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The authors have full responsibility for the originality and content of their own papers.

COMPARATIVE ANALYSIS OF GREEN SYNTHESIS OF SILVER, ZINC AND COPPER NANOPARTICLES USING PLANT EXTRACTS

Ana S. Kesić[1], Katarina M. Marković[1], Mirjana G. Grujović[1], Jelena S. Katanić Stanković[1]
[1]Institute for Information Technologies Kragujevac, University of Kragujevac, Liceja Kneževine Srbije 1A, 34000 Kragujevac, Serbia

Corresponding author e-mail address: akesic@uni.kg.ac.rs (Ana Kesić)

ABSTRACT:
Green synthesis of metal nanoparticles using plant extracts represents an environmentally friendly and sustainable approach for the preparation of nanomaterials with diverse applications. This paper presents a comparative analysis of the green synthesis of silver, zinc, and copper nanoparticles, with particular emphasis on differences in formation mechanisms, particle characteristics, stability, and potential application fields. The analysis is primarily based on the authors' own experimental results, including both published and unpublished studies, supported by relevant literature data.
Nanoparticle formation was monitored by UV–Vis spectroscopy, while interactions between plant biomolecules and nanoparticle surfaces were examined using FTIR analysis. Particle morphology and size were determined by SEM and TEM techniques. The results indicate that green synthesis predominantly leads to the formation of elemental silver nanoparticles, whereas zinc and copper tend to form oxide nanoparticles, ZnO and CuO, due to their higher susceptibility to oxidation. Compared to ZnO and CuO nanoparticles, Ag nanoparticles exhibit faster formation kinetics, narrower size distribution, and improved colloidal stability. In terms of applications, silver nanoparticles show pronounced catalytic and antimicrobial activity, while ZnO and CuO nanoparticles demonstrate significant potential in photocatalysis, environmental protection, and the development of functional materials. This comparative overview provides deeper insight into the advantages and limitations of green synthesis for different metal nanoparticles and supports their targeted application.

Keywords: green synthesis, Ag nanoparticles, ZnO nanoparticles, CuO nanoparticles, comparative analysis

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1. INTRODUCTION

Nanotechnology represents one of the most dynamic fields of modern science, with a wide range of applications in medicine, pharmacy, catalysis, energy, and environmental protection. Due to their high surface-to-volume ratio and unique optical, electronic, and chemical properties, metal nanoparticles exhibit significantly different characteristics compared to their bulk counterparts. Silver, zinc oxide, and copper oxide nanoparticles

are of particular interest because of their pronounced antimicrobial, catalytic, and photocatalytic properties [1–2].

Conventional methods for the synthesis of metal nanoparticles, including chemical and physical approaches, often require the use of toxic reducing agents, organic solvents, and high energy inputs. Such procedures may lead to the formation of harmful by-products and represent a potential risk to the environment and human health. For this reason, in recent years there has been increasing interest in the development of sustainable and environmentally friendly synthesis methods [3].

Green synthesis of nanoparticles is based on the principles of green chemistry and involves the use of biological systems such as plants, microorganisms, and biomolecules for the reduction of metal ions and stabilization of the formed nanoparticles. Plant extracts are particularly attractive due to their simple preparation, availability, low cost, and the presence of various bioactive compounds (phenols, flavonoids, alkaloids, proteins, and terpenoids) that can act as both reducing and stabilizing agents [3].

Mechanism of nanoparticle formation in green synthesis depends on the nature of the metal and the chemical characteristics of the biomolecules present in the plant extract. In the case of silver, a direct reduction of Ag^{+} ions to elemental Ag^{0} occurs, leading to the formation of stable colloidal systems with a pronounced surface plasmon resonance (SPR) maximum. In contrast, zinc and copper show a higher tendency toward oxidation; therefore, oxide nanoparticles such as ZnO and CuO are most commonly formed during the synthesis process. The properties of these nanoparticles are largely determined by their semiconducting nature and the width of their band gap [4].

In this study, the extract of *Agrimonia eupatoria* L. was used for the green synthesis of all nanoparticles (silver, ZnO, and CuO). *Agrimonia eupatoria* L. (family Rosaceae), also known as agrimony, is used as a raw material for the extraction of biologically active components or for the production of pharmaceuticals in the pharmaceutical industry. This plant exhibits anti-inflammatory, neuroprotective, antidiabetic, hepatoprotective, and anticancer properties, in addition to pronounced antioxidant and antibacterial activities [5].

