Prayogik Rasayan

Green Synthesis, Functionalization and catalytic Activity of Palladium nanoparticles for development of Eco-friendly methods

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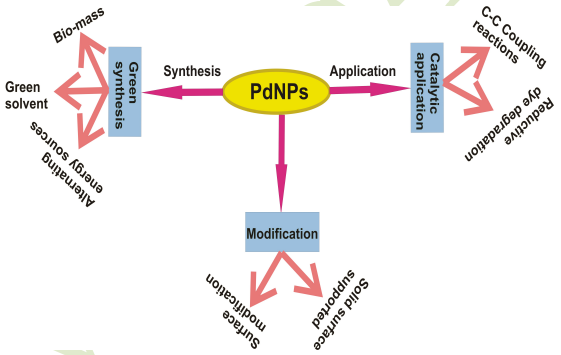
Abstract

During the past few decades metal nanoparticles are in the forefront of research for their unique properties and wide range of versatile applications. Among the several transitional metal nanoparticles palladium nanoparticles (PdNPs) are most interesting for their superior catalytic activity towards several organic reactions and also used as recyclable catalyst. Now being the time when environmental issue is a great concern and needs development of environmentally benign process. Synthesis of PdNPs using non-toxic chemicals and solvents, mild reaction condition, bio-degradable reducing or stabilizing agent, alternative energy sources are energy efficient and also cost effective and considered as green process Functionalization on the surface of PdNPs, nanoparticles showed excellent catalytic activity and can perform organic reactions in eco-friendly conditions. In this review different green synthetic methods, surface functionalization and catalytic activity of PdNPs towards several C-C coupling reactions, toxic dye degradations are discussed.



Keywords: Palladium nanoparticle, green synthesis, functionalization, C-C coupling, Dye degradation

1. Introduction

Now a days metal nanoparticles have drawn more attention of researchers because they play an important role in wide range of fields such as catalysis, diagnosis, medicine, drug-delivery, bio-technology environmental remediation etc. for their large surface area.[1] Among various metal nanoparticles PdNPs are in increasing demand due to novel physio-chemical property in nano-scale and exhibit high catalytic efficiency towards different C-C coupling reaction, hydrogenation of alkene and alkynes, oxidation of alcohols, reduction of toxic dyes etc. The environmental pollution is a big issue in present time and requires development of sustainable and eco-friendly process to protect the environment. PdNPS are not only increase the rate of reaction but also it helps to precede the reaction in milder condition along with recovery and reusing of the catalyst which makes the process became greener. Thus the synthesis of PdNPs using non toxic chemical in a safer pathway is tremendously desired to build out an environmental benign process. The activity of the PdNPs is largely controlled by their shape and size. Again the synthesis process is also responsible for determining the unique physiochemical properties of PdNPs like optical, electronic, shape and size etc. Unfortunately, the PdNPs exhibit thermodynamic instability and undergo aggregation. Hence a support is needed to obtain a stable PdNPs and can be done by surface modification. The surface of nanoparticles can be functionalized with different type of ligands or solid supports either by non covalent or by covalent interaction. This modification also facilitates the ease of separation of the catalyst from the product. Functionalization of the PdNPs not only strongly influences on their catalytic activity but also produces suitable candidate for selective catalytic reactions because they can be designed in such a way to enhance activity for a particular site.[2] Several green synthetic routes for synthesis of PdNPs, surface modification and Applications of PdNPs as catalyst for Suzuki coupling, Heck coupling, Hiyama Cross-Coupling, Sonogashira Cross-Coupling and reductive degradation of toxic dyes are discussed here.

2. Synthesis of Palladium nanoparticles: To synthesize PdNPs different types of synthetic methods have been introduced like physical, chemical, electrochemical and biological methods etc. (Fig.1).

Recently the PdNPs in industrial scale is prepared by physical methods. In this method generally laser ablation, vapor deposition, sonochemical or light irradiation processes are used. Most of the processes of physical methods require expensive sophisticated equipments and drastic condition like high pressure and temperature which is energy intensive.[3]

