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Biosynthesis and characterization of silver nanoparticles using Artemisia Herba-Alba extract and evaluation of their biological activity

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Dedications

I dedicate this work

To my very dear parents

For their patience and comfort in moments of doubt and discouragement.

To my brothers and my sisters

To my wife and my son.

To all my family members.

To all my teachers.

To all my friends.

To all my colleagues.

To all those who are dear to me.

With all my affection and love.

I dedicate this modest work to them.

Yassine

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ABSTRACT

ملخص

RÉSUMÉ

Abstract

Artemisia Herba-Alba is a medicinal plant, and its essential oil is used as an antiseptic and antispasmodic. In this study, green synthesis of silver/silver oxide (Ag/Ag_2O) nanoparticles was successfully synthesized from Artemisia Herba-Alba aqueous leaves extract. The effect of temperature, reaction time, the concentration of $AgNO_3$, the quantity of plant extract, and pH on the synthesis process of Ag/Ag_2O was optimized. More interesting, the results showed that only 5 min were required for reducing 1 mM $AgNO_3$ into Ag/Ag_2O NPs at room temperature. The crystalline nature of Ag/Ag_2O NPs with an average crystallizes size of 10.7-36.8 nm. The green synthesizing Ag/Ag_2O NPs having in general a spherical morphology with particle/aggregate size less than 100 nm. The maximum UV-Vis absorption peak of Ag/Ag_2O NPs was observed at the range of 418- 435 nm giving optical band gaps of 2.05-2.30 eV. The TGA/DTA analysis shows significant organic contents (18 wt%) were physically and chemically adsorbed on the dry weight Ag/Ag_2O NPs. Artemisia herba-alba is a source of phytochemicals for effective and prompt fabrication of Ag/Ag_2O NPs with relevant insecticidal and anti-bactericidal activity against species of high public health importance.

Keywords: Silver /Silver oxide nanoparticles; Artemisia Herba-Alba; Silver nitrate $AgNO_3$; Green Synthesis.

ملخص

نبات الشيح الأبيض هو نبات طبي ، ويستخدم زيته الأساسي كمطهر ومضاد للتشنج. في هذه الدراسة، تم التخليق الأخضر للجسيمات النانوية أكسيد الفضة / الفضة Ag/Ag_2O بنجاح من مستخلص أوراق الشيح الأبيض. اعتمدنا على دراسة تأثير درجة الحرارة ووقت التفاعل وتركيز $AgNO_3$ وكمية المستخلص النباتي ودرجة الحموضة على عملية تخليق Ag/Ag_2O ، أظهرت النتائج أن 5 دقائق فقط مطلوبة لإرجاع 1mM من $AgNO_3$ إلى Ag/Ag_2O NPs في درجة حرارة الغرفة. الطبيعة البلورية لـ Ag/Ag_2O NPs بمتوسط حجم بلوري 36.8-10.7 نانومتر. تمتلك Ag/Ag_2O NPs بشكل عام شكلًا كرويًا بحجم الجسيمات / الركام أقل من 100 نانومتر. ولوحظ الحد الأقصى لامتصاص UV-Vis لـ Ag/Ag_2O NPsفي نطاق 418 -435 نانومتر مما يعطي فجوات النطاق البصري 2.30-2.05 فولت. أظهر تحليل TGA/DTAأن كمية مهمة من المادة العضوية عضوية (18٪) تم امتصاصها فيزيائيًا وكيميائيًا من الوزن الجاف ل NPs Ag/Ag_2O.

الشيح الأبيض هو مصدر للمواد الكيميائية النباتية من أجل التصنيع الفعال والسريع لAg/Ag_2O NPs. مع فعالية كمبيد حشري ومضاد للجراثيم كما أنها ذات أهمية للصحة العامة.

الكلمات المفتاحية: التخليق الأخضر، أوراق الشيح، جسيمات أوكسيد الفضة النانونية.

Résumé

Artemisia herba-alba est une plante médicinale, et son huile essentielle est utilisée comme antiseptique et antispasmodique. Dans cette étude, la synthèse verte de nanoparticules d'argent/oxyde d'argent (Ag/Ag_2O) a été synthétisée avec succès à partir d'extrait aqueux de feuilles d'Artemisia Herba-Alba. L'effet de la température, du temps de réaction, de la concentration d'$AgNO_3$, de la quantité d'extrait végétal et du pH sur le processus de synthèse d'Ag/Ag_2O a été optimisé. Plus intéressant, les résultats ont montré que seulement 5 min étaient nécessaires pour réduire 1 mM $AgNO_3$ en Ag/Ag_2O NPs à température ambiante. La nature cristalline des NP Ag/Ag_2O avec une taille de cristallisation moyenne de 10,7 à 36,8 nm. La synthèse verte des NPs Ag/Ag_2O ayant en général une morphologie sphérique avec une taille particule/agrégat inférieure à 100 nm. Le pic d'absorption UV-Vis maximal des NPs Ag/Ag_2O a été observé dans la plage de 418 à 435 nm, ce qui donne des bandes interdites optiques de 2,05 à 2,30 eV. L'analyse TGA/DTA montre que des teneurs organiques significatives (18 % en poids) ont été physiquement et chimiquement adsorbées sur les NPs Ag/Ag_2O en poids sec. Artemisia herba-alba est une source de composés phytochimiques pour la fabrication efficace et rapide de NP Ag/Ag_2O avec une activité insecticide et anti-bactéricide pertinente contre les espèces d'une grande importance pour la santé publique.

Mots clés : les nanoparticules d’argent /l’oxide d’argent ; Artemisia Herba-Alba ; nitrates d’argent $AgNO_3$; biosynthèse.

Abbreviations list

NPS	Nanoparticles
DPPH	2,2-diphényl 1-picrylhydrazyle
ABTS	Acide 2,2'-azino-bis-3-éthylbenzothiazoline6-sulfonique
NMR	Nuclear magnetic resonance
nm	Nanometer
Au	Gold
Pt	Platinum
Pd	Palladium
Ag	Silver
Rh	Rhodium
E_0	Energy electron beam (ev)
CVD	Chemical vapor deposition
MRI	Magnetic resonance imaging
CT	Computed tomography
Ag NPs	Silver nanoparticles
UV-Vis	Ultraviolet visible
XRD	Diffraction des Rayons X
SEM	Scanning electron microscopy
EDX	Energy dispersive x
TGA/DTA	Thermogravimetry differential thermal analysis
FT-IR	Fourier transform infrared
$AgNO_3$	Silver nitrate
λ	Wavelength
T	Transmittance
A	Absorbance

Eg	Optical bandgap
Ag_2O	Silver oxide
SPR	Surface plasmon resonance
θ	Bragg angle of diffraction

Figures List

Tables List

Contents

Chapter II: Nanoparticles: green synthesis and characterization

Chapter III: Materials and Methods

Chapter IV: Results and Discussion

General introduction

General introduction

One of the major trends in science and technology today is the race to miniaturization.

Make ever smaller is the key word of many scientists and industrialists. Make ever smaller to better know and use the fundamental laws of the behavior of matter. Always make it smaller to be faster. Always make it smaller to be cheaper.

The development of science and technology over the past decade is characterized by intensive studies on the properties of nanoscale objects [1]. The analysis and generalization of these studies as well as a number of successful inculcations of nano-industrial products suggest that further progress in this direction will help solve many of the problems facing humanity, now and in the future.

Nanotechnology could be, according to various specialists, the element of a new industrial era: that of small technologies [2]. They constitute a field of research and technological development involving the manufacture of structures, devices and systems from nanoscale objects or nano objects. The use of the term 'nanotechnology' can be misleading since it is not a single technology or scientific discipline. Rather, it is a multidisciplinary grouping of physical, chemical, biological, technical and electronic processes, materials, applications and concepts whose main characteristic is size [3].

Interest in nanoscale systems is mainly due to their exceptional physical and chemical properties, compared to their massive states of higher sizes. These properties make nanomaterials a rapidly expanding subject, of both fundamental and practical interest.

In recent years, various inorganic nanomaterials such as nanoparticles have been created or modified in order to achieve superior properties with greater functional versatility. In particular, nanoparticles, due to their size, of the order of 1 to 100 nm, were examined for their use as tools for a new generation of technological devices [4]. In addition, due to their dimensions and shapes similar to those of several biological structures (membrane cell genes, proteins and viruses), they have been proposed to study biological processes as well as to detect and treat diseases [5].

Different physical and chemical processes are widely used to synthesize metal nanoparticles. However, these production methods are generally expensive, labor-intensive and potentially dangerous in the environment and living organisms [6].

The progress of science and technology at the nanometer scale has stimulated extensive efforts to develop new cost-effective strategies, and at the same time safe and friendly environment for the production of nanoparticles with the desired characteristics [6].

The synthesis green or ‘biosynthesis’ has opened the door to the sustainable production and safe handling of nanoparticles, and proved to be the best method due to its kinetics slower, ease of manipulation and control of the growth of the crystals for the stabilization of the nanoparticles [7]. This method uses many ecological resources such as plant extracts. The use of the latter has taken on a considerable importance, thanks to the improvement of the properties of chemical, physical and biological particles synthesized by this method [8].

Among many metal nanoparticles, the nanoparticles of silver oxide have reached a significant importance due to their properties, distinctive, and their availability compared to other noble metals such as silver and gold.

The present work has for objective to develop and characterize nanoparticles of silver oxide by the process of green chemistry have been using the extract of the leaves of Artemisia Herba-Alba and study their activity as antibiological.

Our study is structured around four chapters:

- ✓ The first chapter deals with a literature survey carried out on the species Artemisia Herba-Alba.
- ✓ The second chapter was devoted to a review of the literature on the nanoparticles, their classification, their properties, chemical and physical, and their processes of synthesis.
- ✓ In the third chapter, we first presented the experimental protocol used as well as the technical analysis.
- ✓ In the fourth chapter, we have characterization adopted, the set of results has been discussed in this chapter. Finally, a general conclusion summarizes the main results obtained and the prospects that should be undertaken for further study.

Chapter I:

General on Species Artemisia Herba-Alba

A medicinal plant is a plant used for its therapeutic properties. This means that at least one of its parts (leaf, stem, root, etc.) can be used for the purpose of healing. They have been used for at least 7000 years before our era by men and are the basis of phototherapy.

I.1. Presentation of the genus Artemisia

The genus Artemisia belongs to the Asteraceae family: it is one of the most widespread and studied genera of this family; it contains a variable number of species ranging up to 400 species, distributed throughout the world. More than ten species have been identified in Algeria; some are rare and scattered in high mountains, or confined within certain limits; others, on the contrary, are particularly abundant and widespread over large areas [9].

The Romans in the first century used dry flower heads obtained from several species of the genus Artemisia [10], for the treatment of disease caused by roundworm, enterovirus, tapeworm infections and it has become an important part of the pharmacopoeia at the beginning of the 20th century. Artemisia species have been the source of remedies such as Artemisia herba alba, Artemisia Campestris.

The species that belong to the genus Artemisia have therapeutic properties, and not only are they used in traditional medicine [11], but also in the food and pharmaceutical industry, the parts of the plant used in herbal medicine include the leaves and flowering tops. It has been reported that the genus Artemisia is rich in secondary metabolites such as flavonoids, caffeoylquinic acids, coumarins, essential oils.

I.2. Artemisia Herba Alba:

Artemisia Herba Alba in French Armoise White Grass is a monthly plant very responsive in arid to semi-arid areas [11]. It is a species of the genus Artemisia (Mugwort) which belongs to the Asteraceae family. Herbaceous and can measure from 30cm to 50cm high [12]. Its stems are floriferous and slender, a little hairy and its leaves are oblong, cut into segments of dark green color on the face and cottony white on their lower part (figure 1), it also has small yellow tubular flowers; it gives off a very strong odor, sometimes unpleasant.

Figure I.1: Artemisia Herba-Alba

The flowering period is from July to October; its fruits are ovoid achenes. The parts of the plant used in herbal medicine are in particular the leaves and the flowering tops. It has been reported that the genus Artemisia is rich in secondary metabolites such as flavonoids, caffeoylquinic acids, coumarins, essential oils [12]. Species that belong to the genus Artemisia have therapeutic properties, and they are not only used in traditional medicine, but also in the food and pharmaceutical industry.

I.3. Nomenclature:

Artemisia Herba-Alba has different names depending on the region:

Table I.1: Some vernacular names of Artemisia Herba Alba.

Anglais	Arabe	Français
white wormwood	شيح	armoise blanche
Desert wormwood	شيحة	absinthe des steppes

I.4. Classic classification:

Table I.2: Systematic classification

Classification	Specificname
Reign	Plantae
Phylum	Spermaphytes
Subphylum	Angiosperms
Class	Dicotyledons
Subclass	Asteridae
Order	Asterales
Family	Asteraceae or compound
Tribe	Anthemideae
Sub-tribe	Artemisiinae

I.5. Phytogeography

Artemisia herba alba is a spontaneous plant very widespread in North Africa and the Middle East, it likes dry and hot climates, and exists in the form of large populations in desert areas. Artemisia herba-alba is considered an Irano-Turanian species. The existence of Iranian-Turanian flora in North Africa is much debated [13].

Figure I.2: Global distribution of White Mugwort determined

I.6. Plant ecology

Mugwort has a wide geographical distribution covering, in Algeria, about 4 million hectares; Mediterranean shrub that abounds in the Middle East, in the South of Algeria and in Morocco on deep sands [13]. Artemisia herba-alba exists in bioclimates ranging from semi-arid to Saharan. It seems indifferent to altitudes and can live in warm to cool winter regions. In the south, this plant grows on brown steppe soils of medium texture and in the extreme south on sandy soils. It is drought resistant, tolerates gypsum and moderately high salinity levels. It grows in clay steppes where rainfall is around 200mm / year. Its development is linked to the nature of the soil. Indeed, it must be low permeability, compacted and plugged. Accompanied by the alfa "stipatenacissima", it often covers very large areas in the highlands. Its presence is more frequent on the edges of the Wadis in the day as (Depression of the steppe with impermeable soil which are more or less humid sectors). It constitutes a means of combating erosion and desertification [13].

I.7. Botanical description

White Wormwood is a herbaceous plant with woody and branched stems, 30 to 50cm, very leafy with a thick stump. The leaves are small, sessile, pubescent and silvery in appearance. The flowers are grouped in clusters, with very small (3 / l.5 mm), ovoid heads. The involucre has imbricated bracts, the outer ones orbicular and pubescent. The floral receptacle is bear with 2 to 5 yellowish flowers per capitulum, all hermaphroditic[14].

It is distinguished by a characteristic odor of thymol oil and a bitter taste hence its astringent character. Artemisia herba-alba flowers in October - November, fruits and disseminates these seeds in December [15]. This fall bloom is an adaptive strategy adopted by many species in arid regions. It would allow the seeds to escape predation during the summer period. In its annual cycle, the leaves of white sagebrush show a seasonal polymorphism. The first that develop in winter in general are large and jagged [16]. The following ones are becoming smaller and smaller and less and less cut up, which allows the reduction of the transpiring surface because this polymorphism constitutes one of the adaptive characters of the species to drought. Artemisia herba-alba can reduce its weight during the dry season by more than 70%. This decrease considerably lowers the transpiration of the plant. For the underground part, it takes the form of a main root, woody and thick, distinct from the secondary roots and which sinks into the ground like a pivot. The root penetrates deeply up to 40 to 50 centimeters and branches out only at this depth [15].

That the density and depth of root branches vary with the aridity of the climate. In a desert region, this species has a shallow root system with a large number of particularly abundant lateral branches between 2 and 5 cm deep [17]. This shape and method of lateral extension of the roots allows, when the aridity increases, better interception of infiltrated water.

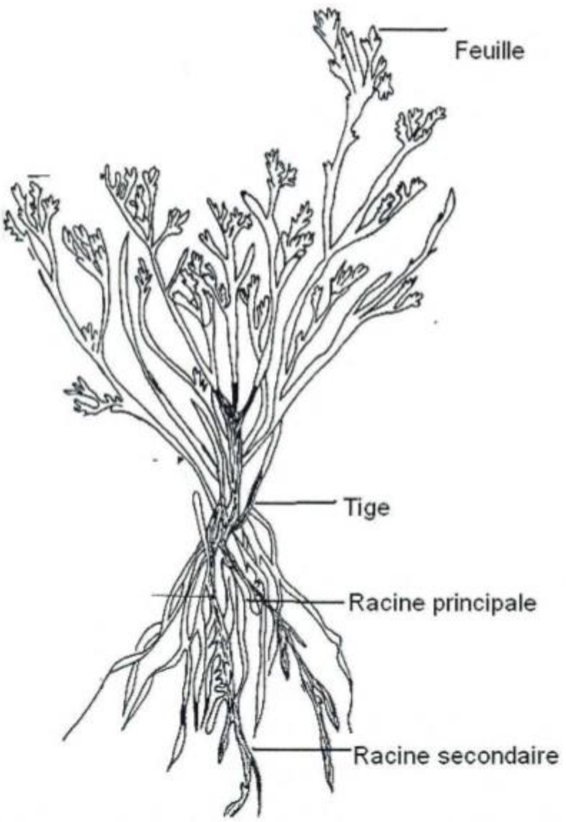


Figure I.3: General morphology of the plant Artemisia herba-alba

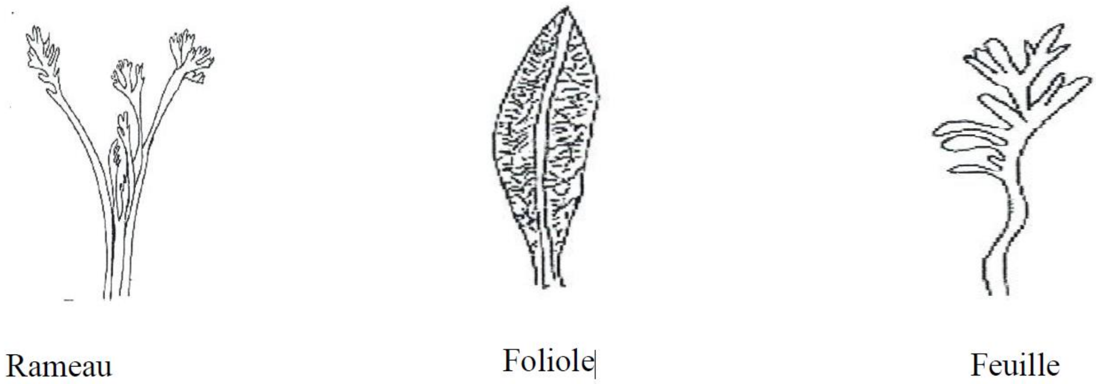


Figure I.4: Morphology of the leaf of Artemisia herba Alba

I.8. Chemical composition

Table I.3: Composition of essential oils extracted from Artemisia herba-alba (%) [18,19]

Chemical components	Alegría	Tunisia
β –thujone	41.2	**30.0**
β - pinene	0.2	**-**
Myrcene	0.5	**-**
p-cymene	0.8	**1.5**
terpinene-4-ol	0.2	**2.8**
Thymol	0.1	**-**
Camphor	20.2	**-**
γ-terpinene	0.2	**1.1**
α-pinene	0.1	**-**
α- thujone	-	**25.7**
1-8, cineole	3.7	**6.0**
Camphene	3.2	**0.8**
Bornylacetate	**-**	**5.7**

I.9. Use of Artemisia herba-alba

White mugwort is a medicinal and aromatic plant used for a long time in traditional medicine, it is considered as a material full of medicinal and nutritional substances (fodder plant), it is also a source of substances (essential oil) which have remarkable effects biologically [18].

