Received: 31 July 2018 | Revised: 2 November 2018 | Accepted: 17 November 2018
DOI: 10.1002/aoc.4758

FULL PAPER

WILEY Applied Organometallic Chemistry

Green chemical synthesis of Pd nanoparticles for use as efficient catalyst in Suzuki-Miyaura cross-coupling reaction

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Funding information
Science and Engineering Research Board, Grant/Award Number: EMR/ 2015/ 001912; Council of Scientific and Industrial Research, Grant/Award Number: 01(2910)/17/EMR-II

Herein, we report the synthesis of tiny spherical Pd nanoparticles (NPs) by green chemical method under ambient conditions using flower extract of *Lantana camara* plant. The size of the Pd NPs is tunable from 4.7 to 6.3 nm by systematically controlling the concentration of either metal ions or plant extract. The synthesized Pd NPs were well characterized by different spectroscopic, microscopic and diffractometric techniques. The Pd NPs offered good size-dependent catalytic activity in the Suzuki-Miyaura C-C coupling reaction under mild reaction conditions in (1: 1) water-ethanol mixture. The catalyst is stable and exhibited excellent reusability up to three cycles of coupling reaction after which the catalytic activity decreases.

KEYWORDS
catalyst, C-C coupling, green synthesis, *Lantana camara*, Pd NPs

1 | INTRODUCTION

Synthesis of palladium (Pd) nanoparticles (NPs) has received considerable attention in recent years due to their interesting physical, chemical, optical and thermodynamic properties in the nanoscale region.[1] Because of these unique properties, Pd NPs find various applications in different areas such as catalysis,[2–5] sensing,[6,7] biomedical[8] and plasmonic waveguiding.[9,10] Consequently, much attention has been focused on the synthesis of Pd NPs of controlled sizes and shapes. Generally, Pd NPs are synthesized by various wet syntheses processes such as chemical reduction,[11–14] sonochemical,[15] polyol reduction methods,[7,16] etc. However, most of the conventional chemical methods involve a reducing agent and a stabilizer in a suitable solvent.[11–13,17] Wherein the chemicals used are quite harmful and toxic enough to cause environmental hazard while adopting for large-scale production of Pd NPs.[18] Also, most of the conventional reducing agents involved in chemical methods produce toxic byproducts which might get adsorbed on the surface of Pd NPs and thereby imparted adverse effects in biological applications.[19] Therefore, the choice of the need of reducing and capping agents is to be considered seriously from both an economic and green chemistry perspective.[20–22] Hence, there is immense interest in recent years in developing environmentally friendly and sustainable methods for the synthesis of Pd NPs. In this regard, the biogenic method involving plant extract has received considerable attention because; such methods are considered to be very effective in developing a rapid, clean, nontoxic, and eco-friendly technology.[23–27] Another advantage associated with the use of plant extract is that no additional capping agent or stabilizer is required as phytochemicals present in the plant extract or their by-product formed during reaction stabilize the formed Pd NPs.[28,29] Additionally, the phytochemicals are also useful in controlling the size and shape of Pd NPs.[30] The most prominent examples of plant used so far include *Pulicaria glutinosa*,[4] *Delonix regia*,[23] *Euphorbia thymifolia*,[24] *Stachys lavandulifolia*,[27] *Sapindus mukorossi*,[30] *Glycyrrhiza* *glabra*,[31] *Pistacia atlantica kurdica*,[32] *Origanum vulgare*,[33] watermelon rind[34] and so on. However most of the above-mentioned plants are either economically important or edible or have medicinal values. However, to the best of our knowledge, reports on the synthesis of Pd NPs using wild weeds are not available yet.

Considering the benefit of plant extracts, herein; we intend to design a facile, cheap and environmentally friendly method to synthesize size-tunable spherical Pd NPs using the flower extract of *Lantara camara* plants. North-East region of India is rich in biodiversity and *Lantana camara* is readily available throughout Arunachal Pradesh as wild sage. The population of *Lantana camara* is very high in this region which is spreading very fast due to their invasive nature. However, such plants are not utilized properly by any researchers for their gainful utilization. It is reported that the extract of flowers of *Lantana camara* is composed mainly of sugars, phospholipids, glycolipids, alkaloids, phenolics, tannins, etc. and the amount of these substances are more in the extract of flowers than that of other parts of the plant.[35,36] Also it is reported that polyphenolics can be extracted efficiently using water as extracting solvent which also increases the versatility of the process as it further minimizes the use of toxic solvents.[36] The polyphenolics act as better green reducing agents for noble metal and other transition metal ions.[25,26,37] Considering these aspects, we believe that the use of flower extract of *Lantana camara* as reducing-cum-stabilizing agent for the preparation of Pd NPs can provide a new platform to this noxious plant making it a value-added weed for nanotechnology-based industries in future. So, we report in this manuscript a fast, low-cost and environmentally safe synthesis method for Pd NPs using phytochemicals present in flower extract of *Lantana camara* plant both as reducing and capping agent.