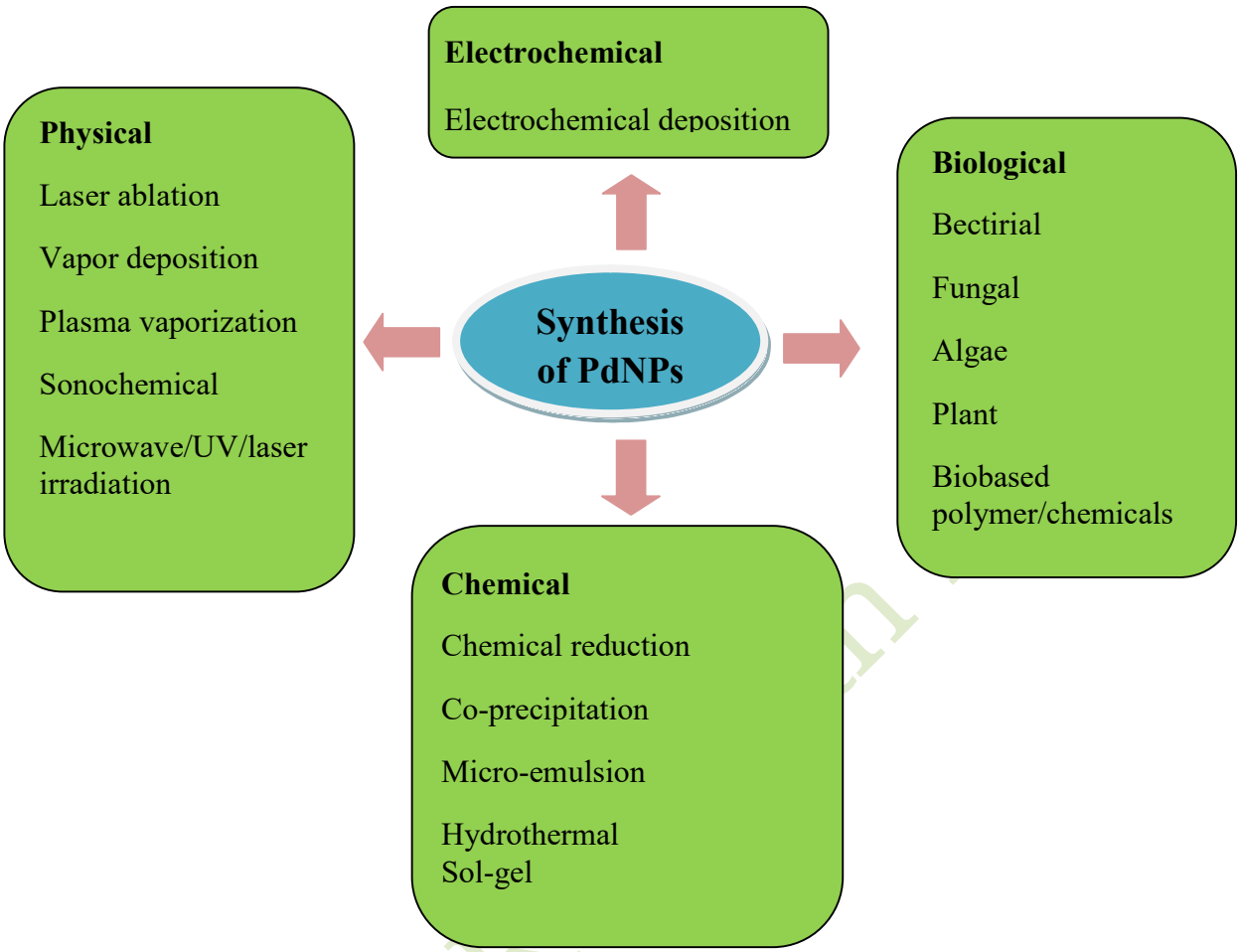


Figure1: Different synthetic methods for synthesis of PdNPs.

In chemical process the palladium nanoparticles are synthesized by reduction of palladium ion to zerovalent atom followed by nucleation in presence of stabilizing agent which also controlled the shape and size of the nanoparticles. The common methods used in chemical synthesis of nanoparticles are chemical reduction, co-precipitation, micro-emulsion, sol-gel, hydrothermal etc. The limitation of the chemical methods is that in most cases toxic and hazardous chemicals are required for preparation of PdNPs.[3]

In case of electrochemical deposition process the palladium cation is reduced and deposited on cathode in an electrolytic cell from the solution of palladium salt by the action of electricity. The size of synthesized PdNPs in this method can be controlled by addition of stabilizing agent like poly N-vinyl pyrrolidone (PVP) and adjusting the applied current. The stabilizing agent inhibits electro deposition of Pd and faster the rate of PdNPs formation. The size of the nanoparticles is inversely proportional with the applied current density.

Since the above discussed physical and chemical methods have several drawbacks and the PdNPs synthesized by these processes have restricted application especially in the field of bio-medical, so researchers are searching for newer methods which will be efficient, low cost and environmentally safe for preparation of PdNPs nanocatalyst. Indeed execution of a chemical process as sustainable needs usage of a catalyst which is safe, cheaper, easy to synthesize, easily recovered and reused with minimum Pd leaching. The methods of synthesis of PdNPs using bio-mass (biogenic synthesis), in solvent free condition or utilizing alternating solvent rather than common toxic solvents and utilization of alternating energy sources like the ultrasonic and microwave irradiation are cost-effective, simple, rapid and eco-friendly, hence called green synthesis.

Over the past few decades synthesis of metal nanoparticles by biogenic process through utilization of bio-mass have gained significant attention because the renewable and nontoxic nature of bio-mass makes the process environmentally benign. Microorganisms (bacteria and fungai), algae and plant mediated synthesis of PdNPs are most important.

Synthesis of PdNPs using microorganisms is encouraging because microorganisms are abundant and can successfully bio-reduce the palladium cation through enzymatic catalysis to produce proper shape and size controlled biocompatible PdNPs. Different types of bacteria and fungai are utilized to synthesize PdNPs. The first report on bacteria mediated PdNPs synthesis is the production of 50 nm sized PdNPs by addition of biomass of sulfate- reducing bacterium Desulfovibrio desulfuricans into the precursor salt of Pd in presence of electron donor sodium pyruvate.[3] Another sulfate-reducing bacterium Desulfovibrio fructosivorans and metal-reducing bacterium Shewanella oneidensis are able to synthesize PdNPs. The cyanobacteria Calothrix pulvinate and Anabaena flos-aquae, gram negative Paracoccus denitrificans and Pseudomonas putida, E.Coli are also utilized to for green synthesis of PdNPs.[3]

Fungai have several advantages over bacteria like (i) it has higher biomass and easy to culture, (ii) higher bioaccumulation of metabolites, (iii) higher uptake capability and high wall binding capacity to metals. Although the fungai have such advantages yet the reports on fungai mediated synthesis of PdNPs in literature are very few compare to bacteria. The extract of *Agaricus bisporus* mushroom has been utilized to synthesize PdNPs. Porous PdNPs were synthesized from medicinal chaga mushroom (*I. obliquus*). The size and shape of the synthesized PdNPs were controlled by the concentration of extract. The biomass of the baker's yeast *Saccharomyces cerevisiae* has been used to synthesize PdNPs of size 10-20 nm.[4]

Synthesis of PdNPs using microorganisms is a time consuming for slow and multistep process. These methods also require selection of appropriate microorganism because each one provides definite enzymatic activity for interaction with the metal ion and careful to the cultural method and condition to avoid contamination with other microorganisms. Therefore the utilization of microorganisms has several limitations and makes its application in green synthesis of palladium nanoparticle challenging.

