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Synthesis of Silver Nanoparticles for Thermal Energy Storage Applications: A Novel Method Using Grewia Asiatica L. Fruit Extract

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Abstract-

Introduction: Today's necessity and enormous applications of nano-particles continuously persuade researchers to find out novel, non-toxic, eco-friendly, and cost-effective synthesis protocols. Metallic Nanoparticles due to their high thermal conductivity are extremely useful to mix with Phase Change materials to enhance the effective thermal conductivity of thermal energy storage for different applications.

Methods: In this article, we report a novel method for the synthesis of silver nanoparticles (Ag NPs) by using the fruit extract of Grewia Asiatica L. These phytosynthesized silver nanoparticles were then characterized and examined using Ultraviolet-Visual Spectroscopy, Fourier Transform Infrared Spectroscopy, and Field Emission Scanning Electron Microscopy techniques for their analysis.

Results: The size of phytosynthesized Ag NPs was found almost spherical in shape and have a diameter of ~ 180 nm. In addition to thermal energy storage applications, synthesized Ag NPs may also find potential applications in the field of drug delivery, bio-imaging, and thermal coolant owing to the known properties of Grewia Asiatica L. Fruit and Ag NPs.

Conclusions: Silver nanoparticles are of much importance in thermal energy storage applications and such cost-effective methods can make the mixing of nanoparticles in PCM commercially viable. Further, these nano-particles may find potential applications in the field of bio-imaging, drug delivery, and biosensors.

Keywords: Silver Nano-particles; Thermal Conductivity; Thermal Energy Storage; Phytosynthesis; Grewia Asiatica L.

1. Introduction

In today's world, every nation wants to be self-reliant in the field of energy generation and most of the generation of energy is required to be from clean energy resources instead of conventional fossil fuel-based resources. The seeming rise in the need for energy is contributing to a situation in which environmental pollution is becoming an increasingly urgent problem. The majority of the world's energy in the modern era comes from non-renewable, conventional & traditional sources. These more conventional methods of energy generation result in the emission of considerable quantities of greenhouse gases, which in turn contribute to both climate change and the pollution of the air. At this moment, every nation on earth is turning to renewable energy sources as a possible solution to the problem of how to fulfill the world's growing energy requirements in the future. On the other hand, one of the most significant drawbacks of renewable energy sources is that they operate only on an intermittent basis. The disparity between the amount of energy that is demanded and the amount that is supplied is putting pressure on the research community to come up with some energy storage devices that will allow for more effective energy utilization.

Globally researchers are looking forward to constructing a system that stores energy and relies on solar thermal energy. Latent heat storage, which differs from sensible heat storage in that it is isothermal and has a high energy storage capacity, has become the focus of a significant amount of attention in recent decades. Thermal energy storage that makes use of nano-enhanced phase change materials is capable of storing a substantial amount of energy and then making that energy available when it is required. When phases change, energy is stored and released. The solid–liquid phase transition is most favored by researchers because it allows for a tremendous quantity of storage of energy during the phase transition, it only causes a tiny volume shift, and it is also advantageous from an economic point of view. In addition to inorganic, organic, and eutectic forms of phase change materials, there are also eutectic phase change materials.

Phase change materials are available for low to high thermal energy storage applications such as photovoltaic/thermal (PV/T), building, air/water heating, drying, space heating/cooling, etc. In these kinds of thermal applications, organic phase change materials, particularly fatty acids, can be of great assistance. The melting and freezing points are the same, they exhibit self-nucleation qualities, and they are generally less corrosive than other elements. Animal fats and vegetable oils are two examples of bio-based materials from which fatty acids can be extracted, waste feedstock as well as Waste cooking oils and fats, can be used to obtain these as well. Due to its renewable raw resources, it has the potential to reduce carbon footprints, environmental impacts, and sustainability.

