



Republic of Iraq
Ministry of Higher
Education
and Scientific Research
University of Diyala
College of Science
Department of Physics



**Physical Properties of CuO Nanoparticles
prepared by Sol - Gel and Hydrothermal
methods for Antibacterial Effects**

A thesis

Submitted to the Council of the College of Science
University of Diyala in Partial Fulfillment of Requirements for the
Degree of Doctor of Philosophy in Physics

By

WISAM MAHMOOD MOHAMMED

Supervised By

Prof. Dr.
Tahseen H. Mubark

Prof. Dr.
Raad M.S.Al-Haddad

2020 A.D.

1441 A.H.



جمهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعة ديالى
كلية العلوم



قسم الفيزياء

الخصائص الفيزيائية لجزيئة CuO النانوية المحضرة بطريقة Sol-Gel وHydrothermal وتأثيرها كمضاد بكتيري

أطروحة مقدمة إلى مجلس كلية العلوم - جامعة ديالى وهي جزء من
متطلبات نيل شهادة الدكتوراه فلسفة في الفيزياء

من قبل

وسام محمود محمد

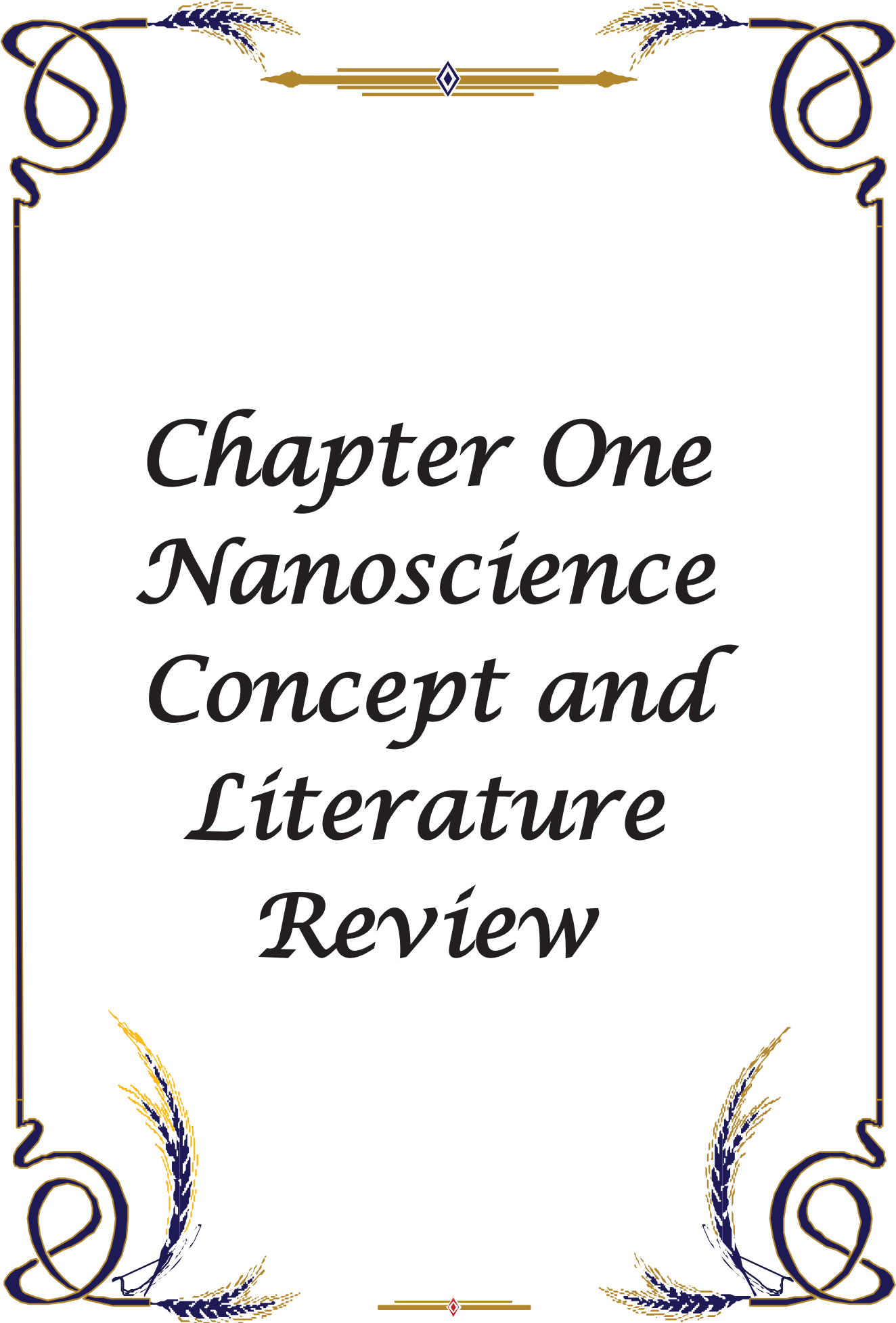
إشراف

أ.د. رعد محمد صالح الحداد

2020 م

أ.د. تحسين حسين مبارك

1441 هـ



Chapter One
Nanoscience
Concept and
Literature
Review



Chapter Two
Theoretical Part



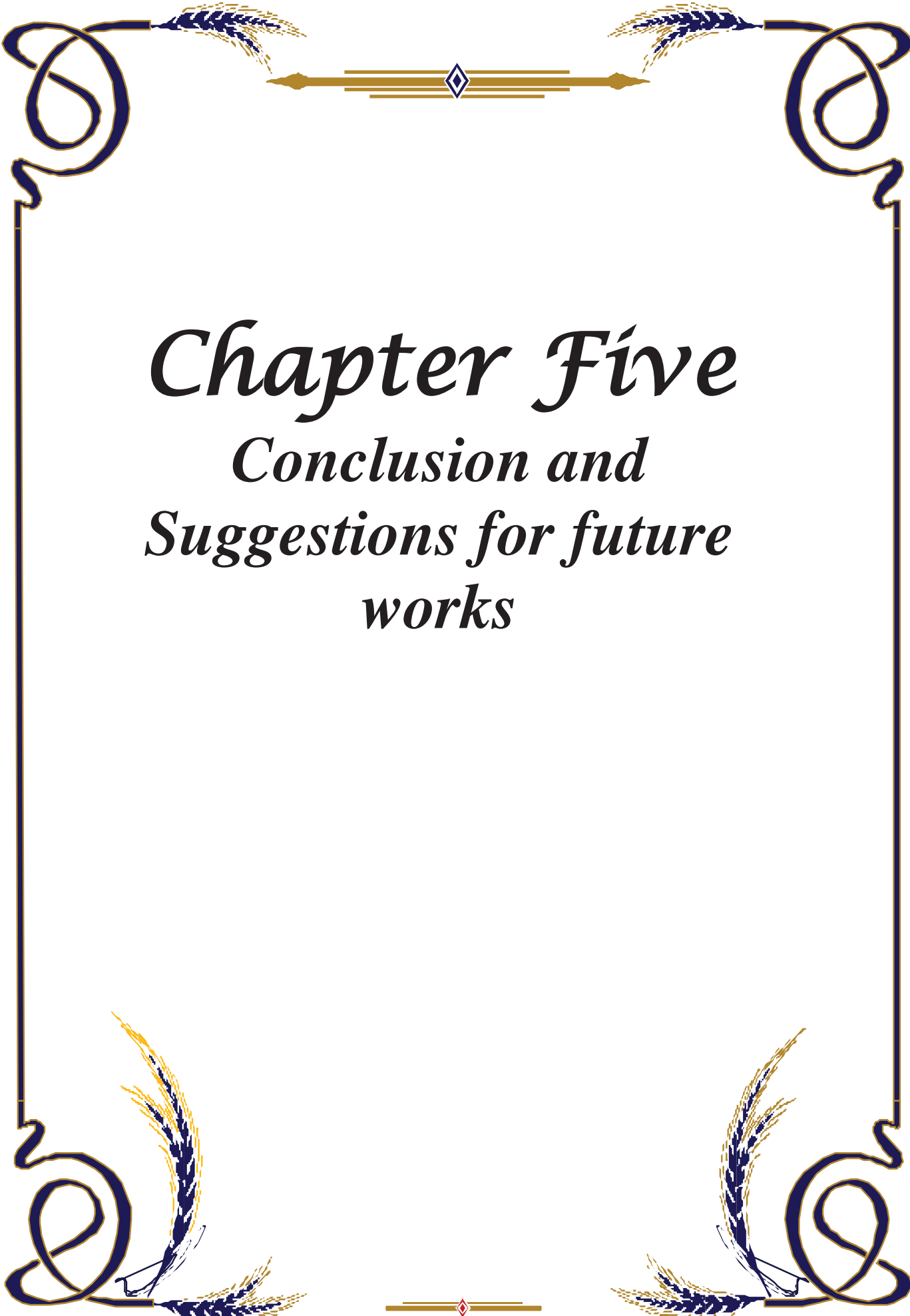
Chapter Three

*Experimental
Part*



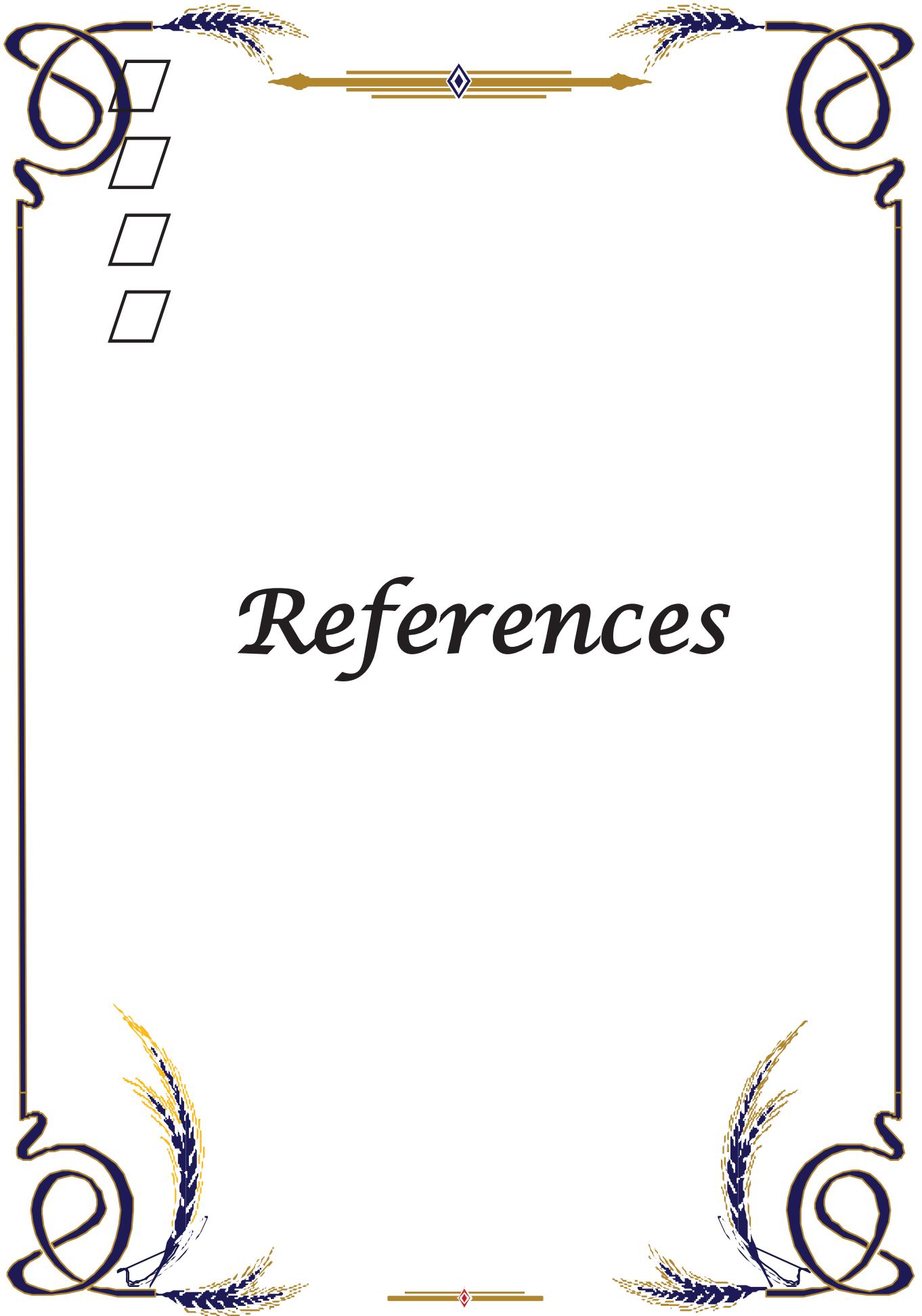
Chapter Four

*Results and
Discussion*



Chapter Five
Conclusion and
Suggestions for future
works □





References

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

[وَمِنْ ذِكْرِ مَفَاتِحِ الْغَيْبِ لَا يَخْلُقُهَا إِلَّا هُوَ وَيَعْلَمُ مَا فِي

الْبُرِّ وَالْبَحْرِ وَمَا تَسْقُطُ مِنْ وَرَقَةٍ إِلَّا يَعْلَمُهَا وَلَا حَبَّةٌ

فِي ظُلُمَاتِ الْأَرْضِ وَلَا رَطْبٌ وَلَا يَابِسٌ إِلَّا فِي كِتَابٍ

مُبِينٍ]

صدق الله العظيم

(سورة الانعام - الآية 59)



Dedication

To ...

