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Study of synthesis of copper and copper oxide nanoparticles and its applications

A Thesis

"Submitted for the degree of Master of Science as a partial fulfillment for requirements of the master of Science"

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2016

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ACKNOWLEDGEMENT

First of all I would like to thank Allah the almighty for giving me the strength, health and well to do this research.

Words are not enough to describe my deep thanks to ***Prof. Dr. Mostafa M. Khalil,*** *Professor of inorganic chemistry, Faculty of Science, Ain Shams University, for suggesting the program of this work, his guidance and supervision in the course of the work, and for his stimulating criticisms and help in the preparation of the manuscript.*

I would like to express my deep thanks and gratitude to ***Dr. Muhammad Ismael Muhammad Ismael****, Lecturer of Physics Faculty of Science, Port Said University for his invaluable help and support throughout the progress of this work.*

Last but not Least, my thanks are due to my family, especially my husband, for support and encouragement which gave me the strength to finish this work.

Hend Yahya

Aim of the work

In this work, the synthesis of copper using plant extract as stabilizing agents and synthesis of copper oxide nanoparticles by simple precipitation under different preparation conditions such as temperature, precipitation agent and sequence of addition. Structural characterization of the prepared materials using X-ray diffraction (XRD), electron microscopy (TEM, SEM), Uv-visible, and (FTTR) spectroscopy.

Determination some of the physical properties of the copper and copper oxide nanoparticles. Applications of copper nanoparticles as antimicrobial agents will be investigated.

Chapter 1
Introduction

1.1 What Is Nanoparticles?

The prefix nano- is derived from the Greek word *νάνος* or the latin word *nannus*, both meaning dwarf.It is used as an official SI unit of distance of one-billionth of a meter or length 10^{-9}**. (NPS)** are solid particles which have all three external dimension at the nano scale**,**it show large surface area to volume ratio**, Ahmed et.al(2011)**. A bulk material have constant properties regardless of its size, but at the nano-scale size dependent properties are often observed sothey have drastic modification of physico-chemical properties contrast to bulk materials.It can demonstrate actions depending on shape,size,biological actions and chemical composition so they are considered a bridge between bulk material and atomic or molecular structure.Nano-scale particles often have very different physical (e.g. melting point, hardness), chemical (e.g.reaction rates, reactivity), electrical (e.g. conductivity) and optical (e.g. transparency, color) properties from that of bulk particles at the same substance. **Figure (1)** shows some common objects in nano meters size**.** **Nanomaterials** have at least one external dimension and its size range from (1-100) nanometers**.** Particle size has effect

on three important group of basic properties in any material. The first one called cell parameters or structural characteristics (lattice symmetry).Bulk oxides have well defined crystallographic structures of stable system. But, thermodynamic stability changes due to decrease particle size that can induce modification of cell parameters and/or structural transformations. In extreme cases, the nanoparticle can disappear due to high surface free energy and interactions with its surrounding environment. It must have a low surface free energy to display structural or mechanical stability because phases which have low stability in bulk materials can become very stable in nanostructures.

