OPTICAL STUDY OF NANOPARTICLES

PROJECT REPORT

Submitted by

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Register No : AB19PHY025

Under the guidance

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Submitted to the

Mahatma Gandhi University, Kottayam

In partial fulfillment of the requirements for the award of

BACHELOR DEGREE OF SCIENCE IN PHYSICS

ST.TERESA'S COLLEGE (AUTONOMOUS)

ST.TERESA'S COLLEGE (AUTONOMOUS)

ERNAKULAM

CERTIFICATE

This is to certify that the project titled "Optical study of Copper Nanoparticles" was completed successfully by Ms.Aishwarya Sunil K, a candidate for the B.Sc Physics programme at St. Teresas College, roll no: AB19PHY025, under the supervision of Dr. Mary Vinaya of the Physics Department, in partial fulfillment of the requirements for course completion during the academic year 2021-2022. Her efforts and endeavors culminated in this report. The subject has been approached with sincerity and discipline.

I certify that this project report is genuine and original work that has not been submitted to any other university for the award of a degree or diploma, and that it has been completed in accordance with the institution's guidelines.

Supervising Guide

Susan

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Department of Physics * St. Teresa's College (Autonomous) * Ernakulam

PLACE : ERNAKULAM

DATE : 10.05.2022

ST.TERESA'S COLLEGE (AUTONOMOUS)

ERNAKULAM-KOCHI-11
(AFFILIATED TO MG UNIVERSITY, KOTTAYAM)

B.Sc PHYSICS

PROJECT REPORT

Name : AISHWARYA SUNIL K

Register No : AB19PHY025

Year of work : 2021-22

This is to certify that this project work entitled **'OPTICAL STUDY OF COPPER NANOPARTICLES'** is an authentic work done by AISHWARYA SUNIL K.

Staff member in-charge

Dr. Mary Vinaya

Head of the Department

Dr.Priya Parvati Ameena Jose

Submitted for the university examination held at St. Teresa's College, Ernakulam.

DATE :

EXAMINERS

DECLARATION

I hereby declare that the project work titled "Optical Study of Copper Nanoparticles" submitted by Aishwarya Sunil K to St.Terasa's College in partial fulfillment of the requirement for the award of the degree of Bachelor of science in Physics is a bona fide record of the project work completed under the supervision of Dr. Mary Vinaya, faculty member of the Physics Department. Moreover, I declare that the work described in this project has not been submitted to, or will not be submitted to, this institution or any other institute or university for the award of any degree or diploma, in whole or in part.

Aishwarya Sunil K

Place: ERNAKULAM

Date: 10.05.2022

AISHWARYA SUNIL K

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OPTICAL STUDY OF COPPER NANOPARTICLES

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ABSTRACT

This project, titled "Optical Study of Copper Nanoparticles," at Deva Matha College in Kurvilangad, Kottayam, focuses on the complete observation of copper nanoparticles as they transition from bulk to nano size. The project's primary objective is to investigate the optical behavior and processes that underpin it. In addition, at the end of the project, some important ideas and facts that were learned during the project are also included.

Material science and technological innovation require the development of more efficient methods for the synthesis of copper nanoparticles. This study synthesized copper nanoparticles by reducing copper sulfate with sodium borohydride in water without the use of inert gas. Ascorbic acid (natural vitamin C) has been used as a protective agent during the synthesis process and storage to prevent the oxidation of nascent copper nanoparticles. The inclusion of polyethylene glycol (PEG) functioned as a size controller and capping agent. The spectrophotometer is used to look at the size, structure, and composition of the Cu nanoparticles that were made.

The surface plasmon resonance phenomenon is known to be controllable during synthesis by varying the reaction time, pH, and copper sulfate/surfactant ratio. The peak of the surface plasmon resonance shifts from 561 to 572 nm, while the apparent color changes from red to black, which is partly due to the particle size change. When the solution is oxidized, its color changes from red to violet to blue.

INTRODUCTION

Nanotechnology is the commercial adaptation of matter on an atomic, molecular, and supra molecular scale. It is naturally broad in scope, embracing fields as widely divergent as surface science, organic chemistry, molecular biology, semiconductor physics, energy storage, and engineering, micro fabrication, and molecular engineering. The related advancements are equally diverse, ranging from modifications of conventional device physics to completely new approaches regarding the molecular self-assembly, from developing new nanoscale materials to direct control of matter at the atomic level.