My Country, Iraq

To...

My Parents father and mother

To...

My brothers and sisters

To...

My wife and my sons and my daughters

To...

My Friends

To...

*The people who love and supported me all the
time*

WISAM M. MOHAMMED

ACKNOWLEDGEMENT

First of all I thank the Almighty *Allah*, whose Grace enabled me to continue this work and overcome all difficulties and our prophet *Muhammad* (peace and blessings of Allah be upon him) who invites us to science and knowledge.

I would like to express my deep thanks and gratitude to university of diyala , college of science, department of physics to allow me to complete the study of doctoral , and I would like to express my deep thanks and gratitude my supervisor Prof. Dr. **Tahseen H. Mubark** for providing necessary facilities and help. I am very grateful to my supervisor Prof. Dr. **Raad M.S.Al-Haddad** for his suggestion of this project and his encouragement through this research work.

I would like to express my profound gratitude to Prof. Dr. **Sabah A. Salman and Prof. Dr. Nabeel B.Ali** for his kind cooperation and constant support. I am highly indebted to Assist. Prof Dr. **Ziad T. Khodair** for his constant encouragement throughout my Ph.D. study in the Department of Physics, College of Science, University of Diyala.

Special thanks are extended to the University of Diyala, College of Science, specially The dean of College of Science, Prof. Dr. **Tahseen H. Mubarak** and the head of the physics department, Dr. **Ziad T. Khodair** for their support and encouragement. and all the Staff of the Department of Physics for their assistance.

I would also like to thank the staff of the Library of College of Science(**Adnan and Raafat**), who continued to provide excellent service, tireless support and scientific resources to all students.

I do not forget to thank Assist. Prof. Dr. **Sabah**(Baghdad University), and biology Department staff for their support.

I am grateful to the staff of laboratory health public and my colleagues at preparatory Hitteen industrial and my colleagues at preparatory Jalawla industrial.

My greatest indebtedness goes to my **Father, Mother,my Wife ,my sons,my daughter ,my sisters and my Brothers** for their valuable advice, and to my Friends (**Aws, Ahmed, Ali, Adnan, Abo Ayman, zaid, mahdi, muhand**) for their endless support.

Published Accepted Research Articles

*Wisam M. Mohammed, Tahseen H. Mubark, Raad M. S. Al-Haddad
"Effect of CuO Nanoparticles on Antimicrobial Activity Prepared by Sol-
Gel Method". International Journal of Applied Engineering
Research. Vol 13, Number 12, pp. 10559-10562, (2018). (Scopus)

*Wisam M. Mohammed, Raad M.S. Al-Haddad, Tahseen H. Mubark
"Characterization of Copper Oxide Nanoparticles Prepared by
Hydrothermal Method for Antibacterial Effect". Indian
Journal of Natural Sciences
Vol.9 , Issue 54 , June ,(2019).

Abstract

Different sized CuO nanoparticles synthesized by using two methods sol-gel and hydrothermal. In sol-gel method CuO nanoparticles obtained by using Copper nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}]$, and citric acid were dissolved in de-ionized water. The powder, which was further annealed at different temperature (200,300,400,500, and 600) $^\circ\text{C}$. In the hydrothermal method CuO nanoparticles obtained by using Copper chloride hydrate $[\text{CuCl}_2 \cdot 2\text{H}_2\text{O}]$, and Hexamine ($\text{C}_6\text{H}_{12}\text{N}_4$) were dissolved in de-ionized water and stirred by magnetic stirrer to get homogenous solution and transferred into 50 ml Teflon -lined stainless steel vessels (autoclave), and annealed at (200,300, and 400) $^\circ\text{C}$ for 1 hour. The nanoparticles were characterized by XRD, UV-Visible spectroscopy, FTIR, AFM,TEM. The X-ray diffraction spectra of the CuO NPs prepared in the two methods at different temperatures were exhibited the monoclinic structure of CuO which was confirmed from the standard card (JCPDs, No. 05-0661). The lattice constants were found to be $a=4.688$ $^\circ\text{A}$, $b=3.427$ A , $c=5.132$ A . The crystalline size of CuO NPs prepared in hydrothermal method was found to be (11.2)nm is smaller than the crystalline size of CuO NPs prepared by sol-gel method was found to be (15.3)nm at the same temperature 200 $^\circ\text{C}$. From the results of UV-Visible show a red shift in the absorption spectra due to the increase in the particles size with increase in annealing temperature. The study of the topography of the surface of the particles of CuO NPs by using atomic force microscopy where it was through that measurement study of surface roughness particle size nanoparticles rate plus size distribution of the particles prepared .It is observed that the increased temperature is accompanied by an increase in the size of nanoparticles ,surface roughness increased as increases of the temperatures. In FTIR Spectra were recorded in solid phase using the KBr pellets technique in the range

of 4000-400 cm^{-1} . FTIR spectra exhibiting only one vibration mode occurring at approximately 500 cm^{-1} for all samples assigned for Cu-O stretching vibration, conforming the formation of highly pure CuO nanoparticles. A weak band at round 2340 cm^{-1} may be attributed to the vibration of atmospheric CO_2 . The result of the TEM of the CuO NPs prepared by sol-gel & Hydrothermal methods at different temperatures these indicate that the increased temperature was accompanied by an increase in nano size. the size depends on the temperature value where the higher the temperature the larger the nanoparticles size was analysed by Image J. The shape of nanoparticles is spherical. The results of antibacterial activity using CuO NPs which prepared by sol-gel and hydrothermal methods at different temperatures against G(+ve) bacteria and G(-ve) bacteria by well diffusion. In this study, the copper oxide nanoparticles showed remarkable antibacterial activity against both Gram-positive bacteria and Gram-negative bacteria. The extent of inhibition of bacteria growth observed it was found to be variable and size dependent. The smallest size NPs synthesized at lowest temperature (200) $^{\circ}\text{C}$,showed a significant inhibitory effect against both Gram(+ve) and Gram(-ve) bacteria as compared to the CuO samples sintered at high temperature. and positive control, a known antibiotic tetracycline against G(+ve) and (-ve) bacteria, that the copper oxide nanoparticles inhibit the growth of both G(+ve) and G(-ve) bacteria and the zone of inhibition decrease with the increase in annealing temperature. the zone of inhibition is maximum when the particles size is minimum these results demonstrate the excellent antibacterial behavior of CuO NPs synthesized at low temperature.

