Sudan University of Science and Technology

College of Graduate Studies

Green Synthesis of Silver Nanoparticles Using Cinnamon Extract

التحضير الآمن لجسيمات الفضة النانوية بإستخدام مستخلص القرفة

A dissertation Submitted in Partial Fulfilment for the Requirement of a Master Degree (M. Sc) in Physics

Prepared by:

Alameen Galal Mohamedahmed Alameen

Supervised by:

Dr. Abd Ellateef Abbass

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Dedication

This study is wholeheartedly dedicated to our beloved parents, who have been our source of inspiration and gave us strength when we thought of giving up, who continually provide their moral, spiritual, emotional, and financial support. To my brothers, sisters, relatives, mentor, friends, and classmates who shared their words of advice and encouragement to finish this study. And lastly, thank you my God for the guidance, strength, power of mind, protection and skills and for giving us a healthy life.

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My heartfelt gratitude to all of my teachers upon the long journey of education. During this journey, I was extraordinarily fortunate in having many nice teachers who gave interesting feedback and valuable lessons in different knowledge, as well as overcame many hard times. Without them I would never be able to carry out my studies. I am sorry that no names written, but indeed no one forgotten.

I would also like to thank my parents for their wise counsel and sympathetic ear. You are always there for me. Finally, there are my friends. We were not only able to support each other by deliberating over our problems and findings, but also happily by talking about things other than just our search.

Last but not least, thank you very much, everyone

Alameen Galal

Abstract

Nowadays, noble metals nanoparticles are considered as the promising metals due their fascinating physical properties. Among the noble metals, silver nanoparticles (Ag-NPs) exhibit a sharp and distinct absorption band in the visible region of electromagnetic spectrum associated with localized surface Plasmon resonance. Moreover, Ag NP has high resistance to oxidation and antibacterial activity which make it desirable for a wide range of applications particularly in biomedical sciences. This led researchers to use materials with low toxicity to synthesis silver nanoparticles which is termed green synthesis. In this method, wide range of natural plant extract is used as the reducing agent instead of poisonous materials.

In this work, cinnamon bark extract was used as the reducing agent to synthesize silver nanoparticles using the well known method called Turkevich method. During synthesis, the color was changed after addition of cinnamon bark extract, indicating the formation of silver nanoparticles. UV-Vis spectrometer was further confirmed the formation of silver nanoparticles due appearance of absorption peak in visible region owing to localized surface plasmon resonance. In addition, the effect of cinnamon quantity and boiling time on the formation of silver nanoparticles was investigated. The obtained results showed that the boiling time has significant effect on the particle size while the quantity of cinnamon extract had no effect on the particle size but instead enhanced interaction rate.

المستخلص

في الوقت الحاضر المعادن النبيلة النانويه تعتبر مهمه وواعده بسبب خصائصها الفيزيائيه المميزه ومن تلك المعادن النانويه جسيمات الفضه النانويه (Ag-NPs) والتي تظهر نطاق إمتصاص حاد ومميز في المنطقه المرئيه من الطيف الكهرومغناطيسي المرتبط برنين البلازمون السطحي الموضعي.

بالإضافه لذلك تتمتع جسيمات الفضه النانويه أيضاً بمقاومه عاليه للأكسده والنشاط المضاد للبكتيريا مما يجعلها أكثر ملاءمه للإستخدام في الكثير من التطبيقات خاصة في العلوم الطبيه الحيويه، مما جعل الباحثين يستخدمون طرق ومواد ذات سُمّيه منخفضه لتحضير جسيمات الفضه النانويه والتي يطلق عليها طريقة التحضير الأمن والتي يتم فيها إستخدام مجموعه واسعه من المستخلصات النباتيه الطبيعيه كعامل إختزال بدلاً من المواد السامّه .

في هذا العمل تم إستخدام مستخلص لحاء القرفه كعامل مختزل لتحضير جسيمات الفضه النانويه بإستخدام طريقة Turkevich. أثناء عملية التحضير تغير لون المحلول بعد إضافة مستخلص لحاء القرفه مما يشير إلي تشكل جسيمات الفضه النانويه. وقد تم أيضاً إستخدام مطياف الأشعه فوق البنفسجيه للتأكد من تشكل جسيمات الفضه النانويه، حيث ظهرت ذروة إمتصاص في المنطقه المرئيه بسبب رنين البلازمون السطحي الموضعي. بالإضافه إلي ذلك تمت دراسة تأثير كمية القرفه المضافه وزمن الغليان علي تكوين جسيمات الفضه.

أظهرت النتائج التي تم الحصول عليها علي أن زمن الغليان له تأثير كبير علي حجم الجسيمات بينما كمية مستخلص القرفه لم يكن لها تأثير علي حجم الجسيمات بل عزز من معدل التفاعل.

Keywords and acronyms

Keywords

Cinnamon bark- turkevich method - Localized surface Plasmon resonance (LSPR) - Mie theory-Silver nanoparticles.

Acronyms

SPP: Surface Plasmon Polariton.

LSPs: Localized Surface Plasmon.

LSPR: Localized Surface Plasmon Resonance.

Ag-NPs: Silver Nanoparticles.

UV-VIS: Ultraviolet-Visible Spectroscopy.

MNPs: Metal Nanoparticles

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Chapter 1

Introduction

1.1 Overview

It has been known that the nature has gone through evolution over the 3.8 billion years since life is estimated to have appeared on earth (Bhushan, 2016). Nature consists of many materials, objects, and processes which function from the macroscale to nanoscale. Nanoscale refers to the length scale from 1 nm to 100 nm and sometimes extended to several hundred of nanometers (Yang and Leong, 2010). Actually, there are two research fields associated with the nanoscale, namely nanoscience and nanotechnology. These two fields have become more and more popular in the last 50 years. The nanoscience is defined as field of research that studying and manipulating materials at the nanoscale while the word nanotechnology refers to the field of research that deals with the development of materials and devices by exploiting the properties of particles on the nanoscale. Nanomaterials are an object that has at least one dimension in the nanoscale. One of the most important characteristics of nanomaterials is their small size and large surface area. Due to these special properties, nanomaterials exhibit specific physical and chemical properties which are completely different from their bulk form. As the results, nanomaterials exhibit a wide range of applications in physics, chemistry and biology.

Recently, metal nanoparticles have attracted much attention due to their promising physical properties owing to the localized surface Plasmon resonance (LSPR). LSPR is defined as the collective oscillation of free electrons in metals nanoparticles (Zayats et al., 2005). This phenomenon occurs when metal nanoparticles interact with electromagnetic radiation and results in magnification of electric field near nanoparticles surfaces by two orders of magnitude. The resulted local field is depends on the particle size, size distribution, shape and the dielectric of environments. According to these specific properties, new applications of metals nanoparticles are growing rapidly in all field of scientific research (Nalwa, 2001).

Silver nanoparticles (Ag-NPs) have attracted much attention of researchers from various academic laboratories due to their novel chemical, physical, and biological properties as compared to other metals (Sharma et al., 2009). For examples, Ag-NPs exhibit high thermal and electrical conductivity, catalytic activity, surface-enhanced Raman scattering, chemical stability, and nonlinear optical behavior (Krutyakov et al., 2008). These properties take Ag-NPs to the top of the priority list, to be used in inks, in electronics for medical purpose (Monteiro et al., 2009). Moreover, Ag-NPs are widely used due its antimicrobial properties against microbes such as bacteria, fungi, and virus (Ahamed et al., 2010). Furthermore, due to their proven antimicrobial properties, Ag-NPs are widely used in commercial products, such as plastic, food packaging, and textiles, which have increased their market value to a great extent (Fabrega et al., 2011).

