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# Biosynthesis of Poly(ethylene glycol)- supported Palladium nanoparticles using Colocasia esculenta leaf extract and their catalytic activity for Suzuki -Miyaura cross- coupling reaction

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**A simple and green protocol for the synthesis of poly(ethylene glycol) stabilized palladium nanoparticles under ambient conditions from the aqueous extracts of *Colocasia esculenta* leaves has been reported. The nanoparticles are characterized by UV-visible spectroscopy, FTIR spectroscopy, XRD and SEM analysis. The prepared Pd NPs showed excellent catalytic activity towards Suzuki-Miyaura cross coupling reaction for a wide variety of aryl halides and phenyl boronic acid substrates. The catalytic system was found to be recyclable and could be reused in subsequent catalytic runs without significant loss of activity.**

From the inception, the palladium-catalyzed carbon–carbon bond forming reactions developed by Heck, Negishi and Suzuki have made a vital impact in the development of modern synthetic organic chemistry.[1,2] Such coupling reactions have wide applications in the production of polymers, agrochemicals, and pharmaceutical intermediates.[3,4] Their widespread use is mainly due to the mild conditions associated with these reactions and also with their compatibility to a wide variety of functional groups. Nowadays, metal nanoparticles (NPs) are considered to be very attractive and efficient catalysts compared to their bulk counterparts since they have a high surface to volume ratios and also their surface atoms are very active. In recent years, much attention had been focused by the researchers on palladium nanoparticles (Pd NPs) synthesis because of their remarkable physical, chemical, optical and thermodynamic properties.[21] Because of these unique properties, Pd NPs find many applications in the field of catalysis[5] and drug delivery[6]. Nowadays, Pd NPs of various sizes and shapes are synthesized by different wet synthetic processes such as chemical,[7] sonochemical[8] and polyols reduction.[9] These types of synthetic processes are generally simple, provide high growth rate and high yield. However, these methods are not environment friendly and therefore some alternative methods are in continuous search for the synthesis of NPs. Biological materials such as plant extracts, microorganisms etc can be used as nanofactories for the synthesis of NPs as they have the reduction potential required for the synthesis and also in addition, they act as stabilizers.[10,11] The use of biological materials such as plant extract for the synthesis of NPs offer several advantages of eco-friendliness and are compatible for pharmaceutical and other biomedical applications as they do not use any toxic chemical for their synthetic protocols.[22] Also, the processes are cost effective, environment friendly and can easily be scaled up for large scale synthesis. Hence, there is a huge demand for these types of simple, inexpensive and easily accessible catalysts which can be generated through green procedure for these coupling reactions. As far as biosynthesis of Pd NPs is concerned; very few reports are available for their synthesis. Few recently reported biological synthesis for Pd NPs are peel extract of *Annona squamosa* (sugar-apple),[12] leaf extract of *Anacardium occidentale* (cashew nut),[13] *Cinnamom zeylanicum* (cinnamon) bark extract,[14] and *Musa paradisiaca* (banana) peal extracts.[15] The biologically synthesized Pd NPs have been used for various applications in recent years such as in azo dye decolorization[16] and as a catalyst for Heck reaction.[17] Therefore, immense opportunities are available for synthesizing Pd NPs using biological materials which can be used for various environmental and biological applications. The present work deals with biosynthesis of Pd NPs using *Colocasia esculenta* Linn. (*C. esculenta*) leaf extract as reducing agent followed by evaluation of catalytic activity of biosynthesized Pd NPs in Suzuki cross coupling reactions. *C. esculenta*, locally known as 'kochu' (**Figure 1**) in Assam, a North Eastern State of India is widely available and used by folks in traditional system of medicine in north-eastern India.

Due to the compositional abundance of ascorbic acid, thiamine, riboflavin, niacin, carbohydrates, fats etc. in its leaves may be responsible for its reductive potency.[18] In this context, one of our laboratory groups has recently reported the utilization of *C. esculenta* leave extract for the preparation of poly(ethylene glycol) (PEG)-supported silver NPs and they

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assessed the free radical scavenging, antibacterial and larvicidal activity of the prepared NPs.[19]

**Figure 1.** Image of *Colacasia esculenta* Linn plant

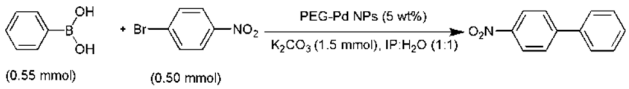
In the work presented here, the authors described the reduction potency of *C. esculenta* Linn. Leaves for the preparation of poly(ethylene glycol)-supported palladium NPs. The prepared NPs were characterized using various spectroscopic and microscopic tools. The Suzuki cross coupling reaction between boronic acids and aryl halides with different types of functional groups were assessed with the prepared NPs resulting good to high yield of the product.

