SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

UNIVERSITI SAINS MALAYSIA

GREEN SYNTHESIS OF SILVER NANOPARTICLES BY KYLLINGA BREVIFOLIA LEAF EXTRACT

by

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Dissertation submitted in partial fulfillment of

The requirements for the degree of Bachelor of Engineering with Honours

(Materials Engineering)

Universiti Sains Malaysia

June 2015

DECLARATION

I hereby declare that I had conducted, completed the research work and written work and written the dissertation entitled “Green Synthesis of Silver Nanoparticles by Kyllinga Brevifolia Leaf Extract”. I also declare that it has not been previously submitted for award of any degree or diploma or other similar title of this for any other examining body or University,

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ACKNOWLEDGEMENT

Praise be to Allah, The Lord of The Worlds

With the name of Allah S.W.T, I am truly grateful for the endless amount of the strength and guidance to complete this research.

First and foremost, I am heartily thankful to my supervisor, Professor Dr. Azizan B. Aziz for his detailed and constructive comment, and for his important support throughout this work, whose encouragement, guidance and support from the initial to final level enabled me to develop an understanding of this research title. His patience, time understanding and trust in my ability are highly appreciated. I express my deepest gratitude to him for guiding me throughout the journey.

A world of thanks also goes to the staff of the Pirometallurgy and Hidrometallurgy Laboratory of School of Materials and Mineral Resources Engineering(SMMRE) who were directly or indirectly involved in the process of completing this research especially Mr. Zulkarnain, Mr. Rashid, Mr. Khairi, Mr. Azrul, Mr. Kamuridan and Mr. Zaini for their generous assistance, useful views and tips throughout my research period.

Last but not least, I would like to thank to my family, Siti Fatimah Bt. Muhammad and friends whom I owe a debt of attitude for their prayers, encouragements and moral support throughout the whole duration of studies in the way to make this research a reality. My regards and blessings to all of those who supported me in any respect during the completion of this project.

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LIST OF ABBREVIATIONS

0-D	Zero dimensional
1-D	One dimensional
2-D	Two dimensional
3-D	Three dimensional
dn	Discrete nanomaterials
nd	Nanoscale device materials
FCC	Face-centred cubic
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray spectroscopy
UV-VIS	Ultraviolet- Visible spectrophotometer
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
Wt%	Weight percentage
At%	Atomic percentage

KB1	5 mL Kyllinga brevifolia leaf extract with 1.0 mM $AgNO_3$
KB2	10 mL Kyllinga brevifolia leaf extract with 1.0 mM $AgNO_3$
KB3	15 mL Kyllinga brevifolia leaf extract with 1.0 mM $AgNO_3$
KB4	20 mL Kyllinga brevifolia leaf extract with 1.0 mM $AgNO_3$
KBpH9	pH 9 of Kyllinga brevifolia leaf extract with 1.0 mM $AgNO_3$
KBpH10	pH 10 of Kyllinga brevifolia leaf extract with 1.0 mM $AgNO_3$
KB1h	1 hour incubation time for leaf extract react with silver ions
KB6h	6 hour incubation time for leaf extract react with silver ions
KB12h	21 hour incubation time for leaf extract react with silver ions

LIST OF SYMBOLS

$AgNO_3$	Silver nitrate
AgCI	Silver chloride
AgBr	Silver bromide
AgI	Silver iodide
CdSe	Cadmium selenide
H_2O_2	Hydrogen peroxide
NO_3	Nitrate
Ag	Silver
Au	Gold
Al	Aluminium
Cu	Copper
C	Copper
O	Oxygen

SINTHESIS HIJAU NANOPARTIKEL ARGENTUM BENGAN EKSTRAK DAUN KYLLINGA BREVIFOLIA

ABSTRAK

Kebelakangan ini, kimia dan proses hijau telah merungkap peranan tumbuhan dalam biosintesis nanopartikel. Kaedah ini merupakan satu pendekatan yang mesra alam untunk mengurangkan penggunaan bahan-bahan kimia. Kertas kerja ini adalah laporan mengenai sintesis hijau nanopartikel argentum menggunakan ekstrak daun Kyllinga brevifolia sebagai ejen penurun dan penstabil. Proses pencirian bagi nanopartikel argentum yang terhasil adalah mikroskop imbasan elektron (SEM), spektroskopi ultraungu-ternampakan (UV-VIS), spektroskopi perubahan infra merah fourier (FTIR) dan pembelauan sinar X (XRD). Nanopartikel argentum yang dihasilkan adalah dalam bentuk kuasi-sfera dengan saiz bergantung kepada pemboleh ubah yang digunakan. Sifat kristal nanopartikel argentums adalah kiub berpusat muka (FCC) berorientasi (111) seperti yang ditunjukkan oleh corak XRD. Protein dalam ekstrak daun Kyllinga brevifolia berkemungkinan menjadi ejen penurun dan ejen pelitup. Ekstrak daun Kyllinga brevifolia mengandungi lapisan organik yang agak nipis dan mudah untuk dibasuh.