However, a fundamental issue with organic-based phase change materials is that they have a low heat conductivity, which limits the scope of their applicability in a variety of applications, including those used in the home and industry. Chemical modification and the inclusion of 3D, 2D, 1D, and 0D additives are the two most common and well-known approaches to improving thermal conductivity. The first method is not appropriate due to its lower success rate and more involved processes. The second approach, on the other hand, is more advanced than the first since it lessens the dispersion of phonons and increases the rate at which heat is transmitted thanks to the construction of a thermally conductive chain.

The outstanding contact interaction, suitable homogeneity, high dispersion, and vast specific surface region of 0D nanoparticles all contribute to their widespread application. These OD nanoparticles have strong thermal conductivity; hence a tiny amount can dramatically boost phase transition materials' thermal conductivity. Nanoparticles of metal and metal oxide are employed as 0D additives the vast majority of the time. The most significant advantage gained by the incorporation of nanoparticles is an increase in the rate of heat transfer, which in turn augments the charging and discharging rates, resulting in a more rapid melting and solidification process [1-7].

Nanotechnology is playing a vital role in scientific development nowadays and the astonishing properties of metal nano-particles attract researchers for finding imminent applications for metal nano-particles in the field of drug discovery, disease diagnosis, bio-sensing, etc. [8-12]. Metal nano-particles have various applications such as bio-imaging, drug delivery, antifungal, antimicrobial, and especially energy-related applications [13-17]. This has motivated researchers to focus on the use of Nano metal particles for energy storage devices or to use them to increase the efficiency of well-known energy storage systems [18-22]. Silver nanoparticles in particular are very important because it has a thermal conductivity of 429 W/mK at room temperature and can considerably enhance the thermal conductivity of phase change materials for thermal energy storage applications. Phytosynthesis is a unique method for the easy and cost-effective formation of novel metal nanoparticles [23-28].

Multiple investigators have increased phase transition material thermal conductivity with metal and metal oxide nanoparticles. Palmitic acid (PA)/titanium dioxide nanocomposite was developed by Sharma et al. for use in thermal applications. 0.5%, 1%, 3%, and 5% TiO_2 nanoparticles enhanced palmitic acid (PA) thermal conductivity by 12.7%, 20.6%, 46.6%, and 80%, respectively [29]. Atef et al. numerically analyzed nano-enhanced phase change materials based on paraffin and nanoparticles (Al_2O_3, MgO, SiO_2, and SnO_2) at 1%, 3%, and 5% v/v. Nanoparticles in the base phase change materials increased melting and heat transfer [30]. Barreneche et al. created some nano-enhanced phase change materials from CA and PA.

This formulation employed co-precipitated CuO nanoparticles. 1.0, 1.5, and 3.0% nanoparticles were added. 3 wt% CuO increased PA thermal conductivity by 60% [31]. Saxena et al. developed nano-enhanced phase change materials samples utilizing n-octadecane as the basic phase change materials and TiO_2 as high-conductive nanoparticles from continuous pyrolysis. Advanced moist impregnation disseminated the nanoparticles. Nanoparticles increased nano-enhanced phase change materials' thermal conductivity by 37% [32].

Kumar et al. tested paraffin with SiO_2 nanoparticles. The authors chose 0.5, 1.0, and 2.0 mass% nanoparticles. These formulations increased thermal conductivity by 12.78%, 22.78%, and 33.34% [33]. Martin et al. tested CA-MA eutectic composition and SiO_2 nanoparticles. The authors mixed 0.5, 1.0, and 1.5 wt% nanoparticles with phase change materials to make this formula. Thermal conductivity increased 142% in the CA-MA eutectic composition with 1.5 wt% SiO_2 [34]. Table 1 demonstrates how 0D nanoparticles improved thermal conductivity.