For the preparation of PEG supported Pd NPs, about 10 gm of the leaves was washed properly with deionized water to remove dust and grounded by using domestic blender. The whole content was stirred in a round bottom flask for about 20 minutes in 60 ml distilled water at 50 $^0$C and was filtered with muslin cloth at ambient temperature. The filtered aqueous extract was kept for further experiments.

For the preparation of Pd NPs@PEG, 25 mL of 0.001 M $PdCl_2$ was prepared in 5% (w/v) PEG-4000 solution. To it, 5 mL of the aqueous extract (obtained as above) was then added. The pH of the solution was maintained within 10 and 11 by using 0.1 M NaOH. Then, the solution was refluxed at 60 $^0$C for one hour. The formation of the NPs was indicated by the color change from light brown to dark brown. The matrix supported NPs were separated by centrifugation at 12,000 rpm for 15 minutes. The separated NPs were washed three times with distilled water and ethanol in order to make the NPs free from biomaterials and dried in an oven at 60 $^0$C for two hours.

To investigate the effectiveness of the catalyst in Suzuki-Miyaura reaction, phenylboronic acid and 4-bromonitrobenzene were chosen as model substrates using isopropanol:water (1:1) as the solvent system, $K_2CO_3$ as a base and the reactions were performed under aerobic condition and at room temperature without adding any ligands or additive (Scheme 1).

In a 50 ml round-bottomed flask, a mixture of aryl halide (0.5 mmol), boronic acid substrate (0.55 mmol), potassium carbonate (1.5 mmol), nanocatalyst (5 wt% with respect to boronic acid substrate) were added and stirred in isopropanol:water (1:1) solvent system at room temperature for the required time. The reaction was monitored by TLC. After completion of the reaction, mixture was diluted with water and the product was extracted with distilled ethyl acetate (3 times). The combined extract was washed with brine (3 times) and dried over anhydrous $Na_2SO_4$. The product was purified using column chromatography technique [60-120 mesh silica gel, ethyl acetate-hexane solvent mixture.




Scheme 1 Model reaction

The synthesis of Pd NPs using *C. esculenta* leaf extract was first monitored visually and then with the help of UV-visible spectroscopy (**Figure 2**). Many reports showed that basic condition was indispensible for the synthesis of NPs using plant extract.[20] Keeping this in mind, we had initially adjusted the pH of the reaction solution within 10 and 11 using 0.1 M NaOH solution.

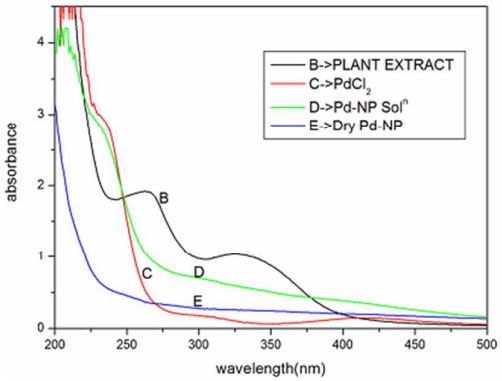



**Figure 2.** UV-Visible spectra of B) plant extract, C) $PdCl_2$ solution, D) Pd NPs solution after bioreduction, and E) dry Pd NPs.

During visual monitoring of the reaction a gradual shifting of the color from light brown to dark brown was observed within 1 hr at moderate temperature (45 $^0$C). Metal NPs are associated with free electrons that are responsible for Surface Plasmon Resonance (SPR) peaks, due to combined vibration of electrons under alkaline condition might be effective for the utilization of the active component of the leaf extract. The change of color from light brown to dark brown was observed due to excitation of SPR of Pd NPs formed. In the UV-Vis spectroscopy, a distinct peak near 300 nm was observed for $PdCl_2$ solution due to $Pd^{2+}$ ions present in the solution. However, as time proceeded, with the formation of Pd NPs, the peak near 300 nm began to disappear and vanished within 2 h. This was due to the metal charge transfer from $Pd^{2+}$ to Pd(0). The appearance of a broad continuous spectrum, which gradually increases in intensity from visible to UV region suggests the complete reduction of $Pd^{2+}$ to Pd(0).

