Biogenic Synthesis of Palladium Nanoparticles using Malus Domestica Extract and their Catalytic Activity towards the Suzuki Coupling Reactions

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2017

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This thesis is submitted as a partial fulfillment of the requirements for the degree of

Masters of Science (MS) in Nanoscience and Engineering

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Islamabad, Pakistan

February, 2017

Dedication

$$D\text{edicated}$$

To my mother, for her support and prayers, my father for being my mentor and advisor, and my siblings for their love and care

Acknowledgements

Abstract

Green methods for nanoparticles synthesis have numerous advantages over typical physical and chemical procedures. These methods are simple, eco-friendly, facile and don't pose any health risk to human body. Herein, we report an environmental friendly procedure for the production of palladium nanoparticles using an aqueous extract of *Malus domestica* (apple). This aqueous extract has the capability to act both as a source of reducing and capping agent. In an aqueous extract complete reduction of $PdCl_2$ salt was observed in 1.5 hours and the synthesized nanoparticles were further characterized by using ultraviolet-visible visible (UV-Vis), spectroscopy, powder X-rays diffraction (XRD), Scanning electron microscope SEM) and Fourier-transform infrared (FT-IR) spectroscopy. FTIR data suggested the presence of proteins and ascorbic acid in the extract of plant. Such proteins, ascorbic acids, and similar phytochemicals have been attributed to act as reducing and stabilizing agents. It was observed by XRD that synthesized nanoparticles were crystalline in nature (JCPDS: No.05-0681, space group: Fm3m (225)). Additionally, enhanced catalytic activity was shown by these synthesized nanoparticles in Suzuki coupling reaction with only 2 mol % loading of the catalyst. During the reaction, progress and completion of reaction was monitored by Gas Chromatography and all the products were analyzed by GC-MS, IR and from their melting points.

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Abbreviations

Meaning	Acronym
Gas Chromatography	GC
Mass Spectroscopy	MS
Scanning Electron Microscopy	SEM
Thin Layer Chromatography	TLC
Fourier Transform Infrared Spectroscopy	FTIR
Transmission Electron Microscopy	TEM
Palladium Nanoparticles	PdNPs
Silver Nanoparticles	AgNPs
X Ray Diffraction	XRD
Carbon-Carbon	C-C
With respect to	w.r.t.
Scanning Electron Microscope	SEM
X-Ray Diffraction	XRD
Mechanism	mech
Palladium	Pd
Nano Particles	NPs
Application	app

Chapter 1

Introduction

1.1. Nanoscience and Nanotechnologies

Nanoscience is generally composed of two words i.e. "*nano*" and "*science*". The word nano is often used as a prefix in nano-seconds, nano-ampere, nanometer etc. and its value is 10^{-9}. This prefix has its origins in Greek νᾶνος (Latin, *nanus*) meaning "DWARF". Study of any subject that comes in the regime of nanometer is known as nanoscience. The idea of nanotechnology was initially introduced by Richard Feynman at an American physical society meeting on 29th December 1959. He delivered a lecture which was entitled, "There's a Plenty of Room at the Bottom"[1]. Recently, nanotechnology gets more attention in the scientific community as properties of materials get change at an atomic scale [2] Nanotechnology is a broad term demonstrating the phenomena's occurring at an atomic level approximately at one billionth of a meter (nano-scale) as shown in Figure 1.1.
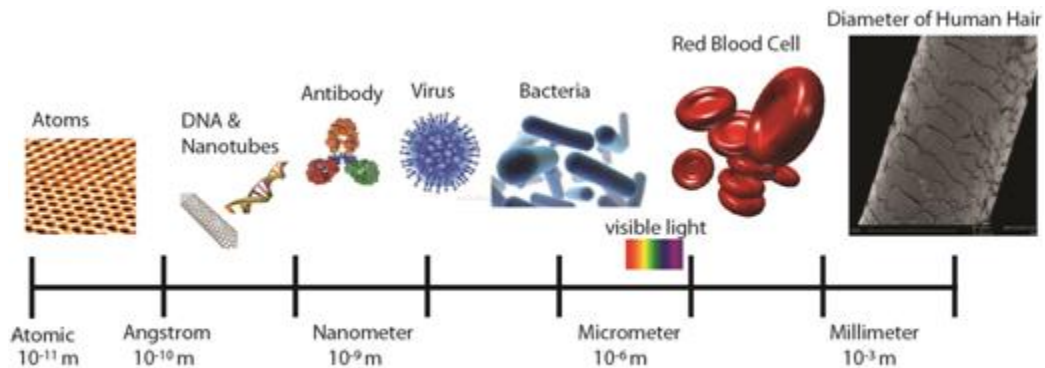
Figure 1.1 Nanotechnology relative scale [2]

$$1 \text{ nm} = 10^{-3}\mu m = 10^{-6}mm = 10^{-9}m$$

A nanometer (nm) or 10^{-9}m means a small number of atoms or molecules. Norio Taniguchi first used the term "nanotechnology'' in one of his publications on

fundamental concepts of nanotechnology [1]. Nanotechnology is an interdisciplinary field, with applications in the advances of biomedical devices, optical and electrical field as well as in energy generation and environmental research. Nano dimensional materials with size domain of 1-100 nm act as a link between atomic and bulk materials, thus possessing distinctive physical and chemical properties. These nanomaterials exhibit unique structural features and excellent functional characteristics, therefore plays a significant part in research, science and also in products used in everyday life [3, 4]. These nanostructural materials such as nanorods, nanotubes, metallic and non-metallic nanoparticles, nanospheres and thin films have several innovative applications [5, 6].

Scientists deal with basic perceptive and scientific advances from development of new physical, chemical, biological and electrical properties of systems having size range between 1-100nm.

The two factors that differentiate nano-materials from bulk are surface to volume ratio and quantum confinement effects.

a. Surface Area to Volume Ratio (S/V)

Surface to volume ratio increases with the decreasing size of particles. To calculate S/V ratio for a sphere, the relationship is given as

$$\frac{Surface\ area\ of\ sphere}{Volume\ of\ sphere} = \frac{4\pi r^2}{(^4/_3)\pi r^3} = \frac{3}{r}$$

S/V ratio increases with the decrease in radius of a sphere. Due to this factor, nanomaterials have more reactivity compared to bulk materials [7].

b. Quantum Confinement Effects

Quantum confinement effect is seen when diameter of a material is so small that it can be equivalent to the de Broglie wavelength of the electron wave function. This results in confinement of electron within small region of material. This phenomenon that occurs

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is called quantum confinement [8]. At this scale, the electrical, optical and magnetic properties deviate from bulk materials.

Energy of electron change with the decrease in size of electron, that's why quantum effects are prominent in nano-materials.

1.2. Nanomaterials and their Classifications

Nanomaterials are defined as materials which possess grain sizes on the order of billionth of a meter. On the basis of different parameters, nanomaterials are usually classified which is given in Table 1.

Table 1 Classification of nanomaterials w.r.t. different parameters

Classification	Examples
Dimensions • 0 dimensions < 100nm • 1 dimensions < 100nm • 2 dimensions < 100nm	Nanoparticles, quantum dots and nano shells. Nanowires, nanorods, nanofibers Thin films, nanobelts etc.
Phase Constituents • Solids based on Single-phase • Solids based on multi-phase • Systems based on multi-phase	Particles and layers of amorphous and crystalline nature Coated particles Colloidal compounds and aerogels etc.
Manufacturing Process • Reactions based on gas phase • Reactions based on liquid phase	Chemical vapour depositions etc. Sol gel based methods etc. Ball milling etc.

1.3. Applications of Nanomaterials

Nanomaterials manifest unique, beneficial physical, chemical and mechanical properties that can be exploited for wide range of applications. Applications of nanotechnology is almost is in every field e.g., food technology, agriculture, chemistry, environment, communication, electronics, pharmaceuticals, energy and photo catalysis as shown in Figure 1.2 [9-11].
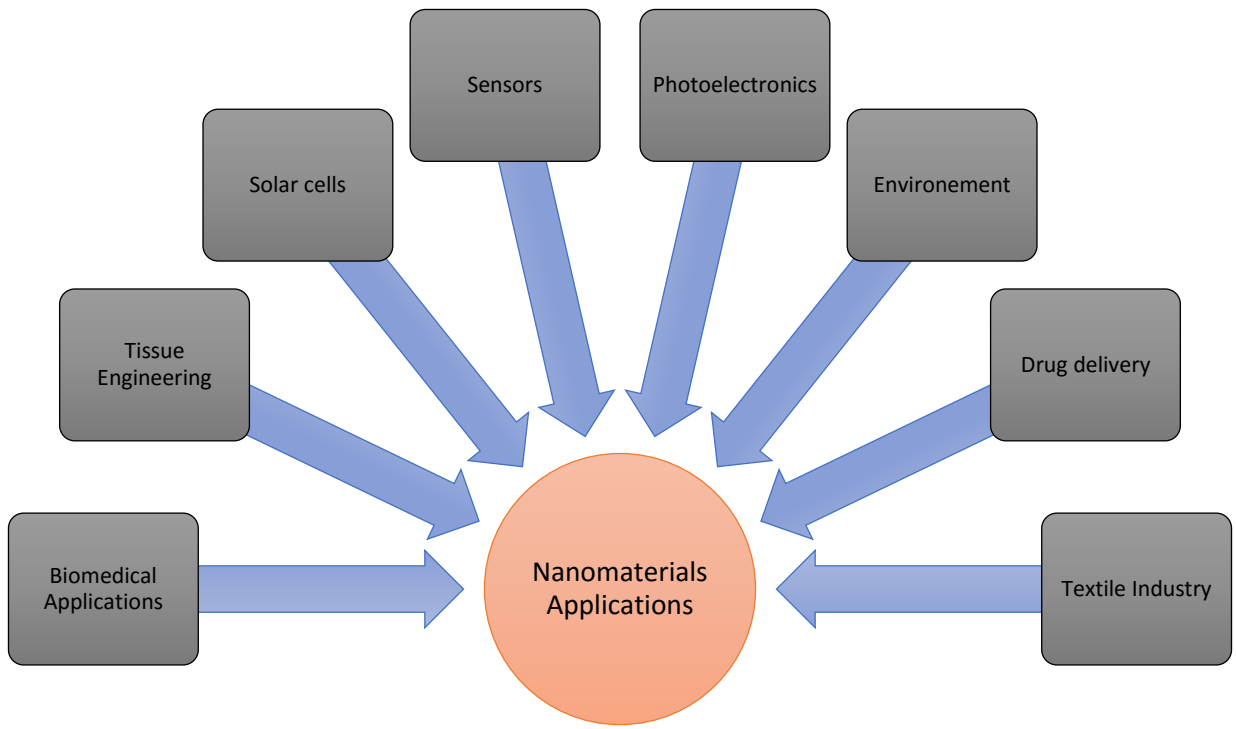
Figure 1.2 Applications of nanomaterials

Nanomaterials have high surface to volume ratio and high number of dangling bonds which enhance their catalytic activity. Many nanoparticles such as Au, NiO and bimetallic Ni-Fe have been used in methanol electro-oxidation and also for ammonium perchlorate thermal decomposition and dehydrodechlonation of trichloroethylene to hydrocarbons respectively [12-14].

Noble-metal nanoparticles have exceptional optical properties due to phenomenon of surface Plasmon resonance. Based on these features, nanoparticles of gold have been exploited to detect DNA and proteins in different assay types. In commercialized

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biomedical assays oligonucleotide coated Au nanoparticles have been used for ultra-sensitive identification of biomarkers for various ailments [15, 16].

In dye sensitized solar cells, TiO_2 thin films and nanoparticles have been used as photo anodes and the highest efficiency around 20% has been obtained by such materials. In order to create portable and economical LEDs nanomaterials have been used. Many nanomaterials like NiO, PbTe, PbSe and silicon nanowires etc are reported to be used in energy storage applications. [17-19].

Nano titanium dioxide and silver dioxide nanoparticles have been exploited in range of areas such as textile industries, antibacterial applications, drug delivery and in tissue engineering etc [20, 21].

1.4. Synthesis of Nanomaterials

Nanomaterials can be synthesized generally by two approaches,

- Top down approach. In this approach macrostructures are milled or etched to form nanostructured materials.
- Bottom up approach. In this approach the nanomaterials are synthesized by self-assembly and chemical synthesis method.

The various synthetic methods reported for the synthesis of nanomaterials are summarized in the Table 2.

Table 2 Synthetic routes for nanomaterials

Top-Down Procedures (Physical methods)	Bottom-Up Procedures (Chemical Methods)
Laser Ablation	Sol-Gel method
Chemical Vapour Deposition (CVD)	Spray pyrolysis
Ball milling	Thermolysis
Electro Deposition	Micro Emulsion

These conventional physical and chemical methods produce toxic by-products and also, hazardous chemicals are required to transform bulk or macro materials into nanoparticles. Another problem associated with the use of these chemical methods is that toxic molecules and surfactants adsorb or bind at the surface of nanoparticles which prevent their usage in various applications such as in biomedical science.

1.5. Green Nanotechnology

Green nanotechnology means how nanotechnology can be useful for the environment, by using eco-friendly materials and recycling of products, less energy will be used in the manufacturing processes [22, 23]. Industrial revolution in twentieth century results in formation of huge quantity of harmful products that not only pose health risks to humans but also to our environment. Now, scientists are trying to mitigate this problem by introducing facile and green methods for synthesis of nanoparticles. These "green" nanotechnology processes use environmental friendly reactants and conditions. Different methods are being introduced for synthesis of nanoparticles using "green Chemistry" principles. Green nanotechnology not only promotes basic research but also goal-oriented research in both academic and engineering fields for the synthesis of Green Nanoparticles (GNPs).