In chemistry, Pd is regarded as one of the most efficient metal catalysts.[2,4,5,14,38] The high surface-to-volume ratio in the nanometer dimension even makes Pd NPs more effective catalyst.[3,24,39] Subsequently Pd NPs are widely used as catalyst in low-temperature oxidation/reduction of automobile pollutants,[40–42] coupling reactions,[2,4,24,30–32,43–45] hydrogenation reaction[23,46] as well as other organic reactions. However, Pd earned a reputation as a catalyst for their remarkable success in C-C coupling reactions which is considered to be one of the most powerful and a versatile method for the synthesis of asymmetric biaryl compounds from aryl boronic acids and aryl halides. These asymmetric biaryl compounds find wide applications in the production of agrochemicals, natural products, pharmaceuticals and functional materials.[47,48] Many studies have reported on the improvements in the activity and selectivity of these catalysts where Pd NPs are formed during the reaction that acts as the active catalyst.[46,49,50] However, ligands used in the system and the corresponding catalysts have several disadvantages such as the use of expensive, toxic phosphine ligands and organic solvents, harsh reaction condition, low yield, environmental problems caused by the side product formation, inert atmosphere conditions. Also, the phosphine ligands are readily oxidized to their corresponding phosphine oxides, which can prevent the easy recovery and recycling of the catalyst. For these reasons, the focus is to make the experimental conditions more environmentally benign and to develop ligand-free palladium catalysts. Consequently, many studies have been engaged in recent times to search for the effective solvents in the context of green chemistry.[51–53] Water is commonly considered as a benign solvent in view of its non-toxicity and abundant natural occurrence. Around 80% of the chemical waste from a reaction mixture corresponds to the solvent. Therefore, the use and release of clean water instead of organic solvents is the significant concern with respect to environmentally friendly organic synthesis.[52–54] Recently, many reports have been published on the successful use of Pd NPs synthesized by plant extract as catalysts in cross-coupling reactions in water and/or a water-alcohol mixture.[4,24,27,30] Due to the ability to dissolve bases in water for activating aryl boronic acids, the reaction proceeds much faster in an aqueous medium.[55] Taking into the consideration of the effectiveness of Pd NPs in Suzuki-Miyaura reaction, herein we also report the use of plant extract reduced Pd NPs as a catalyst for Suzuki-Miyaura coupling reaction in 1: 1 water-ethanol mixture using K_2CO_3 as a base at room temperature.

2 | EXPERIMENTAL

2.1 | Materials and method

Palladium chloride ($PdCl_2$), phenyl boronic acids and their substituted products were purchased from Sigma–Aldrich. Flowers of *Lantana camara* were collected from Papumpare district of Arunachal Pradesh, India. Solvents used were purchased from Merck India and were distilled before use. All other reagents were used without further purification. All the glassware's were cleaned in a bath of freshly prepared aqua–regia solution ($HCl: HNO_3 = 3:1$, V/v) and then rinsed thoroughly with double distilled water. All solutions were prepared in double distilled water.

2.2 | Isolation of flower extract

The phytochemicals from the flowers of wild growing *Lantana camara* were isolated by following the previously reported method.[26] For the synthesis purpose, a 4.0 gL^{-1} solution of the extract was prepared in distilled water. The amount of total phenolics in the flower extract of *Lantana Camara* plants were determined with the Folin–Ciocalteu reagent using gallic acid as a standard following our previously reported method.[25] A calibration curve was plotted ($R^2 = 0.994$) with the series of gallic acid standards from which the total phenolic contents values were determined. Results are expressed as mg of gallic acid equivalents (GAE). The amount of phenolic contents present in the flower extract is 69 mg GAE/g of the extract (GAE: gallic acid equivalent).

2.3 | Synthesis of palladium nanoparticles (Pd NPs)

The Pd NPs were synthesized by the reduction of palladium salt in an aqueous medium using phytochemicals present in the flower extract of *Lantana camara* plant as reducing agent–cum–stabilizer. In a typical synthesis, 2.0 ml of 0.4 wt% aqueous extract solution was taken in a cleaned glass vial containing 1.6 ml of water and was heated to 55 °C under constant magnetic stirring. To the stirring extract solution, 0.4 ml of 0.01 M aqueous $PdCl_2$ solution was added dropwise, and the stirring was continued for 2.0 hr at the same temperature. The progress of the reaction was monitored visually from the color change of the reaction mixture from light yellow corresponding to the mixture of extract and $PdCl_2$ ions to greenish within a short span of time. The resulted colloidal suspension was then purified by dialysis using cellulose membrane (HiMedia; MW cut-off between 12000 to 14000) against distilled water. The purified colloidal suspension was used for different spectroscopic and microscopic analysis. This set of reaction and the resultant suspension was designated as sample Ex-Au-1 (Table 1). To study the effect of metal ion concentration or the concentration of the extract, we have carried out similar sets of reaction by varying the concentration of $PdCl_2$ and extract maintaining the other reaction conditions same (Table 1).

