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ORIGINAL PAPER

Acacia concinna pods: a natural and new bioreductant for palladium nanoparticles and its application to Suzuki–Miyaura coupling

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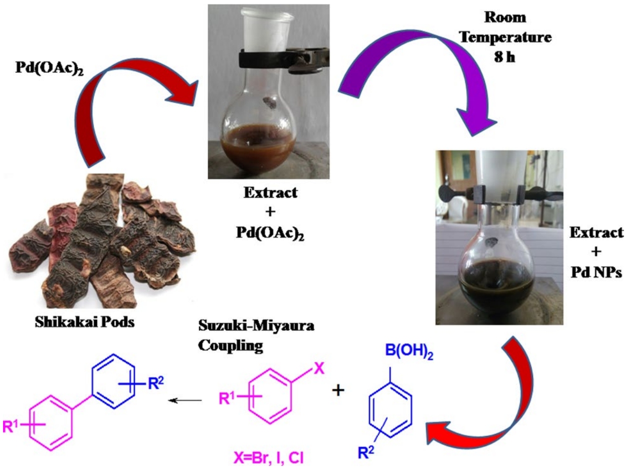
Abstract

In this study, efficient, simple and greener approach is applied for the synthesis of palladium nanoparticles using aqueous extract of *Acacia concinna*, i.e., soap pods. The extract is mainly composed of saponin terpenoid which contains hydroxyl groups in its structure. This performs a versatile role as surfactant, reducing and stabilizing agent for palladium nanoparticles. The average particle size is found about 20 nm by using 30% extract (v/v) of *A. concinna* (soap-pod tree). Diverse techniques are used to characterize synthesized nanoparticles such as UV–visible, TEM and XPS analysis. The synthesized nanoparticles showed excellent activity in Suzuki–Miyaura coupling. The synthesized Pd NPs can be effectively reused for at least five times with excellent yield of product. Results confirmed this protocol as eco-benign, environmental-friendly, nontoxic and alternative to conventional other chemical methods.

Graphical abstract



Keywords *Acacia concina* · Bioreductant · Palladium nanoparticles · TEM · XPS

Introduction

The twelve principals of green chemistry suggests for using solvents which will not be harmful to all kinds of living things. So, according to the principal and along with environmental and economical point of view, water can be considered as green and efficient solvent for carrying out the organic reactions [1–3]. Some of the research groups and review articles that have focused the unique

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reactivity and selectivity of organic reactions which cannot be achieved in organic solvents are often obtained in water [4–6]. In addition to this, several important and useful reactions have been exploited using water as the solvent. But sometimes, the development of methods in water is strongly limited by (1) the low solubility of organic substrates in water and (2) the sensitivity of chemical groups toward hydrolytic degradations. One of the solutions to circumvent these issues comprises the addition of a phase transfer agent (surfactants), or to use salting-in agents [7–9]. On commercial scale, many such synthetic cationic, anionic and nonionic surfactants are available for carrying out the reactions in aqueous medium. Some of the surfactants are biodegradable in nature, and hence, there is no harm using it in organic transformation [10–12].

In nature, there are several such surfactants available which can be used for carrying out the organic reactions [13, 14]. One of the best nonionic, natural surfactant, saponin, is emerging as an effective surfactant. The aqueous extract of *Acacia concinna*, i.e., soap pods mainly composed of terpenoid saponin, and they are generally biodegradable and considered in manufacturing of detergents, cosmetics, and many other products [15, 16]. The outer pericarp of *A. concinna* pods has been traditionally used in India for bathing purpose due to the formation of good lather or foam in water. It has an excellent cleansing action on dirt like detergents or soaps [17]. In addition to this they have some medicinal properties such as anti-inflammatory and antimicrobial activities [18, 19]. However, there has not been much scientific study to understand its surfactant activities and micellar behavior.