1.6.   Green Methods for the Synthesis of Nanoparticles

In last decade, different scientists explored plant and microbe mediated protocols for the synthesis of nanoparticles. Microbe mediated procedures are not as popular as plant mediated synthesis because usually professionals are required to prepare cultures and also it's important to control pH and temperature [24].

On the other hand, plant mediated production of nanoparticles have several advantages. Synthesis of nanoparticles using this method is fast, facile and simple. Plants contain phytochemicals including, enzymes, proteins and amino acids that play role in stabilization and biogenic production of nanoparticles [25, 26]. To date, very few studies have been carried out for the biological synthesis of palladium NPs using plants extracts.

Researchers have synthesized Ag, Au, Pd, Zn, Pt and other nanoparticles using plants extract [27]. Ag nanoparticles have remarkable importance in the area of diagnosis, catalysis and highly specific biomolecular detection [28, 29]. Many researchers have reported green methods for the synthesis of silver nanoparticles. These nanoparticles are the subject of substantial research in medical and industrial processes [30, 31].

Similarly, gold nanoparticles have high technological applications such as in the field of organic photovoltaics, sensory probes, drug delivery, and catalysis and in electronic conductors due to their distinctive optical and electronic properties. Recently, many researchers' synthesize Au nanoparticles using plant extracts [27]. Similar to gold and silver nanoparticles, many other nanoparticles have also been synthesized using plant extracts and have been used for various purposes.

1.7.   Problem Statement

Conventional physical and chemical methods use harmful and toxic reagents which pose danger to human body and to our environment. To overcome these difficulties, scientists are now using "Green methods" for the formation of nanoparticles. Green chemistry has lot of advantages as shown in Figure 1.3.
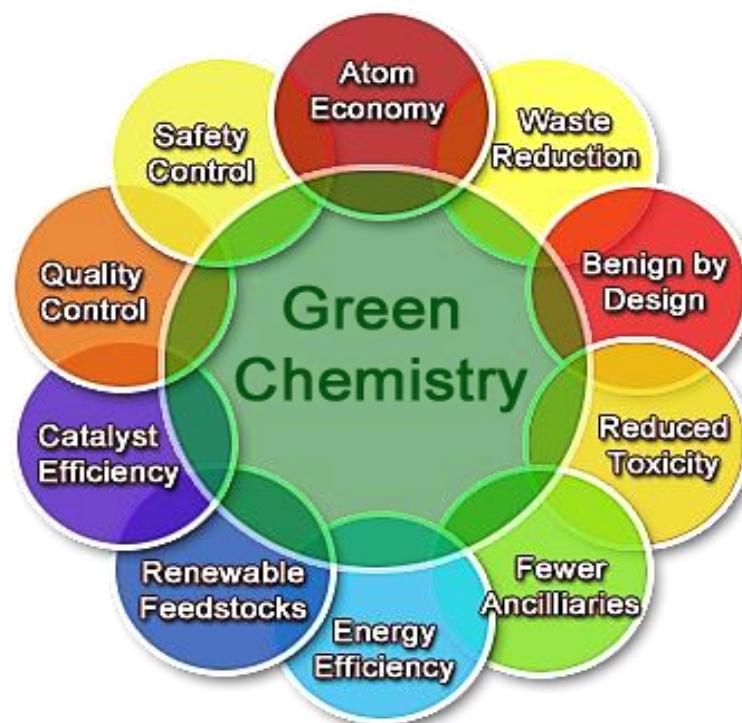
Figure 1.3 Advantages of Green Chemistry [30]

The aim of green methods is to minimize the toxic and hazardous effects of chemical and physical synthesizing methods and green chemistry is considered as designing those methods that would prevent production of hazardous wastes which pose health risk to human body and threat to environment. There are several advantages of using plant extract which are as follow:

- The biogenic production of metallic nanoparticles such as gold, silver, palladium and platinum using plants (extracts of plants, living plants and inactivated plants) is usually considered as suitable alternative to physical and chemical procedures.

- Metallic nanoparticle production using plant extract is very cheap and therefore for bulk production of nanoparticles, plant mediated synthesis provides economical and valuable alternative.

- Plant extract acts as both reducing and stabilizing agent for production of metallic nanoparticles.

- Biomolecules such as enzymes, amino acids, proteins and vitamins are usually present in the extract of plant and this method is environmentally friendly.

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1.8. Objectives

The aims and objectives of this research are

- Green synthesis of palladium NPs using extract of *Malus domestica*
- Characterization of palladium NPs
- Investigation of catalytic potential of Pd NPs in the Suzuki coupling reactions

Malus domestica is a fruit which are rich with several phytochemicals such as flavones, proteins and ascorbic acids.

Plant mediated synthesis of palladium nanoparticles have advantages such as ease of preparation at low cost, tunable catalytic activities and range of sizes and composition can be obtained. Properties such as ease of handling and storage over long period of time provide significant advantages of using plant mediated synthesis of nanoparticles.

Chapter 2

Literature Review

2.1. Palladium Nanoparticles

In the periodic table Palladium belongs to group 10. Its outermost electron shell configuration is (Pd $4d^{10}5s^{0}$) which is very much different in comparison to other members of group e.g. (Ni $3d^{8}$ $4s^{2}$; Pt $5d^{9}$ $6s^{1}$). In Pd configuration the totally vacant fifth O-shell is an exceptional phenomenon that changes its properties from other members of group 10. It has lowest melting point and is least dense. In concentrated nitric acid and in concentrated sulphuric acid Pd dissolves slowly. Pd exists in 0, +1, +2 and +4 common oxidation states, though +3 and +6 oxidation states has also been reported. Pd shows +3 oxidation states unambiguously in few compounds and in cross coupling reactions such compounds have been proposed as intermediates.

2.2. Applications of Palladium Nanoparticles

Palladium nanoparticles have extensive applications in the fields of catalysis.

2.2.1. Palladium Nanoparticles as Catalysts

Palladium (Pd) plays a key role in chemical reactions and also in pollution reduction. In many industrial applications, PdNPs are used as catalysts such as automobile exhaust cleaning, preparation of vinyl acetate and acetylene hydrogenation. Blackburn and Schwartz published the first successful reaction of Pd catalysis involving aerobic oxidation of secondary alcohols to ketones in 1977 [32]. After that, reactions involving oxidations with palladium catalysts were studied for glycerol [33], α,β-unsaturated alcohols [34], benzyl alcohol [35], and 2- hexane [36].

2.2.2. Suzuki Coupling Reactions

In 1979, Suzuki coupling reaction was first published and considered as one of the most important C-C bond formation reaction [37].
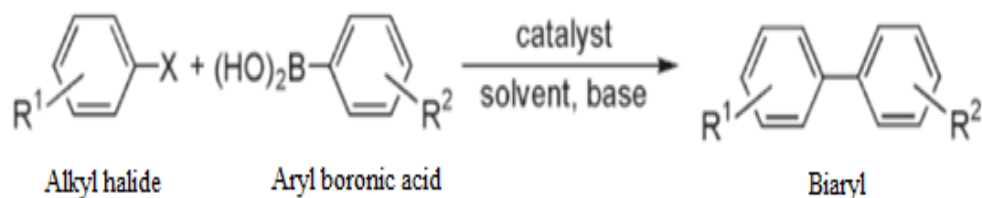
Figure 2.1 Schematic rep. of Suzuki coupling reaction [37]

Figure.2.1 shows generic scheme for the Suzuki coupling reaction which occurred with the support of catalyst in the basic media when aryl boronic acid reacts with alkyl halide and results in C-C bond coupling and formation of biaryls. This reaction has several advantages and these biaryls acts as intermediates in polymer synthesis, intermediates in pharmaceuticals and also in advanced materials.

This reaction is very popular due to its versatility for the synthesis of biaryls. Under these reaction conditions, not only variety of functional groups can be used to synthesize different intermediates which are further used in the synthesis of complex drug molecules. Furthermore, the starting material of this reaction i.e. boronic acid is highly stable, nontoxic and highly selective for cross coupling reactions.
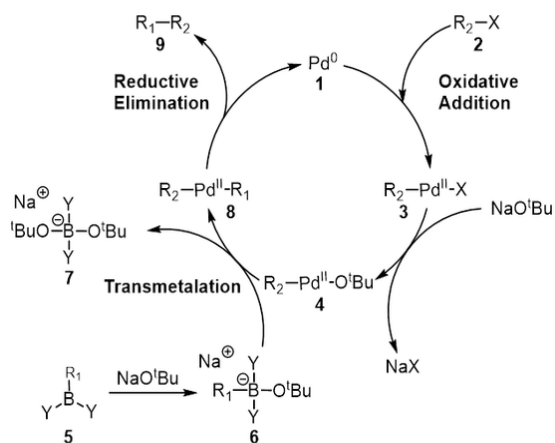
Figure 2.2 Scheme for Suzuki coupling reaction [37]

The scheme for the Suzuki coupling reaction is given in Figure 2.2. The first step of this reaction is oxidative addition, where Pd catalyst attaches to the halide which

results in the increase of oxidation state of palladium catalyst from 0 to 2. In the next step, base which is present is solution helps in the activation of boronic acid which results in enhancement of ligand polarization. It results in transmetalation of reaction. Base also plays role in the enhancement of nucleophilicity of organic group of boron atom. On the other hand, aryl palladium halide plays role to form alkoxy palladate. Reductive oxidation is the last step of reaction which regenerates Pd (0) catalyst and also releases biaryl products. Palladium catalyst which is regenerated from the reaction can be used in other reactions as a catalyst.

After the synthesis of palladium nanoparticles, wide ranges of palladium nanoparticles have been exploited as a catalyst in various reactions. Nanoparticle have high surface to volume ratio so they show higher catalytic activity than bulk materials. For nanoparticles, no ligands are often required as pre catalyst. High turnover number (TON) of the product was due to low concentration of metal in solutions. Therefore, after exploitation of PdNPs as a catalyst in Suzuki coupling reactions it provides facile procedure that results in low production cost.

2.3.   Syntheses of Pd NPs

2.3.1. Chemical and Physical Procedures

For the production of PdNPs, different physical and chemical properties have been studied over the last decade. Synthesis of palladium nanoparticles has gained much interest in the scientific community due various applications of palladium nanoparticles. These palladium nanoparticles are successfully used in the field of catalysis, plastics coatings, fuel cells and sensors applications [38, 39]. The biologically inspired procedure for the production of nanoparticles is becoming a main branch of nanotechnology. Generally two approaches are used for the synthesis of Pd nanoparticles. The first approach is "top down approach" while second one is "bottom up" approach. In bottom up approach, nanoparticles are usually synthesized by self-assembly of atoms and molecules. These self-assembled atoms and molecules form

nuclei and then grow into particles of nanoscales [40]. However, in the top down technique bulk substance is broken down into small sized particles either by grinding, milling or by thermal and laser ablation methods [41].

In bottom up approach, chemical synthesis methods are the most promising mean for the production of nanoparticles. Various organic and inorganic reducing agents have been investigated for the formation of nanoparticles [42]. Most frequently used reducing agents are ascorbic acids, sodium borohydrides, block copolymers and poly ethylene glycol. Similarly, for the stabilization, different capping agents are used. These methods have several advantages such as large quantity of nanoparticles produced, fast reduction etc. However, these methods results into environmentally toxic by-products. Therefore, biogenic methods become a growing wanton due to eco-friendly procedures.

A bunch of chemical procedures have been studied so far for the formation of Pd nanoparticles. The two more common types of procedures for the formation of Pd nanoparticles are free space and confined space reduction methods. These confined free space methods involve use of reverse micelle, dendrimer and mesoporous material [43, 44].

Water/sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/nheptane micro emulsion method has also been used for the synthesis of Pd nanoparticle [45] where fixed ratio of AOT and water play crucial role for the formation of Pd nanoparticles. However, effect of pH and temperature is less crucial in this case. It is an example of reverse micelle procedure for the production of Pd nanoparticles. These methods involve two main principles including controlling interaction between micelle and by manipulating interfacial properties [46].

Similarly, Minna Cao et al; used cucurbit[6] uril as a protecting agent for the production of Pd nanoparticles [47]. In this method molar ratio of cucurbit [6] and Pd salt played a key part in the synthesis of Pd nanoparticles. Such NPs used were in Suzuki–Miyaura cross coupling reaction.

2.3.2. Microbial Methods

Methods used for the synthesis of nanoparticles using microorganisms are widely reported. Among micro-organisms, fungi get scientific attention as fungi are considered as nano factories. Microbial methods are environmentally friendly and can easily be scalable. Various methods have been reported so far by using microbes as reducing and stabilizing agents. A sulphate reducing bacterium, Desulfovibrio desulfuricans (NCIMB 8307) have been used as a reducing agent for the production of palladium nanoparticles [48]. This bacterium anaerobically reduces and stabilizes Pd nanoparticles. The reduction occurs in few minutes in the presence of formate as an exoreic electron donor. Similarly, De Windt et al;[49] used a bacterium *S. oneidensis* MR-1 for the reduction of Pd(II) salt to Pd(0) salt in the presence of formate which acts as an electron donor. The reduction occurs on the surface of cell wall of the mentioned bacteria and colour of biomass changed to black at the end of the reaction.