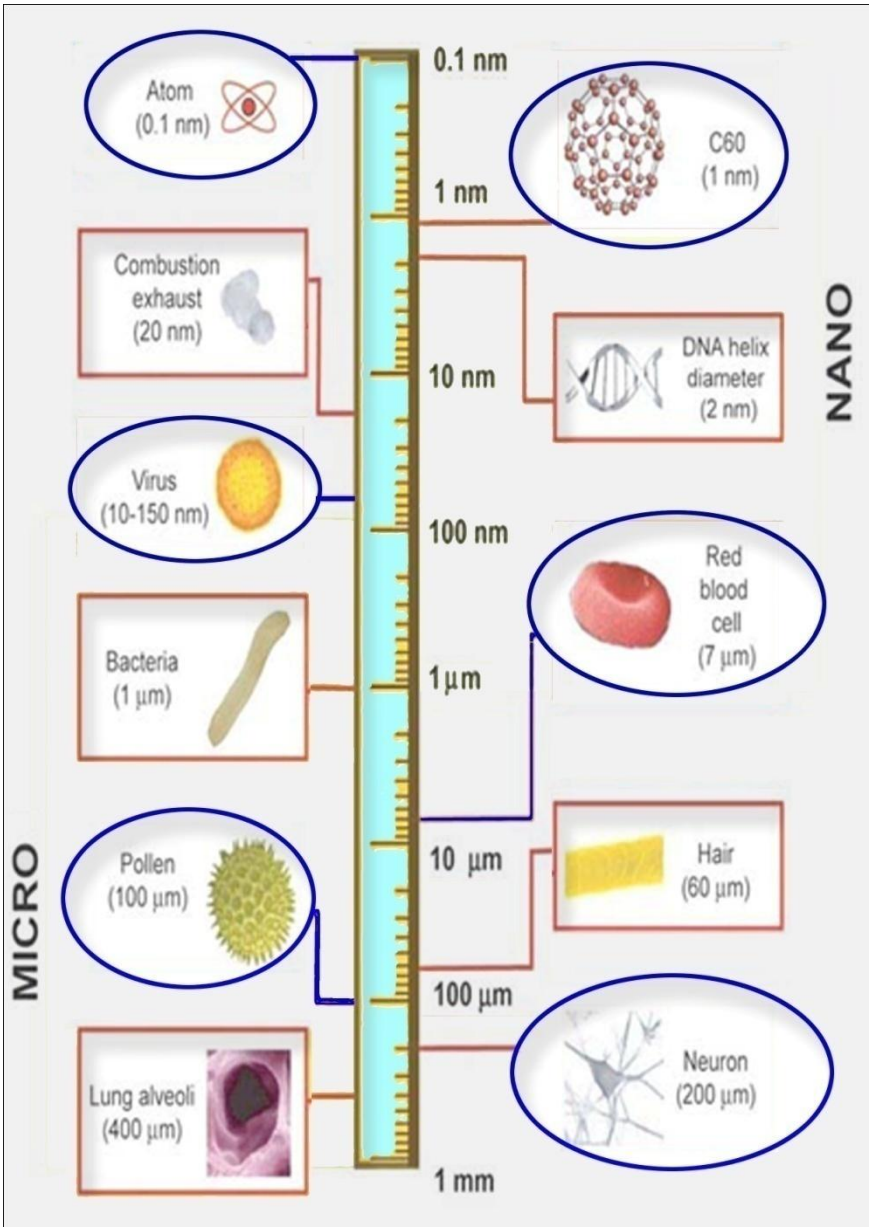

Fig.1.1 some common objects in nanometer

1.2Classification of nanomaterials: Nanomaterials can be classified by different methods according to dimensions,

phase composition, manufacturing process and their structural configuration.

1.2.1 Nanomaterials can be broadly classified into four categories: 0D, 1D, 2D and 3D **(Pokropivny and Skorokhod,2007)** according to dimensions:

a. Zero dimensional nanostructure: materials with nanostructure all its dimensions are only nanometers wideor none of its dimensions are larger than a few nanometers (e.g. Spheres and Clusters etc.)

b. One dimensional nanostructure: materials with nanostructures have only one dimension larger than the other two nanodimensions. Examples of such as structure include chains or bundles of molecules or polymers. (e.g.coatings, film, multilayer's , etc.)

c. Two dimensional nanostructure: materials with nanostructures that have two dimensions which are larger than the third nanodimension.Such as films of nanomaterials which have few nanometers in thickness, but much larger widths and lengths. (e.g.Fibers,Tubes, Platelets,Wires, etc.)

d.Three dimensional nanostructures:3Dmaterials with nanostructures which none of its dimension may be in the nanorange, they take honey comb-like structures or a matrix of particles formed by the aggregation of

nanoparticles.(e.g. Particles, QuantumDots, Hollow Spheres etc.)