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Powder X-ray diffraction technique was used to determine the crystal domain size and the structure of the NPs formed. The XRD pattern for both $PdCl_2$ and Pd NPs were taken and ~~is~~ shown below (**Figure 3).**

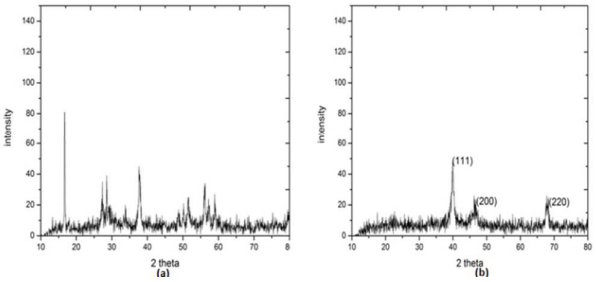


**Figure 3.** XRD patterns for (a) $PdCl_2$ and (b) Pd NPs respectively

From the XRD pattern of Pd NPs, three peaks were observed at 40.260, 45.780 and 68.670 corresponding to reflection to the (111), (200) and (220) planes respectively that could be indexed to fcc phase of Pd NPs (JCPDS≠89-4897). The broadening of the XRD peak indicates that the synthesized particles are in the nano range. Scherrer's formula was used for the determination of average crystalline size of Pd NPs. Since there are three distinct peaks in the XRD spectrum of Pd NPs, the prominent peak at 40.260 corresponding to (111) crystal plane has been considered to calculate the crystal domain size

$$D = K\alpha/\beta\cos\theta$$

Where, D represents average crystal domain size, K is the Scherrer's constant, K=0.9 in this case, α= 15.74 nm which is the wavelength of X-Rays, β is the peak angular width (full width half maxima, FWHM) and θ is the diffraction angle. The FWHM value for this case is 0.7868. Now applying the Scherrer's formula for the crystal domain size of the NPs, it was found to be about 19.35 nm.

The typical FT-IR spectra for the plant extract and PEG assisted Pd NPs are shown below **(Figure 4).**

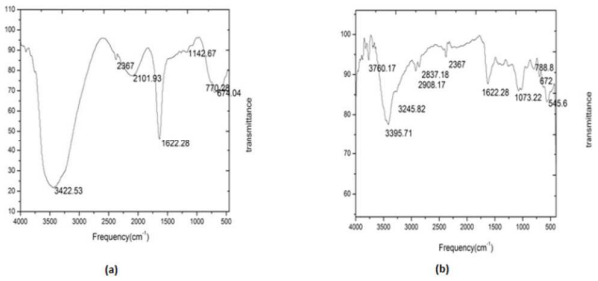


**Figure 4.** FT-IR spectra of (a) biosynthesized Pd-NPs and (b) the plant extract.

The composition of the leaf extracts shows the abundances of ascorbic acid (vitamin C), thiamine, riboflavin, niacin, carbohydrates (glucose, fructose and sucrose), fats etc. as mentioned earlier.[18] These biomolecules have numbers of hydroxyl groups. For the plant extract, in the IR spectrum, the peak observed at 3423 $cm^{-1}$ is due to surface hydroxyl groups. The other prominent peak at 1622 $cm^{-1}$ is due to the C=C stretching vibration of ascorbic acid present in the leaf extract.[28] The peak at 2102 $cm^{-1}$ is due to C-H stretching vibration of sugar present in the leaf extract.[29] Surface hydroxyl groups available in the plant extract of the bioactive molecules primarily reduce $Pd^{2+}$. The presence of the peaks at 3395 $cm^{-1}$, 1622 $cm^{-1}$ and 1073 $cm^{-1}$ in the IR spectrum of Pd NPs indicated that different polyol compounds adsorbed on the palladium surface which might be responsible for capping and stabilizing Pd NPs.

The SEM images for the Pd NPs are shown in the below **(Figure 5):**

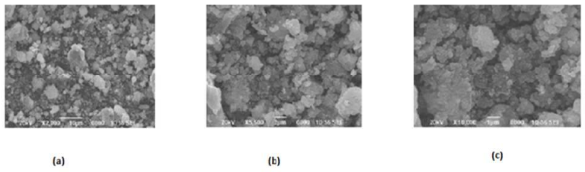


**Figure 5.** SEM images for PEG stabilized Pd NPs at (a) 10 µm, (b) 2 µm and (c) 1 µm magnification

The surface morphology of the NPs was studied by using SEM analysis. The SEM images of PEG stabilized Pd-NPs are visualised at (a) 10 µm, (b) 2 µm and (c) 1 µm scale respectively. From the SEM images we can say that the NPs are of irregular shapes and of different sizes. This might be due to the agglomeration of the Pd-NPs.