TABLE 1 Reaction recipe for the synthesis of Pd NPs using flower extract of *Lantana camara*

Entry No.	Sample code	$[PdCl_2]$ (M)	[Extract] (wt%)	$(d_{TEM})_{av}$
1.	Ex-Pd-1	1.00×10^{-3}	0.20	5.1 nm
2.	Ex-Pd-2	0.75×10^{-3}	0.20	5.6 nm
3.	Ex-Pd-3	0.50×10^{-3}	0.20	6.3 nm
5.	Ex-Pd-4	0.75×10^{-3}	0.30	4.7 nm

2.4 | General procedure for Suzuki–Miyaura coupling reaction

In a 50 ml round-bottomed flask, a mixture of 4-bromonitrobenzene (1 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (1.5 mmol) and Pd NPs catalyst (0.007 mol%) was added and stirred in ethanol-water (1: 1) solvent system at room temperature for the required time. The reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the mixture was diluted with water, and the product was extracted with ethyl acetate (two times). The extracted product was dried over Na_2SO_4. The product was purified in a column chromatography using silica gel (100–200 mesh) as stationery and ethyl acetate-hexane solvent mixture as mobile phase respectively. The purified product was used for characterization and identification.

To check the reusability of the catalyst, the aqueous part containing the catalyst was centrifuged at 7000 rpm for 15 min after completion of the reaction. The isolated mass was re-dispersed in the solvent system and placed in a round-bottomed flask, and a fresh reaction with the same amount of starting materials was carried out.

2.5 | Characterization

For UV–vis spectroscopic analysis, requisite volume of an aqueous suspension of Pd NPs was transferred into a quartz cuvette of path length 1.0 cm, and the spectrum was recorded in an Agilent Cary60 spectrophotometer in the wavelength region of 300–800 nm against water as a blank. For transmission electron microscopic (TEM) studies, a drop of an aqueous suspension of Pd NPs was cast on a carbon-coated copper grid. The excess solutions were soaked with a tissue paper followed by drying in air. The micrographs were then recorded in a high–resolution JEOL electron microscope (JEM 2100EM) at an accelerating voltage of 200 kV. ImageJ software (National Institute of Health) was used to measure the size and interplane spacing values of the nanostructures. X-ray photoelectron spectroscopy (XPS) analyses of the dried powder samples were performed in Thermo Fisher Scientific, UK make ESCALB Xi$^+$ X-ray photoelectron spectrometer using Al k_α radiations with incident energy of 1486.61 eV. The instrument was operated at 15 kV and 300 W at ambient temperature under ultrahigh vacuum. X–ray diffraction (XRD) study of the Pd NPs deposited on microscopic glass

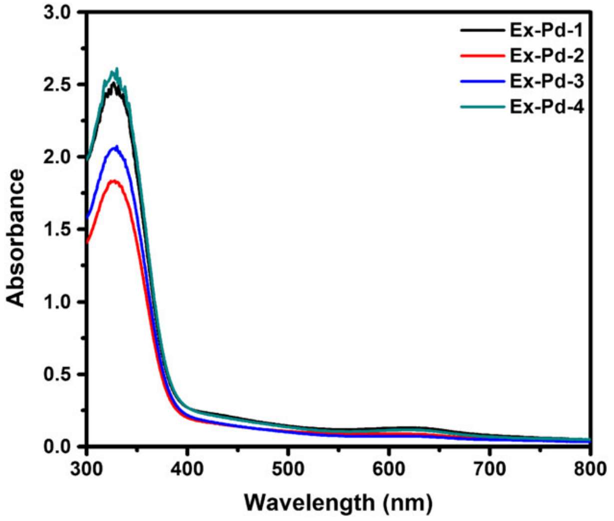


FIGURE 1 UV–vis spectra of colloidal Pd NPs recorded after 2.0 hr of reaction

slide was carried out in a Phillips X'pert Pro multipurpose diffractometer at an accelerating voltage of 40 kV using Cu k_{α} radiation ($\lambda = 1.54$ Å) as X–ray source. Fourier transforms infrared spectra (FTIR) of the powder samples were collected in a Thermo Scientific Nicolet iS5 spectrometer in the range of 4000–400 cm^{-1}. The pellets for recording the FTIR spectra were prepared by mixing the powder sample with dried KBr in the weight ratio of 1:100. ^{1}H and ^{13}C NMR spectra were recorded in a JNM ECS 400 MHz NMR spectrophotometer (JEOL) using tetramethylsilane (TMS) as the internal standard. Chemical shift values are expressed in ppm. Coupling constants are expressed in Hertz.

3 | RESULTS AND DISCUSSION

A series of reaction between the flower extract of *Lantana camara* plant and $PdCl_2$ were carried out in an aqueous medium at 55 °C for 2.0 hr. The formation of Pd NPs was monitored initially by visual observation of the change in color of the reaction mixture from light yellow to greenish with time which was then further confirmed by UV–vis spectroscopy. Figure 1 shows the UV–vis spectra of an aqueous solution of the suspension of colloidal

