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Synthesis of Silver Nanoparticles by ecofriendly nvironmental method using Piper nigrum, Ziziphus spina-christi, and Eucalyptusglobulus extract

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Abstract. In the present study, silver nanoparticles (AgNPs) were prepared using an eco-friendly method synthesized in a single step biosynthetic using leaves aqueous extract of Piper nigrum , Ziziphus spina-christi, and Eucalyptus globulus act as a reducing and capping agents, as a function of volume ratio of aqueous extract(100ppm) to AgNO3 (0.001M), (1: 10 ,2: 10 ,3: 10). The nanoparticles were characterized using UV-Visible spectra, X-ray diffraction (XRD). The prepared AgNPs showed surface Plasmon resonance centered at 443, 440,and 441 nm for sample prepared using extract Piper nigrum , Ziziphus spina-christi, and Eucalyptus respectively. The XRD pattern showed that the strong intense peaks indicate crystalline nature and face centered cubic structure of silver nanoparticles for all samples were prepared .The average crystallite size of the AgNPs was 20-45 nm. Morphology of the AgNPs were carried out using FESEM. Observations show that the AgNPs synthesized were spherical(Cluster) in shape. with diameters of 13 to 53 nm.

Key words ;AgNPs; Surface plasmon resonance; Piper nigrum ;Ziziphus spina-christi; Eucalyptus.

1. Introduction

Nanotechnology is considered to be one of the most important modern techniques of science. New properties of nanoparticles or nanomaterials such as morphology, particle size and distribution have enabled these materials to be an infrastructure in many applications, whether medical, such as those involved in drug delivery or biomedicine in the treatment of certain diseases and cosmetics in addition to environmental applications, and chemical industries, Catalysts, electronics, optics and other applications [1–3]. Silver nanoparticles (AgNPs) are unique nanoparticles with good chemical stability, unique antibacterial effect and anti-inflammatory activity [4, 5]. It can be used in many biomedical applications such as wound dressings, topical creams, disinfectant sprays and fabrics due to its antiseptic and biocide effect against microorganisms. They work by disrupting the unicellular membrane of microorganisms that thus disturb their enzymatic activities. In addition, recently, the synthesis of AgNPs for the diagnosis and treatment of cancer has received the attention of many scientists [6,7].

However, the synthesis of nanoparticles by chemical or physical methods is either expensive or associated with environmental risks due to the inclusion of certain toxic chemicals during the synthesis process. Biological Synthesis Inspired by Nanoparticles an alternative environmentally friendly process promised to synthesize nanoparticles because they do not involve the use of toxic chemicals during synthesis. Biological synthesis of nanoparticles is an environmentally friendly method involving the use of microorganisms [8-10], enzyme [11], and plant or plant extract [12]. Of all biological methods, the advantages of aggregate nanoparticles that use plants are to eliminate the complex process of preserving cell cultures [12]. In addition, it is a process capable of synthesizing nanoparticles. However, in order to replace chemical methods, biological methods must be developed in terms of accelerating the synthesis rate. On the other hand, due to serious issues, ad hoc research on the development of green chemistry and other biological processes has led to an environmentally friendly approach to the synthesis of mineral nanoparticles [13]. Plant sources such as leaves, bark, fruit extracts [14, 15] and organisms [16, 17] are commonly used in this approach. The plant extraction method is a cost-effective, time-efficient green method and provides a combination of crystalline nanoparticles of a wide range of sizes and shapes. Here, we used Papper , Rhamnus, and Eucalyptus act as a reducing and capping agents, and compared the composition of silver nanoparticles as a function of mole ratio aqueous extract to silver nitrate (AgNO3) concentration (1: 10 ,2: 10 ,3: 10).

2. Experimental details

2.1 Materials and methods

2.1.1 Plant material Leaves of *Piper nigrum , Ziziphus spina-christi*, and *Eucalyptus globulus*. were obtained from local markets in Ramadi/ Iraq. Preparation of plant leaf extract 10 g powder of dry leaves were taken in a round flask along with 100 mL of Distilled water, allowed to stirrer at room temperature for 30 min under reflux condition. The extract obtained was filtered through Whatman No. 1 filter paper. The filtrate are drying and stored at 4 °C for further experiments.

