



GREEN SYNTHESIS OF CELLULOSE-SUPPORTED Pd(0) NANOPARTICLES USING RESVERATROL AS BIOREDUCTANT AND THEIR CATALYTIC ACTIVITY FOR SUZUKI-MIYaura AND HECK COUPLING REACTIONS

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ABSTRACT

The cellulose supported Pd(0) nanoparticles [Pd(0)NPs@Cellulose] have been synthesized using resveratrol as a bioreductant which have been isolated from heartwood of *Artocarpus lakoocha roxb.*. The synthesized Pd(0)NPs@Cellulose have been characterized by UV-Vis, FTIR, XRD, TEM, XPS and ICP-AES analysis. The cellulose supported Pd(0) nanoparticles [Pd(0)NPs@Cellulose] have homogeneous particle size distribution in the range of 20-40 nm. The catalytic activity of Pd(0)NPs@Cellulose have been studied in the Suzuki-Miyaura and Heck cross-coupling reactions under microwave heating. The optimum reaction conditions have been established for a yield in the range of 88% and 98%. The recovered catalyst has showed its activity up to 10 cycles without major lose of yield of product.

Keywords: Pd nanoparticle, catalyst, resveratrol, suzuki-miyaura, heck coupling.

INTRODUCTION

The synthesis of metallic nanoparticles (NPs) has great attention in scientific community due to environmental contamination caused by the chemical methods (Iravani, 2011; Zhu *et al.*, 2012; Raveendran *et al.*, 2003; Kalidindi and Jagirdar, 2012; Varma, 2012). Usually, synthesis of NPs using various chemical and physical methods either involves expensive equipments or hazardous chemicals which have harmful effects on the environment (Peralta-Videa *et al.*, 2011). Moreover, in chemical synthesis, the surface of NP's may adsorb the residuals of some toxic chemicals and it prevents the reactivity of NPs (Byrappa *et al.*, 2008).

Recently, emphasis has been given for development of environmentally friendly and sustainable methods for preparation of NPs (Campelo *et al.*, 2009). Nanoparticles can be synthesized by using different sources such as plant materials (Nasrollahzadeh *et al.*, 2015 and Sajadi *et al.*, 2018), marine organisms etc (Otari *et al.*, 2013). Methods using plant extracts for preparation of NPs have been given more attention from environment and economical points of view (Khazaei *et al.*, 2017; Khodadadi *et al.*, 2017; Maham *et al.*, 2018; Nasrollahzadeh *et al.*, 2015; Issaabadi *et al.*, 2018;

Maryami *et al.*, 2017; Nasrollahzadeh and Sajadi, 2016). Flavonoids and polyphenols present in plant extract act an important role in NPs preparation as they have bioreductant and stabilizing properties (Baruah *et al.*, 2015).

Using different plant extracts a number of metal NPs viz. Au, Ag, Pd, Pt, Cu, Ag-Au, Au-Pd and Cu-Au have been successfully synthesized and reported elsewhere (Nasrollahzadeh *et al.*, 2015; Sajadi *et al.*, 2015; Baruah *et al.*, 2015; Basavegowda *et al.*, 2015; Khan *et al.*, 2014; Lu *et al.*, 2018; Baran *et al.*, 2018). These NPs have virtual applications in different fields like optoelectronics, detection of small molecule analytes, biological labeling and catalyst (Coccia *et al.*, 2012). Among the metallic nanoparticles, Pd nanoparticles have wide applications in the area of heterogeneous catalysis such as hydrogenations, oxidations, carbon-carbon and carbon-heteroatom cross-coupling and electrochemical reactions (Dhakshinamoorthy *et al.*, 2015). Suzuki-Miyaura and Heck reactions are the very significant Pd NPs catalyzed reactions (Baruah *et al.*, 2015; Chen *et al.*, 2014; Zhou *et al.*, 2012) which have enormous application in the field of drugs, pharmaceuticals, agrochemicals and advanced materials (Nasrollahzadeh and Banaei, 2015; Azarian *et al.*, 2015; De Rivera *et al.*, 2013).

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In this paper we report a green and sustainable method to synthesize cellulose supported Pd(0) NPs[Pd(0)NPs@Cellulose] using the bio-reductant resveratrol and its application in Suzuki-Miyaura and Heck coupling reaction. Resveratrol was extracted from the heart wood of the medicinal plant *Artocarpus lakoocha* Roxb(ALR) which was reported in our previous publications (Borah *et al.*, 2017).