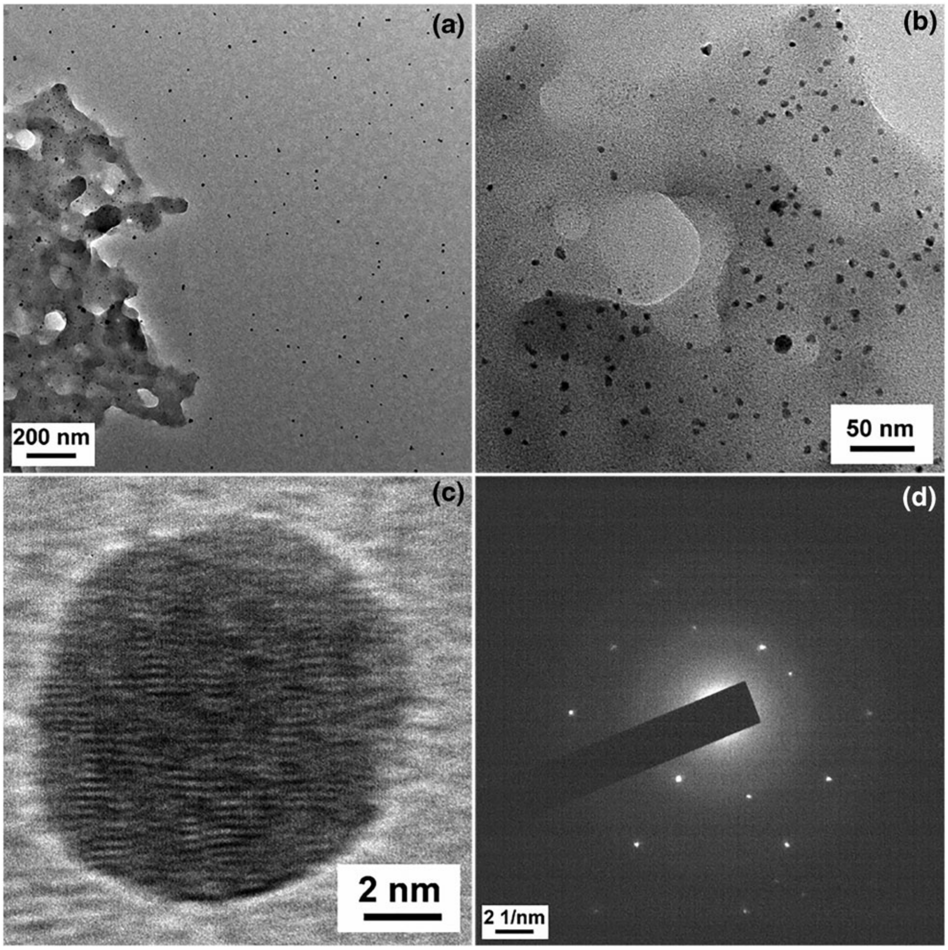


FIGURE 2 Low (a) and high (b) magnification TEM images of Pd NPs recorded from sample Ex-Pd-1. (c) High resolution TEM image and (d) selected area electron diffraction (SAED) pattern recorded from single polygonal Pd NPs

Pd NPs. All the spectra are dominated by absorption peak at 327 nm due to surface plasmon resonance (SPR) indicating the formation of Pd NPs. Nasrollahzadeh et al. reported similar observations for Pd NPs synthesized using extracts of *Euphorbia granulate plant*.[56]

The microscopic analyses of the samples were done in a transmission electron microscope (TEM). Figure 2A shows the TEM image of sample Ex-Pd-1 recorded after 2.0 hr of reaction. The micrograph shows the presence of nearly uniform ultra-small sized spherical Pd NPs. The average size of these Pd NPs as measured from the magnified TEM image (Figure 2B) is 5.1 nm. The particle size distribution of the sample is shown Figure S1a in the Supporting Information (SI). The high-resolution TEM (HRTEM) image of such spherical Pd NP (Figure 2C) shows the presence of lattice fringes those are more likely wavelike with an inter-planner spacing of 0.23 nm. This *d*-spacing value corresponds to the (111) lattice plane of fcc Pd.[5,30] The SAED pattern recorded from such samples show bright spots indicating the formation of crystalline Pd NPs.

To study the effect of concentration of Pd^{2+} on the size of Pd NPs, we recorded the TEM images of samples Ex-Pd-2 and Ex-Pd-3 prepared with Pd^{2+} ion concentration 0.75 and 0.5 mM, respectively, keeping the concentration of extract constant at 0.2 wt%. The TEM image (Figure 3A) of sample Ex-Pd-2 again shows the formation of spherical Pd NPs. In this case, the average size of the Pd NPs is 5.6 nm. Whereas the average size of Pd NPs observed in sample Ex-Pd-3 is 6.3 nm as measured from the respective TEM image shown in Figure 3B. The comparison of the microscopic results of samples Ex-Pd-1, Ex-Pd-2, and Ex-Pd-3 indicate that at constant extract concentration decrease in the concentration of Pd^{2+} ions did not show any significant change in the size or morphology of Pd NPs. The particle size distribution of these samples (Ex-Pd-2 and Ex-Pd-3) are shown in Figure S1b and S1c in the SI. Another set of the reaction was carried out to check the effect of the extract on the size of Pd NPs, with the concentration of extract and Pd^{2+} ion of 0.3% and 0.75 mM, respectively. The TEM image of this sample (Figure 3C) shows the formation of again spherical Pd NPs. However, the average size of these spherical Pd NPs is 4.7 nm. The particles size distribution of this sample is shown in Figure S1d in the SI. To know the