Given that an atom's typical diameter is between 0.15 and 0.6nm, a considerable share of the material in a nanoparticle is included within a few atomic diameters of its surface. As a consequence, the surface layer's properties may take precedence over the bulk material's. This effect is enhanced when nanoparticles are dispersed in a medium with such a different composition, as the interactions between the composite material and the nanoparticles at their interface become significant. Although a bulk material's physical properties should stay constant irrespective of its size, this is frequently not the situation at the nanometre scale.

Owing to the combination of free electrons, bulk metals are quite often lustrous, malleable, and tractable, as well as extremely conductive. When metals are reduced to the micron scale, their physical and chemical properties remain unaffected, but their surface-to-volume ratio unquestionably rises. However, a further slight decrease to the nanoscale (100nm) results in substantial changes in properties; for example, surface plasmon resonances are observed when light interacts with the nanoparticles (NPs). Between 100 and 3nm in size, metal NPs' optical parameters are affected by surface plasmon resonances, including both absorption and scattering of light, resulting in the formation of NP hues.

The surface plasmon resonance (SPR) phenomenon is the consequence of the resonance effect due to the interactions of the conduction electrons of metal

nanoparticles with incident photons. The size and symmetry of metal nanoparticles, as well as the nature and structure of the dispersion medium, all influence the interaction. Quantum confinement has been observed in semiconductor particles, surface plasmon resonance has been observed in certain metal particles, and magnetic samples have exhibited super paramagnetism.

The notable and occasionally exceptional nanomaterials are not solely due to the material's surface properties predominating over its bulk properties. Nanoparticles exhibit a wide range of unique properties in comparison to the bulk material. For example, the bending of bulk copper atoms and clusters on a 50nm scale. Copper nanoparticles relatively smaller than 50 nm in diameter are taken into account as super hard materials, lacking the malleability and ductility of bulk copper. Not all property transitions are advantageous. Due to the confinement of electrons and the subsequent quantum effects, nanoparticles exhibit a variety of unexpected visible properties. Gold nanoparticles, for example, typically appear dark red to black in solution due to their extremely high surface area to volume ratio.

There are extensive research in the synthesis and characterization of metallic copper and copper oxide [I] nanocrystals, not only to expand synthetic capabilities, but also to distinguish their electrical, catalytic, sensing, and surface properties. Copper nanoparticles are promising materials with superior properties and a cheaper compared to other metallic nanomaterials such as gold and silver. The purpose of this study is to evaluate the synthesis of copper nanoparticles and their optical properties as they shift from bulk to nanoscale. Due to Cu's high oxidation potential, it seems the synthesis of Cu nanoparticles is quite complicated. It is highly flammable, and the oxide phases are more thermodynamically stable. Due to their high oxidation rate, Cu NPs often seem to have major limitations. Oxidation can be overlooked if synthesis is conducted out in the involvement of CO and hydrogen. On the other hand, maintaining these gases is very stressful, and their use is widely ignored.

Pure copper NPs are extremely rare, are synthesized unless the entire analysis was performed in an inert atmosphere. Nevertheless, the stabilization of NPs in the presence of air is unknown. Cu nanomaterials are typically shielded with a capping agent to prevent oxidation and to control crystal development by reducing the crystal's surface energies. However, capping agents and stabilizers can reduce but not stop oxidation due to their molecular action.

Laser ablation, thermal decomposition, chemical reduction, and polyol synthesis are all constantly being implemented techniques for preparing NPs. Chemical reduction is given preference because it is simple, cost-effective, and effective, and it permits for good control of size and size dispersion by adjusting control variables. The rate of growth of the NPs is dependent on a number of variables, including metal ion concentration, reductant type, pH, and temperature. Additionally, time is a key factor in the development and manufacturing of NP. The abundance of nuclei at any point caused a reduction in the size of NPs, as smaller metal nuclei grow and at once incorporate metal ions.

