nanorods modified electrode, the latter presents a much better linear range of glucose concentration and a shorter response time. CuO flowers/G (graphite) electrode have a high sensitivity of 709.52 µA/mM.cm^2 with the initial injection of 0.5 mM glucose and a low detection limit of 4 µM. On the other hand, after continuous injection of 0.5 mM glucose, the CuO nanorod/G electrode showed a stable sensitivity of 371.43 µA.mM^{-1}.cm^{-2} within 10 seconds, and the detection limit for glucose was 4 µM, as well as a wide linear response from 4 µM to 8 mM. It has been demonstrated that the CuO nanostructure modified electrodes have good selectivity of glucose in the presence of dopamine and ascorbic acid [14].

Nanoplatelets of CuO were grown on Cu foils by a one step, template free process by J. Wang et al. [14]. The CuO nanoplatelets grown on Cu foil were integrated to be an electrode for glucose sensing. The electrode prepared exhibits a sensitivity of 3490.7 µA mM^{-1} cm^{-2} to glucose which is much higher than that of most reported enzyme-free glucose sensors and the linear range was obtained over a concentration up to 0.80 mM with a detection limit of 0.50 M[15].

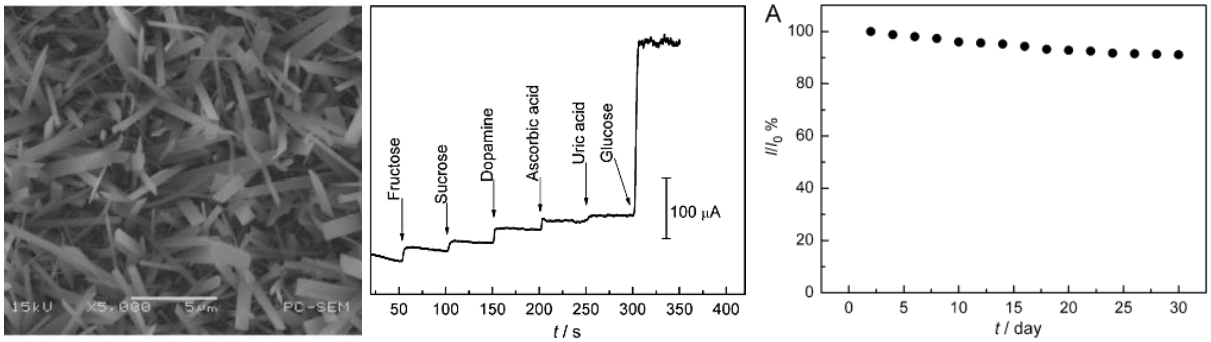

Figure II.7: *A) SEM images of CuO nanoplatelets electrode, B) Flow injection amperometric response to injections of 0.1 mM/l interferences of fructose, sucrose, uric acid, dopamine, ascorbic acid and 0.1 mM/l glucose and C) Stability of the sensor stored at ambient conditions over 30 days[15].*

Exhilaratingly, the electrode based on the CuO nanoplatelets is resistant against poisoning by chloride ion, and the interference from the oxidation of common interfering species, such as uric acid, ascorbic acid, dopamine and carbonhydrate compounds, can also be effectively avoided. Finally, this electrode is a potential candidate for routine analysis of glucose concentrations in human blood serum or other biological fluids [15].

In 2014, Yuchan Zhang et al. prepared a nanowires of copper oxide (CuO NWs) by a facile two-step procedure consisting of wetchemistry synthesis and subsequent direct calcination. The CuO NWs were further employed to construct a non-enzymatic glucose sensor with excellent performance toward glucose detection in 50 mM NaOH solution. The as-developed non-enzymatic glucose sensor showed a fast response time (less than 5 s) and a wide dynamic range with excellent sensitivity of 648.2 μA cm^{-2} mM^{-1} and 119.9 μA cm^{-2} mM^{-1} toward glucose detection at an applied potential of +0.55 V and +0.3 V (vs.Ag/AgCl), respectively. In conclusion, the developed non-enzymatic glucose sensor was successfully applied to the measurement of glucose in human serum samples with good accuracy and high precision. These features make CuO nanowires a good candidate in the development of non-enzymatic glucose sensor[16].

