*ORIGINAL PAPER*

# WASTE TO VALUABLE MATERIALS: GREEN SYNTHESIS OF SILVER NANO-RODS FROM SPENT COFFEE GROUND EXTRACT

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***Abstract.*** *Green synthesis of metal nanoparticles is a promising approach to producing nanoparticles using natural and environmentally friendly resources. It involves the use of various biological agents such as fungi, bacteria, algae, and plants. This method avoids the use of toxic chemicals and reduces the environmental impact of conventional methods of nanoparticle synthesis. Green synthesis of silver nanoparticles (AgNPs) has potential applications in biomedical, environmental, and industrial fields. Conventional coffee brewing techniques produce large quantities of spent coffee grounds that contain bioactive compounds. Silver nano-rods (AgNRs) have been synthesized from filter coffee waste. This is the first report about the synthesis of AgNRs shape from spent coffee ground (SCG). The reduction of Ag (I) to Ag (0) was achieved by spent coffee ground aqueous extract. The obtained nanostructures were characterized by ultraviolet spectroscopy (UV-Vis), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX). They showed a SPR band at a wavelength of 445 nm. The SEM images demonstrated that AgNRs generally contained a rod shape and average size of 100 nm. Elemental composition of AgNRs was analyzed by EDX. A strong peak was observed at around 3 and 3.5 keV. X-ray diffraction (XRD) patterns revealed the crystalline structure of AgNRs. The shape or size of the nanoparticles has an important role in all nanotechnology applications. It was presented a perspective for usage of spent coffee as a valuable material with great potential of application in medicine, pharmacy, and electronic industries. Green synthesized AgNRs from spent coffee may become promising candidates for nano opto-electronics and nanosensors due to their conductivity.*

***Keywords:*** *Spent coffee ground; green synthesis; silver nano-rods.*

## 1. INTRODUCTION

At the end of 1950 Richard Feynman first talked about nanotechnology and introduced the theory that it would be possible to manipulate atoms and molecules directly. In recent years, nanotechnology and nanomaterials have been widely used in many fields. Thus, metallic nanoparticles have attracted great attention due to their potential applications in many research areas such as remediation, energy generation, biological activity, photonics, optoelectronics, and catalysis [1-5]. The physical and chemical methods for the synthesis of silver nanoparticles (AgNPs) have been documented by many researchers [6,7]. But the toxicity of these methods is a major problem [8]. Green synthesis methods produce AgNPs that are more stable using various plant materials extracts (seeds, fruits, leaves, flowers, and roots) since they contain flavonoids, polyphenols, tannins, etc. as reducing and stabilizing

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agents for the synthesis AgNPs [9-12]. This method is environmentally friendly, non-toxic, and inexpensive. The resulting AgNPs have antioxidant, antimicrobial, and anticancer activities, electrical and thermal conductivity, and interesting optical characteristics [13-17]. The number of dimensions is used to classify nanoparticles [18]. They are zero-dimensional (0-D), one-dimensional (1-D), two-dimensional (2-D), and three-dimensional (3-D)[19,20]. 1-D silver nanostructures are more advantageous than other silver nanostructures because they can enable free movement of electrons in one direction. 1-D structures mainly show three different morphology such as nano-rods, nano-wires, nano-tubes [21]. Silver nano-rods (Ag-NRs) are more useful than others in the electrical industry [22]. They can be used in many electronic devices due to their strong conductivity such as conductive inks, adhesives, and pastes [23].

Green synthesis of AgNPs has been investigated using waste materials (peels, leaves, seeds, fruits, and tea waste) because of their abundance and cheap [24-26] In addition, green synthesis of AgNPs from vegetal waste materials has been used in recent years, as the primary goals of researchers include sustainability, energy efficiency, renewability, and reduction of chemical derivatives [15,27-29]. There are only a few reports on the synthesis of Ag-NRs using the plant extract-mediated route. Almost all nanoparticles obtained by green synthesis are spherical [30].

After tea, coffee is the most widely consumed agricultural product in the world; about 8.5 million tons of coffee waste is generated annually from production, industry and restaurants [31]. The coffee wastes contain functional groups such as hydroxyl, carboxyl, ether, aldehyde, and ketone, making them suitable for fertilizer, biodiesel, animal feed and adsorbent applications [32-34]. Great amounts of coffee waste are not used effectively and remain as garbage that causes serious environmental. Waste coffee pulps represent a significant water and soil contamination risk through degradable contents which may be phytotoxic [35]. Our knowledge this study is the first report about the synthesis of Ag-NRs shape from spent coffee grounds (SCG). Since coffee includes significant bioactive contents, the nano-rods capped and stabilized by these compounds could be valuable materials for the food, pharmaceutical, and optics industries. The work adds to the confirmation of previous reports on the biosynthesis of metal nanoparticles from waste plant materials.