GREEN SYNTHESIS OF SILVER NANOPARTICLES BY KYLLINGA BREVIFOLIA LEAF EXTRACT

ABSTRACT

In recent years, green chemistry and process have revealed the role of plants in biosinthesis nanoparticles. This method is an eco-friendly approach lifted in reducing the use of chemicals. This paper is a report on green synthesis of silver nanoparticles using Kyllinga brevifolia leaf extract as a reducing and stabilizing agent. The characterization of silver nanoparticles produced are Scanning Electron Microscope (SEM), Ultraviolet-visible spectroscopy (UV-VIS), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD). Silver nanoparticles are produced in the form of quasi-spherical with the size depending on the variables used. Crystal properties of silver nanoparticles is face-centered cubic (FCC) oriented (111) as shown by XRD patterns. Proteins in Kyllinga brevifolia leaf extract is likely to be agents of degradation and capping agents. Kyllinga brevifolia leaf extract contains organic layers are relatively thin and washable.

CHAPTER 1

INTRODUCTION

1.0 Introduction

A nanoparticle can be defined as a microscopic particle that owns a structure which at least one dimension in the nanometer size range (1-100nm) (Luque et al., 2012). Nanoparticles have remarkably different physical and chemical properties as compared to bulk due to its small size and large surface to volume ratio (Iravani, 2011). Metal nanoparticle are made up by a single metallic element or more than one metal (Johnston and Wilcoxon, 2012). Among the noble metal nanoparticles, silver is one of the most popular. Silver nanoparticles own an inhibitory effect toward many bacterial strains and microorganism which exist in medical and industrial process (Song et al., 2010)

Green synthesis of silver nanoparticles was carried out using plan extract as a reducing agent. In recent years, silver nanoparticles have been widely used in many consumer goods, such as medical devices, cleaning agents, and clothing. Generally, the method for the silver nanoparticles preparation involves the reduction of silver ions in the solution or in high temperature in gaseous environments (Sun et al., 2014). However, reducing agents, such as sodium borohydride, may increase the environmental toxicity or biological hazards. Moreover, the capping agents like polyvinyl alcohol (PVA) or gelatin, have to be used to protect the silver nanoparticles from aggregation and the high temperature may also increase the cost. Hence, the development of green synthesis of silver nanoparticles by using environment friendly solvents and non toxic reagents is of great interest (Mittal et al., 2013).

Synthesis of nanoparticles via conventional methods uses toxic chemicals and generates hazardous intermediates and products (Luque et al., 2012). Green synthesis of nanoparticles has been developed which is a safe and eco-friendly alternative approach. By using microorganism cells or plant extract in biosynthesis of nanoparticles, it can reduce the usage of hazardous materials in chemical processes and decrease or eliminate the generation of undesirable products (Luque et al., 2012). The biomass secretes biomolecules that can function as reducing and capping agents during reaction which can reduce Ag^+ to Ag^0 for the formation of stable silver nanoparticles (Gan and Li, 2012). However, the major challenge is the control on over size distribution, shape and crystallinity of nanoparticles.

In this research project, green synthesis of silver nanoparticles was carried out using Kyllinga brevifolia leaf extract as reducing and capping agent. This plant extract are widely used in medicinal application especially in traditional method. Biosynthesis of silver nanoparticles was conducted by varying the different variable during the reaction of extract added into fix concentration of silver nitrate. The effect of Kyllinga brevifolia leaf extract as reducing agents for the formation of silver nanoparticles was observed and studied.

1.1 Problem Statement

In the synthesis of nanoparticles, the challenges part is the enormous surface area or large surface to volume ratio, a huge surface energy needs to be overcome (Cao, 2004). The desired physical properties can be achieved by having nanomaterials with desired size, uniform size distribution, morphology, crystallinity, chemical composition and microstructure (Cao, 2004). However, metal nanoparticles formed will have a change in its chemical and physical properties depending on the number of atoms in a particle, its shape and type of organization (Schodek et al., 2009).

1.2 Objective

i. To synthesized silver nanoparticles by green synthesis method using Kyllinga brevifolia leaf extract as reducing and capping agent.
ii. To analyze and compare the morphology, size and shape of silver nanoparticles synthesized using different variable of Kyllinga brevifolia leaf extract.