Chemical reduction processes, in general, facilitate the reduction of metal salts in a wide variety of solvents and reducing agents. Cu Nanoparticles are synthesized in this study without the use of an inert gas besides the chemical reduction of Cu+2 in an aqueous medium. By using ascorbic acid, copper ions were reduced to metallic copper nanoparticles. Due to ascorbic acid's low reducing ability, it was preferred as a reducing agent. As a result, the driving force of the reaction is minimal, and the Cu NPs need not aggregate properly.

Cu NPs, on the other hand, are prone to oxidation since copper oxides are more thermodynamically stable than pure copper once prepared at appropriate atmospheric pressures without inert gas protection. Correspondingly, it has been highlighted that Copper NPs aggregate vigorously in the lack of suitable protection. Starch was used to limit nanoparticles from expanding and to protect them from oxidation and aggregation. The overall aim of this study was to synthesize copper

NPs via chemical reduction and to interpret them using a UV visible spectrophotometer.

AIM AND OBJECTIVES

- To synthesize the copper nanoparticle by chemical reduction method
- To study the optical behaviour of copper nanoparticle when transition from bulk to nanoscale.
- To estimate the resonance peak at certain wavelengths

REVIEW OF LITERATURE

Sulekh Chandra et al. (2011) has conducted a study on the Synthesis and characterization of copper nanoparticles by reducing agent. Cu nanoparticles were synthesized by solution reduction process successfully. The influence of parameters on the size of Cu nanoparticles was studied and the referential process parameters were obtained.

Ayesha Khan and Audil Rashid (2016), has studied on the development of improved methods for the synthesis of copper nanoparticles is of high priority for the advancement of material science and technology.

Thi My Dung Dang and Thi Tuyet Thu Le (2011), has studied on the copper nanoparticles which were synthesized through the chemical reduction of copper sulfate with sodium borohydride in water without inert gas protection.

Umme Thahira Khatoon; et al. (2013) has conducted a study on how nano particles are characterized and assessed by UV-Vis spectrometer, SEM-EDS and particle size analysis. SEM-EDS and particle size analysis contributed to the analysis of size, shape and composition of copper nanoparticles.

METHODOLOGY

EXPERIMENTAL MATERIALS

1) Material

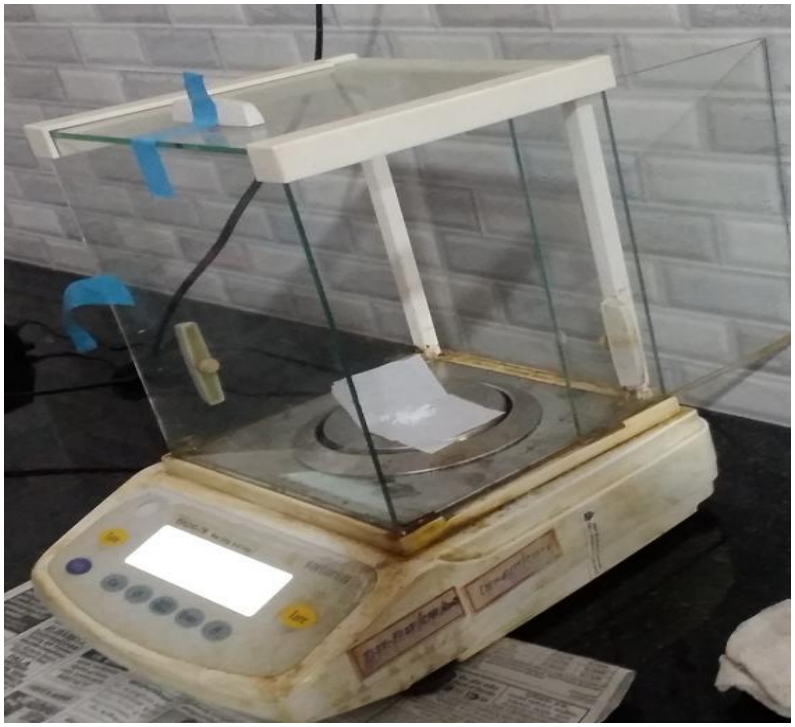
All the chemical compounds were analytical grade and were used directly from the supplier without undergoing extensive purification. In ultra pure water, a 98 % pure copper sulphate pentahydrate salt $CuSO_4.5H_2O$ (0.01248g) was dissolved. Poly ethylene glycol (PEG) (0.6g) was used as a capping agent to prevent aggregation and ascorbic acid (0.01761g) as an antioxidant for colloidal copper. Sodium hydroxide (NaOH) (0.02g) was used to adjust the pH and accelerate the reduction reaction in water. Sodium borohydride was the primary reducing agent ($NaBH_4$) (0.01891g).