To study the effect of different solvents, bases and amount of the catalyst we have chosen 4-bromonitrobenzene and phenylboronic acid as our model substrates and the results are summarized in Table 1. Screening of solvents using $K_2CO_3$ as base showed that isopropanol : water (1:1) was found to be the most effective solvent system with excellent yield (Table 1, entry 7). Our analysis also proved that presence of base was very essential for the coupling reactions, since the reaction did not proceed in the absence of a base (Table 1, entry 2). The

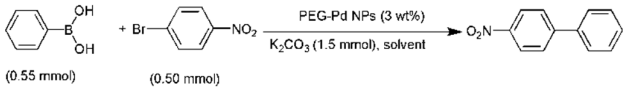


Table 1: Effect of solvents and bases on Suzuki-Miyaura cross coupling reaction of 4-bromonitrobenzene and phenylboronic acid:[a]

| Entry | Solvent | Base | Time (h) | Yield(%)[b] |
|---|---|---|---|---|
| 1 | No solvent | $K_2CO_3$ | 5 | 15 |
| 2 | $H_2O$ | No base | 24 | No reaction |
| 3 | $H_2O$ | $K_2CO_3$ | 24 | 35 |
| 4 | DMF | $K_2CO_3$ | 24 | 70 |
| 5 | MeOH:MeCN (1:1) | $K_2CO_3$ | 26 | 45 |
| 6 | MeOH:$H_2O$ (1:1) | $K_2CO_3$ | 28 | 36 |
| 7 | Isopropanol:$H_2O$ (1:1) | $K_2CO_3$ | 1.5 | 90 |
| 8 | Isopropanol:$H_2O$ (1:1) | $Na_2CO_3$ | 2.5 | 90 |
| 9 | Isopropanol:$H_2O$ (1:1) | KOH | 3 | 85 |

[a]Reaction Condition: 0.5 mmol 4-bromonitrobenzene, 0.55 mmol phenylboronic acid, 1.5 mmol base, 3 wt% catalyst and 4 ml solvent. [b]Isolated yield.

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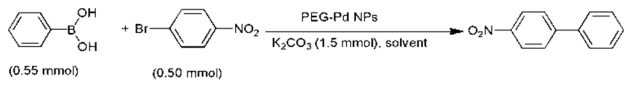
reaction can also proceed in the presence of other inorganic bases like $Na_2CO_3$, KOH with comparable yield of the cross coupling products (Table 1, entries 8 and 9).

After optimizing the reaction condition for the solvent system and the appropriate base, we studied the effect of amount of catalyst on the reaction rate and its efficiency. The results are summarized below **(Table 2).** From this observation it was found that 5 wt% catalytic amount of the catalyst was the optimized amount for the coupling reaction.

**Table 2**: Effect of catalytic amount on Suzuki coupling reaction

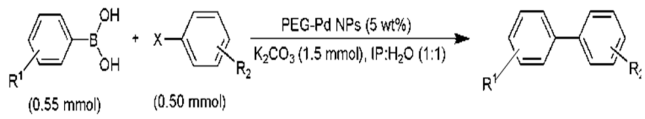



| Entry | Amount of the catalyst[a] (wt/%) | Time (h) | Yield[b] |
|---|---|---|---|
| 1 | 3 | 1.5 | 90 |
| 2 | 5 | 1.5 | 94 |
| 3 | 6.5 | 1.3 | 94 |
| 4 | 10 | 1 | 94 |

[a]wt% w.r.t. the phenylboronic acid derivative. [b]Isolated yield.

To evaluate the scope and limitation of the current procedure, reactions of a wide range of electronically diverse aryl bromides and iodides with different phenylboronic acid substrates were examined using the prepared PEG@Pd NPs as a catalyst (**Table 3**).

**Table 3**: Suzuki-Miyaura cross-coupling reactions of various aryl halides with arylboronic acids using Pd NPs@PEG as catalyst:[a]




| Entry | $R^1$ | X | $R^2$ | Time (h) | Yield[b] (%) |
|---|---|---|---|---|---|
| 1[23] | H | 4-Br | H | 1.5 | 92 |
| 2[24] | H | 4-Br | $NO_2$ | 1.5 | 94 |
| 3[24] | H | 4-I | MeO | 2 | 95 |
| 4[25] | 2-MeO | 4-Br | H | 1.5 | 95 |
| 5[23] | 4-MeO | 4-I | MeO | 1 | 92 |
| 6[26] | 2-Me | 4-I | MeO | 1 | 92 |
| 7[27] | 3-Me | 4-Br | MeO | 2 | 91 |
| 8[24] | 4-CHO | 4-Br | H | 2 | 90 |
| 9 | 4-CHO | 4-I | MeO | 1.5 | 90 |
| 10 | 4-*tert*-butyl | 4-Br | $NO_2$ | 1.5 | 83 |
| 11[24] | 2-CHO | 4-Br | H | 1.5 | 96 |
| 12 | 2-$NH_2$ | 4-Br | H | 2 | 94 |
| 13[24] | H | 4-Cl | $NO_2$ | 24 | 15 |

[a]Reaction Condition: 0.5 mmol halobenzene, 0.55 mmol phenylboronic acid derivative, 1.5 mmol base, 5 wt% catalyst and 4 ml solvent. [b]Isolated yield.