Bandgar and his group [16] showed the use of aqueous extract of soap pods in the synthesis of some coumarin derivatives. Adding up to this, saponin extract has been used for the synthesis of metal nanoparticles (MNPs). Kim et al. used the aqueous extract of *Sapindus mukorossi* for the synthesis of gold nanoparticles illustrating the effectiveness of the saponins [20]. Balakrishnan et al. [21] studied the micellar characteristics of a nonionic, natural surfactant, saponin, and it was found to be 0.045 wt% UV–visible study. But till date, micellar behavior of these surfactants is not much studied. Looking toward these applications and its effectiveness, we decided to find out its use in the synthesis of Pd NPs and Suzuki–Miyaura coupling. The extract may help in solubilizing the organic molecules due to good micellar properties (Fig. 1).

Numerous various solid materials such as chitosan, cellulose, starch and bio-macromolecule Schiff-based supported homogenous or heterogeneous palladium catalysts or palladium nanoparticles have been designed for Suzuki reactions [22–28]. They constitute an important class of catalysts. But in continuation with our earlier study on effect of surfactant [29] and role in the synthesis of metal nanoparticles, here in, we wish to report the role of extract of *Acacia concinna* in the synthesis of Palladium nanoparticles.

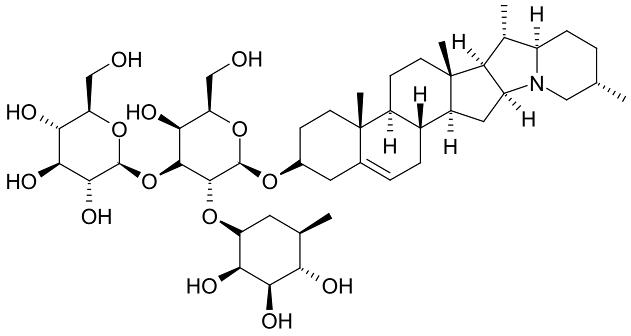


Fig. 1 Structure of saponin

Synthesis of metal nanoparticles using plant extracts is very cost-effective and therefore can be used as an economic and valuable alternative for the large-scale production of MNPs. Extracts from plants may act both as reducing and capping agents in nanoparticle synthesis. The major part of the soap-pod extract consists of saponin; it has found that it contains mainly two functionalities, i.e., hydroxyl and ether [30, 31] and that could acts as reducing and stabilizing agent for MNPs. As per our earlier concept with nonionic surfactant Triton × 100 [32], hydroxyl functional groups can act as a reducing and stabilizing agents in the synthesis of palladium nanoparticles and so started experiment on Pd NPs synthesis by using plant extract.

Materials and methods

Materials

The pods of *Acacia concinna* obtained from the crop fields of West Maharashtra, India. $Pd(OAc)_2$ was purchased from Spectrochem India.

Method

The outer pericarp of the fruits was separated from the seeds and dried at room temperature for 2 days. About 30 g of it was then soaked in 100 mL of water for 24 h, and the solution was filtered through Whatman filter paper No. 1. The filtrate was used as it is for further study without any prier treatment or purification. To synthesize the Pd NPs, $Pd(OAc)_2$ was used as precursor and 10 mL filtrate of 30% w/v as aqueous extract. It was stirred at room temperature for 8 h. The bioreduction of the $Pd(OAc)_2$ was confirmed by the slow color change from yellow to black after 8 h (Fig. 2).

A At starting (Extract + Pd(OAc)₂) **B** After formation (Extract + Pd NPs)