Recently algae have gained importance for biogenic synthesis of PdNPs. They can accumulate the heavy metal ions and modify into ductile shapes and they are rich with carbohydrate, vitamin and many bioactive compounds like antioxidants, pigment, chlorophyll etc. which are responsible for reduction of metal ions. Indeed, algae are easily harvested and their negatively charged surface promotes the nucleation and growth of nanoparticles. Therefore algae are suitable precursor for low-cost, efficient, rapid and large scale production of palladium nanoparticle. *Spirulina platensis* alga has been utilized to synthesize spherical shape PdNPs of size 10-20 nm.[5] Ameri et al have synthesized spherical palladium nanoparticles of diameter 13-33 nm range in microwave within 3 minitues utilizing brown algae.[6] The brown alga, Padina boryana have been utilized to synthesize spherical shaped PdNPs of average size 11 nm.[7] Momeni et al. have reported the biosynthesis of PdNPs using marine alga Sargassum bovinum. The synthesized PdNPs were octahedral shaped with size 5 to 10 nm.[8]

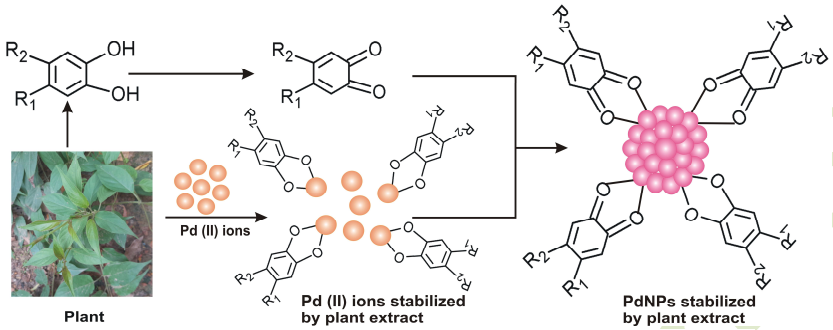


Figure 2: Formation of stabilized PdNPs by plant extract reduction.

Plant mediated biogenic synthesis of PdNPs have attracted much more attention of researchers during the past few decades compared to microorganism for their several advantages. The synthesis of PdNPs utilizing plant extract is one step synthesis process, very simple, mild reaction condition, not require careful culture and maintenance. Additionally the plant extract can act as both reducing and stabilizing agent, so external stabilizing is not needed. Therefore this process is also safe and cost effective. Plants are rich with several secondary metabolites like terpenoids, polyphenols, flavinoid, saponins, steroids, vitamins etc. and these bio-active compounds play significant role for synthesis of PdNPs.These compounds posses poly hydroxyl groups which can co-ordinate and reduce Pd(II) ions to give PdNPs stabilized by carbonyl groups formed by oxidation of hydroxyl groups as well as poly hydroxyl compounds (Figure 2). The concentration of phytochemicals is varies considerably with the type of plants and effects on the size and shape of PdNPs as well as affect on their catalytic activity. There are so many reports on synthesis of PdNPs utilizing different parts (leaf, bark, fruit, flower, root etc.) of plants. The leaf extract of Anacardium occidentale have been utilized to synthesize spherical shaped PdNPs of size range 2.5 to 4.5 nm.[3] The leaf extracts of other plants Melia azedarach, Parthenium hysterophorus, Allium fistulosum, Basella alba and Tabernaemontana divaricate also used for preparation of spherical PdNPs of size 10-20 nm and 2-6 nm respectively.[3] Bark extract of Terminalia arjuna have been utilized to synthesize PdNPs of average size 8.9 nm. The shapes of the synthesized PdNPs were mostly spherical along with

triangular, hexagonal etc.[9] Bark extract of Cinnamomum zeylanicum also been utilized to prepare spherical shaped PdNPs of size 15-20 nm.[3] The fruit extract of Gardenia jasminoides have been utilized to fabricate spherical PdNPs of size 3-5 nm. Fruit extract of other plants like Piper longum, Pistacia atlantica, Rosa canina etc. also been used to yielded Spherical PdNPs.[3] In addition flower extract of Hibiscus sabdariffa L. and Moringa oleifera used to fabricate spherical PdNPs of 5-8 nm and 2-18 nm size range respectively. Again Spherical PdNPs have been synthesized from root extract of Salvadora persica L. and Asparagus racemosus L. of 2.2-15 nm and 1-6 nm size respectively. Various examples of plant mediated green synthesis of PdNPs are shown in Table 1.

Table 1: Green synthesis of PdNPs using various parts of plants

Sl. No.	Name of plant	Part of plant	Shape and size of PdNPs	Reference
1.	Lantana camara	Flower	4.6 - 6.3 nm, Spherical	1
2.	Piper nigrum	Fruit	2–7 nm, spherical	1
3.	Euphorbia granulate	Leaf	25–35 nm, spherical	1
4.	Water melon	Rind of fruit	96 nm, spherical	1
5.	Beta vulgaris	Juice	5 nm, spherical	3
6.	Boswellia serrata	Gum	2-9 nm, spherical	3
7.	Couroupita guianensis Aubl	Fruit	5-15 nm, spherical	3
8.	Musa paradisiacal	Peel	50 nm, spherical	3
9.	Silybum marianum	Seed	10-25 nm, spherical	3
10.	Punica granatum	Peel	20-24 nm, spherical	3
11.	Green tea	Leaf	7-10 nm, spherical	1
12.	Cissus quadrangularis	Stem	12-26 nm, spherical	3
13.	Chrysophyllum cainito	Leaf	25-50 nm, flower like aggregates	1
14.	Stachys lavandulifolia	Leaf	5-7 nm, spherical	1
15.	Glycyrrhiza glabra	Root and branches	3-6 nm, not reported	1

However, the synthesis of PdNPs using microorganism and plant based material is green but the microorganism mediated synthesis is very slow and localized heat is required to prepare PdNPs by deforming the active enzyme from microorganism. In case of plant mediated synthesis it takes few minutes to several hours for formation of PdNPs. Utilization of microwave irradiation or ultrasonic vibration in these synthesis methods makes the process very faster by homogeneous heating of the reaction mixture. The synthesis of PdNPs in aqueous medium using sodium ascorbate by microwave irradiation is very fast and effective process to produce highly stable monodisperse PdNPs of 2-7 nm.[1] K. Seku et.al have synthesized microwave assisted PdNPs from *Frankincense* resin (FR) obtained from the tree of *Boswellia sacra.* The synthesized particles are spherical in nature with approx 11 nm in size.[10] Synthesis of PdNPs through single step by eco-friendly microwave irradiation technique utilizing hemicellulose as reducing agent has been reported. The average size of the synthesized PdNPs is 10 nm. Spherical shaped PdNPs of 12-14 nm sized are also synthesized by microwave irradiation from Albizia Gum.[10]