Most applications of Ag-NPs are critically depends on the size and shape of nanoparticles. Therefore, researchers have used different route to synthesis sliver Ag-NPs with various size and shapes. Actually, there are two different methods that have been used to synthesis metal nanoparticles namely physical and chemical methods (Sharma et al., 2009). Examples of the most common physical method are exploding wire technique, plasma, chemical vapor deposition, microwave irradiation, supercritical fluids, sonochemical reduction, Gamma radiation and pulsed laser ablation. On the other hand, the most chemical methods used are chemical reduction of metal salts, microemulsions, thermal decomposition of metal salts and electrochemical synthesis. Among these methods, the most common methods for synthesis of metal NPs is chemical reduction by organic and inorganic reducing agents due to the following advantages: low preparation cost, very fast and yielding NPs without aggregation (Iravani et al., 2014). Recently, the organic and inorganic chemicals that were used as the reducing agent were replaced by natural plants, and termed green synthesis method. This method have attracted much attention due to the following advantages: environment friendly technique, No need to use high pressure and temperature, easy to fabricate, relatively low cost compare to other existing physical or chemical techniques, and does not involve use of harsh toxic solvents (chemicals) in the preparation process.

In this work, silver nanoparticles (Ag-NPs) were synthesized by modified Turkevich method using Cinnamon bark as the reducing agent. The effect of Cinnamon quantity, and boiling time were evaluated to optimize the synthesis method producing Ag-NPs. All samples were characterized at room temperature using UV-Vis spectrophotometer with the aim to confirm the formation of Ag NPs in an aqueous solution.

1.2 Literature review

The words "green synthesis'' has become more and more popular in the last decades. Green synthesis is associated with the used of herbal extracts in synthesis of nanoparticles. Actually there are different sources of plant parts that has been used to synthesis metal nanoparticles. For example N. Vigneshwaran, et.al reported a novel synthesis of Ag-NPs using soluble starch as reducing and stabilizing agent, and the obtained Ag-NPs has found to be stable in aqueous solution over a period of three months at room temperature (Vigneshwaran et al., 2006). In 2010 S. P. Dubeya, et.al, used fruit extract of Tanacetum vulgare (type of plant commonly found in Finland) to prepared both silver and gold nanoparticles (Dubey et al., 2010). Recently, mixing of leaf extract with noble metals salts has been developed as a valuable strategy to prepare metal nanoparticles.

1.3 Problem statement

The Ag-NPs are very important in our life, because they have several applications e.g. medical purposes, agriculture, and industrial. Chemical reduction is the most frequently applied method for the application of nanoscale materials and structures. Usually nanomaterials may provide solutions to technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatment. This increasing demand must be accompanied by green synthesis methods. The global efforts to reduce generated hazardous waste, green chemistry and chemical processes are progressively integrating with modern developments in science and industry. Implementation of these sustainable processes should adopt of green chemistry and these may guided in minimizing the use of unsafe products and maximizing the efficiency of chemical processes. Hence, any synthetic route or chemical process should address these by using environmentally benign solvents and nontoxic chemical. There are several methods to produced Ag-NPs, like chemical approach and physical approach, Green synthesis practices depend on biological materials like plants, algae, and bacteria and alternative of synthetic chemical reducing agents. Several plant parts (stems, bark, roots and leaves) can be subjugated as capping and stabilizing agents in the green synthesis of Ag-NPs.

In this project we used one of methods that called Turkevich method and new material extract (bark cinnamon) to prepare Ag-NPs from silver nitrite aqueous solution and studied the effect of cinnamon extract on the ions of silver in solution.

1.4 Research Objectives

1.4.1 General Objective

The main objective of this work is to synthesis Ag-NPs using Cinnamon bark as the reducing agent.

1.4.2 Specific Objectives

- To synthesis Ag-NPs by modified Turkevich method.
- To use the Cinnamon bark extract as the reducing agent.
- To study the effect of Cinnamon quantity and boiling time on the formation of Ag-NPs.

- To determine the absorption spectra of Ag-NPs by using **UV-Vis** spectrometer in order to confirm the formation of Ag-NPs.

1.5 Dissertation layout

This study composed from five chapters. In chapter one, brief introduction, the aim of this study and the problem statement are expressed. Chapter two focuses on the theoretical background and physical concept of Plasmon types, effects of nanoparticles shape, size, and environmental, application**s** of Ag-NPs**.** Chapter three focuses on the materials, method and characterization techniques. The result and discussions were presented in chapter four. Chapter five focuses on the conclusion, Recommendation, and references.

Chapter 2

Theoretical background

2.1 Overview

Nanotechnology is an important branch of recent research dealing with design, synthesis, and manipulation of particles structure (shape or size) having size between 1-100 nm (Varadan et al., 2008). The rapid growth in this technology has opened novel field of researches and applications, including the synthesis of nanoscale materials and exploration or utilization of their exotic physicochemical and optoelectronic properties.

Nanotechnology is attract much attention particularly in the last fifteen years because it rapidly gaining importance in a number of areas such as health care, cosmetics, food and feed, environmental health, mechanics, optics, biomedical sciences, chemical industries, electronics, space industries, drug-gene delivery, energy science, optoelectronics, catalysis, reorography, single electron transistors, light emitters, nonlinear optical devices, and photoelectrochemical applications (Korbekandi and Iravani, 2012). Nowadays, nanomaterials are seen as solution to many technological and environmental challenges in many fields such as solar energy conversion, catalysis, medicine, and water treatment. In the context of global efforts to reduce hazardous waste, the continuously increasing demand of nanomaterials must be accompanied by green synthesis methods.

2.2 Nanoparticles

In general, nanoparticles can be defined as objects ranging in size from 1-100 nm (Yang and Leong, 2010). This due the fact that in this size regime the physical property of materials becomes size dependent and completely differ from their bulk form. There are several types of nanoparticles like silver, gold nanoparticles and alloy nanoparticles and Magnetic nanoparticles like Fe_3O_4 (magnetite) and Fe_2O_3 (maghemite) etc. Nanoparticles possess a variety of shapes and their names are characterized by their different shapes. For example, there are nano-spheres that are spherical, nano-reefs, nano-boxes, nanoclusters, nanotubes etc (Buzea et al., 2007). These shapes or morphologies sometimes arise spontaneously as an effect of a templating or directing agent during synthesis. For example during miscellar emulsions or anodized alumina pores.

2.3 Synthesis of metals nanoparticles

In general, synthesis of metal nanoparticles (MNPs) is categorized into two approaches namely, top-down approach or bottom-up approach (see Fig. 2.1 right hand side) (Murphy, 2002). The Top-down approach involves a process of breaking down of large structure to create small structure. Physical techniques such as lithography (Tapasztó et al., 2008), laser ablation, sputtering deposition, pulsed electrochemical etching, and vapor deposition are most commonly used in this approach. Bottom-up approach is refers to the buildup of a materials from the bottom atom by atom, or molecule by molecule (see Fig. 2.1 left hand side). The most common methods used the bottom-up approach are sol-gel processing , chemical vapor deposition , plasma or flame spraying synthesis, laser pyrolysis, and micro emulsion.

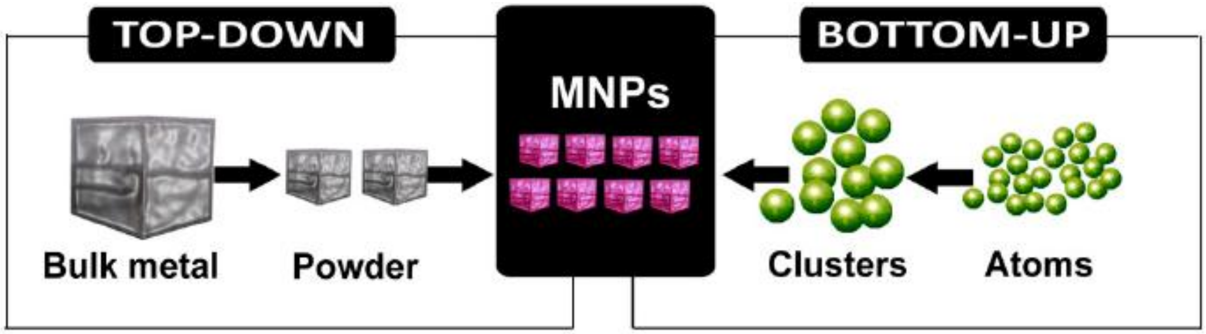


Fig. 2.1. Schematic diagram explaining chemical and physical methods that used to synthesis nanomaterials.