## 2. MATERIALS AND METHODS

### *2.1. MATERIALS*

The filter coffee waste (FACW) collected from the local coffee shop in Tokat/ Turkey was used in this report. Firstly, the collected SCG was washed twice with deionized water and filtered. The filtered material was oven-dried at 80°C for 3 hours. Then it was stored in a plastic box not allowing air. All chemicals were of analytical grade and bought from Merck, Germany. Deionized water was obtained from a Milli-Q water purification system (Millipore, USA).

*2.2. METHODS*

### 2.2.1. Preparation of aqueous extract

An amount of 5 g waste materials was weighed and put into a flask and added (100 mL) deionized water. It was boiled for 5 min. The aqueous extract was filtered using Whatman filter paper No. 1 and refrigerated until use.

### 2.2.2. Synthesis of AgNRs

Silver nitrate ($AgNO_3$) (0.1698 g) was weighed and solved 100 mL of deionized water. It was dissolved completely. A volume of 20 mL of SCG extract was mixed with 100 mL $AgNO_3$ solution. The reaction mixture was placed on a stirring plate and heated at $60^0$C for 4 h as reported elsewhere. The color of the solution turned from light yellow to dark brown. The synthesized AgNRs were subjected to centrifugation at 5000 rpm (NF 200/ NUVE, Ankara, Turkey) for 15 min, and then washed with deionized water two times, and dried by lyophilization.

### 2.2.3. Instruments

The formation of AgNRs was performed by UV-Vis absorption spectroscopy using Lamda 35 UV/Vis Spectrometer (Perkin Elmer, USA) in the wavelength range of 200-800 nm. The shape, and size of bio-synthesized AgNRs were determined by Scanning Electron Microscopy (SEM-Quanta 450 FEG, FEI Company, USA) The purity of AgNRs was determined by Energy Dispersive X-ray spectroscopy (EDX) detector. Powdered samples were taken on straps with carbon bands. They were gold-plated under the vacuum. Gold-plated samples were analyzed under high vacuum. For obtaining the best screen and the particle size, appropriate voltage was used. X-ray diffraction (XRD) analysis of AgNRs was examined by Panalytical brand XRD device with EMPYREAN model (Worcestershire, UK). AgNRs were analyzed by using CuKα radiation ($\lambda$ = 1.5418 nm) with the scanning 2θ ranging from 20 to 80°C.

## 3. RESULTS AND DISCUSSION

Previous studies have shown that plant metabolites contain proteins, alkaloids, terpenoids, sugars, phenolic acids, and polyphenols. These molecules play an important for in the bio-reduction of silver ions ($Ag^+$ to $Ag^0$), yielding AgNPs. The plant-mediated synthesis of AgNPs is nontoxic, easy, and very economical.

According to the findings of this study, AgNRs were successfully biosynthesized from spent coffee waste. The reduction of silver ($Ag^+$) ions by the treatment of $AgNO_3$ with SCG extract took place in 10 min. The reaction progress was monitored by UV-Vis spectroscopy. The change in the color of the reaction mixture was continuously observed from light yellow to dark brown in an hour of incubation (see the inset image of Fig. 1). This colloidal brown color indicated the formation of AgNRs, which corresponded to the surface plasmon resonance (SPR) absorption spectrum. The AgNRs exhibit a brown color, which arises due to the surface plasmon vibration of metal nanoparticles.

