Green Synthesis and Characterisation of Copper Oxide Nanoparticles Using *psidium guajava* Leaf Extract

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Submitted by

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CANDIDATE'S DECLARATION

I, Ammu Varughese, Roll No: 2K18/PTE/01student of M Tech Polymer Technology, hereby declare that the project Dissertation titled "Green Synthesis and Characterisation of Copper Oxide Nanoparticles Using *psidium guajav*a Leaf Extract" which is submitted by me to the Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology is original and not copied from any source without proper citation. This work has not previously formed the basis for the award of any Degree, Diploma Associateship, Fellowship or other similar title or recognition.

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CERTIFICATE

I hereby certify that the Project Dissertation titled "Green Synthesis and Characterisation of Copper Oxide Nanoparticles Using *psidium guajava* Leaf Extract" which is submitted by Ammu Varughese, Roll No: 2K18/PTE/01, Department of Applied Chemistry, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology is a record of the project work carried out by the student under our joint supervision. To the best of our knowledge this work has not been submitted in part or full for any Degree or Diploma to this University or elsewhere.

Place : Delhi	(Dr POONAM)	(Dr RAMINDER KAUR)
Date : 26/08/2020	SUPERVISOR	SUPERVISOR

ABSTRACT

Green synthesis of nanoparticles has gained enormous attention in today's world due to ongoing demand to develop sustainable, safe, economical and eco-friendly process for synthesizing a wide variety of materials including metal/metal oxides nanoparticles, hybrid and bioinspired materials. In the current study, green synthesis of copper oxide (CuO) nanoparticles (NPs) has been carried out by utilising extract of *psidium guajava* leaf as capping agent and cupric acetate as metal precursor. The biosynthesized nanoparticles were characterized utilizing wide assortment of methodologies for example powder X-beam diffraction (PXRD), FTIR, TGA and HRTEM. The PXRD result confirms the synthesis of CuO NPs in pure phase having monoclinic symmetry. The average particle size using PXRD was found out to be ~33nm.

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LIST OF ABBREVIATIONS

atm	Atmosphere
CO_2	Carbon Dioxide
Conc. H_2SO_4	Concentrated Sulfuric acid
CuO	Copper Oxide
DI water	De-ionized water
DNA	Deoxyribonucleic acid
DTU	Delhi Technological University
eV	electron volt
$FeCl_3$	Iron (III) Chloride
FTIR	Fourier Transform Infrared Spectroscopy
g	Grams
hrs	Hours
IR	Infrared
kV	Kilovolt
M	Molar
ml	Millilitre
N_2	Nitrogen
NaOH	Sodium Hydroxide
nm	Nanometre
NPs	Nanoparticles
PC	Personal Computers
pH	Potential of Hydrogen
rpm	Revolutions Per Minute
SLS	Sodium Lauryl Sulfate
SRL	Sisco Research Laboratories Pvt. Ltd.
TEM	Transmission Electron Microscopy
TGA	Thermo-Gravimetric Analysis
XRD	X-Ray Diffraction
Wt%	Mass fraction of a substance

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Over the last few decades, the synthesis of nanomaterials (such as metal/metal oxide NPs, quantum dots (QDs), carbon nanotubes (CNTs), graphene, etc.), having dimension within the range of 10-100 nm, have become an extensive area of research due to their prospective applications in extensive area of science and technology [1-5]. Though bulk synthesis of nanoparticles can be carried out rapidly using conventional methods i.e. physical and chemical methods, they require use of hazardous chemicals. Keeping this in mind, the use of green synthesis approach, that makes use of mild reaction conditions and non-hazardous precursors, have been emphasized for promoting environmental sustainability [6]. The biological systems that are actively used in the green synthesis of NPs include plants and their derivatives (phytosynthesis), microorganisms like fungi, bacteria, algae and yeast [7-8]. Among all the available methods, phytosynthesis is the ideal methodology for metal oxide NPs synthesis, inferable from the several benefits associated with it [9].

Phytosynthesis of metal oxide NPs establishes a strong bond between nanosynthesis and natural plant material [10]. Plants comprises of large number of bioactive compounds, and most of the plants have demonstrated record for their antibacterial properties. The phytosynthesis of the metal oxide NPs can be achieved by simply mixing metal solution with plant extract. Subsequently, NPs will be produced because of the metal ion reduction.

Among a variety of transition metal oxides, CuO have gained considerable attention attributed to its excellent electrical, physical, magnetic and optical properties. Hence it is selected for the present study. In the current study, *Psidium guajava* leaves have been utilized for carrying out the phytosynthesis of CuO NPs, due to the existence of high amount of phytochemicals in it [11-12].

1.1. NANOPARTICLES

Metal & metal oxide nanoparticles correspond to the particulate diffusion of solid units with at least one dimension in the nanometre scale (1-100nm) [13]. The incredibly little size and enormous surface-to-volume proportion are the notable highlights of nanoparticles, which influences its physical and chemical properties [14]. The utilization of nanoparticles incorporates antimicrobial action, bio detecting sensors, electrometers, memory plans, optics, PC transistors and remote electronic rationale.

NPs consists of 3 layers which has been schematically represented in Figure 1.1. The following are the 3 layers of NPs [15]:

- The **core** that can be synthesized by utilizing various methodologies, precursors and reaction conditions.
- A **shell** that might be added based on the desired properties of the final products.
- A **surface** that can be easily functionalised.

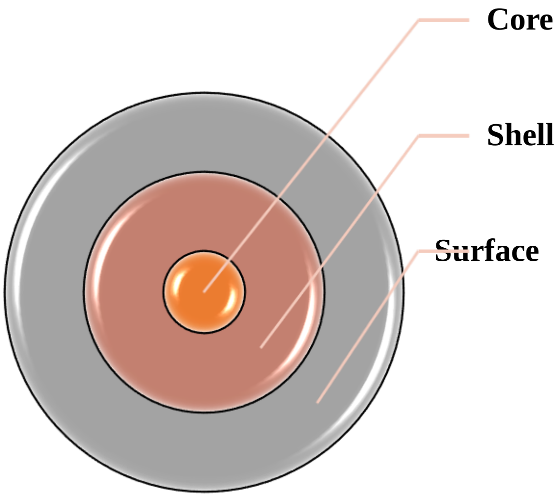

Figure 1.1: Schematic representation of various layers of NPs

Metal oxide NPs have been synthesised by either a bottom-up approach or top-down approach**.** A schematic representation of both top-down and bottom-up methodologies are illustrated in Figure 1.2. In bottom-up approach, the nanoparticles are formed primarily by the gathering of atoms, molecules or clusters, and then subsequently, assemble them to ultimate material by utilising biological or chemical methodologies; while in top-down approach, the bulk material is reduced into a nanosized material, by using various physical and chemical methodologies [16]. Figure: 1.3 illustrates the various nanoparticle synthesis methodologies.