2.3.3. Plant Mediated Synthesis

Earlier, it was believed that plants have the potential to degrade accumulated metallic ions from their nearby environment. Now scientists could identify the reason behind plants role in the reduction and stabilization of inorganic metallic ions. It has been observed that organic entities present in plants play vital role in the reduction and stabilization of nanoparticles.

| Plant extract | Metal ion solution | Extract +Metal ion soln. | Synthesis process | Nanoparticle formation |

Figure 2.3 Plant mediated Synthesis of nanoparticles [50]

Usually living plants are used for the synthesis of nanoparticles as shown in Figure 2.3. Often, plant leaves, shoots, roots and fruit extracts have been exploited for this purpose. Plants extracts contains some important constituents such as enzymes, alcohols and other phytochemicals that play crucial role in the reduction of metallic salt as shown in Figure 2.4. In these syntheses methods, wide range of sizes and shapes of nanoparticles have been obtained which could be attributed to the presence of these energetic bio molecules in the living plants and their collaboration with aqueous metallic salt solution. These methods have several advantages including simple working environment such as pH and temperature. Since most of the reactions are carried out at room temperature by simple mixing of metallic salt and plant extract.
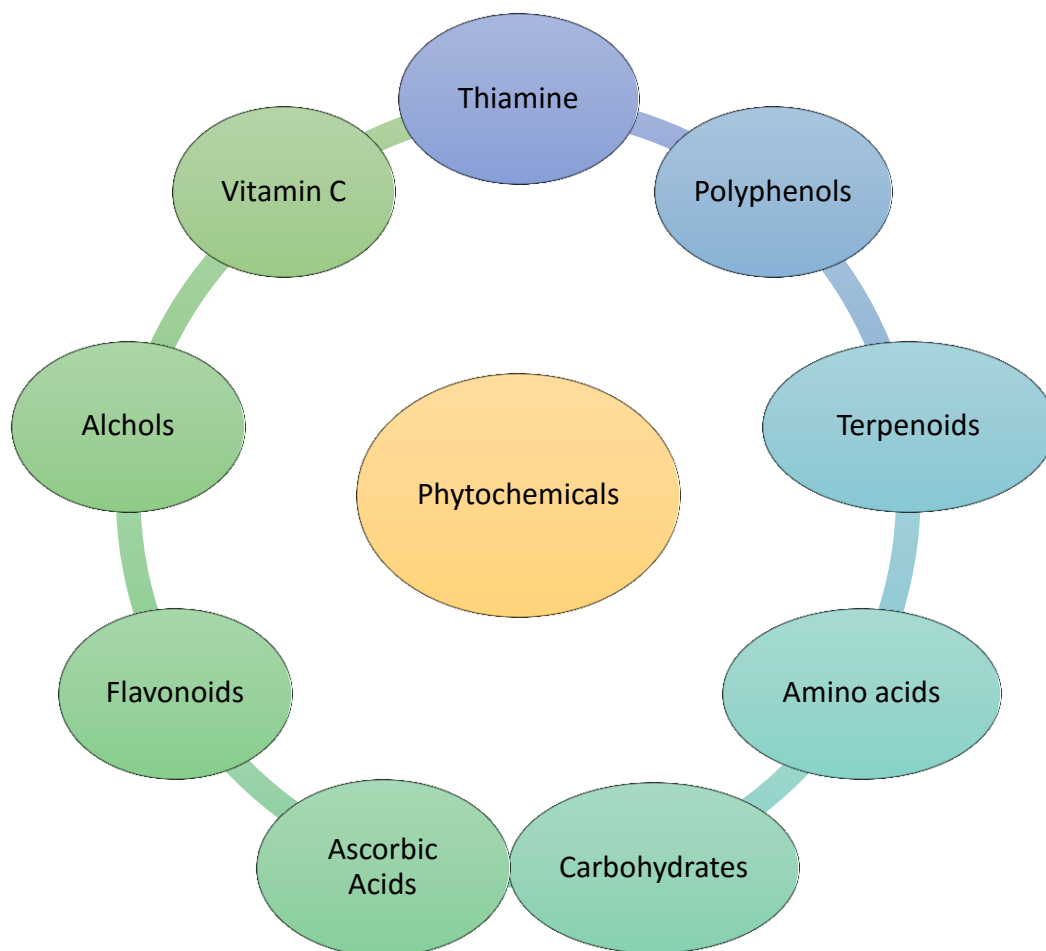
Figure 2.4 Role of Phytochemicals in formation of PdNPs

So far, scientist used only few plants for the production of Pd nanoparticles e.g. 4.5nm sized Pd nanoparticles were obtained using dried powder of *Anacardium occidentale* leaf [50] whereas morphology as well as shape of nanoparticles were analysed by TEM. In this case, researchers have added 300mg dried powder of the mentioned plant to the aqueous solution of PdCl$_2$ salt. Under constant stirring and at 80 $^{\circ}$C temperature, reduction was carried out to obtain dark brown colour. Leaves of the plant contain lot of polyols which were considered to play crucial part in reduction of Pd (II) salt (Figure 2.5).
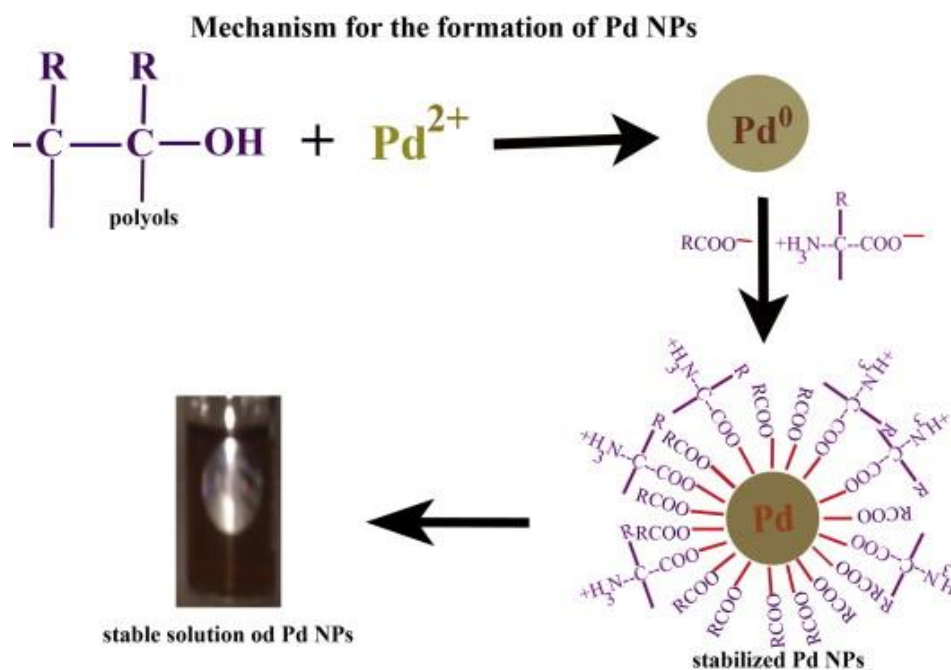
Figure 2.5 PdNPs synthesis mechanism by using *A. occidentale* [50]

Similarly, without any surfactant and extra reagent, only broth of Cinnamomum camphora leaf was used as reducing agent for salt of Pd [51]. By varying initial concentration of Pd ions, different ranges of Pd nanoparticles were produced. The average size was 6.0nm. The mentioned plant broth contains huge amount of polyols and heterocyclic constituents which were assumed to stabilize the nanoparticles. Furthermore, 15nm sized Pd nanoparticles were obtained using Soybean (Glycine max) leaf extract [52]. In UV-Vis spectroscopy Pd^{+2} ions showed absorption peak at 420nm which

disappeared after forty eight hours, indicating the formation of Pd nanoparticles. According to authors, proteins and amino acids found in the leaf extract of the plant supported the reduction of Pd^{+2} ions. Similarly, dried fruit extract of Gardenia jasminoides Ellis has some antioxidants constituents including, geniposide, chlorogenic acid, crocins and crocetin compounds [53]. These compounds contained hydroxyl groups, carbonyl and carboxylic compounds which played crucial role for the synthesis of nanoparticles. In this case after 1.5 hours, the initial orange colour which was due to crocetin was disappeared and dark brown colour formed, indicating the formation of Pd nanoparticles. Colour of solution remains unchanged even after twelve hours and the obtained nanoparticles had face centered cubic structure. TEM image showed that particles have spherical, rod like and polyhedral structures. The particles were uniformly dispersed at 70 ^{0}C. In a similar study, average size of 20nm of palladium nanoparticles were synthesized by using leaf extract of *Artemisia annua* [54]. This plant extract is rich in polyols and compounds with carbonyl groups which were considered to be the reason for Pd (II) salt reduction. These synthesized nanoparticles were further used as a catalyst where it was observed that nanoparticles were regenerated many times without reduction in their catalytic activity.

A recent study showed the formation of Pd nanoparticles with 38nm size using methanolic extract of *Catharanthus roseus* leaf [55]. The reaction was completed at 60°C in one hour. UV-Vis spectroscopy showed absorption spectra in range of 360-400nm. Since extract is rich in compounds with hydroxyl groups, such compounds played important role in the reduction of metallic salts (Figure 2.6).
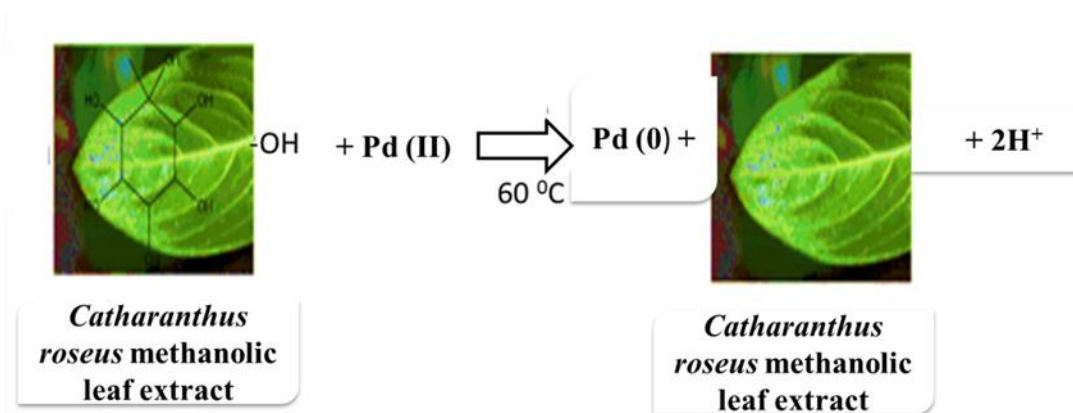
Figure 2.6 Pd (II) ions reduced by the *C. roseus* extract [55]

In another study, *Delonix regia* leaf extract was studied for production of Pd nanoparticles [56]. The average size obtained in this experiment was 2-4nm and calculated mean diameter was 19nm. Water-soluble phenolic acid and flavonoid constituents present in the extract of plants could likely play role for the Pd (II) ions reduction (Figure 2.7).
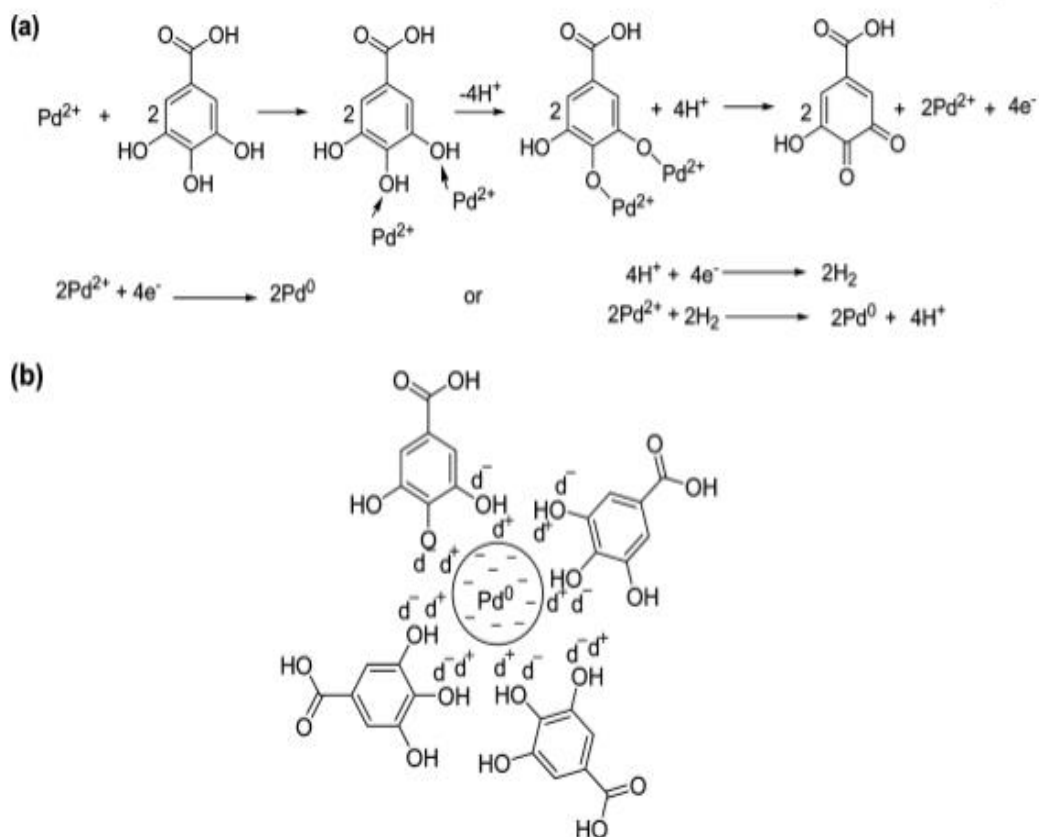
Figure 2.7 (a) Reduction of PdCl$_2$ salt (b) Gallic Acid role in Pd-NPs formation [56]

Figure 2.7 demonstrates reduction mechanism of Pd (II) salt using gallic acid. Gallic acid is at the ring of benzene, while hydroxyl groups performing reduction process and Pd (II) salt is converted to Pd (0) nanoparticles. Gallic acid formed an intermediate with PdCl$_2$ salt thus helped in the oxidation of gallic acid. This complex played role in transformation of gallic acid to quinone Pd^0 NPs formation.