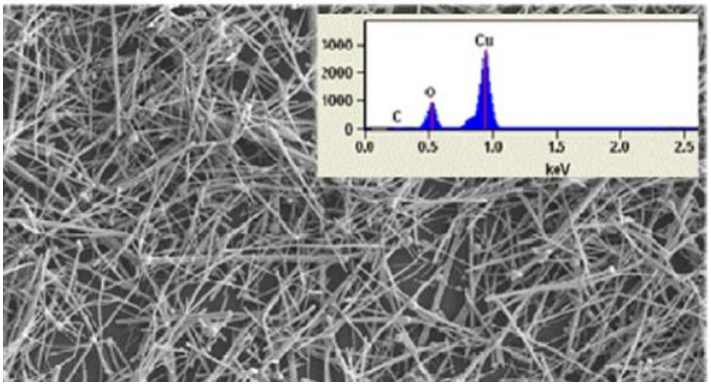

Figure II.8: *Typical SEM image of CuO NWs. Inset shows the EDX spectrum of CuO NWs.*

Another research has been presented by a et al. in 2014, it's related to the elaboration of CuO on titanium (Ti) substrate as working electrode to detect glucose which is inexpensive and convenient. The CuO/Ti films have been successfully prepared via a hydrothermal method and used to construct an amperometric non-enzymatic glucose sensor. The CuO films based glucose sensors exhibit enhanced electrocatalytic properties which show very high sensitivity (726.9 μA mM^{-1} cm^{-2}), low detection limit (2 μM), and fast response (2 s). In addition, reproducibility and long-term stability have been observed. Low cost, convenience, and biocompatibility make the CuO films directly grown on Ti substrate electrodes a promising platform for amperometric non-enzymatic glucose sensor. .

From this work we find that the CuO/Ti electrode shows high sensitivity, low detection limit, good stability,reproducibility, and fast response time. [17].

In 2015, F. Sun et al. was studied a novel CuO thin films composed of porous nanosheets (NSs) formed on indium tin oxide (ITO) by a simple, low temperature solution method, and used as working electrodes to construct non-enzymatic glucose sensor after calcinations. It can be found from the figure II.9.A, that the nanosheets have many porous structures, which may provide large surface area and high surface energy for the catalytic reaction. The results indicate that the CuO/ITO electrode exhibits a low operating potential of +0.35 V and high sensitivity of 2272.64 μA$mM^{-1}cm^{-2}$. Moreover, the CuO/ITO electrode also showed good stability, reproducibility and high anti-interference ability. Thus, it is a promising material for the development of non-enzymatic glucose sensors. Finally, the CuO/ITO electrode had strong and sensitive current response to glucose, which may be attributed to the large surface area of the porous nanosheets (NSs) structure and fast electron transfer ability between CuO NSs and ITO[18].