2.4 Silver nanoparticles

Ag-NPs are of interest because of their unique properties like optical, electrical, and thermal properties (Sharma et al., 2009). Ag-NPs are being incorporated into products that range from photovoltaics to biological and chemical sensors. Examples include conductive inks, pastes and fillers which utilize Ag-NPs for their high electrical conductivity, stability, and low sintering temperatures. Additional applications include molecular diagnostics and photonic devices, which take advantage of the novel optical properties of these nanomaterials. An increasingly common application is the use of Ag-NPs for antimicrobial, coatings, and many textiles, keyboards, wound dressings, and biomedical devices now contain Ag-NPs that continuously release a low level of silver ions to provide protection against bacteria.

2.5 Plasmon

Plasmon is defined as the collective oscillations of the free electrons in the conduction band of metals due to existence of an internal electric field. According to the dimensions of metal there are two main types of Plasmon namely bulk Plasmon **(**three dimensions (**3D)**, surface Plasmon **(**two or one dimension (**2D** or **1D**)**)**. Section 2.5.1 and section 2.5.2 will give details about these types.

2.5.1 Bulk Plasmon

This mode of Plasmon occurs only in bulk metals. When an external field is applied to a given metal, the free electrons will make longitudinal oscillations through the metal. These oscillations occur at certain frequency called plasma frequency $\boldsymbol{\omega_p}$ and is given by following equation (Borys, 2011).

$$\boldsymbol{\omega_p = \sqrt{\frac{n e^2}{\varepsilon_0 m}}} \qquad \textbf{(2.1)}$$

Where **n** is the electrons density, **e** is charge of electron and **m** is mass of electron and $\boldsymbol{\varepsilon_0}$ is the permittivity of free space. Bulk Plasmon cannot be excited by photon due to missmatching between longitudinal oscillation of free electrons in metals and transverse oscillation of light. Thus Instead of photon, electrons beam can be used to excite the bulk Plasmon (Amendola et al., 2017).

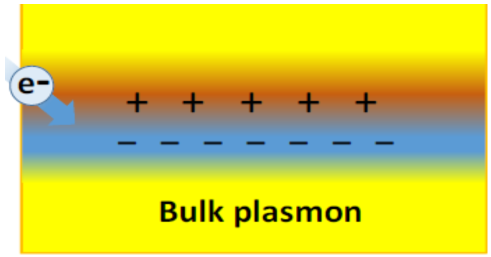


Fig.2.2 Schematic diagram illustrating Bulk Plasmon(Amendola et al., 2010).

2.5.2 Surface Plasmon resonance

Plasmon resonance is an optical phenomenon arising from the collective oscillation of conductive electrons in a metal when the electrons are disturbed from their equilibrium positions (Lu et al., 2009). Such a disturbance can be induced by an electromagnetic wave (light), in which the free electrons of a metal are driven by the alternating electric field to coherently oscillate at a resonant relative to the lattice of positive ions.

Actually, there are two modes of surface Plasmon, the first mode called surface Plasmon polariton (**SPPs**), and the second mode called localized surface Plasmon (**LSPs**) (Stewart et al., 2008). The following sections will give details about these modes.

2.5.2.1 Surface Plasmon Polariton (SPP)

This mode of Plasmon occurs only at the interface between metal and dielectric (2D structure) such as thin film (see Fig.2.3). Once the **SPP** is excited, it propagates between the thin metal and dielectric material a few nanometer before absorbed by metal or scattered in other directions. It is important to note that in order to excite the **SPP,** the momentum of incident light must be matched with the momentum of surface Plasmon. Actually, prism is commonly used to manipulating the momentum of photon.

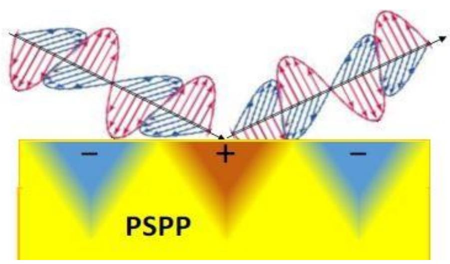


Fig. 2.3 Schematic diagrams illustrating SPP (Amendola et al., 2010)**.**

2.5.2.2 Localized surface Plasmon (LSPs)

This mode occurs in metal particles whose size is lower than the wavelength of incidence light.

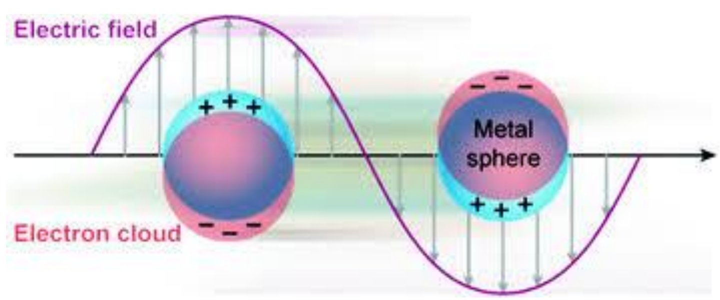


Fig. 2.4 Schematic diagram illustrating localized surface Plasmon (Borys, 2011).

When metal particles exposed by light, the electric field of the incident light induced an electric dipole in the metal particles. Since the charge distribution depends on the electric field orientation, many surface electron moves to one side of the metal particles leaving a net positive charge on the other side.

When the oscillation frequency of electron matches the frequency of incident light, a resonance is setup resulting in strong in absorption band in the visible region of the electromagnetic spectrum. Localized surface Plasmon occurs in silver and gold nanoparticles (1-100 nm) size range and can amplify the electric field of incident electromagnetic radiation near the NPs surface by two orders of magnitude.

2.6 Tuning of the localized surface Plasmon resonance

The position of the absorption band (resonance wave length) of the localized surface Plasmon resonance is playing an important role in its applications. In real fact, the resonance wave length is depends on three different parameters, namely shape and size of nanoparticles as well as the dielectric constant of the environment. Details about these parameters will be given below.

2.6.1 Effect of shape

In addition to size, the specific geometry of **Ag** nanostructure can have a strong effect on its LSPR properties (Cobley et al., 2009). Fig. 5.2 shows extinction spectra for Ag nanostructures with a set of basic geometries (sphere, cube, octahedron, and right bipyramid) calculated using Mie theory (for the sphere) and the DDA method (for other geometries), respectively, together with the spectra acquired experimentally. A number of general themes can be observed. The number of resonances increases as the symmetry of a structure decreases. For example, the spectrum of the cube contains a couple of peaks or shoulders beyond the strong dipole peak near 450nm, whereas the spectrum of the sphere only shows one resonance peak. The additional peaks arise because of the lower symmetry of a cube relative to a sphere, making it possible to polarize the electrons in more than one way.

This trend is also visible in the spectra for the right bipyramid and absorption and scattering, however, other factors like size may play a more prominent role in the magnitude of the scattering and absorption cross sections of a nanoparticle.