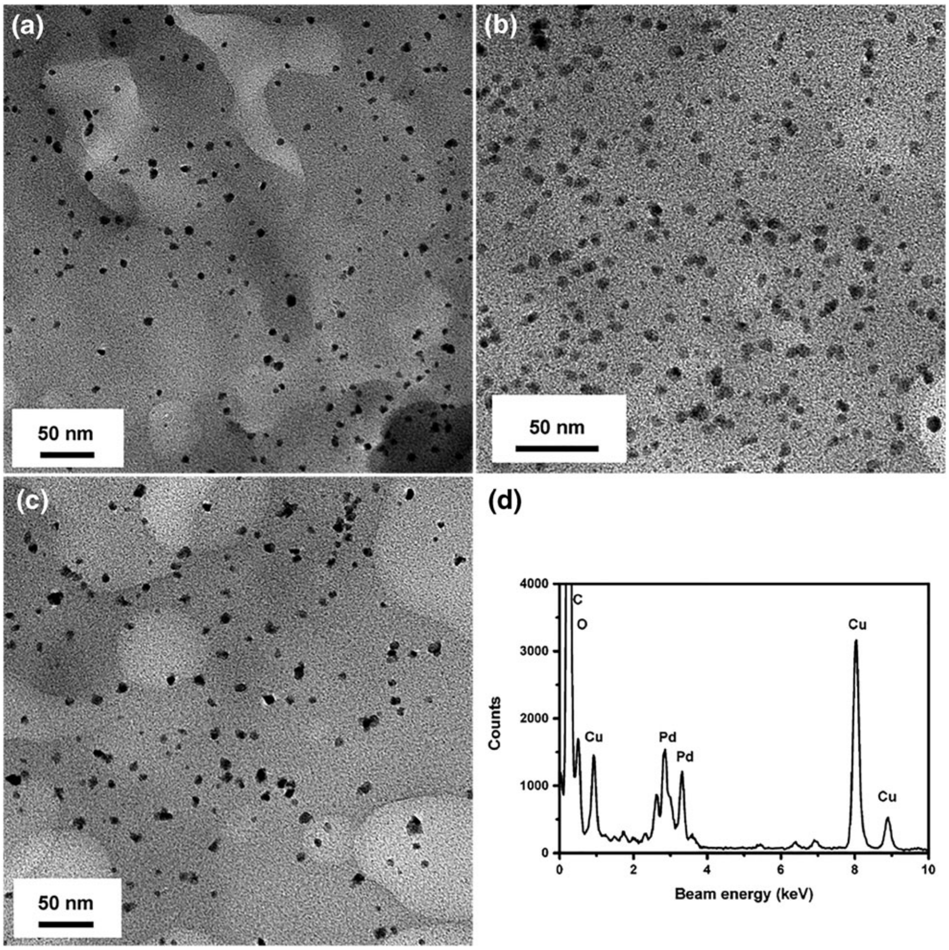


FIGURE 3 TEM images of Pd NPs recorded from samples (a) Ex-Pd-2, (b) Ex-Pd-3 and (c) Ex-Pd-4. (d) EDX spectrum recorded from sample Ex-Pd-3

composition of the formed Pd NPs, we have recorded the EDX spectra of sample Ex-Pd-3 during TEM analysis. The spectra (Figure 3D) confirmed the presence of peak due to elemental Pd indicating the formation of pure Pd NPs as peak due to any other impurities could not be noticed. Further to investigate the surface compositions and chemical state of the plant extract derived Pd NPs, X-ray photoelectron spectra (XPS) were recorded from sample Ex-Pd-1. Wide survey scans were recorded first followed by a detailed scanning of the edge of Pd-3d (Figure 4). The charging effect on the sample was corrected by setting the binding energy of the carbon (C-1 s) at 284.6 eV and this carbon peak was used as a reference position for scaling all the other peaks. Figure 4b shows that the peak appears as a spin-orbit doublet at 337 eV ($3d_{5/2}$) and 343.1 eV ($3d_{3/2}$) for Pd^0 in the product. The peaks due to C-1 s, O-1 s and N-1 s in the survey spectrum (Figure 4a) arise due to the presence of extract on the surface of Pd NPs.

The crystalline properties and phase structures of the synthesized Pd NPs were studied using powder XRD technique. Figure S2 in the SI shows the XRD patterns of the (Table 1). The diffractograms show the presence of diffraction peaks at 2θ = 38, 46, and 66° which are characteristic peaks of Pd as reported earlier.[50] The additional peaks appeared in the diffractogram might be due to some complex formed between Pd (II) and the organic moiety present in the extract as reported earlier.[33]

Further, to confirm the capping of Pd NPs by biomolecules, we recorded the FTIR spectra of plant extract reduced Pd NPs and the plant extract which are presented in Figure 5. FTIR spectra of the extract showed IR bands at 3276, 2933, 2361, 1590, 1399 and 1022 cm^{-1}. The bands observed at 3276 and 1590 cm^{-1} correspond to –O-H and –C=O stretching modes, respectively. On the other hand, the bands at 1399 and 1022 cm^{-1} are due to –C-O and -C-O-C stretching modes, respectively. Whereas the FTIR spectra of Pd NPs (sample Ex-Pd-3) showed the IR bands at 3399, 1627, 1433 and 1022 cm^{-1} which are due to –O-H, -C-H, –C=O and –C-O-C stretching modes, respectively. This observation confirmed that the phytochemicals present in the extract are anchored on the surface of Pd NPs providing stability to them from aggregation.