Moreover, some medicinal plants like *Coleus aromaticus* and *Myristica fragrans* were also studied for PdNPs formation [57]. From the leaves of these plants usually essential oil was extracted which was used as reducing and stabilizing agent for PdNPs formation. The average size of particles obtained in this case was 2.8nm. This extract contained terpenoids and phenolic ether derivatives which were assumed to play role in reduction of Pd (II) salt. These nanoparticles played an important role in the organic

pollutants degradation such as methyl red, methyl orange, eriochrome black T, methylene blue, rhodamine B, ortho-, meta- and para-nitrophenols

In another report, Hippophae rhamnoides Linn leaf extract was exploited for the growth of palladium nanoparticles [58]. The synthesized Pd nanoparticles were characterized by using techniques such as XRD, FTIR, UV-Vis spectroscopy and SEM. The plant was rich in polyphenols such as flavonoids and phenolic compounds which were actually supposed to do $PdCl_2$ reduction and stabilization. Range of sizes was observed between 2.5nm to 14nm and their catalytic activity was further observed in Suzuki Miyaura coupling reactions. 100 percent yield of product was obtained when iodobenzene reacted with phenylboronic acid and PdNPs were used as a catalyst. In another report, leaf broth of *Piper betel* was exploited for the Pd nanoparticles synthesis [59]. The produced NPs had spherical shape with the size of 4±1 nm. Further study suggested that flavonoids and proteins found in extract played role in reduction and stabilization process.

In a similar report, researchers employed leaf extract of *Solanum trilobatum* to photo-synthesized Pd NPs [60]. The reaction between $PdCl_2$ salt and plant extract occurred at room temperature. Similarly, in another report, *Andean blackberry* leaf extract was also reported to use for Pd nanoparticles synthesis [61]. These nanoparticles were crystalline in nature with shape of decahedron and diameter of 55-60nm.

Table 3 Plants and parts used for synthesis of Pd nanoparticles

Plant	Part used	Size and shape of NPs obtained	Biomolecules involved	Reference
Anacardium occidentale	leaves	2.5-4.5nm, spherical	polyols and proteins	[50]
Andean blackberry	leaves	55-60nm, decahedron	flavonoids, ellagic acid, tannins	[61]
Artemisia annua	leaves	20-30nm, spherical	polyols	[54]
Catharanthus roseus	leaves	38nm, spherical	4-methylmyoinositol	[55]
Cinnamomum camphora L.	leaves	3.2-6.0nm, quasi-spherical	flavones, terpenoids and polysaccharides	[51]
Delonix regia	leaves	2–4nm, shape not given	water soluble polyols	[56]
Soybean	leaves	~15nm, spherical	proteins, amino acids	[52]

Table 3 shows a range of plants whose leaf extracts have been studied for synthesis of Pd NPs. The data also shows the constituents (biomolecules) concerned with the synthesis of Pd nanoparticles and their size and morphology is also discussed in Table 3.

Similar to leaf extract, extract of some fruits have also been exploited for synthesis of Pd nanoparticles. In a recent study, *Berberis vulgaris* fruit extract was used

for reduction of Pd (II) ions into Pd nanoparticles [62]. The reaction was performed at 80 °C. It only required 10 minutes for completion of reaction. Flavonoids, vitamin C, phenolic acids and similar compounds present in this fruit extract of this plant were considered have function as reducing and stabilizing agents for Pd (0) nanoparticles synthesis. Formation of PdNPs using barberry fruit extract is shown in the Figure 2.8. The major phytochemical in this extract was vitamin C that reduced metal ions to nanoparticles. The primary structure had some hydroxyl groups and it underwent oxidation-reduction reaction. As a result of this reaction, transfer of electrons takes place and NPs are formed after reduction of Pd (II) ions. Authors further investigated catalytic activity of Pd nanoparticles. For the reduction of nitroarenes to amines, reaction occurred at 50 °C temperature in the presence of 1:2 alcohol water mixtures. The catalytic activity was investigated by researchers and observed that nitrobenzene reduced to aniline with the help of sodium borohydride. The phenomenon of reduction occurred on the surface of catalyst and the rate of reaction depended on the degree of adsorption of nitro compounds on the surface of catalyst. The catalyst was used five times and no significant reduction in their catalytic activity was observed.
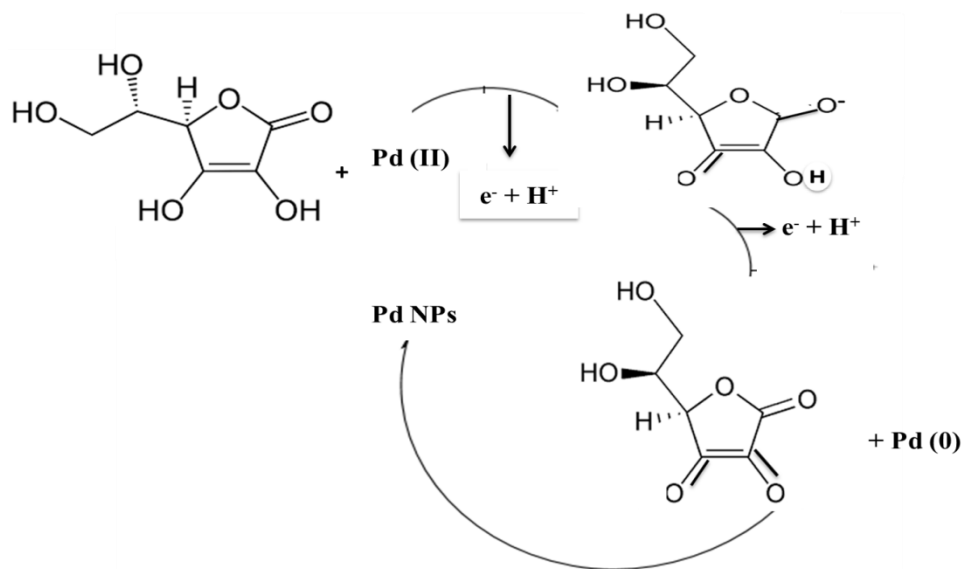
Figure 2.8 PdNPs synthesis using extract of *B.vulgaris* [62]

Similarly, *Pistacia Atlantica* fruit extract has constituents such as phenolic and triterpenoidic groups [63]. For the synthesis and stabilization of NPs, the extract was

studied and these groups were present in excess in the mentioned plant and were responsible for reduction of Pd^{2+} ions. The average size of synthesized PdNPs 60nm with spherical morphology for as prepared PdNPs. In another report, peel extract of *Annona squamosa L* was used for the formation of Pd nanoparticles from Pd $(OAc)_2$ solution [64]. At 60 °C reaction was carried out and PdNPs obtained had spherical morphology with size in the range of 80 ± 5 nm. Water soluble hydroxy functional groups in the plant extract are assumed to start the process of reduction. These compounds also act as stabilizing agents. In addition, extract of *banana* peel also helps in Pd (II) salt reduction [65]. This extract has carboxyl, amine and hydroxyl groups that help in the reduction of Pd (II) salt. The reaction carried out at 80 °C took only three minutes to complete. The size of these synthesised NPs was found to be around 50 nm.

The summary of plants where fruit extracts has been used for reduction of salt is given in Table 4. The nature of constituents (biomolecules) present in the plant extract and their morphology and average size is also given in the table. It shows that compounds with -OH groups plays role in reduction of Pd (II) salt.

Table 4 Plant and parts used for the production of Pd (0) nanoparticles

Plant	Part used	Size/shape of NPs obtained	Biomolecules involved	Reference
Annona squamosa L	fruit peel	80±5nm, spherical	hydroxyl groups	[64]
Banana Peel	fruit peel	50nm, crystalline	Carboxyl groups	[65]
Berberis vulgaris	fruit	18nm, spherical	phenols, flavonoids	[62]
Gardenia jasminoides Ellis	fruit	3–5nm, shape not given	chlorogenic acid,	[53]
Pistacia atlantica	fruit	60nm, spherical	water-soluble polyols	[63]

Extract of other parts of a plant also have been found to play role in reduction of salts. In one of studies, *Antigonon leptopus* which is a famous terrestrial weed had constituents such as flavonoids, phenolic acids and proteins [66]. The extract of these weeds had been studied for the synthesis of Pd nanoparticles. In this experiment, reaction between $PdCl_2$ salt and weed extract was performed at 95 °C. The reaction completed within five minutes and the indication for synthesis of PdNPs was conversion of light yellow colour to dark brown colour. In another report, extract of *tea and coffee* was used for the production of Ag and Pd nanoparticles [67]. All these nanoparticles were produced in bulk amount and the average size of particles was around 20-60 nm. The reaction was performed at room temperature and the prepared PdNPs had spherical shape. In this plant extract polyphenols were present which were considered to have a function in reduction and stabilization of nanoparticles. In another report, *Asparagus racemosus Linn* root extract had been investigated for the formation of Pd and Pt nanoparticles [68]. These nanoparticles were highly stable and the average size of

particles was in the range of 1-6nm. They were highly crystalline with spherical morphology. In the extract phototropins and flavones were supposed to act as reducing agents for the formation of Pd nanoparticles. In addition, Cinnamom *zeylanicum* bark extract had compounds for example linalool, cinnamaldehyde and methyl chavicol. These compound have specific aroma and are used for reduction of Pd salt. In the bark of *Cinnamom zeylanicum* polyols which includes terpenoids, flavones and polysaccharides were mostly present which acted as reducing and stabilizing agents [69]. Hearth wood extract of *Artocarpus lakoocha Roxb* had also been reported for production of Pd nanoparticles [70]. For Suzuki and Heck coupling reactions, cellulose supported Pd NPs were supposed to play an important role as shown in Figure 2.9. The average size of particles was 10-30nm size. They have higher stability, with high crystallinity and have spherical morphology.
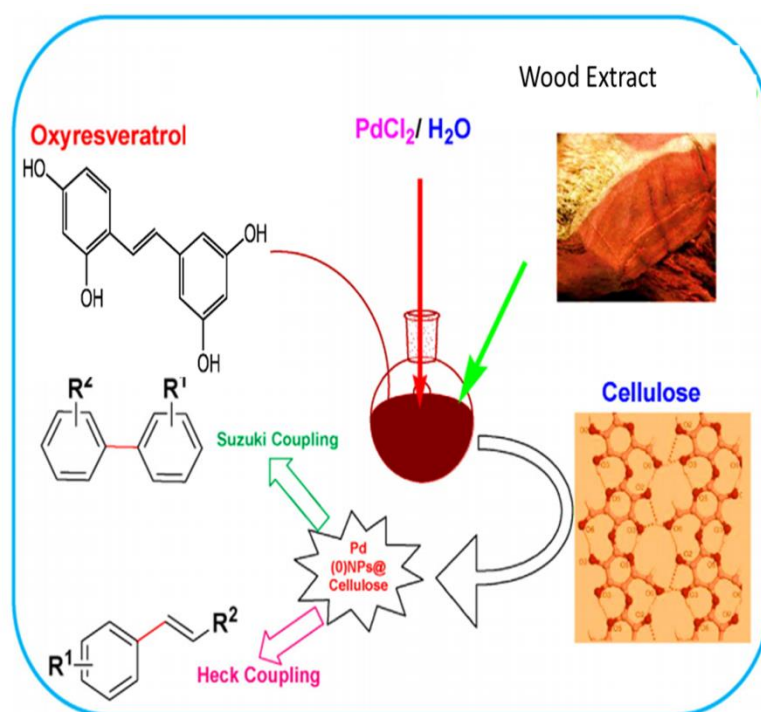
Figure 2.9 PdNPs Synthesis and its application in Suzuki Heck Coupling reaction [70]

A recent report shows *Pulicaria glutinosa* extract was used for formation of PdNPs [71]. These synthesized nanoparticles show enhanced catalytic activity in Suzuki coupling reactions. This plant had excessive amount of hydroxyl groups which were

actually responsible for reduction process. Flavonoids, polyphenols and presence of other phytochemicals in plant extract played a vital role in synthesis of NPs. *Terminalia chebula* extract has also been studied for the production of Fe and Pd nanoparticles [72]. Size was estimated to be 80nm for amorphous iron while less than 100nm size for cubic Pd nanoparticles. In the plant extract, polyphenol compounds present were supposed to play vital role of reducing and capping agents. Moreover, *Vitis vinifera* extract was exploited for Au, Ag, Pt and Pd nanoparticles synthesis where Pd nanoparticles have spherical morphology [73]. They have size in the range of 5-10nm. In this case, for Pd (II) ions reduction again polyphenols were considered to be responsible. Reaction between *Euphorbia granulates* plant extract and $PdCl_2$ salt was performed for five minutes [74]. The temperature for reaction was maintained at 80 °C where reduction was due to existence of flavonoids and phenolic acids in the extract.