I.9.1. Medicinal use

It is the most famous mugwort in Algeria. CHIH is a very popular remedy that is often used: to facilitate digestion, calm abdominal pain and certain liver ailments and antidiabetic. Its roots are indicated against certain nervous disorders. Artemisia herba alba is widely used in traditional medicine for gastric disorders such as diarrhea and abdominal pain. It is also used as a remedy for inflammation of the gastrointestinal tract [21]. By far the most frequently cited is the use of Artemisia herba Alba As so in the treatment of diabetes mellitus. Several scientific studies have also proven the effectiveness of white mugwort as an anti-diabetic, anti-parasitic, antibacterial, antiviral, antioxidant, anti-malarial, antipyretic, antispasmodic and antihemorrhagic. This species has been used as a decoction for fever, menstrual and nervous problems.

On the other hand, wormwood has been used since ancient times for the treatment of digestive disorders [22]. The active parts of the plant are all very bitter. They are used internally, either pure or in mixtures, to stimulate appetite, the secretion of digestive juice and bile, against intestinal colic as well as against intestinal parasites. It can be used in particular to treat arterial hypertension, heart failure, certain edemas, portal hypertension or hypokalaemia [23].

I.9.2. In pastoralism

- **Food use:** In food, white mugwort is considered the aroma of certain drinks such as tea or coffee. Nevertheless, its use in the food industry remains very limited because of the toxicity of beta-thujone, the level of which must not exceed 5 mg / kg [20].
- **Forage use:** Artemisia herba-Alba represents an important forage resource, it is the main plant species grazed especially in spring and summer. It constitutes a very important source for the livestock. The biomass of this steppe plant constitutes a substitute food for raising livestock in times of scarcity[24].

For a long time, white mugwort has been recognized by pastoral and nomadic populations for its purgative virtues. It is used in particular as an anthelmintic in sheep. It is used by the people of Nague to relieve gastrointestinal complaints. In Tunisia, it is used for digestive diseases and for anti-diabetic treatment. Artemisia herba-alha is used as an anti-diarrhea, against abdominal cramps, and for healing external injuries. It is used against diabetes and jaundice. It is recommended for neurological disorders [25]. It is also used in traditional medicine to aid digestion, soothe abdominal and liver pain, in the treatment of diabetes and as an anthelmintic. The roots are effective against convulsions. In high doses, mugwort is abortive, neurotoxic and hemorrhagic. Thujone is the toxic and bioactive substance in mugwort and the most toxic form is alpha-thujone. It has convulsive effects and also heavy consumption of white mugwort has a purgative effect, especially on sheep, and can cause death in young lambs [24].

I.9.3. Biological uses

- **Antioxidant activity**

Many medicinal plants contain large amounts of antioxidant compounds, which could be isolated and then used as antioxidants for the prevention and treatment of free radical-related disorders. In a study by Djeridane [25], the purpose was the evaluation by a chemical method of the antioxidant capacity of phenolic compounds in some Algerian medicinal plants, including A. herba-alba. These medicinal plants showed stronger antioxidant activity and content in phenolics than the common nutritional plants. It has been also noted in this study that these Algerian plants are strong radical scavengers and can be considered as good sources of natural antioxidants for medicinal and commercial uses [26]. Raw and cooked ground beef patties were treated with an aqueous extract of A. herba-alba, rosemary, fennel and rue at levels of 5 mm of 10% (w/w vegetable matter to water) extract for every 100 g of meat. Patties were kept under refrigeration (4º) for a period of 16 days, and samples were drawn at 4-day intervals. Results showed that cooked meat was more susceptible to oxidative deterioration than raw meat. In addition, A. herba-alba had a somewhat

less effective role than the other herbs [26]. In another study, 21 plant samples were collected from different Jordanian locations and used for antioxidant evaluation. The level of antioxidant activity, determined by DPPH and ABTS assays, showed that Artemisia herba-alba has a moderate antioxidant activity compared to the other plants [27].

Abid compare the long-term effects of Artemisia herba-alba decoction with a green or black tea decoction, prepared without sugar, on the antioxidant processes in rats. The conclusion of this study showed that Artemisia, as well as green tea decoctions, increased the total antioxidant status, whole blood glutathione peroxidase activity and zinc and copper status, and prevented weight gains and increased conjugated dienes, plasma glucose, lipids and iron status. The beneficial antioxidant effects were in descending order: Artemisia decoction ≥ green tea decoction > black tea decoction. So, Artemisia could constitute a good adjuvant to combat obesity, hyperglycemia, hyper-triglyceridemia, hyper-cholesterolemia and particularly oxidative stress [28].

The effects of seven medicinal plants including Artemisia herba-alba on protein degradation, lipid peroxidation, erythrocyte deformability and osmotic fragility of erythrocytes exposed in vitro to 10 mM H_2O_2 for 60 min at 37°C have been examined. The result was that Artemisia herba-alba did not protect erythrocytes against lipid peroxidation [29].

- **Anti-venom activity**

Aqueous extracts of 12 medicinal plants traditionally used in Jordan for the inhibition in humans of snake and scorpion venoms were evaluated for their possible anti-venom activity. Among the plants tested, 9 extracts were found to inhibit the hemolytic activities of both venoms. The most active plant extract was Artemisia herba-alba, which gave 100% inhibition [30].

- **Antifungal activity**

The antifungal activity of Artemisia herba-alba was found to be associated with two major volatile compounds isolated from the fresh leaves of the plant. Carvone and piperitone were isolated and identified by GC/MS, GC/IR, and NMR spectroscopy. Antifungal activity was measured against Penicillium citrinum (ATCC 10499) and Mucora rouxii (ATCC 24905). The antifungal activity (IC50) of the purified compounds carvone and piperitone was estimated to be 5 µg/ml and 2 µg/ml against Penicillium citrinum, and 7 µg/ml and 1.5 µg/ml against Mucora rouxii, respectively [31]. In another study, the antifungal activity of the essential oils of 25 Moroccan medicinal plants, including A. herba-alba, against Penicillium digitatum, Phytophthora citrophthora, Geotrichum citri-aurantii, and Potrytis cinerea. A. herba-alba essential oil showed only weak antifungal activity at 250 µg/ml concentration [32]. In addition, the effect of A. herbaalba, Eucalyptus, and Rosmarinus essential oils was evaluated on the mycelial growth and toxigenesis of Penicillium aurantiogriseum and P. vindication. A significant decrease in mycelial dry weight was obtained with the addition of 0.05-2.5% of each of the three essential oils in yeast extract sucrose broth. The inhibition of mycelium growth was tested on malt extract agar, Czapeck yeast agar, yeast extract sucrose agar and broth at constant pH, and was highly effective for A. herba-alba, followed by Eucalyptus. A complete inhibition of toxin production was observed with 0.44% of each essential oil for P.aurantiogriseum and 0.22% for P. viridicatum [33]. The effect of A. herba-alba and Oreganum oils on spore germination, mycelial elongation and sporulation were studied in three fungi. All three stages of fungal asexual reproduction were affected but mycelium growth was the most sensitive, followed by spore germination and then sporulation of the three fungi studied. Zygorrhynchus sp. was found to be the most sensitive followed by Aspergillus niger and then Penicillium italicum. A. herba-alba was less active on the three phenomena studied than the Oreganum oil. [34]. In addition, A. herba-alba essential oil demonstrated a synergistic action on the inhibition of mycelium growth in Zygorrhynchus sp. and Aspergillus niger isolates, when associated with sodium chloride or fatty acid [33]. The essential oils extracted from 10 Algerian plants; including A. herba-alba, were analyzed for their potential activity against Candida albicans. A moderate efficiency was obtained with the essential oil from A. herba alba which showed an antifungal effect 5617-fold lower than that measured with amphotericin B. [34].

The inhibitory effects of Artemisia flower heads (Artemisia herba-alba), on the growth and aflatoxin production of a toxigenic strain of Aspergillus flavus was tested using different concentrations. The plant inhibited aflatoxin formation by 85-90% of that of control at a concentration of 10% [35].

The in-vitro antifungal activity of A. herba-alba essential oil has been evaluated on various microorganisms. The oil showed a very strong action vs. Candida and Microsporum. [36]

- **The nematicidal activity**

The in-vitro nematicidal activity of methanolic extracts (20 μg/ml) from twenty Jordanian plant species against two species of root-knot nematodes was evaluated. The leaf extract of Artemisia herba-alba was the most effective causing 22, 51, and 54% mortality after 24, 48 and 72 h of exposure, respectively [37].

- **The antimicrobial activity**

The antimicrobial activity of A. herba-alba has been evaluated in many studies of experimental nature. In studies examined the essential oils of A. herba-alba reported that it had a great potential on microbial activity against strains of Staphylococcus aureus, Micrococcus luteus, Escherichia coli, Salmonella typhimurium, Bacillus cereus, and Entrococcus faecalis. Furthermore, antimicrobial activity of A. herba-alba have been confirmed in some yeast strains of Candida [33].

Chapter II:

Nanoparticles, green synthesis and characterization

Nanosciences and nanotechnologies represent the most promising research field in sciences of material today. They constitute a domain of technological developments implicating the manufacture of structures, implements and systems from objects of nanometric size. These scientific developments which gave birth to nanosciences [38].

In the course of last years, the materials of nanometric size were attracted attention thanks to their specific physical and chemical ownership different from those of the material in the corresponding massive state. This new ownership which makes the world of nanoparticles a research domain in uninterrupted evolution by developing new strategies of synthesis of these nanomaterials of size and form controlled [39].

II.1. Historical aspects

Nanotechnology, although considered to be a recent phenomenon, is also obvious in the ancient civilizations. The history of nanoparticles goes back up to Roman epoch, when they were in most cases used for the fancy colouring of the glass. However, the concept of nanoparticles was unknown in epoch. In fact, very few people know that even in the sixth century BC, nanotechnology was commonly used in the region of Attica [39]. During the Archaic and Classical periods, around 620-300 BC, in the region of Attica, the production of decorated vases reached an extraordinary artistic level thanks to the development of a very original manufacturing technique that obtained a magnificent black/red dichromatism, the secret of Greek vases. During this technique, spinel nanoparticles formed inside a vitreous layer a few microns thick. [40]

Celtic red enamels dating from (400 to 100 BC) contain copper and copper oxide nanoparticles while most of the red tesserae used in Roman mosaics were made of glass containing copper nanocrystals. [39]

Roman craftsmen achieved unusual color changes by adding noble metal to the glass before being molten. During the period (1066-1485 AD) saw the emergence of enamelled ceramics with striking optical effects obtained from metal nanoparticles [39]. Ancient Indian and Chinese medicines used soluble gold, for therapeutic purposes, it has been shown that these substances contain gold nanoparticles mixed with larger particles [41]. , however; ancient civilization did not understand the unique properties and potential of their preparations as we now understand them. [42]

A revolution in nanotechnology only took place after Faraday's work on colloidal gold in 1857, which ignited the idea of metallic nanoparticles [43]. At a conference in 1959, physicist Richard Feynman declared: 'The principles of physics, as far as we can judge, do not oppose the possibility of manipulating things atom by atom'. With this statement, the American physicist suggested to the scientific community to explore the universe of the infinitely small. [43]

The term "nanotechnology" was first coined in 1974 by Norio Tanigushi, but it was unknowingly used by Eric Drexler in his 1986 book Engines of Creation: The Coming Era of Nanotechnology. [44]

Here is the history of nanotechnology that allows us to observe the evolution:

- 1981: Scanning electron microscope that could process atoms Individual.
- 1985: Discovery of fullerene, 60 carbon atoms in a circle (C60).
- 1992: Discovery of carbon nanotubes stronger than steel; they can be Used for drug delivery, energy storage and energy transmission.
- 1993: Discovery of quantum dots.
- 2000: Construction of passive nanoparticles for applications as nanopiles To fuel and in products for everyday use, including cosmetics.
- 2005: Construction of active nanoparticles for targeted drugs and others Structures

II.2. Definitions

II.2.1. The definition of the nanoscale

More specifically, the nanometric said ladder is between 1 and 100 nm (ISO / TS27687 (2008). It involves in the order of characteristic greatness of the nanometric processes in which ratio surface volume has a preponderant role. Besides the particles dimensions of which are understood between 100 and 500 nm also introduce of potential nano-specific characteristics [46].

II.2.2. The nano world.

The prefix 'nano-' is connected to the nanometer, the unit of measurement of length of the international system worth one billionth of a meter (10^{-9}m). In nature, this scale is common: an assembly of atoms 0.1 nm forms molecules, proteins, matter, etc. For humans, the manipulation of the material at this size is recent and makes it possible to manipulate the physical properties and chemical materials, this is called nanotechnology [45].

II.2.3. Nanomaterials

Today, nanotechnology is one of the most important trends in the Materials science. Is considered a nanomaterial any natural material, formed Accidentally or manufactured containing free particles, in aggregate form or In the form of agglomerate, of which at least 50 % of the particles, in the numerical distribution By size, have one or more external dimensions between 1 nm and 100 nm In all industrial countries, there is a considerable rise in nanosciences And nanotechnologies. They consist of building, understanding and controlling functionality objects between 1 and 100 nm in size [46].

Nanomaterials are materials made up of all or part of nano-objects that make them Confer improved or specific properties of the nanometric dimension. Among the Nano-objects, we can distinguish three main families:

- **Nanoparticles:** These are nano-objects whose particle size is Less than 100 nm. The term "nanoparticles" is rather reserved for particles Synthesized and intended for industrial uses. These nanoparticles known and produced for several years and whose tonnages are high as the Titanium dioxide (they represent 95% of the nanoparticle market) [47]. The Nanoparticles can be in the form of powder, suspension, Solution or gel.
- **Nano-fibers**: nanotubes, nano-filaments These are materials of which a of dimensions is less than 100 nm. This name is generally, used to designate slender nano-objects whose dimensions range from 1 to a few Tens of nanometers for the section and 500 to 10,000 nanometers for the Length [48]
- **Nano-films**: nano-layers with a thickness of less than 100 nm [49].

Nano-objects can be used either as such or to develop new materials and usually grouped into three categories:

- **Materials nano-structured in surface** These nanomaterials are covered Either of one or several nano-coats, or nanoparticles which form one Well defined surface, allowing to endow the surface of ownership (resistance in Erosion.) Or new functionalities (sticking, hardness etc). Of such Surfaces already exist, for instance to color packing in glasses, Bring a self-cleaning function or reinforce the surface of polymers.

- **Nanomaterials in volume** It is the nanomaterials which have one Nanometric intrinsic structure (microstructure, porosity, network Monocrystalline) who confers on them particular physical ownership. Nano-objects are, in that case, the essential elements of the massive material.
- **Nano-charged or nano-reinforced nanomaterials** These materials are Worked out by enlistment of nano-objects in an organic or mineral matrix at the end to bring a new functionality or to change proprieties Mechanical, optic, magnetic and thermal. Various nano-objects are already Used in numerous industrial and environmental applications as for instance: The dioxide of titanium used as protection in Ultraviolet radiance in solar creams and photo-catalyst for Cleanup of water and air under solar radiation. Nano-objects are therefore classified according to Figure 1 below:

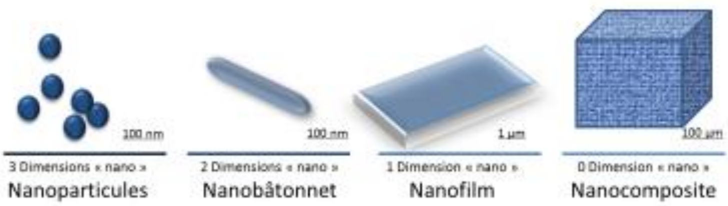


Figure II.1: The classification of nano-objects according to their degree of nanometric dimension.

From the point of view of size, nanoparticles are located on the scale of the world living between the helix DNA (diameter 2 nm) and a virus (diameter 100 nm) as shown in Figure II.2 below:

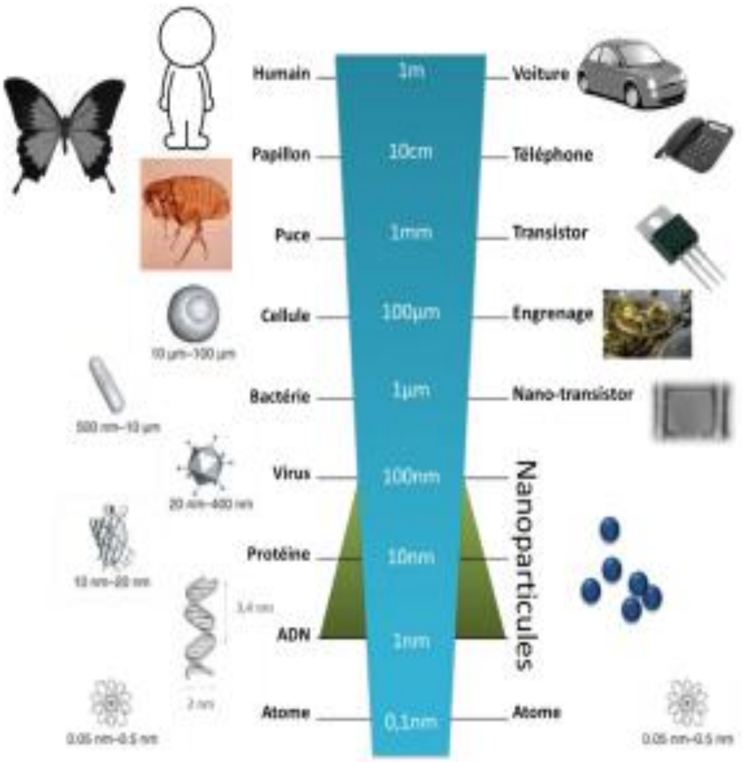


Figure II.2: Situation of nanoparticles in relation to the size scale of life and technologies (freely inspired by Invitrogen).

II.3. Properties of nanomaterials

The best-known physical properties of nanomaterials are: (i) a significant fraction of surface atoms, (ii) significant surface energy, (iii) spatial confinement, and (iv) reduced imperfections. Here are some examples

- **Mechanical properties**: Nanomaterials can achieve theoretical strength. Generally, nanomaterials have few defects in their Structure, and the improvement in mechanical strength is simply due to the reduced probability of defects [50].
- **Optical properties:** Nanomaterials exhibit a variety of unusual and interesting optical properties. A wide range of optical effects can be generated with many useful applications. Nanoscale structures made of metals such as gold can support surface plasmon modes, resulting in a highly colored particle that can change with their sizes [51].

The electrical conductivity of nanomaterials can be significantly improved with minimal structural defects [52].

Nanomaterials exhibit significant paramagnetic behavior at the nanoscale due to the enormous surface energy [53].

Thermal conductivity: Due to the covalent bond vibration in the nanomaterial structure, leads to very high thermal conductivity. Its thermal conductivity is 10 times higher than that of metal [54].

II.4. Classifications of nanoparticles

II.4.1. Classification of nanoparticles according to their dimensions [55]

- Nanoparticles of dimension 0: materials in dispersed, random or random form Organized as in colloidal crystals for optics or magnetic fluids.
- Nanoparticles of dimension 1: materials in the form of nanowires or Nanotubes.
- Nanoparticles of dimension 2: materials in the form of a thin film, As in deposits of aggregates or thick coatings obtained by plasma projection or electrochemical means.
- Nanoparticles of dimension 3: materials in compact form as in Ceramics and nanostructure metals.

II.4.2. Classification by origin

Nanomaterials can be classified according to their origin into natural or artificial [56].

It is generally accepted that substances derived from the nanotechnology sector are derived from intentional anthropogenic activities are called manufactured nanomaterials such as Than titanium dioxide, carbon black, amorphous silica. There are also nano-sized substances present unintentionally, whether they are of natural origin (volcanoes, forest fires, cosmic dust) or from polluting emissions such as: combustion engine emissions, sometimes are called particles ultrafine.

II.4.3. Classification by chemical composition

Nanomaterials can be organic, inorganic or mixed in nature [61].

II.4.4. Classification by structure

- Nano-objects: Any object whose dimensions in space are at scale Nanoscale, (between 1 and 100nm) [62].

