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Microwave Assisted Green Synthesis of Ag, Ag_2O, and Ag_2O_3 Nanoparticles

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Abstract: In this study, nanoparticles containing Ag, Ag_2O, and Ag_2O_3 mixture were synthesized by using a microwave-assisted green synthesis method. For the reduction of Ag^+ to Ag^0, *Rhododendron ponticum* plant extract was used while the microwave synthesis method was used for the formation of silver oxides. Nanoparticles synthesized under 90 °C, 450 W, and 30-minute microwave synthesis conditions were characterized by UV-Vis, XRD, and STEM. As a result of characterization, Ag-NPs were found to show maximum absorbance peak at 432 nm in the UV-Vis spectrum, crystallite size was 46 nm according to XRD analysis, and nanoparticles showed in a spherical_homogeneous distribution by STEM analysis. Our results showed that the phytochemicals in the plant extract of *R. ponticum* reduce Ag^+ ions to Ag-NPs and that the mixture of silver and silver oxide can be synthesized quickly and easily with microwave heating support. This study is important to increase the use of Ag_2O and Ag_2O_3 nanoparticles in industrial production and medical applications. In particular, nanoparticles of silver and silver(I) oxide show great promise for widespread usage in medical polymers and nanodrugs. Because in this study, toxic chemicals were not used in the synthesis of silver oxide nanoparticles and it is a safe synthesis because there is no risk of explosion.

Keywords: Silver oxide nanoparticles, Green synthesis, Microwave synthesis, Ag_2O_3 nanoparticles, Ag_2O nanoparticles.

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INTRODUCTION

Nanotechnology involves the adaptation of atomic materials at the nanometer level to achieve the desired shape and properties according to the field of application (1). Recently, there has been an increase in studies aimed at developing rapid, inexpensive, and environmentally friendly methods in nanoparticle synthesis methods (2). These studies focused on using everything from plants to bacteria as a reducing agent in reducing noble metal ions. The green synthesis method has been developed as a product of this orientation (4-10). Compared with traditional methods; In addition to being inexpensive, easily available, it does not contain toxicity against human and ecological systems (4,5,11). On the other hand, the mechanism of action is not fully known, and shape and size control has not been achieved in metal nanoparticle synthesis.

Similarly, many plant extracts have been used in the synthesis of metal nanoparticles and similar results have been obtained. Plant extracts such as Artocarpus hetrophyllus, *Azadirechta indica, Callistemon lanceolatus, Centella asiatica, Lippia citriodora, Fenugreek, Paeonia emodi, and Pinus longifolia* play an important role in reducing toxicity during the reduction of metal ions (12-19). Studies on Ag2O nanoparticles synthesized using these plants are summarized in Table 1. Bio-synthesized Ag-nanoparticles have many application areas such as solar energy systems, coatings, battery production, sensors, medical devices, biological studies, and biotagging (20-23).

Silver has three different oxidative forms: Ag_2O, AgO, and Ag_2O_3. Silver oxides are widely used in the production of medical devices, in the production of zinc-mixed alkaline batteries (22,24). Although AgO and Ag_2O oxidative forms of silver are easily obtained, the industrial production of Ag_2O_3 is quite difficult. Generally; although $AgClO_4$ is frequently used in the chemical synthesis method, the presence of ClO_4^- ion is very harmful to both human health and the environment. In addition, there is a high risk of explosion during the synthesis.

In this study, *Rhododendron ponticum* plant, a forest waste, was used as a reducing agent. Although green synthesis has been used for nanoparticle synthesis in the last two decades, the microwave-assisted synthesis method has been preferred for the first time for oxide formation. As a result, the use of environmentally friendly, rapid microwave synthesis method for oxide formation adds innovation to this study.

Characterization of the synthesized silver and silver oxide mixture was done by UV-Vis, X-Ray diffractometry, and STEM (Scanning Transmission Electron Microscopy) analysis. As a result of these, by combining two different synthetic methods (green synthesis method, microwave synthesis method), it attracts attention with its ease of use advantage compared to other studies in the literature with a cheap, easy, healthy, and safe synthesis method.