List of Contents

No	contents	Page
Chapter one		
Nanoscience Concept and literature Review		
1.1	History of Nanomaterial	1
1.2	Nanoparticles	2
1.3	Quantum Confinement	2-4
1.4	literature review	4-10
1.5	Aim of this work	11
Chapter Two		
Theoretical Part		
2.1	Distinguish Proper of Nanoparticle	12
2.1.1	Quantum Size Effects [QSE]	12
2.1.2	Surface to Volume Ratio	12-14
2.2	Properties of Nanoparticles	15
2.2.1	Electronic Properties	15
2.2.1.1	Semiconducting Nanoparticles NPs	15-16
2.2.1.2	Surface Effect and Nanoparticle Stability	16-17
2.2.2	Optical Properties	17
2.2.2.1	Optical Absorption and particle size Dependent	17-18
2.2.2.2	Surface Plasmon Resonances (SPR)	18-20
2.2.2.3	propagation of surface plasmons	21-23
2.3	Nanoparticles Synthesis	23-25
2.4	Nanoparticle Morphology:	25-26
2.5	Preparation Methods of Nanoparticles	26
2.5.1	sol-gel method	26-27

2.5.2	Hydrothermal method	27-28
2.6	The Kinetics of Phase Transformations of Solid nanosphere	28
2.6.1	Nucleation	28-32
2.6.2	Particle Growth	32-33
2.6.3	Growth Termination	33
2.7	Estimated the Nanoparticles Size	33
2.7.1	Estimate the Size from UV-Vis Spectrum Absorption	33-34
2.7.1.1	Effective Mass Approximate Model (EMA)	34-35
2.7.1.2	Tauc Relation to Calculate the optical Energy Gap	35
2.7.2	Estimate the Nanoparticles Size from X-ray Diffraction	35
2.7.2.1	Scherrer Equation	35-36
2.8	Estimate the Lattice constant of Nanoparticles from X-ray Diffraction	36
2.9	Properties of Copper oxide	36-37
2.10	Biological potentials of CuO NP _s	38
2.10.1	Antimicrobial Activity of Nanoparticles	38-39
2.10.2	The Bacterial cell wall	39-40
2.10.3	Bacterial – Nanopartical Interactions	40-41
2.10.4	Bacterial Types	42-44
2.11	Ultraviolet – visible (UV - Vis) Spectrophotometer	44-45
2.12	Fourier Transform Infrared Spectroscopy (FTIR)	45-46
2.13	Atomic Force Microscopy (AFM)	46-47
2.14	Transmission Electron Microscope:	47-49
CHAPTER THREE		
Experimental Part		
3.1	Flow chart of the work	50
3.2	Material and Chemical	51

3.3	Synthesis of CuO nanoparticles by Sol-Gel procedure	52
3.3.1	Calculating weight of materials	53
3.3.2	CuO Nano particles preparation by sol-gel method	53-54
3.3.3	CuO nano particles preparation by hydrothermal method	54-55
3.4	Distilled and Deionized water	55
3.5	Characterization of CuO	56
3.5.1	Ultraviolet – visible Spectroscopy (UV - Vis)	56
3.5.2	X – ray Diffraction (XRD)	56
3.5.3	Transmission Electron Microscopy (TEM)	56
3.5.4	Atomic Force Microscopy (AFM)	56
3.5.5	Fourier transfer infrared (FTIR)	56
3.6	Biomedical application of CuONP _s	57
3.6.1	study antibacterial activity of CuO NPS(<i>in vitro</i>)	57
3.6.1.1	McFarland preparation	57
3.6.1.2	Nutrient Broth Preparation	57
3.6.1.3	Muller hinton Agar Preparation	57
3.6.1.4	Nutrient Agar Preparation	58
3.6.1.5	Preparation of antibiotic	58
3.6.1.6	Microorganisms	58
3.6.1.7	Well Diffusion Assay	58-59
3.6.1.8	Minimum inhibitory concentrations (MIC)	59-61
Chapter Four		
Results and Discussion		
4.1	structural properties of CuO	62
4.1.1	X-ray Diffraction(sol- gel method).	62-63
4.1.2	X-ray Diffraction(hydrothermal method).	64-65

4-2	Optical Properties	66
4.2.1	UV-Visible of CuO NPs(sol-gel method)	66-69
4.2.2	UV-Visible of CuO NPs(hydrothermal method)	69-72
4-3	morphological properties of CuO NPs	72
4.3.1	Atomic force microscopy(AFM)	72
4.3.1.1	Atomic force microscopy of CuO NPs prepared by sol-gel method	72-74
4.3.1.2	Atomic force microscopy of CuO NPs prepared by hydrothermal method	74-76
4.3.2	Transmission Electron Microscopy(TEM).	77
4.3.2.1	Transmission Electron Microscopy of CuO NPs prepared by sol-gel method	77-80
4.3.2.2	Transmission Electron Microscopy of CuO NPs prepared by hydrothermal method	80-82
4.4	FTIR of CuO NPs	83
4.4.1	FTIR of CuO NPs prepared by sol-gel method	83
4.4.2	FTIR of CuO NPs prepared by hydrothermal method	84
4-5	Optimum Parameters synthesized of CuO NPS	85
4-6	A study of antibacterial activity using CuO NPs.	85
4.6.1	study of antibacterial activity using CuO NPs. Prepared by Sol-gel Method	85-90
4.6.2	study of antibacterial activity using CuO NPs. Prepared by Hydrothermal Method	90-95
Chapter Five		
Conclusion and Suggestions for future works		
5-1	Conclusion	96
5-2	Suggestions for future works	97
	References	98-116

<i>List of Figures</i>		
No	Name of Figure	Page
Chapter one		
Figure (1-1)	Different dimensional structures	4
Chapter Two		
Figure (2-1)	Example to illustrate increase in surface to volume ratio	13
Figure (2-2)	Fractions of gold atoms at corners, edges, and particle surfaces in the octahedron.	14
Figure (2.3)	Schematic of surface plasmon oscillations induced by an oscillating electric field in a metal sphere. The displacement of the conduction electrons (green color) relative to the nuclei (gray color) is shown. The frequency of the surface plasmon resonance is denoted ω_p	19
Figure(2.4)	shows CuO NPs size as well as own exterior plasmon (SP) Note: AR is the standard aspect ratios for Nano-rods (length divided by width)	20
Figure(2.5)	(a) Illustration of charge distributions of different orders of surface plasmon resonant modes. (b) Corresponding electric field patterns of a silver nanosphere in air.(c) Illustration of the assumption of a surface plasmon resonant mode of spherical nanoparticle and surface plasmons on the interface of plane metal and dielectric medium.	23