To probe the effectiveness of the synthesized Pd NPs in the Suzuki-Miyaura reaction, we chose 4-bromo nitrobenzene (1 mmol) and phenylboronic acid (1.2 mmol) as model substrates. For the initial investigation, the model reaction was performed at room temperature with 2 ml of an aqueous suspension of catalyst (0.014 mol%; sample Ex-Pd-1), using 1.5 mmol of K_2CO_3 as a base under aerobic and ligand-free condition. However, 62% (Table 2, entry 1) of yield was isolated after a span of 12 hr. The low yield of the product led us to check the effect of co-solvent on the reaction because; it has been reported that the addition of co-solvent to an aqueous system assist in the complete dissolution of the organic substrates, and

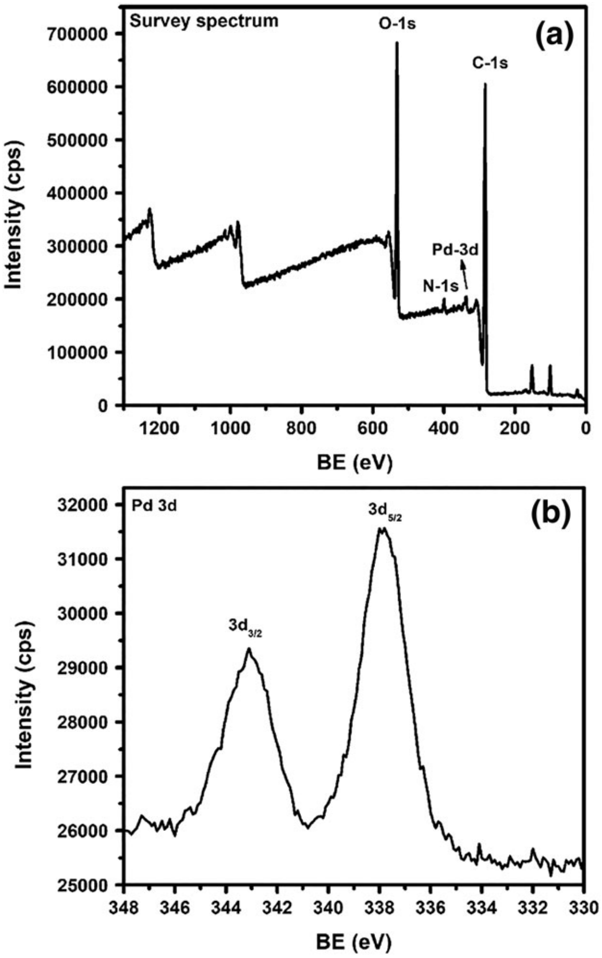


FIGURE 4 X-ray photoelectron spectra of Pd NPs recorded from sample Ex-Pd-1: (a) full scan, and (b) Pd 3d region

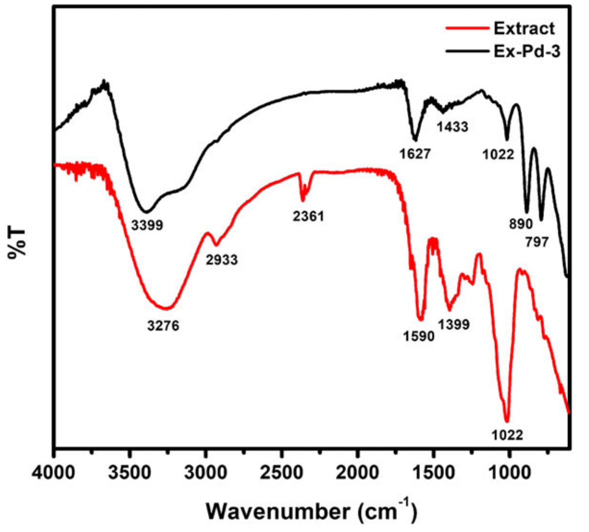
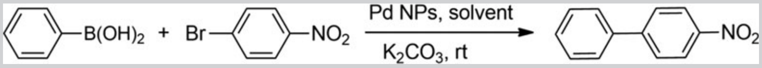


FIGURE 5 FTIR spectra of pure extract and extract reduced Pd NPs

TABLE 2 Optimization of the reaction condition for catalyst, solvent and base[a]

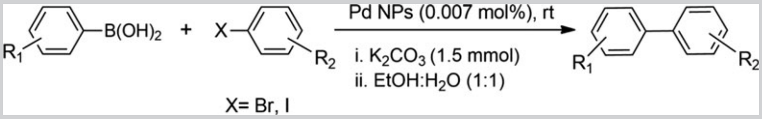


Entry	Pd NPs (mL; mol%)	Solvent (vol)	Time (hr)	Yield (%)[b]
1	2.0; 0.014	-	12	62
2	2.0; 0.014	MeOH (2 ml)	3	93
3	2.0; 0.014	EtOH (2 ml)	3	93
4	2.0; 0.014	*i*-PrOH (2 ml)	3	93
5	1.5; 0.0105	EtOH (2 ml) + Water (0.5 ml)	3	93
6	1.0; 0.007	EtOH (2 ml) + Water (1 ml)	3	93
7	0.5; 0.0035	EtOH (2 ml) + Water (1.5 ml)	3	85
8	1.0; 0.007	EtOH (2 ml) + Water (1 ml)	3	88