- Nanoparticles: A nanoparticle is an assembly of thousands of atoms, forming an object of nanometric size (1 to 100 nm) [57].
- A nano-composite: consists of nano-objects incorporated into a matrix or polymer. Depending on their nature, nano-objects can modify the properties of the material: mechanical strength, flexibility/rigidity, thermal, electrical properties, Magnetic.
- Nano-porous materials: Nano-porous materials are materials containing Nanoscale nanopores that may contain a gas or liquid [58].
  - Nanostructured materials are materials that have a structure Internal or surface at the nanoscale [58].

II.4.5. Classification of nanomaterials according to their sizing

The first classification scheme for nanomaterials was presented by Gleiter in 1995 [59] and explained in more detail by Skorokhod in 2000 [60]. Pokropivny and Skorokhod [62] reported the different classes of nanomaterials.

II.5. State of the art on the elaboration of nanoparticles

A nanoparticle is an assembly of a few hundred to a few thousand of atoms leading to an object of which at least one of the dimensions is of size Nanoscale. The combination of the different reducing and stabilizing agents (Table 1) a gave rise to several methods of synthesis of nanoparticles of different shapes and Sizes. As shown in Table 1, metals such as Au, Pt, Pd, Ag and Rh With a redox potential E0 > 0.7 V will react with weak reducers under Ordinary conditions [63]. The reducing agent and the stabilizing agent may be different from the chemical point of view, but one can also use the same chemical agent to play Both the role of reducer and stabilizer.

Metal species	E^0/V	Reducing agent	Conditions	Rate
$Au^{3+,+}$, $Pt^{4+,2+}$, Pd^{2+}, Ag^{+}, Rh^{3+}, Hg^{2+}, Ir^{3+}	$\geqslant +0.7$	Organic acids, alcohols, polyols	$\geqslant 70$°C	Slow
		Aldehydes, sugars	<50°C	Moderate
		Hydrazine, H_2SO_3, H_3PO_2	Ambient	Fast
		$NaBH_4$, boranes, hydrated e^-	Ambient	Very fast
Cu^{2+}, Re^{3+}, Ru^{3+}	$<+0.7$ and $\geqslant 0$	Polyols	>120°C	Slow
		Aldehydes, sugars	70–100°C	Slow
		Hydrazine, hydrogen	<70°C	Moderate
		$NaBH_4$[60]	Ambient	Fast
Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, In^{3+}, Sn^{2+}, Mo^{3+}, W^{6+}	<0 and $\geqslant -0.5$	Polyols	>180°C	Slow
		Hydrazine, hydroxylamine	70–100°C	Slow
		$NaBH_4$, boranes[14,60]	Ambient	Fast
		Hydrated e^-, radicals	Ambient	Very fast
Cr^{3+}, Mn^{2+}, Ta^{5+}, V^{2+}	<-0.6	$NaBH_4$, boranes[14]	$T, P >$ ambient	Slow
		Hydrated e^-, radicals	Ambient	Fast

Table II.1: Guide for the choice of reducing agents and reaction conditions for synthesis Metal particles.

The synthesis of metal nanoparticles is now carried out by two main approaches summarized in Figure II.3, these are the top-down approach and the "Botton-up".

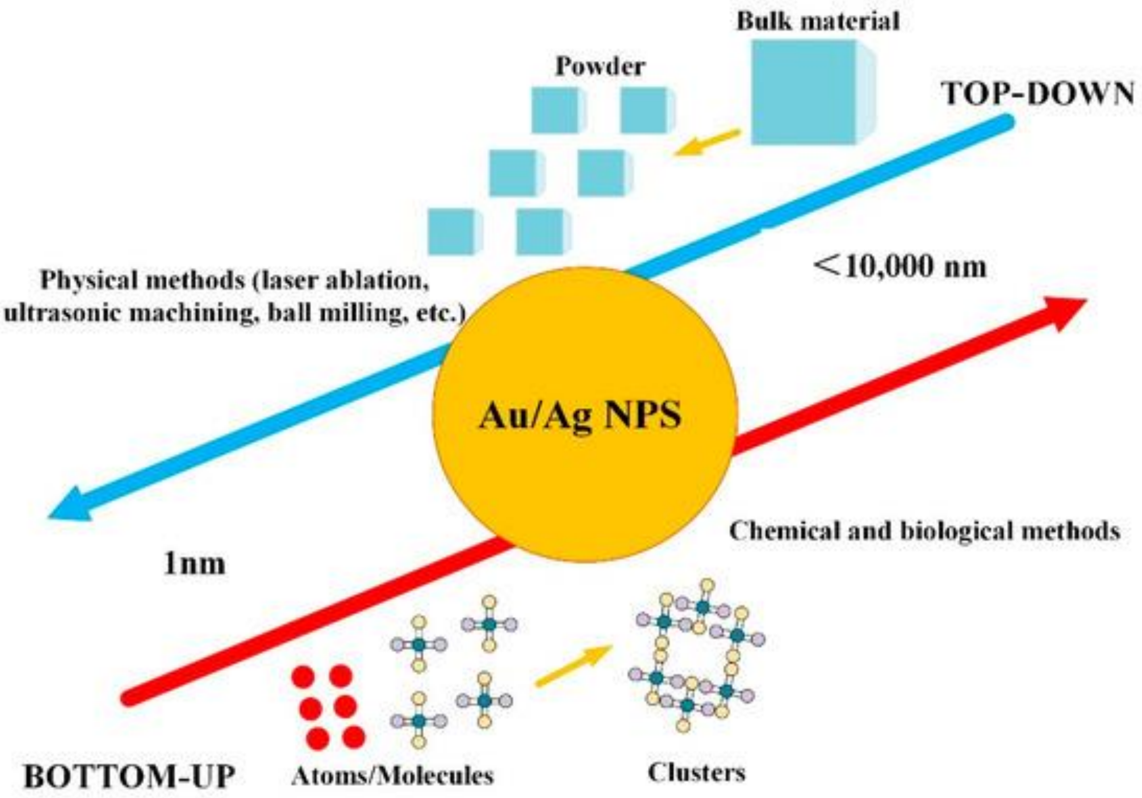


Figure II.3: Two different methods to fabricate Au/Ag NPs: top-down and bottom-up.[70]

II.5.1. Synthesis of nanoparticles by top-down approach

Starting from a massive material, it consists in transforming the latter into small particles of Nanometric size. In this case, the nanoparticles are mainly made by Reduction in the size of metal or metal oxide fragments. As an example, we Can cite:

II.5.1.1. Mechanosynthesis

Mechanosynthesis is a process of powder metallurgy. As its name indicates it, it consists of using mechanical energy to reduce the grain size of the material. It is a process of grinding metal powders in order to reduce the size of the Particulate matter. This method does not control the size and morphology of particles Because the structures are gradually fractionated until the particles of Nanometric dimensions. The particles obtained by this method have a size included Between 0.5 and about ten microns. This technique is very elaborate and requires a lot In addition, efficiency and performance are not always there.[65]

II.5.1.2. Lithography

Lithography involves duplicating an increasingly smaller pattern in a layer of Photosensitive polymer resin deposited on the surface of a substrate. The resin is subsequently Exposed to radiation (UV, X...) Or a beam of charged particles (electrons, Ions). Unlike powder methods, lithography allows for more control Easily the morphology and organization of nano-objects on a surface. Although this Approach allows precise control of the size, shape and position of structures, The quality of the nanoscale structures produced is not always optimal because of the Defects (lens) generated during elaboration. In addition, the development time is long and

The major disadvantage is its limitation of resolution due in particular to the problems of Diffraction related to the wavelength of the radius used (X or UV.) [66-68].

II.5.2. Synthesis of nanoparticles by bottom-up approach

Unlike the top-down approach, this approach makes it possible to obtain Nanoparticles by nucleation and growth processes from isolated atoms. it Involves the use of physico-chemical phenomena at the atomic and molecular scale In order to chemically transform a precursor into metal particles. Assembly and Positioning of atoms, molecules or particles makes it possible to carry out Simple or elaborate nanostructures. In general, in the "Bottom-up" approach, a distinction is made two categories of reactions: reduction and decomposition reactions. Both reactions can take place in the gas, liquid or solid phase. The processes for developing nanomaterials by a bottom-up approach are based on generally on physical and chemical transformation pathways. The ways of chemical transformation grouped under the name of "chemistry of colloids" are particularly rich both by the large number of compounds that could be synthesized than by the flexibility of the processes allowing to vary a large number of parameters. Since no general trend emerges from these methods, it is therefore Important to determine the best synthesis method as well as the most stabilizer appropriate for the intended application [69].

II.5.3. Processes for the development of nanoparticles by physical means

Physical synthesis is based on homogeneous vapor nucleation supersaturated followed by particle growth by condensation. Thus, depending on the chemical nature of the material, saturated vapors can be generated in various ways. Supersaturation can be carried out by cooling or by chemical reaction or by a combination of these two processes. Supersaturated vapors can grow by homogeneous in the gas phase or heterogeneous in contact with the surface.

Physical methods offer a wider variety of host matrices and the possibility Make it easier to control the size, shape and local environment of nanoparticles. However, they require heavier equipment and do not allow most of the time Than the synthesis of materials in the form of thin films. The synthesis of nanoparticles by Physical route can be carried out from solid, liquid or gaseous precursors [69].

- **Laser pyrolysis.**

It is a synthesis method for obtaining particles whose size is the order of 10 to 50nm in diameter with a narrow dispersion. Its principle is based on the interaction between the cross-jets of a CO_2 infrared laser beam and a stream of reagents in a reactor under controlled atmosphere. Energy transfer causes an elevation of Temperature in the reaction zone leading to the dissociation of precursors and formation nanoparticles. Precursors can be gaseous or liquid. In the case of a liquid, the precursor is injected into the reactor as an aerosol. Chemical efficiency can Go up to 90% in the case of gaseous precursors. Among the different methods of nanoparticle synthesis, laser pyrolysis stands out for its flexibility and the variety of compounds that it can produce both in terms of chemical composition and morphology and crystallinity. This method is used to produce spherical nanoparticles extreme purity of small diameter, low size distribution and low yield agglomeration [70]

- **Chemical vapor deposition (CVD) synthesis**

The CVD process is probably the most widely used bottom-up approach today for the preparation of nanotubes, nanowires and nanoparticles. Its principle is based on the Decomposition of a gaseous precursor that adheres to and accumulates on a substrate (silicon or quartz slat). In general, a catalyst is deposited on the surface of the substrate Thus activating the chemical reaction between the substrate and the gaseous precursor [71,72].

II.5.4. Processes for the development of nanoparticles by chemical (colloidal) means

These are the oldest methods used for the preparation of dispersions nanoscales in matrices. The first use of the colloidal method dates back to faraday who from 1857 prepared colloids of au [73]. Colloidal methods allow prepare large quantities of products and are suitable for the production of nanoparticles. These methods are based on fairly simple principles although it remains difficult to control certain reactions uniformly. They have the advantage of being quite inexpensive and requires less energy than other synthesis processes nanoparticles. They are also the simplest to implement and are the basis of a large part of the production of nanomaterials [74]. Among them, we distinguish in general: reductions (chemical, electrochemistry, sonochemistry, photochemistry ...), methods conventional (sol-gel) and thermal decomposition of metal compounds in media aqueous or organic in the presence of surfactants, ligands or polymers [75].

- **Reduction**

The reduction of an ion or complex can be done by a chemical reducer or biological or by the production of reducing species such as radicals or electrons by radiolysis, photolysis or sonochemistry.

- **The sol-gel process**

It is a method for obtaining colloidal nanoparticles in phase liquid. It was developed for the production of nanomaterials and for coatings [76]. This process is mainly used for the production of oxide nanoparticles metallic and composite nano powders. The main advantage of the sol-gel method rests on the fact that it is a low temperature process and moreover, it allows access to materials organic-inorganic hybrids. The main precursors used in this process are metal alkoxides ($Ti(OC_2H_3)4$, $Si(OC_2H_3)_4$), chlorides and nitrates [77-78].

- **Chemical decomposition**

The most commonly used metal precursors are complexes organometallic. The thermal decomposition of these metal precursors induces separation between the metal atoms and the organic part of the precursor. The solubility of atoms decreases strongly resulting in the supersaturation of the medium which leads to the precipitation of particles. This method avoids the use of reducing agents. However, the limiting factor of this method is the temperature necessary for decomposition because it causes a restriction in the stabilizers and solvents that can be used. The stabilizers most often used are polymers. The latter make it possible to control nanoparticle size during growth [79-80]

II.5.5. Biological methods (Biosynthesis)

Biosynthesis is presented as an alternative method to chemical methods and physical. Efforts have therefore been made for the synthesis of nanoparticles at from biological materials in an aqueous medium. This is how lemongrass, the tea leaves [81], algae [82], human cells [83], fungi, microorganisms [84] and proteins [85] have been used to synthesize nanoparticles of various shapes and sizes. However, by this approach, it is very difficult to control the chemical composition and purity of the particles obtained. In addition, the reaction mechanism is far from being established [81].

II.6. Applications of Nanoparticles

Nanoparticles, due to their unique properties, have a wide range of applications across various fields. Here are some of the key applications

II.6.1. Medicine and Healthcare

- Diagnosis of diseases. Gold nanoparticles and iron oxide nanoparticles are commonly used in imaging [86].

- Cancer treatment drug delivery: nanoparticles can be engineered to deliver drugs directly to targeted cells, improving the efficacy and reducing the side effects of treatments. For example, liposomes and polymeric nanoparticles are used to encapsulate drugs and release them at specific sites within the body [87].

- Diagnostic Imaging: Nanoparticles enhance the contrast in imaging techniques like MRI, CT scans, and ultrasound, aiding in the early detection: Silver and gold nanoparticles can be used for photothermal therapy, where they are targeted to cancer cells and heated with laser light to destroy the cells. Nanoparticles can also carry chemotherapeutic agents directly to tumors [88,90].
- Antimicrobial Agents: Silver nanoparticles exhibit strong antimicrobial properties and are used in wound dressings, coatings for medical devices, and in antibacterial textiles [87].

II.6.2. Environmental Applications

- Water Treatment: Nanoparticles like titanium dioxide and silver nanoparticles are used in water purification systems to remove contaminants, pathogens, and heavy metals from water [89].
- Pollution Control: Nanoparticles can help in the degradation of pollutants and the removal of hazardous substances from the environment. For example, iron nanoparticles are used to clean up oil spills and detoxify polluted groundwater [91].

II.6.3. Energy

- Solar Cells: Nanoparticles enhance the efficiency of photovoltaic cells by improving light absorption and charge separation. Quantum dots and perovskite nanoparticles are prominent in this application [92].
- Batteries: Nanomaterials are used in lithium-ion batteries to increase energy density, charge capacity, and lifespan. Silicon nanoparticles, for instance, are used in anodes for high-performance batteries [93].
- Hydrogen Production: Nanoparticles, particularly those of metals like platinum, are used as catalysts in the production of hydrogen through water splitting [94].

II.6.4. Electronics

- Sensors: Nanoparticles improve the sensitivity and specificity of sensors used in detecting gases, chemicals, and biological agents. Carbon nanotubes and graphene are widely used in nano sensors [95].
- Transistors and Memory Storage: Nanoparticles are used to develop smaller, faster, and more efficient transistors and memory storage devices in electronics. Quantum dots and nanowires play a significant role in this area [96].

II.6.5. Cosmetics

- Skin Care Products: Nanoparticles, such as titanium dioxide and zinc oxide, are used in sunscreens to provide UV protection without leaving a white residue. They are also used in anti-aging creams and moisturizers to enhance skin absorption and efficacy [97].

II.6.6. Food and Agriculture

- Food Packaging: Nanoparticles improve the properties of food packaging materials, making them more durable, antimicrobial, and capable of preserving food freshness for longer periods [98,99].
- Agricultural Applications: Nanoparticles are used to deliver nutrients and pesticides more efficiently to plants, reducing the amount of chemicals needed and minimizing environmental impact [100].

These applications highlight the versatility and potential of nanoparticles in transforming various industries, contributing to advancements in technology, healthcare, and environmental sustainability.

Table II.2: Examples of current applications of nanomaterials: sector of activity

SECTOR OF ACTIVITY	EXEMPLE D'APPLICATIONS ACTUELLES ET POTENTIELLES
Automotive, aeronautics and aerospace	Reinforced and lighter materials, exterior paints with effect of brighter color, anti-scratch, anti-corrosion and anti-dirt. Sensors optimizing engine performance, ice detectors on aircraft wings, more durable and recyclable tyres. Additives for diesel allowing better combustion...
Electronics and communication	High density memory and miniaturized processors, solar cells, handheld electronic library, ultra-fast computers, technology wireless, flat and flexible screens...
Food	Active packaging, additives such as dyes, anti-caking agents and innovative emulsifier...
Chemistry and materials	Pigments, fillers, corrosion inhibitors, multifunctional catalysts, antibacterial and ultra-resistant coatings...
Construction	Self-cleaning and anti-pollution cements, anti-fouling glazing. Paintings innovative varnishes and glues...
Pharmacy and health	Medicinal products and active agents, anti-allergic medical adhesive surfaces, tailor-made medicinal products specifically dispensed, surfaces biocompatibles for implants. Innovative vaccines and imaging...
Cosmetics	Transparent sunscreens, abrasive toothpaste, makeup better hold...

Energy	New types of batteries, smart windows, insulating materials more efficient...
Environment and ecology	Reduction of carbon dioxide emissions, ultra water production pure from seawater, pesticides and fertilizers more effective and less Damaging...
Defense	Miniaturized surveillance systems, precise guidance systems, textiles light and protective repairing themselves...

II.7. Silver Nanoparticles

Silver nanoparticles (AgNPs) are tiny particles of silver that range in size from 1 to 100 nanometers [101]. These nanoparticles exhibit unique properties due to their small size and high surface area, which differ significantly from those of bulk silver [102]. Key characteristics of silver nanoparticles include their strong antimicrobial activity, optical properties, and electrical conductivity [103]. Ag NPs are synthesized through various methods, including chemical, physical, and biological (green) approaches, with the biological methods gaining popularity for their eco-friendliness [104]. Silver nanoparticles are used in numerous applications such as medical devices, drug delivery systems [105], antimicrobial coatings, water purification, and in electronics for their conductive and optical properties [106].

Chapter III:

Materials and Methods

In recent years, the green synthesis of metal oxide nanoparticles has attracted considerable attention. A very simple, effective and environmentally friendly protocol was developed to synthesize green nanoparticles using an aqueous extract of various plants, phenolic compounds extracted from plants play a major role as that reducing and styling agent of metal ions during synthesis. The green synthesis, the characterization and application of nanoparticles (NPs) is becoming a major challenge in nanotechnology. This technique is very safe and environmentally friendly.

The purpose of this chapter is to present a simple protocol for the green synthesis of silver oxide nanoparticles using the extract of the leaves of Artemisia Herba-Alba, as well as the conditions experimental used in this study. For investigation, the characterizations of Nanoparticles obtained were analyzed using standard techniques such as UV Vis, FT-IR, DRX, SEM, EDX, TGA and DTA to confirm the nature of the final products obtained by the green synthesis.

III.1. The Green synthesis from plant extracts

The green synthesis of nanoparticles represents a step forward compared to others methods because it is simple, cost-effective and relatively reproducible, and often gives more stable materials. Microorganisms can also be used to produce nanoparticles, but the rate of synthesis is slow and only a limited number of sizes and shapes lend themselves to the method compared to pathways involving plant-based materials. In the green synthesis method, there is no requirement of high pressure, energy, temperature or toxic chemicals. Therefore, nowadays, many researchers are turning away from the use of synthetic methods. Plants produce nanoparticles more stable compared to other means and it is very simple to develop them. The risk of contamination is also lower [107].

Current green synthesis practices often involve the use of natural sources such as extract from plant leaves, non-hazardous solvents (examples water and ethanol), biodegradable and biocompatible materials and energy-efficient processes in the preparation of nanoparticles [108].