MATERIALS and METHODS

Plant selection and preparation

Located about 150 genera and 4.000 species of shrubs in Turkey is a cosmopolitan family *Ericaceae* including the small tree-like community (25). *R. ponticum* is a species of this family. Turkey's Black Sea coast, at the edge reach that level up to 2500 m altitude, lovers of the acidic growing conditions, evergreen, is a perennial shrub species (26). *R. ponticum* has been used as medicinal plants in treatments due to its pain-relieving properties (tooth, back, joint and rheumatic pain) (27,28).
R. ponticum was collected and washed thoroughly and dried in a non-direct sunlight environment. The dried leaves of the plant are dried into a fine powder with the help of a grinder and stored at +4 °C for use in the synthesis process.

Silver and silver oxide synthesis

On the one hand, 20 mg of plant powder was mixed in 20 mL of pure water at 70 °C for 6 hours, then filtered. On the other hand, $AgNO_3$ solution was prepared with a concentration of 1 mM. It was taken from 10 mL of plant extract stock and 50 mL of $AgNO_3$ solution and mixed in a beaker. The mixture in the beaker was then placed in 20 mL of microwave synthesizer containers and subjected to experimental conditions of 30 min, 90 °C, 450 W. As a result of the synthesis, particles settled to the bottom of the containers were observed. The collapsed part is washed several times with pure water, then was centrifuged at 10.000 rpm for 20 min.

Physical characterization

To achieve physical characterization of silver nanoparticles, we first determined the UV-Vis spectrometric analysis (TERMO, Model Multiscanner spectrophotometer) for obtaining the maximum absorbent peak between 300 and 700 nm, then powder X-ray analysis for calculating the average silver nanoparticle size (Brand name-Panalytical, Model-Empyrean Advance, made in the Netherlands). It was then characterized by scanning transmission electron microscopy (TESCAN, MAIA3 XMU) analysis, which is one of the most commonly used methods to analyze the morphology and size of the vacuum-dried sample.

RESULTS AND DISCUSSION

In this synthetic reaction, Ag^+ ions are reduced to Ag^0 (AgNP formation) thanks to the phytochemicals contained in the plant extract. Afterward, silver oxide mixtures were obtained as a result of exposure to microwaves of 90 °C and 450 W for 30 minutes.

Generally, it is very difficult to give a formation mechanism for metal nanoparticles obtained by green synthesis. While the reducing agent is clearly known in the chemical synthesis method, it is not known which phytochemicals in the plant have a reducing effect in green synthesis. Scheme 1. will be a reasonable representation for the AgNPs to be obtained in this study.

Table 1. Biosynthesis of Ag_2O NPs using various plant extracts with size and shape.

Plant's name	**Morphology**	**Size (nm)**	**Characterization Techniques**	**Refs**.
Artocarpus hetrophyllus	Spherical	14	XRD, UV-Vis, FTIR, DLS, TEM	12
Azadirechta indica	Spherical and sheet	60-100	UV-Vis, FTIR, XRD, SEM, Zeta potential	13
Callistemon lanceolatus	Spherical and hexagonal	3-30	UV-Vis, FTIR, XRD, SEM, HRTEM	14
Centella asiatica	Spherical	11-12	XRD, UV-Vis, SEM, EDS, FTIR	15
Lippia citriodora	Spherical	20	XRD, TEM, EDS, FTIR, TGA	16
Fenugreek	Spherical	31.5	UV-Vis, FTIR, TEM, Zeta potential	17
Paeonia emodi	Spherical	38.29	XRD, TEM, SEM, EDX, FTIR, UV-Vis	18
Pinus longifolia	Spherical and sheet	1-100	UV-Vis, SEM	19

$$\text{Plant phytochemicals} \xrightarrow{e^-} Ag^+ \longrightarrow Ag^0 \text{ (AgNPs and AgONPs)}$$

Scheme 1. Mechanism of AgNPs and AgONPs synthesis.

Many attempts have been made in the microwave synthesis system, especially for Ag_2O_3 synthesis. In most of the trials, only Ag_2O form nanoparticles were synthesized at high temperatures. Ag_2O-Ag_2O_3 mixtures were obtained by subjecting only the plant extract-$AgNO_3$ mixture solution to 450 W microwave at 90 °C for 30 minutes. These optimized synthesis conditions are of great importance for the reproducibility of the experiment.