Figure (2.6)	Top down and bottom up Approach	24
Figure(2.7)	Schematic diagram showing the nucleation of a spherical solid particle in a liquid	29
Figure (2.8)	Free energy diagram for nucleation	32
Figure (2.9)	Monoclinic Structure of CuO	37
Figure(2-10)	Bacterial cell structure:(A) (G+ve)Gram-positive (B) (G-ve)Gram-negative	39
Figure (2-11)	shows the mechanisms of nanoparticles that causes bacterial death	41
Figure (2.12)	schematic of (UV - Vis) Spectrophotometer	44
Figure(2.13)	show absorbance spectrum of CuO nanocrystalline	45
Figure(2.14)	schematic diagram of FTIR spectrometer	46
Figure (2.15)	schematic of AFM spectroscopy	47
Figure (2.16)	Typical TEM functioning	48
Figure (2.17)	shows a TEM image of CuO nanoparticles	49
Chapter Three		
Figure (3-1)	Flow chart of the work and characterization technique	50
Figure (3-2)	The out line of sol-gel method	52
Figure (3-3)	Illustrated sol-gel steps technique	54
Figure (3-4)	a-hydrothermal system b-Autoclave	55
Figure(3-5)	Agar plate with wells of 6 mm diameter	60
Figure (3-6)	a- Schamatic of incubator b- block diagram of incubator	61

Chapter Four		
Figure (4-1)	XRD spectra of CuO NPs prepared in the sol-gel method at different temperatures	62
figure (4-2)	XRD spectra of CuO NPs prepared in the hydrothermal method at different temperatures	64
Figure (4-3)	Absorbance of CuO NPs prepared in the sol-gel method at different temperatures	66
Figure (4-4)	Shows the energy gap of CuONPs prepared by sol-gel method at different temperature	67
Figure(4-5)	shows the variation of Energy gab with different tempreature of CuO NPs prepared by sol –gel method.	68
Figure(4-6)	shows the variation of absoabance and wave length with different tempreature of CuO NPs prepared by sol –gel method.	69
Figure (4-7)	Absorbance of CuO NPs prepared in the hydrothermal method at different temperatures	70
Figure (4-8)	Shows the energy gap of CuONPs prepared by hydrothermal method at different temperature	70
Figure (4-9)	shows the variation of Energy gab with different tempreature of CuO NPs prepared by hydrothermal method.	71
Figure(4-10)	shows the variation of absoabance and wave length with	72

	different temperature of CuO NPs prepared by hydrothermal method.	
Figure (4-11)	(A) show 3D AFM images for surface graphical and (B) show statistical distribution of particle size of CuO NPs prepared by sol-gel method at different temperature	73-74
Figure (4-12)	(A) show 3D AFM images for surface graphical and (B) show statistical distribution of particle size of CuO NPs prepared by hydrothermal method	75
Figure(4-13)	shows the variation of Average roughness with different temperature of CuO NPs prepared by (a) sol-gel (b) hydrothermal methods.	76
Figure (4-14)	shows a TEM image of CuO nanoparticles prepared by sol-gel method at 200°	77
Figure (4-15)	shows a TEM image of CuO nanoparticles prepared by sol-gel method at 300° C	78
Figure (4-16)	shows a TEM image of CuO nanoparticles prepared by sol-gel method at 400° C	78
Figure (4-17)	shows a TEM image of CuO nanoparticles prepared by sol-gel method at 500° C	79
Figure (4-18)	shows a TEM image of CuO nanoparticles prepared by sol-gel method at 600° C	79
Figure(4-19)	shows the variation of Grain size with different temperature of CuO NPs prepared by sol-gel method.	89
Figure (4-20)	shows a TEM image of CuO nanoparticles prepared by hydrothermal method at 200° C	81

Figure (4-21)	shows a TEM image of CuO nanoparticles prepared by hydrothermal method at 300° C	81
Figure (4-22)	shows a TEM image of CuO nanoparticles prepared by hydrothermal method at 400° C	82
Figure(4-23)	shows the variation of Grain size with different tempreature of CuO NPs prepared by hydrothermal method.	82
figure(4-24)	FTIR spectra of CuO NPs prepared by sol-gel method annealed at different temperature	83
Figure(4-25)	FTIR spectra of CuO NPs prepared byhydrothermal method annealed at different temperature.	84
Figure(4-26)	Antibacterial activity of CuO NPs prepared by sol-gel against staph-aureus	87
Figure(4-27)	Antibacterial activity of CuO NPs prepared by sol-gel against E.coli	87
Figure(4-28)	Antibacterial activity of CuO NPs prepared by sol-gel against Serratia	88
Figure(4-29)	Antibacterial activity of Cuo NPs prepared by sol-gel against Bacillus	88
Figure(4-30)	Antibacterial activity of CuO NPs prepared by sol-gel against Klebsiella	89
Figure(4-31)	Antibacterial activity of CuO NPs prepared by sol-gel against P.aeruginosa	89
Figure(4-32)	Antibacterial activity of CuO NPs prepared by sol-gel against Enterobactor	90
Figure(4-33)	Antibacterial activity of CuO NPs prepared by hydrothermal against staph-aureus	91

Figure(4-34)	Antibacterial activity of CuO NPs prepared by hydrothermal against E.coli	92
Figure(4-35)	Antibacterial activity of CuO NPs prepared by hydrothermal against Serratia	92
Figure(4-36)	Antibacterial activity of CuO NPs prepared by hydrothermal against Bacillus	93
Figure(4-37)	Antibacterial activity of CuO NPs prepared by hydrothermal against Klebsiella	93
Figure(4-38)	Antibacterial activity of CuO NPs prepared by hydrothermal against P.aeruginosa	94
Figure(4-39)	Antibacterial activity of CuO NPs prepared by hydrothermal against Enterobactor	94

<i>List of Tables</i>		
No	Name of Tables	Page
Chapter Two		
Table (2-1)	The comparsion between the walls of the two bacteria strain kinds	40
Chapter Three		
Table(3-1)	chemical properties of the materials used to synthesis metal oxides (CuO)	51
Chapter Four		