Modification of PdNPs by surface functionalization

Since PdNPs acquire high surface energy, they have very much tendency to aggregate during their synthesis or utilization as catalysts and hence stabilization of synthesized PdNPs is required to protect PdNPs. This can be achieved by introduction of chemical functional group on the surface of PdNPs (called surface functionalization) or PdNPs are produced on a solid support (called solid supported PdNPs) or both. Several types of organic compounds like dendrimer, polyol, surfactant, polymers etc. and inorganic materials are act as stabilizing scaffold and the electrostatic or steric interaction produced by coating of ligands on nanoparticle surface helps to stabilize the nanoparticles.[11] Indeed these stabilizing agents can also enhance the catalytic activity and make the PdNPs as selective catalyst. Moreover, the advantage of supported PdNPs is that these are easily recoverable, reusable and low deactivating power. There are various reports on synthesis of supported PdNPs in literature. P.Gao et.al. have reported the synthesis of urea linked porous organic polymer supported PdNPs. They prepared the PdNPs in two steps, at first synthesize UPOP by reaction of 1,4-diisocyanatobenzene and tris(2-aminoethyl)amine in DMF solvent then synthesized UPOP added to the H_2PdCl_4 solution to obtained spherical PdNPs of size range 4-8 nm.[12] The mineral clay kaolinite has been used as supporting platform to synthesize PdNPs. The kaolinite is modified by grafting with amino alcohol triethanolamine and ionic liquid 1-(2-hydroxyethyl)-3-methylimidazolium to increase the compatibility and size controlled synthesis of PdNPs. The synthesized particles are mono-disperse with size 4-6 nm. Synthesis of zirconia supported vacant phosphotungstate stabilized Pd nanoparticles ($Pd–PW_{11}/ZrO_2$) also been reported.[13] Another example is synthesis of PdNPs supported by sodium dodecyl sulfonate (SDS)-intercalated layered double hydroxide (LDH) nanocomposites. The uniformly dispersed PdNPs of average size 3.6 nm are prepared through ultrasonic method.[14] Galleti et al. have reported the synthesis of chitosan supported PdNPs. Nanoparticles are yielded by reduction of palladium acetate in ethanol which act as reducing agent as well as solvent and reaction has performed under micro-wave condition.[15] Synthesis of polyvinyl chloride stabilized PdNPs have been reported. PVP-PdNPs are obtained by reduction of palladium chloride by KOH in tetra ethylene glycol l(TEG) in both microwave irradiation and normal pressure condition. The synthesized

particles are mostly spherical in nature with 5-15 nm size range and the particles from microwave irradiation are bigger than normal pressure condition.[16] More examples are shown in Table-2.

Table-2: Green synthesis of supported PdNPs

Support	Reducing agent	Size of PdNPs	Reference
Fe_3O_4 magnetic NPs	Flower extract of Fritillaria imperialis	20-30 nm, quasi-spherical	1
Biopolymer Chitin	Chitin	20-59 nm	33
Silica-cyclodextrin	-	3-10 nm	18
Chitosan nanofiber	EtOH	5-50 nm	1
Pyrene functionalized reduced grapheme	EtOH	20-25 nm	19
Poly vinyl Pyrrolidine	-	3-6 nm	20
Kaolin	Modified chitosan(EtOH)	15-20 nm	1
Graphene nanosheet	Cyclodextrin(EtOH)	5-15 nm	1
Thiourea modified chitosan	Ellagic acid	3-5 nm	1

3. Applications of PdNPs

For the enhanced unique physiochemical property exhibited in nanoscale, palladium nanoparticles have wide range of applications from chemical catalysis to biomedical fields. High surface to volume ratio and very high porosity makes the palladium nanoparticle more useful than the bulk palladium. Applications of PdNPs as catalyst for C-C coupling reaction and reductive degradation of toxic dyes are focused in this review (Fig.3).

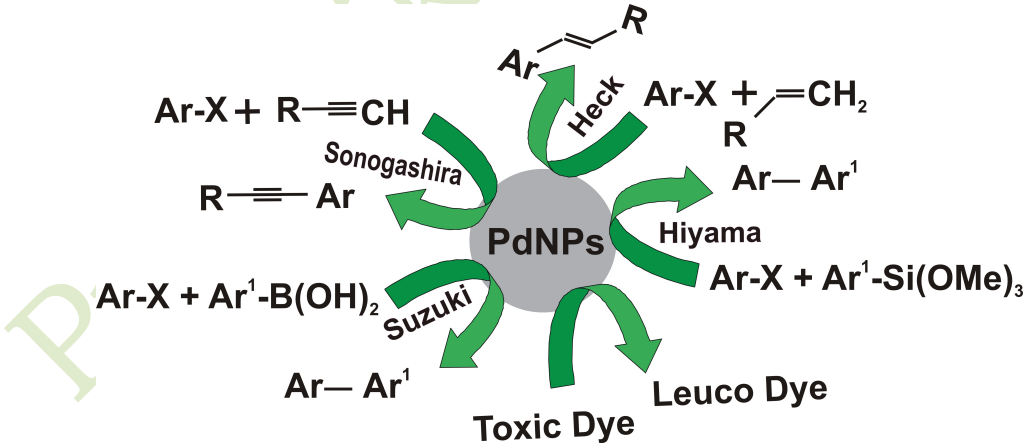
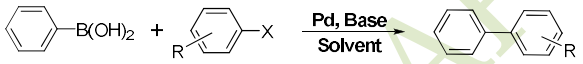


Figure3: Application of PdNPs as catalyst

Catalytic activity towards C-C coupling reaction:

Development of green and efficient method for formation of C-C bond has gained significant attention of researchers for organic synthesis. Cross coupling reactions are generally catalyzed by palladium metal. But palladium nanoparticle can replace the traditional bulk metal for their excellent catalytic activity, selectivity, recyclability and recyclability nature. Different cross coupling reactions performed by catalysis of PdNPs and their advancement in green approach have been discussed here.