Accordingly, the aim of this study is a comparative analysis of the green synthesis of silver, zinc oxide, and copper oxide nanoparticles with respect to their formation mechanisms, process kinetics, morphological characteristics, colloidal stability, and potential application fields, based on the authors' experimental results as well as relevant literature data.

2. EXPERIMENTAL

All precursor salts used for the green synthesis—silver nitrate ($AgNO_3$), zinc acetate ($Zn(CH_3COO)_2{\cdot}2\ H_20$), and copper sulfate ($CuSO_4\ {\cdot}5\ H_20$)—were purchased from Sigma-Aldrich. Data were analyzed using OriginPro 2019b – 64 bit, and the synthesis of all nanoparticles (Ag, ZnO, and CuO) was monitored with a PerkinElmer Lambda 365 spectrophotometer in the 200–800 nm wavelength range. All synthesized nanoparticles (Ag, ZnO, and CuO) were characterized by TEM using an FEI Talos F200X microscope and by FTIR spectroscopy with a PerkinElmer Spectrum One FT-IR to analyze their microstructure and functional groups. A magnetic stirrer (MAGE 12/17) and a laboratory

microcentrifuge (Scilogekj DM0412) were used for nanoparticle synthesis and separation.

2.1. Preparation of plant extracts

The previously described method was used for the preparation of the aqueous plant extract [5]. Dried and powdered plant material (60 g) was soaked in 800 mL of distilled water, and the maceration process was repeated three times at room temperature. Fresh solvent was used every 24 h, and the samples were filtered through filter paper. The obtained filtrates were then concentrated using a rotary evaporator at 40 °C. The dry aqueous extract was stored at 4 °C until further use [6].

2.2. Synthesis of silver nanoparticles

Silver nitrate ($AgNO_3$) was used for the synthesis of Ag nanoparticles. The aqueous plant extract was employed as a reducing and stabilizing agent. The procedure was carried out under control using a magnetic stirrer. The optimized synthesis conditions were determined by varying parameters such as the concentration of starting components, pH, and temperature. The formation of AgNPs was monitored by UV–Vis spectrophotometry and visual color change (from light yellow to dark brown) to determine the optimal conditions. Using the aqueous plant extract, the highest yield of AgNPs was obtained after 3 h of reaction, at 25 °C, pH 6, with 5 mM $AgNO_3$ and 1% plant extract. After synthesis, the suspension was centrifuged using a laboratory microcentrifuge for 20 minutes at 4500 rpm. The remaining material was centrifuged once more and then resuspended in demineralized water. The precipitated nanoparticles were dried in a hot air oven at 40 °C and stored at 4 °C. Dana [6,7,8].

2.3. Synthesis of ZnO nanoparticles

The aqueous extract of *Agrimonia eupatoria* L. was used as a reducing and stabilizing agent in the synthesis of ZnO nanoparticles. The extract (20 mL, 1%) was prepared, filtered if necessary, and heated to 50 °C under constant stirring. A solution of zinc acetate (0.55044 g in 30 mL of distilled water, 0.1 M) was added dropwise to the extract under continuous stirring. The pH of the reaction mixture was adjusted to 12–13 using 1 M NaOH. The total reaction volume was 50 mL. After standing overnight, the resulting suspension was centrifuged (4500 rpm, 2 × 20 min), washed several times with distilled water and once with ethanol, and then dried overnight at up to 200 °C to obtain ZnO nanoparticles. The formation of ZnO nanoparticles was confirmed by UV–Vis spectroscopy, with a characteristic absorption peak at 365 nm.

2.4. Synthesis of CuO nanoparticles

The aqueous extract of *Melissa officinalis* was used as a reducing and stabilizing agent in the synthesis of CuO nanoparticles. A 5 mM solution of $CuSO_4 \cdot 5H_2O$ (0.062 g in 50 mL of distilled water) was prepared, and the aqueous plant extract (1 g/L) was obtained by dissolving the appropriate amount of dried plant material in distilled water,

followed by brief ultrasonic treatment and filtration. The extract was added dropwise to the copper(II) sulfate solution under constant stirring, and the pH of the reaction mixture was adjusted to approximately 8 using 0.1 M NaOH. The formation of CuO nanoparticles was monitored by UV–Vis spectroscopy, with a color change from blue through green to brown. For the specific batch, the resulting suspension was centrifuged at 4,000 rpm for 20 minutes twice in distilled water and once in ethanol, and then left to dry at room temperature in the same cuvettes, yielding CuO nanoparticles.