1.3 Scope of Project

Silver nanoparticles were synthesized via plant-mediated synthesized method where Kyllinga brevifolia leaf extract were used as reducing and capping agent. Four parameter were studied in this project. The parameter ere listed below:

i. Effect of amount of Kyllinga brevifolia leaf extract towards the fixed concentration and amount of silver nitrate.
ii. Effect of pH value of Kyllinga brevifolia leaf extract towards the fixed concentration and amount of silver nitrate.
iii. Effect of incubation time of reaction between Kyllinga brevifolia leaf extract and silver nitrate towards the fixed concentration and amount of silver nitrate.
iv. The effect of Kyllinga brevifolia leaf extract as reducing agent towards the biosynthesis of silver nanoparticles.

Characterization on synthesized silver nanoparticles were carried out to analyze the morphology, size and shape of silver nanoparticles. These 4 characterization were listed as below:

i. Scanning Electron Microscopy (SEM)
ii. Ultraviolet-visible Spectroscopy (UV-VIS Spectroscopy)
iii. Fourrier Transform Infrared Spectroscopy (FTIR)
iv. X-ray Diffraction (XRD)

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

Nanotechnology provides the tools and technology platform for the investigation and transformation of biological systems, and biology offers inspiration models and bioassembled components to nanotechnology. Nanobiotechnology is defined as a field that applies the nanoscale principle and techniques to understand and transform bio systems (Gan and Li) and which uses biological principles and materials to create new devices and systems integrated from the nanoscale (MubarakAli et al., 2011). The development of nanotechnology has opened up novel fundamental and applied frontiers in material science and engineering (Iravani, 2011). It is a creation and exploitation of material which includes fundamental understanding of physical properties and phenomena of nanomaterials and nanostructures (Cao, 2004). The main concerns in nanotechnology are the synthesis of nanoparticles of variable sizes, shapes, chemical compositions and controlled disparity and their potential use for human benefits (Kumar and Yadav, 2009)

2.1 Nanomaterials

Nanomaterials is defined as materials where some controllable relevant dimension is of the order of 100 nm or less (Schodek et al., 2009). To exhibit nanoparticles, the at least one dimension of the materials should be on nanoscale (Vajtai, 2013). Properties, behaviors and features of nanomaterials differ from bulk materials. For nanoscale, the length (e.g., size, diameter, edge) of nanomaterials should be measure on nanometer scale.

2.1.1 Classes of Nanomaterials

There are three types of nanomaterials, which include discrete nanomaterials, nanoscale device materials and bulk nanomaterials. Discrete nanomaterilas (dn materials) are free standing materials elements with the scale of 1-10 nm in at least one dimension like nanoparticles. Nanoscale device materials (nd materials) are usually thin films where material elements are in nanoscale that contain within the device. Bulk nanomaterials are constructed by discrete nanomaterials or nanoscale device materials. This material is available in bulk quantities with the structure controlled at nanoscale (Ramesh, 2009)

Nanomaterials are classified according to their dimensions but not confined to nanoscale range which is <100 nm. It can be categorized as zero-demensional (0-D), one-dimensional (1-D), two dimensional (2-D) and three-dimensional (3-D) (Schodek et al., 2009).

a) Zero-dimensional (0-D)

Dimensions of nanomaterials are measurable within nanoscale. The most well-known example nanoparticles. Nanoparticles can be:

i. Amorphous or crystalline
ii. Single crystalline or polycrystalline
iii. Composed of single or multichemical elements
iv. Exhibits various shapes and forms
v. Individually or incorporated in matrix
vi. Metallic, ceramic or polymeric.

b) One-dimensional (1-D)

1-D nanomaterilas have one dimension not confined to the nanoscale. This makes the nanomaterials to be in needle-like-shaped (Schodek et al., 2009). Examples for 1-D nanomaterials include nanotubes, nanorods and nanowires. 1-D nanomaterials can be:

i. Amorphous or crystalline
ii. Single crystalline or polycrystalline
iii. Chemically pure or impure
iv. Standalone materials or embedded in within another medium
v. Metallic, ceramic or polymer

c) Two-dimensional (2-D)

2-D nanomaterials are materials with two dimensions outside of the nanoscale and exhibits plate like shape (Schodek et al., 2009). Nanofilms, nanolayers and nanocoatings are the examples of 2-D nanomaterials (Schodek et al., 2009). 2-D nanomaterials can be:

i. Amorphous or crystalline
ii. Composed by various chemical compositions
iii. Used as a single layer or multilayer structures
iv. Deposited on a substrate
v. Integrated in a surrounding matrix materials
vi. Metallic, ceramic or polymeric

d) Three-dimensional (3-D)

3-D nanomaterials also known as bulk nanomaterials (Ramesh, 2009). These materials are still classified as nanomaterials although it consists of three arbitrary dimensions above 100 nm (Schodek et al., 2009). This is due to the materials have nanocrystalline structure which bulk nanomaterials can be made up of a multiple arrangement of nanosize crystals with various orientation (Schodek et al., 2009). It can be also be explained that bulk nanomaterials consists of features at nanoscale which include dispersions of nanoparticles, bundle of nanowires, nanotubes and multianolayers. 3-D nanomaterials can be :

i. Amorphous of crystalline
ii. Chemically pure or impure
iii. Composite materials
iv. Metallic, ceramic or polymeric