Suzuki cross coupling reaction



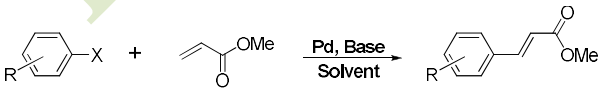
Scheme 1: Suzuki Coupling reaction

Suzuki coupling reaction has discovered by Akira Suzuki in 1979, which is an important reaction among the several and widely utilized reactions for selective construction of carbon-carbon bond. In this reaction cross coupling occurs between an organoboron compound and organic halide or psuedohalide to form C-C bond in presence of base and catalyzed by metals (scheme 1). Performance of Suzuki reactions in green solvent in presence of compatible, recyclable, reused and active PdNPs is environmentally benign process in perspective of green chemistry. Coleus amboinicus conjugated PdNPs(synthesized from leaf extract of Coleus amboinicus) are act as efficient catalyst for Suzuki reaction in PEG-400 green solvent under ultrasound irradiation. The reaction completed within 30 minutes and the catalyst reused up to seven cycles without significant loss of catalytic activity[1]. Similarly the PdNPs synthesized from leaf extract of Thymbra spicata and Stakys lavandulifolia along with fruit extract of Rosa canina also been utilized as excellent catalyst for Szuki reaction in aqueous methanol. The catalysts are reused up to 7-8 cycles with very low Pd leaching.[1] Plant extracts can synthesize and stabilize PdNPs on solid supports and supported PdNPs exhibit enhanced stability and recyclability of nanocomposite. PdNPs synthesized from fruit extract of strawberry on the surface of Fe_3O_4 used as efficient catalyst to perform Suzuki reaction aqueous ethanol with negligible Pd leaching.[1] Another

example of supported PdNps other than synthesized from plant extracts is poly(2-hydroxyethyl methacrylate)/KIT-6 conjugated PdNPs, used as catalyst for Suzuki reaction of aryl halide with phenyl boronic acid to give good yield for aryl iodide. But in case of bromides and chlorides the process needs higher temperature for better yield in aqueous medium.[17] The catalyst reused upto nine cycles without significant loss of activity. Graphene supported PdNPs have been used as catalyst for Suzuki coupling between aryl bromides and potassium aryltrifluoroborates in aqueous methanol.[17] PdNPs immobilized on an amine-functionalized LDH catalyst (PdNP@NH_2-LDH-Al-MCM-41) have been utilized for Suzuki cross coupling of several aryl bromides with different aryl boronic acids in ethanol at 80 °C and exhibit excellent catalytic activity, recyclable up to five cycles without losing activity with TON up to ~ 47 and TOF ~ 47 h^{-1} .[17] The PdNPs work better in presence of ionic liquids or microwave irradiation. Phosphonic acid stabilized PdNPs synthesized by using sodium ascorbate as biocompatible reductant has been utilized as very efficient catalyst for Suzuki coupling reaction performed in aqueous or aqueous ethanol media. For the Suzuki reaction of aryl halide with tolyl bororonic acid very low PdNPs loading (0.002 mol%) is required for complete conversion within 30 minutes under microwave irradiation at 80° C.[1] Biopolymer supported PdNPs are more effective catalyst to synthesize substituted biphenyls by unconventional technique from aryl halides with several types of substitution. Glucose stabilized PdNPs have been used as excellent catalyst for Suzuki reaction of aryl halides containing electron donating and also electron withdrawing substituent with variety of aryl boronic acids. In another example, Cellulosed supported PdNPs have been reused up to ten cycles with no loss of reactivity.[17] Nano cellulose obtained from waste cotton cloth can be used as solid support for PdNPs synthesis. The in-situ synthesized nano cellulose supported PdNPs without additional reagent in Suzuki coupling reaction exhibit efficient catalytic activity towards aryl halides even least reactive aryl chlorides[1].

Heck Cross Coupling reaction

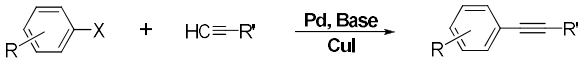
Mizoriki–Heck reaction is one of cross coupling reactions developed by Mizoriki and Heck in early 1970s where alkenylation of aryl, vinyl and alkyl halides takes place (scheme 2). This reaction is applied for synthesis of several drugs and intermediates like naproxen, prosulfuron, ethylhexyl-p-methoxycinnamate and comonomers of styrene polymers etc.[17] PdNPs have been widely used as catalyst to carry out Heck reaction for easily recoverable and reusable nature.



Scheme 2: Heck Coupling reaction

PdNPs synthesized from bark extract of Terminalia arjuna utilized to perform Heck reaction of iodobenzene and methyl acrylate in presence of triethyl amine as base in aqueous DMF system at 90° C. The reaction completed within 5 hours with 95.5% yield.[9] PdNPs supported on several polymers or inorganic backbones shows excellent catalytic activity and they are easily recoverable for the presence of solid supports. PdNPs supported on triazine functionalised meso porous covalent organic polymer used as catalyst for cross coupling reaction between several substituted aryl halides with styrenes and acrylates. The catalyst exhibit excellent catalytic activity, gives good yields in case of both electron deficient and electron rich aryl bromides with hindered styrenes.[17] The processes where water used as solvent are eco-friendly method. PdNPs supported on ethylenediamine-functionalised cellulose used as catalyst for Heck reaction of styrene and methyl acrylate with aryl halides in aqueous medium. To perform this reaction in water as green solvent higher mol% ofPdNPs is required. Nazhad et al. have synthesized a silica-cyclodextrin (SCD) substrate as supports of PdNps and the supported PdNPs act as catalyst for organic reactions in water. Among the alpha, beta and gama CD, silica-gama CD is best to perform the Heck reaction in aqueous medium.[18] PdNPs encapsulated within a N-doped carbon layer (Pd@N-C) utilized to catalyze Heck reaction of Iodobenzene with styrene and methyl acrylate which shows better activity than that of Pd/N-C-200 and confirms lower degree of leaching of the catalyst.[18] Khan et al. also prepared a novel catalyst, pyrene functionalized PdNPs supported on reduced graphene oxide (HRG-Py-PdNPs) and used as catalyst in Heck reaction of acrylic acid with various aryl halides in water. They also compare the reactivity of reduced grapheme supported Pd metal, PdNPs itself and HRG-Py-PdNPs and observed that HRG-Py-PdNPs showed excellent catalytic activity towards Heck reaction in aqueous medium.[19] To obtain complete conversion in Heck reaction in traditional heating methods, it takes long time even several hours. But utilization of microwave irradiadtion makes the process very fast. Martin et al. have synthesized polyvinyl pyrrolidine stabilized PdNPs (PVP-PdNPs) and utilized as catalyst of Heck reaction of iodobenzene with different alkenes in ethanol. The reactions are completed within very short time (12 min) with good yield and the catalyst shows excellent selectivity towards E-isomer.[20]