1.2.2 Nanomaterials are also classified according to phase composition as:

a.Single Phase Solids (e.g.amorphous particles ,crystalline and layers etc.)

b.Multi-Phase Solids (e.g.coated particles, matrix composits etc.)

c.Multi-phase Systems (e.g.aerogels,colloids ,ferro fluids etc.)

1.2.3 Nanomaterials are classified according to manufacturing process into:

a.Gas phase reaction

(e.g.condensation,flamesynthesis,CVD etc.)

b.Liquid phase reaction

(e.g.precipitation, sol-gel, hydrothermal processing etc.)

c.Mechanical procedures

(e.g.plastic deformation, ball milling etc.)**(Sharma and Bhargava, 2013)**

1.2.4 Nanomaterials can also classified according to structural configuration into:

a.metal-based materials: materials which have metal as main component of this particle include nanosilver, nanogold and metal oxides(e.g titanium dioxide and quantum dots)

b.carbon-based materials: nanomaterials which composed mostly of carbon, taking form of a hollow spheres,ellipsoids,or tubes. Spherical and ellipsoidal carbon nanomaterials called fullerenes, but cylindrical carbon nanomaterials called nanotubes.

c.Dendrimers: nanomaterials are nanosized polymers built from branched units.The surface of a dendrimer has numerous chain ends,which perform specific chemical functions which be useful for catalysis and also used for drug delivery because this structure has interior cavities in which other molecules can be placed.

d.Composites: nanomaterials called bulk-type materials because nanoparticles combine with other nanoparticles or with larger.

1.3. Metallic Nanoparticles: The term metal nanoparticles is used to describe nano sized metals with dimensions (width , length or thickness) within the size range 1-100 nm.

In recent years**,** scientists become interested in discovering of different methods of synthesis of metal nanoparticles because oftheir special properties and potential applications. It is mainly noble metals, **(Lu et al. 2009, Zheng et al. 2007, Dotzauer et al. 2009, Singh and**

Raykar 2008). It has grabbed exceptional attention due to their catalytic, thermal, anomalous optical **(Krolikowska et al., 2003 and Huang et al.,2007),**chemical **(Kumar et al., 2003**), photo electrochemical **(Chandrasekharan and Kamat, 2000)**, magnetic **(Alivisatos, 1996,Coulthard et al., 1998)** and electronic **(Peto et al., 2002,Ekinci et al. 2008)** properties.They are used in many applications for benefit of humans such as biomedical applications **(Arunachalam and Annamalai, 2013),** cancer therapy **(Tzeng and Green, 2013)**, drug delivery **(Ganeshkumar et al., 2013, Khan et al., 2014)**, Anti-metastatic **(Karuppaiya et al., 2013)**, theranostic applications **(Ahmed et al., 2012),** degradation of organic pollutants **(Cheng et al., 2013)**, bioremediation systems **(da osta et al., 2013)** , colorimetric sensor **(Barman et al., 2013), (Xia et al., 2013),** catalysis **(Paul et al., 2014, Cortie and vanderLingen, 2002, Mancin et al., 2013, Mandal et al., 2013),** optical applications **(Murphy et al., 2005)**, agriculture **(Mishra and Singh, 2015),** cosmetics **(Kokura et al.,2010),** biodiesel production **(Verma et al., 2013),** bioimaging, biosensing **(Selvan et al., 2010)**, antimicrobial**,** antioxidant and cytotoxic activities **(Reddy et al. 2014).** It also used inbiological system because many proteins are tenth of nm in size.Its structures can be accurately designed

on the nanometer scale**(Eustis and El-Sayed, 2006; Rosi and Mirkin, 2005; Shenhar and Rotello, 2003; Katz and Willner, 2004; Mody et al., 2009).**

Among these nanomaterials, the most important nanomaterials such as(Cu,Ag,Au,Pt, ……..).