2.1.2 Properties of Nanomaterials

The properties of nanomaterials depend on its size and morphology (Vajtai, 2013). Properties of nanomaterials which differ from bulk materials are:

a) Morphology of nanomaterials

Overall size and shape of nanomaterilas are the factors in controlling other properties. Shape is important factor in the classification of nanomaterials as it is done according to their dimensionality or aspect ratio. The surface-to-volume ratio and other properties are all change by aspect ratio, porosity and surface roughness (Vajtai, 2013).

b) Mechanical Properties

Nanomaterials own unique mechanical properties as a result of shorter bond length and reduced number of defects. Decrease in size enhances the mechanical properties of materials (Cao, 2004). It may achieve the theoretical strength with magnitude of one or two order higher than the single crystals in the bulk form (Cao, 2004). In bulk solid materials, the change of bond length requires high pressure and substantial amount of energy due to the strong bonds in solid (Vajtai, 2013). However, in nanomaterials, forces near the surface atoms in solids cause asymmetry and able to change its bond length.

c) Magnetic Properties

Bulk materials and nanostructured materials have different magnetic properties. The characteristic size of nanomaterials strongly affect its magnetic properties. As compared with the magnetic domain size of materials, diameter of nanoparticles or the grain size of nanostructured material is smaller (Vajtai, 2013). Classification of nanomaterials can be accomplished based on the type of interaction between magnetic particles. It can be ranged from no interaction in a well-distributed nanoparticle system to a system to a strongly interacting nanostructured materials (Vajtai, 2013).

d) Electrical Properties

In nanomaterials, the conduction of electrons is delocalized. This allows the electron to move freely in all dimensions and scattered by phonons, impurities and interfaces as they travel their paths (Schodek et al., 2009). As surface scattering increases, the electrical conductivity reduces with a decreased dimension. This leads to quantum effect where electron confinement causes the discrete energy sates replace the energy band and allows conducting materials to act as semiconductors and insulators (Vajtai, 2013). Besides, there is also the presence of classical effect as a reduction in scattering events where mean-free path for inelastic scattering becomes comparable with the size of the system (Vajtai, 2013).

e) Optical Properties

Similar to electrical properties, quantum confinement also governs optical properties where a larger energy difference between neighboring discrete energy levels in density of state due to lower dimensionability and smaller size (Schodek et al., 2009). Electrons and holes are spatially confined and formed electric dipoles as the size of a nanocrystal is smaller than the de Broglie wavelength. Increased band gap causes the optical absorption peak of a semiconductor nanoparticle shifted to a shorter wavelength (Cao, 2004).

Surface plasmon resonance is the main reason for the changes in colour of metallic nanoparticles with their sizes. It is the coherent excitation of all the ‘free’ electrons within the conduction band, resulting to an in-phase oscillation (Cao, 2004). A surface Plasmon resonance is produced when the size of a metal nanocrystal is smaller than the wavelength of incident radiation (Cao, 2004)

2.2 Nanoparticles

Nanoparticles are cluster of atoms, ions or molecules with dimensions of the order of 1-100 nm (Johnston and Wilcoxon, 2012). It is utterly small in size with large surface to volume ratio (Iravani, 2011), large surface energy, spatial confinement and reduced imperfections (Gan and Li, 2012). These makes nanoparticles have improved chemical and physical properties such as mechanical properties, biological and sterical properties, catalytic activity, thermal and electrical conductivity, optical absorption and melting point (Iravani, 2011). The distinct properties of nanoparticles are the interest for variety of application. It is beneficial in the field of catalysis, electronics, biomedical analysis, groundwater purification (Gan and Li, 2012) and antimicrobial activity (Iravani, 2011). The most common metallic nanoparticles are gold and silver which one used in the field of nanobiotechnology and biomedical.

2.2.1 Metal Nanoparticle

Metal nanoparticles as shown in figure 2.1 are defined as particles (Sau and Rogach, 2012). Electrons in nanoparticles are enclosed to spaces of a few atoms width across.