Sonogashira Cross-Coupling Reactions

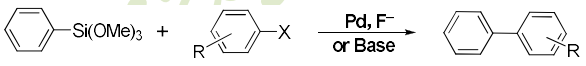


Scheme 3: Sonogashira Coupling reaction

Sonogashira Cross-Coupling reaction has been discovered in 1975 which successfully accomplished in broad area of research like drug discovery, synthesis of heterocyclic compounds along with natural compounds. This reaction involves the generation of C-C bond by coupling between aryl or vinyl halides and terminal alkynes (Scheme 3). Generally the transitional metals such as Cu, Pd etc. can catalyze this reaction but the formation of explosive copper acetilide as side product during this reaction, copper is less favored. Even the removal of high boiling solvents to reuse the Pd metal enhances the cost and also toxic Pd contaminated the product.[17]

Recent developments in synthesis of supported PdNPs overcome such limitations because the recovery of such PdNPs is very simple and also they acts more actively as well as selectively. Sajiki et al. have reported the sonogashira coupling reaction between different aryl iodides with aliphatic and aromatic terminal alkynes in presence of carbon supported PdNPs as catalyst. They used both type of aryl iodides containing electron donating and withdrawing groups and explored that aryl iodides containing electron withdrawing groups gives better results than molecules containing electron releasing groups.[21] PdNPs immobilized on SBA-propyl-imine-furan utilized towards sonogashira coupling of phenylacetylene with various aromatic halides under reflux condition. The reactions are completed within very short time with excellent yield and the catalyst is highly efficient up to seven cycles.[21] In another example, PdNPs encapsulated into polypyrrle globules are act as efficient catalyst towards sonogashira reaction between bromo and iodo arenes along with their nitro substitution with phenyl acetylene. The reaction is carried out under 100°C in presence of 1 mol% of PdNPs and 2 mol% of CuBr in argon atmosphere and the reaction has completed within 4 hours.[22] Shunmughanathan et al. have prepared a novel catalyst melamine-based microporous network polymer supported PdNPs which is able to carry out this reaction in water as green solvent. They have optimized the reaction condition using iodobenzene with phenyl acetylene and further implemented with bromobenzene system.[17] Another example of PdNPs supported on ethylenediamine-functionalized cellulose acts as excellent heterogeneous catalyst to perform Sonogashira reaction in water at 100°C. When the reaction carried out in presence of 0.4 mol% of catalyst and 100 mol% of K_2CO_3 gives excellent result in 7 hr. The catalyst easily recovered and reused up to 4 cycles without loss of activity.[23] Utilization of microwave irradiation or ultrasonication makes the process became rapid and also eco-friendly. Graphene oxide supported PdNPs has been exploited as excellent catalyst for sonogashira reaction of electron rich iodo substrates with phenyl actelene under microwave irradiation and reaction completed within 40 min.[24] The reports on microwave assisted sonogashira reaction catalyzed by PdNPs are very less.

Hiyama Cross coupling reaction



Scheme 4 Hiyama Coupling reaction

Hiyama cross coupling reaction invented in 1988 and widely used in organic synthesis for construction of C-C bond by coupling between organo silicon with organic halides (scheme 4).This reaction is analogus to Suzuki reaction and activated by fluoride ions. Recently the fluoride ions are replaced by PdNPs. This reaction is mostly applicable due to low toxicity, low cost and commercial availability of organosilicon. Sarkar et al. have reported the colloidal PdNPs stabilized by PEG act as catalyst for Hiyama reaction of aryl trimethoxy silane with aryl iodides and bromides containing electron donating and electron withdrawing groups in water.[17] But this catalyst failed to catalyze the reaction of aryl chlorides. Similarly another example reported by Brindaban et al. is in situ generation of PdNPs stabilized by surfactants also gives excellent yields towards Hiyama reaction of substituted aryl bromides and iodides with aryl siloxanes.[25] They also demonstrate the coupling of several substituted allyl acetates with vinyl or aryl siloxanes in presence of in situ generated PdNPs.[17] PdNPs stabilized by Tris-Imidazolium Salt exhibit excellent efficiency towards fluoride-free Hiyama coupling of vinylsilanes with aryl iodidesin aqueous methanol and sodium hydroxide act as base.[26] Application of microwave irradiation in Hiyama reaction the reaction became faster and aryl chlorides also undergoes Hiyama reaction to give products. PVP supported PdNPS are act as catalyst for Hiyama reaction of aryl chlorides and bromides with phenyl trimetoxy silane under microwave irradiation at 110°C and completed within 6-9 min.[24]

Dye degradation

Several synthetic organic dyes are extensively used in various industries such as textile, pharmaceutical, printing, cosmetic, photography leather, food processing etc. but these synthetic dyes are highly toxic and harmful to human health as well as environment. They are causes of pollution of air, water or soil. The effluents from these industries are enriched with different types of dyes and lead to increase BOD and COD as well as inhibit the photosynthesis of aqueous plants. Hence the degradation of such toxic synthetic organic dyes is most urgent necessary.[27] Metal nanoparticles are broadly used as catalyst for reductive degradation of dyes for their high stability and excellent catalytic activity due to high surface area to volume ratio. By reductive degradation the toxic dyes form non toxic leuco dyes which also play vital role in data storage media, holographic industry etc. The colloidal PdNPs synthesized from bark extract of Terminalia arjuna shows excellent catalytic activity towards sodium borohydride reductive degradation of methylene blue and rhodamine-B dyes[9]. Similarly the PdNPs synthesized from gum of *Boswellia serrata* also utilized for reductive degradation of coomassie brilliant blue G-250, rhodamine B and methylene blue dyes and exhibit excellent activity.[27] In another example, PdNPs prepared from agro-waste empty cotton boll peels aqueous extract utilized as catalyst for reduction of toxic azo-dyes Congo red, Methyl orange, Sunset yellow and Tartrazine with sodium borohydride. In all cases the PdNPs has showed good catalytic activity.[28] Kalathil et al. have reported on degradation of methyl orange through a sustainable process by electrically active biofilm in presence of hollow PdNPs. They also carried out the same experiment in presence of solid PdNPs and revealed that hollow PdNPs are much more active than the solid one, this may be due to cage effect and large specific surface area.[29] Malik et al. have synthesized PdNPs from flower extract of Matricaria recutita and applied as nanocatalyst for reduction of an azo dye congo red and reused the catalyst up to five cycles without