Table 1 Some of the recent works on thermal conductivity enhancement through the use of 0D nanoparticles

Year, Author, Method	PCM/0D nanoparticle system	Result
2017, Sharma et al. [27], Experimental	PA/TiO_2	The thermal conductivity was enhanced by 80%
2019, Barreneche et al. [29], Experimental	CA, PA/ CuO	60% increment in the thermal conductivity
2019, Kumar et al. [31], Experimental	Paraffin/SiO_2	The thermal conductivity was increased by 33.34%
2019, Martin et al. [32], Experimental	CA-MA/SiO_2	The thermal conductivity was increased up to 142% by the addition of 1.5 wt% SiO_2 nanoparticles
2020, Saxena et al. [30], Experimental	n-octadecane /TiO_2	The thermal conductivity was increased by 37%
2021, Atef et al. [28], Numerical	Paraffin /$Al2O_3$, SiO_2, MgO, SnO_2	The heat transfer rate and melting rate significantly improved with the addition of nanoparticles
2022, Anand et al. [21], Experimental	CA/α-MnO_2	The developed phase change materials had excellent thermal energy storage capability lying between 145 and 164 kJ/ kg with excellent thermal reliability.

2. Objectives

The use of natural extracts in the creation of metal nanoparticles has been explored but is still limited. Maryam et. al. has phytosynthesized silver nanoparticles using green tea leaves. They demonstrated that silver nanoparticles distributed in deionized water had an improvement in thermal conductivity of around 45% over the base fluid. This suggests that silver/water nanofluid has a lot of promise for cooling applications [35].

Zhannat et. al. synthesized silver nanoparticles using commercially available green tea leaves and demonstrated that phytosynthesized silver nanoparticles increased the ablated area by 102% and reached a greater maximum temperature during RFA than clean tissue [36]. Rajeshwari et al formulated a Coccina grandis leaf extract that was used in the bio-reductive production of nanosized Ag particles, demonstrating the utilization of a biological reducing agent that is natural, renewable, and inexpensive to create metal nanostructures [37].

They discovered that the silver nanoparticles possess photocatalytic activity and that these particles may be utilized in water purification systems. Javed et al presented a green synthesis method for silver nanoparticles synthesized by the Astragalus tribuloides Delile root extract. The synthesized silver nanoparticles exhibited an LSPR absorption band at 430 nm. They showed that their green synthesized silver nanoparticles have remarkably better antioxidant, antibacterial, and anti-inflammatory properties than the extract itself [38].

Grewia Asiatica L. is a fruit plant commonly known as Phalsa. Many studies show that Phalsa can be a reducing agent for synthesizing metal nanoparticles [23-27]. It has strong antimicrobial, antidiabetic, anti-inflammatory, antioxidant, and anticancer properties. Given these properties, we have used Grewia Asiatica L. fruit extract to reduce silver nitrate solution for the synthesis of silver nano-particle.

The Grewia Asiatica L. fruit extract also acted as a capping agent for synthesized silver nanoparticles. To the best of our knowledge, we have developed a unique protocol for the phytosynthesis of silver nanoparticles by using Grewia Asiatica L. fruit extract as a reducing agent.

3. Materials & Methods

3.1 Materials & Collection of Plant Material (Fruit)

Silver Nitrate (AgNo3) having 99.9% purity om Merck was as a precursor solution. Fresh Grewia Asiatica L. fruits, commonly known as Phalsa, were collected in the month of May-June 2022.

3.2 Formulation of Fresh Grewia Asiatica L. Fruit Extract & Aqueous Solution of Silver Salt

To remove dirt and dust particles, fresh Grewia Asiatica L. fruits were given thorough rinsing and cleaning with running tap water. The first step, rinsing, gets rid of any other polluted organic contents. The next step, washing five times in double-distilled water, eliminates any remaining residue. The cleaned fruits were shaded and air-dried at room temperature for three hours. After piling the fruits (about 10 grams) into a beaker that contained 200 millilitres of double-distilled water, the mixture was brought to a boil for 18 minutes. The extract was allowed to cool down before being filtered using Sartorius filter discs (Grade 292) a total of four times. The extract was brought to its final volume of 185 ml, and then it was kept at a temperature of 4 degrees Celsius until it was used again. It took 0.3397 gm of 99.99% pure Silver Nitrate (AgNO3) salt (Merck) dissolved in 200 ml of deionized water to make an aqueous solution of silver ions that had a concentration of 10 mM.