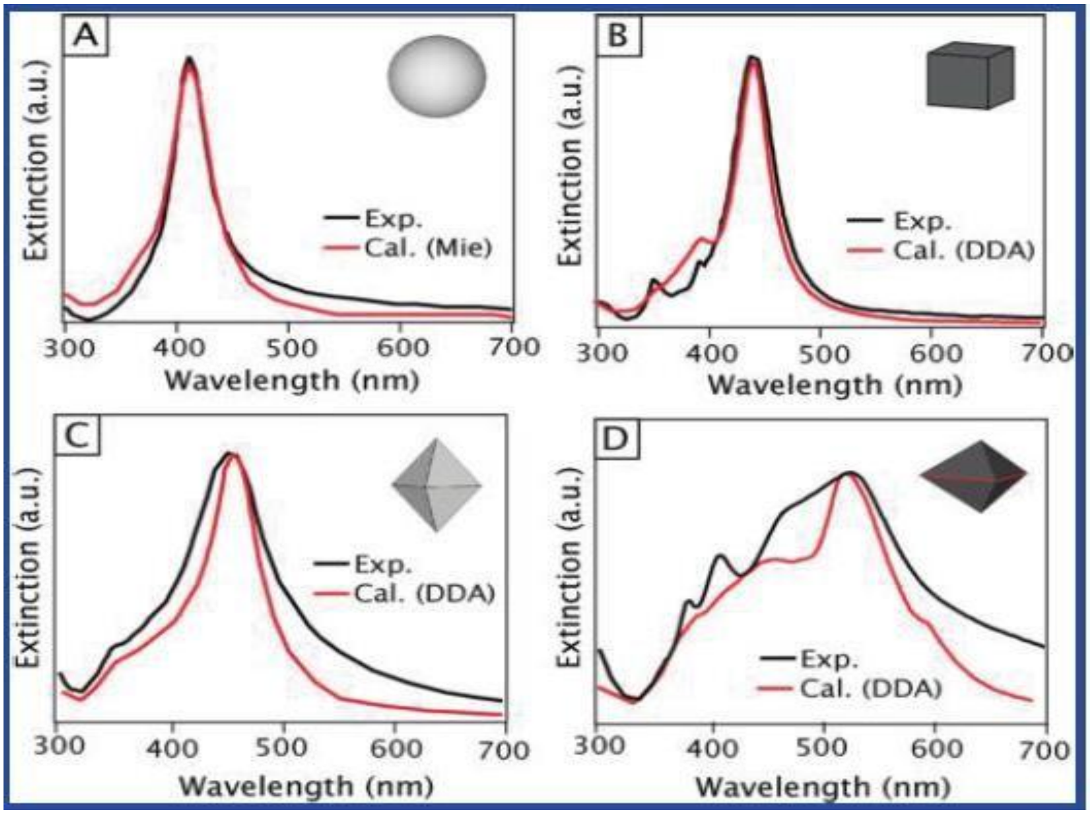


Fig.2.5 shows extinction spectra for Ag with different shapes (Rycenga et al., 2011).

2.6.2 Effect of size

Metal particles in the nanometer size range have gained considerable interest in recent years as they serve as building blocks of next generation Nano devices(Kamat, 2002). Nanoparticles possess unique optical, electrical, and magnetic properties, which are strongly dependent on the size and shape of the particle (Creighton and Eadon, 1991, Cao et al., 2001). The size of a nanoparticle determines Plasmon features that include the ratio of absorption to scattering, the number of LSPR modes, the ratio of absorption to scattering, the number of **LSPR** modes, the peak position of an **LSPR** mode, and the extent of **PSP** localization (Hutter and Fendler, 2004).Therefore, size is an important variable that must be carefully considered to achieve a balance between many competing factors. Fig. 2.6 show in (A) Extinction (black), scattering (green), and absorption (red) spectra of Ag Nano spheres **(A)** 40nm and **(B)** 140nm in diameter calculated using Mie theory in water. The extinction spectrum for the larger spheres **(B)** is dominated by scattering and has a broad shoulder due to contributions from the quadrupole Plasmon modes. The smaller spheres have a narrow LSPR peak, and the absorption and scattering cross sections are nearly equal.

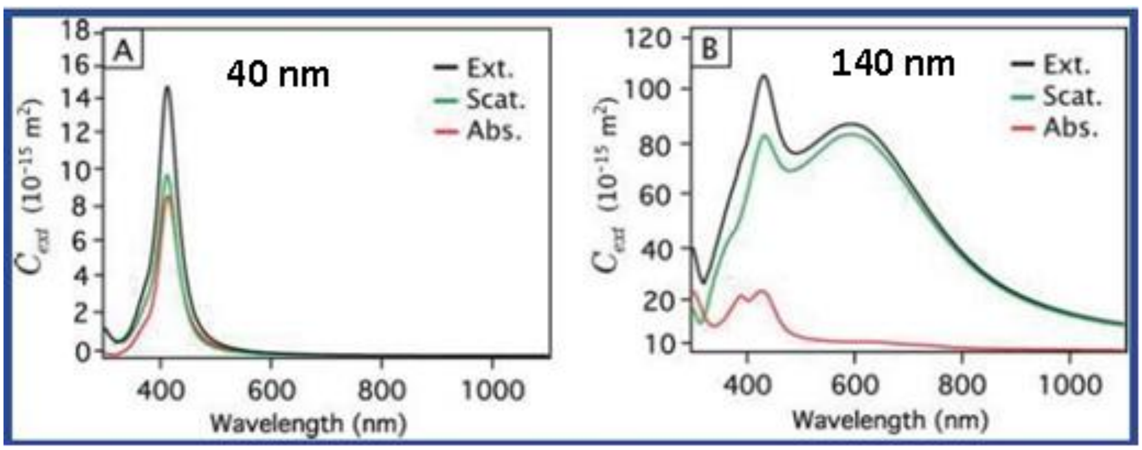


Fig.2.5 shows the absorption, scattering, and extinction spectra of silver Nano sphere with diameter (A) 40 nm and (B) 140 nm (Rycenga et al., 2011).

2.6.3 Effect of dielectric of the environment

The dielectric environment of nanoparticle has a good impact in the localized surface Plasmon resonance **LSPR**. It is plays a role in plasmon shifting effect. An increase in the relative permittivity of the dielectric medium results in a decrease in the restoring force of electron oscillation and therefore shifts the Plasmon resonance towards longer wavelength.

2.7 Applications of silver nanoparticles

Nowadays, Ag-NPs become the most commonly used nanomaterials both in everyday life, and in research laboratories. These nanoparticles are incorporated into many commercial products including clothing, textiles, furniture, and household appliances such as refrigerators, cosmetics, and even children toys (Seltenrich, 2013). The following subsection will give some important application of Ag-NPs.

2.7.1 Applications in medicine

Silver is known for its antimicrobial properties and has been used for years in the medical field for antimicrobial applications and even has shown to prevent HIV binding to host cells (Nino-Martinez et al., 2008). Additionally, silver has been used in water and air filtration to eliminate microorganisms (Chou et al., 2005).

2.7.2 Applications in industrial

The nanoparticles are used in industry as electronics and electrical purposes. Ag-NPs are used as antimicrobial agents in a diverse range of applications, including air sanitizer sprays, socks, pillows, slippers, face masks, wet wipes, detergent, soap, shampoo, toothpaste, air filters, coatings of refrigerators, vacuum cleaners, washing machines, food storage containers, cellular phones.

2.7.3 Scientific Applications

The remarkable physical, chemical and optical properties of silver nanomaterial allows for their utilization in various scientific applications. These properties significantly depend on the size, shape and surface chemistry of the nanomaterial.

Metallic nanoparticles, including nano silver are a promising tool for sensing applications, including detection of DNA sequences (Pastoriza-Santos and Liz-Marzán, 2008). Laser desorption ionization mass spectrometry of peptides (Roduner, 2006). Colorimetric sensors for Histidine, determination of fibrinogens in human plasma. Enhanced IR absorption spectroscopy. Colorimetric sensors for measuring ammonia concentration. Biosensors for detection of herbicides, and glucose sensors for medical diagnostics (Biswas and Dey, 2015).

Chapter 3

Methods and techniques

3.1 Introduction

In this chapter, the experimental method and materials used were described in details. At the end of the chapter, a brief description of the UV-Vis spectrometer used in the characterization of Ag-NPs is presented. The UV-vis spectroscopy was used to determine the absorption band of localized surface plasmon resonance (LSPR) associated with silver nanoparticles.