Table (4-1)	XRD parameters of CuO prepared by sol- gel method	63
Table (4-2)	XRD results of CuO prepared by hydrothermal method	65
Table (4-3)	variation of energy gap with annealing temperature of CuO NPs prepared by Sol-gel method	68
Table (4-4)	variation of energy gap with annealing temperature of CuO NPs prepared by hydrothermal method	71
Table (4-5)	surface topography characteristics of CuO NPs prepared by sol-gel method at different temperature (200,300,400,500,600)° C	76
Table (4-6)	surface topography characteristics of CuO NPs prepared by hydrothermal method at different temperature (200,300,400)° C	76
Table (4-7)	Shows optimum parameters synthesized of CuONPs	85

List of Abbreviation

Symbols	Description
0D	Zreo dimension
1D	One dimension
2D	Two dimension
S:V	Surface area to volume ratio
NPs	Nanoparticles
QSE	Quantum size effect
Cu	Copper
CuO	Copper Oxide
SPR	Surface plasmon resonance
D _{av}	Grain size
m	Meter
nm	Nanometer
DW	De-ionized water
M	Molarity

W_t	Weight
$M.W_t$	Molecular weight
T	Temperature
μ	Micro
μg	Microgram
m_l	Millilitre
L	Litre
UV-Vis	Ultraviolet-Visible Spectroscopy
XRD	X-ray diffraction
FTIR	Fourier transform infrared
TEM	Transmission electron microscopy
AFM	Atomic force microscopy
E.Coli	Escherichia coli
S.aureus	Staphylococcus aureus
P.areginosa	Pseudomonas areginosa
CFU	Colony forming unit
NA	Nutrient agar
NB	Nutrient broth
MA	Mullerhinton agar

List of symbols

Symbols	Description	Unit
D_{av}	Grain size	nm
E_g	Energy gap	ev
FWHM	Full-width at high maximum	Degree
M	Mass	mg

λ	Wavelength	nm
θ	Diffraction angle	Degree

1.1 History of Nanomaterial

New and improved products are produced for numerous applications. Physicist Richard Feynman [1] introduced the concept of nanotechnology in 1959 in his talk “There’s Plenty of Room at the Bottom.” ‘Nano science’, is a combination of Nano, meaning “dwarf” and the word science. Nanometer refers to 10^{-9} or one billionth of a meter. For comparison, a human hair is 100,000 nm thick. Nano science deals with the science of materials and technologies in the scale range of 1-100 nm. That means the nano science deals with a few hundred to a few thousand atoms or atomic clusters, whereas microscopic world is made out of trillions of atoms or molecules. Nanoparticles are larger than individual atom and molecules, but are smaller than bulk solid; hence they obey neither absolute quantum chemistry nor laws of classical physics and have properties that are different from those expected. [2]. Properties not seen on a macroscopic scale are now becoming important on Nano scale such as – quantum mechanics, optics, magnetism, surface reactivity, and thermodynamics. The Nano scale is that materials that can have different properties at the Nano scale – some are better at conducting electricity or heat, some are stronger, some have different magnetic properties, some reflect light better or change colors as their size is changed [3].

1-D nanostructures are confined in two spatial directions e.g., nanowires, nanotubes etc.

0-D nanostructures are confined in all three spatial directions e.g., nanoparticles, quantum dots etc.

1.2 Nanoparticles:

Nanoparticles are of great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures. A bulk material should have constant physical properties regardless of its size, but at the nano-scale this is often not the same. Size-dependent properties are observed such as quantum confinement in semiconductor particles and surface plasmon resonance (SPR) in some metal particles [5]. The properties of materials changed as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant. For bulk materials larger than one micrometer the percentage of atoms at the surface is minuscule relative to the total number of atoms of the material.

The interesting and sometimes unexpected properties of nanoparticles are partially due to the aspects of the surface of the material dominating the properties in comparison with the bulk properties. Nanoparticles exhibit a number of special properties relative to bulk material. Nanoparticles have a very high surface area to volume ratio [6]. This provides a tremendous driving force for diffusion, especially at elevated temperatures. The large surface area to volume ratio also reduces the incipient melting temperature of nanoparticles [6]. Moreover nanoparticles have been found to impart some extra properties to various day-to-day products.

1.3 Quantum Confinement:

In any material, substantial variation of fundamental electrical and optical properties with reduced size will be observed when the energy spacing between the electronic levels exceeds the thermal energy kT . In small nanocrystals, the electronic energy levels are confinement of the

electronic wave function to the physical dimensions of the particles. This phenomenon is called quantum confinement and therefore nanocrystals are also referred to as quantum dots [1]. The quantum confinement effect can be observed once the diameter of the particle is of the magnitude as the wavelength of electron wave function. When the materials are so small, their electronic and optical properties deviate substantially from those of bulk materials. A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle [2]. During this state, band gap remains at its original energy due to continuous energy state. However, as the confining dimension decreases and reaches a certain limit, typically in Nano scale, the energy spectrum turns discrete. As a result, band gap becomes size dependent. This ultimately results in a blue shift in optical illumination as the size of the particles decreases. Specifically, the effect describes the phenomenon which results from electrons and electron holes being squeezed into a dimension that approaches a critical quantum measurement, called the exciton Bohr radius. Quantum confinement describes the increase in energy which occurs when the motion of a particle is restricted in one or more dimensions by a potential well. When the confining dimension is large as compared to the wavelength of the particle, the particle behaves as if it were free. As the confining dimension decreases, the particle's energy increases. A quantum dot [9] is a well that confines in all three dimensions such as a small sphere, a quantum wire confines in two dimensions, and quantum well confines in one dimension Figure 1-1

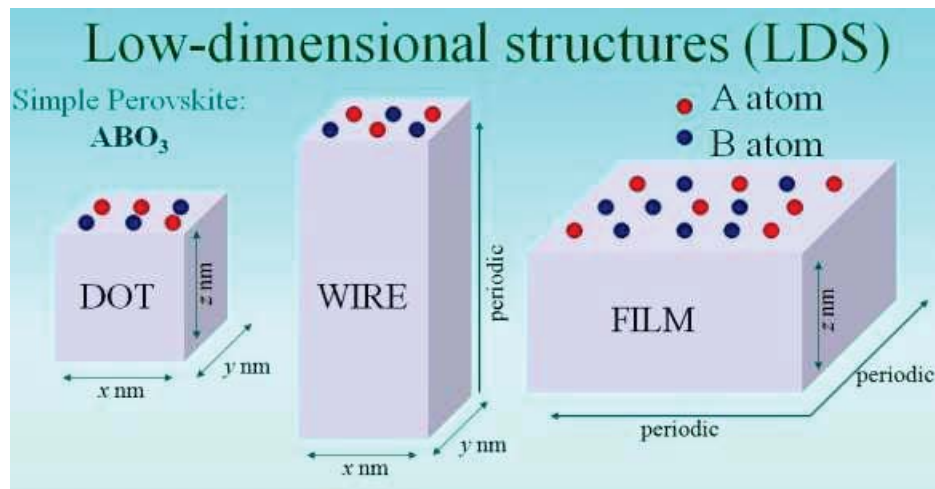


Figure (1-1): Different dimensional structures.[9]