Several reports suggested that natural plants polymers also played role in synthesis of NPs. For example, *Anogeissus latifolia,* popularly known as *"gum ghatti"* had been studied for the production of Pd nanoparticles [75]. The size obtained was about 4.8nm size. In this plant compounds like carboxylic, hydroxyl groups and proteins were assumed to be responsible for stabilizing these nanoparticles.

Table 5 Other parts of Plants used for Synthesis of PdNPs

Plant	Part used	Size/ shape of NPs obtained	Biomolecules involved	Reference
Anogeissus latifolia	gum	4.8±1.6nm, spherical	hydroxyl, carboxylate groups, proteins	[75]
Asparagus racemosus Linn	root	1-6nm, spherical	phototropins, flavones	[68]
Artocarpus lakoocha Roxb	hearth wood	10-30nm, spherical	hydroxyl groups	[70]
Cinnamomum zeylanicum Blume	bark	15–20nm, spherical	terpenoids	[69]
Gum olibanum	gum	6.6nm, spherical	Hydroxyl/carbo xylic groups	[76]
Pulicaria glutinosa	whole plant	20-25nm, spherical	flavonoids and polyphenols	[71]
Red grapes	pomace	5-10nm, spherical	polyphenols	[73]
Tea and coffee extract	coffee/tea powder	20–60nm, spherical	caffeine/polyph enols	[67]

The summary of plants where root and gum extracts has been used for reduction of salt is given in Table 5.

Similarly, *gum olibanum*, which is a biopolymer were used for the Pd (II) ions reduction into Pd (0) NPs. The NPs formed were spherical shaped, polydispersed and 6.6 ± 1.5nm in size [76]. In the gum hydroxyl/ carboxyl groups and proteins were again considered to be liable for the reduction of Pd salt. *Sour cherry* tree gum was used for the

formation of Pd nanoparticles [77]. The average size was about 5± 2nm with spherical morphology.

For environmental remediation, bimetallic nanoparticles played most important role. By using plant extracts several bimetallic nanoparticles have already been synthesized. In this connection, grapes leaf extract was used for the synthesis of Fe/Pd nanoparticles. Such nanoparticles have been exploited in removing orange II in 12 hours and also as the environmental remediation. Similarly, *Cacumen Platycladi* leaf extract was used to produce Au/Pd nanoparticles [78]. The average size of particles were 7.4 nm and water soluble polyhydroxy biomolecules like flavonoids and reducing sugars played a vital function in reduction of Pd salt. In another study, *Myrtus communis L.*leaf exract was used for synthesis of Pd/TiO$_2$ nanoparticles [79]. *Theobroma cacao L.* seed extract was also used for the formation of Pd/CuO nanoparticles [80]. It has compounds such as flavonols for example; epicatechin, catechin and their polymeric derivatives have an important role in the reduction process. Average size of Pd/CuO NPs was about 40nm. Pd/CuO nanoparticles synthesis was performed in an aqueous media through phenolic antioxidant shown in Figure 2.10.
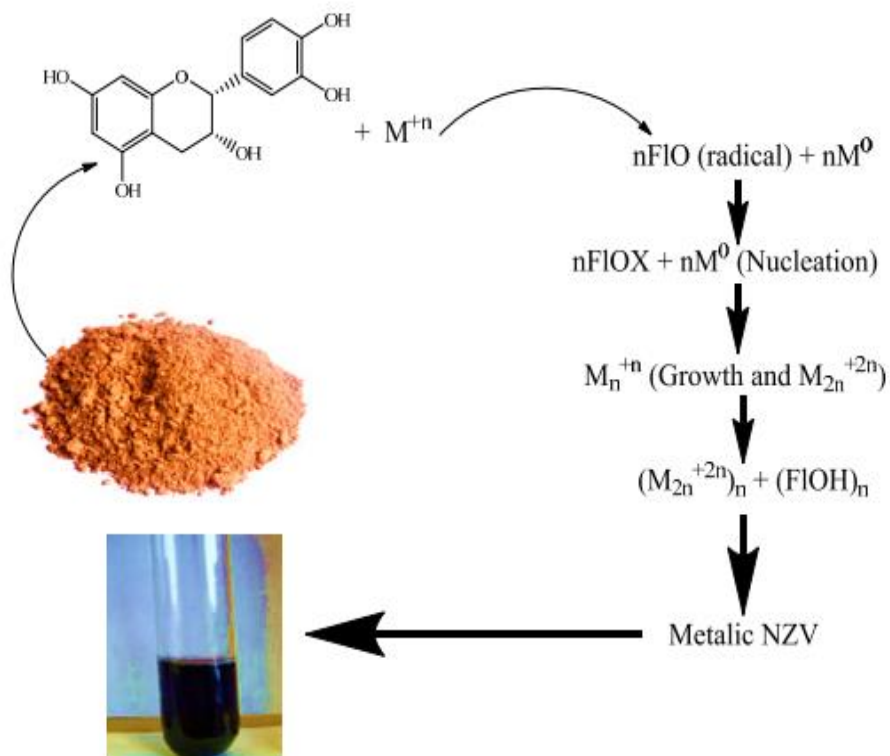
Figure 2.10 Synthesis of Pd/ CuO NPs by *Cocoa* seeds extracts [80]

Recently, for the production of magnetic catalysts as well as for heterogeneous catalysts numerous attempts have been made. For example, *Euphorbia stracheyi Boiss* root extract was studied for the production of Pd/Fe_3O_4 nanoparticles [81]. This was due to existence of phenolic constituents present in the extract. They had spherical shape with 10nm size. Similarly, *Euphorbia condylocarpa M.Bieb* root extract nanoparticles such as Pd/Fe_3O_4 had been synthesized [82]. In this investigation, flavonoids and phenolic acids in the extract were supposed to play role in the reduction process. The average size was about 39nm.

Chapter 3

Characterization Techniques

The following characterization techniques have been used to study synthesized Pd nanoparticles.

- X-ray diffraction to study the crystallographic structure.
- Scanning electron microscope was used to study surface morphology.
- Fourier transformation infrared spectroscopy.
- UV-Vis spectrophotometer (PG Instrument T90)
- Transmission Electron Microscope

3.1.   X-ray Diffraction (XRD)

X-ray powder diffraction (XRD) is a tool which is used for phase identification of a crystalline material. The material is first finely powdered and homogenized, so that its average bulk composition is analyzed. The XRD study of a crystalline material gives its structure and the spacing between consecutive atomic plans.

X-ray diffractometers consist of three basic elements i.e. an X-ray tube, a sample holder, and an X-ray detector. To produce X-rays first the filament is heated in a cathode ray tube. The heated filament produces electrons, which are then accelerated by the applied voltage to hit the target. These electrons produce the inner shell transition in the target material, which in turn produces the X-rays.

The X-rays produced are targeted towards the crystalline material where they suffer multiple diffractions while passing through the atomic plans of crystalline material. A diffraction pattern is observed using X-ray detector, and are then analyzed in terms of their intensity peaks, which are further studied to obtain the structure and atomic spacing of a crystalline material.

X-rays typically used in diffraction analysis penetrates to a depth of 1-2 μm, depending on the atomic number and density of sample. It is powerful technique for identification of unknown sample.

3.1.1. Bragg's Law

Constructive interference of X-ray beam and crystalline specimen is the core concept of X-ray diffraction technique. The constructive interference produced by the interaction of monochromatic X-ray beam and specimen must obey the Bragg's law.

In this law three parameters are related to each other as In powder X-ray diffraction the sample is randomly oriented so it is scanned in a range of 2θ angles and all possible orientations of diffracted radiations are recorded.

nλ=2dsinθ

Where,

λ = wavelength of incident light

θ = diffraction angle

d = line spacing (Inter atomic distance)

As the EMR fall on the sample they got diffracted according to the specific inter-atomic-spacing of each sample as shown in Figure 3.1. These diffracted X-rays are then detected, refined and estimated. In powder x-ray diffraction the sample is randomly oriented so it is scanned in a range of 2θ angles and all possible orientations of diffracted radiations are recorded.
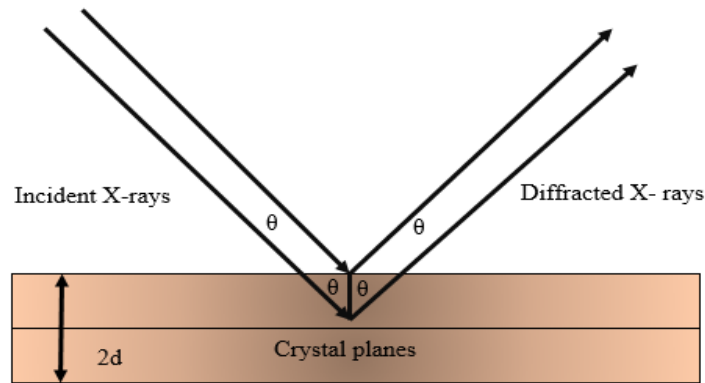
Figure 3.1 Schematics of Bragg's law

3.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a technique used to study materials surface. SEM gives an image with the magnification of about 10x-300,000x. It is not only used to obtain topographical data but also gives surface composition of the sample.

In SEM, specimen's surface data is obtained by interaction of an electron beam with the sample. This interaction results in the reflected or backscattered electron beam, which is collected and then displayed on a cathode ray tube (CRT). The image generated on screen shows the topographical data of the specimen.

An advantage of SEM is that a small amount of sample is required for analysis. Usually conducting sample is used, if the sample is an insulator, then coating of a thin film of some conducting metals such as gold and carbon are required. It is important that coating is uniform as improper coating leads to distortion or agglomeration of the coating material.

Interaction of Electronic Beam with Specimen

As the electrons interact with sample they get scattered into it. The scattering range depends upon the energy of electrons, atomic number and density of the constituent elements. This interaction happens via two ways i.e. elastic and inelastic collision as shown in Figure 3.2. As a result of elastic collisions b*ack scattered electrons* (BSE) are

produced and inelastic collisions generate *Secondary electrons* (SE)*, characteristic x-rays* and *auger electrons.*
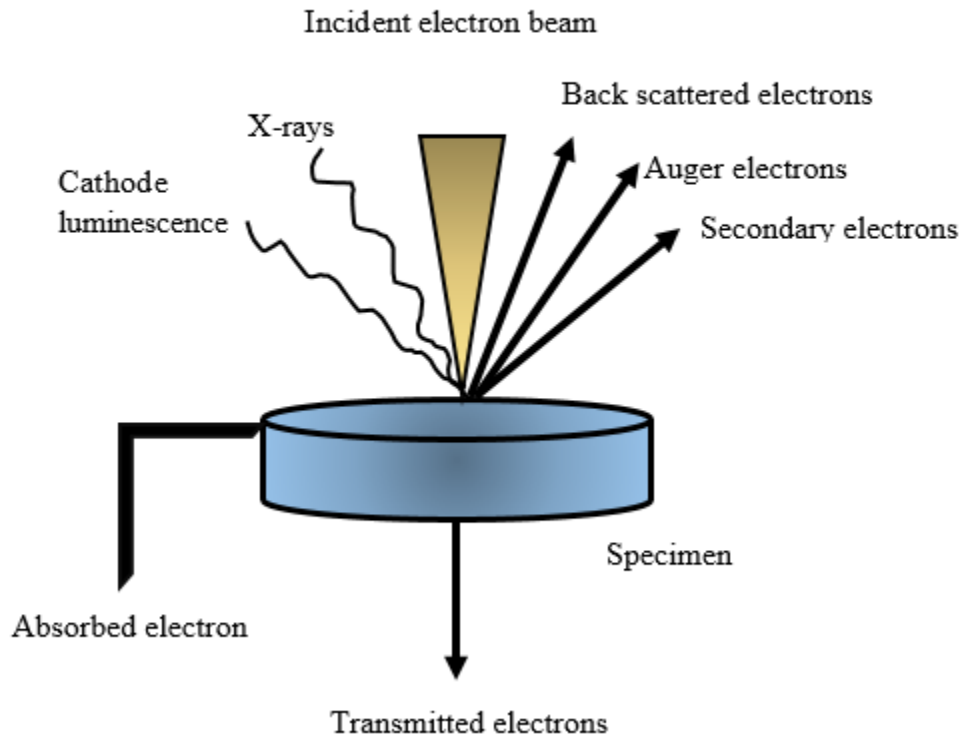
Figure 3.2 Scattering of electron beam after interaction with specimen

On cathode ray tubes, the signals emitted in the form of photons or electrons are collected and image is generated. On cathode ray tube, three types of images can be obtained.

3.3. Fourier-Transform Infrared Spectroscopy (FTIR)

Dispersive infrared spectrophotometer has several limitations including inaccuracies in wavelength, slow monitoring process, narrowness of focusing slit causing light loss and thus poor sensitivity. These imperfections in DIS lead to the development of FTIR.