loss of activity.[30] Supported PdNPs exhibit better activity as well as easy to recover and recycle. For example PdNPs and Fe_3O_4 NPs dispersed on PEI modified graphene oxide sheets, a novel nano catalyst utilized for catalytic degradation of methylene blue in presence of $NaBH_4$. This catalyst easily separated from the reaction mixture by the use of external magnetic field and recycled up to nine cycles with significant TON value.[31] Another example, biopolymer chitosan-carbon nanotube supported PdNPs can act as excellent catalyst for degradation of dyes Congo red, Methyl orange, Methylene blue and Methyl red.[32] Chitin fabricated PdNPs used as recyclable nano catalyst towards reductive degradation of acidic blue 193 and the degradation process was very fast, estimated $t_{1/2}$ of 1.6 minute and rate constant k_1 of 424.9×10^{-3} min^{-1}. The catalyst was highly efficient, even the reaction completed within 15 min after 5 cycles of the catalyst.[33]

4. Conclusion and future prospective

In recent time the developments of green and sustainable processes has gained much more interest in every parts of chemistry. Since the applications of PdNPs have continuously increased in versatile fields and hence to fulfill the demand of PdNPs requires developments of new methodologies by which PdNPs can be synthesized very rapidly along with low costs and eco-friendly process. The traditional chemical and physical methods for PdNPs synthesis have several drawbacks and they are not environmentally benign. The synthetic process involving synthesis of PdNPs from biological species or utilizing green solvents or alternative energy sources are green process because these process are rapid, low cost, mild reaction condition and uses renewable materials or green solvents. Modification of PdNPs by functionalization or solid supports makes the PdNPS more active as well as more selective.

In this review the different synthetic processes of PdNPs preparation focusing the green processes are discussed. The modifications of PdNPs have been introduced by synthesis of PdNPs on surface of different solid materials. The application of PdNPs both not supported and solid supported as catalyst towards C-C coupling reactions Suzuki coupling, Heck coupling, Sonogashira coupling and Hiyama coupling discussed with advancement by performing the reactions in green solvents or execution of an alternative energy sources such as microwave irradiation or ultrasonic condition to make the process became greener. The reductive degradations of toxic dyes in presence of PdNPs as catalyst have also been considered here.

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6. Notes and References

1. Piermatti O., Green Synthesis of Pd Nanoparticles for Sustainable and Environmentally Benign Processes, Catalysts **2021**, 11, 1258.

2. Gavia D. J. and Shon Y.-S., Catalytic Properties of Unsupported Palladium Nanoparticle Surfaces Capped with Small Organic Ligands, ChemCatChem. **2015**, 7(6): 892–900.

3. (a) Joudeh N., Saragliadis A. , Koster G., Mikheenko P. and Linke D., Synthesis methods and applications of palladium nanoparticles: A review, Front. Nanotechnol. **2022**, 4:1062608.

   (b) Bloch K, Pardesi K, Satriano C and Ghosh S, Bacteriogenic Platinum Nanoparticles for Application in Nanomedicine. Front. Chem., **2021,** 9, 624344.

   (c) Vinodhini S., Scholastica M. et al., Green synthesis of palladium nanoparticles using aqueous plant extracts and its biomedical applications, Journal of King Saud University – Science, **2022,** 34, 102017

4 . Loshchinina E. A., Vetchinkina E. P. , Kupryashina M. A. , Diversity of Biogenic Nanoparticles Obtained by the Fungi-Mediated Synthesis: A Review, Biomimetics, **2023**, 8(1), 1;

5. Sayadi H. , Salmani N., Heidari A. , Rezaei M. R., Bio-synthesis of palladium nanoparticle using Spirulina platensis alga extract and its application as adsorbent, Surfaces and Interfaces, **2018,** 10**,** 136-143

6. Ameri A., Shakibaie M. et al. "Forootanfar H. Rapid and Facile Microwave-Assisted Synthesis of Palladium Nanoparticles and Evaluation of Their Antioxidant Properties and Cytotoxic Effects Against Fibroblast-Like (HSkMC) and Human Lung Carcinoma (A549) Cell Lines". Biol. Trace Elem. Res. **2019,** 197:132–140.

7. FuadAmeen S. H. et al., Padina boryana mediated green synthesis of crystalline palladium nanoparticles as potential nanodrug against multidrug resistant bacteria and cancer cells, Scientifc Reports, **2021**, 11:5444

8. Momeni S., Nabipour I., A Simple Green Synthesis of Palladium Nanoparticles with Sargassum Alga and Their Electrocatalytic Activities Towards Hydrogen Peroxide, Appl Biochem Biotechnol, **2015**, 176(7):1937-49.

9. Garai C., Hassan Sk. et al. "Green synthesis of Terminalia arjuna conjugated palladium nanoparticles (TA-PdNPs) and its catalytic applications". Journal of Nanostructure in Chemistry, **2018,** 8, 465.

10. (a) Seku K. , Sulaiman S. et al., Microwave-assisted synthesis of palladium nanoparticles using Frankincense resin and evaluation of their catalytic properties, Materials Letters, **2020**, 278, 128427.

    (b) Shivakumar M., Manjunath S. et al., Biological activity of PdNPs derived from hemicellulose via microwave assisted green synthesis, Current Research in Green and Sustainable Chemistry, 2021, 4, 100150

    (c) Khazaleh M., Reddy B.G., Biogenic synthesis of palladium nanoparticles with *Albizia* gum for degradation of Congo red and 4-nitrophenol dyes, Optical Materials, **2023**, 142, 113970

11. Phan T. T. V., Huynh T.C., Manivasagan P. et al., An Up-To-Date Review on Biomedical Applications of Palladium Nanoparticles, Nanomaterials **2020**, 10, 66;

12. Gao P., Xiao Y., Dong Z., Pan H., Wang W., Facile synthesis of palladium nanoparticles supported on urea-based porous organic polymers and its catalytic properties in Suzuki-

Miyaura coupling, Journal of Saudi Chemical Society, 2020, 24, 282-287

13. (a) Ngnie G., Dedzo G. K. and Detellier C., Synthesis and catalytic application of palladium nanoparticles supported on kaolinite-based nanohybrid materials, Dalton Trans., **2016**, 45, 9065-9072