To achieve catalyst robustness and reusability we have used cellulose as a viable solid support. Cellulose contains anhydroglucose units linked by β -1-4 glycosidic linkage to make a molecular chain. The hydrogen bonding of hydroxyl groups and oxygens of the adjacent ring molecules balanced the linkage and produce the linear configuration of the cellulose chain. Cellulose includes micro fibrils up to 30 nm width that are three dimensionally linked to each other. The metal nanoparticles can be stabilized in these cavities *via* oxygen-metal electrostatic attraction. The pore size of cellulose micro fibrils also changes the size of the metal catalyst nanoparticles. Thus, cellulose can act as a solid support for the synthesis of metal nanoparticles (Habibi, 2014; Wu *et al.*, 2013; Xu *et al.*, 2008; Wu *et al.*, 2008). To enhance the rate of reactions and product yield (Leadbeater, 2005) we have carried out all the reactions under microwave heating.

MATERIALS AND METHODS

Materials

Cellulose (CAS: 9004-34-6, microcrystalline, 20 μ m, pH: 5-7), PdCl₂ (99%), arylboronic acids, arylbromides, methyl acrylate, acrylonitrile, bases and solvents were purchased from Sigma Aldrich, USA. The reagents and solvents were used as received without any further purification.

Methods

Analytical methods

Powder X-ray diffraction (XRD) was performed on a Rigaku X-ray diffractometer (model : ULTIMA IV, Rigaku, Japan) with Co-K α (λ =1.7902Å). The 2 θ values ranging from 5° to 100° and scanning rate of 3°min⁻¹ using a generator voltage of 40 kV and a generator current of 40 mA. TEM (Transmission electron microscopy) and HRTEM (high resolution transmission electron microscopy) images were recorded on a JEOL-2100 electron microscope operating at an accelerating voltage of 60-200 kV at CSIR-NEIST, Jorhat, Assam, India. X-ray photoelectron spectrum (XPS) was recorded on Thermo Fisher Scientific: ESCALAB Xi⁺ spectrophotometer at CSIR-NEIST, Jorhat, Assam, India. The C (1s) electron binding energy corresponding to graphitic carbon was used for calibration of the Pd (3d) core-level binding energy. UV-Visible spectra were recorded using Specord 200 in the range 200-800 nm in

ethanolic suspension of the NPs and Spectrum 100 FTIR-Spectrometer (resolution: 4 cm⁻¹) was used for recording IR spectra using KBr pellets. The ¹H and ¹³C NMR spectra were obtained at room temperature with a Bruker Advance DPX 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The products were purified by column chromatography using silica gel (200-300 mesh) and petroleum ether (60-90 °C).

Isolation of Resveratrol from heartwood of *Artocarpus Lakoocha* Roxb

Artocarpus lakoocha Roxb was collected from Jorhat district of Assam, India. Branches of plants were cut into very small pieces (~ 1 cm³) prior to extraction. The pieces were dried in an oven at 50°C to get constant weight and crushed in a Wiley Mill and sieved through mesh of standard size to obtain particles of 150 μ m size. A round bottom flask was charged with a 10 g of ground sample and 500 mL methanol and was refluxed for 7 h at constant temperature. After extraction the solution was filtered off and evaporated to dryness to get the solid product. The light brown colored product was then filtered, washed with cool water and vacuum dried and characterized by FTIR, NMR and Mass spectroscopy.

Synthesis of cellulose supported Pd(0) nanoparticles [Pd(0)NPs@Cellulose] using extracted and purified resveratrol

300 mg cellulose and 20 mg PdCl₂ was mixed in a 250 mL round bottom flask containing 200 mL solution of resveratrol (10 mg). The mixture was then stirred at room temperature followed by heating at 50 °C for 20 min until the light brown colored solution became black. The black precipitate of Pd(0)NPs@Cellulose was filtered, washed, dried and finally kept under N₂ atmosphere in a desiccator. The as synthesized Pd(0)NPs@Cellulose was extensively characterized by XRD, TEM, ICP-AES, XPS, FTIR and UV-Vis absorption spectroscopy.