3.2 Materials and tools

Materials and tools used to synthesis Ag-NPs were:

- Silver nitrate ($AgNO_3$) with purity 99%**.**
- Distilled water and ethanol.
- Beakers and hot plate with magnetic stirrer (see Fig.3.1)
- Cinnamon back (see Fig.3.3 a).

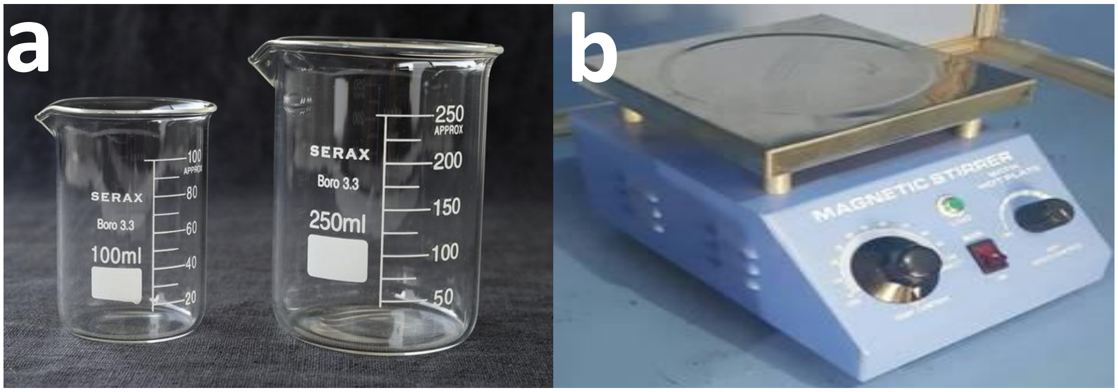


Fig. 3.1 show (a) beakers (b) Magnetic stirrer with hot plate

3.2.1 Silver nitrate

Silver nitrate is an inorganic compound with chemical formula $AgNO_3$. Silver nitrate can be prepared by reacting silver, such as a silver bullion or silver foil, with nitric acid, resulting in silver nitrate, water, and oxides of nitrogen. Reaction by products depends upon the concentration of nitric acid used.

$$3\ Ag + 4\ HNO_3\ \text{(cold and diluted)} \rightarrow 3\ AgNO_3 + 2\ H_2O + NO$$

$$Ag + 2\ HNO_3\ \text{(hot and concentrated)} \rightarrow AgNO_3 + H_2O + NO_2$$

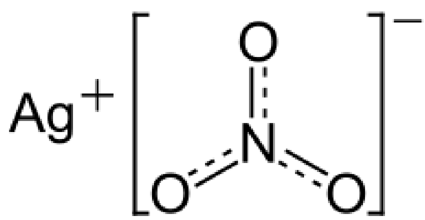


Fig.3.2 The chemical formula of silver nitrate

3.2.2 Cinnamon bark

Cinnamon comes from the bark of trees native to China, India, and Southeast Asia. Cinnamon has a long history of uses particularly in traditional medicine. For example, many ancient societies used cinnamon for bronchitis. The traditional uses include gastrointestinal problems, loss of appetite, and control of diabetes, as well as a variety of other uses. Cinnamon bark is commonly used as powders or liquid extracts. Although there are many kinds of cinnamon, cassia cinnamon (also known as Chinese cinnamon) is the most familiar type. Cinnamon consists of a variety of compounds, including cinnamaldehyde, cinnamate, cinnamic acid, and numerous essential oil (Rao and Gan, 2014).

The most important compound to our work is cinnamaldehyde which will be the focus of this research. It is an organic compound with the chemical formula C_9H_8O belonging to the aldehydes group and known as active ingredient that gives cinnamon the distinctive flavor and aroma. Actually, cinnamaldehyde is the main constituent of cinnamon bark oil, since is exist with ratio of about 65.00 to 80.00% (Rao and Gan, 2014). Since aldehydes groups are readily oxidize, the cinnamaldehyde is considered to be a powerful reducing factor. Therefore, cinnamaldehyde is expected to reduce silver ion (Ag^+) to silver atom (Ag^o). **Fig. 3.3** shows (a) natural cinnamon bark (b) chemical syntax of cinnamaldhyde.

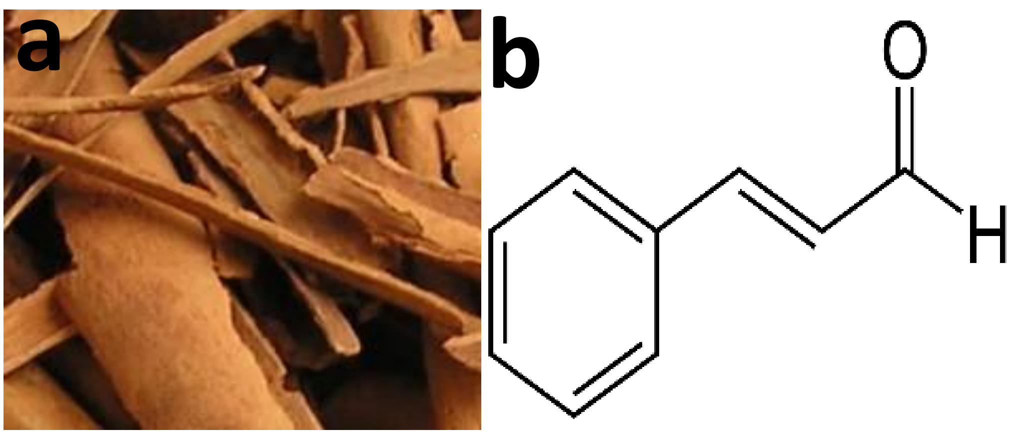


Fig.3.3 show (a) natural cinnamon bark (b) chemical syntax of cinnamaldhyde.

3.3 Experimental procedure to synthesize Ag nanoparticles

Silver nitrate ($AgNO_3$, 99%) was purchased from loba Chemie (india). All glassware was washed with ethanol and distilled water and dried before used. Cinnamon cortex was purchased from Elarabi market of Khartoum. Cinnamon was washed several times with distilled water to remove dust. Cinnamon extract was prepared as follow. 40g of washed cinnamon was added to 200 ml distilled water in beaker and boiled for 10 min. The obtained solution was filtered and stored at low temperature for further use. To optimize the synthesis parameters, different boiling time and cinnamon to silver salt solution ratio were applied. In typical experiment, cinnamon extract with different quantities was added to silver nitrate solution (1mM) in beaker to get different cinnamon to silver nitrate solution ratio (0.5:10, 1:10, 1.5:10 and 2:10). The mixed solution was boiled for 20 Min. In other experiment, the optimum ratio (1.5:10) which showed more pronounced peak with high intensity related to absorption band of LSPR was used to optimize boiling time. Similarly, the mixture of cinnamon and silver nitrate with the ratio of 1.5:10 was boiled at different time (10, 30, 40 and 50 min). In both experiments, after 5 minutes, the color was changed indicating the formation of Ag-NPs. Fig. 3.4 showed the steps of preparation of Ag-NPs