(b) Patel A., Patel A., Synthesis and characterization of supported stabilized palladium nanoparticles for selective hydrogenation in water at low temperature, RSC Adv**., 2021,** 11(14): 8218–8227

14. Li J. & Bai X., Ultrasonic synthesis of supported palladium nanoparticles for room-temperature Suzuki–Miyaura coupling, Journal of Materials Science, **2016**, 51, 9108–9122

15. Raspolli A. M., Galletti C. A., Bertoldo M., Piccinelli F., Chitosan as biosupport for the MW-assisted synthesis of palladium catalysts and their use in the hydrogenation of ethyl cinnamate, Applied Catalysis A: General, **2013**, 468, 95-101

16. Walbrück K., Kuellmer F., Witzleben S., Guenther K., "Synthesis and Characterization of PVP-Stabilized Palladium Nanoparticles by XRD, SAXS, SP-ICP-MS, and SEM", Journal of Nanomaterials, 2019, https://doi.org/10.1155/2019/4758108

17. (a) Ayogu J. I. and Onoabedje E. A., Prospects and Applications of Palladium Nanoparticles in the Cross-coupling of (hetero)aryl Halides and Related Analogues, Chemistry Open, **2021**, 10, 430–450

(b) Patil P.S., Jadhav N.S., Inamdar A.F. et al., Recyclable Pd nanoparticles immobilized on amine functionalized LDH for the Suzuki–Miyaura cross-coupling reaction, Chemical papers, **2023**.

18. (a) Nezhad A. K. and Panahi F., Size-Controlled Synthesis of Palladium Nanoparticles on a Silica–Cyclodextrin Substrate: A Novel Palladium Catalyst System for the Heck Reaction in Water, ACS Sustainable Chem. Eng. **2014**, 2, 5, 1177–1186

(b) Pei X., Xiang D., Luo Z. et al., Catalytic performance of palladium nanoparticles encapsulated within nitrogen-doped carbon during Heck reaction, Journal of Catalysis, **2021**,400, 20-27

19. Khan M., Ashraf M., Shaik M.R., Adil S.F., Islam M.S., Kuniyil M., Khan M., Hatshan M.R., Alshammari R.H., Siddiqui M.R.H. and Tahir M.N., Pyrene Functionalized Highly Reduced Graphene Oxide-palladium Nanocomposite: A Novel Catalyst for the Mizoroki-Heck Reaction in Water. Front. Chem. **2022**, doi: 10.3389/fchem.2022.872366

20. Martins D.L. , Alvarez H.M., Aguiar L.C.S., Antunes O. A.C., Heck reactions catalyzed by Pd(0)-PVP nanoparticles under conventional and microwave heating, Applied Catalysis A: General **2011**, 408, 1(2), 47

21. (a) Mori S., Yanase T., Aoyagi S., Monguchi Y., Maegawa T., Sajiki H., Chem. Eur. J. **2008**, 14, 6994–6999.

(b) Mohajer F., Ziarani M.G., Badei A., Decorated palladium nanoparticles on mesoporous organosilicate as an efficient catalyst for Sonogashira coupling reaction, Journal of the Iranian Chemical Society, **2020**, 18(3):1-13

(c) Mohajer F., Heravi M.M.et al., Copper-free Sonogashira cross-coupling reactions: an overview, *RSC Adv.*, **2021**, 11, 6885-6925

22. Magdesieva T.V., Nikitin O. M., Zolotukhina E. et al., Palladium–polypyrrole nanoparticles-catalyzed Sonogashira coupling, Mendeleev Commun., **2012**, 22, 305–306.

23. Keshipour S., Shojaei S., Shaabani A., Palladium nano-particles supported on ethylenediamine-functionalized cellulose as a novel and efficient catalyst for the Heck and Sonogashira couplings in water,Cellulose, **2013**, 20, 973–980.

24. Salih K. S. M., and Baqi Y., Microwave-Assisted Palladium-Catalyzed Cross-Coupling Reactions: Generation of Carbon–Carbon Bond, Catalysts **2020**, 10, 4.

25. Ranu B. C. , Dey R., Chattopadhyay K., A one-pot efficient and fast Hiyama coupling using palladium nanoparticles in water under fluoride-free conditions, Tetrahedron Letters, **2008**, 49,3430–3432.

26. Planellas M. , Moglie Y. et al., Heck, Sonogashira, and Hiyama Reactions Catalyzed by Palladium Nanoparticles Stabilized by Tris-Imidazolium Salt, EurJOC, **2014**, https://doi.org/10.1002/ejoc.201400162

27. Kora A. J., Rastogi L. , Catalytic degradation of anthropogenic dye pollutants using palladium nanoparticles synthesized by gum olibanum, a glucuronoarabinogalactan biopolymer, Industrial Crops and Products, **2016,** 81, 1-10

28. Narasaiah B. P., Mandal B. K., Remediation of azo-dyes based toxicity by agro-waste cotton boll peels mediated palladium nanoparticles, Journal of Saudi Chemical Society, **2020,** 24(2), 267-281

29. Kalathil S. and Ghosh Chaudhuri R., Hollow Palladium Nanoparticles FacilitatedBiodegradation of an Azo Dye by ElectricallyActive Biofilms, Materials **2016**, 9, 653.

30. Malik M.A., Alshehri A.A., Abomuti M.A., Danish E.Y., Patel R., Bioengineered Matricaria recutita Extract-Assisted Palladium Nanoparticles for the Congo Red Dye Degradation and Catalytic Reduction of 4-Nitrophenol to 4-Aminophenol. Toxics **2021**, 9, 103.

31. Li S., Li H. et al., Highly efficient degradation of organic dyes by palladium nanoparticles decorated on 2D magnetic reduced graphene oxide nanosheets, Daltontrans, **2015**, DOI: https://doi.org/10.1039/C5DT01036E

32. Sargin I., Baran T., Arslan G., Environmental remediation by chitosan-carbon nanotube supported palladium nanoparticles: Conversion of toxic nitroarenes into aromatic amines, degradation of dye pollutants and green synthesis of biaryls, Separation and Purification Technology, **2020**, Volume 247, 116987

33. Ahmed H. B., Saad N., Emam H. E., Recyclable palladium based nano-catalytic laborer encaged within bio-granules for dye degradation, Surfaces and Interfaces, **2021,**Volume 25, 101175

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