Fig. 2 Visual eye detection of Pd NPs

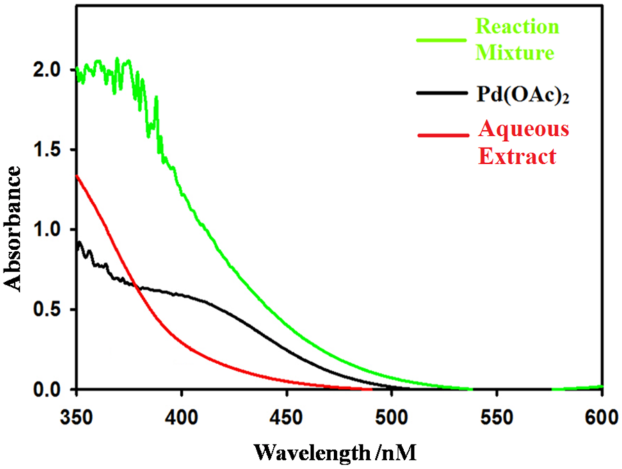


Fig. 3 UV study of reaction mixture

Characterization of Pd NPs

The UV–visible measurements were carried out to identify the formation of Pd NPs under same reaction conditions. Figure 3 shows the UV–visible spectra of the aqueous extract, $Pd(OAc)_2$ and reaction mixture. It confirms the disappearance of peak of $Pd(OAc)_2$ from the reaction mixture and formation of Pd NPs. The NPs was separated from reaction mixture by centrifugation method and was analyzed by TEM analysis. The average size of the nanoparticles found to be 20 nm (Fig. 4). Again, the formation of NPs was further confirmed by XPS analysis (Fig. 5); the analysis found to correct one. High content of saponins present in aqueous extract of soap pod has a hydroxyl functionality which is responsible for reduction in $Pd(OAc)_2$.

Result and discussion

After the initial success in the synthesis of Pd NPs, we next focused attention toward exploring its effectiveness in Suzuki–Miyaura coupling. The reaction carried out by two ways, i.e., by separating the Pd NPs and to carry out the reaction in aqueous conditions, another way to generate the Pd NPs in situ and to continue Suzuki–Miyaura coupling (Scheme 1). First, NPs were separated from the aqueous extract and used in a model reaction with iodobenzene and phenyl boronic acid by employing different bases such as NaOH, KOH, K_3PO_4, K_2CO_3, Na_2CO_3 and TEA (Table 1, Entry 1–7) at room temperature. Among the bases used, Na_2CO_3 was found to be the best choice for the present conditions giving 98% of the desired biaryl and with rest of the bases obtained inferior results. Reaction did not much work well under the absence of basic conditions. Another procedure, i.e., in situ generation of Pd NPs and continuing the Suzuki coupling, also gave the same yield by utilizing Na_2CO_3 as a base. Product was separated from reaction mixture by extracting with it by ethyl acetate, and the catalyst was recovered by centrifugation of aqueous layer. Hence, we followed the second procedure, i.e., in situ generation of NPs and to carry out the reaction in aqueous extract. The product obtained was characterized by ^1H and ^{13}C NMR spectroscopy; it confirms the formation of desired product.

Comparison with differently synthesized Pd NPs by diverse methods is shown in Table 2; it highlights qualities as well as demerits of the earlier literature methods. However, it is noteworthy that the in situ generated Pd-NPs using *Acacia concinna* pods extract in the present method has a comparatively similar/excellent activity compared with other known Pd NPs.

After screening the base and method of reaction, we tried different substituted aryl halides and various boronic acids using synthesized Pd NPs. All the results are mentioned in Table 3.

A variety of functional groups can be tolerated for aryl halides including methyl, nitro, cyano, methoxy as well as aryl boronic acids. The results conclude that electronic character of aryl halides or boronic acids has no obvious effect on the Suzuki–Miyaura coupling under optimized reaction conditions. It is noteworthy that less activated aryl chlorides afforded corresponding product in excellent yield (Table 3, Entry 3b).