2) Synthesis of copper nanoparticles

To begin with, all the test tubes used to store the experiment's five key components are washed with soap and then rinsed with distilled water obtained from the distillation unit, which condenses water twice and

Transferring to the test tube

Heating various components on a hot plate



Test readings

collects the distilled water for use. Second, all components are dissolved completely in distilled water. The following step involves drying all of the test tubes on a hot plate and allowing them to cool. Then, using a digital weighing machine, weigh all the components. Then, using distilled water, completely dissolve all the components.

Copper nanoparticles are prepared in four steps. The first step is to dissolve copper(II) sulphate pentahydrate salt,$CuSO_4.5H_2O$(0.0127g) in distilled water to obtain a pale blue solution that is placed on a magnetic stirrer and vigorously stirred. Following that, while vigorously stirring,

poly ethylene glycol (0.602g) which was dissolved in water and was initially prepared, is added to the aqueous solution containing the copper salt. The solution was converted from blue to white during this step. In the third step, ascorbic acid (0.01761g) was added to the synthesis solution, followed by sodium hydroxide (0.0184g). A change in colour from white to yellow occurred during the aqueous phase.

Subsequently, a solution of $NaBH_4$ (0.01691g) in distilled water was prepared and rapidly added to the solution. In the aqueous phase, a colour change from yellow to black/red is occurred instantaneously. This dark colour indicated the start of the reduction reaction. The reaction required BH_4- as an electron donor. To let the reaction to happen, the mixture was rapidly stirred for about 10 minutes in the air.

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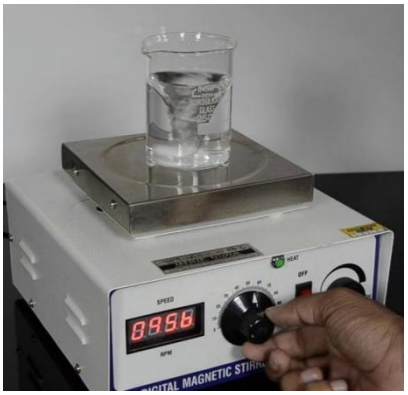
3) <u>Characterization</u>

UV-visible absorption spectroscopy was used to examine synthesized samples in the wavelength range of 190-1100m using a double beam spectrophotometer.

UV-visible spectrophotometry is a term that refers to absorption and reflectance spectroscopy in the visible and adjacent visible regions of the electromagnetic spectrum.

4) <u>Instruments used for the synthesis</u>

A) <u>Magnetic stirrer/mixer:</u> is a laboratory instrument that uses a rotating magnetic field to affect a stir bar dipped in a liquid to spin rapidly, thereby stirring it. A rotating magnet or a series stationary electromagnets placed beneath the vessel containing the liquid can generate the



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rotating field. It is used in chemistry and biology where other stirring methods, such as motorized stirrers and stirring rods, are impractical.

B) <u>Hot plate</u>:Although the hot plate can be used independently, it is commonly used to replace one of the burners on an oven range or kitchen stove. Hot plates are typically used in laboratories to heat glassware or their contents. Certain hot plates also include a magnetic stirrer, which automatically stirs the heated liquid.

C) <u>UV-visible spectrophotometer:</u> compares the intensity of light after it passes through a sample to the intensity of light before it passes through the sample.

The basic components are a light source, a sample holder, a diffraction grating or a prism to separate the various wavelengths of light, and a detector. Single-beam or double-beam spectrophotometers are available. A cuvette containing only a solvent must be measured first in a single beam instrument. The light source is a xenon flash lamp that covers the UV, visible, and near-infrared wavelengths between 190 and 1100nm.

The lamp flashes are concentrated on a fibreglass, which initiates the light beam onto a cuvette filled with the sample solution. The beam passes through the sample, with the sample components trapping specific wavelengths. After the cuvette, the residual light is collected and focused into a spectrograph via a glass fibre. The spectrograph is made up of a grating that splits light into different wavelengths and a CCD sensor stores the information.