Copperhas face centered cube (F.C.C)crystal structure with atomic weight 63,54 and atomic number 29 so it occupies the first position of subgroup IB also include Ag and Au.Because of the atomic and electron structure of copper,It shares many characteristics with these other nobelmetals. It has very high thermal and electrical conductivity.Pure Cu is very soft and malleable.

1.4.Copper-based nanoparticles have great interest because of low cost, availability and properties possessed are similar to that of other metallic Nps. They represent an ideal compromise between cost and interesting properties so they become an industrially important material. It consider most widely used material in the world because It finds applications in heat transfer systems as super strong materials which there is an innovative technique for improving heat transfer by using ultra-fine solid particles dispersed in the base fluids because nanoparticles prevent the sedimentation**(Liu et al. 2006; Nada et al. 2008)**., It can give more yields and reaction rate

in mild reaction conditions when compared to other traditional catalysts and due to their electrical,optical **(Tanabe 2007)** and magnetic devices **(Gritaonandia et al. 2008),**biomedical and antifungal and antibacterial applications **(Kim et al. 2006),** so used to coat hospital equipments. It also used in catalysis **(Son et al. 2004, Sarkar et al. 2008, Haq and Raval 2007)**,sensors and used in environmental remediation **(Liu et al. 2007).** Moreover, Copper nanoparticles in the colloidal form (nanofluids) have many new applications and advantages such as they have used as better coolants than conventional particles (microscale) because they have extraordinary thermal conductivity and they avoid any increase in pressure drop in the flow field **(Daungthongsuk and Wongwises 2007).**They are also used as an antifriction liquid in motor oil that permits less wear among motor metal components **(Yu et al. 2008),** although the lubricating power could be assured by aperfect particle dispersion.Copper nanoparticles are very reactive because of high surface to volume ratio, which allows them to interact with other particles and increase their antimicrobial efficiency so they have antimicrobial activity and act as antimicrobial agent in various fields.

It has ahigh toxic effect on microorganismssuch as bacteria**(***Pseudomonas aeruginosa , Staphylococcus Aureus,E-Coli***)** and non-toxic effect on animal cells soit is considered to be an effective bactericidal metal. It is safe for human beings such aswater treatment application andfood package application because it is receptive to oxidation a lot of physical and chemical methods have been used to synthesize Cu nanoparticles. The most importan tchemical synthesis of metallic copper nanoparticles is either carried out in organic or aqueous phasedue to avoid the copper potential oxidation. The biosynthesis of pure metallic copper nanoparticles is also important method to synthesis copper nanoparticles and can be carried out in aqueous phase.

1.5 Methods for synthesis of metallic nanoparticles:

The synthesis is considered to be a pivotal point in producing nanoparticles with defined properties. Different methods used in synthesis of metallic nanoparticles. For example, Nano-structured metal colloids have been synthesized by physical or chemical method and any method includes"top-down"and"bottom up" methods.

1. The **'top-down'** methods mean the mechanical grinding of bulk materials then make stabilization of the resulting nanoparticles by the addition of

polymers **(Amulyavichus et al., 1998, Gaffet et al., 1996)**.various physical and chemical treatments for Size reduction.Top down synthesis methods make defect in the surface structure of the product and this is a major restriction because the surface chemistry and the other physical properties of nanoparticles are certified on the surface structure **(Thakkar et al., 2010)**.

The top down synthesis generally depend on physical methods of production as shown in **figs.1.2.** and **fig.1.3.2.**The**'bottom-up'**method of synthesis mostly depend on biological and chemical methods of production as shown in **figures 1.2.** and **figure 1.3.**

2.The wet-chemical 'bottom-up method' of nanoparticle preparation mostly depend on the chemical reduction of metal salts, electro-chemical pathways or the controlled disintegration of metastable organometallic compounds. Various stabilizers such as polymers, donor ligands and surfactants that are used to control the growth of the primarily formed nano-clusters and to prevent them from conglomerate.In practice, the apparatus used by the precursory chemist to control the particle size are size selective separation and size selective synthesis **(Teranishi and Miyake.,1998,Reetz and Maase.,1999)**.