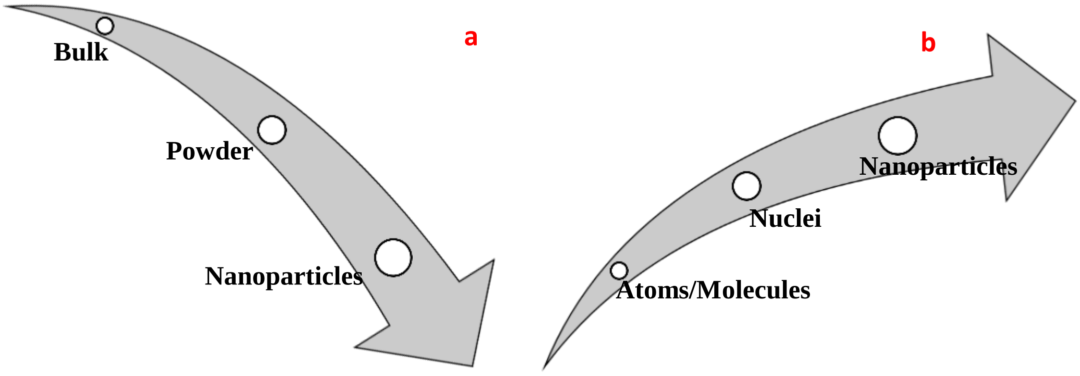

Figure 1.2: Schematic representation of nanoparticle synthesis a) top-down, b) bottom-up

But, both the bottom-up and top-down approaches have certain shortcomings that are tabulated in Table-1 [17]. These shortcomings had been subdued by adopting the Green Chemistry approaches for the metallic NPs synthesis.

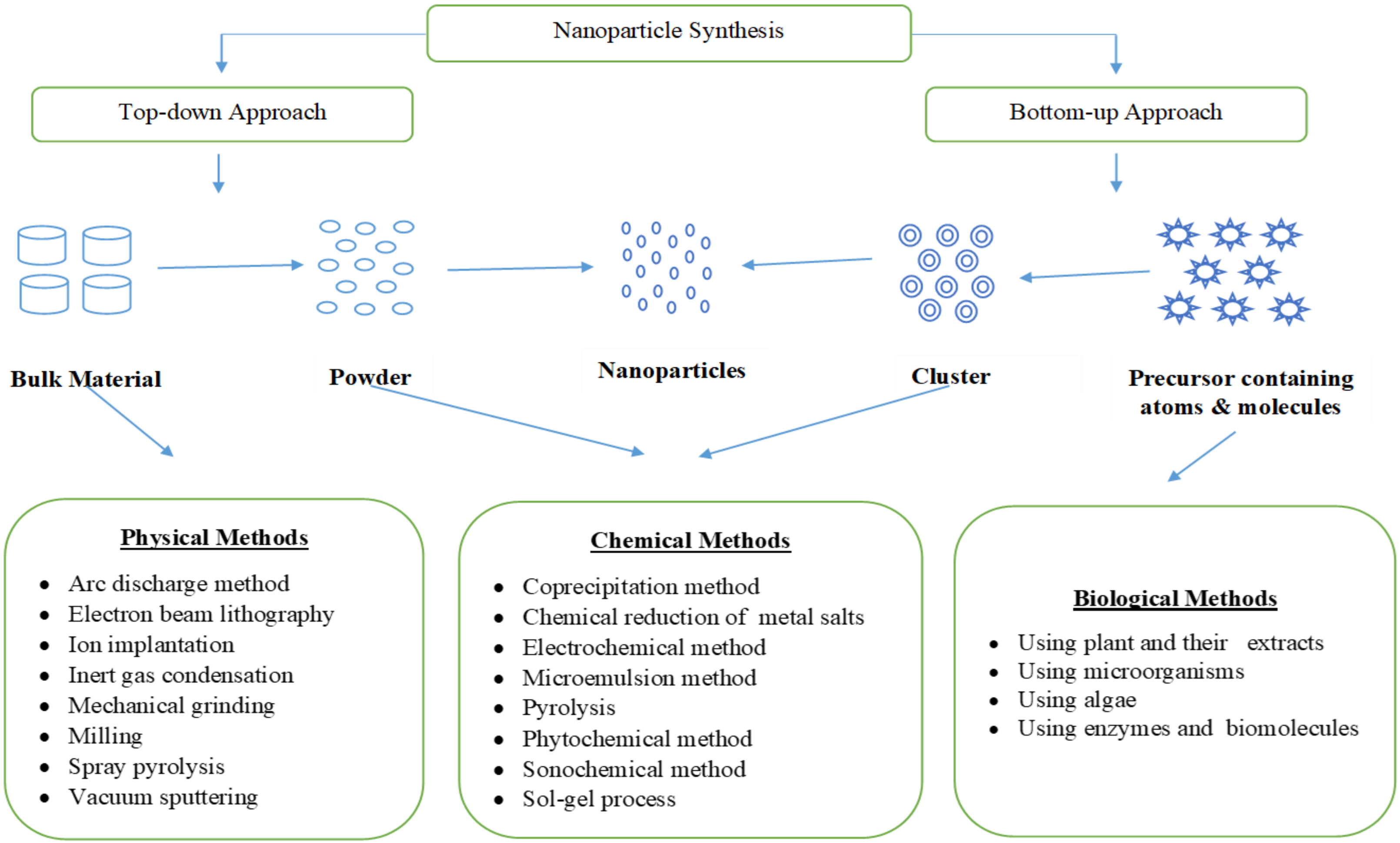

Figure 1.3: Various Nanoparticle Synthesis Methods

Table 1: Major Drawbacks of Bottom-up and Top-down Approaches for the Synthesis of Nano-particles

Bottom-up Approach	• Utilises toxic chemicals, different synthetic capping agents, stabilizing agents and non-polar organic solvents for the synthesis of metallic NPs. • Not environmentally benign.
Top-down Approach	• Synthesised metallic NPs has surface imperfections, which affects the physical & surface chemical properties. • During the synthesis procedures, a massive amount of energy is required to maintain high-temperature and high pressure conditions. • Outwardly controlled tools are utilized for shaping, milling and cutting the materials into preferred shape and order.