3.3 Green Synthesis of Silver Nano Particles

As a precursor solution, we combined two hundred millilitres of the aqueous solution containing 10 millimoles of AgNO3 with ten millilitres of Grewia Asiatica L. fruit extract. The hue of the combined substance eventually turned out to be beige. The reaction was allowed to proceed for another 15 minutes, but there was no noticeable change in the colour of the mixed solution. After that, the solution mixture was stirred on a magnetic hot plate using a cum stirrer at 45 degrees Celsius.

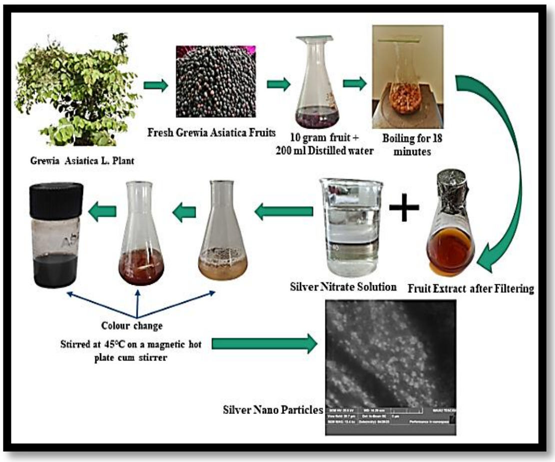

Figure 1 Schematic diagram for the phytosynthesis of Silver Nanoparticles

Within 45 minutes, the colour of the solution in the mixture changed from beige to golden yellow, and then from golden yellow to a dark brownish tint. This colour change indicated the creation of Ag NPs, which is the reduction of Silver ions (Ag+) to Ag-NPs (Ag0). To guarantee that the reaction was carried out to its full potential, the solution was agitated at the same temperature for a further half an hour, or until there was no discernible shift in colour. The artificially produced Ag-NPs were stable for several months and exhibited good dispersion. Figure 1 shows a simplified depiction of the phytosynthesis process.

3.4 Characterization

UV-Vis, FTIR, and FE-SEM were used to examine phytosynthesized silver nanoparticles. UV-Vis Spectrophotometer (Evolution 201) at Babasaheb Bhimrao Ambedkar University, Lucknow, evaluated the absorption spectra of Grewia Asiatica L. fruit extract and phytosynthesized silver nanoparticles. FTIR Spectra were recorded to determine the organic functional groups which may be present in Grewia Asiatica L. fruit extract. working as capping agents on the surface of phytosynthesized Ag NPs. FTIR spectra of phytosynthesized Ag NPs were recorded at Babasaheb Bhimrao Ambedkar University, Lucknow in the transmittance mode (at a resolution of 1 cm-1. Sample) scanned between 4000 cm^{-1} to 667 cm^{-1}. With the help of a Field-Emission Scanning Electron Microscope (TESCAN MAIA3 with EDX) at Central Advanced Facilities for Material Characterization (CAFMC) of Veer Bahadur Singh Purvanchal University, Jaunpur, we have studied the morphology and particle size of synthesized silver nanoparticles. FE-SEM samples were created by spin coating a clean glass substrate with a few drops of diluted phytosynthesized silver NP solution and drying under IR light.

4. Results

Figure 2 (a, b) displays the UV-Vis spectra of the fruit extract of Grewia Asiatica L. as well as the silver nanoparticles that have been phytosynthesized. In the spectrum of fruit extract, an absorption peak can be seen in the ultraviolet area at around 311 nanometers. One possible explanation for this is that the extract contains a wide variety of different functional groups. Figure 2(b) presents the UV-Vis Spectra of Silver Nanoparticles that were Produced via Phytosynthesis. The spectra showed that there was a prominent absorption peak at a wavelength of around 418 nm, which is a peak that is unique to silver nanoparticles and is caused by surface plasmon resonance (SPR). This was made abundantly clear by the transformation of the combination from a translucent to a dark brown tint. The free electrons in silver nanoparticles get excited, causing a color shift that can be attributed to surface plasmon resonance (SPR). The appearance of a plasmon peak is determined by the nature of the synthesized nanoparticles, namely their shape, and size. Therefore, we can also validate the creation of silver nanoparticles by the use of ocular observation.