[a] Phenylboronic acid (1.2 mmol), 4-bromo nitrobenzene (1 mmol). [b] Isolated yield.

thereby increase the efficiency of the reaction.[4,32,52,53] Thereby, in the next assessment we checked the effectiveness of different alcoholic co-solvents like ethanol, isopropanol, methanol, etc. (Table 2, entries 2–4). We were pleased to note that the addition of the alcoholic co-solvents dramatically increased the % yield of the reaction in our system up to 93% within 3 hr. All the alcoholic solvents delivered the same yield; hence we preferred ethanol as the most apposite solvent for the transformation (Table 2, entry 3) due to its more environmentally friendly behavior compared to other alcohols. After this satisfactory result, we decided to optimize the reaction condition for the amount of catalyst. For this, we decreased the amount of aqueous suspension of catalyst gradually from 2 ml to 1.5 ml, 1 ml, and 0.5 ml, respectively (Table 2, entries 4, 5, 6 and 7). After completion

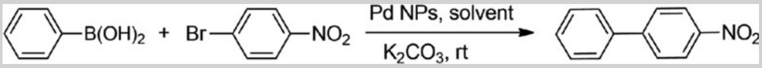
TABLE 3 Suzuki-Miyaura cross-coupling reactions of various aryl halides and aryl boronic acids catalyzed by Pd NPs (sample Ex-Pd-1)[a]



Entry	R_1	R_2	X	Time	Yield (%)[b]	TOF[c] (h^{-1})
1	H	4-NO2	Br	3 hr	93	2105.6
2	H	4-COCH3	Br	2 hr	88	913.2
3	H	4-OMe	Br	90 min	90	1245.2
4	4-OMe	H	I	40 min	94	2926.4
5	4-OMe	H	Br	90 min	94	1300.6
6	4-OMe	4-NO2	Br	100 min	94	1170.5
7	4-OMe	4-OMe	Br	35 min	95	3380.0
8	4-Me	H	Br	50 min	92	2291.3
9	4-Me	4-OMe	Br	60 min	92	1909.4
10	4-tertbutyl	4-NO2	Br	60 min	91	1888.6
11	3-OMe	H	Br	90 min	85	1176.1
12	4-Cl	H	I	3 hr	82	588.0
13	4-Cl	4-COCH3	Br	4 hr	84	435.8
14	4-Cl	4-NO2	Br	3 hr	82	567.2
15	4-F	4-OMe	Br	2 hr	85	882.0

[a] Reaction conditions: aryl halide (1 mmol), aryl boronic acid (1.2 mmol), in air. [b] Isolated yield. [c] Turnover frequency (TOF): moles of aryl halide converted per mole of Pd per *h*.

TABLE 4 A comparison between the yields and catalyst loading for different plant extract mediated synthesized Pd NPs and their activity towards Suzuki-Miyaura cross coupling reaction



Entry	Catalyst loading	Solvent system	Time	Yield (%)	Reference
1	0.1 mmol%	EtOH-H_2O	30 min	97%	[57]
2	2 mol%	H_2O	2 hr	95	[34]
3	5 mg	H_2O	2 hr	93	[31]
4	1 mol%	^{i}PrOH-H_2O	3.5 hr	89	[50]
5	5 wt%	^{i}PrOH-H_2O	30 min	94	[30]
6	0.002 g	H_2O/60 °C	55 min	95	[32]
7	0.007 mol%	EtOH-H_2O	3 hr	93	This work

and purification, it was noticed that 2 ml, 1.5 ml and 1 ml of the catalyst resulted in the same conversion of 93%, but 0.5 ml of the catalyst offered 85% yield (Table 2, entries 4, 5, 6 vs. 7). So, this series of experiments concluded that 1 ml of the catalyst suspension (0.007 mol%) is enough for the desired transformation in 3 hr (Table 2, entry 6). As K_2CO_3 is a mild base, we did not feel it necessary to check the effect of other bases on the reaction but carried out the reaction in 1 mmol of K_2CO_3 keeping other parameters constant (Table 2, entry 8). But the study yielded a slight decrease in the % yield of the reaction. Thus, the best condition for the desired cross-coupling reaction was with 0.007 mol% of Pd catalyst, 1.5 mmol of K_2CO_3 and 4 ml of solvent (1: 1) ethanol: water (Table 2, entry 6).

With the optimized reaction condition in hand, we examined the effect of size on the catalytic activity of Pd NPs. So, when we repeated the coupling reaction with sample Ex-Pd-4, we observed the conversion of 92% within 1 hr. This confirmed that with smaller sized Pd NPs, the coupling reaction took place at a faster rate. Further, we also examined the scope and limitation of the reaction using different electron donating and withdrawing group substituted arylhalides and arylboronic acids respectively as summarized in Table 3. From the substrate study analysis it was observed that the coupling product from the electron donating group substituted halides and boronic acids (Table 3, entries 3, 4, 5, 7, 8, 9 and 11) consumed less time and offered excellent yield compared to the electron withdrawing group substituted substrates (Table 3, entries 2, 13, 14 and 15). The turn over frequency for the different reaction catalyzed by Pd NPs is also presented in Table 3. A comparative result of the coupling reaction of the most relevant works is presented in Table 4 which shows that our system is more effective than some of the other reports.