2.1.2 Green synthesis of silver nanoparticles: For synthesis of silver nanoparticles,10 ml of 1 mM $AgNO_3$ (Shanghai Jiuling Chemical Co., Ltd.) aqueous solution, were added to 1 ml(100ppm) of plant extract and left at room temperature for one hour. The change in color was observed indicating the formation of silver nanoparticles.

2.2 Characterization of green synthesis silver nanoparticles

Silver nanoparticle was characterized using an UV-vis spectrum for the detection of surface Plasmon resonance property (SPR) of AgNPs conducted at room temperature using Shimadzu UV-Vis 1800 spectrophotometer at wavelengths ranging from 300 to 800 nm using double beam UV-visible spectrophotometer (PD-303 UV).

The structure evolution of the green synthesized AgNPs using thymus vulgaris aqueous extract was was examined by high-resolution X-ray diffraction (HR-XRD) using X'Pert Pro MRD diffractometer (PANalytical Company) system equipped with Cu-Kα-radiation wavelength (λ = 0.15418 nm) operating at 40 kV and 30. Morphology and microstructure of the thin films were investigated by scanning electron microscopy (FESEM) using Jeol JSM-6460 LV microscope operating at 10 kV.

3. Results and Discussions

3.1 Characterization of green synthesis gold nanoparticles.

3.1.1 UV spectral analysis

During the mixing process of the silver nitrate solution (colorless) and the pepper extract (greenish solution), the solution color changes due to the reaction process to yellowish brown. The change in color gives an initial indication of the formation of nanoparticle particles [9]. The appearance of silver particles in non-silver color is attributed to the Surface plasmon resonance. Surface plasmon resonance occurs in certain metals such as silver due to the arrival of its particle diameter to the nanometer. Therefore, the spectral analysis device is used at wavelengths of visible light to prove the formation of nanoparticles. The UV-Visible absorption spectra of the colloidal silver nanoparticles as a function of cocnetration of extract shown in Figure 1. An increase in absorbance can be noticed in the UV-Vis spectrum for AgNPs using *Piper nigrum* extract (Fig. 1.a). Also, the peak area at 439 to 443 nm has increased with increasing concentration of extract. The sharp peak at around 443 nm evidences the formation of silver nanoparticles [20], while the increase in intensity could be due to increasing number of nanoparticles formed as a result of reduction of silver ions present in the aqueous solution [21].Figure 1.b show the UV-Vis spectrum for AgNPs prepared using *Ziziphus spina-christi*. It was observe that the peak area at 423 to 441 nm has increased with increasing concentration of extract, the peak intensity were less than that for simple prepared using *Ziziphus spina-christi* extract. The absorbance for AgNPs were prepared using extract, *Eucalyptus globulus* show increase intensity compared with the other sample (Fig1.c).It noticed that the peak area at 432 to 440 nm has increased with increasing concentration of extract.