3. RESULTS AND DISCUSSION

In this section, the characterization of the synthesized silver (Ag), zinc oxide (ZnO), and copper oxide (CuO) nanoparticles is presented using three complementary experimental techniques: transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), and UV–Vis spectrophotometry. This approach allows a comprehensive analysis of their morphology, chemical composition, and optical properties.

3.1. Transmission electron microscopy (TEM) characterization of AgNPs, ZnONPs and CuONPs

The TEM analysis reveals distinct differences in morphology and particle size distribution among the synthesized nanoparticles (Fig. 1.).

Silver nanoparticles (AgNPs) exhibit predominantly spherical morphology with relatively uniform size distribution, indicating efficient reduction and stabilization by plant biomolecules, in agreement with previously reported results [5].

In contrast, ZnONPs show more irregular shapes and a broader size distribution, which may be attributed to their formation through intermediate hydroxide species and subsequent conversion to oxide structures.

CuONPs are characterized by pronounced agglomeration and less uniform morphology, with a wider size distribution compared to AgNPs, as also reported in the literature [9]. This behavior can be explained by the higher tendency of copper to undergo oxidation and form oxide phases, as well as weaker stabilization by biomolecules.

Overall, the observed differences confirm that the nature of the metal precursor plays a crucial role in determining nanoparticle morphology, size distribution, and degree of aggregation during green synthesis.

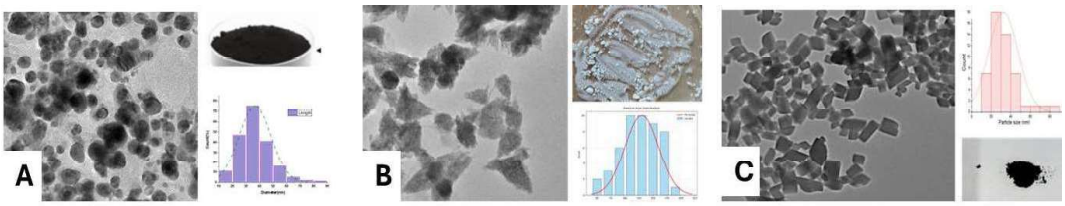

Fig. 1. TEM micrographs and corresponding particle size distribution histograms of green-synthesized nanoparticles: (A) AgNPs obtained using *Agrimonia eupatoria* extract [5], (B) ZnONPs and (C) CuONPs synthesized using plant extract [9].

3.2. FTIR analysis of AgNPs, ZnONPs and CuONPs

FTIR analysis was employed to identify the functional groups of biomolecules involved in the reduction and stabilization of nanoparticles. The spectra of plant extracts exhibit characteristic absorption bands corresponding to O–H, C=O, and C–O vibrations, indicating the presence of phenols, flavonoids, and other bioactive compounds.

In the spectra of AgNPs and ZnONPs, shifts and changes in the intensity of these bands are observed compared to the plant extract, confirming their involvement in the synthesis and stabilization processes. These changes are more pronounced in the case of AgNPs, suggesting stronger interactions between biomolecules and the nanoparticle surface.

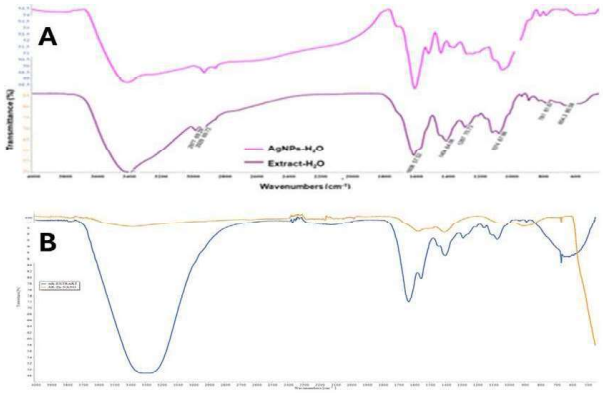

Fig. 2. FTIR spectra of (A) *Agrimonia eupatoria* extracts and corresponding AgNPs [5], and (B) *Agrimonia eupatoria* extracts and corresponding ZnONPs.

3.3. UV-vis analysis of AgNPs, ZnONPs i CuONPs

UV–Vis spectrophotometry was used to monitor the formation and optical properties of the synthesized nanoparticles (Fig. 3). Changes in the absorption spectra, as well as visible color changes of the reaction mixtures, provide important information about the reaction progress and nanoparticle formation.