1.4 Literature Review:

- **Ojas Mahapatra et al [2008]** studied \square Copper oxide nanoparticles with particle size ranging from $\square\square 0$ to $1\square 0\square$ nm were prepared by chemical procedure. copper hydroxide was generated as a precursor which was thermally decomposed to $\text{Cu}\square$ nanoparticles . the nanoparticles were tested for antibacterial activity a against *Klebsiell apneumonias* , *pseudomonas aeruginosa* , *salmonella paratyphi* and *shigella* strains \square [10].

- **Guogang Ren et al [2009]** studied \square Copper oxide nanoparticles where characterized and investigated with respect to potential antimicrobial applications . \square was found that nanoscaled $\text{Cu}\square$, generated by thermal plasma technology, transmission electron microscopy \square T $\square\square\square$ demonstrated particle sizes in the range $\square 20\text{--}95\square$ nm. $\text{Cu}\square$ nanoparticle in suspension showed activity a against arange of bacterial pathogens including methicillin- resistant *staphylococcus aureus* $\square\square$ R $\square\square\square$ and *Escherichia coli*, with minimum bactericidal concentrations $\square\square\square$ Cs \square ranging from $\square 100\text{--}5000\square$ $\mu\text{g/ml}$ "[11].

- **O. Akhavan et al [2010]** studied Cu nanoparticles with average diameter of about 20 nm were accumulated on surface of sol-gel silica thin films heat treated at 300 °C in air. Heat treatment of the Cu nanoparticles at 300 °C in a reducing environment resulted in effective reduction of the nanoparticles and penetration of them into the film. While the thin films heat treated at 300 °C exhibited a strong antibacterial activity against *Escherichia coli* bacteria, the reducing process decreased their antibacterial activity. However, by definition of normalized antibacterial activity $\frac{\text{antibacterial activity}}{\text{surface concentration of coppers}}$ it was found that Cu nanoparticles were more toxic to the bacteria than the Cu nanoparticles by a factor of ~ 2.1 . Thus, the lower antibacterial activity of the reduced thin films was assigned to diffusion of the initially accumulated copper-based nanoparticles into the film. The Cu nanoparticles also exhibited a slight photocatalytic activity for inactivation of the bacteria $\sim 22\%$ improvement in their antibacterial activity. Instead, the normalized antibacterial activity of the Cu nanoparticles covered by a thin oxide layer highly increased $\sim 3\%$ improvement in the photocatalytic process. A mechanism was also proposed to describe the better antibacterial activity of the Cu than Cu nanoparticles in dark and under light irradiation.[12]

-**Sunita Jadhav et al [2011]** studied copper oxide nanoparticles were prepared by electrochemical reduction method using tetra butyl ammonium bromide TBA^+ as structure directing agent in an organic medium vis. The nanoparticles were tested for antibacterial activity against human pathogens like *Escherichia coli* (*E. coli*) and *staphylococcus* strains and which was proved to be excellent[13].

-**Yong – Wook Back et al [2011]** studied the microbial toxicities of Copper oxide nanoparticles were evaluated for *Escherichia coli*, *Bacillus subtilis*, and *streptococcus aureus* in laboratory experiments. The metal oxide were dispersed thoroughly in culture medium. The bacteria were counted in terms of colony forming units (CFU). The CFU was reduced in a culture medium containing metal oxide nanoparticles[14].

-**Zhanyu Wang et al [2011]** This is first study investigating the toxicity of nanoparticles (NPs) to algae in the presence of dissolved organic matter (DOM). A type of DOM could significantly increase the toxicity of Cu nanoparticles to prokaryotic alga *microcystis aeruginosa* [15].

-**Azam et al [2012]** studied Cu nanoparticles were synthesized using a gel combustion method. In this approach cupric nitrate trihydrate and citric acid were dissolved in distilled water at a molar ratio of 1:1. XRD spectra confirmed the formation of single phase Cu nanoparticles. A minimum crystallite size of 20 nm was observed in the case of Cu nanoparticles annealed at 300°C. All Cu nanoparticles exhibited inhibitory effects against both Gram-positive and Gram-negative bacteria. The size of the particles was correlated with its antibacterial activity [1].

- **Guy Applerot et al [2012]** studied To date, There is still a lack of definite knowledge regarding the interaction of Cu nanoparticles with bacteria and the possible permeation of the nanoparticles into bacteria cells. This study aimed at shedding light on the size dependent effect from the micro scale down to the small nanoscale antibacterial activity of Cu [1].

-**Azam et al [2012]** studied Nanosized particles of metal oxides were synthesized by sol-gel combustion route. The particles size were observed to be 12, 22, 20 nm for Zn, Cu and Fe₂O₃ respectively. We use these nanomaterials to evaluate their antibacterial activity against both Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) and Gram-positive (*Staphylococcus aureus* and *Bacillus subtilis*) bacteria [1].

- **R. Sathyamoorthy et al [2013]** studied Hierarchical CuO micropeony was synthesized by an environmentally benign reflux condensation approach without using any surfactant or templates. X-

ray diffraction (XRD) analysis revealed the formation of CuO exhibiting monoclinic crystal structure. Fourier transform infrared spectroscopy (FTIR) further confirmed the formation of single phase CuO. Scanning electron microscopy (SEM) analysis showed that the hierarchical CuO architecture is composed of numerous interpenetrating nanosheets that radiated from the center to form floral pattern with a diameter of 1–2 μm . Photoluminescence (PL) spectra of CuO exhibited both UV and visible emissions. The photocatalytic activity of hierarchical CuO microsphere was evaluated by monitoring the photodegradation of methyl orange dye while the antibacterial activity was studied against gram-positive and gram-negative bacteria's. Results demonstrated that CuO hierarchical architecture possesses good photocatalytic as well as antibacterial activity.. [19].