1.2. GREEN CHEMISTRY

Over the past decade, the researchers have been shown augmented attention on ‘Green Chemistry’ [14-17]. Green chemistry is a part of chemistry that aims to exploit efficiency and diminish lethal effects on human health and environment by adopting following 12 fundamental principles [18]:

- Atom Economy
- Catalysis

- Design for Degradation
- Design for Energy Efficiency
- Design Safer Chemicals
- Inherently Safer Chemistry for Accident Prevention
- Less Hazardous Chemical Synthesis
- Prevention
- Reduce Derivatives
- Real-time Analysis for Pollution Prevention
- Safer Solvents & Auxiliaries
- Use of Renewable Feedstocks

1.3. GREEN SYNTHESIS

It is the biological synthesis method used to synthesise the metal and metal oxide NPs by adopting the green chemistry approach, as shown in Figure 1.4. Green synthesis is clean, reliable, biocompatible & eco-friendly method to synthesise NPs. Based on green chemistry perspective, the minimum steps involved in the preparation of NPs are [19]:

- Choice of solvent medium (water, supercritical CO_2, etc) used for the synthesis
- Choice of a non-toxic stabilising agent (starch, citric acid, etc)
- Choice of an eco-friendly reducing agent (sugar, β-D-glucose, etc)

The major attractive features of green synthesis methodology are [20]:

- Uses benign reducing and capping agents
- Yields little or non-hazardous by-products
- Offers better control of dispersivity, size and shape of metal nanoparticles
- Eliminates the need for purification of synthesised NPs

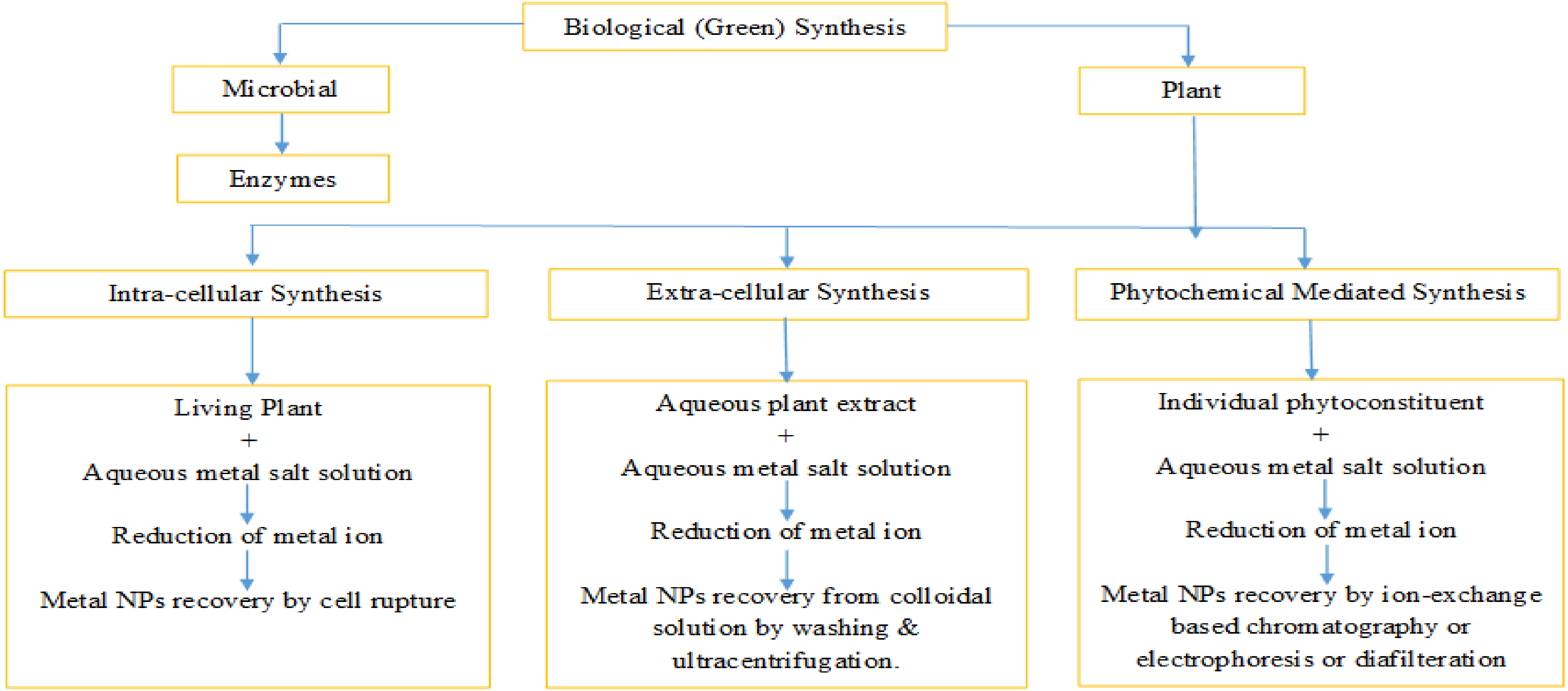

Figure 1.4: Green Synthesis Methodology

Green synthesis is mainly classified as microbial synthesis (where bacteria, fungi, yeast, viruses and actinomycetes are used for the synthesis of NPs), and phytosynthesis (where parts of the whole plant are utilised for the synthesis of NPs). The advantages of phytosynthesis over microbial synthesis are [21]:

- Do not involve complex and multistep processes like microbial isolation, culturing, etc.
- Very rapid process
- Cost-effective process
- A faster rate of synthesis
- More stable products

1.3.1. Phytosynthesis

Plants with rich genetic variability possess a variety of biomolecules, which helps in the reduction of metal ions into NPs in a one step process. Further, plant metabolites (phenolic compounds, sterols, etc.) acts as an excellent reducing agent. In comparison with the whole plant tissue as an extract, the plant extract materials shown better control over the results. A general mechanism of photosynthesis of metal oxide NPs are illustrated as Figure 1.5.