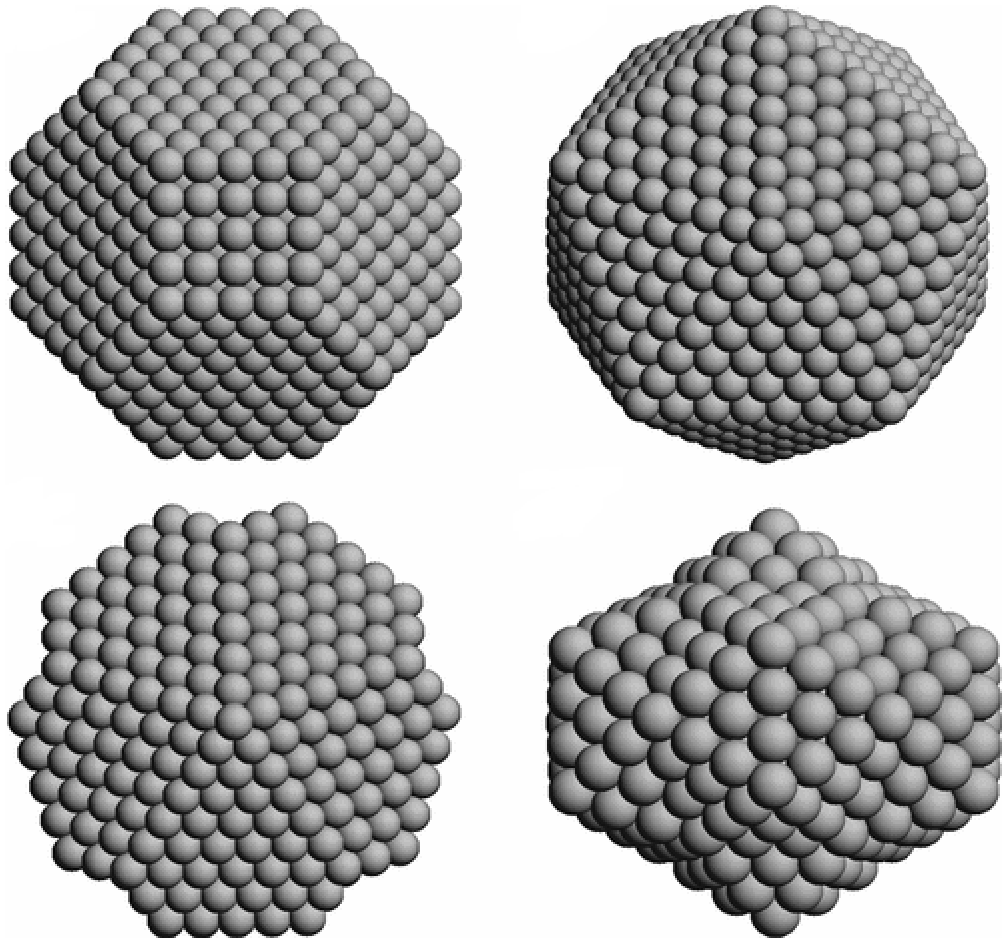

Figure 2.1: Metallic nanoparticles (Bochicchio and Ferrando, 2013)

Due to the presence of discrete electronic energy levels and loss of overlapping electronics bands, metal nanoparticles give rise to typical quantum size behavior (Luque et al., 2012). In addition to exciting electronic properties, distinct physical properties of metal nanoparticles such as lower melting point than bulk metal also presented. Higher surface-to-volume ratio in metal nanoparticles makes it to own larger fraction of catalytically active atoms on surface than bulk metal (Luque et al., 2012). The have great potential as highly active and selective catalysis. Their unique properties which differ from bulk species allow metal nanoparticles to have applications in fields like conductors, chemical and biosensors, photovoltaic devices, drug delivery, fuel cells, light-emitting diodes, industrial lithography and catalysis (Xia et al., 2013).

2.2.2 Silver Nanoparticles

Silver nanoparticles are usually obtained from silver salts such as silver nitrate ($AgNO_3$), silver chloride (AgCl), silver bromide (AgBr) and silver iodine (AgI) (Bagchi et al., 2012). Silver can also deploy on a variety of substrates such as activated carbon, activated carbon fibers (ACF), polyurethane, zeolites and ceramics (Bagchi et al., 2012). Silver colloids can be prepared using various chemical methods. All these methods are generally chemical reduction of silver ions, Ag^+ in aqueous or non-aqueous solution using different reduction agents such as citrate, borohydride (Pozo, 2010), ascorbate and elemental hydrogen. The reduction of silver ions in aqueous solution yields stable, colloidal dispersion in water or organic solvents with particle diameter of several nanometers (Singhal et al., 2011).

Chemical reduction of silver nanoparticles starts with the reduction of different complexes with Ag^+ ions to form silver atoms (Ag) and agglomerate into oligomeric clusters. Eventually these clusters form colloidal silver particles. The solutions will show yellow colour with an intense band in the 400- 500 nm range and other less intense or smaller bands at longer wavelength in the absorption spectrum when the colloidal particles are much smaller than the wavelength of visible light (Singhal et al., 2011)

2.2.3 Synthesis of Metallic Nanoparticles

Two vital processes are involved in the formation of nanoparticles, which are nucleation and growth (Lu, 2012). Homogeneous, heterogeneous or secondary nucleation in a supersaturated solvent happens as the initial nucleation (Luque et al., 2012). Then, continues with growth of nuclei through molecular addition which causes the concentration of the target element to fall below critical point ends the nucleation process (Luque et al., 2012). The growth process will stop when the concentration of the precipitates achieves equilibrium (Lu, 2012).

