Available online at sjuoz.uoz.edu.krd

Science Journal of University of Zakho

Vol. 10, No. 4, pp. 193 –196, October-December 2022

p-ISSN: 2663-628X
e-ISSN: 2663-6298

SOLID STATE SYNTHESIS OF SILVER NANOPARTICLES USING VIOLURIC ACID AS A NOVEL REDUCING AGENT

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Received: *28 Aug., 2022 /* ***Accepted:*** *20 Sep., 2022 /* ***Published:*** *17 Oct., 2022* ***https://doi.org/10.25271/sjuoz.2022.10.4.1021***

ABSTRACT:

Metal Nanoparticles (NPs) are recognized as the most attractive materials due to their distinct physical and chemical characteristics. Several chemical and physical fabrication techniques have already been tested to obtain NPs of appropriate size and shape. Although the chemical-based solution methods provide NPs within a proper size and shape and can be reasonably controlled, they require a large amount of raw material including solvents, capping agents, etc., which usually lead to toxic output and waste. In this study, the author tested an easy and environmentally friendly solid-state synthesis pathway for synthesizing silver (Ag) NPs within a suitable size and shape, using a novel reducing agent. Silver carbonate (Ag_2CO_3) was allowed to react with Vio2luric acid ($C_4H_3N_3O_4$) as a reducing agent through a solid-state grinding method for one hour. The results confirmed that Violuric Acid can be considered a promising reducing agent that forms well-shaped spherical Ag NPs within an average particle size of about 60 nm.

Keywords: Silver Nanoparticles, Solid-State Synthesis, Violuric Acid.

1- INTRODUCTION

Silver along with other noble metals is the focus of many researchers due to its unique properties (Jain, Huang, El-Sayed, & El-Sayed, 2008). Silver, in the bulk state, compared with other noble metals possesses the highest thermal and electrical conductivities, and lowest melting and boiling points (Chen, Wiley, & Xia, 2007). It is also the most reactive noble metal so its cations showed a toxic effect on many kinds of micro-organisms (Singh, Singh, Prasad, & Gambhir, 2008).

However, Ag NPs are even more interesting owing to the specific property under light irradiation called localized surface plasmonic resonance (LSPR). Ag NPs have been used in many applications including electronic devices (Shen, Zhang, Huang, Xu, & Song, 2014), analytical techniques (Liming Wang et al., 2015), photocatalytic (Sajadi et al., 2018), solar thermal generation (Talabani, Hamad, Barzinjy, & Demir, 2021), biomedicine (Gherasim, Puiu, Bîrcă, Burduşel, & Grumezescu, 2020), antibacterial agents (Hamad, Khashan, & Hadi, 2020), anti-cancer therapies (Kovács, Igaz, Gopisetty, & Kiricsi, 2022) and many more.

One of the most interesting concerns in nanotechnology is the ability to synthesize desired NPs within specific size and shape for a certain application. For this, two main approaches have been employed; namely top-down and bottom-up approaches (Dang-Bao, Favier, & Gómez, 2021). Top-down, in turn, is creating the nanomaterial starting from bulk by chopping away the extra material, while bottom-up is starting from atoms and molecules as building blocks and assembling them to get the desired nanomaterial (Pryshchepa, Pomastowski, & Buszewski, 2020). Further, the syntheses of NPs can be also categorized by the nature of the utilized process, namely physical, chemical, and biological methods (Iravani, Korbekandi, Mirmohammadi, & Zolfaghari, 2014). In the physical method, physical agents like heat, electric discharge, or electromagnetic irradiation are used (Rajput, 2015). Despite the low yield, high cost, high energy usage, and no uniform size distribution of physical methods they are considered as environmentally friendly methods with no toxic outputs (Jamkhande, Ghule, Bamer, & Kalaskar, 2019).

Chemical synthesis, in turn, is the production of NPs through chemical reactions from the preliminary material. Chemical methods consume organic solvents to synthesize NPs. In general, the chemical method utilizes three main materials, metal precursors, reducing agents, and stabilizing/ capping agents (Babu Kalidindi, Sanyal, & Jagirdar, 2011). The preference for the chemical approach is the high yield but the drawback is that it is expensive and the materials involved are hazardous and toxic (Talabani et al., 2021).

Most chemically fabricated Ag NPs are formed by four chemical reactions: citrate (Turkevich) method (S. H. Lee & Jun, 2019), borohydride reduction (Sholikhah, Pujiyanto, Lestari, Sarmini, & Lubis, 2018), Tollens (silver mirror) reaction (Dondi, Su, Griffith, Clark, & Burley, 2012), polyol process (Lalegani, Ebrahimi, Hamawandi, La Spada, & Toprak, 2020).