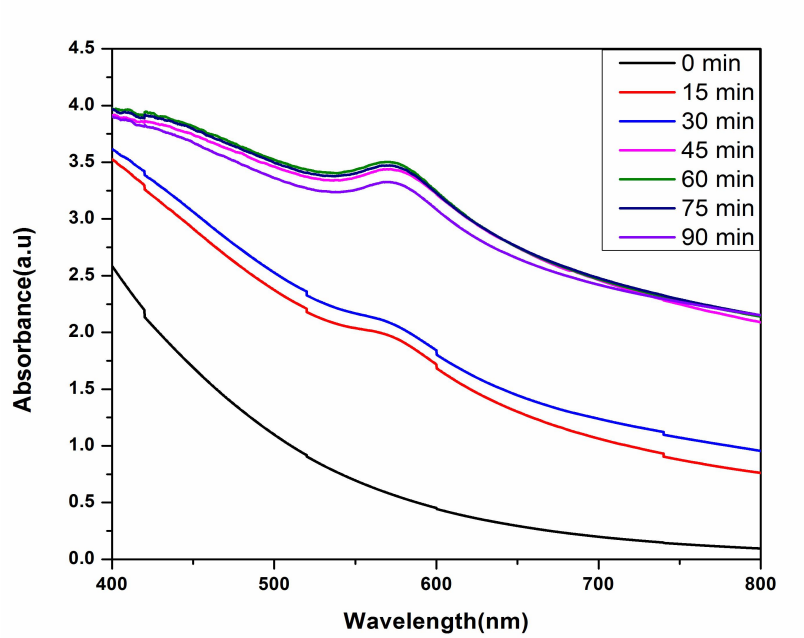
UV/Vis spectrophotometry is most commonly used with liquid samples, but it can also be used to evaluate the absorbance of gases and even solids. Typically, samples are placed in a clear cell called a cuvette. Cuvettes are usually rectangular, with an internal width of approximately 1 cm.

RESULTS AND DISCUSSION

Due to the collective oscillation of conduction electrons at the surface of small metal nanoparticles, visible electromagnetic waves are absorbed. The surface plasmon resonance effect is the scientific term for this phenomenon. The reason for the importance of this effect is that it could be used as a tracer for the presence of metal nanoparticles using a simple UV-visible spectrometer. For particles that are smaller than 20 nm in diameter (for gold), the size dependence of the plasmon resonance is a complicated phenomenon. One highly promising property is that resonance's bandwidth rises as the particle size is reduced due to enhanced electron scattering at the surface. The resonance shift and bandwidth variation are thus satisfying parameters for describing metal nanoparticles.

Numerous samples were taken from the synthesis solution over time: one immediately after pouring the ascorbic acid solution, another instantly before pouring the $NaBH_4$ solution, and then 5, and 10 minutes later, as depicted in the figure.Plasmon absorbance (562nm) can only be seen when the solution is red, about 10 minutes after the strong reducing agent was added. This is even though the absorption of the strong reducing agent had already increased by 5 minutes, which suggests that there are small clusters or nanoparticles in the solution.

The yellow solution lacked plasmon resonance prior to the addition of $NaBH_4$. When $NaBH_4$ was added, a rapid increase in absorbance at low wavelengths occurred, suggesting the onset of particle formation (light red). When the solution turned red, the Cu nanoparticles' plasmon resonance was visible at 562nm. The reaction was allowed to take place in the air. After the synthesis was complete, the solution was kept at room temperature, and the oxidation process was substantively monitored regularly by observing the solution's colour change. After a few hours, the solution that was initially black returns to a pale blue colour due to the oxidation process.



5) <u>Effect of reaction time</u>

Time is an essential aspect,in the synthesis of metal nanoparticle. Generally speaking, having a greater number of nuclei accessible at any given time results in a reduction in the size of the nanoparticle, because smaller metal nuclei grow and consume metal ions simultaneously.

To investigate the impact of reaction time on the formation of the product and its stability, were prepared by using the procedure described, with the only variable being the period of stirring with ascorbic acid prior to pouring the sodium borohydride.