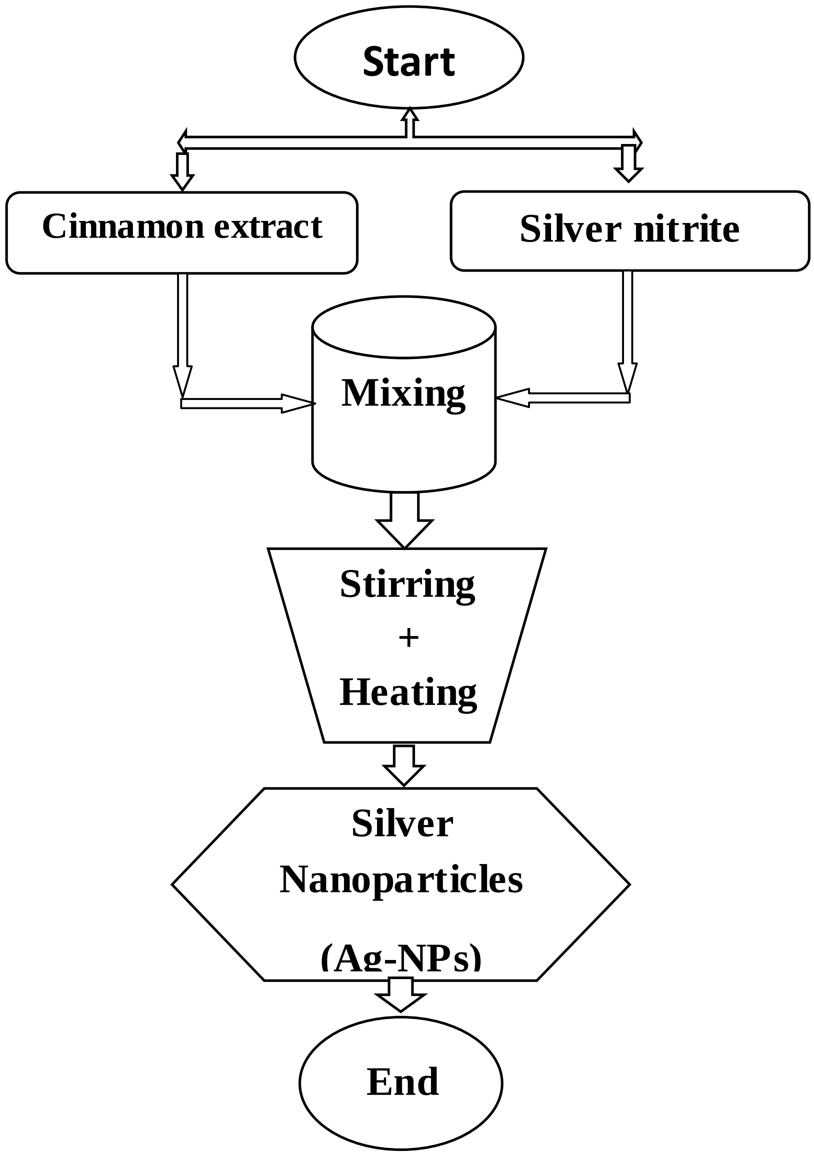


Fig.3.4 Schematic diagram for preparation of silver nanoparticles (in solution) by turkevich method

3.4 Characterization technique

3.4.1 UV-VIS Spectrophotometer

The instrument used in ultraviolet-visible spectroscopy is called a UV-Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample (I_o).The ratio (I/I_o) is called the transmittance. The UV-visible spectrophotometer can also be configured with an integrated sphere to measure reflectance. In this case, the spectrophotometer measures the intensity of light reflected from a sample (I), and compares it to the intensity of light reflected from a reference material (I_o). The ratio (I/I_o) is called the reflectance. In a UV-Vis (ultraviolet-visible light) spectroscopic measurement, light absorption as a function of wavelength provides information about electronic transitions occurring in the material (Förster, 2004). There are two types of UV spectrophotometer (single beam and double beam). In a single beam UV spectrophotometer, all of the light passes through the sample cell (Chen et al., 2013). I_o must be measured by removing the sample. This was the earliest design, but is still in common use in both teaching and industrial labs. In a double-beam UV spectrophotometer, the light is split into two beams before it reaches the sample (see Fig.3.5). One beam is used as the reference and the other beam passes through the sample. The measured UV-vis spectrum can be obtained as absorption, transmission and reflection spectrum. Absorption and transmission apply for gas and solution or transparent glass samples, while reflection applies only for solid samples. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are typically rectangular in shape and commonly with an internal width of 1 cm. Cuvettes are made of high quality fused silica or quartz glass because these are transparent throughout the UV, visible and near infrared regions.

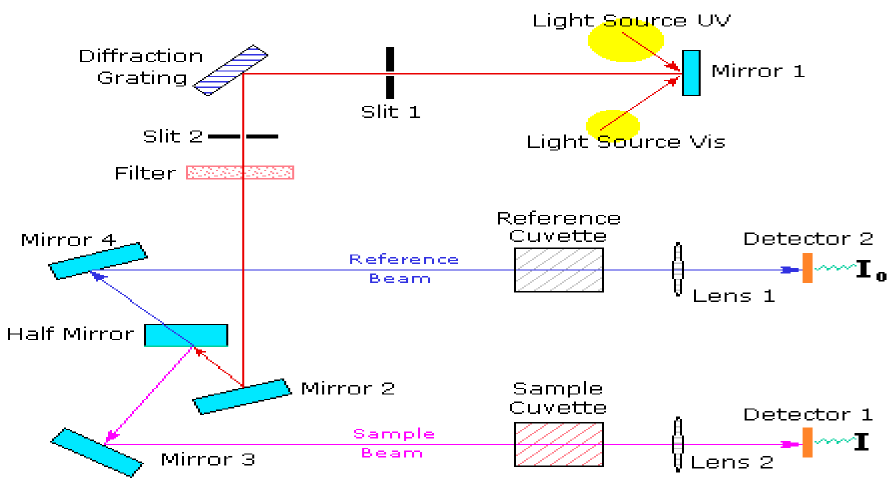


Fig. 3.5 A dual-beam UV-vis spectrophotometer.

Fig. 3.6 UV-vis spectrophotometer.