The different plant contains a different concentration of biomolecules, which affects the morphology of the synthesised NPs [22]. The major factors which affect the phytosynthesis are:

- the concentration of the extract
- the reaction temperature
- the pH.

Phytosynthesis of nanoparticles involves 3 phases [23]:

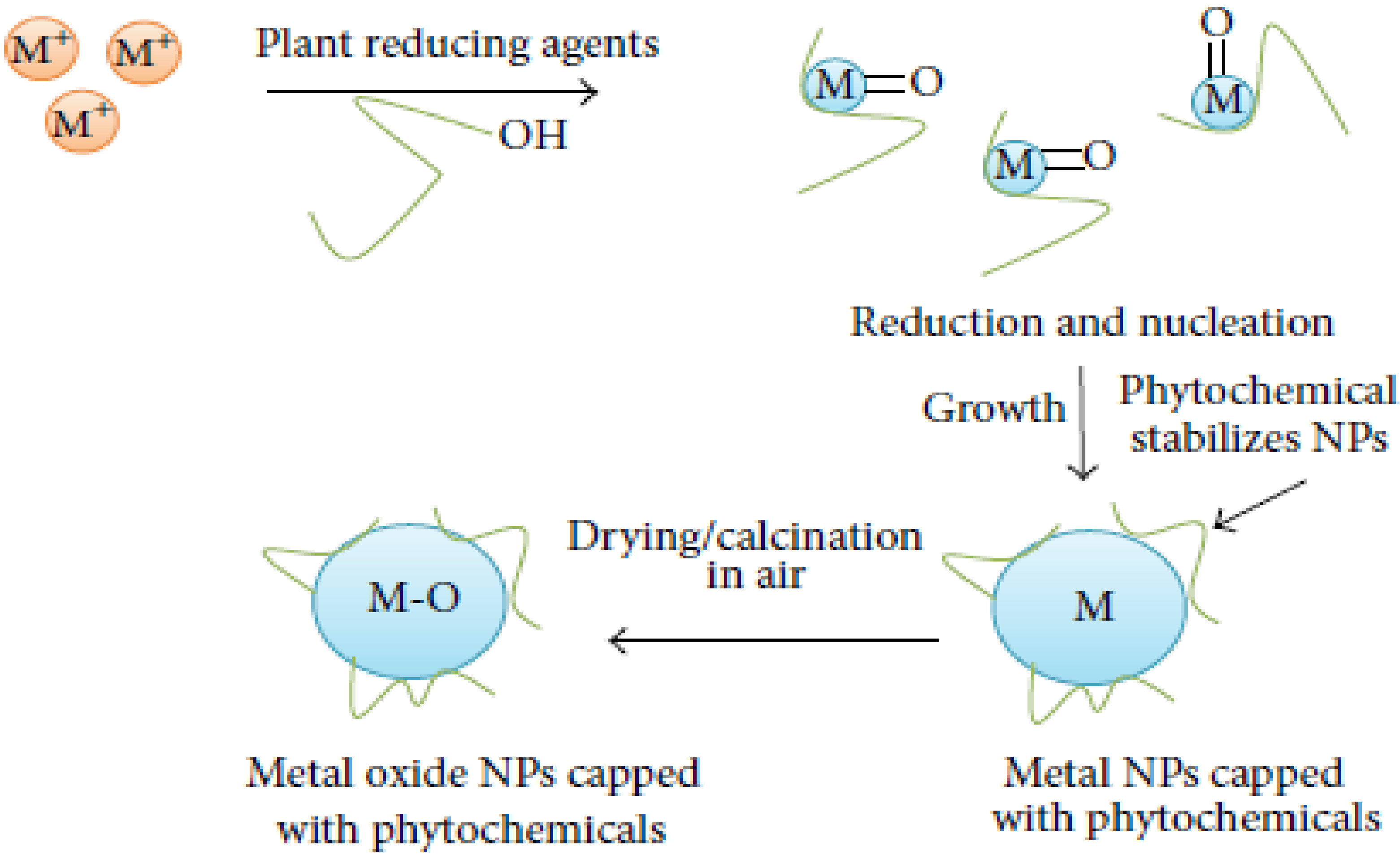

Figure 1.5: Mechanism of Phytosynthesis of Metal Oxide Nanoparticles

a) **Activation phase:** Metal ions got reduced and the new structure were formed by nucleation.

b) **Growth phase:** Further formation of new structure and metal ions reduction with rise in thermal stability.

c) **Termination phase:** Formation of the final shape of NPs.

1.3.1.1. *Psidium guajava* (Myrtaceae)

Psidium guajava (Figure 1.6) is a medicinal plant commonly known as guava and has a place in Myrtle family as Myrtaceae [24]. *Psidium guajava* is found in various areas of the tropical and subtropical zones and has been reported to have antidiarrheal [25], antispasmodic [26], antioxidant [27], anti-allergy [28], antibacterial [29], anti-cough [30], anti-inflammatory [31], and anticancer activities [32].

Figure 1.6: *Psidium guajava* (Guava) Leaf

1.4. COPPER OXIDE NANOPARTICLES

CuO is a potential p-type semiconductor with a narrow band gap of 1.2 eV [33]. CuO is widely used in catalysis [34-37], electrochemistry [38-39], solar energy conversion [40], sensors/biosensors [41-43], energy storage [44], biocidal agents [45-46] etc. In the nanometre scale, it holds great electrochemical action, gives the high surface area, shows appropriate redox potential and amazing stability in solutions [47]. The physical and chemical properties of CuO nanostructures were strongly dependent on their morphology and crystallinity [48]. Researches has reported that the CuO NPs has excellent antimicrobial activity than other metal and metal oxide NPs [49-50]. The synthesis of CuO NPs utilizing various parts of plants has discussed in Table 2. For the CuO NPs synthesis most of the researchers has utilised copper sulfate pentahydrate ($CuSO_4.5H_2O$), copper acetate (monohydrate) ($(CH_3COO)_2Cu\cdot H_2O$) and copper chloride di-hydrate ($CuCl_2.\ 2H_2O$) as metal precursors.