Catalytic reactions

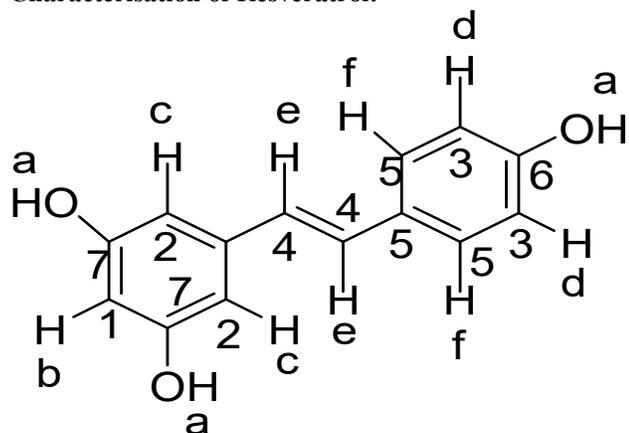
Suzuki-Miyaura cross-coupling reaction

To set up the reaction, a mixture of 15 mg Pd(0)NPs@Cellulose (0.103mmol Pd), 0.75 mmol phenylboronic acid, 0.5 mmol arylbromide and 1 mmol K₂CO₃ (2 eq.) was mixed with 5 mL water in a 10 mL microwave glass vial and allowed to stir at 80 °C at the appropriate time in a microwave. After completion of the reaction (monitored by TLC), the catalyst was separated by filtration, washed with acetone and reused. The residue was extracted from the filtrate using water- ethyl acetate mixture (1:3) followed by washing with brine and drying over Na₂SO₄. The products were obtained by column chromatography of the residue using ethyl acetate/hexane (1:9) as eluent.

Heck coupling reaction

In a typical procedure, a mixture of 20 mg Pd(0)NPs@Cellulose (0.138 mmol Pd), 0.75 mmol alkene (e.g., methyl acrylate), 0.5 mmol aryl iodide and 1 mmol K₂CO₃ (2 eq.) was added to water (5 mL) in a 10 mL microwave glass vial and was stirred at 80°C for the required time. The progress of the reaction was observed by TLC. After completion of the reaction, the catalyst was filtered off, washed with acetone and reused. The residue was extracted from the filtrate using water-ethyl acetate mixture (1:3) followed by washing with brine and drying over Na₂SO₄. The products were obtained by column chromatography of the residue using ethyl acetate/hexane (1:9) as eluent.

Characterisation of Resveratrol:



The purified resveratrol was fully characterized by FTIR, ¹H and ¹³C NMR and GCMS analysis which was also reported in our previous publication (Borah *et al.*, 2017).

IR (KBr, cm⁻¹): (O-H) 3334.9, (O-H) 3247.1, (C-H) 3034.4, (C=C) 1610.0, (C=C) 1592.0, (C=C) 1519.1, (C-C) 1458.4, (C-C) 1401.8, (C-C) 1314.9, (monosubstituted C-H) 1217.5, (monosubstituted C-H) 1147.9, (monosubstituted C-H) 1108.0, (monosubstituted C-H) 972.7, (monosubstituted C-H) 824.9, (monosubstituted C-H) 674.2 cm⁻¹.

(¹H NMR, 500 MHz, DMSO-d₆, δ ppm): H_a 5.35(s,1H), H_b 6.12(s,1H), H_c 6.38(s,1H,J=1.5 Hz), H_d 6.70(t,1H,J=7.5Hz), H_e 6.95(d,1H,J=15.1Hz), H_f 7.38(s,1H,J=7.5Hz). (¹³C NMR, 125 MHz, DMSO-d₆, δ ppm):102.8(1), 104.7(2), 115.8(3), 127.4(4), 130.6(5), 157.79(6), 159.8(7). MS (m/z): 228 (base peak).

RESULTS AND DISCUSSION

Characterisation of Pd(0)NPs@Cellulose

The formation of Pd(0)NPs@Cellulose using resveratrol was initially observed from color change. The light brown color solution of resveratrol (Fig. 1A) upon addition of PdCl₂ and cellulose gradually changes to black (within 20 min) (Fig. 1C) indicating the generation of Pd(0)NPs@Cellulose (Figure 1D). The formation of Pd(0)NPs@Cellulose was identified by XRD, TEM, ICP-AES, XPS, FTIR and UV-Vis absorption spectroscopy.