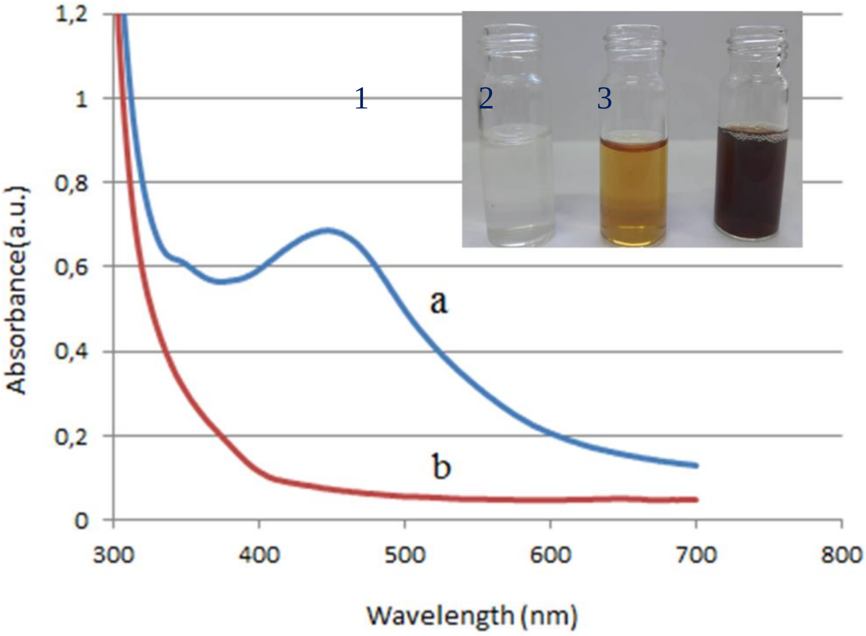


**Figure 1. UV-Vis absorption spectra of AgNRs (a) and SCG extract (b) The aqueous solution of silver nitrate (1), SCG extract (2), and AgNRs (3).**

The potential for the synthesized AgNRs to absorb UV-Vis radiation was investigated and the spectrum is shown in Fig. 1. The color of the reaction mixture changes during the bio-reduction of silver ions by coffee waste aqueous extract. The bio-synthesized AgNRs exhibited an absorption peak at 445 nm, attributed to the SPR band, which demonstrates the characteristic absorption behavior of silver nanostructures. Another peak of low intensity was observed at 340 nm. These findings agree with previous reports highlighting that the SPR band of AgNRs was mentioned to be located in the wavelength range 300 to 460 nm [29].

SEM images (Fig. 2) present the details about the morphology and nano-structure of the prepared particles, revealing that the synthesized samples have rod-like shapes and an average size of 100 nm. Nano-rods have a typical length of 10-150 nm. Due to their physical properties, nano-rods are attractive constituent to be studied and ideal candidates for several applications such as optics, electronics, and medical devices. In addition, nano-rods had great structural stability.

It was discovered that conductivity of the nano-rods is better than spherical shape particles. This is due to the increase of the aspect ratio of the particle lead to the increased of excitation of surface plasmon in the nanostructure.

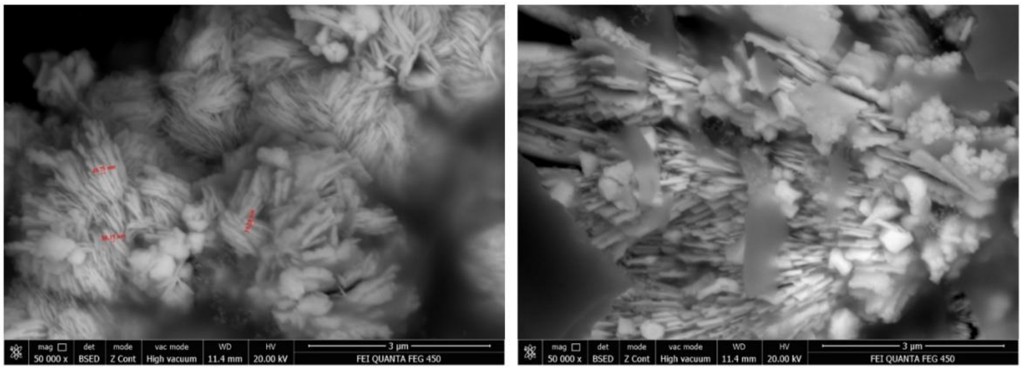

**Figure 2. SEM images of synthesized AgNRs at different magnifications.**

Fig. 3 demonstrates the elemental composition of AgNRs, as determined by the EDX spectrum. The strong peak of AgNRs in the EDX spectrum at around 3.0 and 3.5 keV confirmed the AgNRs formation [30].