UV-Vis Absorption Analysis

UV-Vis analysis is the most widely used technique for the determination of different materials such as transition metal ions, organic compounds, and biological molecules. The first evidence that the synthesis reaction took place; it was understood that the color of the colorless $AgNO_3$ solution turned brown by the addition of *R. ponticum* extract. After this evidence, the primary characterization of silver and silver oxide nanoparticles was done by UV-Vis analysis. In the UV-visible spectrophotometric observations of silver nanoparticles synthesized using *R. ponticum* extract, a maximum absorbance was observed at 432 nm (Figure 1). According to previous papers, it can be said that the spectrum values for Ag nanoparticles vary between 420-450 nm depending on the particle size, plant extraction concentration, chemical environment, and dielectric medium (20-23). For the nanoparticles that are stable and monodisperse, the spectral peak is narrower and sharp whereas for colloidal aggregates (or agglomerates of AgNPs) a much broader peak, usually the visible in the spectrum can be observed.

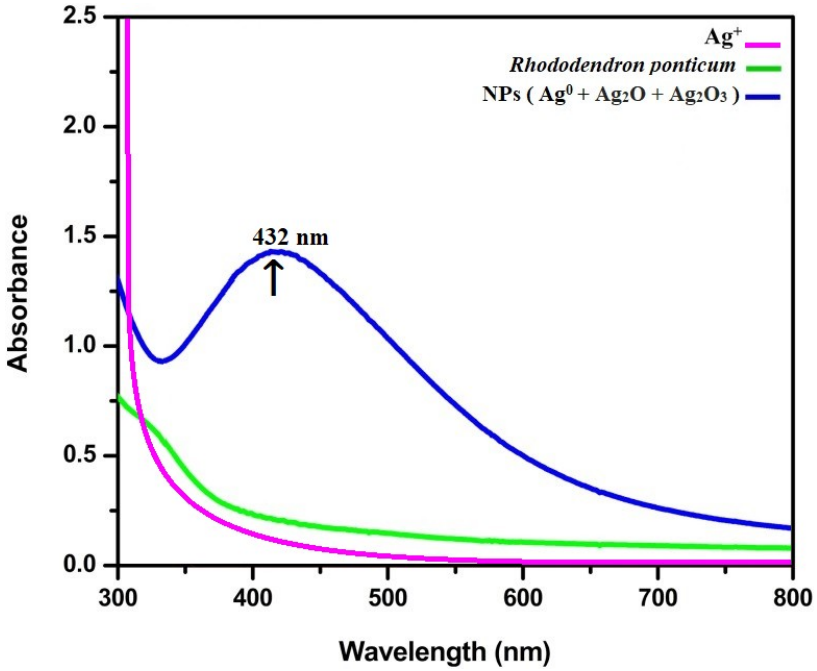

Figure 1. UV–Vis absorption spectra.

XRD analysis

XRD analysis data of pure Ag^0, Ag_2O, and Ag_2O_3 nanoparticles in mixture form synthesized by microwave synthesis method are shown in Figure 2. As seen from the powder X-ray analysis data, six 2θ values that were intensely seen from 20 to 80 were seen. Evaluation of the powder X-ray analysis is important to clearly learn the nature of the nanoparticles formed. The standard 2θ values for silver nanoparticles given in the literature were confirmed to be in the form of nanocrystals as a result of overlapping with the 2θ values (38.23°, 46.36°, 64.62° and 77.57°) we obtained as a result of synthesis. It is also clearly seen that other peaks other than 38.23° seen in the XRD spectrum are a mixture of silver and silver oxides.