Figure 1.7: Copper Oxide Nanoparticles

Table 2: Plants used for the phytosynthesis of CuO NPs

Plant	Part of plant used	Size (nm)	Shape	Reference
Aloe barbadensis Mill	Leaf	15-30	Spherical	51
Aloe vera	Leaf	500	Spherical	52
Anthemis nobilis	Flower	36-61	Spherical	53
Calotropis gigantean	Leaf	20-30	Spherical	54

Camellia japonica	Leaf	15-25	Spherical	55
Carica papaya	Leaf	140	Rod	56
Gloriosa superba	Leaf	5-10	Spherical	57
Rauvolfia serpentine	Leaf	10-20	Sponge	58
Rheum palmatum	Root	10-20	Spherical	59
Tamarix gallica	Leaf	~60	Spherical	60
Theobroma cacao	Seed	40	Spherical	61
Thymus vulgaris	Leaf	<30	Spherical	62

1.5 OBJECTICVE OF THE RESEARCH WORK

During this M.Tech programme, the aim of my research was the "**Green Synthesis and Characterisation of Copper Oxide Nanoparticles Using *psidium guajava* Leaf Extract**". For the environment friendly and green synthesis of copper oxide nano-particles, the study was conducted to accomplish the following sub-objectives:

- To develop a green methodology for the synthesis of CuO NPs.
- To identify the leaf for the phytosynthesis of CuO NPs.
- To identify the phytochemicals participated in the synthesis process.
- To comprehend the role of phytochemicals in the biochemical reduction & stabilisation of CuO NPs.
- To develop a CuO NPs with minimal particle size, crystallinity & high thermal stability.

CHAPTER 2

MATERIALS AND METHODS

2.1. MATERIALS USED

Cupric acetate monohydrate (Merck, ≥ 98.0 %), Sodium lauryl sulfate (Sisco Research Laboratories ≥ 98.0 %) and fresh *psidium guajava* leaves collected from the Delhi Technological University (DTU) campus.

2.2. METHODOLOGY

2.2.1. Extraction of *psidium guajava* Leaf Extract:

Fresh *psidium guajava* leaves collected from the DTU campus were first cut into small pieces. These leaves were then washed thoroughly using double distilled water to eliminate debris. These cleaned leaves were then dried in the presence of sunlight for 5 days. After that the dried leaves were ground into a fine powder using pestle mortar & stored in dry place.

Psidium guajava leaf extract was prepared by heating the solution of *psidium guajava* leaf powder and distilled water (1:10 wt. %) at 100°C for 30 minutes in Erlenmeyer flask till the colour of solution changes to dark brown (indicating phytochemical extraction). The dark brown solution is sifted through a filter paper (Whatman No.1), after cooling it down in to room temperature. The obtained infusion was used for the phytosynthesis of CuO NPs. The steps for the preparation of *psidium guajava* Leaf Extract are presented in Figure 2.1.

Figure 2.1: steps for preparation of leaf extract a) *psidium guajava* leaves, b) *psidium guajava* leaves dried under sunlight for 5 days, c) *psidium guajava* leaf extract

2.1.2. Phytosynthesis of CuO NPs:

To phytosynthesise CuO NPs 1M of cupric acetate monohydrate was dissolved in 10 ml of distilled water at room temperature using magnetic stirrer (250 rpm). After that, 30 ml of *psidium guajava* leaf extract was added into the cupric acetate solution drop wise, with continuous stirring. Later the solution was kept on magnetic stirrer (250 rpm) for 24 hrs at 60 °C leading to the formation of gel that was dried in hot air oven at temperature of 60 °C. The green precipitate thus obtained was calcined at temperatures of 400 °C for 6 hrs in the muffle furnace, forming black CuO nanoparticles.

2.2.3. Phytosynthesis of CuO NPs in presence of sodium lauryl sulfate

To phytosynthesise CuO NPs 1M of cupric acetate monohydrate was dissolved in 10 ml of distilled water at room temperature using magnetic stirrer (250 rpm) and sodium lauryl sulfate (SLS; 4 g) was added into p*sidium guajava* leaf extract (30 ml). After that, SLS - leaf extract solution was drop-wisely added into the cupric acetate solution, while continuous stirring. Later the solution was kept on magnetic stirrer (250 rpm) for 24 hrs at 60 °C leading to the formation of gel that was dried in hot air oven at temperature of 60 °C. The green precipitate thus obtained was calcined at temperatures of 400 °C for 6 hrs in the muffle furnace, forming black CuO nanoparticles.

2.3. CHARACTERISATION TECHNIQUES

PXRD pattern of phytosynthesized sample was recorded using high-resolution Bruker D8 Advanced X Ray diffractometer over the range of $2\theta = 10\text{-}80°$ by employing Cu-Kα radiation ($\lambda = 1.5418$ Å). Perkin-Elmer TGA4000 was used for carrying out the Thermo-gravimetric analysis (TGA) in the temperature range of 50-800°C at a heating rate of 10 °C/min under flowing nitrogen (50 mL/min). FTIR spectra of the phytosynthesized sample was recorded using a Perkin-Elmer 200i FTIR spectrometer employing KBr disks. TEM of the sample was recorded using Jeol/JEM 2100 HRTEM operated at an acceleration voltage of 200KV.

2.3.1. Transmission Electron Microscopy [TEM]

As it is difficult to identify the nanostructures using conventional light spectroscopy, TEM offers as a powerful alternative to identify the features of materials whose dimension is ≤100nm in size. Figure 2.2 demonstrates a typical TEM. The TEM results depend upon 4 variables:

- specimen thickness
- resolving power of the microscope
- sample stability and composition
- energy spread of the electron beam

TEM provides morphologic, compositional and crystallographic information on samples utilizing energetic electrons.

Figure 2.2: Transmission Electron Microscopy (Jeol/JEM 2100)

2.3.2. Powder X-Ray Diffraction Analysis [PXRD]

X-rays are high-energy electromagnetic waves ($\lambda = 10^{-3} - 10^{1}$ nm). Figure 2.3 demonstrates a typical X-ray diffractometer. X-rays are generally generated by using synchrotron radiation sources, sealed tubes or rotating anodes. XRD analysis is based on the capability of crystals to diffract X-rays in a typical fashion permitting a specific study of the structure of crystalline phases. The resultant diffraction pattern contains several micro & macrostructural features of samples, such as:

- **Peak Intensity**: provides details of crystal structure (atomic positions, temperature factor or occupancy), texture, and helps in quantitative phase analysis.
- **Peak Position**: provides lattice parameters, space group, chemical composition, macro-stresses and qualitative phase analysis.
- **Peak Shape**: helps in sample broadening contributions (micro-strains and crystallite size).