From the substrate study, it is found that the rate of Suzuki coupling reaction depends on the nature of the functional group present on the aryl halide and the arylboronic acids. If electron donating group is present on the arylboronic acid then the reaction requires less time to complete. However, in the presence of electron withdrawing substituents the reaction requires more time for completion. The progress of the reaction was monitored by TLC and the products formed were characterized by $^1$H NMR and $^{13}$C NMR analyses and melting point determination.

From the green chemistry perspective, the reusability of catalysts makes them more attractive. Accordingly, we also investigated the reusability of our catalyst. To examine the reusability of the catalyst, the model reaction (scheme 1) was carried out. After completion of the reaction, the reaction mixture was filtered through Whatmann 40 filter paper. The catalyst being insoluble and remains as residue, it was collected and dried. The filtrate was extracted with ethyl acetate. The collected Pd NPs were dried and taken in a round bottomed flask and a fresh reaction with the same amount of starting material was carried out. We find that the catalyst is reusable up to third cycles without any significant loss of the catalytic activity. After third cycle slight loss of activity was observed (**Figure 6**). After fifth cycle a significant loss of activity of the catalyst was observed. This may be due to the deactivation of the catalyst during the course of the reaction and recovery process.

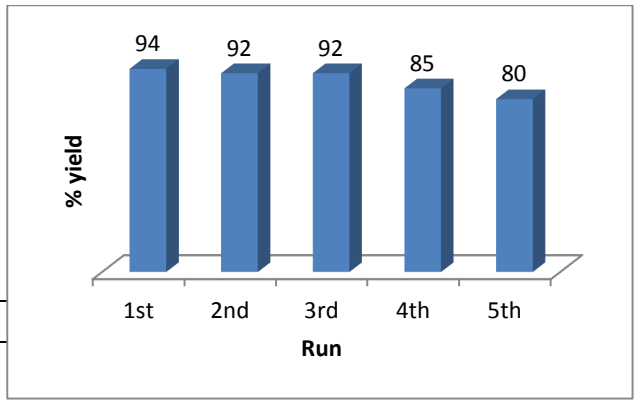



**Figure 6**. Reusability checking of the Pd nano catalyst

In conclusion, we have developed a very efficient and green process for the synthesis of Pd NPs using *C. esculenta* plant extract which exhibits excellent reactivity under mild conditions for Suzuki cross-coupling reaction of aryl halides and phenylboronic acid derivatives. The reaction also take much lesser time and less amount of catalyst compared to some of the conventional method.[30-32] It is found that a wide range of functional groups are compatible in the reaction conditions and also gives very high yield of the cross-coupling products. In the UV-Visible wavelength range, the synthesized NPs show good surface plasmon resonance behaviour. The polyol components and the heterocyclic compounds found in the plant leaves were considered to be responsible for the reduction of Pd(II) which eliminated the use of toxic reducing agents. Therefore, we can consider the synthetic process as green synthesis. The *C. esculenta* plants are easily available in North-Eastern region which can further be applied for the

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synthesis of other transition metal NPs as well. From the technical point of view, these Pd NPs obtained may have the potential applications not only in the field of catalysis, but also in the medical field. Success of such a biological synthesis of metallic NPs is an alternative to chemical synthesis protocols and low cost reductants for the synthesis of Pd NPs.

Notes and references

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## Graphical Abstract:

**Biosynthesis of Poly(ethylene glycol)-supported Palladium nanoparticles using *Colocasia esculenta* leaf extract and their catalytic activity for Suzuki –Miyaura cross-coupling reaction**

Raju Kumar Borah, Hirak Jyoti Saikia, Abhijit Mahanta, Vijay Kumar Das, Utpal Bora and Ashim Jyoti Thakur*

A green and efficient method for the development of PEG supported Pd NPs has been developed from aqueous extract of *Colocasia esculenta* leaf. The prepared NPs shows excellent catalytic activity for Suzuki-Miyaura cross coupling reaction for a wide varieties of aryl halides and phenyl boronic acid substrates at room temperature.