FTIR overcomes all drawbacks associated with dispersive instrument and is a single beam technique. The fundamental principle of FTIR is based on interferometer

which produces interferogram and a mathematical tool known as Fourier transformation is used to process and analyse the resultant frequency spectrum. In order to analyse functional groups, bond types and impurity of samples, FTIR is used. The IR region is further divided into three sub regions known as:

- Far-IR (400-20 cm^{-1})
- Mid-IR (4000-400 cm^{-1})
- Near-IR (14000-4000 cm^{-1})

3.3.1. The Interferometer

An optical device used to measure infrared frequencies is known as interferometer. Interferometer produces unique types of signals known as interferogram, encoded with all infrared frequencies.
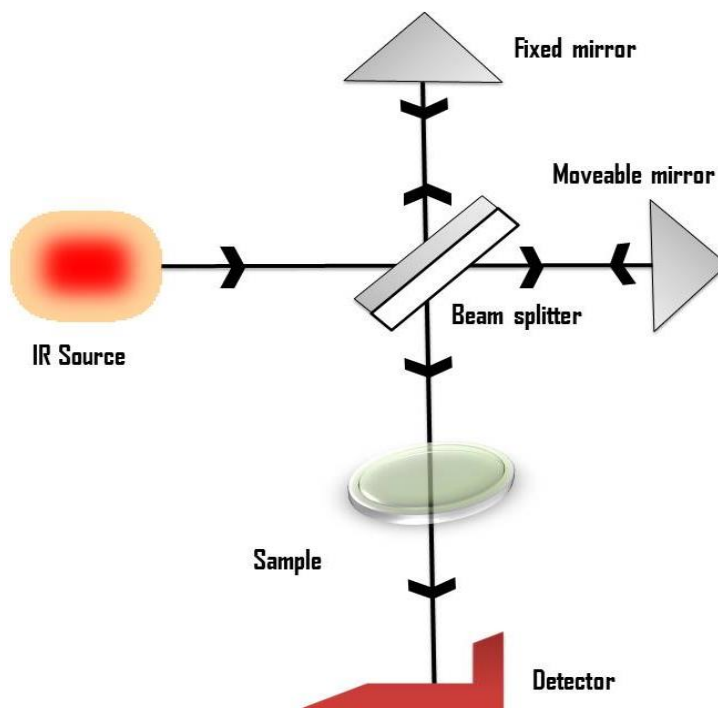
Figure 3.3 Optical diagram of Michelson's Interferometer

The three basic parts of an interferometer are fixed mirror, moveable mirror and beam splitter. Between two potassium bromide (KBr) plates, beam splitter is sandwiched. It is a semi-silvered mirror or germanium (Ge) thin film. Both mirrors are positioned at

right angle to each other as shown in Figure 3.3. Beam splitter splits the light received from the IR source that is reflected to the fixed mirror and transmitted towards moveable mirror. When these beams reflect back they recombine at beam splitter. This signal is called interferogram. One half of the interferogram goes towards sample followed by detector while other half moves towards back source. Collection time of these signals is one second .The sample is in the form of KBr pellets.

Advantages of FTIR

Advantages of FTIR over dispersive IR are given below:

- All frequencies can be measured simultaneously within seconds. This is also known as felgett advantage.
- Fast scan is another advantage of FTIR as it has high sensitivity and optical throughput. Sensitivity is enhanced as no slit is used and all radiant energy is utilized.
- The only moving part of the instrument is the moving mirror which reduces the mechanical breakdown.
- The resolution of instrument is up to $0.1cm^{-1}$.

Experimentation

A Fourier transform infrared spectrum was collected in transmittance mode on Perkin Elmer FTIR spectrometer. The scan of spectrum was run ranging from $450cm^{-1}$ to $4000cm^{-1}$. Samples were dispersed and hydraulic pressed along KBr powder in a pellet form. Most common interferometer used in FTIR spectroscopy is Michelson interferometer.

3.4. Ultraviolet/Visible Spectroscopy (UV/Vis)

The absorption of radiations by organic and inorganic molecules in ultraviolet (10-400 nm) and visible (400-800 nm) is based on the same principle and hence results in excitation of identical molecular species that is why, they are scrutinized concurrently as UV/Vis spectroscopy. UV/Vis causes transition between electronic energy levels, therefore it is also known as electronic spectroscopy.

3.4.1. Basic Principle of UV/Vis Spectroscopy

The basic principle of UV/Vis spectroscopy is that the molecules excite from ground to excited state upon absorption of UV/Vis radiations. The radiation wavelength depends on difference of energy between ground and excited state of electron. The most common observation is that one photon absorption causes excitation of only one electron while others remain unaffected. This is due to absorption of particular wavelength of UV/Vis region by molecule.

Franck- Condon principle states that position isn't changed by vibrating atoms of molecules because electronic transitions take place expeditiously. Electronic transition of atoms is based on Frank Condon principle. The four types of electronic transitions are related with UV/Vis absorption are:

1) $\sigma \rightarrow \sigma^*$ (saturated hydrocarbons)
2) $n \rightarrow \sigma^*$ (saturated molecules containing hetero-atoms)
3) $\pi \rightarrow \pi^*$ (conjugated systems)
4) $n \rightarrow \pi^*$ (hetero-atoms containing double or triple bonds)

The two key characteristics of absorption are position and intensity. At particular wavelength intensity depends on number of molecules that absorb the radiation of that specific wavelength. The intensity of absorption is expressed as molar absorptivity (ϵ) and can be measured either as absorbance (A) or transmittance (T). Both are expressed as:

$$A = \log(^{I}/_{I_o}) \qquad \text{Or} \qquad A = log \, ^{1}/_{T}$$

$$T = \, ^{I}/_{I_o}$$

Where,

I_o = incident radiation intensity

I = transmitted radiation intensity

3.4.2. Beer-Lambert Law

Beer-Lambert law states that in a sample, absorbance is directly proportional to path length and concentration travelled by UV/Vis radiation.

$$\text{i.e;} \qquad A \propto cl$$

$$A = \in cl$$

Where,

A = particular wavelength absorbance.

$\in$ = molar absorptivity or molar extinction coefficient (L/mol cm), at particular wavelength it is constant for solute. It calculates how much light is absorbed by solute at particular wavelength.

c = concentration of the sample in moles per liter (mol/L) of the solution.

l = path length of the sample solution in centimeters (cm).

The solute molecules get closer to each other when solution is concentrated and influence their properties including $\in$. Solutes act as solvents at very high concentrations and absorbance gets altered. For solutes having absorbance greater than 1, Beer's law doesn't apply.

3.5. Transmission Electron Microscope (TEM)

Transmission electron microscope (TEM) is used to determine the internal structure of materials. TEM samples are usually prepared with specific thickness that allows the electrons to be transmitted through the sample which helps to determine finest details of the internal structure as such as of individual atoms. Magnifications higher than 300K are usually obtained for many materials. Individual atoms can be imaged under optimal conditions because the TEM are usually employed to evaluate the finest crystallography of materials such as films or grains. The fundamental principle of transmission electron microscope is quite similar to the principle of optical microscope

but it uses electrons as an alternative to light. As source of light, TEM uses electrons. Resolution of TEM is better than light microscope as electron has lower wavelength.

Objects in the range of few angstroms i.e. 10^{-10}m can be observed with the help of TEM. Small fine details up to atomic level can be seen with the help of this technique. It is one of most valuable tool in biomedical sciences, material science and other research areas.

The interaction of high energy beam of electron to the thin sample can be used to see fine features including crystal structure, dislocations with in structures and grain boundaries. It is also used to analyze layer growth, composition of layers and semiconductors defects. TEM has high resolution thus can be used to investigate the quality, shape, size and density of quantum wells, wires and dots.

Chapter 4

Material and Methods

4.1. Chemicals required

- PdCl$_2$ (99.9%) obtained from Sigma Aldrich
- 4-bromobenzonitrile (99.5%) purchased from Sigma Aldrich
- Phenylboronic acid (95%) purchased from Sigma Aldrich
- Potassium phosphate tribasic (98%) purchased from Sigma Aldrich
- 4-bromotoluene (99.5%) purchased from Sigma Aldrich
- 4-bromoanisole (99.5%) purchased from Sigma Aldrich
- Ethyl 4-bromobenzoate (99.5%) purchased from Sigma Aldrich
- 4-bromonitrobenzene (99.5%) purchased from Sigma Aldrich
- 3-chlorobromobenzene (99%) purchased from Sigma Aldrich
- 4-chloronitrobenzene (99%) purchased from Sigma Aldrich
- Methyl 4-iodobenzoate (98%) purchased from Sigma Aldrich

All chemicals were used without further purification.

4.2. Experimentation

Experimentation work was carried out in the following steps:

4.2.1. Preparation of Plant Extract

Apples were purchased from a local fruit market in Islamabad, Pakistan. A fresh apple was washed, chopped and then grinded using a kitchen grinder. At 3,000 rpm the crushed material was centrifuged for ten minutes and by using filter paper the liquid extract was obtained. The entire residue was left on the filter paper and pure liquid extract was obtained [83].

4.2.2. Synthesis of Palladium Nanoparticles

In order to carry out reaction, 1mM PdCl$_2$ solution was prepared and 95ml of it was taken in a round bottom flask and 5ml of fruit extract was added to it. The round bottom flask was mounted with condenser under stirring condition. The temperature of reaction was maintained at 90 ^{o}C. Colour of solution turned to light yellow after addition of plant extract. After one hour, the colour of solution started to change and became light brown. After 1.5 hours the colour of solution completely turned to dark brown and no further change in colour was observed after two hours. This dark brown colour indicated formation of PdNPs and complete reduction of PdCl$_2$ salt. The reaction mixture was allowed to cool down and later centrifuged at 9000rpm. During centrifugation they were washed three times in the ultra-pure water. The supernatants were removed each time with centrifugation and after overnight drying at 70°C in an oven, black powder was obtained.

4.2.3. Suzuki coupling reaction

The Suzuki coupling reaction was carried out as follow. Nitrogen gas was back-filled three times in a Schlenk flask. In the presence of nitrogen supply, palladium nanoparticles stabilized with organic compounds of apple extract (1 mg, 0.01 mmol, 2 mol %),) with aryl halides (0.5 mmol, 1 equiv) phenylboronic acid (91.4 mg, 0.75 mmol, 1.5 equiv), and K$_3$PO$_4$ (212 mg, 1 mmol, 2 equiv) were added followed by 2 mL toluene. This flask was heated in an oil bath at 100°C and was sealed with Teflon screw cap. Thin Layer Chromatography and gas chromatography-mass spectrometry was used to monitor progress of reaction. In a separating funnel all contents of flask were taken out. These contents were further extracted with water (5-6 mL) and ethyl acetate (EtOAc) (12 mL, 4-3). Over anhydrous sodium sulfate the organic phase was dried and then filtered. In a rotary evaporator all volatile materials were evaporated. By Column chromatography the crude products were further purified. The biaryl products were characterized by data obtained by these techniques gas chromatography-mass spectrometry, IR, and with their melting point.

Chapter 5

Results and Discussions

In this work, fruit extract of *Malus domestica* (apples) was used as a reducing and stabilizing agent for synthesis of PdNPs. Many phytochemicals and other constituents are present in the extract of apple which are antioxidant, phyto nutrients, flavonoids and polyphenols such as quercetin, epicatechin, and procyanidin B2. The synthesized nanoparticles were further used for catalysis. These nanoparticles showed high catalytic activity. The palladium nanoparticles used for Suzuki coupling reaction has only 2 mol % catalytic loading. The schematic representation for formation of PdNPs is shown in Figure 5.1.
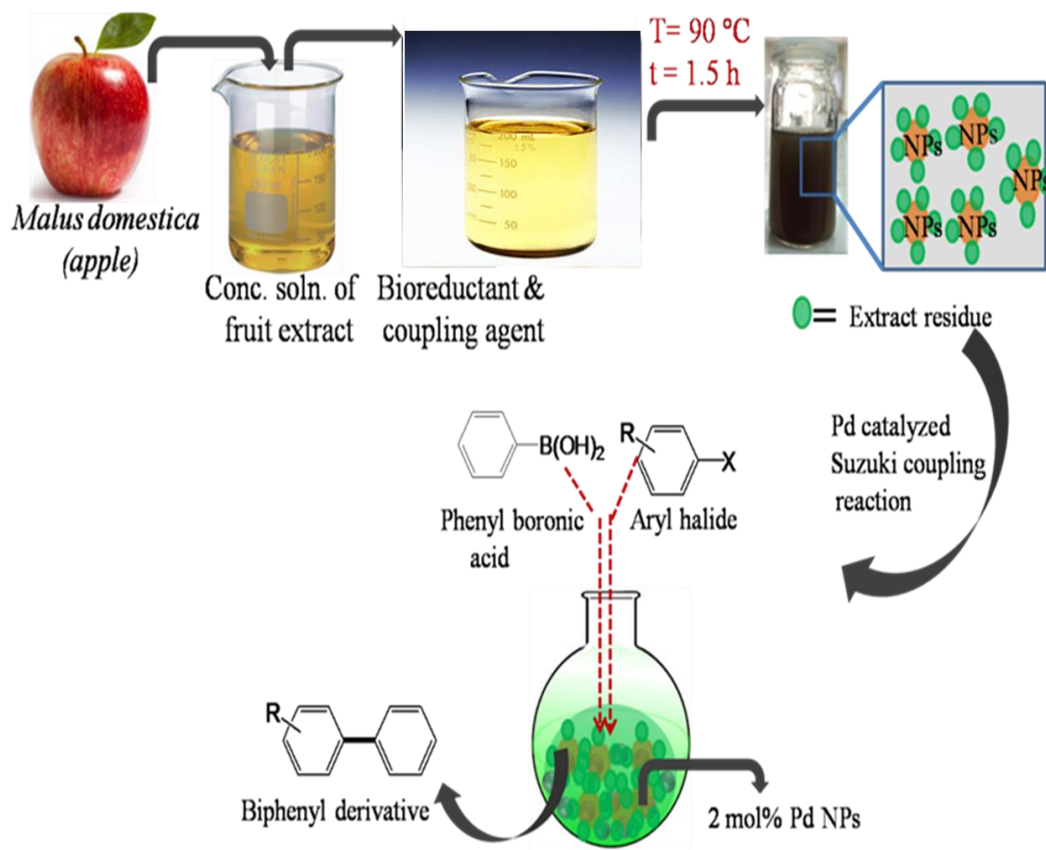
Figure 5.1 Schematic diagram PdNPs synthesis using extract of *Malus domestica*

5.1. Characterization of NPs

Palladium nanoparticles were characterized through following techniques:

5.1.1. UV-Vis Spectroscopy

All the UV measurements were performed using Biowave II spectrophotometer (Biochrom, Cambridge, UK). As a reference solvent, ultra-pure water was used and for further analysis quartz cuvettes were used. The samples were diluted with ultrapure water and all UV measurements were performed after that.