To avoid the disadvantages of chemical methods, biological or green synthesis methods, for NPs preparation, have been introduced and considered viable choices. The synthesized NPs through biological methods are considered to be one-pot, inexpensive, eco-friendly, and more stable than the traditional methods. On top of that, the production of hazardous chemicals, within the green method, is avoidable to the highest extent (Rafique, Sadaf, Rafique, & Tahir, 2017). In the green synthesis method, microorganism and plant extracts are utilized as an alternative to chemical solutions and agents (Okafor, Janen, Kukhtareva, Edwards, & Curley, 2013).

Recently a facile, one-pot scalable solid-state technique has been used to produce metallic and metal oxide NPs. In this procedure, only the metal precursor and a reducing agent are used in a mortar and pestle system and the corresponding metal NPs is produced after grinding the materials for a proper time. This process can produce NPs in the absence of chemical solvent and can be conducted at room temperature (LP Wang & Hong, 2000).

Debnath *et al.* (Debnath, Kim, Kim, & Geckeler, 2010) reported a seminal work for the production of Ag NPs through a solid-state milling method with high-speed vibration. They used poly (Vinylpyrrolidone) as the reducing agent for Ag ions reduction. The process is performed at room temperature (RT) without utilizing any extra solvent. Another attempt was done by Zhang *et al*. (Zhang, Tian, Xiao, Sun, & Li, 2015) to introduce a method for Ag NPs preparation. They mixed the metal precursor $AgNO_3$ with the reducing agent Ascorbic Acid (AA) and grinding the mixture in a solid-state reaction at room temperature for about 30 min. Hebeish *et al.* (Hebeish, Shaheen, & El-Naggar, 2016) reported the preparation method for synthesizing Ag NPs. The synthesis process has been conducted using starch to reduce and stabilize NPs in the presence of sodium hydroxide through the solid-state grinding method. Later, K. H. Lee *et al.* (K. H. Lee et al., 2018) synthesized currency metal (Ag, Au, Cu) NPs through the solid-state method by grinding metal acetates and solid hydrazine and oxides at room temperature.

In this study, the author investigated the preparation procedure for synthesizing Ag NPs using the solid-state grinding technique at room temperature. Silver Carbonate (Ag_2CO_3) as a metal precursor and Violuric Acid (VA) as a reducing agent was ground in a mortar for about one hour. The color of the mixture changed from white to reddish-orange powder after about 1 hour milling indicating the production of the Ag NPs. Numerous characterization techniques were used to characterize the final product. Scanning Electron Microscopy (SEM) was employed to obtain the topography and the grain size of the synthesized NPs. While X-Ray diffraction (XRD) is used to compute the crystalline size and analyze the degree of crystallinity of the NPs. Energy Dispersion X-Ray (EDX) spectroscopy was used to analyze the purity and composition of the final product. UV-Vis spectroscopy is used to detect the SPR absorption peak of the NPs.

2. MATERIALS AND METHODS

The procedures and interactions for the one-step solid-state synthesis of Ag nanoparticles at Finely ground silver carbonate (Ag_2CO_3) and Violuric Acid ($C_4H_3N_4O_4$) were combined (feed molar ratio = 1:1 (R = 1:1) and milled for one hour at room temperature in an agate mortar. The reactions began rapidly throughout the milling. Ag NPs were produced when the reduction of Ag^+ to Ag^0 atoms was performed by low-valent nitrogen atoms of ($C_4H_3N_3O_4$), resulting in the release of nitrogen (N_2). Finally, Ag NPs were produced, then cleaned and air-dried. The final product, *i.e.*, Ag NPs, was then analyzed using XRD, SEM, EDX, and UV-Vis spectrophotometers. UV-Vis Spectroscopy was performed using a double-beam spectrophotometer (Super Aquarius Spectrophotometer-1000). The structure of synthesized silver nanoparticles has been studied using XRD diffractometer PAN analytical X'Pert PRO (Cu kα=1.5406 A^0). The rate of the scanning was 1^0/min in 20^0 to 80^0 of the 2Θ range. Voltage and currents are 45 KeV and 40 mA respectively. The SEM characterization is performed using (SEM Quanta 450).

3. RESULTS AND DISCUSSION

After synthesizing Ag NPs to evaluate the functional aspects of the prepared nanoparticles their physiochemical properties should be examined. These different characterization techniques are usually performed using different analytical methods including X-Ray Diffractometry, Scanning Electron Microscopy, UV-Vis Spectroscopy, and Energy Dispersion X-Ray Spectroscopy, which have been used to characterize the NPs.