Generally, desired nanoparticles can be produced by controlling the parameters such as metal precursor, stabilizer and reducing agent. Stabilizers control the size and shape of particles and reduce the tendency to agglomerate (Johan et al., 2012). Solution synthesis or water-in-oil emulsion are the choices for fabrication of metallic nanoparticles.

i. Solution synthesis

Chemical reduction of metal salts in solution phase is most commonly used for fabrication of metallic nanoparticles. Upon aggregation, nanoparticles are produced through reduction of metal ions (Vajtai, 2013). In the embryonic stage of nucleation, metal salt is reduced to provide zero valent metal atoms. After the reducing agent is added, stirring is needed to ensure that the reducing agent is evenly distributed throughout the solution. An excess amount of reducing agent is added into the reaction solution to prevent oxidation of synthesized nanoparticles (Luque et al., 2012). Table

2.1 shows the summary of various solution-phase reduction processes employed to make metal nanoparticles.

Table 2.1: Summary of various solution-phase reduction processes employed to make metal nanoparticles (Pradeep and Ashokreddy, 2012)

Method	**Metal/reducing agent**	**Example**
1. $NaBH_4$ route	Metal ion/BH_4^-	Au, Ag
2. Citrate route	Metal ion/Cit^{3-}	Au, Ag
3. Polyol route	Metal ion/ethylene glycol	Ag, Pd
4. Polyvinylpyrrolidone (PVP) route	Metal ion/PVP	Pd

ii. Water-in-oil emulsion

In this method, oil phase is added to an aqueous solution of metal ions with the addition of water-soluble cosolvent into the formed emulsion (Luque et al., 2012). Usually, reducing agent is last added into the system. Nanoparticles produce via this method have improved size control where they have more uniform size and lower tendencies to aggregate.

Fabrication of metallic or bimetallic nanoparticle can also be synthesized via in situ method. The surface of the stabilizer is deposited with metal precursors. After that, the stabilizer is soaked in reducing agent.

2.3 Application of Metal Nanoparticles

i. Biomedicine

Silver nanoparticles perform well for their anti-fungal, anti-inflammatory and anti-viral activities. It can inactivate microbes through the interaction with enzymes, protein or DNA to restrain cell proliferation (Gan and Li, 2012). The interaction of silver and thiol-containing compounds is vital in bacterial inactivation. Besides, it was revealed that silver nanoparticles are effective in controlling HIV infection. Interaction with glycoproteins of HIV-1 occurred on silver nanoparticles in the size ranges from 1-10 nm and inhibited the binding of virus to the host cells (Gan and Li, 2012).

Disinfection properties are imparted to the materials and devices for biomedical application due to the antibacterial properties of silver nanoparticles (Amiji, 2011). To prevent infection with pathogenic bacteria, extracellularly synthesized silver or gold nanoparticles are incorporated in a few types of materials such as cloths and some medical devices in hospital (Gan and Li, 2012). For instance, impregnation of polymeric medical devices with silver nanoparticles helps to raise their antibacterial activity (Pozo, 2010). Moreover, surgical masks and implantable devices are the example of silver impregnated medical devices.

The use of silver nanoparticles in medicine for burn treatment, dental materials and sunscreen lotions is discovered (Pozo, 2010). For example, it is used on typical ointments and creams. It functional to prenent of burns and open wounds.

ii. Catalysis

Heterogeneous catalytic reactions require high surface area as the process occurs only at surfaces (Vajtai, 2013). They behave differently from larger-grain counterparts due to their distinct features. Under the same conditions, surface catalysis with different reactions is promoted as different crystal planes and different defect sites such as steps and kinks on the surface. For homogeneous catalysis, atoms at edge and corners are important. Their ratio varies dueing the reaction and ir is common to have surface reconfiguration (Vajtai, 2013). For nanomaterials, the number of this kind of defects is higher based on their size and shape. Therefore, manipulation of these parameters offer well-regulated reactions in a multichannel process.

The use of nanoparticles as catalysts is known as nanocatalysis. The variation in sizes and synthesis method leads to different catalysis properties. Decomposition of H_2O_2 to oxygen is catalyzed by metals such as Au, Ag and Pt and metal ions (Pozo, 2010). Furthermore, luminal H_2O_2 system are catalyzed by metal ions. Upon the injection of silver colloid, emission of chemiluminoscence from luminal H_2O_2 system is greatly enhance (Pozo, 2010).