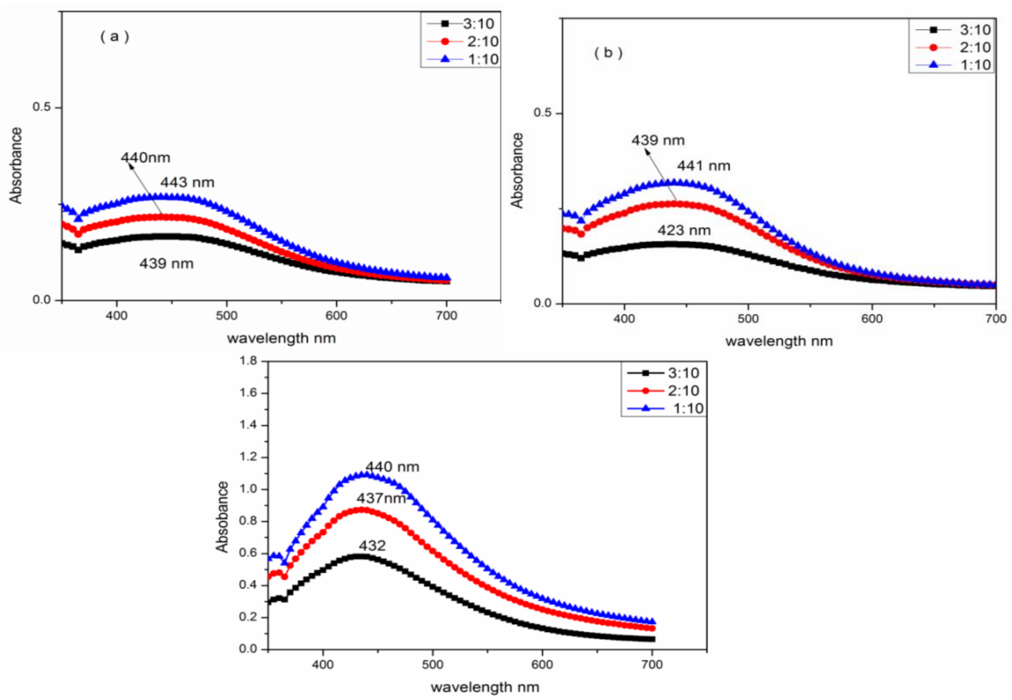

Figure (1): Ultraviolet-visible absorption spectrum of silver nanoparticles prepared using: (a) papper ,(b) Rhamnus, (c) Eucalyptus

3.1.2 X-ray diffraction (XRD)

The X-ray (XRD) patterns of dried silver nanoparticles synthesized using Leaves of *Piper nigrum* , *Ziziphus spina-christi*, and *Eucalyptus globulus* extract showed Bragg reflections representative of the fcc structure of Ag nanoparticles. Figure 2 (a) shows the X-ray diffraction spectra of AgNPS prepared using *Piper nigrum* extract as a function of salt: extract ratio , where a peaks at the angle of 38.2 and 44.4, corresponding to the (111) and (200) planes of silver, respectively after matching with the standard X-ray model of silver (JCPDS No. 04-0783) . The pattern above shows that the diffraction pattern of any peaks cannot be repeated to other materials and this indicates the purity of the prepared sample and free of any additional impurities [ ]. X-ray diffraction measurements showed a different pattern for the samples prepared. The pattern of the 1:10 pattern was better than the other samples. The 3:10 sample did not show exact values compared to the rest of other samples due to the increased concentration of the extract compared to the other samples. The concentration of silver salt, which reduces the proportion of silver particles in the solution, means an increase in the dilution of the resulting solution. Sherrer formula [13] was used to calculate the particle size. It was found that the best size was for model 1:10 which is 20 nm while the ratio of 2:10 was 40nm. Figure 2 (b) shows the X-ray diffraction pattern of nanoparticles where a peak is observed at 2θ equal to 38,and 43 which related to the Silver after its conformity with the standard model of X-ray diffraction of silver (JCPDS No. 04-0783). The X-ray diffraction measurements showed a different pattern of the prepared samples as a function of salt: extract ratio. The diffraction pattern of the prepared at 1:10 better than the other others, while the sample with a ratio of 3: 10 did not show precise values compared to the rest of the samples due to the increased concentration of the extract compared with the concentration of silver salt, which reduces the percentage of silver particles in the solution, which means an increase in dilution of the resulting solution. was used to calculate the granular size where it was found that the best size of the sample prepared at 1:10, while it was 45nm for ratio 2:10.XRD pattern for AgNPs prepared using Eucalyptus was shown in Figure 2 (c).It notice that the higher peak intensity was found for sample prepared using Rhamnus compare with other sample prepared using. The behavior for these sample were found look like to samples prepared using papper and Eucalyptus. Figure 2 (c) illustrated that pattern were same behavior, also was the best compare with other where the intensity was highest for peaks

