Silver and Zinc Oxide Nanoparticles

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Contributor: Norfarina Bahari , Norhashila Hashim , Khalina Abdan , Abdah Md Akim , Bernard Maringgal , Laith Al-Shdifat

The versatility of Ag-NPs and zinc oxide NPs (ZnO-NPs) in rendering themselves to many applications, including in sensors, renewable energies, environmental remediation, bio-therapeutic devices, clothing, antimicrobial is currently being explored.

nanoparticles honey green synthesis reducing agent

1. Honey-Mediated Silver Nanoparticles

The synthesis of Ag-NPs using honey typically involves the addition of a silver salt precursor, such as $AgNO_3$, to a honey solution. **Table 1** summarizes the various silver salt precursors used for Ag-NPs synthesis, conditions, morphologies of the resulting Ag-NPs, and their applications. According to a study by Khorrami et al. [1], the appearance of a brownish-yellow color followed by a dark brown color after a few hours of contact confirms the formation of Ag-NPs through the suggested reaction.

$$Ag^{+}NO_3^{-} + \text{Honey (OH, COOH, etc.)} \rightarrow Ag^{0}\ \text{NPs} \qquad (1)$$

Table 1. Silver salt/precursor used, synthesis condition, Ag-NPs morphology, and their applications.

Silver Salt/Precursor	Synthesis Condition	Shape	Size (nm)	Application	References
$AgNO_3$	- Reaction temperature, 30 °C. - Incubation time, 72 h in dark conditions.	Spherical	50 to 98	Antioxidant, antibacterial	[2]
$AgNO_3$	- Reaction temperature, 35 °C - Stirred vigorously for 24 h.	Spherical	42.7	Antibacterial	[1]

Silver Salt/Precursor	Synthesis Condition	Shape	Size (nm)	Application	References
$AgNO_3$	- centrifuged at 12,000 rpm for 1 h. - ph mixture at 5 to 10.	Spherical	20.0	Na	[3]
$AgNO_3$	- pH mixture at 6.5 to 8.5.	-	15.63 to 26.05	Na	[4]
$AgNO_3$	- Continuous stirring until color changes to brown under room temperature conditions.	Spherical	50 to 90	Anticancer, antimicrobial, immunomodulatory	[5]
$AgNO_3$	- Continuous stirring until color changes to brown under room temperature conditions.	Spherical	60 to 85	Antimicrobial, immunomodulatory	[6]
$AgNO_3$	- pH mixture was adjusted to 9.5	Spherical	42 to 80	Antifungal	[7]
$AgNO_3$	- stirred for 1 min. - pH mixture was adjusted to 6.5.	Spherical	5 to 25	Catalytic degradation of methylene blue	[8]

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forms the $Ag(OH)_x$ complex. Eventually, Ag^0 is obtained, which increases the nucleation rate. The OH groups in the solution also open the glucose ring. The rate of reaction increases with honey concentration. The effect as a reducing agent, in this case, shows that a higher concentration of the reactant increases the rate of the reaction. However, with a high concentration of honey, the concentration of OH groups can be reduced due to the buffering capacity of honey. This can inhibit the formation of intermediate complexes and decrease the reduction and nucleation of silver ions. To summarize, the mechanism described above transforms Ag^+ ions to Ag^0 particles through the linear form of glucose. Then, glucose molecules are adsorbed on the reduced silver, acting as capping agents.

Na—not applicable.

It has been suggested that the reduction process of Ag^+ ions to Ag-NPs could also involve sucrose, glucose, and proteins/enzymes. The addition of NaOH to the solution can impact the size of the NPs formed as it increases the pH of the solution, leading to the production of more gluconic acid from glucose. This occurs because the alkali

abstracts the α-proton from the sugar ring of glucose and causes the opening of its ring structure, leading to the formation of gluconic acid. The Ag^+ is reduced to metallic Ag^0 after the oxidation of glucose to gluconic acid [4]. Ghramh et al. [6] reported that $AgNO_3$ was mixed with the diluted form of honey to prepare Ag-NPs. The change in mixed color was evidence of the formation of Ag-NPs. Sugars (sucrose and glucose) and proteins (possibly enzymes) play a role in the Ag^+ reduction process. In addition, the addition of NaOH, which increases the pH of the solution, had a significant impact on the expected volume of produced NPs. FTIR spectroscopy analysis revealed the existence of multiple functional groups in honey as evidence for the source of reducing and capping agents.