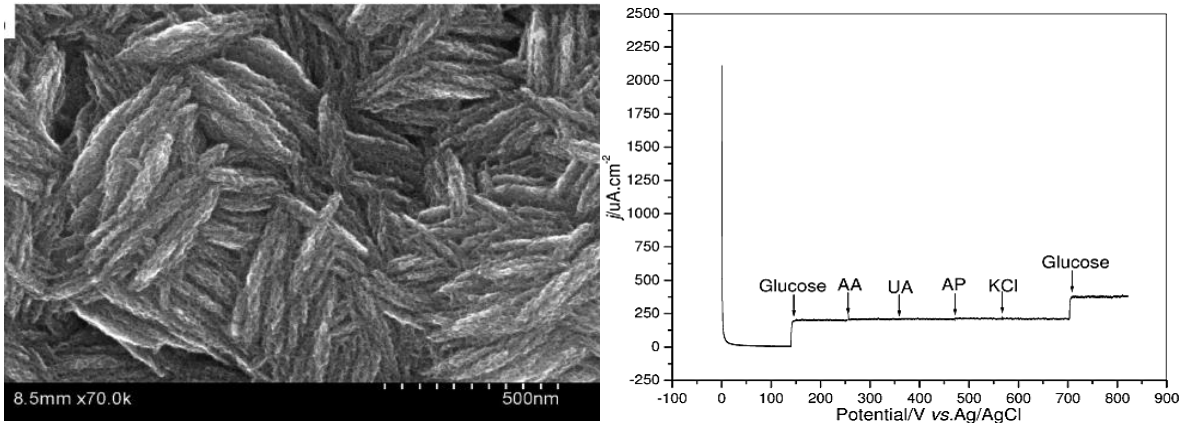

Figure II.9: *A) SEM image of as-prepared CuO film on ITO substrate, B) Amperometric response of the annealed CuO/ITO electrode in 0.1 M NaOH with successive addition of 0.1 mM glucose, 0.01 mM AA, 0.01 mM UA, 0.01 mM AP, 0.1 mM KCl and 0.1 mM glucose at an applied potential of +0.35 V[18].*

In the study of L. Zhang et al. [19], a sensitivity of 33.95 mA mM^{-1} $cm^{-2}$was reported for a CuO electrodes which prepared through in-situ constructing copper (Cu) - metal-organic framework (MOF) films on Cu foam and subsequently converting the films to CuO nanosheet arrays through an electrochemical process.

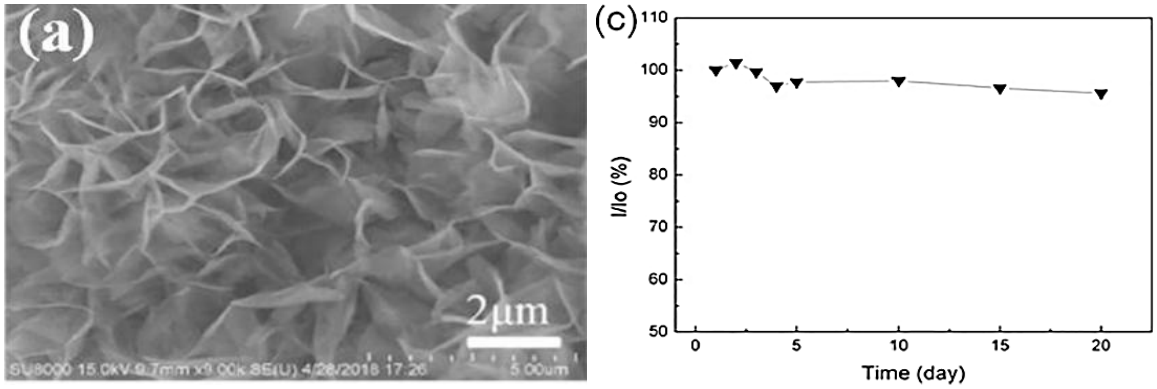

Figure II.10: *A) SEM images of vertical aligned CuO nanosheets prepared by an electrochemical conversion from Cu-MOF, B) long-term stability test of a CuO/Cu electrode stored at room temperature over a 20-day period[19].*

More importantly, the good controllability of electrochemical preparation leads to remarkable reusability, reproducibility and stability of the electrodes. The practical detection of CuO/Cu electrodes on serum samples indicates the results are basically consistent with the clinical reports from hospital, further indicating their attractive potential in practical application.

In 2020, J. Singh et al. were studied in this paper a cubic structured CuO thin films through of electrochemical and thermal annealing processes (figure II.10.A). Cubic nanostructured CuO thin film reveals the outstanding non-enzymatic glucose sensing behavior with a high sensitivity of 1311.83 µA mM^{-1} cm^{-2}, the wide linear range was varied between 0.001 and 1.8 mM, fast response times (less than 5) and low detection limit (LOD) of 0.068 µM [20].