Figure 2.3: X-Ray Diffractometer (Bruker D8 Advanced)

The average crystalline size of the crystals formed was calculated by the Debye-Scherrer equation, i.e.,

$$D = \frac{k\lambda}{\beta \mathrm{Cos}\theta}$$

Where D: Average crystallite size (nm)

k: 0.89

λ: x-ray wavelength (0.15418 nm)

β: Full width at half maximum of the intense peak (radians)

θ: Bragg's angle (radians)

The characteristic spacing between the crystal planes of the sample was calculated by Bragg's law, i.e.,

$$n\lambda = 2d\mathrm{Sin}\theta$$

Where d: lattice spacing between the crystal planes of the sample (nm)

n: order of reflection

λ: x-ray wavelength (0.15418 nm)

θ: Bragg's angle (radians)

2.3.3. Fourier Transform Infrared Spectroscopy [FTIR]

Figure 2.4: FTIR spectrophotometer (Perkin-Elmer 200i)

FTIR is a non-destructive technique for the analysis of materials. Figure 2.4 demonstrates a typical FTIR spectrophotometer. It gives explicit data about the vibrations and rotation of the molecular structures and chemical bonding in this manner making it useful for the analysis of organic materials and certain inorganic materials. No two compounds produce a similar IR spectrum in light of the fact that each and every material is made up of a unique combination of atoms. Hence, an IR spectrum can be used as a fingerprint for identification. IR spectroscopy can be used for the qualitative analysis of different kinds of material. The IR region is usually categorized into three smaller regions i.e., near - IR (400 - 10 cm^{-1}), mid - IR (4000 - 400 cm^{-1}) & far - IR (14000 – 4000 cm^{-1}).

2.3.4. Thermo-Gravimetric Analysis [TGA]

TGA constantly monitors the weight of a test specimen during isothermal or dynamic temperature scans over the range from 30 °C to 1000 °C in air, nitrogen, oxygen, or speciality atmosphere. Figure 2.4 demonstrates a typical TGA instrument. TGA measures the material's composition and thermal stability. TGA offers a quantitative measurement of weight or mass change of materials with respect to the time and temperature. This change is allied with the thermal degradation (decomposition, dehydration & oxidation) and transition of a test specimen. Because of the distinctive order from physicochemical reactions of a test specimen arising at a particular temperature range and heating rate, the corresponding thermo-gravimetric curves are given for specific materials and chemical compounds. These distinctive features are correlated to the molecular structure of the sample.

Figure 2.5: Thermo-Gravimetric Analyser **(Perkin-Elmer TGA4000)**

CHAPTER 3

RESULTS AND DISCUSSION

3.1. QUALITATIVE PHYTOCHEMICAL SCREENING

The chemicals that present naturally in plants are known as phytochemicals. Due to their countless medicinal uses, these phytochemicals are more popular, nowadays [63]. Qualitative phytochemical tests help to understand the role of chemical compounds and their usefulness in medicinal activities [64]. Different phytochemicals had different reducing mechanism. Hence, phytochemical screening is inevitable to understand the mechanism of nanoparticle synthesis. The freshly prepared *psidium guajava* leaf extract was undergone phytochemical screening using simple chemical tests to identify the presence of active phytoconstituent i.e. polyphenol, alkanoids, flavonoids, saponins, tannins, etc. in the sample (Table 3).

Table 3: Phytochemical screening of *Psidium guajava* leaf extract

Component	**Procedure**	**Result**
Flavonoids	A portion of aqueous extract was mixed to 5ml of aq. ammonia solution, followed by the addition of Conc. H_2SO_4 [65].	Absence of yellow colour indicating the absence of flavonoids.
Gum and Mucilages	10ml of extract was mixed to 25ml of ethanol with constant stirring [66].	No white or cloudy precipitate indicating the absence of gum and mucilages

Phenolic Compounds	A few drops of 5% neutral $FeCl_3$ was mixed to 5ml of extract [67].	The presence of phenolic compounds was confirmed by the emergence of dark green colour.
Terpenoids	To a solution of 5ml of leaf extract and 2ml of chloroform, a 2ml of Conc. H_2SO_4 was carefully added along the sides of the test tube [68].	No reddish brown ring were formed at the interface, indicates the absence of terpenoids.
Saponins	A 1ml aliquot of the leaf extract was mixed to 20ml of distilled water and was then shaken vigorously for 15 minutes in a vortex [67].	Persistent foaming indicates the presence of saponins.
Glycosides	Few drops of aqueous NaOH was added into a 1ml of leaf extract [65].	The absence of yellow color formation indicates the absence of glycosides.
Steroids	5ml of extract was added to a 2ml of chloroform and Conc. H_2SO_4 solution and was shaken thoroughly [69].	No reddish brown colour were formed at the lower chloroform layer, indicates the absence of steroids.

Phytoconstituents exhibits an important part in the phytosynthesis of metal oxide NPs and can acts as both effective reducing as well as stabilizing agents. Therefore, in order to understand the mechanism of nanoparticles synthesis screening of phytochemical is inevitable. Phytochemical analysis exhibit positive result for phenolic & saponins content in the leaf extract inferring its significant properties and shows negative results for flavonoids, gum & mucilages, terpenoids, glycosides and steroids.

3.2. STRUCTURAL ANALYSIS OF CUO NPS

The PXRD pattern of phytosynthesized CuO NPs utilizing *psidium guajava* leaf extract in absence and in presence of SLS is presented in Figure 3.1. The presence of PXRD peaks at 2θ value of 32.53°, 35.63°, 38.74°, 48.83°, 53.56°, 58.36°, 61.51°, 65.85°, 66.42°, 68.11°, 72.34° and 75.33° confirms the formation of CuO having monoclinic symmetry with lattice constant *a* = 4.683, *b* = 3.428, *c* = 5.129 Å (JCPDS 80-1268) [70]. Since no additional peak due to the presence of any other phase was observed in absence of SLS this suggests the generation of CuO NPs in pure phase. The average crystallite size of phytosynthesised CuO NPs was calculated as ~33 nm.