For the synthesis of silver oxide nanoparticles using biological agents, we have not yet imagined, but it is suggested that different bimolecular are responsible for the synthesis of nanoparticles. But in intracellular biosynthesis and extracellular nanoparticles, as well as the effect of bioreducing agents on size and forms nanoparticles [109].

The presence of phenolic compounds such as tannins, flavonoids and acids phenolics in plant extract could be responsible for reducing ions metals and the creation of the respective metal oxide nanoparticles [110].

The next challenge for researchers is to find new metal ion bioreduction protocols for green synthesis of metal oxide nanoparticles using plant extracts in particular unused plant parts such as fruit leaves and peels, while guaranteeing easy, low-cost and low-cost mechanisms and environmentally friendly.

III.1.1. Mechanism for green synthesis of nanoparticles by plant extracts

In general, the mechanism of bioreduction of metal in plant extracts consists of three main phases: activation phase, growth phase and termination phase.

- The primary stage is the activation phase in which the metal ions are recovered from their salt precursors by the action of plant metabolites, biomolecules with reduction capacities. In addition, metal ions change from a mono- or divalent oxidation state to a zero valence state and the nucleation of the reduced metal atoms takes place. [111]
- The growth phase, referring to the spontaneous coalescence of nanoparticles in which small adjacent nanoparticles spontaneously unite into larger particles, which is accompanied by an increase in the thermodynamic stability of the nanoparticles. [112]
- The final stage of synthesis is the termination phase during which the Nanoparticles eventually reach their maximum possible activity, this process being strongly influenced by the ability of a plant extract to stabilize metal nanoparticles. [113]

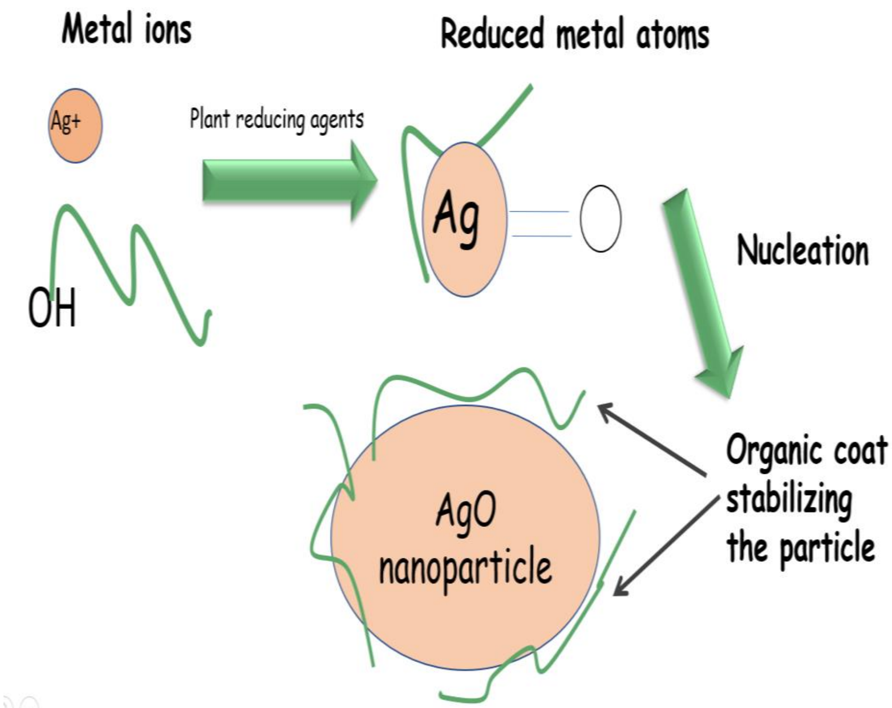


Figure III.1: Green synthesis mechanism.

III.1.2. Effect of secondary metabolites in the bio reduction reaction

The reduction reaction mechanism mainly concerns plant bimolecular (secondary metabolites) such as organic compounds. These secondary metabolites are well known as key sources for controlling various acute diseases. This proposed reduction reaction proved that secondary metabolites are essential factors in the biosynthesis of metal nanoparticles.

Plant extracts contain several functional groups, including H-C, C=C (alkenyl), C=N (amide), O=H (phenolic and alcohol), N-H (amine) and COO- (carboxylic group). Phenolic compounds are the most used in green synthesis. The latter is characterized by the presence of a benzene ring having one or more hydroxyl substitutes.

Our work was carried out at the level of “valorisation et technologie des ressources sahariennes” (VTRS) of Echahide Hamma Lakhdar University of El Oued. This work includes the study of green synthesis and characterization of metal nanoparticles by the extract of leaves Artemisia Herba-Alba.

III.2. Materials and methods

III.2.1. Plant material

As part of green chemistry for the synthesis of silver nanoparticles, we selected Artemisia Herba-Alba a sheet as a reducing agent. This choice is based on the studies conducted on this plant in the VTRS laboratory [123]. They confirmed the presence of several phytochemical compositions, including: alkaloids, polyphenols (flavonoids, tannins) and saponins.

III.2.2. Methodology

III.2.2.1. Sample preparation

The leaves of Artemisia Herba-Alba were harvested in October 2018 from Ain Zatoute –Biskra- (South East of Algeria).

The samples are cleaned and dried at room temperature and away from sunlight, in order to preserve the integrity of its chemical composition as much as possible.

- **Extraction of phenolic compounds:**

For the separation of phytochemicals from solid plant matter in use of organic solvents, in this case solid-liquid extraction is applied. The principle of this method is that the solvent must cross the interface barrier solid-liquid, dissolve the active component inside the solid and drag it outside.

In our study, for the extraction of phytochemicals we chose the technique of extraction by maceration in water during which the solid is put duringa more or less long duration in a liquid.

- **Operating Mode :**

The extract was prepared by placing 50 g of powdered material plant strong (leaves or the bark of fruit) with 500 ml of distilled water in a glass beaker of 1000 ml. The mixture was been stirred regularly for 24 hours at 35°C. The extract was filter redusing a filter paper (WhatmanNo : 42) and stored in a glass container airtight 4° C for future use.

III.2.2.2. Synthesis of nanoparticles of silver oxide

The silver oxide nanoparticles were synthesized by a reduction of iron ions solution of silver nitrate ($AgNO_3$) by phenolic compounds of the extract of the plants Figure III.1.

Adding with four different concentrations (from 2, 3, 4, and 5 mM) of the solution of silver nitrate ($AgNO_3$) to the extract in a volume ratio of 1:10 v/v between the extract and the solution of silver nitrate, it took 20 ml / 200 ml in a 250 ml beaker.

The silver oxide nanoparticles have been immediately obtained with the process of reduction. The mixture is stirred continuously at 75 ° C for 1 hour. The formation of NPs silver oxide is indicated by a color change of the mixture solution of the brown light to dark black. The reasonable mechanism of formation of silver oxide nano particles may be due to the reduction of silver ions, which takes place at the same time that the phenolic compounds in the extract of plants.

A small amount of the solution NPs of silver oxide synthesized has been preserved for the measurements of UV-visible.

The solid product was collected by centrifugation at 3000 rpm for 30 min. The samples of NPs synthesized were washed several times well with distilled water and dried in a drying oven drying at 100 °C for 24 h. The dried powder was annealed at 500 °C for 3 h in an oven. To crystallize completely NPs and eliminate compounds organic remaining of the plant extract. The powders resulting have been stored in containers for different characterizations.

III.2.3. Techniques of characterization

Considering the nanometric character of materials synthetized in this study, we shall introduce in this party, the various techniques of investigation under which a definite description of this last will be shown.

III.2.3.1 Structural and morphological Ownership

III.2.3.1.1. Diffraction of X-rays (DRX)

X-rays are the electromagnetic radiance the length of wave of which is understood between 0.01 and 10 °A. This not destroying technology is the most useful and the most spreading for the identification of nature and the structure of the crystallized products. Besides, the diffraction by X-rays allows having access to physical information on crystals, notably their size and their orientation.

- **Principle:**

This technology is based on the correlations of the crystalline structure of a sample with radiance monochromatic of short length of wave.

When X-rays attain reticular plans of crystalline networks, either they get into contact with the electronic clouds of atoms constituting this plan, in that case the beams of X-rays are partly reflected by the first plan, or they do not meet obstacle and can go on up to the second plan to be again partly thoughtful. These plans are separated by characteristic distance which depends like the analyzed material (reticular distance).

The interferences of rays are going to be alternately useful or destroying. The directions in which interferences are useful, called peaks of diffraction, can be determined by the law of Bragg. [114]

- **The law of Bragg**

When a crystalline species is irradiated by X-ray radiation of wavelength λ under an incidence θ the radiation is diffracted if Bragg's law is verified.

$$\mathbf{n\,\lambda = 2\,d\,sin\,\theta} \qquad (1)$$

With: n is an integer that represents the order of reflection.

λ is the wavelength of X-rays.

d is the interreticular distance.

θ is the angle of incidence of X-rays

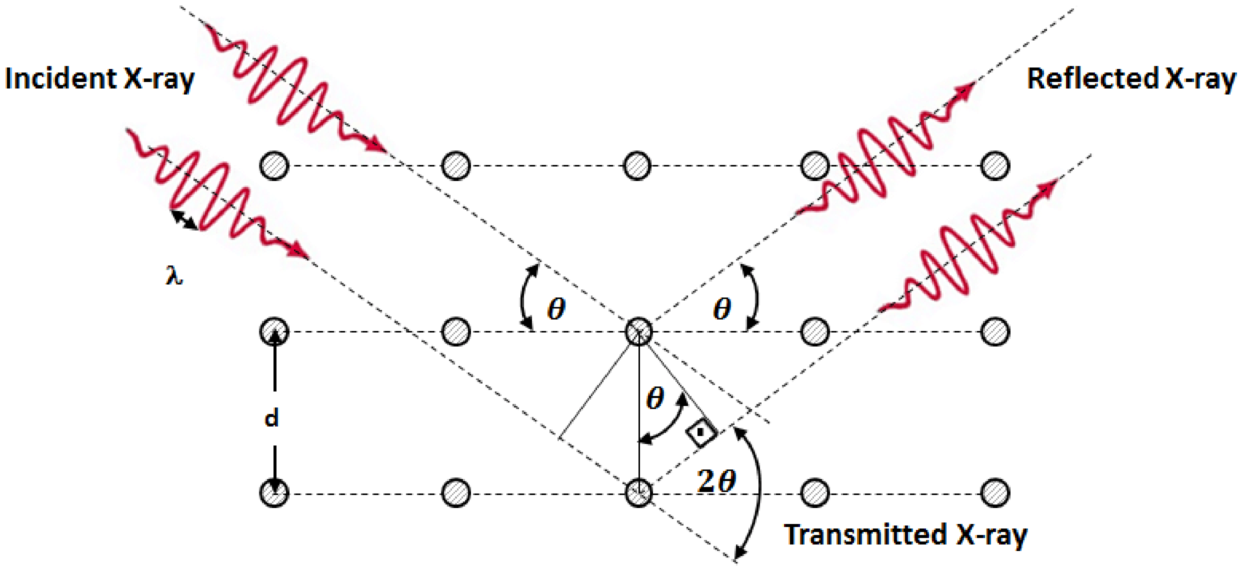


Figure III.2: Diagram illustrating Bragg's law. [115]

In general, the study of the diffractogram makes it possible to trace back to a large amount of information such as the orientation of a single crystal, the structural properties and size and shape of the samples.

Determination of grain size:

many approaches have been described for determining size using XRD, the Debye-Scherrer equation is the most commonly used to determine size. [116]

$$\mathbf{D} = \mathbf{0.9\,\lambda\,/\beta\cos\theta} \quad (2)$$

Where: D is the grain size in nm.

λ is the wavelength of the X-ray beam.

θ is the angle of diffraction.

β is the width at mid-height expressed in radian.

III.2.3.1.2. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) is a technique that allows the observation of the surface morphology of a solid material. This technique therefore offers several advantages in morphology and dimensional analysis.

- **Principle:**

Scanning electron microscopy is a technique using electron-matter interactions. SEM provides images of the surface in relation to the mode of electron scattering by the sample. These images are formed mainly using surface electronic emissions (secondary electrons and backscattered electrons).

The interaction between the E_0 energy electron beam (the primary electrons) and the sample generate low-energy electrons called (secondary electrons). The latter are then accelerated to a detector whose role is to amplify the electrical signal received (at each point, the intensity is converted into an electrical signal). The different particles are analyzed by different detectors that make it possible to reconstruct a three-dimensional image of the surface.

It uses, in addition, the other interactions of the primary electrons with the sample: emergence of backscattered electrons, absorption of primary electrons, as well as the emission of X-ray photons. Each of these interactions is often significant in the topography and/or composition of the surface.

III.2.3.2. Optical properties

III.2.3.2.1. UV-visible absorption spectrometer

UV-visible absorption spectroscopy plays a very important role in the study of the optical properties of nanoparticles. It is based on the study of the interaction of electromagnetic waves and matter.

- **Principle:**

UV-visible absorption spectrometry is based on the transition of valence electrons from a ground state to an excited state after absorption of a photon into the UV-visible.

When electrons encounter a light wave of a frequency corresponding to their vibrational frequencies, the latter absorbs the energy of the light wave and acquire vibrational motion. The vibrating electron interacts with neighboring electrons and converts the vibration into thermal energy. Absorption spectroscopy therefore refers to the measurement of the absorption of light by a material as a function of wavelength.

The greater the numbers of molecules that absorb light of a given wavelength, the greater the light absorption and the higher the maximum intensity of the absorption spectrum. [117]

This spectrophotometer works according to the Beer-Lambert principle which indicates that the fraction of incident radiation absorbed is proportional to the number of absorbent molecules in its path.

Mathematically, this law can be explained as:

$$\log\left(\frac{I_0}{I}\right) = \varepsilon cl \qquad (3)$$

With I_o: Intensity of incident light.

I: Intensity of the light transmitted by the sample solution.

c: sample concentration.

l: length of the sample path.

ε: molar absorption coefficient.

The I/I_o ratio is known as transmittance (T) and the logarithm of the I_o/I inverse ratio is known as absorbance (A).

Consequently

$$-\log\left(\frac{I}{I_0}\right) = -\log T = \varepsilon cl$$

where $\mathbf{A = \varepsilon cl}$

so $\mathbf{A = \log\left(\frac{1}{T}\right)}$ (4)

- **Determination of indirect and direct transition energy band theory:**

The theory of optical energy bands (Figure 4) estimated (Eg) of nanoparticles of metal oxide can be determined by extrapolation from the absorption edge which is given using the Tauc relation [118]

$$(\boldsymbol{\alpha} hv) = A\left(Hv - E_g^{opt}\right)^n$$

Where **α** is the absorption coefficient, **A** is constant, **hv** is the energy of light, and **n** is a constant depending on the nature of the electronic transition, $\mathbf{E_g^{opt}}$ is the energy of the band optical no-(gap) and exponent **n** = 1/2 for the direct allowed transition (Figure III.3),

while n = 2 for the allowed indirect transition. We got the energy gap at from the intersection of the edge of the linear absorption part with the energy axis.

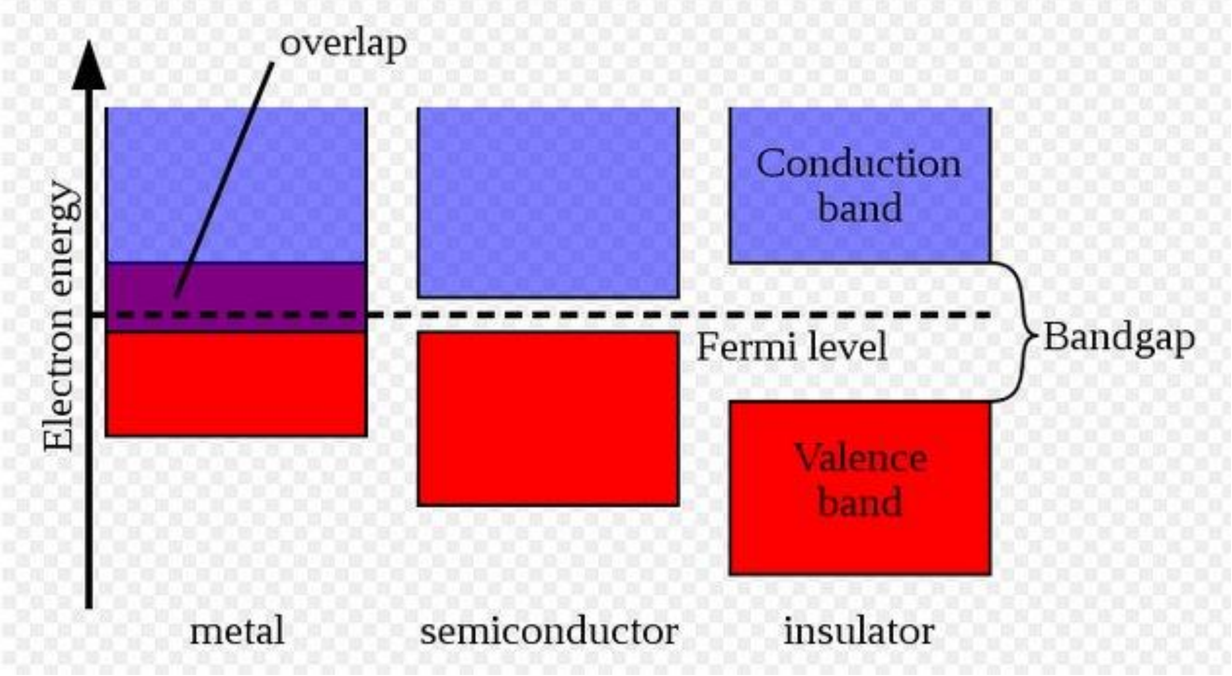


Figure III.3: Simplified diagram of the electronic band structure of metals, semiconductors, and insulators.[119]

III.2.3.2.2. Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR spectroscopy is a technique that provides information on different functional groups from peak positions in the spectrum. Information on the identification and stabilization of nanoparticles can also be deduced from this analysis.

- **Principle**:

The principle of FTIR is based on the absorption of single or double beam infrared radiation by the sample to be analyzed. It allows via the detection of vibration frequencies characteristic of chemical bonds; to carry out the analysis of the chemical functions present in the material.

III.2.3.3. Thermal properties

III.2.3.3.1. Thermogravimetric analysis (ATG)

This technique makes it possible to record the mass variation of a sample according toof the temperature cycle applied to it. The sample is placed in the nacelle of a precision balance. This basket is inserted into an oven to submit the sample at a temperature cycle (ascents, descents, isotherms) while measuring the evolution of its mass. It is possible to choose the atmosphere under which the sample is subjected to this temperature cycle [120].

The analyses were performed using a TGA 4000 device from (Netzsch STA 449 F1). Thermogravimetric Analyzer. Samples of 4 to 10 mg were heated under an atmosphere nitrogen (30 ml/min) at a speed of 10 °C/min by sweeping from 10 to 700 °C.

Chapter IV:

Results and Discussion

Silver NPs were formed by reducing Ag $^{+}$ to Ag^0 using leaf extract of Artemisia Herba-Alba. However, the reaction parameters such as pH, the ratio of $[Ag^+]$ to extracted sample, and a period can significantly affect the reduction process and lead to the formation of Ag_2O as a co-product. Silver/Silver Oxide NPs were formed by reducing Ag^+ to Ag^0 using leaf extract of Artemisia Herba-Alba. However, the reaction parameters such as pH, the ratio of $[Ag^+]$ to extracted sample, and a time frame can significantly affect the reduction process and lead to the formation of Ag_2O as a co-product. The plant extract-mediated synthesis of Ag NPs hypothesized that the presence of bioactive compounds, such as polyphenols (flavonoids) have a hydroxyl (-OH) and ketonic (-C=O) groups that bind to the bulk metal Ag^+ ion cluster them to a few nanometers size. The formation of Ag/Ag_2O NPs could be mediated by the presence of OH^-. This contributes the OH− group to Ag^+ and results in the formation of highly unstable Ag-OH, which is readily oxidized to Ag_2O upon drying and leads to the formation of the Ag/Ag_2O NPs.