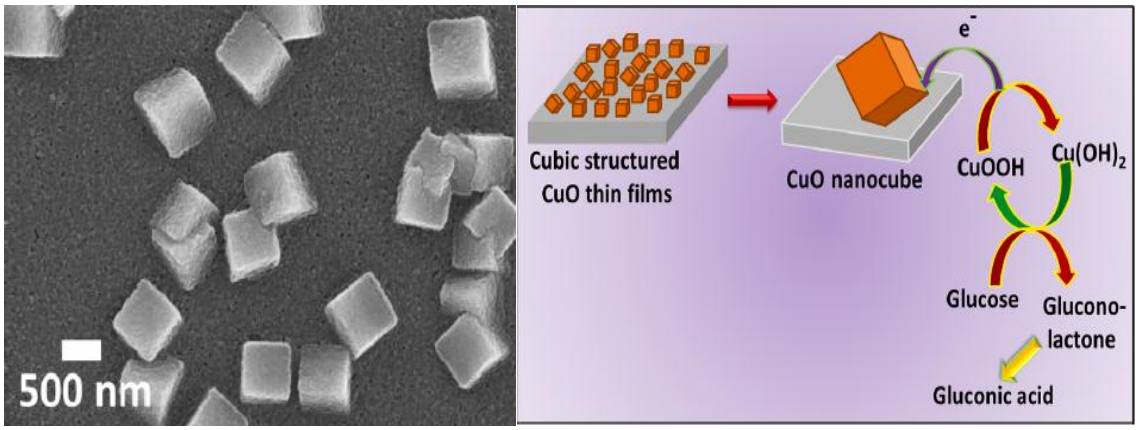

Figure II.11: *A) SEM images of electrodeposited CuO thin film, B) The schematic diagram for glucose sensing mechanism based on cubic structured CuO thin film [20].*

In 2020, A. Inyang et al. were fabricated a non-enzymatic electrochemical glucose sensor by deposition of CuO nanoparticle on fluorine doped tin oxide coated conductive. The CuO nanoparticulate thin film exhibited an excellent electrochemical response towards glucose oxidation, high sensitivity of 1207 µA mM^{-1} cm^{-2}, a linear range of up to 2.2 mM, and fast response of less than 4 s at a potential of 0.55 V vs Ag/AgCl with a limit of detection calculated to be 1.19 µM. In the present work, the performance demonstrated makes the electrode material promising for the development of effective non-enzymatic glucose sensor [21].