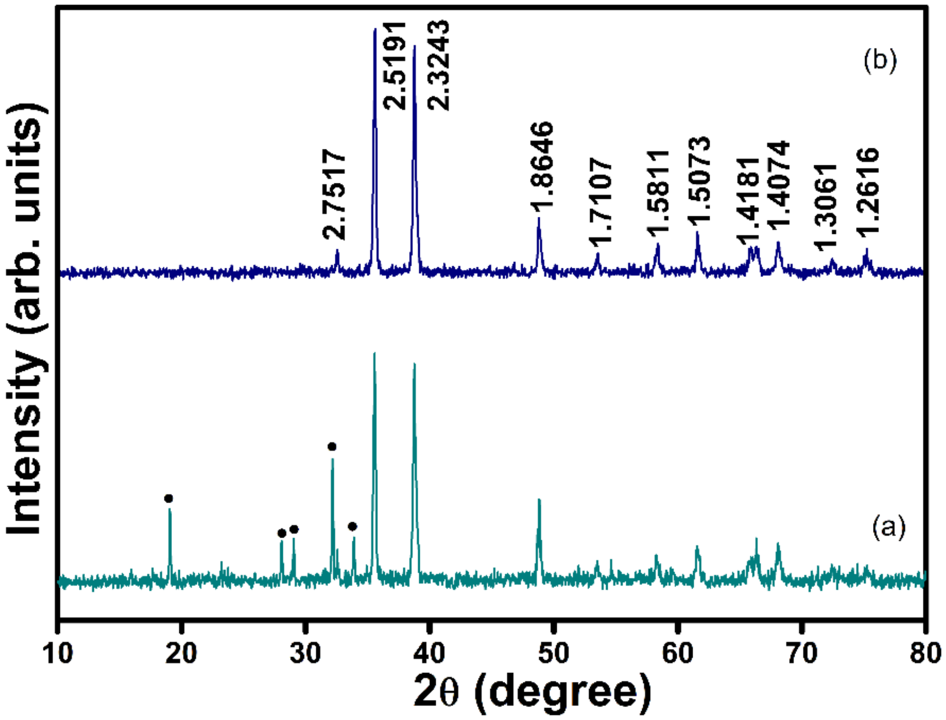

Figure 3.1: PXRD pattern of CuO NPs in presence (a) and in absence of SLS (b). "•" denote reflections due to Na_2SO_4

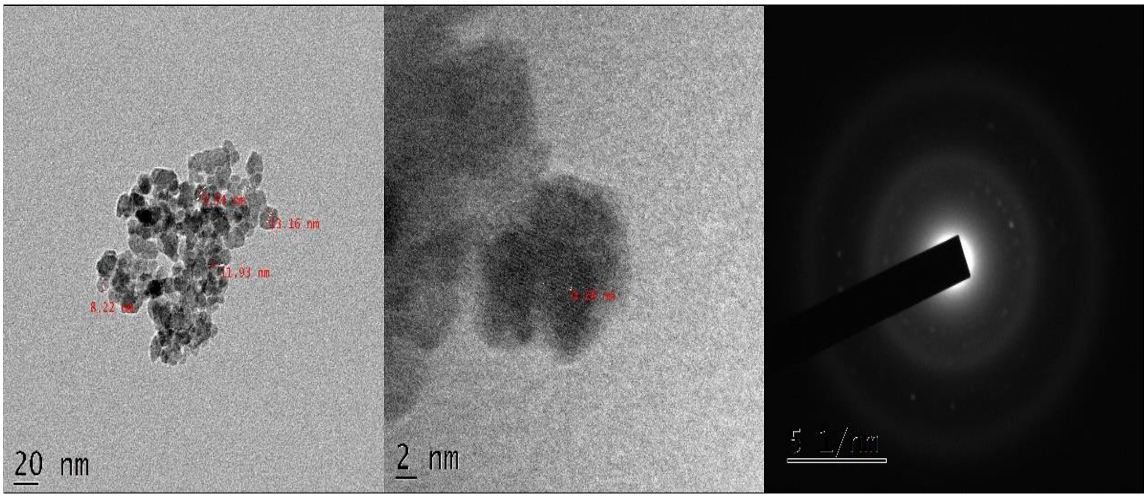

Figure 3.2: HR-TEM image and SAED pattern of CuO nanoparticles

Further confirmation of internal structure, precise measurement of morphology and particle size was done using HR-TEM analysis (Figure: 3.2). Both the average particle size & interplanar spacing values were in close agreement to that obtained from XRD data. However, the SAED pattern of phytosynthesized CuO NPs confirmed its crystalline nature.

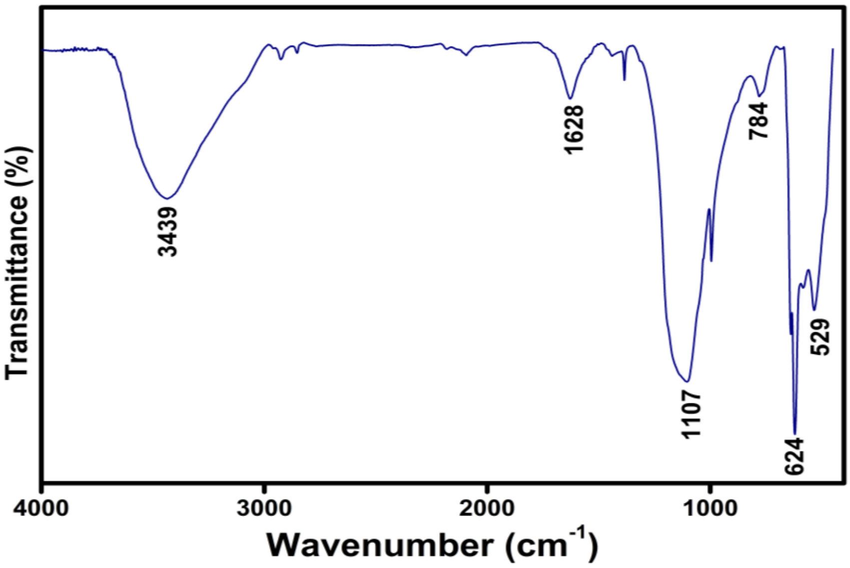

Figure 3.3: FTIR spectrum of CuO NPs

The FTIR spectrum of phytosynthesized CuO NPs is presented in Figure 3.3. The absorption peaks around 784, 624 and 529cm^{-1} corresponds to the Cu–O stretching vibration of CuO NPs in the monoclinic structure. The absorption peaks at 3439 cm^{-1} and 1628 cm^{-1} corresponds to the OH stretching vibration and HOH bending mode of adsorbed water molecules. The absorption peak at 1107cm^{-1} corresponds to the C–O stretching of phenol and alcoholic compounds.