IV.1. UV-Vis Spectroscopy

Visual observation shows the color changed from light yellow to brown within 5 minutes, after a while the color becomes dark brown and this indicates might be the excitation of surface plasmon resonance (SPR). The formation of Ag/Ag_2O NPs was confirmed by observing an absorption peak in the visible range from 418 to 435 due to SPR at different $AgNO_3$ concentrations (Figure IV.1) and different volumes of leaf extract (1.0, 1.5, 2.0, and 2.5 ml) to 100 ml of 1 mm $AgNO_3$ (Figure IV.2). The change in the peak intensity is due to the change in the amount of the leaf extract. This may be due to the high number of Ag/Ag_2O NPs formed resulting from the reduction of $AgNO_3$.

The optimization of the reaction time for Ag/Ag_2O NPs formation was followed at room temperature that in the first 24 hours is shown in Figure IV.3, the reaction rate was fast, to start decreasing after that until it becomes very slow after seven days. Which indicated that most Ag_+ ions were consumed for Ag/Ag_2O NPs synthesis. If we estimate that the formation of Ag/Ag_2O NPs stopped after a week, 89.4% of Ag/Ag_2O NPs formed in 24 hours.

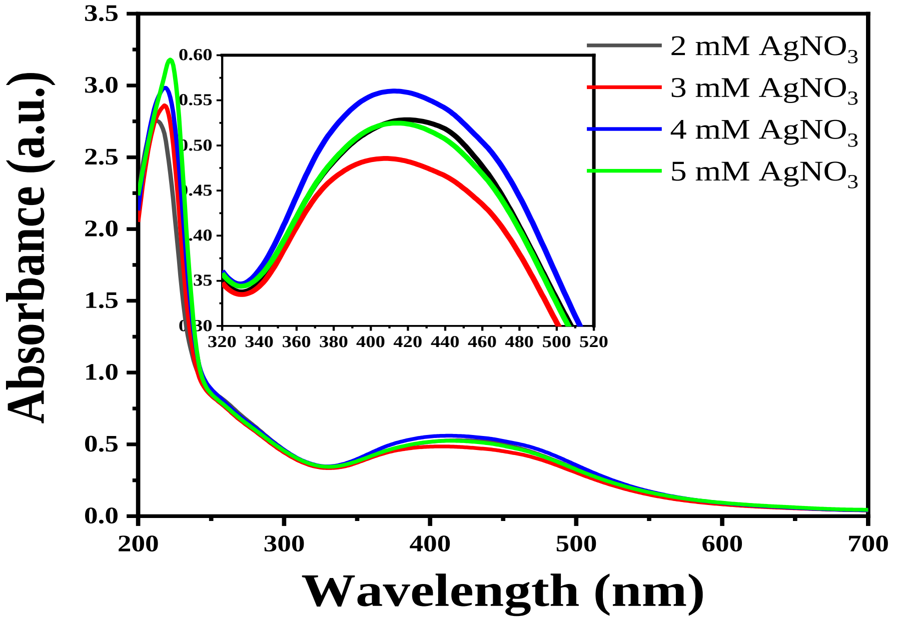


Figure IV.1: UV–Vis absorption spectrum of Ag/Ag_2O NPs synthesized using different 100 ml $AgNO_3$ precursor concentration with 1.0% leaf extract (v/v).

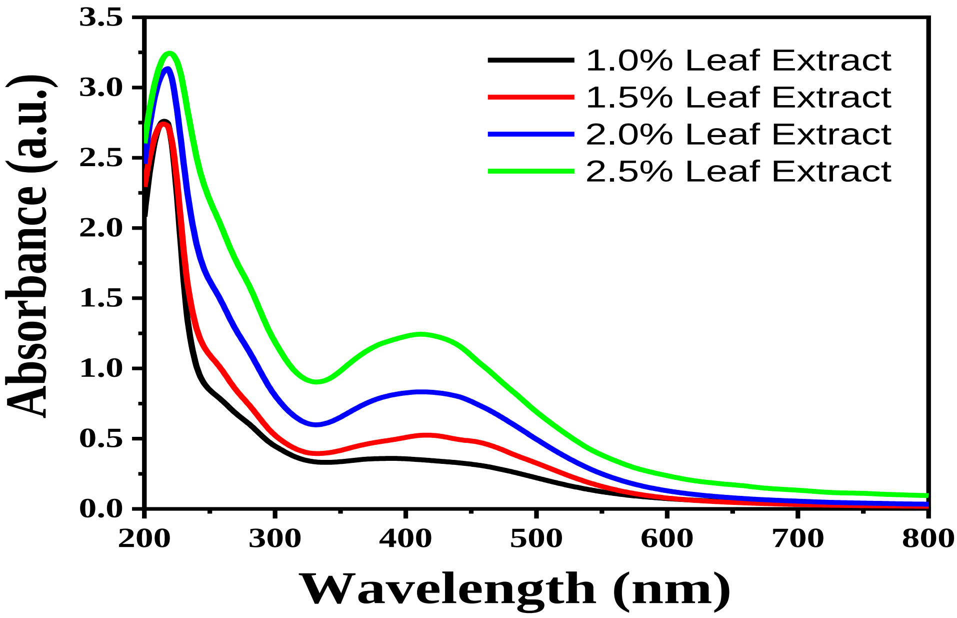


Figure IV.2: UV–Vis absorption spectrum of Ag/Ag_2O NPs synthesized from 100 ml of 1 mm $AgNO_3$with different volume ratio of artemisia herba-Alba leaf extract(v/v):1%, 1.5%, 2%, and 2.5%.

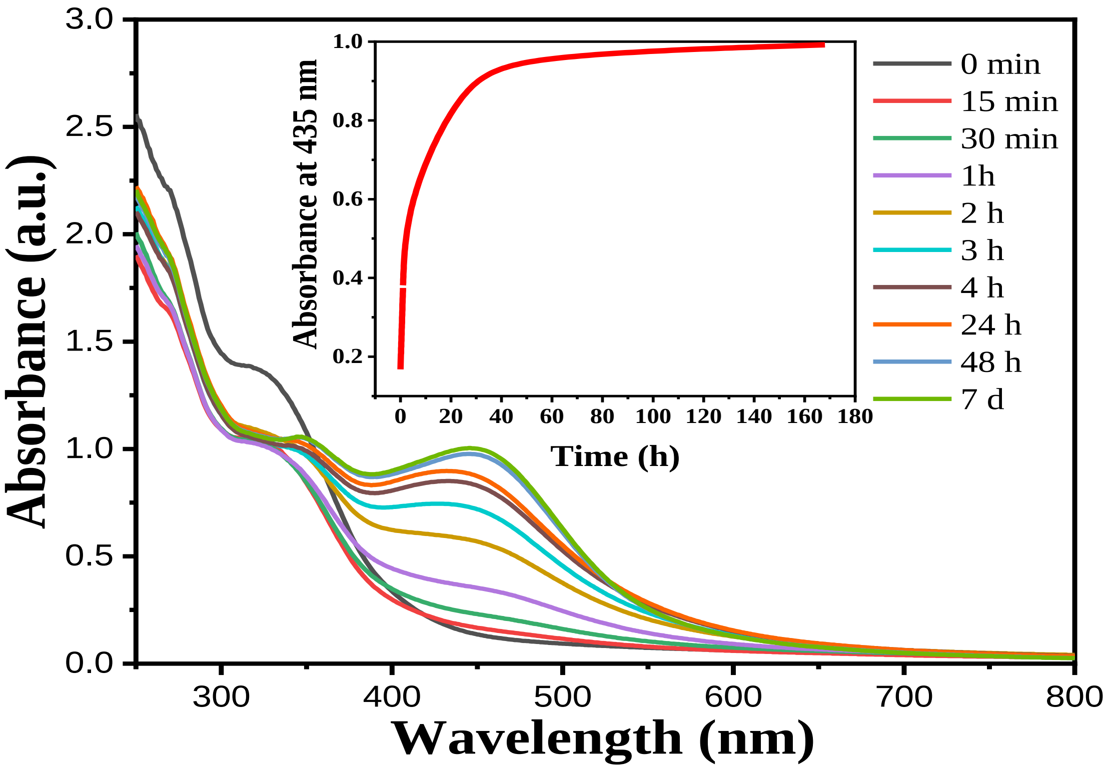


Figure IV.3: UV-vis spectrum absorption of Ag/Ag_2O NPs at different time intervals at room temperature (100 ml of 1 mm $agno_3$and 1ml artemisia herba-Alba leaf extract).

The estimated optical band gap (Eg) of Ag/Ag_2O NPs is calculated using the Tauc relation Eq.(1) [118]:

$$(Ahv) = A(Hv - E_G)^N \qquad (1)$$

Where α is the absorption coefficient, A is constant, hν is the energy of light and n is a constant depending on the nature of the electron transition, E_G Is optical band gap energy. Additionally, Figure IV.3 and Figure IV.4 show the Tauc plot of (αhν) 2 versus hν at different concentrations and different rapport, respectively. We have obtained the energy gap from the intersection of the edge of the linear part of absorption with the energy axis. When (αhν)2 is zero, the photon energy is Eg. The results are listed in Table 1. A (Eg) estimation of Ag/Ag_2O NPs with a different volume ratio of leaf extract was found to be in the range 2.05-2.30 ev. The Bandgap (Eg) slightly decreases from 2.29 to 2.32 ev with increasing the $AgNO_3$ concentration from 2mm to 5mm with 1.0% of leaf extract.

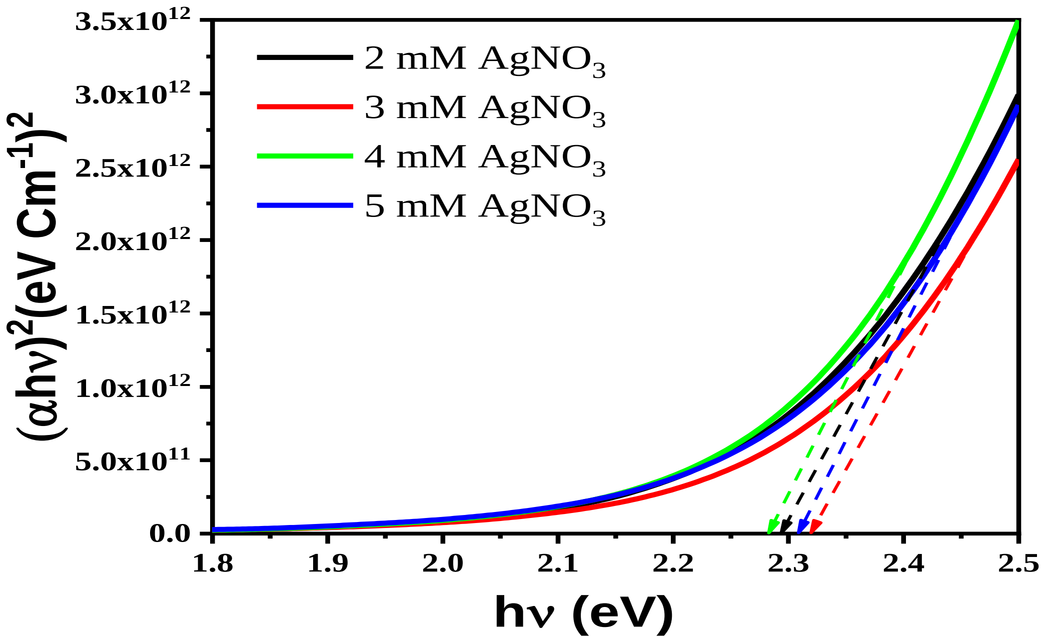


Figure IV.4: Bandgap (Eg) estimation from Tauc's relation of the prepared Ag/Ag_2O NPs with 100 ml of $AgNO_3$ of concentrations with 1.0% of leaf extract.

Table IV.1 : The optical bandgap of the Ag/Ag_2O NPs prepared from different volume ratio of leaf extract (v/v): 1.0%, 1.5%, 2.0%, and 2.5% to 100 ml of 1 mm $AgNO_3$

Volume ratio	**Optical band gap E_g (ev)**	**Precursor concentration**	**Optical band gap E_g (ev)**
1.0%	2.30	2mm	2.29
1.5%	2.27	3 mm	2.32
2.0%	2.21	4 mm	2.28

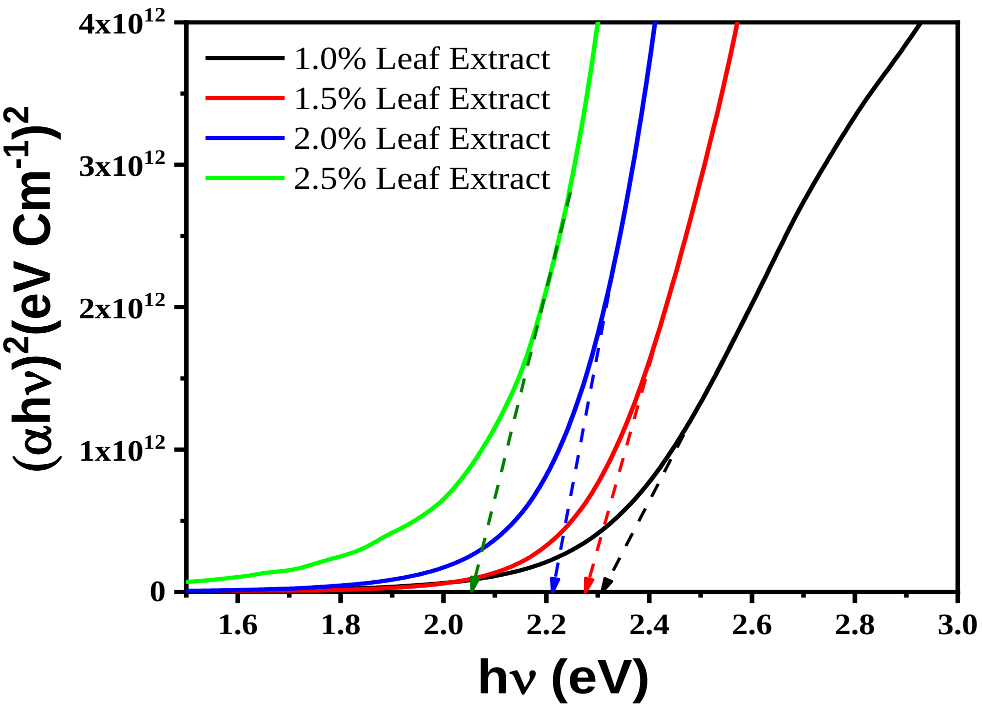


Figure IV.5: Bandgap (Eg) estimation from Tauc'srelation of the prepared Ag/Ag_2O from 100 ml of 1 mm $AgNO_3$ with different volume ratio of leaf extract (v/v): 1.0%, 1.5%, 2.0%, and 2.5%.

IV.2. Fourier transform infrared spectroscopy

FTIR analysis was done to distinguish the nature of the functional groups (reducing and stabilizing biomolecules) in the Artemisia Herba-Alba extract. The resultant FTIR spectrum (**Figure IV.6** and **Figure IV.7**) has displayed a few absorption bands that relate to the functional groups of the biomolecules existing in the plant extract. Three main absorption peaks were observed, the broad Peak centered at 3340 cm^{-1} is assigned to O–H stretching vibrations [74, 75], the intense peak at 1650 cm^{-1} is due to C=O stretching and N–H bending vibrations of the primary amides group which is commonly found in the protein [76]. Besides, the peak located at 650 cm^{-1} corresponds to C–H bending vibrations out of plane [77].

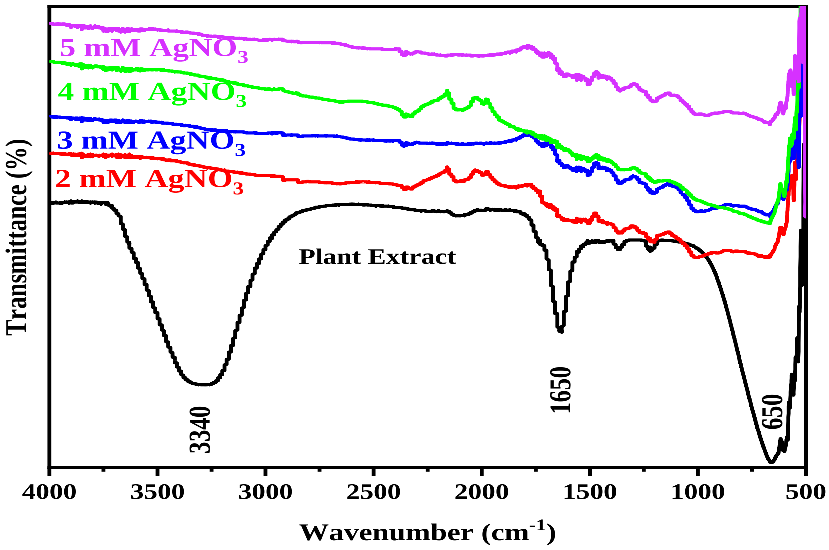


Figure IV.6: FTIR Spectra of artemisia herba-Alba extract and the prepared Ag/Ag_2O NPs solution prepared at 100 ml of $AgNO_3$ of different concentrations (2, 3, 4, and 5 mm $AgNO_3$) and 1 ml of artemisia herba-Alba extract.

The FTIR spectra of AgO NPs synthesized at different precursor concentrations and different (precursor to extract volume ratios) are shown in (Figure IV.5) and (Figure IV.6) respectively. Comparing the FTIR spectra of AgO NPs with the Artemisia Herba-Alba extract in (Figure IV.5) reveals a distinguished decrease in the band's intensity at 3340 cm^{-1} and 1650 cm^{-1} which may indicate that both of the OH group and the proteins presented in Artemisia herba-alba extract have served as bio-reducing and capping agents for AgO NPs synthesis [110].

IV.3. X-Ray Diffraction

XRD patterns of the biosynthesized Ag/Ag_2O NPs prepared from 100 ml $AgNO_3$ solution of different concentrations (2, 3, 4, and 5 mm $AgNO_3$) and different volume ratios (Leaf extract: $AgNO_3$ solution of 1.0, 1.5, 2.0, 2.5% V/V) are shown in Figure IV.7 and Figure IV.8 respectively. A number of Bragg reflection peaks were observed in all the XRD patterns located at 2θ values of 38.16°, 44.34°, 64.57°, and 77.60° corresponding to (111),(200), (220), and (311) planes of metallic face-centered cubic structure (JCPDS 04-0783) of Ag NPs [121, 122]. Whereas the diffraction peaks at 2θ values of 26.90°, 32.69°, 37.94°, 54.9°, 65.54° and 69° related to (110), (111), (200), (220), (311) and (222) planes of face-centered cubic structure (JCPDS 01-076-1393) of crystalline Ag_2O. Noteworthy that the prepared Ag/Ag_2O NPs with the lowest volume ratio of extract to $AgNO_3$ solution (1:100) shown in Figure IV.2 exhibited only one phase of metallic Ag NPs with no additional peaks of Ag_2O phase. The higher contraction of the leaf extracts the higher binding between polyphenols of the extract (hydroxyl, ketonic) to the Ag^+ ions. This contributes the OH^- group to Ag^+ and results in the formation of highly unstable Ag-OH, which is readily oxidized to Ag_2O upon drying and leads to the formation of the Ag/Ag_2O NPs [103].