Besides that, silver is the well-known catalysts fo oxidation of ethylene to ethylene and methanol to formaldehyde (Pozo, 2010). Its catalytic oxidative power is because of its ability to chemosorb oxygen in atomic form (Gan and Li, 2012). Atomic oxygen is able to fit into the octahedral holes of silver and leads to accumulation of oxygen within the bulk of silver (Gan and Li, 2012). Water purification systems such as Katadyn and Ionic systems have been developed due to the ability of silver to adsorb atomic oxygen (Gan and Li, 2012).

iii. Sensor

Noble metal nanoparticles exhibit excellent properties which use as optical biosensors and chemosensors (Pozo, 2010). Nanomaterials are outstanding in functioning as active elements of chemical sensors. As there is interaction between surface atoms and experience changes, materials need to have high dispersion in order to attain high sensitivity (Vajtai, 2013). However, the atoms inside the material unchanged. This brings the meaning of higher surface atom ratio results in larger relative changes in the measured physical property of the material (Vajtai, 2013). Sensors are similar to catalysts as it depends on both the size and shape of the particle. The changes in shape, number and configuration of edge and corner atoms, the signals measured will be different.

2.4 Green Synthesis of Nanoparticles

2.4.1 Green Chemistry

Green synthesis techniques also provide some valuable advantages over the chemical and physical nanoparticles synthesis methods, i.e., cost effectively, environmental compatibility, and simplicity in scaling up for large-scale synthesis, while they require no considerable amounts of pressure, temperature, toxic chemicals, and energy. The size of nanoparticles depends on their formation kinetics and hence the composition of the reaction solution could play an important role in the kinetic of silver nanoparticles formation. Furthermore, there is a potential for extract species to be absorbed onto the surface of the nanoparticles during the particle formation processes which ultimately leads to occurring subsequent surface effects during their application. Thus, investigation on the various plant sources which provide different extract compositions as the reagents for silver reduction could be interested (Pourmortazavi et al., 2014).

The silver nanoparticles have been widely used in many consumer goods, such as medical devices, cleaning agents, and clothing, due to its unique antimicrobial properties. Generally, the method for the silver nanoparticles preparation involves the reduction of silver ions in the solution or in high temperature in gaseous environments (Cheng et al., 2013). Instead of using chemical reduction which is harmful to the environment, bioreduction of metal nanoparticleswith plant extract as reducing agent is used.

There are many important applications for metal nanoparticles in medicine and pharmacy. Gold and silver nanoparticles are the most common ones used for biomedical applications and in emerging interdisciplinary field of nanobiotechnology. For instance, oligonucleotidecapped gold nanoparticles have been used for polynucleotide or protein detection using various detection/characterization methods, including atomic force microscopy, gel electrophoresis, scanometric assay, surface plasmon resonance imaging, amplified voltammetric detection, chronocoulometry, and Raman spectroscopy (Iravani, 2011).

The development of green chemistry for biogenic synthesis of nanomaterials is important. It is an eco-friendly approach which can minimize waste products with the use of organisms. The nanomaterials and nanodevices are used in water and air filters which reduce pollution. It also provide a more efficient alternative for energy production such as solar and fuel cells (Luque et al., 2012).

2.4.2 Biosynthesis of Nanoparticles

Nanobiotechnology is the combination of physical and chemical procedures together with biological principles to produce nanosized particles with particular functions. Biosynthesis of nanoparticles is compatible with green chemistry principles. Bimolecular that secreted by the biomass can work as reducing and capping agents (Gan and Li, 2012). As the cost for physical and chemical processes increases, biosynthesis of nanoparticles is an economical way to generate nanoparticles (Pozo, 2010).

Biosynthesis of metal nanoparticles by plants is currently under exploitation. The biological synthesis of metal nanoparticles (especially gold and silver nanoparticles) using plants (inactivated plant tissue, plant extracts and living plant) has received more attention as a suitable alternative to chemical procedures and physical methods. Synthesis of metal nanoparticles using plant extracts is very cost effective, and therefore can be used as an economic and valuable alternative for the large-scale production of metal nanoparticles. Extracts from plants may act both as reducing and capping agents in nanoparticle synthesis.

2.5 Plant Extracts

The use of plant biomasses or plant is easier and cost effective compared to microorganism-mediated synthesis of nanoparticles (Gan and Li, 2012). Trace elements such as metal and metalloids are hazardous and cause pollution to the environment. Plants are performed well in heavy metal accumulation and detoxification (Iravani, 2011).