The TGA/DTG profile of CuO precursor is presented in Figure 3.4. The TGA curve exhibited a three-step degradation process of the precursor to generate CuO NPs. The first weight loss >166°C (~9%) corresponds to the exclusion of organic solvent molecules and moisture. The second and third weight loss in the region from 166 – 403°C may be due to combustion and pyrolysis of organic compounds form precursor and solvent that leaves the system in the form of CO, CO_2 and other organic gases. At further higher temperatures, no critical weight reduction was detected, thereby supporting the generation of CuO NPs with high purity.

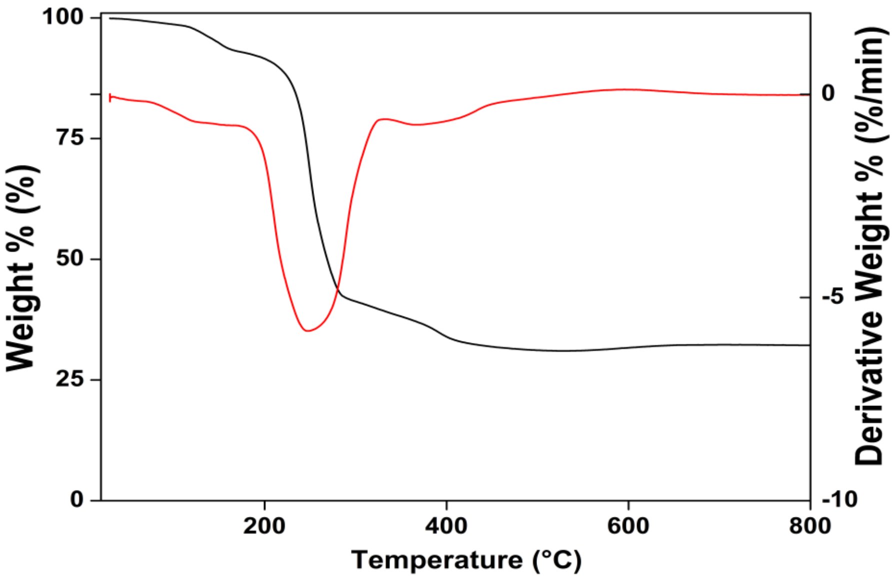

Figure 3.4: TGA/DTG thermograph of CuO precursor (under N_2 atmosphere)

Hence, based on TGA and phytochemical analysis, the proposed mechanism of biochemical reduction & stabilization of CuO nanoparticles is given in Figure 3.5.

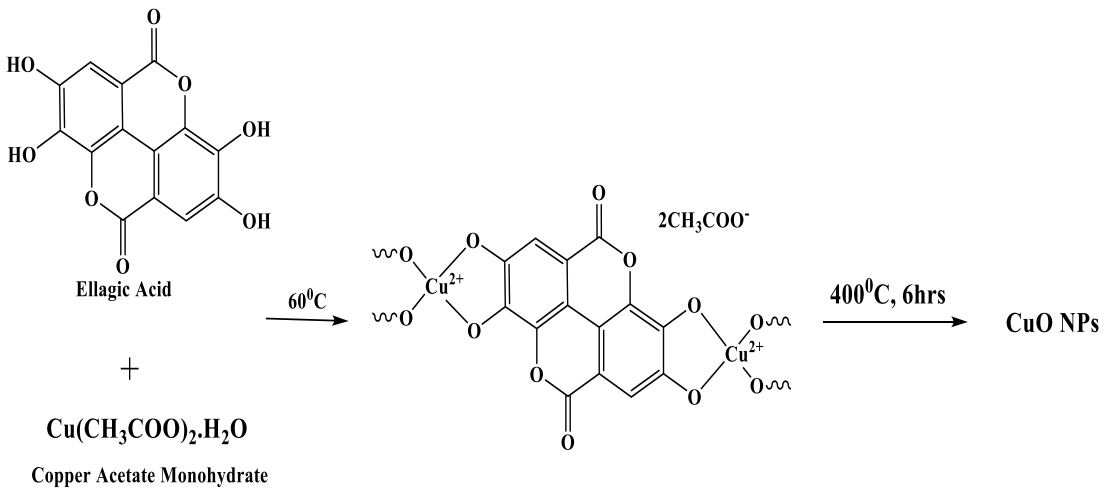

Figure 3.5: Mechanism of the synthesis of CuO NPs

CHAPTER 4

CONCLUSIONS AND FUTURE PROSPECTS

4.1 CONCLUSIONS

In the current study, **"green synthesis and characterisation of copper oxide nanoparticles using *psidium guajava* leaf extract"**, *psidium guajava* leaf had been utilised as capping agent and cupric acetate as metal precursor. A methodology has been indigenized for the synthesis of CuO NPs. The developed methodology is green and viable because of its ease, efficiency, cost-efficient and eco-friendly nature in comparison to other methods. From the experimental studies conducted, the following significant conclusions have been drawn:

- It is identified that the biochemical reduction and stabilization of copper oxide at nano scale level was because of the existence of phytoconstituent (phenolic compounds) in the leaf extract.
- The PXRD spectrum confirms the formation of CuO in monoclinic phase having average crystallite size of ~33nm.
- The HR-TEM revealed that the generated CuO NPs were spherical in morphology and, both the average particle size & interplanar spacing values were in close agreement to that obtained from XRD data.
- The SAED pattern of phytosynthesized CuO NPs confirmed its crystalline nature.
- The TGA/DTG profile of CuO precursor confirms the generation of CuO NPs with high purity.

4.2 FUTURE PROSPECTS

A metal oxide nanocomposite with enriched thermal stability, electrical conductivity and chemical stability, signifies a new generation of novel materials with extensive applications. The metal oxide NP research is still in its budding stage due to the high popularity of metallic nanostructures. Owing to the less toxicity of green methodology, metal oxide NPs synthesised by green methodology is quite cherishing. A better comprehension of phenomena towards the metal oxide NPs synthesis like, biocompatibility, growth mechanism, nucleation, surface chemistry and toxicity will be helpful to diminish the interaction of nanomaterials with the biomolecules in biomedical application. The control of morphology and particle size of metal oxide NP is challenging and seeks more research in this field. Moreover, and the exact mechanism of the binding of capping agent and their exact role in determining the final morphology needs to be investigated further.

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