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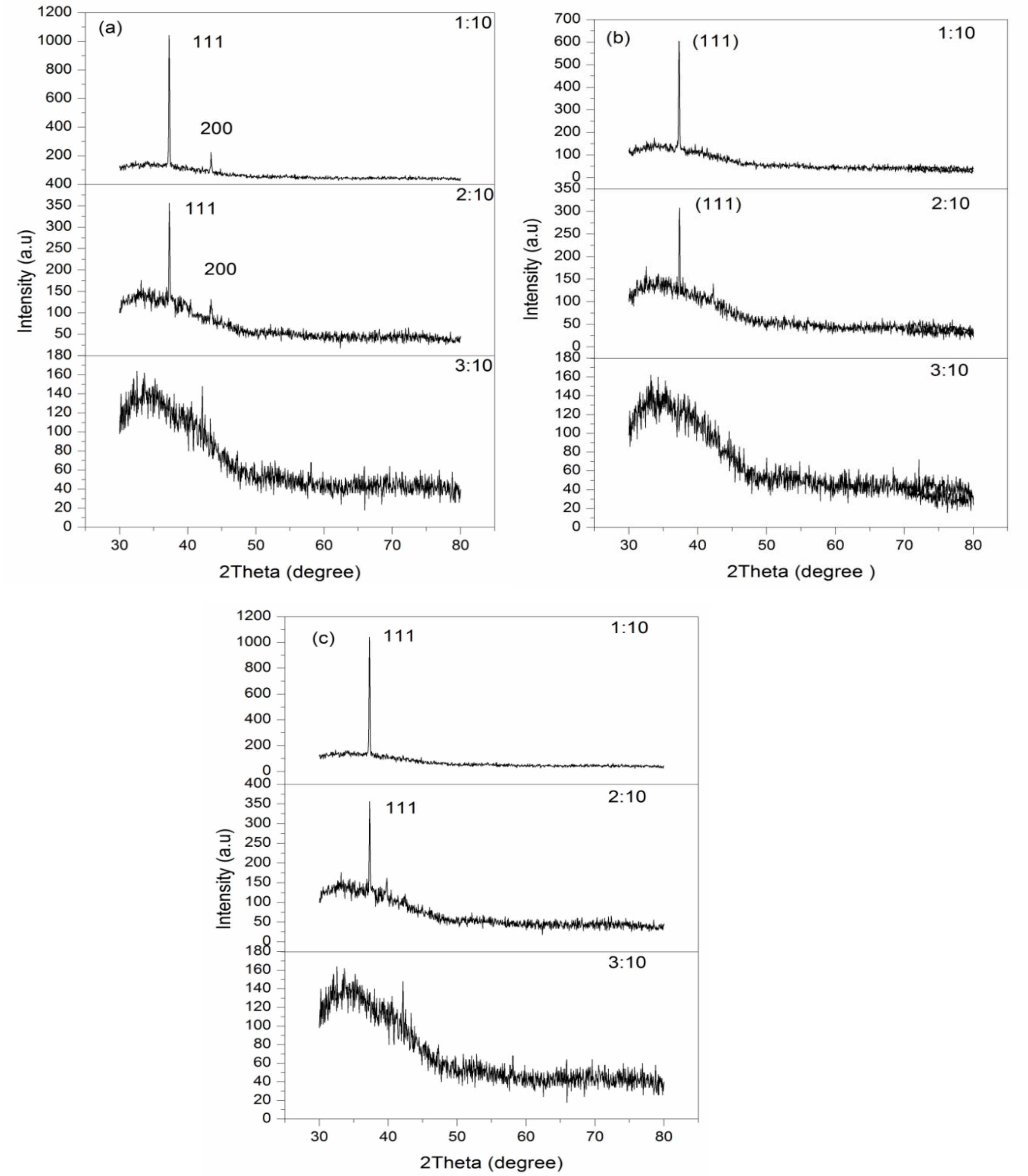

Figure 2: X-ray pattern of silver nanoparticles prepared using: (a) Piper nigrum ,(b) Ziziphus spina-christi, (c) Eucalyptus globulus