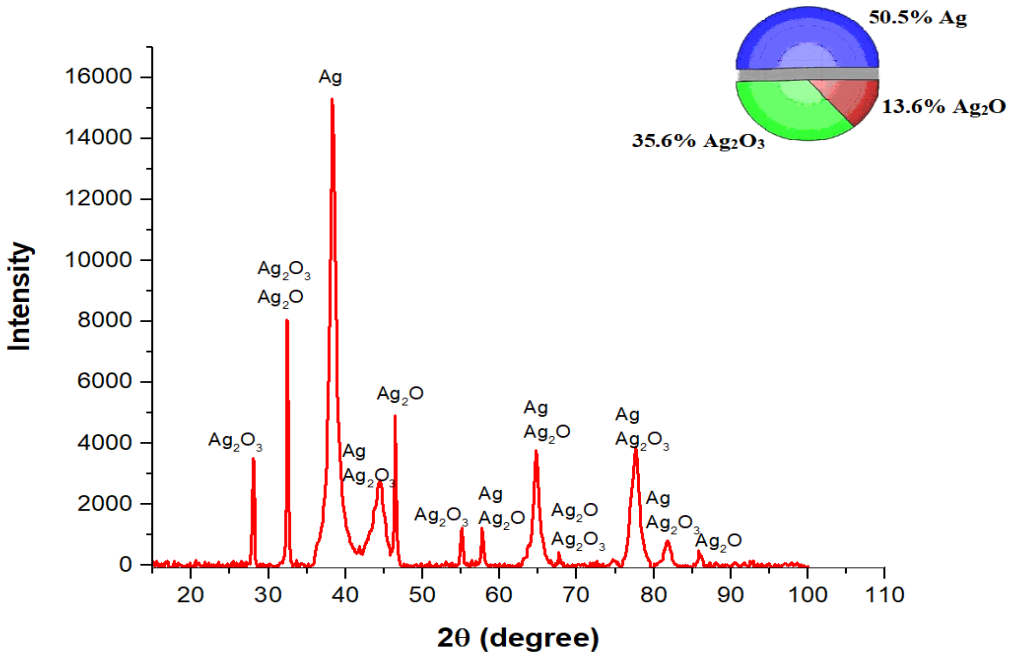

Figure 2: XRD analysis of silver and silver oxide nanoparticles.

This study involving the synthesis of Ag nanoparticles, Ag_2O_3 and Ag_2O nanoparticles with pure Ag nanoparticles were observed together. Semaltianos et al. conducted a study involving silver nanoparticle synthesis by laser ablation from the material in pure water. As a result of the synthesis, they observed Ag_2O_3 nanoparticle mass in addition to pure silver (29).

In another study, they suggested that the formation of AgONP was caused by the interaction of Ag atoms with oxygen atoms or radicals during their decomposition in water. They also stated that the type of oxide formed depends on the partial pressure of oxygen and temperature (30). Sajti et al. stated that AgO formed at low partial oxygen pressure, remained stable in the large temperature range and Ag_3O_4 and Ag_2O_3 formed at higher partial pressures (31).

The Scherrer equation was used to calculate the crystal size of nanoparticles composed of silver and silver oxide mixtures.

$$D = (K \lambda) / (\beta \cos\theta) \quad \text{(Eq. 1)}$$

In the equation, λ is the X-ray wavelength, β is the half-height width of the X-ray peak, the K shape factor constant (0.9), and the angle θ denotes the reference peak width. As a result of this equation, the crystal size of Ag-ONPs was calculated as 46 nm. It was noted that the result obtained was close to the silver oxide values synthesized in the literature as well as the results of the STEM analysis (13,14,18,19,32).

STEM (SEM) study of the AgNPs and AgONPs

STEM images of the synthesized nanoparticles were made to determine the particle size, shape, in short, their morphology of the nanoparticles. Figure 3 shows that the synthesized particles are nano-spheres and the particle size variation is widely distributed. Also from the particle size distribution, it indicates that the nanoparticle sizes generally vary between 40 and 60 nm. As a result, it is possible to say that the average of the particle size variation coincides with the crystal size obtained as a result of X-ray.