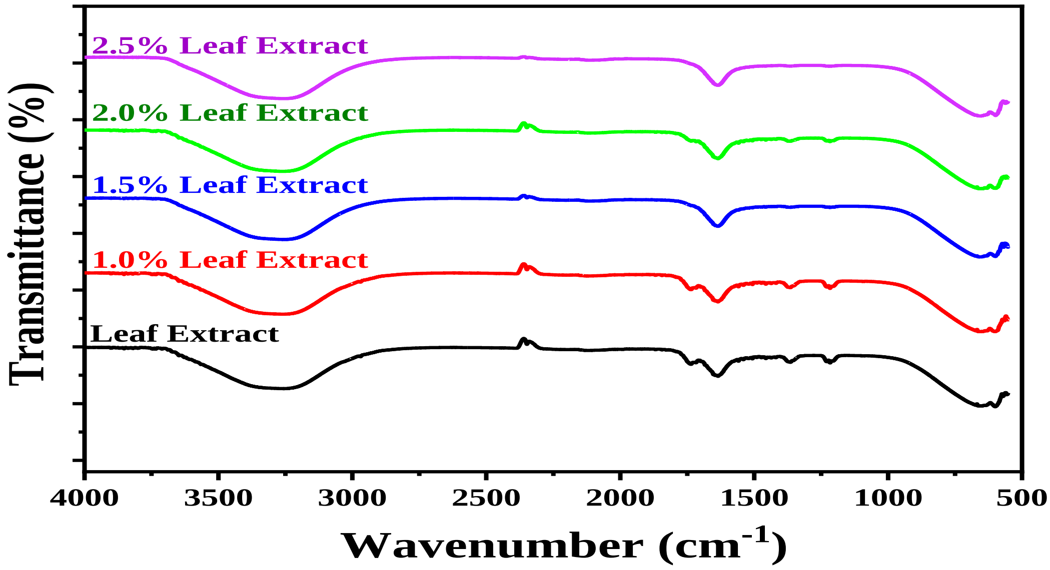


Figure IV.7: FTIR Spectra of Artemisia Herba-Alba extract and the prepared Ag/Ag_2O NPs solution prepared at 100 ml of 1 mm $AgNO_3$ and 1.0, 1.5, 2.0, and 2.5 ml of the as-prepared Artemisia Herba-Alba extract.

The crystallite size of the synthesized nanoparticles was estimated selecting the peak of highest intensity situated at 2θ value of 38.16° using the Scherrer formula eq (1):

$$D = \frac{K\lambda}{B \cos \Theta} \quad (1)$$

Where D is the crystalline size (nm), β is the full width at half maximum of the diffraction peak (FWHM) of the most intense diffraction peak, λ the X-ray wavelength (1.5406 Å) and θ is the Bragg angle of diffraction [102]. The effect of both precursor

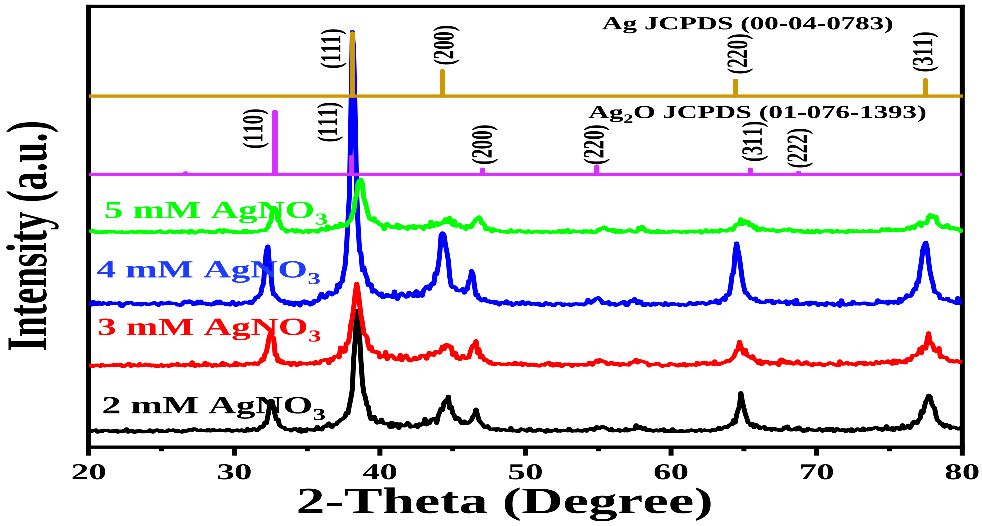


Figure IV.8: XRD patterns of the prepared Ag/Ag_2O NPs solution prepared at 100 ml of $AgNO_3$ of different concentrations (2, 3, 4, and 5 mm $AgNO_3$) and 1 ml of artemisia herba-Alba extract.

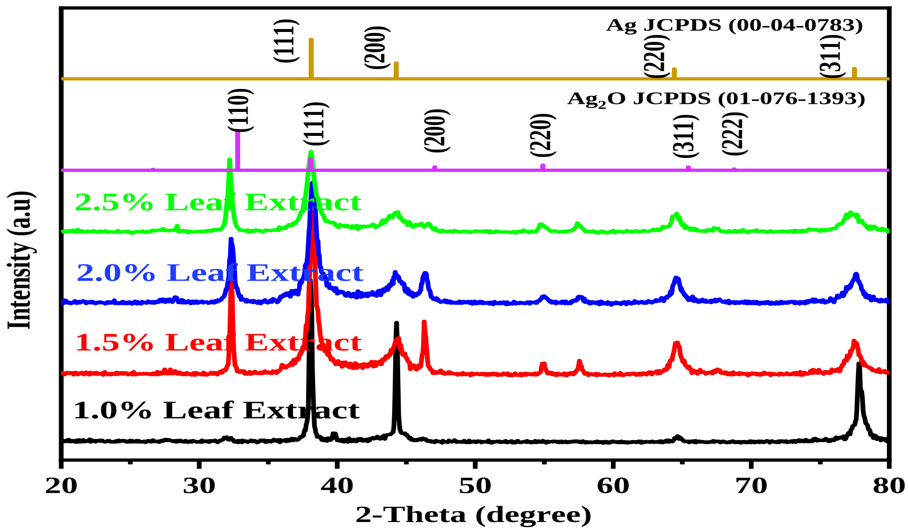


Figure IV.9: XRD patterns of the prepared Ag/Ag_2O NPs solution prepared at 100 ml of 1 mm $AgNO_3$ and 1.0, 1.5, 2.0, and 2.5 ml of the as-prepared artemisia herba-Alba extract.

Concentration and volume ratio on crystallite size of Ag/Ag_2O NPs are shown in Table 2.

Table 2 shows that the crystallite size is affected by both precursor concentration and volume ratio. Increasing the precursor concentration has irregularly affected the Ag and Ag_2O NPs crystallite size. On the other hand, increasing the volume ratio of leaf extract to 1 mm $AgNO_3$ solution from 1:100 to 2.5:100 has decreased the crystallite size of Ag from 20.25 to 10.67 and Ag_2O crystals from 36.79 nm to 12.23 nm.

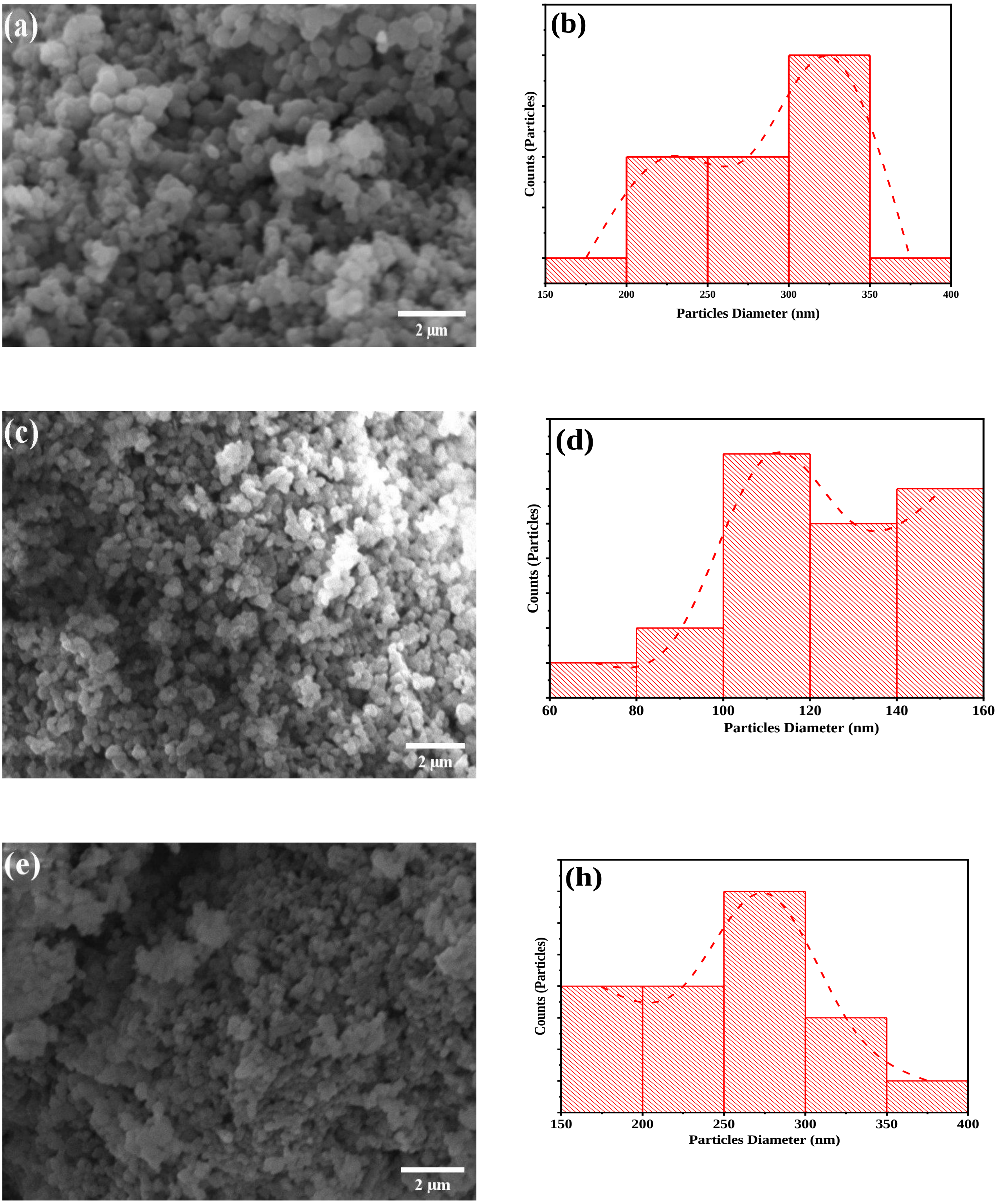
IV.4. Scanning Electron Microscopy

Particle size and morphology of Ag/Ag_2O NPs were studied using the SEM Figure IV.10. The particle size of the prepared Ag/Ag_2O NPs have a tight size distribution with an average size of 150-250nm with a spherical shape. The particle size distribution increases with decreases with increasing the $AgNO_3$ from 2-5 mm.

Table IV.1 : Effect of $AgNO_3$ precursor concentration and volume ratio of leaf extract to $AgNO_3$ solution on the crystallite size of Ag and Ag_2O NPs.

$AgNO_3$ Concentration	**Extract/$AgNO_3$ solution Volume Ratio (ml/ml)**	**Crystallite size Of Ag (nm)**	**Crystallite size Of Ag_2O (nm)**
2 mm	1.0/100	14.95 ± 1.05	36.79 ± 1.45
3 mm	1.5/100	10.67 ± 1.38	16.55 ± 0.61
4 mm	2.0/100	20.25 ± 0.82	12.35 ± 1.12
5 mm	2.5/100	10.79 ± 1.27	12.23 ± 0.56

Ag/Ag_2O NPs were aggregated to form foam like a bunch of particles, and however, individual particles were also observed. The spherical shape of Ag/Ag_2O NPs because of the equivalent growth rate alongside all nucleation directions where the sphere has the littlest surface area per unit volume contrasted with different shapes.


(a)
2 µm
(b)
Counts (Particles)
150
200
250
300
350
400
Particles Diameter (nm)
(c)
2 µm
(d)
Counts (Particles)
60
80
100
120
140
160
Particles Diameter (nm)
(e)
2 µm
(h)
Counts (Particles)
150
200
250
300
350
400
Particles Diameter (nm)

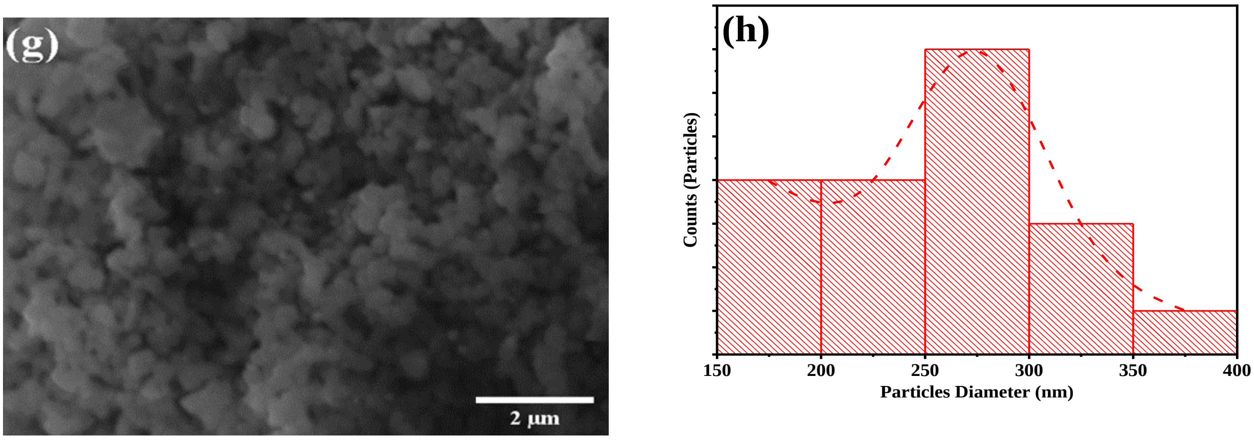


Figure IV.10: SEM images of the prepared Ag/Ag_2O NPs solution prepared at 100 ml of $AgNO_3$ of different concentrations ((a,b) 2 mm, (c,d) 3 mm, (e,f) 4 mm, and (g,h) 5 mm. $AgNO_3$) and 1 ml of Artemisia herba-Alba extract.

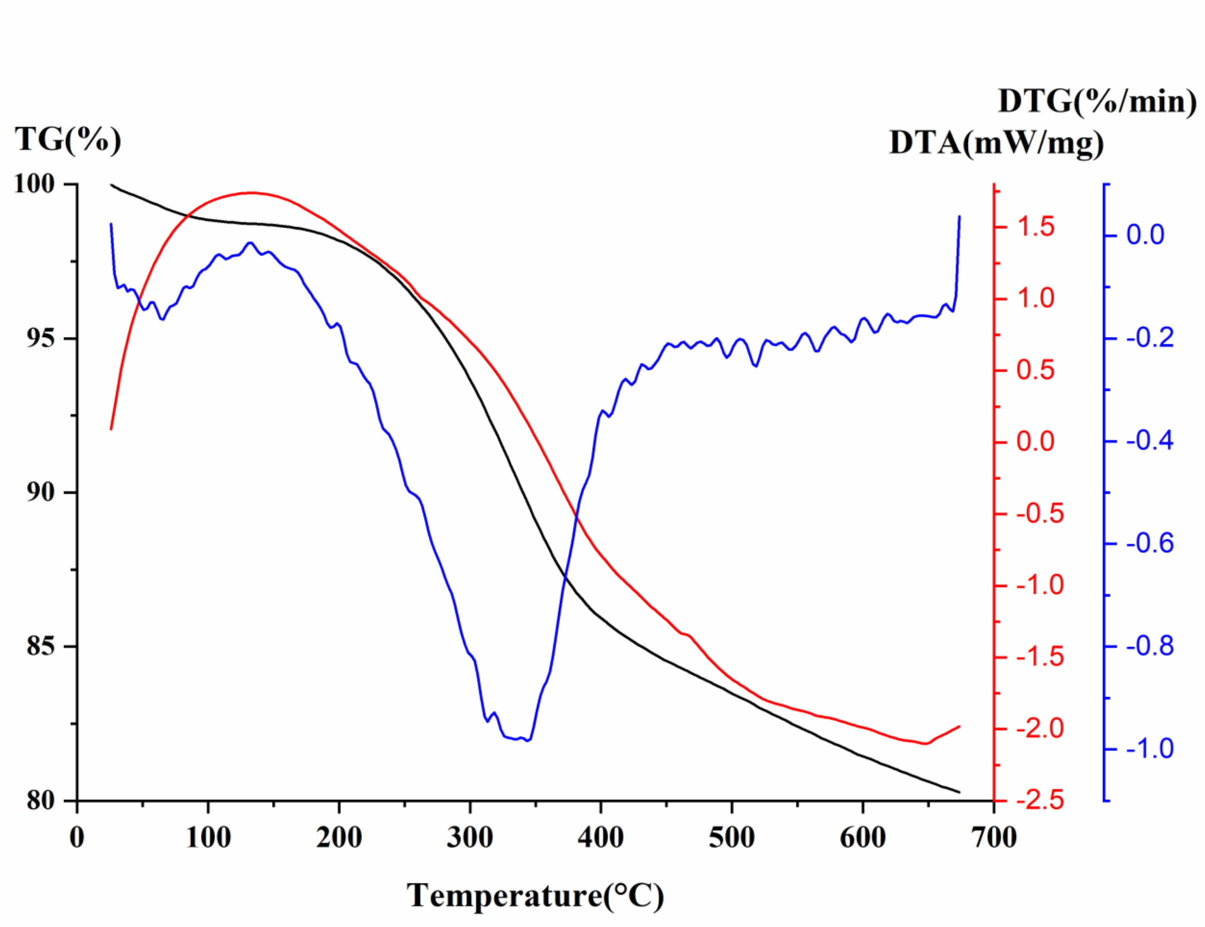


Figure IV.11: TGA and DTA profiles the prepared Ag/Ag_2O NPs solution prepared at 100 ml of $AgNO_3$ of different concentrations 2 mm agno$_3$and 1 ml of artemisia herba-Alba extract.

IV.5. Thermal Analysis and Organic Contents

Figure IV.11 shows a thermogravimetric analysis (TGA/DTA) performed to assess the purity of Ag/Ag_2O NPs in the powder form. Data extracted from TGA/DTA analysis was used to estimate the organic contents adsorbed on the surface of the AgAg_2O NPs and their thermal stability for Oxidation in the air in the temperature range from 25 to 700 [120].

To confirm the stability of Ag/Ag_2O NPs, thermogravimetric analysis was performed under a nitrogen atmosphere at a heating rate of 10 ºc.min^{-1}. Further weight loss was observed during heating from 300 to 700 °C. The first weight of about 2wt% occurs at about 140 ºc due to loss

General Conclusion

General Conclusion

Because of the terrible environmental pollution that has hit the world, the green technology and chemistry are becoming more common and used. Nanotechnology, the field is growing strongly from sophisticated technology and is associated to the construction and use of nanomaterials in the physical range [1 - 100] nm. They also represent theme, which converge and unite the physics, chemistry and biology. They throw challenges of structure, function, and implementation for where the chemistry is particularly sought. Nanobiotechnology is the application of nanotechnology in the fields organic. Chemistries, physicists and biologists have considered each of the nanotechnology as a branch of their own subject, and the collaborations to which they each contribute in equal parts are common. One of the results is the hybrid domain of nanobiotechnology that uses metal nanoparticles are widely in several areas of application due to their exceptional properties. These properties depend on especially their size and shape.

In this study, silver oxide nanoparticles synthesized green by using plant extract leaves of Artemisia herba-alba were studied. The characterizations of the resulting nanoparticles were analyzed using standard techniques such as UV-Vis, FT-IR, XRD, SEM and (TGA/DTA),

The silver oxide nanoparticles have been synthesized by the reaction of reduction of the silver ions due to the presence of phenolic compounds in plant extracts which act as an agent bioreducteur. The characterization techniques used were validated the formation of silver nanoparticles.

UV-Vis and FTIR optical characterization techniques confirmed the training of silver oxide nanoparticles distinguishing between AgO absorption bands, and disappearance of polyphenol absorption bands due to the reduction of silver ions.