4. Field Emission Scanning Electron Microscopy Study

The morphology of green synthesized AgNPs was viewed by FESEM. The FESEM image, as represented in Fig. 4, showed that Particle shapes are usually irregular spheroid and spherical were well dispersed with and particle sizes ranging from 13 to 53 nm. the particle size of nanoparticles through microscopic electron microscopy images, which approximates the values obtained from X-ray diffraction measurements. It is known that the optical and electronic properties of metal nanoparticles are largely affected by the shape of nanoparticles. This finding strongly confirms that the Rhamnus extract may act as a reduction factor in the production of silver nanoparticles

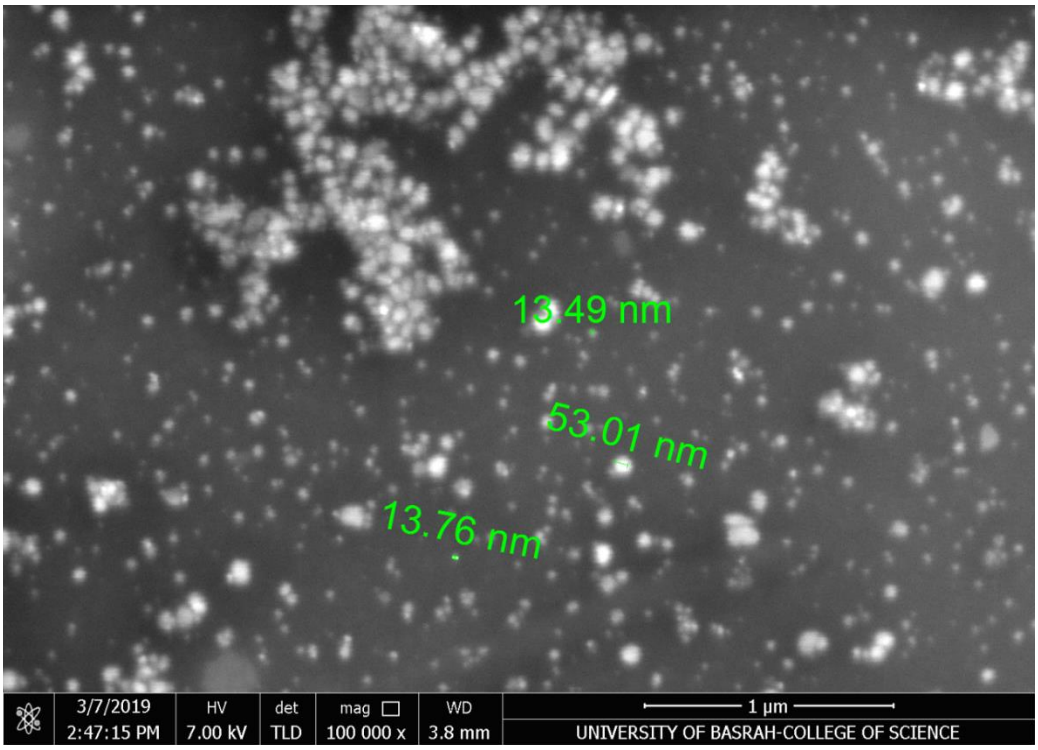

Figure 3: FESEM image of the Ag-NPs

5. Conclusion

Many researchers are highly interested in nanoparticles and the diversity of their fields of application such as electronics, photonics, medicine, and farming. Due to the diversity of organisms ranging from microorganisms to plants, Manufacturing of nanoparticles thus generated has properties that include stable, non-toxic, inexpensive, environmentally friendly and synthesized using green chemistry Unlike conventional chemical and physical processes which often use toxic substances that have the potential to cause environmental toxicity, cellular toxicity, and carcinogenesis. Widely used in the development of nanoparticles, plant use offers a simple, safe and easy to prepare, non-toxic and strong need no preparation or long time to prepare them needed techniques have the potential to commonly use medical procedures for bacteria and fungi techniques. Composite nanoparticles have the potential to be used in the supply of antimicrobial compounds for use as agricultural pesticides In the case of plant extracts, the mechanisms of composition of nanoparticles vary between different plant species.

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