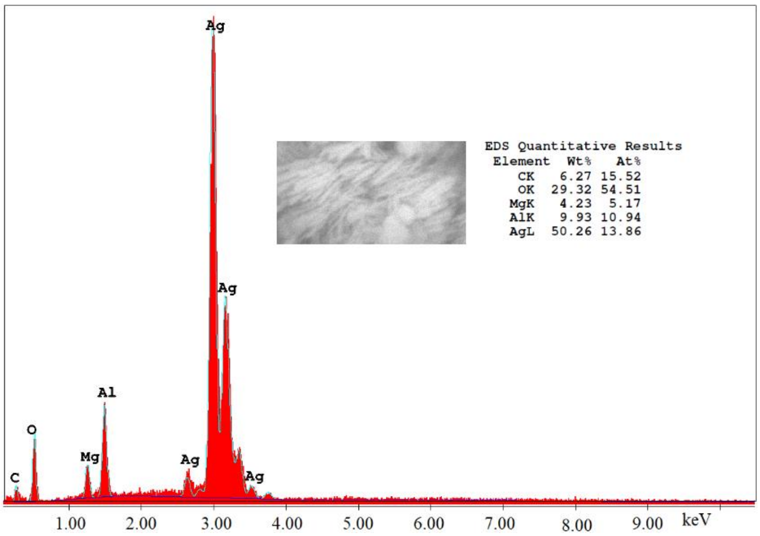

**Figure 3. EDX spectrum of AgNRs**

Other elements presented in EDX spectrums (such as carbon, oxygen, magnesium, etc.) are coming from coffee wastes. Plant materials have also minerals and vitamins. An EDX examination confirmed the presence of silver, while the oxygen signal indicated the possibility that extracellular organic material was probably adsorbed on the surface of the AgNRs [11].

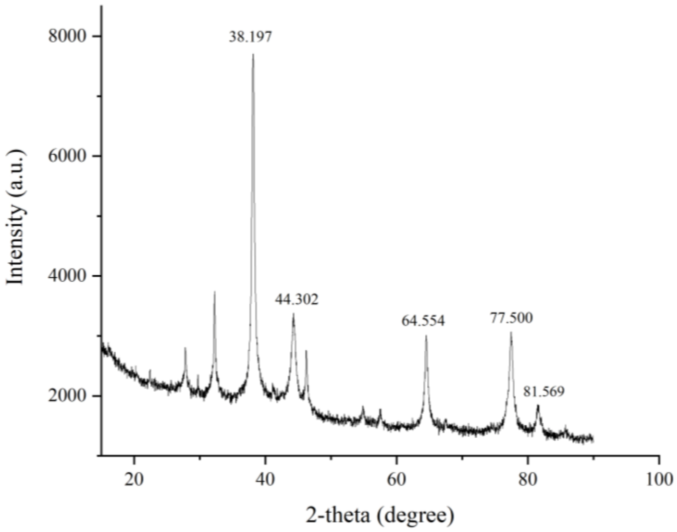

**Figure 4. X-ray diffraction of synthesized AgNRs**

Fig. 4. indicates that AgNRs have cubic face-centered (FCC) structures. As shown in Fig. 4, significant peaks are observed 38.197°(111), 44.302°(200), 64.554°(220), 77.500° (311), and 81.569°(222). XRD analysis shows that the synthesized AgNRs correspond to well-defined surfaces with an arrangement of atoms in a crystal lattice manner. The intense peak 2θ=38.197° corresponds to the (111) reflection as one of the most compressed packed planes, indicative of the FCC structure. These results are consistent with earlier studies as XRD contains similar 2θ patterns. The XRD data also reveals peaks representing organic compounds from the SCG extract (~32°) [39,40].

Zuorro et al. (2022) reported that the green synthesis of AgNPs from spent coffee grounds using water/ethanol extract [38]. Since phenolic compounds in coffee and coffee wastes have metal-reducing properties, they are suitable for nanoparticle production. SCGs have been used for nanoparticle synthesis in the reference study and a few other studies. However, due to the use of chemicals in the methods applied during the synthesis, it can be discussed to be called green synthesis because the green synthesis method aims to use easy, cheap, and environmentally friendly methods. The importance of this study is that it is easy, inexpensive and synthesized in a single step with water extract without the use of any toxic chemicals. AgNRs synthesized by chemical and physical methods have applications in the electrical and optical industries. There are almost no studies in the literature on AgNRs obtained by green synthesis and their applications. The presented work will give an idea for future studies in this direction. Also, AgNRs are potential candidates for energy storage applications.

## 4. CONCLUSION

In this study, it was reported for the first time the synthesis of AgNRs shape by a “green chemistry” method using the extract of spent coffee ground. The method is operationally fast, simple, nontoxic, and eco-friendly. Herein, it was presented a perspective for usage of spent coffee as a valuable material with great potential of application in medicine, pharmacy, and electronic industries. Green synthesized AgNRs from spent coffee may become promising candidates for nano optoelectronics and nanosensors.

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