- **Rajeshwari Sivaraj et al [2014]** studied Copper oxide nanoparticles were synthesized by biological method using aqueous extract of *Acalypha indica* leaf and characterized by UV–visible spectroscopy, XRD, FT-IR, SEM TEM and EDX analysis. The synthesised particles were highly stable, spherical and particle size was in the range of 26–30 nm. The antimicrobial activity of *A. indica* mediated copper oxide nanoparticles was tested against selected pathogens. Copper oxide nanoparticles showed efficient antibacterial and antifungal effect against *Escherichia coli*, *Pseudomonas fluorescens* and *Candida albicans*. The cytotoxicity activity of *A. indica* mediated copper nanoparticles was evaluated by MTT assay against MCF-7 breast cancer cell lines and confirmed that copper oxide nanoparticles have cytotoxicity activity [20].

- **Mehdi Yadollahi et al [2015]** studied carboxymethyl cellulose/CuO nanocomposite hydrogels have been synthesized through the in situ

formation of CuO nanoparticles within swollen carboxymethyl cellulose hydrogels. The aim of the study was to investigate whether these hydrogels have the potential to be used in antibacterial applications. The formation of CuO nanoparticles in the hydrogels was confirmed using X-ray diffraction and scanning electron microscopy studies. In addition, swelling behavior of nanocomposite hydrogels was investigated in various pH values and salt solutions. Furthermore, the CuO nanocomposite hydrogels were tested for antibacterial activities. The antibacterial activity of the nanocomposite hydrogels was studied by inhibition zone method against *Escherichia coli* and *Staphylococcus aureus*. The nanocomposite hydrogels demonstrated excellent antibacterial effects. Therefore, the developed carboxymethyl cellulose/CuO nanocomposite hydrogels can be used effectively for biomedical application". [21].

- **Manyasree D. et al [2017]** In the present study copper oxide (CuO) nanoparticles were synthesized and characterized. The antibacterial activity of CuO nanoparticles was carried out against *Escherichia coli*, *Proteus vulgaris*, *Staphylococcus aureus* and *Streptococcus mutans*. The synthesis was carried out by coprecipitation method using copper sulfate and sodium hydroxide as precursors. The average crystallite size of CuO nanoparticles was found to be 19 nm by X-ray diffraction. FT-IR spectrum exhibited vibrational modes at 320 cm⁻¹, 511 cm⁻¹ and 611 cm⁻¹ were assigned for Cu-O stretching vibration. According to UV-Vis spectrum, two bands were observed at 402 nm and 422 nm. ED's spectrum shows only elemental copper (Cu) and oxide (O) and no other elemental impurity was observed. The antimicrobial assay revealed that *Proteus vulgaris* showed a maximum zone of inhibition (3 mm) at 50 mg/ml concentration of CuO nanoparticles [22].

- **Trifa Sheikhaighaiy et al [2018]** studied [1] Given the gradual development of drug resistance in different bacterial species, it is necessary to search for new drugs with effective broad-spectrum antimicrobial activity. Therefore, recent studies on various Nano metal oxides such as copper oxide and on antibacterial peptides including nisin as antibacterial agents are especially important. The present study aimed to investigate the synergistic effect of nisin conjugated copper oxide nanoparticles [Cu²⁺ NPs] on the genome of *E. coli* selected as a Gram-negative model. After being cultured in a Nutrient Broth medium, the bacteria were treated with Cu²⁺ NPs at 15,30, 40, and 60µg/mL, with nisin at 30, 60, 90, and 120µg/mL, and with nisin-conjugated Cu²⁺ NPs at 10, 20, and 30µg/mL and were then incubated. The optical densities of the samples were read at 600nm and their DN₆₀₀ was extracted. R²PD-PCR was used to study genomic effects, and statistical analysis was performed employing NT-D-PC based on the D_C coefficient, the similarity matrix, and the drawn diagram. Results showed that the combination of Cu²⁺ NPs and nisin had synergistic effects and was able to inhibit growth more than either of them used alone. However, this combination had no synergistic effects on the genome and caused minimal changes in the DN₆₀₀ sequence [23].

- **P. Siriphannon et al [2018]** studied [2] Chitosan-Cu²⁺ nanocomposites [Chi-Cu²⁺] were prepared by facile and eco-friendly technique. The 2% w/v chitosan solution was mixed with 0.5 % w/v sodium tripoly phosphate [TPP] resulting in the formation of ionically cross linked chitosan. The cross linked chitosan was soaked in an aqueous solution containing 0.001, 0.01 or 0.1 mol/L CuSO₄•5H₂O for 24 hrs, in which the Cu²⁺ ions were absorbed into the chitosan network, forming as the chitosan-Cu²⁺ precursors. The chitosan-Cu²⁺ precursors were hydrothermally reacted in two different basic media, i.e. NaOH and

N₂, at 100°C for 2 hrs, resulting in the nano-sized Cu₂O crystals hydrothermally grew and embedded in the crosslinked chitosan matrix. The Cu₂O grown in the Na₂CO₃ possessed larger crystallite size and higher crystallinity than that in the N₂. In addition, the Cu₂O crystallite size in the nanocomposites increased with the increase of initial concentration of Cu₂O starting agent due to the increase of Cu₂O quantity in the chitosan-Cu₂O precursors. The chitosan-Cu₂O nanocomposites prepared by using 0.01 and 0.1 mol/L Cu₂O could exhibit the antibacterial activities after intimate contact with *Staphylococcus aureus* and *Escherichia coli* under ISO 1902:1994 qualitative test method, indicating their potential use as biocontrol agents [24].

- **Nereyda Nino-Martinez et al [2019]** The increase in bacterial resistance to one or several antibiotics has become a global health problem. Recently, nanomaterials have become a tool against multidrug-resistant bacteria. The metal and metal oxide nanoparticles are one of the most studied nanomaterials against multidrug-resistant bacteria. Several in vitro studies report that metal nanoparticles have antimicrobial properties against a broad spectrum of bacterial species. However, until recently, the bacterial resistance mechanisms to the bactericidal action of the nanoparticles had not been investigated. Some of the recently reported resistance mechanisms include electrostatic repulsion, ion pumps, expression of extra cellular matrices, and the adaptation of biofilms and mutations. The objective of this review is to summarize the recent findings regarding the mechanisms used by bacteria to counteract the antimicrobial of nanoparticles. [25].

1.5 Aim Of This Work :

The surface plasmon resonance (SPR) for Cu nanoparticles within high surface energy by using sol-gel and hydrothermal methods.

- Investigation the effect of temperature on the size and morphology of Cu nanoparticles .

-The effect of time of annealing on the size and morphology of produced Cu nanoparticles.

-Comparison between results of the effect of nanoparticles prepared by sol-gel and hydrothermal on the bacteria .

Study the effect of Cu nanoparticles on Gram-positive isolate and the Gram-negative isolated.