The XRD analysis allowed us to observe the presence of two phases of silver oxide, the crystallite size of Ag from 20.25 to 10.67 and Ag_2O crystals from 36.79 nm to 12.23 nm. The Ag/Ag2O NPs were found to be less than 100 nm in size with spherical shapes.

Indeed, from the SEM images we can observe that the particles are agglomerated in roughly spherical form of different sizes.

As part of the continuation of this study, it will be necessary to control the dispersion and the morphology of silver oxide nanoparticles by modifying the conditions and parameters synthesis (reaction time, annealing time and PH).

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Scientific publications

GREEN SYNTHESIS AND CHARACTERIZATION OF SILVER/SILVER OXIDE NANOPARTICLES USING AQUEOUS LEAVES EXTRACT OF ARTEMISIA HERBA-ALBA AS REDUCING AND CAPPING AGENTS

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Artemisia herba-alba is a medicinal plant, and its essential oil is used as an antiseptic and antispasmodic. In this study, green synthesis of silver/silver oxide (Ag/Ag_2O) nanoparticles was successfully synthesized from Artemisia Herba-Alba aqueous leaves extract. The effect of temperature, reaction time, the concentration of $AgNO_3$, the quantity of plant extract, and pH on the synthesis process of Ag/Ag_2O was optimized. More interesting, the results showed that only 5 min were required for reducing 1 mM $AgNO_3$ into Ag/Ag_2O NPs at room temperature. The crystalline nature of Ag/Ag_2O NPs with an average crystallize size of 10.7-36.8 nm. The green synthesizing Ag/Ag_2O NPs having in general a spherical morphology with particle/aggregate size less than 100 nm. The maximum UV-Vis absorption peak of Ag/Ag_2O NPs was observed at the range of 418- 435 nm giving optical band gaps of 2.05-2.30 eV. The TGA/DTA analysis shows significant organic contents (18 wt%) were physically and chemically adsorbed on the dry weight Ag/Ag_2O NPs. Artemisia herba-alba is a source of phytochemicals for effective and prompt fabrication of Ag/Ag_2O NPs with relevant insecticidal and anti-bactericidal activity against species of high public health importance.

Keywords: *silver /silver oxide nanoparticles; Artemisia Herba-Alba; Silver nitrate $AgNO_3$; Green Synthesis, XRD*

1. Introduction

Green synthesis has as of late become a typical methodology for the development of nanoparticles (NPs) [1]. Green synthesis (biosynthesis) method utilized for getting nanoparticles through normally happening reagents like vitamins, sugars, plant extracts, biodegradable polymers, and microorganisms as reducing and capping agents [2]. However, the tweaking of the last properties is without a doubt the most repetitive and moving issue to be tackled before the far and wide utilization of metals and metal oxides NPs acquired by these routes [3]. Over the long decades, microorganisms such as bacteria [4–6], viruses [7], algae [8–11], fungi [12–15], yeast [13, 14], and especially plant extracts [16–19] have played a prominent role in the synthesis of metals and metal oxides NPs for specific applications, for example, bioimaging, drug delivery, and tissue engineering [19,20]. Plant extracts are also common in the green synthesis of metals and metal oxides NPs [22], as they act as a bio-reducing agent as well as a covering agent due to the presence of phytochemicals such as organic acids, flavonoids, alkaloids, phenolic compounds, and terpenoids [23–26].

Silver (Ag) and silver oxide (Ag_2O) NPs are wonderful materials and having great potential for biomedical applications such as wound healing and cancer treatment [27]. To date, an assortment of synthetic, physical, and biological methods has been developed for the synthesis of Ag and Ag_2O with various morphologies for various applications [14],[28]. They are additionally a notable nanomaterial having tremendous applications in the field of oxidation catalysis [29–31], sensors [32–35], cancer cells [36], and photovoltaic cells [37]. There are numerous methods for the synthesis of Ag_2O, for example, photoreduction [38], wet precipitation [39–41], electrochemical synthesis [42–45], in additions to the green biosynthesis methods based on microorganisms [46, 47] and plant extracts [48–52]. Nonetheless, the physical and chemical methods are perilous, harmful, and costly [53, 54]. Despite the unique properties and wide range of applications reported for Ag and Ag_2O NPs, safety concerns have been raised over the usage of Ag and Ag_2O NPs because they pose cytotoxicity effects on the human cells [55].

Plant extract synthesis of Ag/Ag_2O NPs in an aqueous medium is advantageous for biological applications because the resulting particles can often be used directly [56], yet these techniques typically provide Ag NPs of low monodispersity, or with a size that is difficult to control [57]. Generally speaking, the aqueous synthesis of Ag NPs falls under the category of wet chemistry. This including

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the clustering and nucleation of Ag^+ ions within a bulk solution in the presence of a reducing agent. To control particle size, capping and stabilizing agents such as trisodium citrate and polyvinylpyrrolidone (PVP) are typically used to slow and eventually stop the growth of the Ag NPs [58]. The formation of Ag_2O NPs instead of Ag can be performed by combining aqueous solutions of Ag^+ ions and alkali hydroxide. This reaction does not afford appreciable amounts of AgOH due to the favorable energetics for the following (2 AgOH → Ag_2O + H_2O, pK = 2.875). Recently, more attention has been given to the low-cost, non-toxic, simple, and eco-friendly synthesis of Ag and Ag_2O NPs from biological sources due to their antioxidant or reducing properties commonly liable for the reducing and stabilizing out of the synthesized nanoparticles.

Plant-extract synthesis seems to be the best route for large-scale Ag and Ag_2O NPs synthesis. Plant parts of Camellia Sinensis (green tea) [59–61], pine [62, 63], persimmon [64], ginkgo [65], magnolia [66], and Platanus [67] are being used for Ag and Ag_2O NPs synthesis. This technique made particles with a scatter size scope of 10 to 200 nm, yet it was likewise tracked down that the Ag NPs size could be constrained by fluctuating the reaction temperature. The speed at which the Ag NPs were reduced by the plant separate was similar to those of utilizing chemicals to reduce [68]. Thus, this route is considered as the best stage being liberated from harmful chemicals just as giving regular reducing and capping agents for the stabilization of the synthesized Ag and Ag_2O NPs. The use plant extraxt for the synthesis of Ag and Ag_2O NPs is eco-friendly and biocompatibility rout for pharmaceutical and biomedical applications as plant extracts do include toxic chemicals for the synthesis protocol.

The present work disclosed the green synthesis of Ag/Ag_2O NPs by using Artemisia Herba-Alba aqueous leaf extract. The synthesis route of the Ag/Ag_2O NPs was optimized based on the standard characterization techniques, including ultraviolet-visible spectrophotometry (UV–Vis or UV/Vis), Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), and thermogravimetric and differential thermal analysis (TG–DTA) [69],[70]. This work also provides more information on the chemical composition of the Artemisia Herba-Alba aqueous leaf extract originated from Ain Zatoute –Biskra- (South East of Algeria) and investigates their chemical characteristics. Artemisia Herba-Alba, the white wormwood, is a lasting bush in the sort Artemisia that develops generally on the dry steppes of the Middle East (Desert of Egypt), North Africa (Tunisia, Morocco, and Algeria), Western Asia (Arabian Peninsula), and Southwestern Europe. Numerous reports attributed different natural and/or pharmacological activities of Artemisia Herba-Alba to specific segments of its fundamental oil and found that varieties in oil structure were typically connected with considerable changes in movement, specifically the antimicrobial action [71, 72]. The antibacterial and the antispasmodic activity of Artemisia Herba-Alba fundamental oil has likewise been accounted for to have an enemy of anti-leishmaniasis activity [73].

2. Materials and Methods

2.1. Materials

Silver nitrate ($AgNO_3$, 98%, VTRS Laboratory), double distilled water, samples of Artemisia Herba-Alba were harvested in October 2018 from Ain Zatoute –Biskra- (South East of Algeria) used as received.

2.2. Preparation of Artemisia Herba-Alba Leaf extract

Leaves of Artemisia Herba-Alba were washed twice by distilled water, then were dried in the air for 5 days, the preparation of aqueous extract been by adding 500 mL of double distilled water to 50 grams of Artemisia Herba-Alba powder well (w/v ratio 1:10) and then kept under continuous stirring at 35℃ for 24 h. The extract was filtered through Whatman filter paper to obtain the clear filtrate, which was used in Ag/Ag_2O NPs synthesis.

2.3. Biosynthesis of silver/silver oxide nanoparticles

Ag/Ag_2O NPs were synthesized by adding different ratio volume ratios 1 mL to 2.5 mL of leaf extract to 100 mL of 1 mM $AgNO_3$ aqueous solution in a 250 mL-Erlenmeyer flask. The mixture was kept under stirring 150 rpm at room temperature for 2 hours, the bio-reduction of Ag^+ to Ag° can be observed by a color change from yellow to reddish-brown brown after 5 minutes.

2.4. Characterisation of silver/silver oxide nanoparticles

Biosynthesis of Ag/Ag_2O NPs was analyzed by using UV-vis spectrometry (Shimadzu -1800). The UV-Vis measurements were recorded at room temperature in a wavelength region of 300 to 900 nm. The reaction time and stability of the Ag/Ag_2O NPs formation were followed by UV-vis spectrometry using quartz cells and double distilled water as a blank solution. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy measurements of leaf extract and green synthesis Ag/Ag_2O NPs were performed by (Nicolet iS5, Thermo Fisher Scientific), to identify the functional groups carried out in the range of 4000 to 400 cm^{-1}.

Crystalline structure and crystallite size of the synthesized Ag/Ag_2O NPs was obtained using an X-ray diffractometer (XRD, Rigaka Miniflex 600) and CuK radiation with a wavelength of 0.15406 nm in the angular 2θ range 10°< 2 θ<80°. Particle size and morphology of the synthesis Ag/Ag_2O NPs were examined by using (SEM-TESCAN VEGA 3) at an accelerating voltage of 10 KV. Thermogravimetric and differential thermal analysis (TG–DTA) of the silver/silver oxide nanoparticles was studied were performed with a TG apparatus (Netzsch STA 449 F1). Ag/Ag_2O NPs of about 10 mg were heated from 10 to 700 C at a heating/cooling rate of 10 ℃/min and a flow rate of 30 mL/min in the air atmosphere.

3. Results and discussion

Silver NPs were formed by reducing Ag^+ to Ag^0 using leaf extract of Artemisia Herba-Alba. However, the reaction parameters such as pH, the ratio of $[Ag^+]$ to extracted sample, and a period can significantly affect the reduction process and lead to the formation of Ag_2O as a co-product. Silver/Silver Oxide NPs were formed by reducing Ag^+ to Ag^0 using leaf extract of Artemisia Herba-Alba. However, the reaction parameters such as pH, the ratio of $[Ag^+]$ to extracted sample, and a time frame can significantly affect the reduction process and lead to the formation of Ag_2O as a co-product. The plant extract-mediated synthesis of Ag NPs hypothesized that the presence of bioactive compounds, such as polyphenols (flavonoids) have a hydroxyl (-OH) and ketonic (-C=O) groups that bind to the bulk metal Ag^+ ion cluster them to a few nanometres size. The formation of Ag/Ag_2O NPs could be mediated by the presence of OH^-. This contributes the OH− group to Ag^+ and results in the formation of highly unstable Ag-OH, which is readily oxidized to Ag_2O upon drying and leads to the formation of the Ag/Ag_2O NPs
.

3.1. UV-Vis Spectroscopy

Visual observation shows the color changed from light yellow to brown within 5 minutes, after a while the color becomes dark brown and this indicates might be the excitation of surface plasmon resonance (SPR). The formation of Ag/Ag_2O NPs was confirmed by observing an absorption peak in the visible range from 418 to 435 due to SPR at different $AgNO_3$ concentrations (Figure 1) and different volumes of leaf extract (1.0, 1.5, 2.0, and 2.5 mL) to 100 mL of 1 mM $AgNO_3$ (Figure 2). The change in the peak intensity is due to the change in the amount of the leaf extract. This may be due to the high number of Ag/Ag_2O NPs formed resulting from the reduction of $AgNO_3$.

The optimization of the reaction time for Ag/Ag_2O NPs formation was followed at room temperature that in the first 24 hours is shown in Fig. 3, the reaction rate was fast, to start decreasing after that until it becomes very slow after seven days. Which indicated that most Ag_+ ions were consumed for Ag/Ag_2O NPs synthesis. If we estimate that the formation of Ag/Ag_2O NPs stopped after a week, 89.4% of Ag/Ag_2O NPs formed in 24 hours.

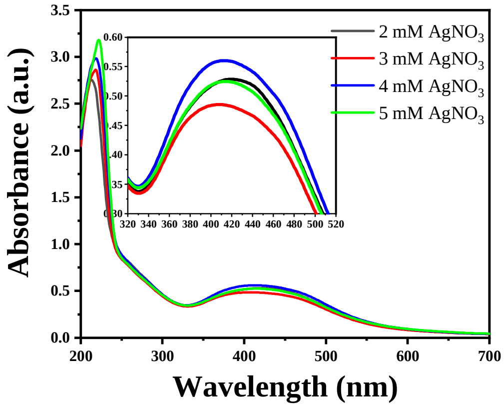

Fig.1 - UV–Vis absorption spectrum of Ag/Ag_2O NPs synthesized using different 100 mL $AgNO_3$ precursor concentration with 1.0% leaf extract (v/v).

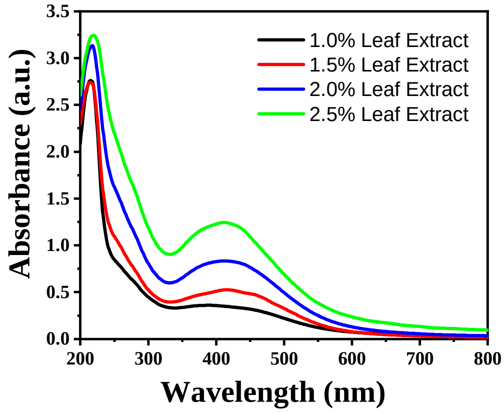

Fig. 2 - UV–Vis absorption spectrum of Ag/Ag_2O NPs synthesized from 100 ml of 1 mM $AgNO_3$ with different volume ratio of Artemisia Herba-Alba leaf extract (v/v):1%, 1.5%, 2%, and 2.5%.

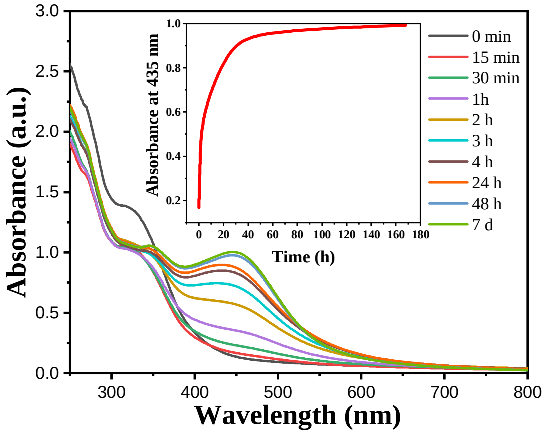

Fig. 3 - UV-vis spectrum absorption of Ag/Ag_2O NPs at different time intervals at room temperature (100 ml of 1 mM $AgNO_3$ and 1ml Artemisia Herba-Alba leaf extract).

The estimated optical band gap (Eg) of Ag/Ag_2O NPs is calculated using the Tauc relation Eq.(1) [74]:

$$(\alpha h\nu) = A(h\nu - E_g)^n \qquad (1)$$

Where α is the absorption coefficient, A is constant, hv is the energy of light and n is a constant depending on the nature of the electron transition, E_g is optical band gap energy. Additionally, Figure 3 and Figure 4 show the Tauc plot of $(\alpha h\nu)^2$ versus hv at different concentrations and different rapport, respectively. We have obtained the energy gap from the intersection of the edge of the linear part of absorption with the energy axis. When $(\alpha h\nu)^2$ is zero, the photon energy is E_g. The results are listed in Table 1. a (Eg) estimation of Ag/Ag_2O NPs with a different volume ratio of leaf extract was found to be in the range 2.05-2.30 eV. The Bandgap (Eg) slightly decreases from 2.29 to 2.32 eV with increasing the $AgNO_3$ concentration from 2mM to 5mM with 1.0% of leaf extract.

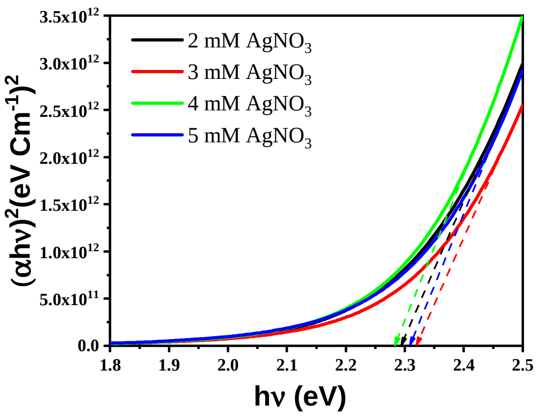

Fig. 4 - Bandgap (Eg) estimation from Tauc's relation of the prepared Ag/Ag_2O NPs with 100 mL of $AgNO_3$ of concentrations with 1.0% of leaf extract.

Table 1
The optical bandgap of the Ag/Ag_2O NPs prepared from different volume ratio of leaf extract (v/v): 1.0%, 1.5%, 2.0%, and 2.5% to 100 mL of 1 mM $AgNO_3$

volume ratio	**Optical band gap E_g (eV)**	**Precursor concentration**	**Optical band gap E_g (eV)**
1.0%	2.30	2mM	2.29
1.5%	2.27	3 mM	2.32
2.0%	2.21	4 mM	2.28
2.5%	2.05	5 mM	2.31

3.2. Fourier transform infrared spectroscopy

FTIR analysis was done to distinguish the nature of the functional groups (reducing and stabilizing biomolecules) in the Artemisia Herba-Alba extract. The resultant FTIR spectrum (Figure 5 and Figure 6) has displayed a few absorption bands that relate to the functional groups of the biomolecules existing in the plant extract. Three main absorption peaks were observed, the broad peak centered at 3340 cm^{-1} is assigned to O–H stretching vibrations [75, 76], the intense peak at 1650 cm^{-1} is due to C=O stretching and N–H bending vibrations of the primary amides group which is commonly found in the protein [77]. Besides, the peak located at 650 cm^{-1} corresponds to C–H bending vibrations out of plane [78].

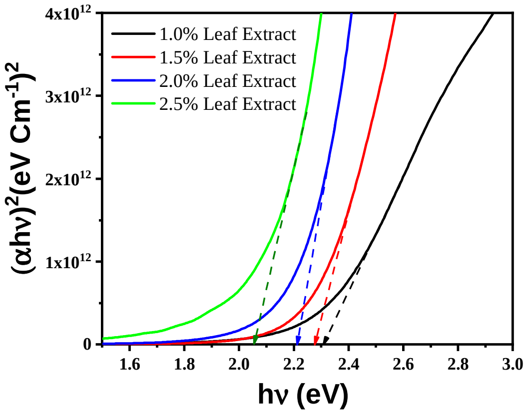

Fig. 5 - Bandgap (Eg) estimation from Tauc's relation of the prepared Ag/Ag_2O from 100 mL of 1 mM AgNO3 with different volume ratio of leaf extract (v/v): 1.0%, 1.5%, 2.0%, and 2.5%.