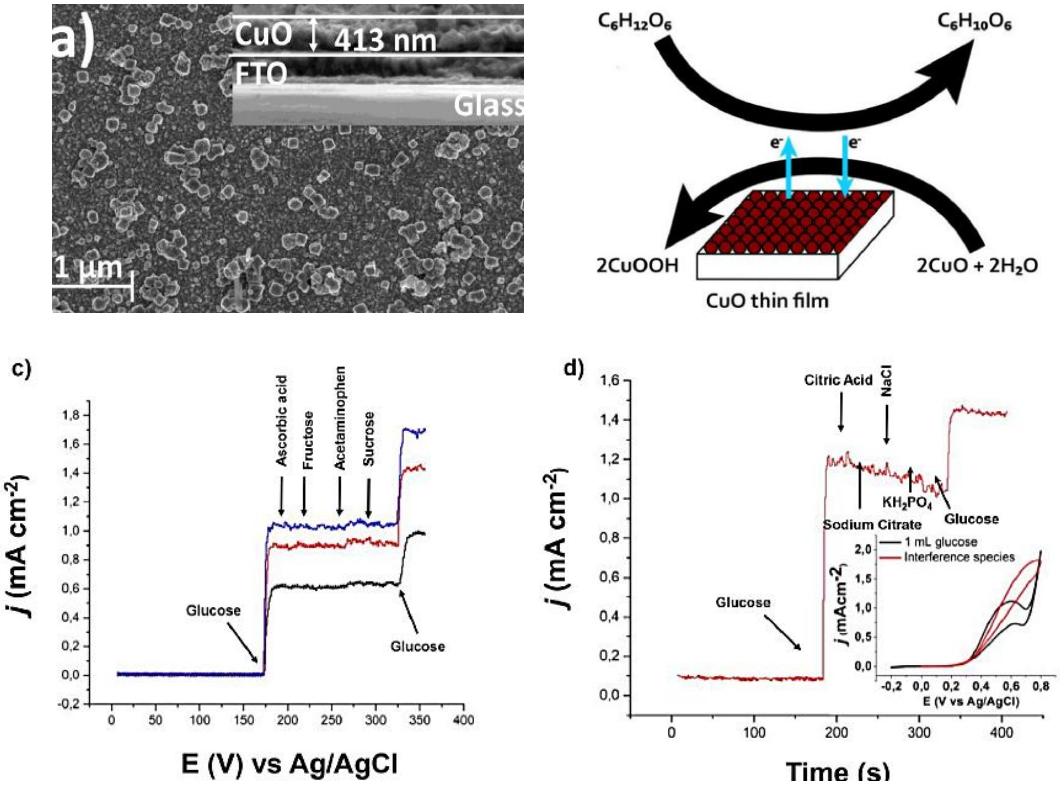

Figure II.12: *A) SEM images of the CuO electrode material (inset: cross section), B) CuO thin film electrochemical glucose sensing, C) selectivity study of the as-prepared electrode to interference species and D) selectivity study of the as-prepared electrode to various salts[21].*

Y-Y. Li et al. were developed the efficient of a non-enzymatic glucose sensor through the strategy of the L-B technique integrated with in situ thermal oxidation. Due to in-situ thermal oxidation, the porous CuO nanobelts formed are sintered together and tightly anchored on the ITO electrode, forming a stable assembly film, which exhibits a high sensitivity of 1876.52 µA mM^{-1} cm^{-2} and low detection limit (60 nM) on the detection of glucose in a wide concentration range. In addition, the CuO porous nanobelts (PNBs) film presented the robust stability and anti-interference capability, which can be successfully demonstrated for the quantitative detection of glucose in human blood serum [22].

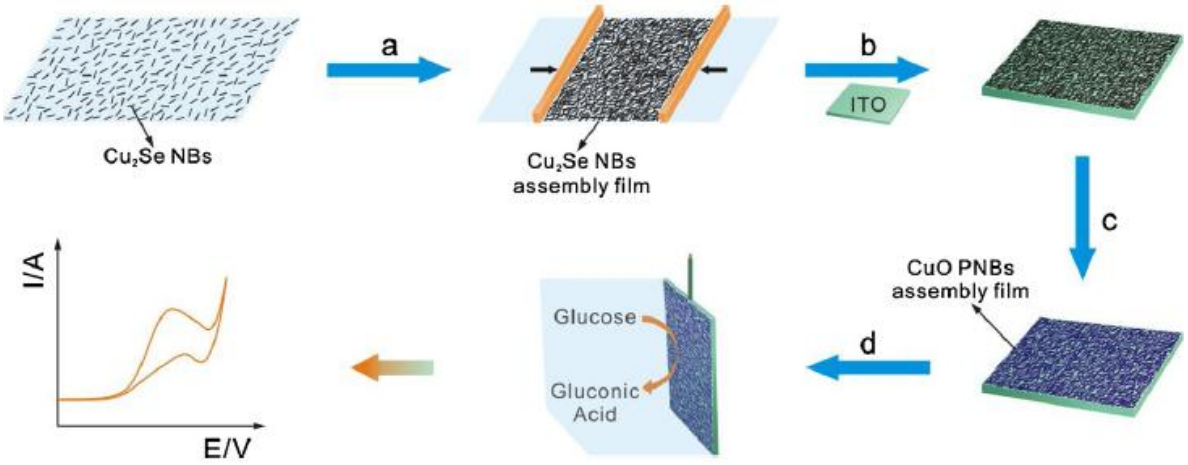

Figure II.13: *Schematic process of the fabrication of a non-enzymatic glucose sensor based on CuO PNBs assembly film deviated from Cu_2Se nanobelts. (a) assembly of Cu_2Se nanobelts via the Langmuir-Blodgett technique, (b) Cu_2Se nanobelts assembly film transferred onto ITO substrate, (c) in situ thermal oxidation, and (d) fabrication and measurements of the electrochemical electrode[22].*