Notably, both findings by Haiza et al. [4] and Ghramh et al. [6] are parallel to those of Hemmati et al. [9]. In the paper, the authors claim that reducing sugar is sugar that can serve as a reducing agent and contains either free aldehyde or free ketone groups. They denote that all monosaccharides (simple sugars) are reducing sugars, while sucrose (table sugar) and maltose are non-reducing sugars. According to the authors, when heated in an alkaline state, reducing sugars are generally converted to gluconate and other compounds that can serve as reducing agents. In addition, alkaline hydrolysis has been proven to convert non-reducing sugars such as sucrose into reducing sugars such as glucose and fructose, which are responsible for the reduction of Ag^+ ions to Ag^0 atoms. Furthermore, the pH value and amount of the alkaline solution employed during the synthesis operations can have a substantial influence on the efficiency of Ag-NP formation [10].

The study by Czernel et al. [7] supports previous findings that the reduction of glucose and fructose in honey is the key factor in the synthesis of Ag-NPs. They found that proteins act as stabilizing agents while an alkaline environment is necessary for synthesis. The researchers observed that at high pH, the removal of a proton from the oxygen ring of glucose facilitated the opening of its ring, leading to the oxidation of metal ions into gluconic acid. The formation of NPs was characterized by a change in the color of the synthesis mixture from pale yellow to light brown. This change was attributed to the surface plasmon resonance (SPR) of the Ag-NPs, as evidenced by its corresponding UV-Vis spectrum.

FTIR measurement was performed to identify the bioactive molecules responsible for the capping and stabilization of Ag-NPs synthesized using honey. According to the study conducted by Al-Zaban et al. [8], FTIR detected the presence of phenolic compounds through a broad and prominent peak at 3350.87 cm^{-1}, which was due to the hydrogen-bonded O-H stretching. The stretching of the aromatic C-H bond produced peak bands at 2957.76 and 2882.84 cm^{-1}. The strong peak at 1634.25 cm^{-1} was attributed to the C-C stretchable alkene functional group. The bands at 1418.21 cm^{-1} were assigned to the N-H stretching vibration of proteins. Furthermore, the peaks associated with the C-O single bond at 1248.41 cm^{-1} and 1044.16 cm^{-1} may correspond to the vibrational frequencies of amide proteins, with frequencies ranging from 1000 cm^{-1} to 1300 cm^{-1} depending on the type of molecule.

The results are consistent with those reported in the 2020 study by Al-Brahim and Mohammed [2], where Ag-NPs were synthesized from *Z. spinachristi* sp. and *A. gerrardii* sp. honey. FTIR detected the presence of phenols or glycosides as stretching vibrations of H-bonded OH groups. Another study led by Ghramh et al. [5] found different peaks in FTIR spectra for different types of honey. The reduction of $AgNO_3$ to Ag-NPs resulted in the formation of

several compounds, with the disappearance of peaks belonging to cyclopentanone, alkene, and bromo compounds, indicating their involvement in the reduction and stabilization of the Ag-NPs.

Sreelakshmi and colleagues [11] reported that the high dispersion levels of the NPs were attributed to the intrinsic properties of the metals, including surface energy and melting point. Additionally, the transmission electron microscopy (TEM) results indicated that no agglomeration occurred, which suggested that the functional groups in the honey played a critical role in firmly anchoring the formation of the Ag-NPs. Furthermore, the co-existence of other elements with silver in honey corresponds to its functional properties, and these entities are proposed to bind efficiently to Ag-NPs, thereby preventing them from agglomerating.

The exact mechanism for the green synthesis of Ag-NPs using honey is not well understood. However, researchers concur that biomolecules such as reducing sugars, proteins, phenols, and flavonoids in honey play a crucial role in reducing metal ions and capping the Ag-NPs. The current authors deduce that the free amino groups and/or carboxyl residues of honey bee biomolecules, which could be proteins or polysaccharides, bind to Ag-NPs. These biomolecules are not only responsible for reducing Ag^{+} to Ag^{o}, but also act as stabilizing capping agents for Ag^{o}, potentially enhancing the biological properties of the produced Ag-NPs. It has been established that amino groups are primarily the main agents in the reduction of Ag^{+} ions and are adsorbed by them to a considerable extent.

2. Honey-Mediated Zinc Oxide Nanoparticles

The stability of zinc oxide ZnO-NPs is influenced by the choice of capping agents utilized in the synthesis process. These agents play a significant role in guiding the formation of diverse ZnO nanostructures. Understanding the particle development process is important for controlling the shape of ZnO-NPs. Honey contains a range of carbohydrates, enzymes, vitamins, OH groups, and amine groups, which can help to complex zinc cations (Zn^{2+}) into the initial molecular matrix. This structure enables zinc species, eventually forming ZnO-NPs, to be stabilized and coated, preventing excessive aggregation and crystal formation. This method provides a simple, environmentally friendly, and economically feasible way to produce various nanopowders [12][13]. A summary of the zinc salt/precursor used, synthesis conditions, ZnO-NPs morphology, and applications are presented in **Table 2**. The reaction between zinc nitrate solution and honey generally leads to the formation of ZnO-NPs.

$$(NO_3)_2{}^{-}Zn^{2+}{\cdot}6H_2O + \text{Honey (OH, COOH, etc.)} \rightarrow \text{ZnO NPs} \quad (2)$$

Table 2. Zinc salt/precursor used, synthesis condition, ZnO-NPs morphology, and their applications.