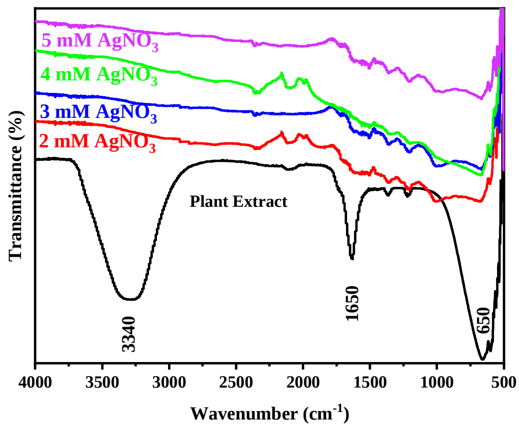

Fig. 6 - FTIR Spectra of Artemisia Herba-Alba extract and the prepared Ag/Ag_2O NPs solution prepared at 100 mL of Ag NO_3 of different concentrations (2, 3, 4, and 5 mM $AgNO_3$) and 1 mL of Artemisia Herba-Alba extract.

The FTIR spectra of AgO NPs synthesized at different precursor concentrations and different (precursor to extract volume ratios) are shown in (Fig. 5) and (Fig. 6) respectively. Comparing the FTIR spectra of AgO NPs with the Artemisia Herba-Alba extract in (Fig. 5) reveals a distinguished decrease in the band's intensity at 3340 cm^{-1} and 1650 cm^{-1} which may indicate that both of the OH group and the proteins presented in Artemisia herba-alba extract have served as bio-reducing and capping agents for AgO NPs synthesis [24].

3.3. X-Ray Diffraction

XRD patterns of the biosynthesized Ag/Ag_2O NPs prepared from 100 mL $AgNO_3$ solution of different concentrations (2, 3, 4, and 5 mM $AgNO_3$) and different volume ratios (Leaf extract: $AgNO_3$ solution of 1.0, 1.5, 2.0, 2.5% V/V) are shown in Fig.7 and Fig.8 respectively. A number of Bragg reflection peaks were observed in all the XRD patterns located at 2θ values of 38.16°, 44. 34°, 64.57°, and 77. 60° corresponding to (111), (200), (220), and (311) planes of metallic face-centered cubic structure (JCPDS 04-0783) of Ag NPs [79, 80]. Whereas the diffraction peaks at 2θ values of 26.90°, 32.69°, 37.94°, 54.9°, 65.54° and 69° related to (110), (111), (200), (220), (311) and (222) planes of face-centered cubic structure (JCPDS 01-076-1393) of crystalline Ag_2O [81]. Noteworthy that the prepared Ag/Ag_2O NPs with the lowest volume ratio of extract to $AgNO_3$ solution (1:100) shown in Figure 9 exhibited only one phase of metallic Ag NPs with no additional peaks of Ag_2O phase. The higher contraction of the leaf extracts the higher binding between polyphenols of the extract (hydroxyl, ketonic) to the Ag^+ ions. This contributes the OH^- group to Ag^+ and results in the formation of highly unstable Ag-OH, which is readily oxidized to Ag_2O upon drying and leads to the formation of the Ag/Ag_2O NPs [82].

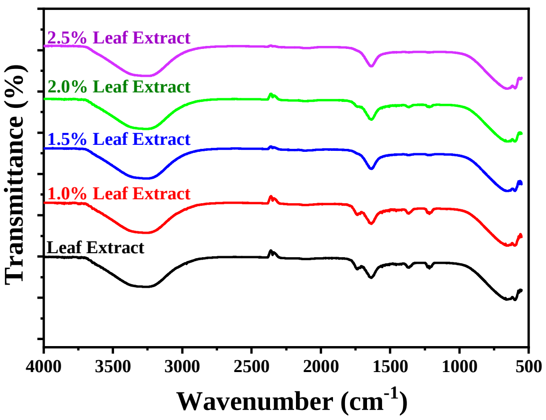

Fig. 7 - FTIR Spectra of Artemisia Herba-Alba extract and the prepared Ag/Ag_2O NPs solution prepared at 100 mL of 1 mM $AgNO_3$ and 1.0, 1.5, 2.0, and 2.5 mL of the as-prepared Artemisia Herba-Alba extract.

The crystallite size of the synthesized nanoparticles was estimated selecting the peak of highest intensity situated at 2θ value of 38.16°using the Scherrer formula Eq (1):

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (1)$$

Where D is the crystalline size (nm), β is the full width at half maximum of the diffraction peak (FWHM) of the most intense diffraction peak, λ the X-ray wavelength (1.5406 Å) and θ is the Bragg angle of diffraction [83]. The effect of both precursor

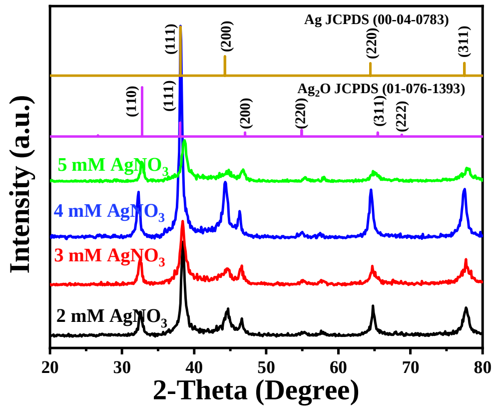

Fig .8 -XRD patterns of the prepared Ag/Ag_2O NPs solution prepared at 100 mL of Ag NO_3 of different concentrations (2, 3, 4, and 5 mM $AgNO_3$) and 1 mL of Artemisia Herba-Alba extract.

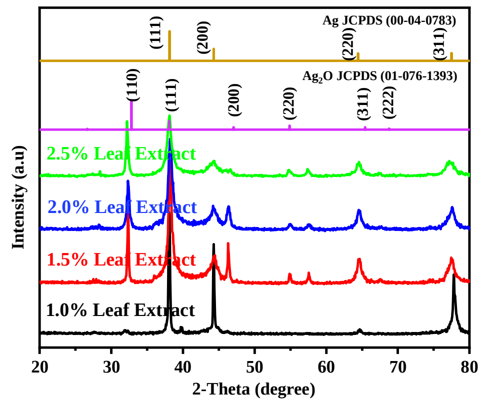

Fig. 9 - XRD patterns of the prepared Ag/Ag_2O NPs solution prepared at 100 mL of 1 mM $AgNO_3$ and 1.0, 1.5, 2.0, and 2.5 mL of the as-prepared Artemisia Herba-Alba extract.

concentration and volume ratio on crystallite size of Ag/Ag_2O NPs are shown in Table 2.

Table 2 shows that the crystallite size is affected by both precursor concentration and volume ratio. Increasing the precursor concentration has irregularly affected the Ag and Ag_2O NPs crystallite size. On the other hand, Increasing the volume ratio of leaf extract to 1 mM $AgNO_3$ solution from 1:100 to 2.5:100 has decreased the crystallite size of Ag from 20.25 to 10.67 and Ag_2O crystals from 36.79 nm to 12.23 nm.

3.4. Scanning Electron Microscopy

Particle size and morphology of Ag/Ag_2O NPs were studied using the SEM (Figure 10). The particle size of the prepared Ag/Ag_2O NPs have a tight size distribution with an average size of 150-250 nm with a spherical shape. The particle size distribution increases with decreases with increasing the $AgNO_3$ from 2-5 mM. Most of the

Table 2

Effect of $AgNO_3$ precursor concentration and volume ratio of leaf extract to $AgNO_3$ solution on the crystallite size of Ag and Ag_2O NPs.

$AgNO_3$ Concentration	Extract/$AgNO_3$ solution Volume Ratio (ml/ml)	Crystallite size of Ag (nm)	Crystallite size of Ag_2O (nm)
2 mM	1.0/100	14.95 ± 1.05	36.79 ± 1.45
3 mM	1.5/100	10.67 ± 1.38	16.55 ± 0.61
4 mM	2.0/100	20.25 ± 0.82	12.35 ± 1.12
5 mM	2.5/100	10.79 ± 1.27	12.23 ± 0.56

Ag/Ag_2O NPs were aggregated to form foam like a bunch of particles, and however, individual particles were also observed. The spherical shape of Ag/Ag_2O NPs because of the equivalent growth rate alongside all nucleation directions where the sphere has the littlest surface area per unit volume contrasted with different shapes.

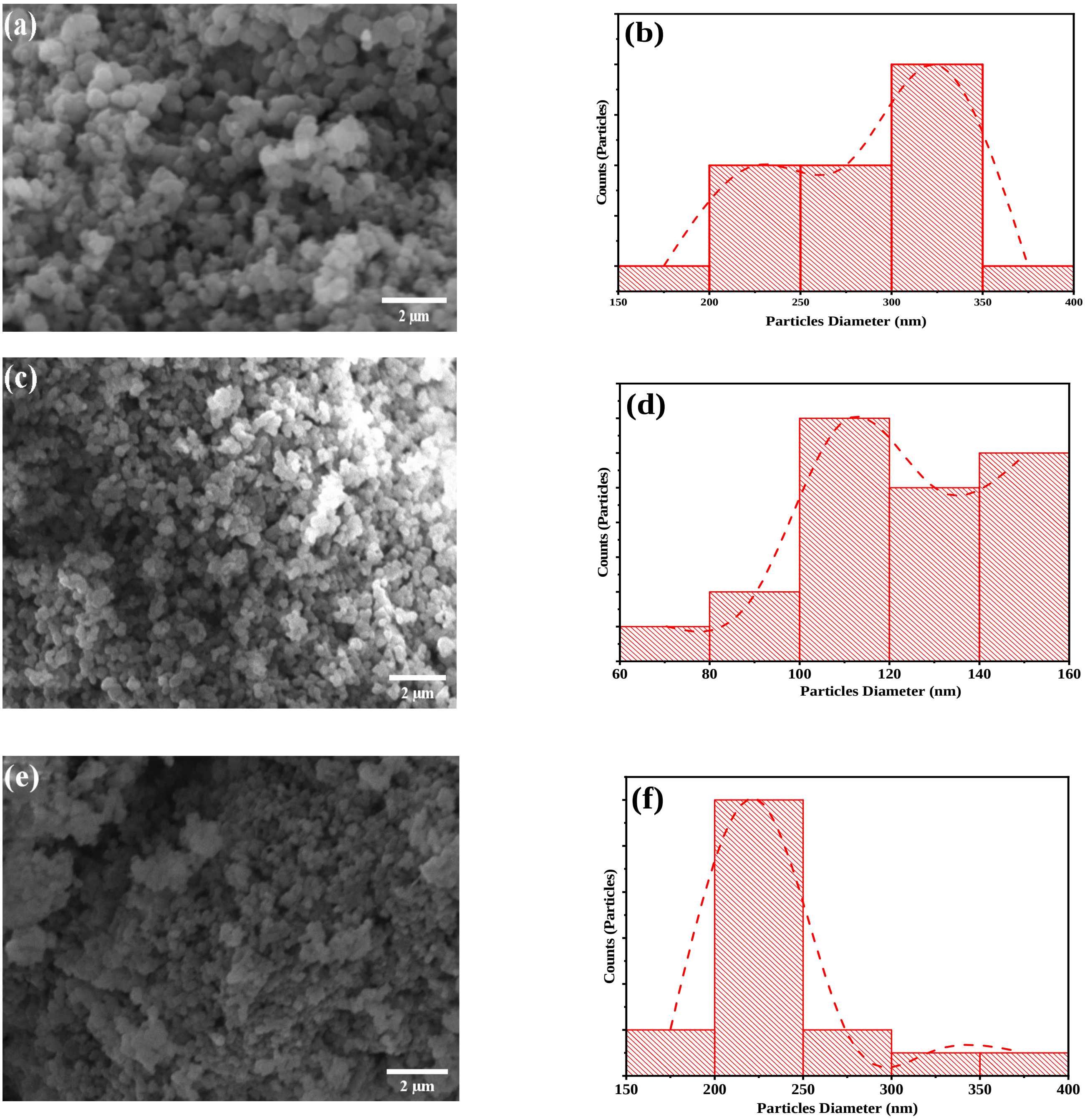

Fig. 10 continues on next page

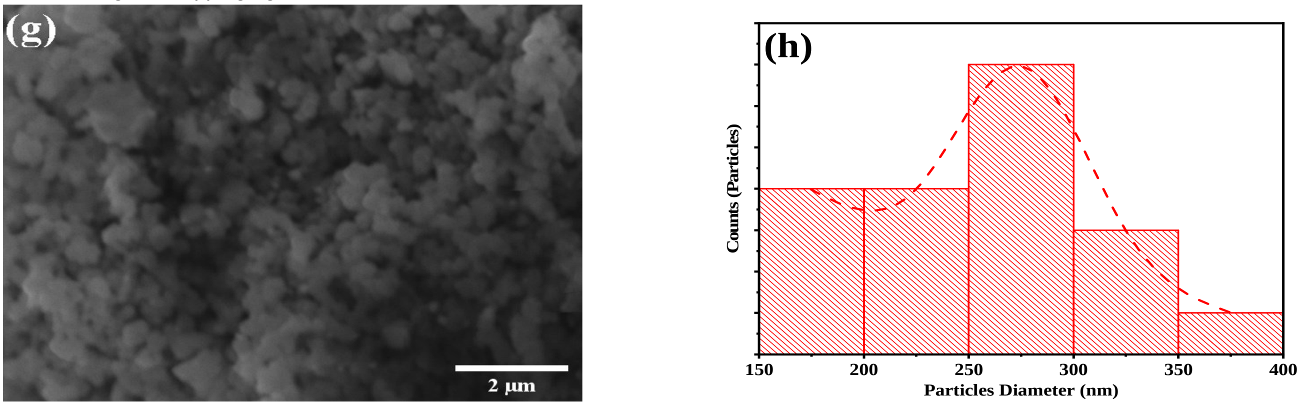

Fig. 10 - SEM images of the prepared Ag/Ag_2O NPs solution prepared at 100 mL of Ag NO_3 of different concentrations ((a,b) 2 mM, (c,d) 3 mM, (e,f) 4 mM, and (g,h) 5 mM. $AgNO_3$) and 1 mL of Artemisia Herba-Alba extract.

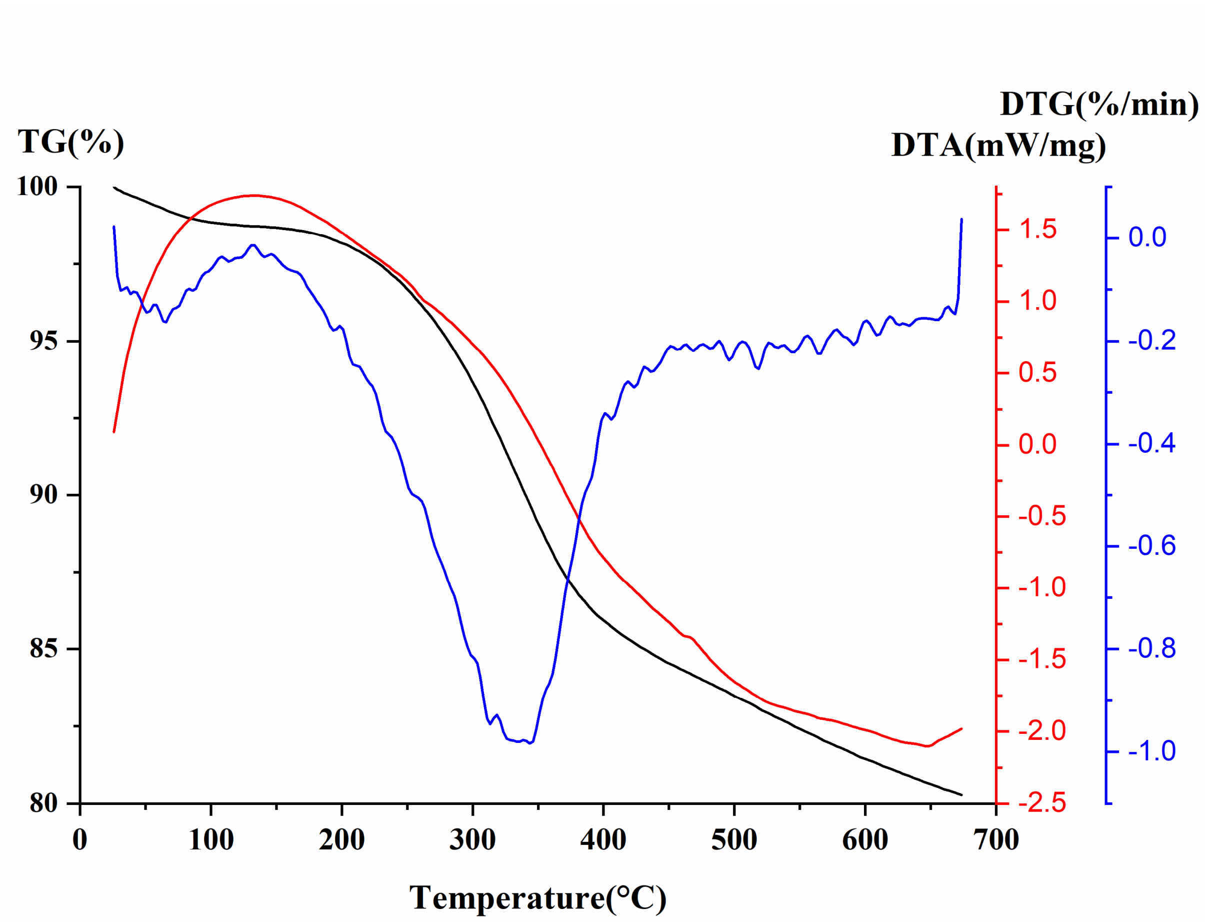

Fig. 11 - TGA and DTA profiles the prepared Ag/Ag_2O NPs solution prepared at 100 mL of $AgNO_3$ of different concentrations 2 mM $AgNO_3$ and 1 mL of Artemisia Herba-Alba extract.

3.5. Thermal Analysis and Organic Contents

Figure 11 shows a thermogravimetric analysis (TGA/DTA) performed to assess the purity of Ag/Ag_2O NPs in the powder form. Data extracted from TGA/DTA analysis was used to estimate the organic contents adsorbed on the surface of the Ag/Ag_2O NPs and their thermal stability for oxidation in the air in the temperature range from 25 to 700 [84]. To confirm the stability of Ag/Ag_2O NPs, thermogravimetric analysis was performed under a nitrogen atmosphere at a heating rate of 10 ºC.min^{-1}. Further weight loss was observed during heating from 300 to 700 ℃. The first weight of about 2wt% occurs at about 140 ºC due to loss of physically adsorbed water (moisture). The second weight loss (18wt%) in the temperature range 350-680 ℃ is due to the oxidation and degradation of the organic and liberation of CO_2 and H_2O [85]. Significant weight loss is observed in the heating step at 300-350 ℃ due to the elimination o f the organic part [86].

4.Conclusion

This study describes a green, simple, and eco-friendly method for the synthesis of Ag/Ag_2O NPs using Artemisia Herba-Alba aqueous leaf extract as a reducing and capping agent. The formation of Ag/Ag_2O NPs and influence of different $AgNO_3$ concentrations and addition of different volumes of leaf extract to $AgNO_3$ solution was studied by ultraviolet-visible (UV-Vis) spectroscopy, Fourier transforms infrared spectroscopy (FTIR), scanning electron spectroscopy (SEM), and X-ray diffraction (XRD) and thermal analysis (TGA/DTA). The formation of Ag/Ag_2O NPs was confirmed by observing an absorption peak in the visible range from 418 to 435 nm due to SPR at different $AgNO_3$ concentrations. The results have shown that the crystallite size of Ag/Ag_2O NPs can be significantly influenced by the precursor concentration and volume ratio. Increasing the volume ratio of leaf extract to 1 mM $AgNO_3$ solution from 1:100 to 2.5:100 (v/v) has decreased the crystallite size of Ag from 20.25 to 10.67 and Ag_2O crystals from 36.79 nm to 12.23 nm. The Ag/Ag_2O NPs were found to be less than 100 nm in size with spherical shapes. The TGA/DTA analysis shows significant organic contents (18 wt %) were physically and chemically adsorbed on the dry weight Ag/Ag_2O NPs. The purposed procedure is green and viable because it's simple, fast, low cost, and friendly to the environment compared to other wet chemistry methods.

Conflict of interest
The authors declare that they have no conflict of interest.
Acknoledgment
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