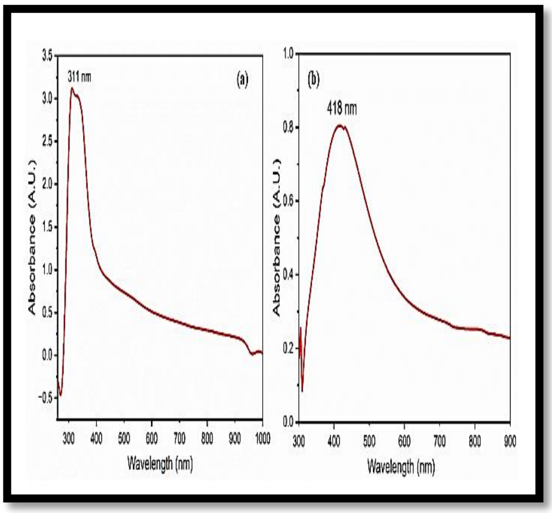

Figure 2: (a) UV Spectra of Grewia Asiatica L. Fruit Extract and (b) UV Spectra of phytosynthesized Silver Nanoparticles

FTIR spectra of phytosynthesized silver nanoparticles are shown in Figure 3. Here spectra exhibit intense peaks at 3347 cm^{-1} (intermolecular hydrogen bonding O-H stretching) and another peak at 2123 cm^{-1} (C≡C stretching).

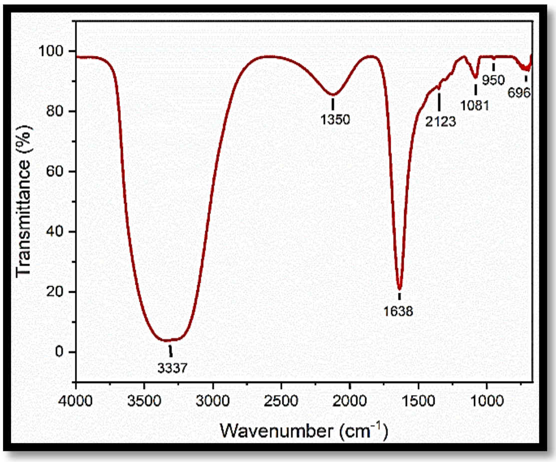

Figure 3 FTIR Spectra of phytosynthesized silver nanoparticles using Grewia Asiatica L. Fruit extract

The peaks at 1638 cm^{-1} and 1350 cm^{-1} may be attributed to the C=O stretching of tertiary amide and C-N stretching of primary aromatic amines respectively. [39]

Figure. 4 exhibits the XRD spectra of synthesized silver nanoparticles. The XRD pattern exhibited sharp reflections which are characteristics of the Face Centred Cubic (FCC) structure of silver. Five peaks have been observed at 2θ values of 38.10, 44.20, 64.49, 77.30, and 81.63 correspondingly indexed as (111), (200), (220), (311), and (222) planes of FCC structure of silver (JCPDS File No. 04-0783). Therefore, it was found that the synthesized silver nanoparticles using Plumeria pudica leaf extract are crystalline in nature. The lattice parameter 'a' was calculated from the most intense peak (111) and was found to be 3.9168 Å which is close to the standard value of 4.0865 Å (JCPDS File No. 04-0783).

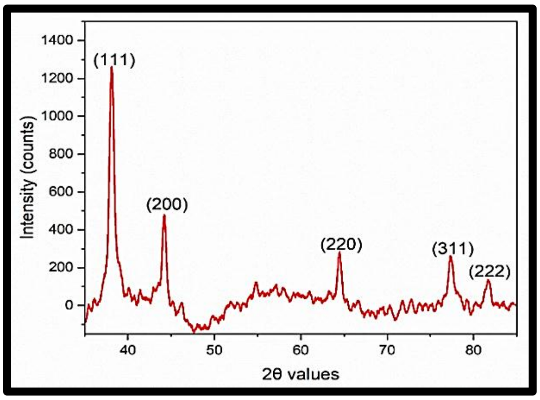

Figure 4 XRD Spectra of phytosynthesized silver nanoparticles using Grewia Asiatica L. Fruit extract

Figure. 5 shows the Scanning Electron Microscopic image of Grewia Asiatica L. fruit extract-synthesized silver nanoparticles.