Zinc Salt/Precursor	Synthesis Condition	Shape	Size (nm)	Application	References
$Zn(NO_3)_2{\cdot}6H_2O$	- Reaction temperature, 60 °C. - Stirred continuously for 1 h.	Quasi-Spherical	39	Photocatalytic degradation of methylene blue, antibacterial, antifungal	[14]

Zinc Salt/Precursor	Synthesis Condition	Shape	Size (nm)	Application	References
	- Drying at 100 °C for 1 h. - Annealed 550 °C, 2 h.				
$Zn(NO_3)_2{\cdot}6H_2O$	- Reaction temperature, 60 °C in oil bath. - Incubated for 6 h. - Annealed 200, 400, 600, and 800 °C for 2 h.	Spherical	30	Na	[12]
$Zn(NO_3)_2{\cdot}6H_2O$	- Continuous stirred at 60 °C until paste formed. - Annealed 400 °C for 2 h.	Plate-like and rod-like structure	26	Na	[15]
$Zn(NO_3)_2{\cdot}6H_2O$	- Stirred for 1 h. - Heating at 100 °C with continuous stirring until powder obtained. [17]	Spherical	23	Antimicrobial	[16]

Na—not applicable.

…e particle …exagonal phase could form both in the solution phase and in the dried state. They determined the critical concentration required to fully understand the growth kinetics of ZnO-NPs and observed that ZnO particles nucleated in solution and increased in size over time. The growth kinetics were detected at the critical concentration and continued during the sedimentation process. Capping agents can be used to inhibit the growth of certain facets and produce ZnO-NPs with a specific morphology.

In a study by Jeyageetha et al. [15], ZnO-NPs were synthesized using honey as a medium and characterized using various techniques. The results showed that the FTIR peaks of metals and their oxides appeared at lower wavenumbers between 400 to 800 cm^{-1}. The study also noted absorption peaks at various wavenumbers that were attributed to specific molecular bonds such as O-H stretching, aliphatic asymmetric C-H stretching, O-H stretching in carboxylic acid, NH bending of amines, C-C stretch of aromatics, -C=N stretches, amide bands of

proteins, O-H stretching vibrations of carboxylic acids, tetrahedral coordination of the Zn ion, and C-H bending of aromatics.

Recently, UV-Vis spectra were acquired in the range of 200 to 800 nm to confirm the existence of ZnO-NPs. A change in color from yellow to brown during the synthesis process was observed, which indicated the reduction of Zn^{2+} ions to ZnO-NPs by electron transfer. FTIR analysis was employed to identify the biomolecules that contributed to capping and stabilizing the synthesized sample. Two absorption peaks at 1449 cm^{-1} and 1124 cm^{-1} were found in the spectra and corresponded to the protein conformations of the capped ZnO-NPs and vibrations of C-O and C-N, respectively. The release of zinc and oxygen from bare zinc oxide was also observed, which indicated the existence of ZnO-NPs on the surface of the nanoparticles and was shown by an absorption peak at 515 cm^{-1}. These findings indicate that the stabilization of ZnO-NPs is formed by the interaction between carboxyl ions and amino acid groups. Other weak peaks are also attributed to the interaction of ZnO-NPs with amino acid residues. It was concluded that components of honey, such as fructose, glucose, sucrose, proteins, minerals, and vitamins, may play a role in the synthesis of ZnO-NPs [14].

Ranjithkumar et al. [18] conducted a study to compare the impact of using honey and cow urine on the properties of ZnO-NPs synthesized through the co-precipitation method, including the crystalline size, structure, morphology, band gap, and thermal properties. The results showed that the hexagonal structure at pH 8 transformed into stable nanospheres at pH 12, with honey having a noticeable impact on the morphological change of ZnO-NPs. Another study by the authors found that honey-assisted ZnO-NPs exhibited high zeta potential, high thermal stability, and strong antibacterial activity against both Gram-positive (*B. subtilis*) and Gram-negative (*E. coli*) bacteria [16]. Furthermore, the results indicated that the ZnO-NPs synthesized with honey had better colloidal stability and more uniform particle dispersion compared to those synthesized with cow urine.

To date, limited research has been conducted on synthesizing ZnO nanoparticles (NPs) using honey, and further investigation is required to determine the specific substances responsible for metal ion reduction. While proteins have been suggested to play a role in stabilizing ZnO-NPs in some experiments, further study is necessary to identify the specific proteins involved in functionalizing these NPs.

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