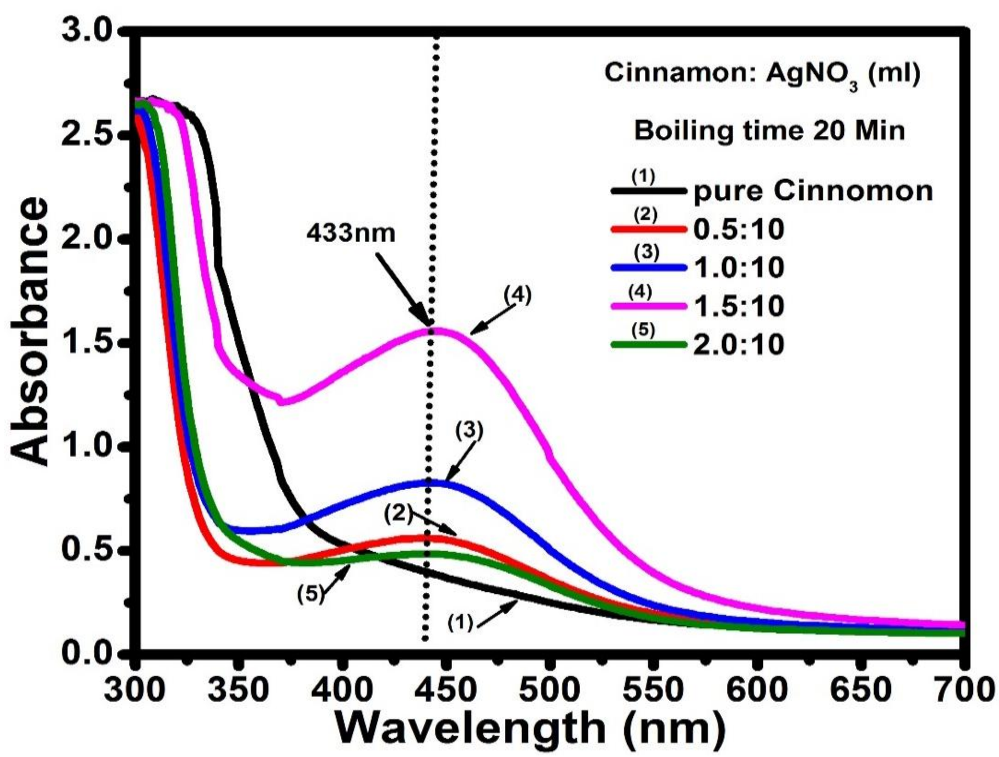
Chapter 4

Result and Discussion

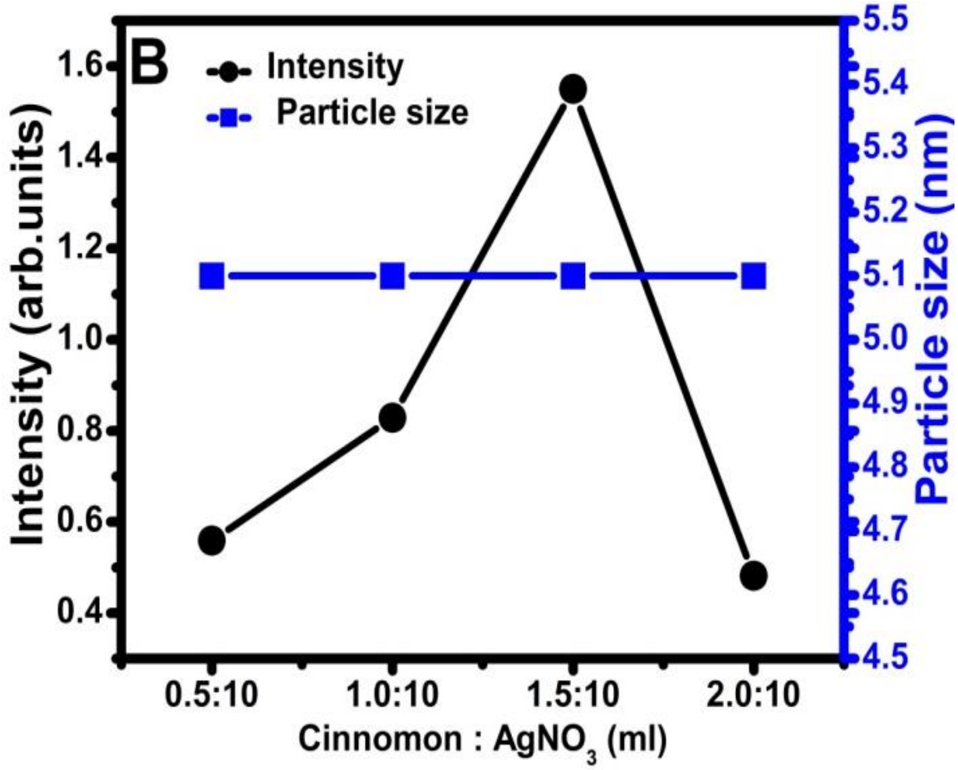
It is well known that for frequencies up to visible light, bulk metals are highly reflective and do not allow electromagnetic radiation to penatrate through them. This is due to the fact that the electrons in metals screen the electric field of the incident light. At high frequencies (Ultraviolet), bulk metals become transparent to electromagnetic radiation (with some degree of attenuation), because the electrons cannot respond fast enough to screen out the electric field of light. These properties will completely be different if the size of metals reduces to nanoscale (Kelly et al., 2003). In general, when the light is expose to a metal particle having size in nanoscale, the oscillating electric field of the light produces a force on the mobile conduction electrons, inducing a dipole moment in the particle. This effect is maximized at resonance frequency, resulting in the phenomenon called localized surface Plasmon resonance (Mayer and Hafner, 2011). This phenomenon occurs in visible-IR regions particularly for noble metals (i.e., Ag, Au), resulting in strong absorption band and changing in color as well. Therefore, the appearance of the absorption band in visible-IR regions will be strong evidence for the formation of metal nanoparticles. Actually, the common technique used for this purpose is UV-Vis spectrometer.

In the present work Ag ion (silver nitrate dissolved in distill water with concentration 1mM) is reduced to Ag-NPs using natural cinnamon bark.

Different boiling time and concentration of cinnamon bark extract were used to optimize the synthesis method (see Fig. 4.1 and 4.2). The first indication of the formation of Ag-NPs was achieved during experimental process which is changes in solution color. When the cinnamon bark extract is added to silver salt solution, the color was changed to pale yellow, yellowish brown and finally to dark brown as a function of boiling time. The change in color of the solution is assigned to the presence of Ag-NPs formed by the reduction of silver salt. In our case, the reducing agent used was Cinnamon bark extract. It was suggested that compound like Cinnamaldehyde may be responsible for reducing Ag salt to Ag-NPs when Cinnamon bark extract is used (Parashar et al., 2009). Further confirmation of the formation of Ag-NPs can be obtained from UV-Vis results (see Fig. 4.1)



(A)



(B)

Fig. 4.1 Shows (a) UV-Vis spectra of pure cinnamon and Ag-NPs produced using different concentration of cinnamon bark. (b) Effect of cinnamon concentration on the intensity of the absorption band and NPs size.

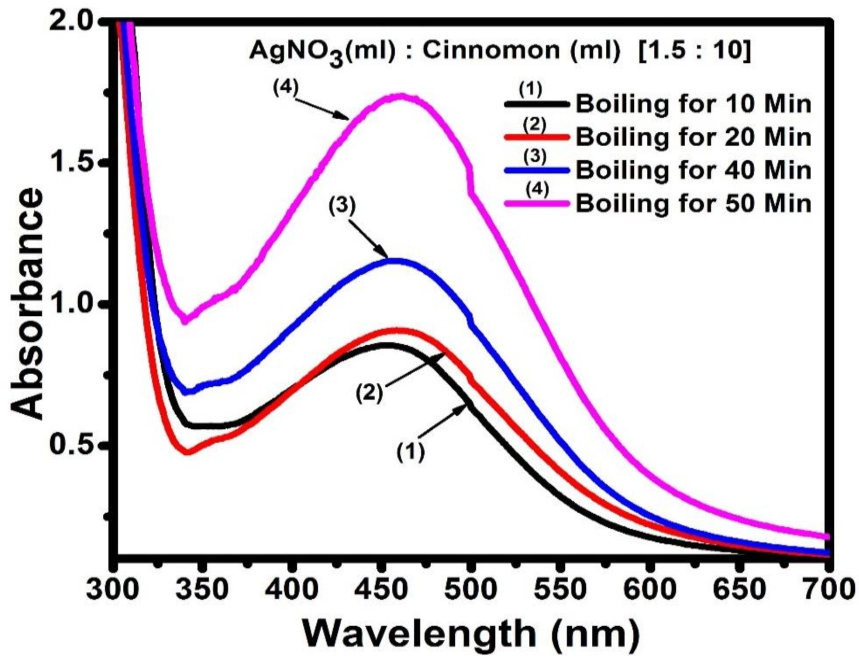
Fig. 4.1A shows absorption spectra for pure cinnamon extract and silver nitrate mixed with different quantity of cinnamon bark extract boiled for 20 minutes. As can be seen from Fig.1A, there is no obvious absorption band was observed for pure cinnamon extract in the visible region. When the cinnamon extract was mixed with silver nitrate, small peak at 433 nm was appeared. This peak is assigned to LSPR absorption band, indicating the formation of Ag-NPs (Pandey et al., 2012). The intensity of this peak is increased with increasing the ratio between cinnamon extract and silver salt solution until the ratio reached 1.5:10 for cinnamon and silver salt, respectively and then the intensity is decreased when the ratio was further increased (see Fig. 4.1B). Of interest is that there is no shift in the peak position for all samples. It has been reported that the appearance of single peak indicating that the NPs is smaller than the mean free path of the conduction electrons (50 nm for Ag) and have spherical shape, since shapes other than sphere produces multiple peaks due to existence of high order modes (see chapter 2, section 2.3.1 and 2.3.2) (Vollmer, 1995). Therefore, in this case the Mie theory can be applied to calculate the size of NPs. According to this theory, there is the relationship between the resonance broadening (γ) and the sizes of nanoparticles (R) given by the following relation.