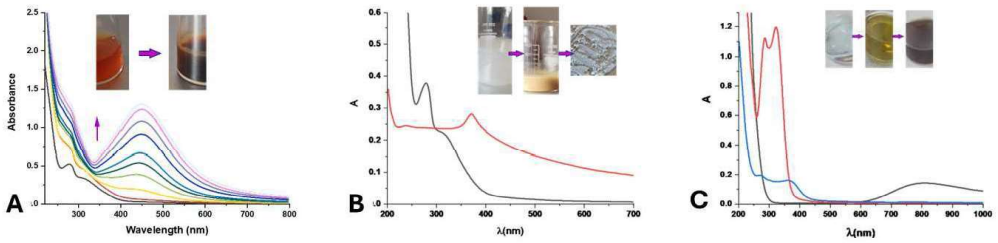

Fig. 3. UV–Vis absorption spectra and corresponding color changes during the green synthesis of (a) AgNPs, (b) ZnONPs, and (c) CuONPs.

In the case of silver nanoparticles, a characteristic surface plasmon resonance (SPR) band is observed in the region of 400–450 nm, whose increasing intensity over time indicates nanoparticle formation and growth, in agreement with previously reported results [5]. A simultaneous color change from light yellow to dark brown further confirms the formation of AgNPs.

For ZnO nanoparticles, the spectrum shows a distinct absorption maximum around 360–370 nm, which is typical for ZnO and associated with its semiconducting properties. The color change is less pronounced compared to silver nanoparticles, which is consistent with the formation mechanism of oxide nanoparticles.

In the case of CuO nanoparticles, no distinct SPR peak is observed; instead, a broad absorption band appears in the UV region, which is characteristic of oxide systems. The color change from blue through green to brown indicates the transformation of Cu(II) ions and the formation of CuO nanoparticles.

These results confirm that UV–Vis spectroscopy is a reliable method for monitoring the green synthesis process and distinguishing between metallic and oxide nanoparticles.

3.4. Comparative analysis of synthesized nanoparticles

A comparative summary of the key characteristics of green-synthesized Ag, ZnO, and CuO nanoparticles is presented in Table 1.

As shown, silver nanoparticles are formed via direct reduction under mild conditions and exhibit faster formation kinetics and higher colloidal stability. In contrast, zinc and copper predominantly form oxide nanoparticles through hydroxide intermediates under alkaline conditions, resulting in moderate formation rates and lower stability. These differences highlight the strong influence of metal nature on the synthesis pathway and the resulting nanoparticle properties.

Table 1. Key differences in green synthesis and properties of Ag, ZnO and CuO nanoparticles

Property	AgNPs	ZnONPs	CuONPs
Dominant phase	Ag^0 (metallic)	ZnO (oxide)	CuO (oxide)
Formation mechanism	Direct	Hydroxide →	Hydroxide →

	reduction	oxide	oxide
Reaction conditions	Mild (pH ~6)	Strongly alkaline (pH 12–13)	Moderately alkaline (pH ~8)
Formation rate	Fast	Moderate	Moderate
UV–Vis feature	SPR (~400–450 nm)	Absorption edge (~365 nm)	Broad absorption
Stability	High	Mode rate	Lower
Key applications	Antimicrobial, catalytic	Photocatalysis, sensors, environmental remediation	Catalysis, antimicrobial, environmental applications

4. CONCLUSION

The obtained results indicate significant differences in the formation mechanisms, morphology, and stability of nanoparticles depending on the nature of the metal precursor. Silver nanoparticles are formed via direct reduction of Ag^+ ions to elemental Ag^0, enabling faster formation kinetics, higher uniformity, and improved colloidal stability. In contrast, zinc and copper tend to form oxide nanoparticles (ZnO and CuO) through hydroxide intermediates, resulting in slower formation rates and greater system heterogeneity.

TEM and FTIR analyses confirm the crucial role of biomolecules from plant extracts in both the reduction and stabilization processes, with more pronounced interactions observed in the case of silver nanoparticles.

Overall, the results demonstrate that the choice of metal precursors strongly influences the green synthesis pathway and the final properties of the obtained nanoparticles, enabling their targeted application in various fields.

In terms of potential applications, silver nanoparticles exhibit pronounced antimicrobial and catalytic activity, whereas ZnO nanoparticles show significant potential in photocatalysis and environmental remediation. CuO nanoparticles, on the other hand, demonstrate promising properties in catalytic processes and environmental applications.

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