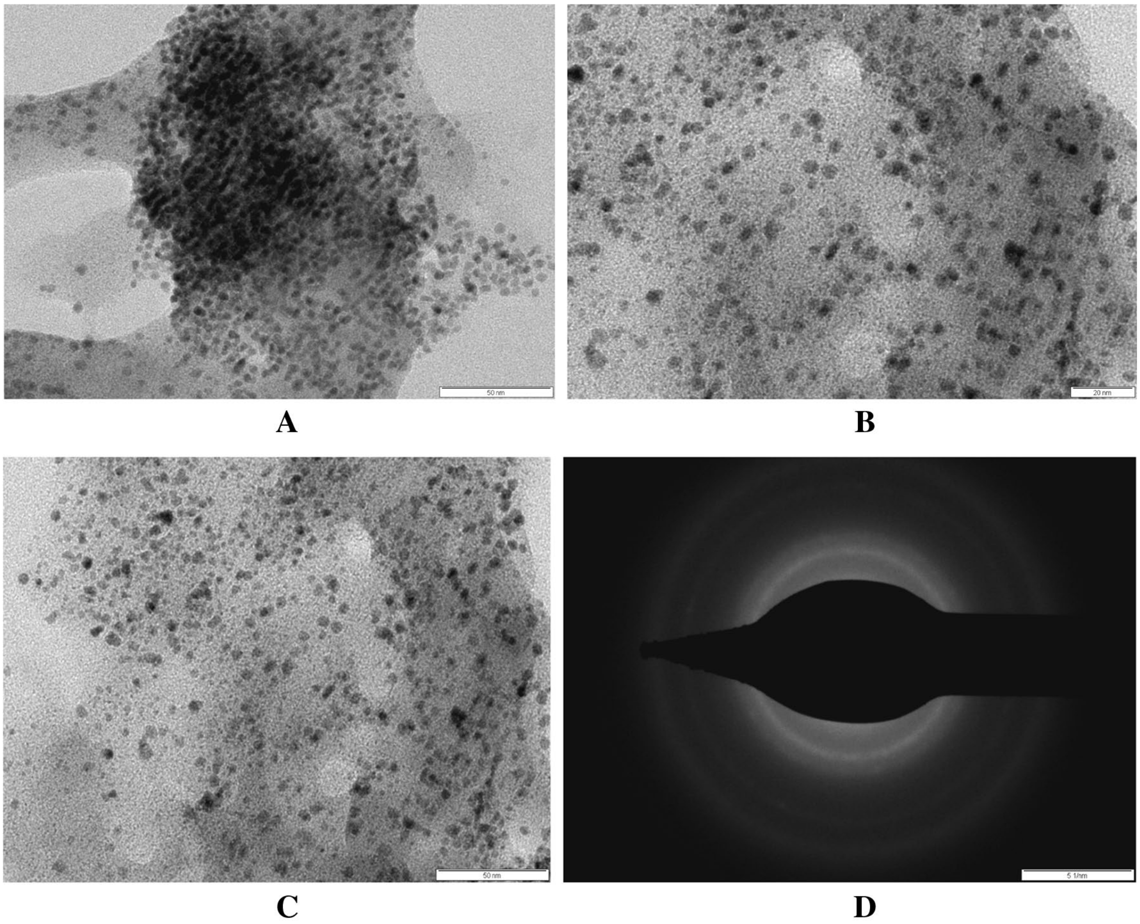


Fig. 4 TEM images of Pd nanoparticles with SEAD pattern

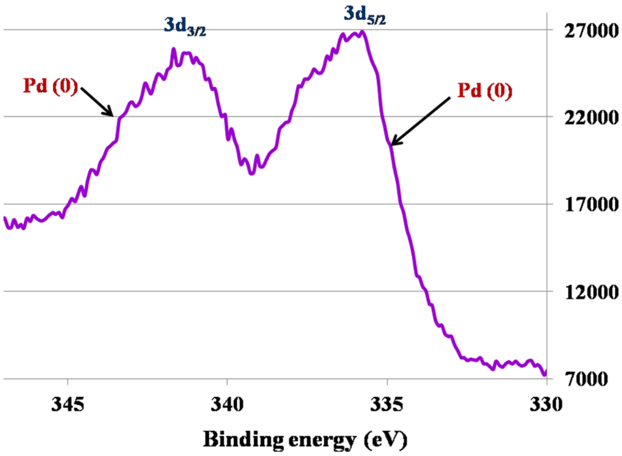
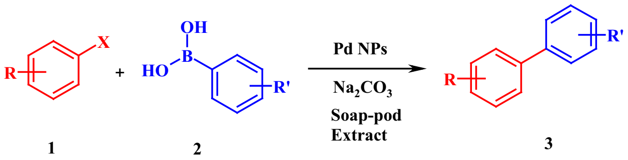