$$\gamma(R) = \Gamma_0 + \frac{AV_f}{R} \qquad (4.1)$$

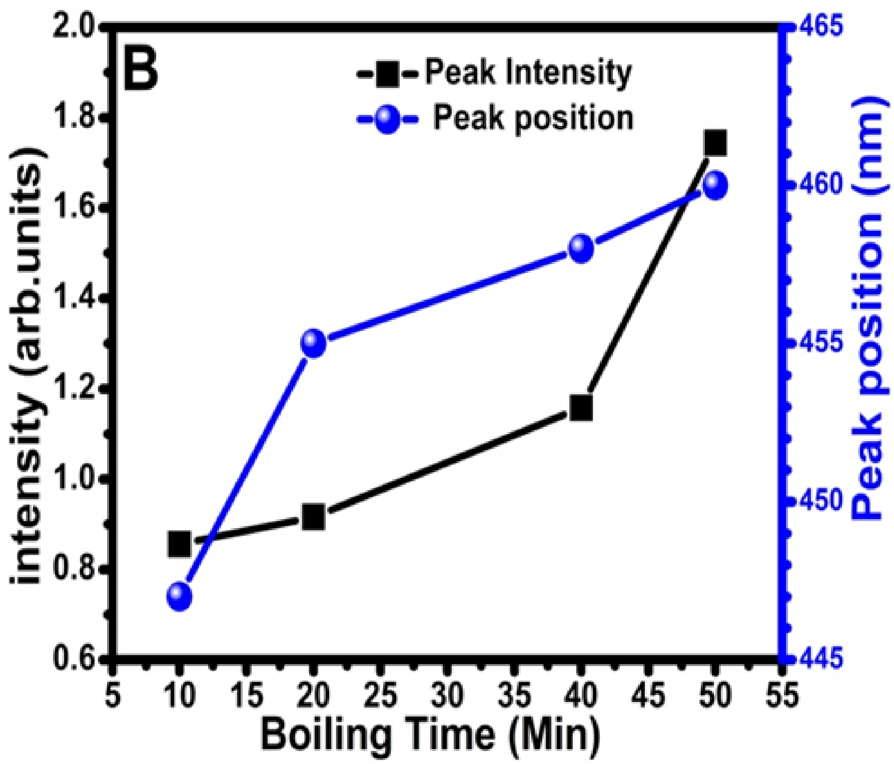
where $\gamma(R)$ is resonance broadening, A is scattering process (3/ 4 in case of Ag), Γ_0 is the velocity of bulk scattering ($5 \times 10^{12} S^{-1}$, for Ag) and V_f is the Fermi velocity (1.4×10^{6}m/s, $for\ Ag$).

Appling equation (4.1), the size of Ag-NPs was found to be 5.1 nm for all samples (see Fig.4.1B), indicating that increasing of the cinnamon extract quantity did not affect the particle size of Ag, but instead enhanced the reaction rate.

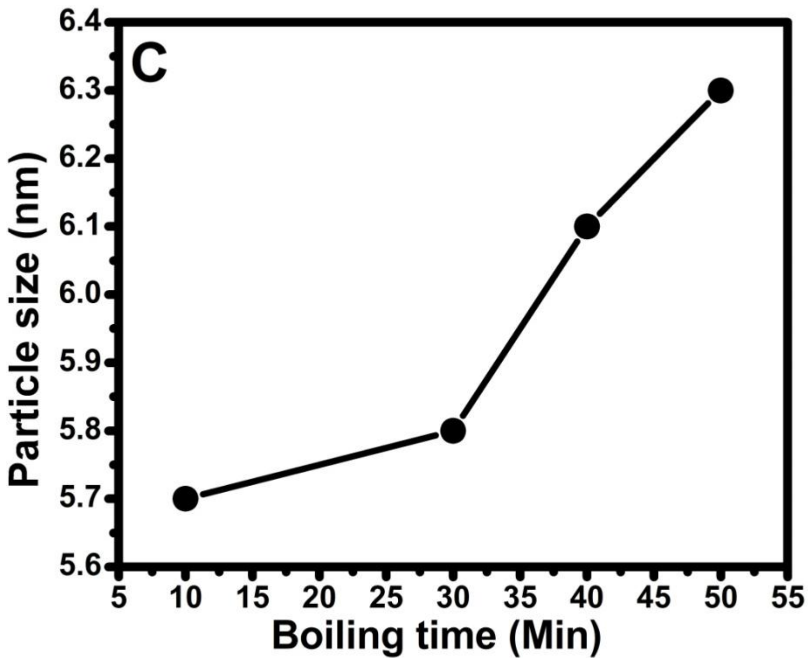
Fig. 4.2A shows absorption spectra of the mixture of silver nitrate and cinnamon bark extract with the ratio of 1.5:10, respectively boiled at different time. Fig. 4.2b and 4.2c shows the effect of boiling time on the position and intensity of the absorption peak and effect of boiling time on the NPs size, respectively.


AgNO3(ml) : Cinnomon (ml) [1.5 : 10]
(1) Boiling for 10 Min
(2) Boiling for 20 Min
(3) Boiling for 40 Min
(4) Boiling for 50 Min
Absorbance
Wavelength (nm)

(A)


B
Peak Intensity
Peak position
intensity (arb.units)
Peak position (nm)
Boiling Time (Min)

(B)



(C)

Fig. 4.2 shows (a) UV-Vis spectra of Ag-NPs produced using silver nitrate mixed with cinnamon bark extract with the ratio of 1.5:10 for cinnamon and silver salt, respectively. (b) Effect of boiling time on the intensity of the absorption band and peak position. (c) Effect of boiling time on NPs size.

As can be seen from Fig. 4.2A, when the boiling time was 10 min there is peak appeared at 449 nm assingned to LSPR. The intensity of this peak is increased with increasing the boiling time (see Fig. 4.2B), indicating an enhancment in the reaction rate. Of interest is that there is shift in the peak position for all samples, indicating that increasing of the boiling time has significant effect on peak position (see Fig. 4.2B). The shift in peak position of the LSPR absorption band is correlated with changes in particle sizes or shapes (Kelly et al., 2003). As already metioned above that the appearance of single peak is sssoaited only with spherical shape, the shift is expected to be due to changes in particle sizes. To confirm that, equation (4.1) was used to calculate the particle size of Ag-NPs. Fig. 4.2c shows the particle size as a function of boiling time. As can be seen the change in boiling time has significant effect on the particle size in agreement with the literature.

Chapter 5

Conclusion and Recommendation

5.1 Conclusion

In this project, Ag-NPs were synthesized by the Turkevich chemical method using cinnamon bark extract as the reducing agent. The prepared samples were characterized using UV-visible absorption spectroscopy. The change in color during synthesis processes and the presence of pronounced peak in the visible region in absorption spectra confirms the formation of Ag-NPs. Further study on the effect of the cinnamon quantity and boiling time on the formation of Ag-NPs was investigated. The obtained results showed that the quantity of cinnamon has significant effect only on the reaction rate and the optimum ratio was found to be 1.5:10 for cinnamon and silver, respectively. In addition, it is also found that increasing of boiling time increased the particle size from 5.1 to 6.3 nm and enhanced the reaction rate too.

5.2 Recommendation

There is no limit that can be set to define a complete work since there is always interesting aspects that require further investigation to complement what has already been done. Therefore, for future work the following are suggested.

1. Only cinnamon bark is used as reducing agent in this work. Research on the other plant extract to reduce silver ions to Ag-NPs should be done.

2. In this work, cinnamon extract is used to reduce silver ions only. In future work other metals such as gold, copper…ect. should be used.
3. In this work, only UV-Vis spectrometer is used to confirm the formation of Ag-NPs. Appling other characterization techniques such transmission electron microscope (TEM) and x-ray diffractometer (XRD) for further information (I.e., morphology, distribution, size and shape) should be done.

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