3.1 UV-Vis Spectroscopy

Once Ag NPs are formed, the energy gap between conduction and valence bands becomes very small within which electrons can freely move. These free electrons result in a Localized surface plasmon resonance (LSPR) absorption band, happening due to the collective oscillation of electrons of Ag NPs in response to the frequency of the light wave (Raza et al., 2013).

The LSPR absorption band lies near different wavelengths depending on the NP structure, for example, LSPR lies near 400 nm for spherical silver NPS, whereas it is in the range of 500-100 nm for triangular Ag NPs (Durval et al., 2021).

The absorbance spectrum of Ag NPs is shown in **Figure 1** exhibiting a distinct peak at around (~360 nm) indicating well production of spherical NPs. Al-Namil *et al.* 2019) showed that Ag NPs can be synthesized through a novel solid-state green method without utilizing any solvent environment. They stated that the SPR absorbance peaks were found in the range of 400-450 nm. Our results show that the produced Ag NPs are smaller in size. This shape distribution and size have been also reflected in the optical properties. It can be stated that smaller NPs possess higher catalytic activities, therefore, using the solid-state synthesis method size and shape of NPs can be adjusted for its better requests such as in catalysis.

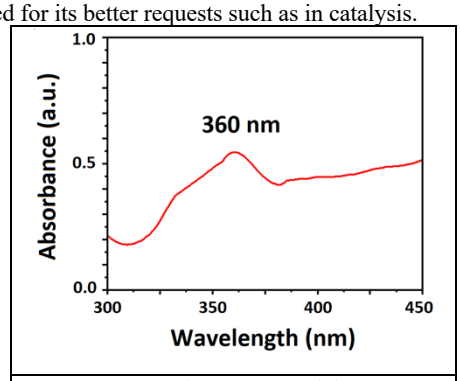

Figure 1: UV-Vis spectrum of the Ag NPs

3.2 X-Ray Diffraction (XRD) Analysis

X-Ray diffraction is one of the most efficient techniques which can be utilized to analyze molecular and crystalline material structures as well as particle size. When X-Ray is reflected from a crystalline structure many diffracted patterns are formed each of which reflects a physical or chemical property of the material (Bykkam, Ahmadipour, Narisngam, Kalagadda, & Chidurala, 2015). **Figure 2**, shows the XRD pattern of the Ag NPs prepared by the present solid-state technique, which indicates distinct peaks corresponding to the crystallinity of the Ag NPs. It can be perceived, from **Figure 2**, that the diffraction peaks at 38.05°, 44.14°, 64.51° , and 77.45° are linked to the (111), (200), (220), and (311) planes, in that order. These diffraction peaks, of a cubic crystal system (a = 4.0686 Å) have been coordinated with the typical JCPDS card No. 65–2901 to monitor the purity and crystalline degree of Ag NPs. The outcomes of this study were consistent with the formerly reported investigations (Khatami, Mehnipor, Poor, & Jouzani, 2016; Li et al., 2011; Roy, Bulut, Some, Mandal, & Yilmaz, 2019; Talabani et al., 2021)

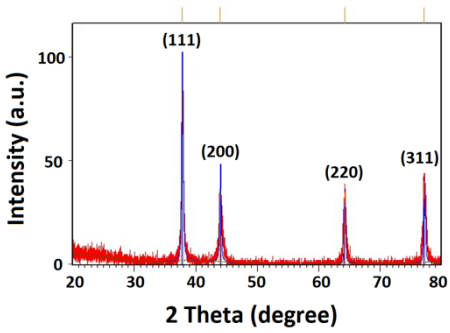

Figure 2: XRD pattern of the Ag NPs

The average crystalline size of the Ag NPs can be computed through the Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Where K is the Scherrer constant with values from 0.9 -1 (shape factor), λ is the X-ray wavelength β is the full width at half maximum (FWHM) of the XRD peaks and θ is the Bragg's angle. The regular crystalline size, by means of the Debye-Scherrer equation, of the Ag NPs was about 45 nm. The variation between the XRD and SEM analysis is due to the fact that XRD provides crystalline size, not particle size.