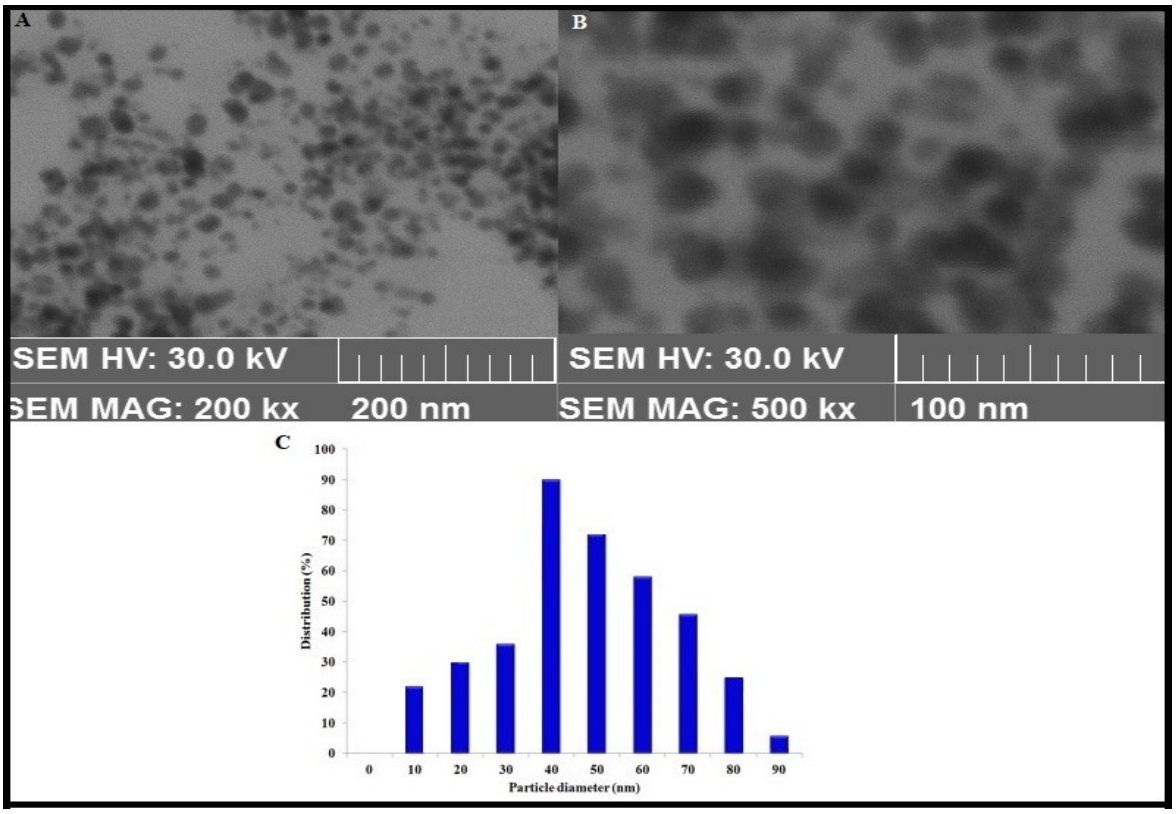

Figure 3. STEM images of the nanoparticles synthesized by *R. ponticum* plant extracts.

CONCLUSION

Easy, fast, cheap, and non-toxic green synthesis method was used in the synthesis of Ag_2O and Ag_2O_3 nanoparticles. In this method, the synthetic reaction was supported by the microwave method using *R. ponticum* plant extract as a substrate. The combination of two separate synthesis methods allowed the rare synthesized Ag_2O_3 nanoparticles to be obtained easily and safely. Silver oxide is a well-known semiconductor metal oxide having vast applications, in the field of electrochemical, electronic, optical properties, oxidation catalysis, sensors, fuel cells, photovoltaic cells, all-optical switching devices, optical data storage systems, and as a diagnostic biological probe, anticancer chemotherapy, antibiotics, and cosmetics. In the study the nanoparticles obtained were physically (UV-Vis analysis, XRD analysis, and STEM analysis) examined; the nanoparticles were found to exhibit a homogeneity in shape and size, and the crystallite size was 46 nm.

Microwave-assisted Ag_2O-Ag_2O_3 NPs are stable due to the presence of vegetable capping agents such as flavonoids, proteins, and phenols whose NPs are resistant to agglomeration. Biomimetic synthesis of Ag_2O-Ag_2O_3 NPs using plant extract and microwave has many advantages such as non-harmfulness, environmentally friendliness, sustainability, biocompatibility, simplicity, and cost-effectiveness. Because of these properties, it is concluded that Ag_2O NPs will have an important and mandatory role in most nanotechnology-based protocols.

In the future, if the biosynthetic experimental conditions are optimized to control the size and shape parameters of silver oxide NPs, photocatalytic performance applications and growth towards more biomedical fields are expected.

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