UV-Vis spectra of $PdCl_2$ and Pd NPs are shown in Figure 5.2. The absorption maxima were observed at 400nm due to Pd (II) ions absorption. After reduction, this peak changes to broad and continuous peak. This peak shows complete reduction of Pd (II) ion to Pd (0) nanoparticles.
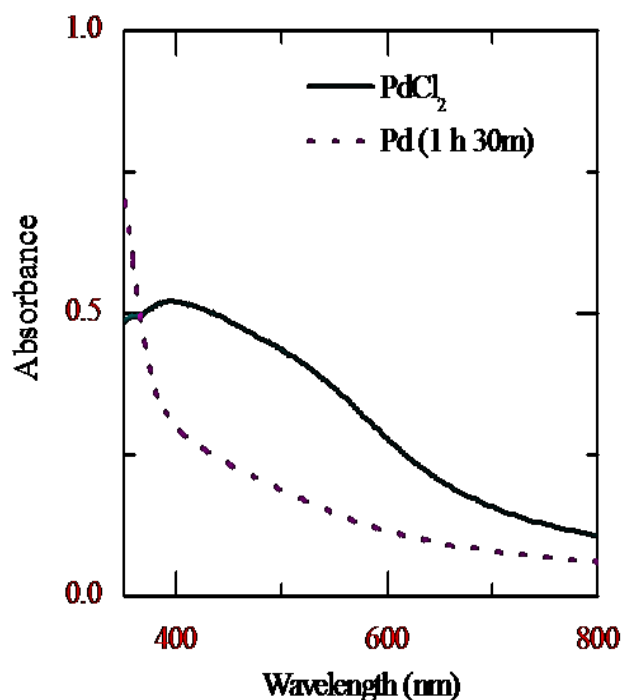
Figure 5.2 UV-Vis absorption spectra showing formation of Pd NPs

5.1.2. X-ray Diffraction

In order to obtain X ray diffraction pattern, a STOE Powder X-ray diffractometer θ-θ (operating voltage 40 kV and current 40mA) was used. It utilizes a scanning rate of 0.5° min^{-1} in the range of 20° to 80° (2θ) with Cu Kα radiation (λ = 1.5418 Å).

XRD analysis showed the crystallinity of the synthesized nanoparticles formed from apple extract. There are three distinctive reflections in the diffractogram at 40.01° (111), 46.02° (200), and 68.05° (220) as shown in Figure 5.3. The preferred growth direction was observed at 40.1^{o} (111) in comparison to other reflection. By using Debye Scherrer formula the crystallite size of particles were found to be about 20nm. These nanoparticles have face centered cubic (fcc) structures of Pd (JCPDS: 05-0681) [71].
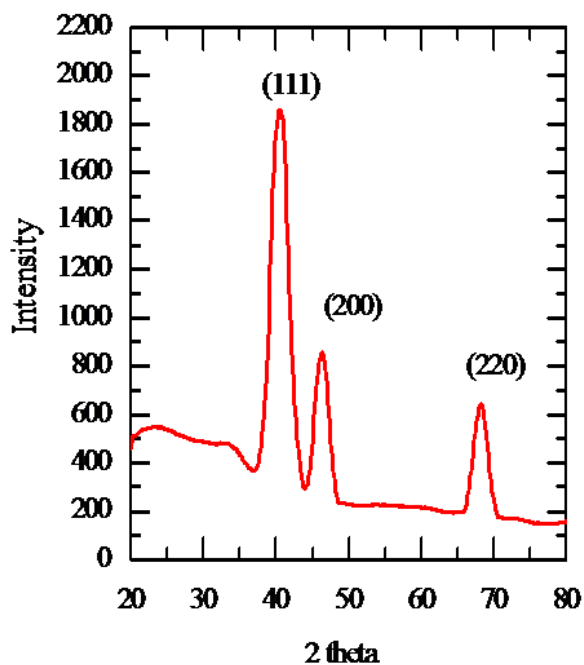
Figure 5.3 XRD diffraction patterns of the as-synthesized Pd NPs

5.1.3. Fourier transforms infrared spectrometer

Through Perkin-Elmer 100 Fourier-transform infrared spectrometer all FTIR measurements were performed. KBr pellets method was used for analysis and all measurements were recorded between 4000 and 400 cm^{-1}. The dried black powder was

mixed with KBr powder and pellets were formed for analysis. For background collection reference, blank KBr pellet was used.

FTIR analysis was performed in order to study the organic compound responsible for reduction and stabilization of nanoparticles. FTIR spectra was not only obtained for PdNPs but also for organic constituents present in the plant extract as shown in Figure 5.4. Apple extract analysis showed various absorption bands such as hydroxyl groups (3422.53 cm^{-1}), Carbon-Hydrogen aromatic stretching (2941.7 cm-1), C-C and C-O bonds (1617.9 cm^{-1} and 1420.4 cm^{-1}) stretching. It showed presence of alcohols, carboxylic groups, proteins and other such phytochemicals present in plant extract. It showed complete proteins, ascorbic acids and other phytochemicals played role in reduction of PdCl$_2$ salt.
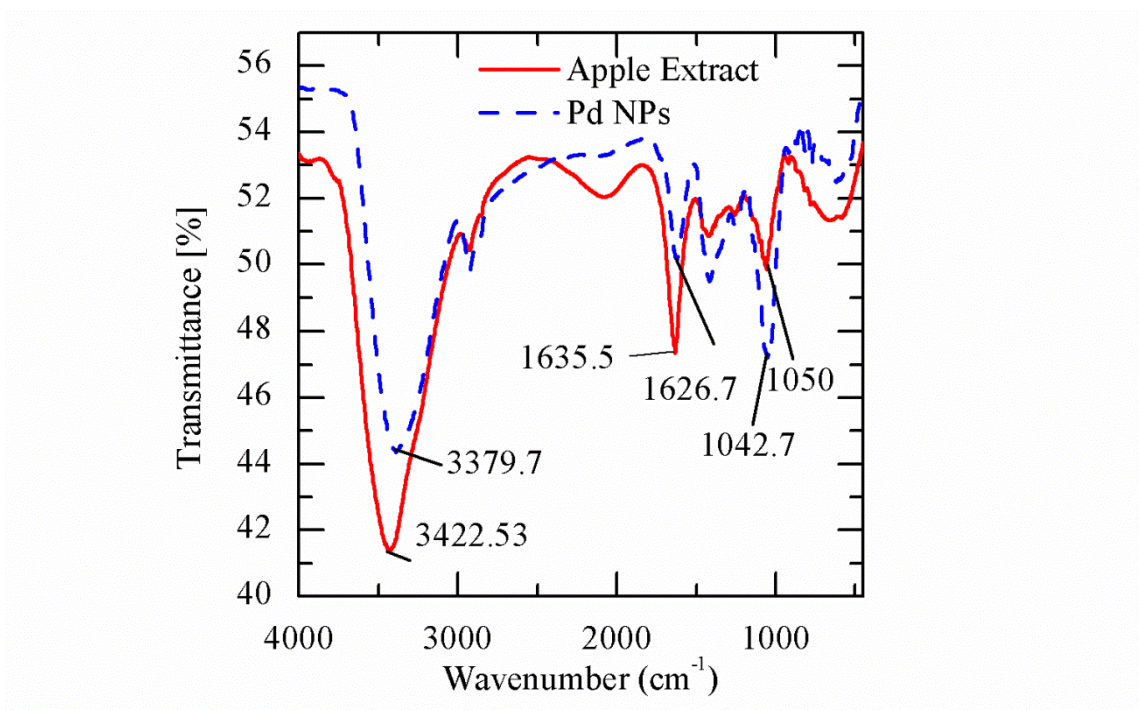
Figure 5.4 FTIR spectra of Pd NPs (red) and apple extract (black)

5.1.4. Scanning electron microscopy (SEM)

SEM analysis was used to analyze morphology of NPs. Sample was studied at various magnifications with a JEOL JSM-6490A apparatus at 15 kV.
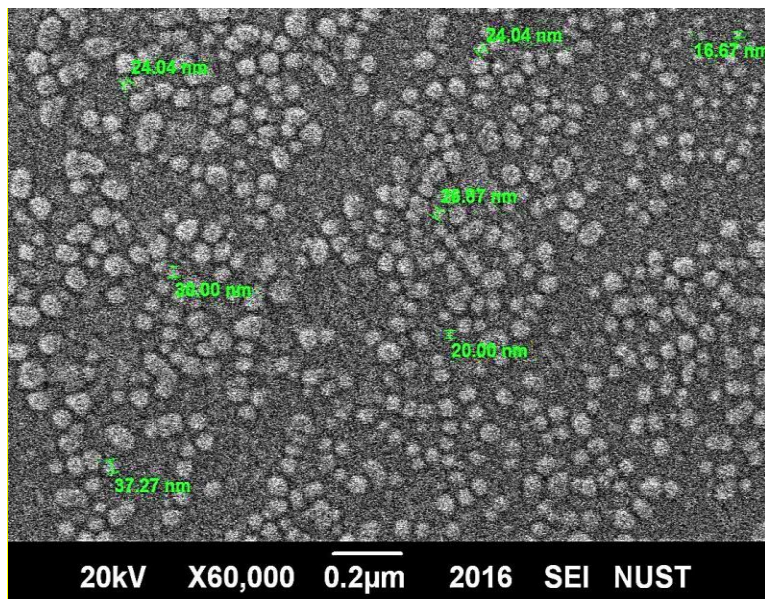
Figure 5.5 SEM image of Pd NPs

Scanning electron Microscope was used to study morphology of nanoparticles. It indicates average size of 25nm for PdNPs as shown in Figure 5.5.

5.1.5. Transmission Electron Microscope

Transmission Electron Microscope was used to analyze as synthesized PdNPs. At 100nm and also at 50nm the morphology and crystallanity of PdNPs has been observed in Figure 5.6 and Figure 5.7.

According to these figures, it has been observed that synthesized nanoparticles are highly crystalline with spherical morphology. These Pd nanoparticles are uniformly dispersed and only a small amount of constituents of apples residue are present. These results indicate successful formation of Pd nanoparticles.
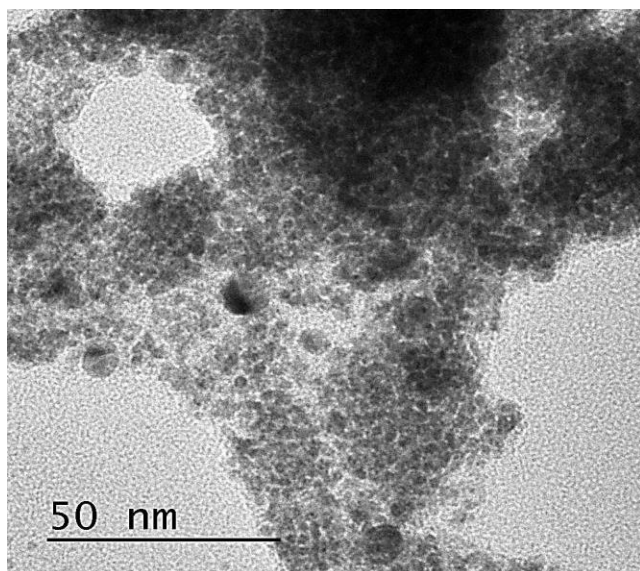
Figure 5.6 TEM image of Pd NPs (50nm)
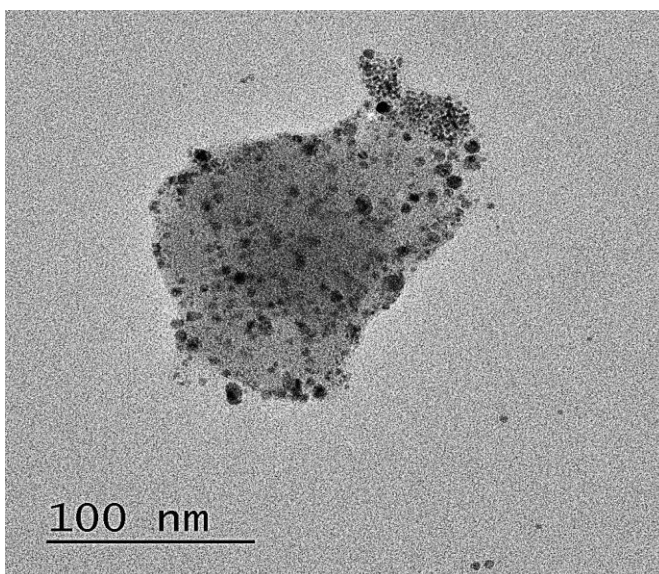
Figure 5.7 TEM image of Pd NPs (100nm)

5.1.6. Gas chromatography

Reactions were monitored by Thermo Scientific ISQ single quadrupole GC–MS operating in EI mode, and equipped with Trace 1300 GC and AI 1310 auto injector. Column type: Trace™ TR-5MS, 5% phenyl polysilphenylene-siloxane, 30m × 0.25mm ID × 0.25µm. GC–MS method: injector 250 °C, oven 50 °C (1 min), 50 °C to 250 °C (20 °C min^{-1}), 250 °C (10 min); carrier gas: He (1.5 mL min^{-1}).