3.3 Scanning Electron Microscopy (SEM) analysis

The shape, morphology, and particle dispersion of the prepared Ag NPs have been assessed using SEM. **Figure 3** shows monodispersed and spherical shape Ag NPs. **Figure 3a** shows that the average NPs size distribution for the synthesized Ag NPs is ranging between 50-70 nm. However, the particle dispersion analysis, using image J software, indicated that the average particle size is roughly 60 nm. The SEM analysis confirms that the synthesized Ag NPs are monodispersed and the agglomeration status is less than the green synthesis method using plant extract (Dhand et al., 2016). This is, in turn, extremely important since one can derive the NPs within the desired shape and size if one can control these parameters.

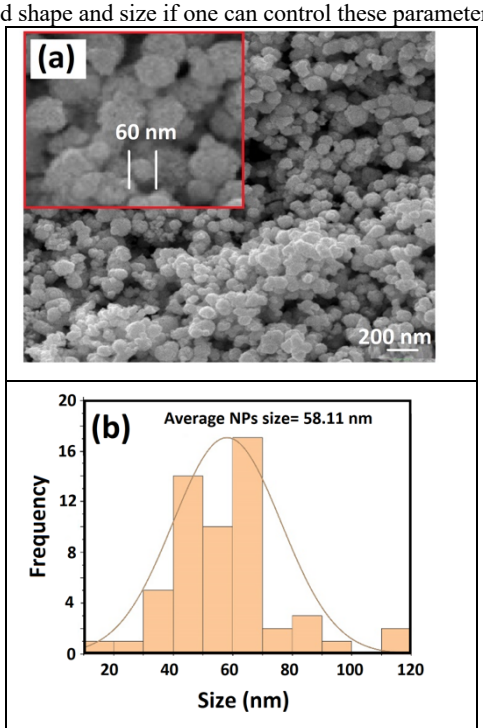

Figure 3: (a) SEM image of Ag NPs and (b) Ag NPs size distribution

3.4 Energy Dispersion X-Ray (EDX) analysis

The elemental analysis of the synthesized Ag NPs was studied through Energy Dispersive X-ray (EDX) analysis (**Figure 4**). This characterization is, also, significant since it provides the purity status of the synthesized Ag NPs. The energy of the typical X-rays permits qualitative analysis to disclose the elements that contribute to the sample, while the resultant intensity signifies quantitative analysis to disclose the amount of the existing elements (Thambiratnam, Reduan, Tiu, & Ahmad, 2020). According to **Figure 4**, the quality of Ag NPs is high and there is no mentionable contamination in the samples. The existence of gold in all samples is owing to the SEM sample preparation meanwhile the samples have been coated with a very thin layer of gold, 100Å, so as to improve the quality of the SEM images. Analogous analysis has been found in previously reported investigations (Ahani & Khatibzadeh, 2017) (Al-Namil et al., 2019; Talabani et al., 2021).

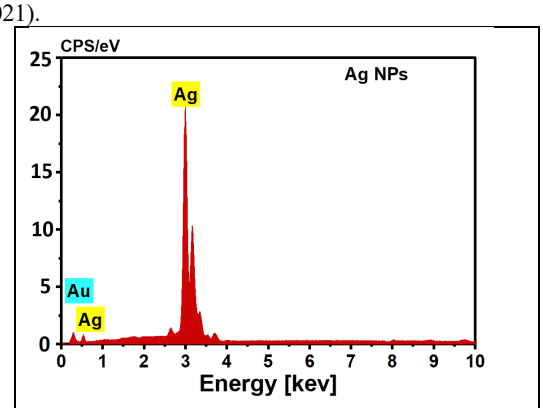

Figure 4: EDX analysis of the synthesized Ag NPs

4. CONCLUSION

In this work, Ag NPs were synthesized effectively through a one-pot, cost-effective, and solid-state synthesis method. Silver Carbonate and Violuric Acid were utilized as a novel reducing agent, combined, and milled for one hour at room temperature. Several characterization techniques have been employed to study the morphology, pureness, degree of crystallinity, structural, and optical properties of the synthesized Ag NPs. It was perceived that small size, ~ 60 nm, monodispersed and spherical Ag NPs can be obtained in this study which led to narrowing the SPR peak to about 360 nm. XRD analysis displayed that the fabricated Ag NPs are crystallized in the face-centered cubic and possess high crystallinity. EDX analysis showed that the quality of Ag NPs is high and there is no mentionable contamination in the sample. This method can produce spherical Ag NPs, which possess a higher surface area to volume ratio than the other shapes, therefore, it is more likely, to generate higher surface energy which is important for many applications. Finally, this method can be generalized for synthesizing other types of nanomaterials.

ACKNOWLEDGMENT

The Author would like to thank the chemistry department at the College of Science, Salahaddin University for kindly providing the materials and also thanks to the Scientific Research Center- Soran University for performing the characterization.

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