Other study carried out in 2021 by M. Palmer et al. were presented the performance of CuO-NiO mixed oxides thin film by plasma assisted nitrogen doping. The as prepared film was also applied as an electrochemical glucose sensor. Device performance electrochemical testing showed that the as-developed sensor (labelled as N-CuO/Cu_2O: NiO) showed an ultrafast response time of 2.5 s with high sensitivity (1131 mA/mM.cm^2). Enhanced electrochemical performance of the N-CuO/Cu_2O:NiO originates from the improved electronic properties of the thin film [23].

II.2.2 Applications of Cuprous oxide Cu_2O

In 2012, L. Wang et al. were used a facile strategy to prepare Cu_2O/Cu electrode as a sensitive nonenzymatic glucose sensor was developed by an electrochemical method. The resulted sensor showed high catalytic activity towards the oxidation of glucose with a wide linear range of 0.05–6.75 mM and detection limit of 37 μM. Also, the good catalytic activity, high sensitivity 62.29 μA mmol L^{-1} and good stability made such Cu_2O/Cu electrode to be a promising candidate for constructing novel enzyme-free sensor. We concluded that the sensor has the advantages of simple and convenient preparation, low production cost, good electrocatalytic activity, high stability and low detection limit. It is possible to be a potential candidate for routine glucose analysis [24].

In 2015, H. Cao and his co-workers were obtained a sensitivity of 2038.2 μA mM^{-1} cm^{-2} from the hollow Cu_2O nanosphere grown on a glassy carbon electrode (GCE) as the biosensor. Hollow Cu_2O were expediently prepared and provided with some advantageous properties such as increased electrocatalytic activity toward glucose, high surface area, and excellent conductivity. Meanwhile, hollow Cu_2O nanospheres distributed in Nafion film provide abundant active sites for sensing of glucose. In conclusion, due to the ease of synthesis and electrode fabrication, high sensitivity and good stability, hollow Cu_2O nanospheres become promising microstructures for electrochemical biosensor devices of glucose [25].

In 2017, X. Yu et al. were prepared a Cu_2O thin film by electrodeposition and used as a non-enzymatic glucose sensor electrode to test electrochemical performance for glucose. The sensor showed the characteristics of a wide detection range of 0.337 mgL^{-1} and high sensitivity of 23.24 $mAcm^{-2}mM^{-1}$. In general, the Cu_2O thin-film electrode exhibited good electrocatalytic performance with respect to glucose, and the response was quick and the anti-jamming performance and stability were excellent. The method described has a low LOD and high sensitivity, and it can be used to detect glucose [26].

In 2017, J. L. K. Jayasingha et al. were fabricated a non-enzymatic glucose sensor by the deposition of Cu_2O nanocubic and Cu_2O microcrystalline on titanium (Ti) substrate and achieved a sensitivity of about 4 ± 0.2 mA mM^{-1} cm^{-2} and 16.3 ± 0.2 mA mM^{-1} cm^{-2} respectively. In conclusion, amperometric sensing measurements of glucose for the nano-cubic Cu_2O/Ti electrode were significantly better than the microcrystalline counterpart prepared under similar electrodeposition conditions without the aid of a template [27].

In 2018, Y. Dai et al. were reported a best sensitivity (99.6 μA cm^{-2} $mmol^{-1}$) for cuprous oxide (Cu_2O) thin layer served as the base for a non-enzymatic glucose sensor in an alkaline medium, 0.1 NaOH solution, with a linear range of 50–200 mg/dL using differential pulse voltammetry (DPV) measurement [28].

In 2021, S. Laidoudi et al. were reported a sensitivity of 2322.5 μA mM^{-1} cm^{-2} for non-enzymatic glucose detection using Cu_2O/ITO electrode. The results indicate that the proposed Cu_2O/ITO sensor exhibits better performances compared to the aforementioned literature report in terms of sensitivity and low cost. As well, this sensor demonstrated a fast response time (~ 3 s), high sensitivity of 2322.5 μA $mM^{-1}cm^{-2}$ in the range of 0.04–0.4 mM, R2 = 0.9989 with a detection limit of 4 μM, high selectivity in the presence of common interfering species and good stability[11].