It can be observed that, a reaction time of up to 60 minutes with ascorbic acid results in well-defined nanoparticles with a declining mean particle size with time. It demonstrates a mechanism of homogenization that results in an increase in the number of nuclei over time. For 90 minutes, despite a strong absorption in an even lower wavelength range, no clear resonance was noticeable. This might reveal a particle with a much smaller size.

Currently, very little is known about the mechanism underlying this phenomenon. Ascorbic acid is well known for its ability to scavenge free radicals, acting as an

antioxidant during the development of copper nuclei. This creates a favourable environment for successive rapid reduction with NaBH4 and culmination with copper nanoparticles. The characteristic red colour of well-defined copper nanoparticles is primarily obtained at 60 minutes and can be noticeably darker at times. Furthermore, it appears as though these particles have the greatest potential for stability in the availability of an ambient atmosphere. Oxidation, particle re-dissolution, or a mix of both could be the reason why the colour changes.

6) Effect of pH

According to the findings conducted in, pH in aqueous media has an effect on the rate of the copper reduction reaction. Moreover, the probable kinetic enhancement could lead to a decline in crystallite size as a consequence of the greater nucleation rate. Increased ascorbic acid concentrations led to a drop in solution pH, which was restored to a range of 6 to 14 by providing 0.02 g of NaOH solution drop wise.

The ultraviolet-visible absorption spectra of five colloidal solutions were generated under normally identical conditions besides a pH range of 6 to 14. All spectra, excluding 6, could be used to extract the plasmon absorption of copper colloids in each solution. At such a low pH, this most likely shows the presence of extremely small particles. For pH values ranging from 8 to 12, the plasmon resonance is readily apparent. The peak is still recognizable at pH 14, but it is considerably weaker. 566, 575, 573 and 554nm are the measured values for pH values between 8 and 14.

The size of the copper particles could be to blame for the big drop in intensity around the peak value at pH 10. The precise location of the plasmon absorption depends on a lot of things, including the particle size, shape, solvent type, and capping agent. In this case, the pH change could have caused some changes in the arrangement of the capping molecules around the copper particles.

8)Effects of [PEG] to [Cu^{2+}] molar ratio

Due to its reliability, low cost, and non-toxicity, PEG is most often used as a surfactant for the preparation of nanomaterials and as a stabilizer for metal

colloids.Previously, it was shown that the size and shape of nanomaterials are highly directly proportional to the concentration of PEG in the solution.

Once nuclei have been formed, they aggregate to lower the total surface energy. Aggregation, which can occur as a result of attractive Van der Waals forces between crystals, should be inhibited or limited in order to constrain the final particle size to the nanometric scale. Yet another method for preventing nanoparticle aggregation is to use materials that cause steric repulsion between individual nanoparticles. PEG is a growth and aggregation inhibitor of this type. It is dependent on the molar ratio (PEG [mol] /Cu2+ [mol]), as demonstrated by our investigation.

The size and shape dispersion of the colloidal particles are dependent on the quantity and concentration of each element used in the formation. The observed strong aggregation could be due to colloidal copper oxidation in water, which improves electrostatic attraction between particles. With greater PEG concentration, colloidal copper's size distribution tends to narrow, while the mean diameter drops. Likewise, it appears that aggregation has been reduced. Overall, it demonstrates that the capping molecule concentration has a significant impact on limiting the mean diameter and particle size distribution of our copper nanoparticles.

We notice maxima at a longer wavelength for a molar ratio of 6:1 with large particles. For greater molar ratios, nevertheless, the plasmon resonance seems to be stabilized between 561 and 564nm. At this stage, it is difficult to determine how much of the variation is due to particle size and how much is linked due to extrinsic phenomena, such as the configuration of the capping layer around the smaller particles.

CONCLUSION

Utilizing chemical reduction method in water, copper nanoparticles were successfully synthesized in this analysis. The appearance of the surface plasmon resonance on these colloids indicated the existence of unoxidized metal nanoparticles. The reaction time, pH of the solution, and relative ratio of PEG to copper sulphate were considered to enhance particle size and oxidation resistance during the synthesis. With increasing reducing agent concentration levels in capping molecules, the size decreases. Copper nanoparticles have a broader range of research implementations, and we can continue working on developing a copper nanoparticle that acts as an anti-biotic, anti-microbial, and anti-fungal agent when incorporated into plastics, coatings, and textiles in the long term.

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