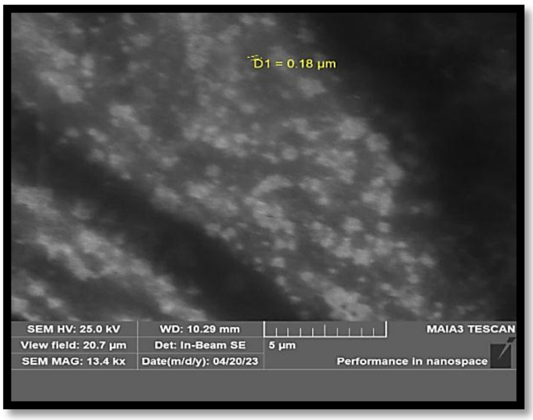

Figure 5 FE-SEM images of synthesized silver nanoparticles

FE-SEM scans showed that synthesized silver nanoparticles were approximately spherical, smooth, and evenly dispersed. The estimated average particle size is ~180 nm.

In Figure 5, we have selected a region for elemental mapping with the help of EDX. The EDX of the nanoparticle dispersion confirmed the presence of elemental silver nanoparticles, uniformly grown and uniformly distributed. The distribution of particle size in EDX data is shown in Figure 6 (a, b).

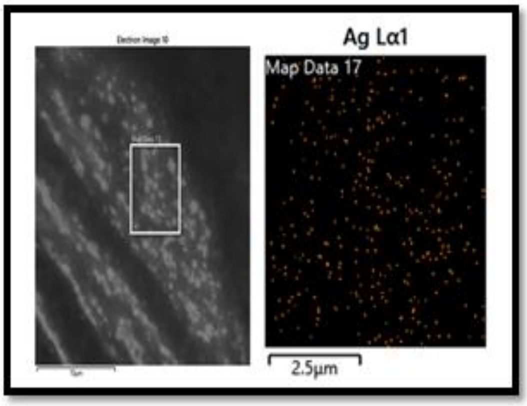

Figure: 6 (a,b): Distribution of particle size in EDX data

5. Discussion

In the present work, we have successfully synthesized silver nanoparticles using Grewia Asiatica L. berry juice as a reducing agent to make it a very simple, cost-effective, and less potentially hazardous process. UV-Vis Spectroscopy, Field

Emission-Scanning Electron Microscopy (FE-SEM), and FTIR methods were used to study and characterize phytosynthesized silver nanoparticles. Nearly round silver nanoparticles were made in a controlled environment. They had a smooth surface and were spread out evenly. FE-SEM images were used to measure the size of phytosynthesized Ag NPs and found that their average size was approximately 180 nm. Due to the high thermal conductivity, silver nanoparticles are of much importance in thermal energy storage applications and such cost-effective methods can make the mixing of nanoparticles in PCM commercially viable. Further, these nano-particles may find potential applications in the field of bio-imaging, drug delivery, and biosensors. Synthesized silver nanoparticles may also be studied for coolant applications.

Author Contributions: Conceptualization, S.K.S. and R.K.G.; methodology, S.K.S., and R.K.G.; software, S.K.S., and R.K.G.; validation, S.K.S., S.S., and A.P.T.; formal analysis, S.K.S., A.K., and R.K.G.; investigation, S.K.S.; resources, S.K.S. and A.P.T.; data curation, S.K.S., and S.P.S.; writing—original draft preparation, S.K.S.; writing—review and editing, S.K.S., A.K., S.S., R.K.G., A.M., D.C., A.S. and A.S.; visualization, S.K.S., A.S., and A.S.; supervision, A.K., R.K.G.; funding acquisition, S.K.S. All authors have read and agreed to the published version of the manuscript.

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