Fig. 5 XPS analysis of Pd NPs



Scheme 1 Typical Suzuki–Miyaura coupling

Reusability study

Reusability of catalyst is imperative aspect of green chemistry. Hence, the reusability of Pd NPs was investigated for model reaction iodobenzene (1 mmol), phenyl boronic acid (1.1 mmol), Na_2CO_3 (3 mmol), $Pd(OAc)_2$ (2 mol%) and 10 mL plant extract at room temperature. After completion of reaction on TLC, product was isolated by extraction with diethyl ether and Pd NPs were separated from aqueous by centrifugation method. Then, for next subsequent run, fresh reactants were taken, the separated Pd NPs was

Table 1 Effect of different bases on the Suzuki–Miyaura coupling reaction

Entry	Base (mmol)	Time (h)	Yield (%)*
1	NaOH (3)	3	60
2	KOH (3)	3	62
3	K_3PO_4 (3)	5	40
4	K_2CO_3 (3)	2	55
5	Na_2CO_3 (3)	1	98
6	Na_2CO_3 (2)	3	80
7	TEA (3)	3	70
8	Without base	12	–

Reaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), Pd NPs (10 mg by wt), Na_2CO_3 (3 mmol) and soap-pod extract (10 mL 30%V/V) at r.t.

*Isolated yield

added into that, and reaction continued till completion of it. It was found that NPs can be effectively reused for at least five times by giving 98, 94, 92, 89 and 85% yield, respectively (Fig. 6). After reusability study, the Pd NPs are analyzed by TEM analysis (Fig. 7), and no any significant change in the structure is observed.

Experimental

General

NMR spectra were recorded on a BrukerAC-300 spectrometer in $CDCl_3$ using tetramethylsilane as internal standard.

Typical procedure for Suzuki–Miyaura coupling

To a 25-mL round bottom flask, a mixture of aryl halide (1 mmol), arylboronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%) and Na_2CO_3 (3 mmol) was added in soap-pod extract (10 mL). The mixture was stirred at room temperature and monitored by TLC. After completion of reaction, the mixture was extracted with diethyl ether (3 × 10 mL). The

Table 2 Comparison with other synthesized Pd NPs

Entry	Catalyst	Conditions	Time (h)	% Yield* [Refs.]
1	Pd-NPs	Pd NPs (10 mg by wt), Na_2CO_3 (3 mmol), soap-pod extract (10 mL, 30%V/V) at r.t.	1	98 [This work]
2	Pd-NPs in Ionic liquid	$Pd(OAc)_2$ (2 mol%), TSIL (20 mol%), Na_2CO_3 (1 mmol), Water (5 mL), 80 oC	1	98 [33]
3	Pd-NPs using surfactant	$PdCl_2$ (0.015 mmol) TBAF (1.5 mmol) at 40–100 °C argon atmosphere	0.5-12	90 [34]
4	Pd-NPs in PEG	$Pd(OAc)_2$ (2 mol%) K_2CO_3 (1 mmol), PEG (4 g), 45 °C	1-5	92 [35]
5	Pd-NPs in water	$PdCl_2$ (1.2 mol%), IL (1.0 ml), Na_2CO_3 (1.05 mmol), water (0.5 ml), 110 °C	4	96 [36]
6	Pd-NPs in $CH_3OH{:}CH_3CN$ (1:1)	K_2CO_3 (2 mmol), $CH_3OH{:}CH_3CN$ (1:1) at r.t.	2-6	99 [37]