Due to the various composition and structure of plants from different sources, it is difficult to synthesize nanoparticles with particular morphology (Gan and Li, 2012). A mixture of agriculture waste or plant biomasses which may contain other impurities is often collected. The production of nanoparticles with desired morphology by certain functional group on a specific part of the plant biomass will raise the level of difficulty to set up the process design (Gan and Li, 2012). Figure 2.2 shows various types of plants used in plants-mediated synthesis of nanoparticles.

Figure 2.2: Various types of plants used in plants-mediated synthesis of nanoparticles (Mittal et al., 2013)

2.5.1 Biological Synthesis of Metallic Nanoparticles by Plants

Synthesis of nanoparticles using plant extracts is by mixing the extract with solution of the metal salt at room temperature and the reaction will be completed with minutes (Mittal et al., 2013). Instead of organic solvents, most of the plant-mediated synthesis of metallic nanoparticles could be carried out in aqueous medium. This more environmentally friendly and cost saving.

Gold and silver nanoparticles have been produced through the process of extracellular synthesis. Plant broths are used on biosynthesis of nanoparticles by plant systems. Reduction of metal ions is accomplished by the compounds extracted and added to the reaction mixture to produce nanoparticles extracellularly (Gan and Li, 2012).

During the biosynthesis process, three distinguishable reaction regimes happened which are short induction period, growth phase and termination period (Gan and Li, 2012). Usually, the growth rate of particles is slower than the reduction and nucleation of metallic seed. This results in higher concentration of small particles. Interaction between metallic ions and biomass occurred through ionic binding with the bioorganic reducing agents such as flavonoids or terpenoids in the absence of other strong ligands. The presence of π-electrons and carbonyl groups in their molecular structures causes the adsorption of bioreducing agents on the surface of metallic nanoparticles (Gan and Li, 2012)

2.5.2 Possible Compounds for Plant-Mediated Synthesis Process

For the formation of nanoparticles, active components in the biomass are the potential bioreducing and stabilizing agents for bioreduction process of metal ions:

i. Flavonoids

It belongs to polyphenol family with water soluble polyphenolic molecules consisting 15 carbon atoms (Gan and Li, 2012). Chalcone, falvone, falvonol, falvanone, anthocyanin and isoflavonoid are the major subgroups in flavonoids.

It presents as the main components in the aqueous extract of many plant broths which involved in the bioreduction process. By the means of interaction with carbonyl groups and π-electrons, flavanones can be adsorbed on the surface of metallic nanoparticle (Fierascu et al., 2010). The internal mechanisms that convert ketone to carboxylic acid in flavonoids are vital for bioreduction of metal ions (Gan and Li, 2012).

ii. Terpenoids

Terponoids, also known as isoprenoids, is the subclass of prenyllipids (terpenes). It is the largest group of small molecular products synthesized by plants. The presence of terpenoids provides some plants with scent, flavour and colour (Gan and Li, 2012). Cinnamon, cloves and cannabis are the examples.

iii. Reducing sugars

Monoses, dioses and oligoses are the examples of reducing sugars. They are polyols with separated aldehyde or kenotic groups (Gan and Li, 2012). When fructose is used, nanoparticle with uniform size can be generated. However, glucose and sucrose will produce particles with different sizes.

2.6 Kyllinga Brevifolia

Kyllinga brevifolia are used in Paraguayan traditional medicine as refreshing beverage and are claimed to possess diuretic, sedative and antispasmodic properties(Helliön-Ibarrola et al., 1999). However, we have found no scientific references on any experimental evaluation either about central nervous system activity, which traditional medicine ascribes to this plant, or about the toxicity of this plant.

The rhizomes of Kyllinga brevifolia (Cyperaceae) were collected in Paraguarı´ Department, Paraguay, in February 1991 and were identified at the herbarium of the Faculty of Chemical Sciences, where a voucher herbarium specimen has been deposited (Helliön-Ibarrola et al., 1999). The guaranı´ name of this plant is Kapi-i katı´ (meaning smelling grass). Fresh rhizome samples were airdried and ground, yielding 459.5 g of powder. The powder was extracted with a mixture of ethanol:water (70:30) by a conventional reflux method for 1 h. The extraction was repeated three times and the filtered hydro-ethanolic extracts were mixed and evaporated under reduced pressure. The concentrated extract was frozen and finally freeze-dried to yield 31 g of lyophilized extract. Thus, 1 mg of lyophilized extract was obtained from 14.8 mg of dry rhizome powder (Helliön-Ibarrola et al., 1999).

Kyllinga brevifolia plants as shown in figure 2.3 also species are native in Asia. Kyllinga brevifolia tend to have a finer leaf texture be shorter growing than other sedges. They thrive under close mowing situations (inch or less) and are very prolific in areas that are poorly drained or frequently wet. These two species are mat-forming sedges and have been observed to take over turfgrasses in the southeastern United States. Green kyllinga brevifolia is very difficult to control once the large mats form. The range of these two