II.3 Comparison between copper oxides based on non-enzymatic sensors for glucose detection

Table 4 presents a comparison of electrocatalytic parameters of proposed sensor with several non-enzyme glucose sensors which were reported in last years. The results indicate that CuO nanosheet/Cu the proposed sensor exhibits better performances among cupric oxide thin films and Cu_2O nanometer thin-film the proposed sensor exhibits better performances among cuprous oxide thin films compared to the aforementioned literature report in terms of sensitivity and low cost. Among the last two, CuO nanosheet/Cu the proposed sensor which showed a high sensitivity and a low detection.

Table II.2: *A performance comparison of CuO thin films.*

Electrode material	**Linear range (up to mM)**	**Detection limit (µM)**	**Sensitivity ($\mu A.mM^{-1}\ cm^{-2}$)**	**Ref**
CuO				
Porous CuO	$1*10^{-3}$ to 2.5	0.14	2900	[13]
CuO flowers/G (graphite)	$4*10^{-3}$ to 8	4	371.43	[14]
CuO nanowires	_	2 5	648.2 119.9	[16]
CuO porous nanosheets (NSs)/ Indium Tin Oxide (ITO)	$2.0*10^{-3}$ to 0.6	1.0	2272.64	[18]
CuO nanosheet/Cu	$1.0*10^{-3}$ to 5.0	0.33	33950	[19]
Cubic nanostructured CuO thin film	0.001 to 1.8	0.068	1311.83	[20]

CuO nanoparticulate thin film	To 2.2	1.19	1207	[21]
CuO Porous nanobelts (PNBs)	$0.1*10^{-3}$ to 2.0	0.06	1876.52	[22]
N-CuO/Cu_2O:NiO	up to 2.74	20	1131	[23]
CuO nanoplatelets	0.8	0.50	3490.7	[15]
CuO/Titanium (Ti)	_	2	726.9	[17]
Cu_2O				
Cu_2O nanometer thin-film	0.0055 to 0.111	1.87	23240	[26]
Cu_2O nanospheres	$1.25*10^{-3}$ to 0.0375	0.41	2038.2	[25]
Cu_2O thin films	_	_	99.6	[28]
Cu_2O/ Indium Tin Oxide (ITO)	40 to 0.4	4	2322.5	[11]
Nano-cubic Cu_2O/Ti (T_{30})	0.017 to 11.650	15.6	28.40	[27]
Microcrystalline Cu_2O/Ti (S_{60})	0.030 to 9.650	28.1	16.29	[27]
Cu_2O/Cu	0.05 to 6.75	37	62.29	[24]

II.4 References

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Conclusion

Conclusion

It is an undeniable fact that with the advancement of nanotechnology, the field of glucose sensors is able to progress at a rapid pace. With newer and better nanostructured metal oxide being introduced frequently by researchers, eventually non-enzymatic glucose sensors would be able to completely replace the enzymatic glucose sensors.

This work has briefly summarized the difference between enzymatic and non-enzymatic glucose sensor. Besides, the properties of copper oxides thin films and the roles played by their different shapes types in the non-enzymatic glucose sensors have also been introduced concisely. Also, in this work we reviewed the conditions and the mechanism of glucose oxidation on the non-enzymatic glucose sensor based on copper oxides electrode.

From the literature, both oxides, Cu_2O and CuO, have better performances owing to his high sensitivity, low detection limit, good stability, reproducibility, and fast response time which made it possible to introduce this oxides as an electrode in the non-enzymatic glucose sensors.

Finally, we compared between some electrocatalytic parameters of proposed sensor with several non-enzyme glucose sensors which were reported in last years. The results indicate that cupric oxide sensor (CuO nanosheet/Cu) exhibits a high sensitivity of 33950 ($\mu AmM^{-1}\ cm^{-2}$) and low detection limit of 0.33 μM.