*Isolated yield

Table 3 Combinatorial library of biaryls synthesized by Suzuki–Miyaura coupling

Entry	Aryl halide (1)	Boronic acid (2)	Time (h)	Yield (%)*	TON	TOF
3a	R = H, X = I	R' = H	1	98	48	48
3b	R = H, X = Cl	R' = 4-OMe	2	80	40	20
3c	R = H, X = Br	R' = 4-Me	1	95	47.5	47.5
3d	R = 4-Me, X = Br	R' = H	1	92	46	46
3e	R = 4-Me, X = I	R' = 4-OMe	1.5	89	44.5	29.66
3f	R = 4-OMe, X = I	R' = H	1.5	88	44	29.33
3 g	R = 4-OMe, X = I	R' = 4-OMe	1	85	42.5	42.5
3 h	R = 4-CN, X = Br	R' = H	1.5	84	42	28
3i	R = 4-NO_2, X = I	R' = H	2	87	43.5	21.75
3j	R = 4-COMe, X = Br	R' = H	1.5	90	45	30
3 k	R = 4-OMe, X = Br	R' = 4-Me	1	87	43.5	43.5
3 l	1-Naphthyl iodie	R' = H	2	80	40	20

Reaction conditions: aryl halide (1 mmol), boronic acid (1.2 mmol), $Pd(OAc)_2$ (2 mol%), Na_2CO_3 (3 mmol) and soap-pod shell extract (10 mL 30%V/V) at r.t.

*Isolated yield

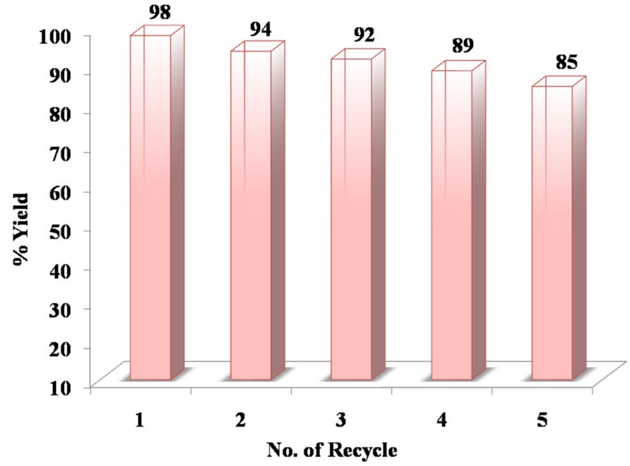


Fig. 6 Reusability study

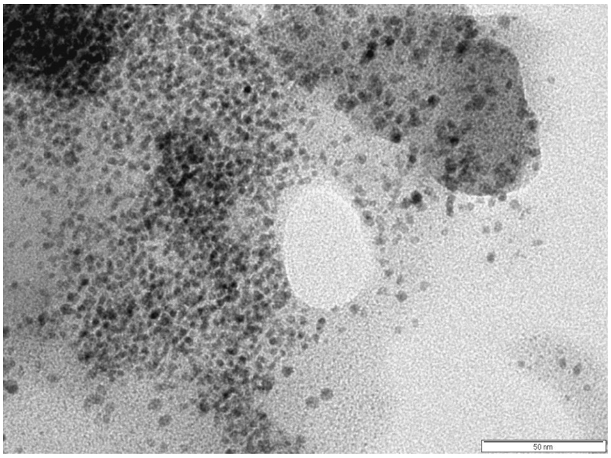


Fig. 7 Pd nanoparticles after reusability study

organic layer obtained was dried over anhydrous Na_2SO_4, filtered and concentrated to furnish the desired biaryl compound which then purified by column chromatography (5% ethyl acetate). The Pd NPs formed during the process was separated from aqueous by centrifugation process and reused for subsequent run.

Conclusion

In conclusion, Pd MNPs generated by the use of aqueous extract *Acacia concinna* pods can be efficiently applied to the Suzuki–Miyaura coupling reaction at ambient temperature. Furthermore, the catalytic system could be recycled up to five times without a decrease in the yield of the reaction. The high activity seems due to the very small size of nanoparticles. The protocol is a simple, eco-benign, environmentally friendly and high yielding with all kinds of aryl halide and aryl boronic acids.

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