It is important to note that one of the key advantages of Pd NPs based catalytic system is their potential recyclability, and to check this property, we have performed the reusability experiment with our model system using 4-bromo nitrobenzene (1 mmol) and phenylboronic acid (1.2 mmol) in water: ethanol system (1:1) at room temperature following the previously optimized condition (Table 2). Our study revealed (Figure 6) that the Pd nanocatalysts could be reused at least for four cycles; however, a gradual decrease in yield was observed which might be due to a decrease in the activity of the catalyst due to possible adsorption of the reactants on the surface of Pd NPs. Another reason might be the loss of Pd NPs during its recovery for successive uses. To understand the fate of the used catalyst and to check the stability, we isolated the Pd NPs after its use in the catalysis reaction and analyzed by both TEM and SEM. The TEM image (Figure 7) of the reused catalyst showed almost similar morphology with no sign of aggregations suggesting that the catalyst are highly stable and could be reused for further runs. However, comparison of the SEM images (Figure S3 in the SI) suggests that there are some

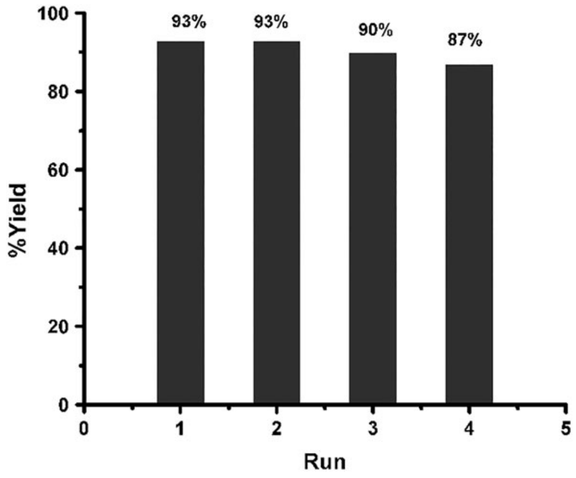


FIGURE 6 Catalytic performance of recovered Pd NPs in Suzuki-Miyaura reaction

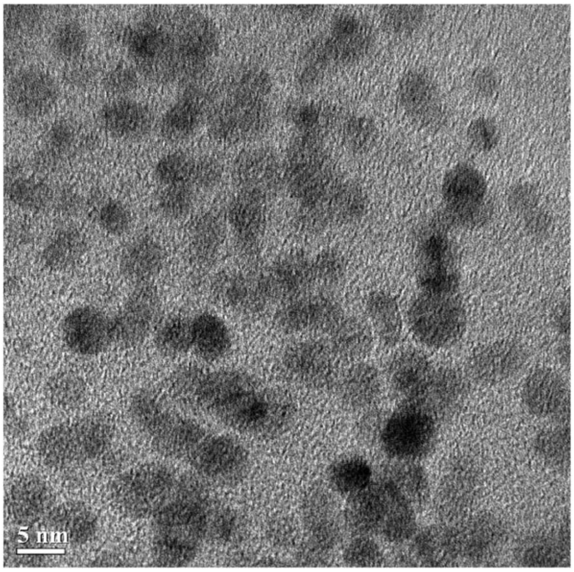


FIGURE 7 TEM images of recovered Pd NPs recorded from sample Ex-Pd-3

changes on the surface of such Pd NPs due to catalysis which might be due to adsorption of the reactants or products on the surface of the catalyst. This probably decreases the catalytic activity of Pd NPs in successive runs. This was further proved by FTIR spectra where (Figure S4 in the SI) where an additional peak was observed on the reused sample due to catalysis.

4 | CONCLUSION

Pd NPs of different sizes have been prepared by chemical reduction of Pd^{2+} ions using flower extract of *Lantana camara* plant. The size of Pd NPs can be systematically controlled by varying the concentration ratio of extract and metal ions. The Pd NPs shows excellent catalytic activities towards Suzuki-Miyaura cross-coupling reaction under ambient reaction conditions. The Pd NPs are highly stable and are reusable for successive batches of coupling reactions. The advantages associated with our method is: (i) the use of non-toxic and eco-friendly reducing agent in the form of flower extract of locally available plants, (ii) no additional stabilizer, capping agent or template is required for size control of Pd NPs, (iii) the use of plant extract as an economic and effective alternative represents an interesting, fast and clean synthetic route for the large-scale synthesis of Pd NPs and (iv) the Pd NPs generated through this plant-mediated process remains stable suggesting that the phytochemicals present in them serve as excellent coatings and stabilizing agents and thus shield these NPs from aggregations.

ACKNOWLEDGMENTS

MHR acknowledges Council of Scientific and Industrial Research (Grant No. 01(2910)/17/EMR-II), India for supporting the research. Thanks are also due to partial support from Science and Engineering Research Board (Grant No. EMR/2015/001912), India. We also thank SAIF NEHU, NEIST Jorhat and SAIF GU for extending their instrumental facilities to us.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

How to cite this article: Phukan S, Mahanta A, Kakati D, Rashid MH. Green chemical synthesis of Pd nanoparticles for use as efficient catalyst in Suzuki-Miyaura cross-coupling reaction. *Appl Organometal Chem*. 2018;e4758. https://doi.org/10.1002/aoc.4758