In order to study PdNPs applications, the catalytic activity of these synthesized nanoparticles was further investigated in Suzuki coupling reaction. The coupling reaction of phenyl boronic acid and various aryl halides were studied.

Entry	X	Product	Yield[a]
1	Br	NC—⬡—⬡	98%
2	Br	EtO$_2$C—⬡—⬡	99%
3	Br	O$_2$N—⬡—⬡	95%
4	Br	Me—⬡—⬡	99%
5	Br	MeO—⬡—⬡	74%
6	Cl	O$_2$N—⬡—⬡	0%
7	Br	Cl⬡—⬡	93%
8	I	MeO$_2$C—⬡—⬡	92%[b]

[a]Isolated yields. [b]6 mol % Pd for 24 h
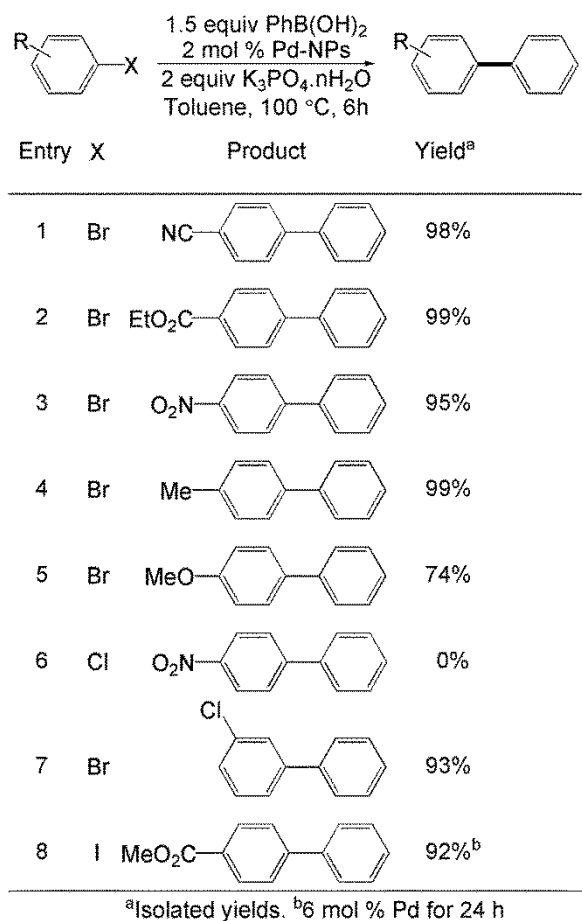
Figure 5.8: Suzuki coupling reaction showing catalytic activity of as synth. PdNPs

Only 2 mol % loading of catalyst was used in these reactions. It results in the formation of biaryls which exhibited good to excellent yields. In Figure 5.8, it can be seen that better yield was observed in electron-deficient aryl bromides (entries 1-3) than the electron-rich ones (entries 4 & 5). In (entry 6) Suzuki coupling reaction was unsuccessful and after twenty four hours only 15% conversion was observed even 10 mol % palladium nanopartilces were employed. As a consequence, selective Suzuki coupling

reaction was underwent by chloro-substituted aryl bromide (at the C–Br bond) leaving the chloro substituent intact for further functionalization (entry 7). Aryl iodide required higher catalyst loading and longer reaction times for complete conversion (entry 8). All reactions were monitored through gas chromatography (GC) and product formed were purified through column chromatography and characterized through GC-MS, FTIR analysis and melting point data of the formed biaryls (S1).

4.3. Suzuki Coupling Catalyzed by Palladium Nanoparticles Supported on Apple Extract

Palladium NPs supported on apple extract were employed as catalyst for Suzuki coupling reactions.

[1, 1'-Biphenyl]-4-carbonitrile
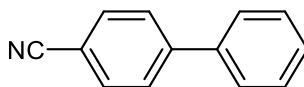
Structure 1:

[1, 1'-Biphenyl]-4-carbonitrile

The common procedure was used on 4-bromobenzonitrile (91 mg, 0.5 mmol, 1 equiv) at 100 °C for 6 h. Through column chromatography purification of crude product was done. Column chromatography (Silica gel, hexanes/DCM; 2:1, R_f 0.30) as white solid; 88 mg, 98%; melting point was obtained 86 °C;

FT-IR (ATR) $\tilde{v}_{max}$ values were: 2224, 1603, 1482, 845, 766, 695 cm^{-1};

GC-MS (EI) m/z (% relative intensity) 180 (13) (M + 1)$^+$, 179 (100) (M)$^+$, 151 (23), 76 (3).

Ethyl [1,1'-biphenyl]-4-carboxylate
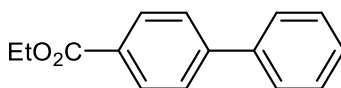
Structure 2:

Ethyl [1,1'-biphenyl]-4-carboxylate

The common method was applied to ethyl 4-bromobenzoate (82 μL, 0.5 mmol, 1 equiv) at 100 °C for 6 h. Through column chromatography purification of crude product was done. Column chromatography (Silica gel, hexanes/DCM; 1:1, R_f 0.40) as pale white solid; 112 mg, 99%, melting point of the compound was 47 °C;

FT-IR (ATR) $\tilde{v}_{max}$: 1704, 1605, 1267, 1103, 856, 743, 696 cm^{-1};

GC-MS (EI) *m/z* (% relative intensity) 227 (12) (M + 1)$^+$, 226 (94) (M)$^+$, 198 (53), 181 (100).

4-Nitro-1,1'-biphenyl
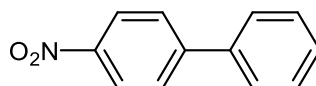
Structure 3:

4-Nitro-1,1'-biphenyl

The common method was applied to 1-bromo-4-nitrobenzene (101 mg, 0.5 mmol, 1 equiv) at 100 °C for 6 h. Through column chromatography purification of crude product was done. Column chromatography (Silica gel, hexanes/DCM; 1:1, R_f 0.45) as solid; 94 mg, 95%; melting point was 114 °C;

FT-IR (ATR) $\tilde{v}_{max}$: 1507, 1337, 1102, 851, 738, 692 cm^{-1};

GC-MS (EI) *m/z* (percentage relative intensity) 200 (11) (M + 1)$^+$, 199 (100) (M)$^+$, 169 (45), 152 (40).

4-Methyl-1,1'-biphenyl
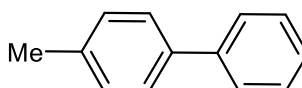
Structure 4:

4-Methyl-1,1'-biphenyl

The common method was applied to 4-bromotoluene (61 μL, 0.5 mmol, 1 equiv) at 100 °C for 6 h. Through column chromatography purification of crude product was done. Column chromatography (Silica gel, hexanes, R_f 0.55) as crystalline semi-solid; 83 mg, 99%; melting point 47 °C;

FT-IR (ATR) $\tilde{v}_{max}$: 1484, 821, 751, 687 cm^{-1};

GC-MS (EI) *m/z* (percentage relative intensity) 169 (12) (M + 1)$^+$, 168 (100) (M)$^+$, 152 (23), 115 (5).

4-Methoxy-1,1'-biphenyl
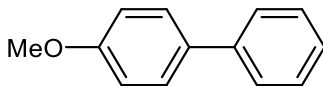
Structure 5:

4-Methoxy-1,1'-biphenyl

The common method was applied to 4-bromoanisole (125 μL, 0.5 mmol, 1 equiv) at 100 °C for 6 h. Through column chromatography purification of crude product was done. Column chromatography (Silica gel, hexanes, R_f 0.35) as white solid; 68 mg, 74%; melting point was 89 °C;

FT-IR (ATR) $\tilde{v}_{max}$: 1603, 1269, 1183, 1033, 832, 757, 686 cm^{-1};

GC-MS (EI) *m/z* (percentage relative intensity) 185 (11) (M + 1)$^+$, 184 (100) (M)$^+$, 169 (44), 141 (43).

3-Chloro-1,1'-biphenyl
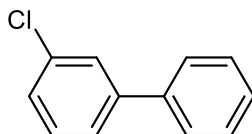
Structure 6:

3-Chloro-1,1'-biphenyl

The common method was applied to 1-bromo-3-chlorobenzene (59 μL, 0.5 mmol, 1 equiv) at 100 °C for 6 h. Through column chromatography purification of crude product was done. Column chromatography (Silica gel, Hexane, R_f 0.55) as oil; 87 mg, 93%;

FT-IR (ATR) $\tilde{v}_{max}$: 1563, 1472, 1404, 1084, 1044, 879, 750, 691 cm^{-1};

GC-MS (EI) m/z (percentage relative intensity) 190 (31) $(M + 2)^+$, 188 (100) $(M)^+$, 152 (25).

Methyl [1,1'-biphenyl]-4-carboxylate
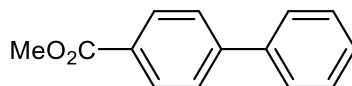
Structure 7:

Methyl [1,1'-biphenyl]-4-carboxylate

The general procedure was applied to methyl 4-iodobenzoate (131 mg, 0.5 mmol, 1 equiv) with a higher catalyst loading (3 mg, 0.03 mmol, 6 mol % (apple) and (7 mg, 0.07 mmol, 14 mol % (coconut) at 100 °C for 24 and 60 h respectively. The crude product was purified through column chromatography (Silica gel, hexanes/DCM; 1:1, R_f 0.45) as crystalline solid; 88 mg, 98%; melting point was 117 °C;

FT-IR (ATR) $\tilde{v}_{max}$: 3252, 1704, 1602, 1435, 1268, 856, 745, 695 cm^{-1};

GC-MS (EI) m/z (percentage relative intensity) 212 (95) $(M)^+$, 181 (100), 152 (31).

These results show that due to chlorine when chloro halide was reacted with phenylboronic acid with only 2 mol% loading of Pd nanoparticles no Suzuki Coupling

product was observed. However, bromine and iodine are good leaving groups, so successful C-C coupling was observed. On the other hand methyl groups are electron donating groups but due to small size of methyl, high catalytic activity was observed. In this case successful reaction of phenylboronic acid and aryl halide in the presence of only 2 mol% loading of Pd nanoparticles was observed.

To conclude our synthesized Pd nanoparticles demonstrate high catalytic activity and even after five reactions.

Chapter 6

Conclusions, Future Work and Recommendations

6.1. Conclusion

Chemical methods cause environmental contamination and also pose health risks to human body, however green protocols for production of metallic nanoparticles are getting scientific attention in the last decade. This is due to the fact that green procedures for production of metallic nanoparticles are not only easy and facile but also environmental friendly. Nanoparticles can be produced in bulk using crude plant extract and by controlling temperature; pH and irradiance huge amount of nanoparticles can be prepared. *Malus domestica* extract has constituents such as alcohol, carboxylic acid, esters, or ethers and other organic constituents which play important role in reduction and stabilization of $PdCl_2$ salt. The average sizes of particles obtained through SEM images suggest 25nm sizes of particles are synthesized. These particles have nearly spherical morphology. Different nanoparticle can be synthesized by using same extract and more efforts should be made for bulk synthesis of these nanoparticles. These nanoparticles can be used in other applications. If new methods for constituent's separation from these plants are made, better quantity of nanoparticles can be produced. So we conclude that;

- Palladium NPs were synthesized and characterized successfully
- Catalytic potential of produced Pd NPs was investigated in Suzuki coupling reactions and our synthesized NPs demonstrated excellent catalytic activity in Suzuki coupling reactions for electron-rich as well as electron-deficient aryl bromides with only 2 mol % catalytic loading
- It has also been demonstrated that chloro-substituted aryl bromide underwent selective Suzuki coupling (at the C–Br bond) leaving the chloro substituent intact for

further functionalization, indicating the potential and scope of such coupling reactions catalyzed by Pd NPs

6.2.   Future Aspects and Recommendations

Future aspects of our works are as follow:

- The plant biomass utilization for the green production of novel metal NPs (silver, gold, platinum, and palladium) would be more important if the NPs are produced extracellularly and in a controlled fashion.
- Owing to the rich biodiversity of plants, their potential for the production of noble metal NPs is yet to be fully studied.
- There are good chances for producing industrial scale production of NPs for important applications
- Efficient control of the size of particle and monodispersity must be extensively studied.

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