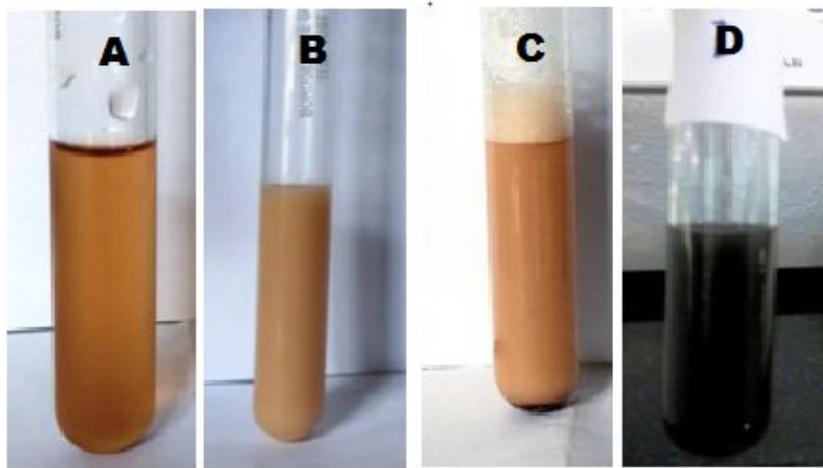


Fig. 1. (A) Solution of resveratrol in water (B) solution of A with cellulose (C) solution B with PdCl₂ (D) solution C after 20 min heating.

The formation of PdNps was monitored by recording electronic spectra (200-800 nm) of the colloidal ethanolic solution of PdNps (Fig. 2). The UV-visible spectrum of PdCl₂ exhibits two peaks at around 222 nm and 380-450 nm, could be due to the ligand to metal charge transfer

transition of the Pd(II) ions and d-d transition, respectively. The non-appearance of any absorption band above 380 nm in the UV-Vis spectrum of Pd(0)NPs@Cellulose is indicative of the formation of Pd(0) nanoparticles (Patel *et al.*, 2005).

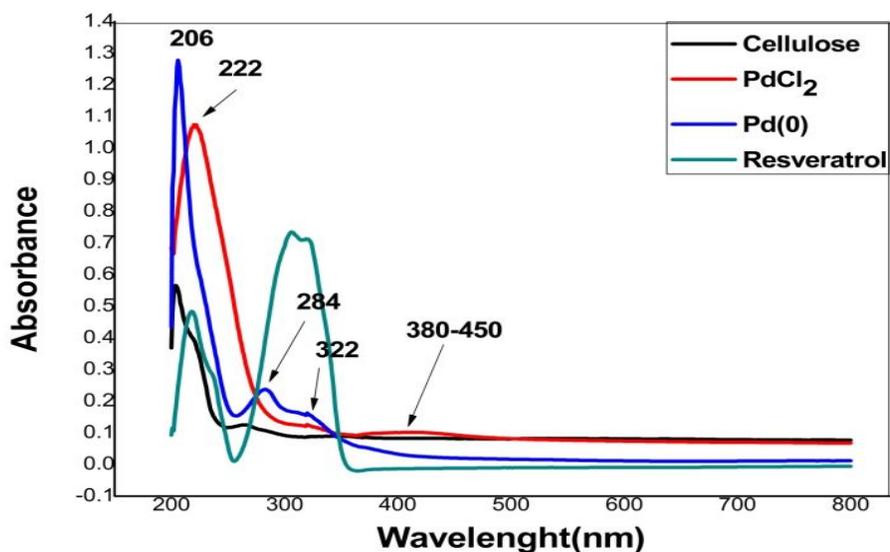


Fig. 2. UV-Visible spectra of PdCl₂, cellulose, resveratrol and Pd(0)NPs@Cellulose.

The comparison of FTIR spectra of cellulose and cellulose supported Pd(0) NPs is shown in Figure 3. The black line indicates the cellulose supported Pd(0) NPs and red line indicates the FTIR of pure cellulose. Strong absorption peak at 3343 cm⁻¹ corresponds to the νO-H of intramolecular hydrogen bonds for cellulose. Peak at 2902 cm⁻¹ is due to the νC-H vibration. Peaks at 1643 cm⁻¹ is because of O-H bending vibration, 1426 cm⁻¹ is CH₂ scissoring motion, 1367 cm⁻¹ is CH₂ wagging, 1062 cm⁻¹ is C-O-C pyranose ring stretching vibration and peak at 897 cm⁻¹ is the cellulose β-glycoside linkages (Kumar *et al.*, 2014). A decrease in intensity of peak at 3344 cm⁻¹

indicates the formation of Pd(0)-oxygen linkage in which Pd metals are stabilized by -OH group of cellulose by metal-ligand interactions. Due to these metal-ligand interactions, weak absorption peaks were observed in the FTIR spectrum of cellulose supported Pd(0) NPs. This indicates that the -OH group of cellulose acts as a stabilizing agent of Pd(0) nanoparticles. Thus Pd(0) NPs formed inside the cavities of cellulose. Shifting of all peaks in FTIR spectrum of cellulose supported Pd(0) NPs indicates the formation of Pd(0) NPs inside the cavities of cellulose template (Mochochoko *et al.*, 2013).

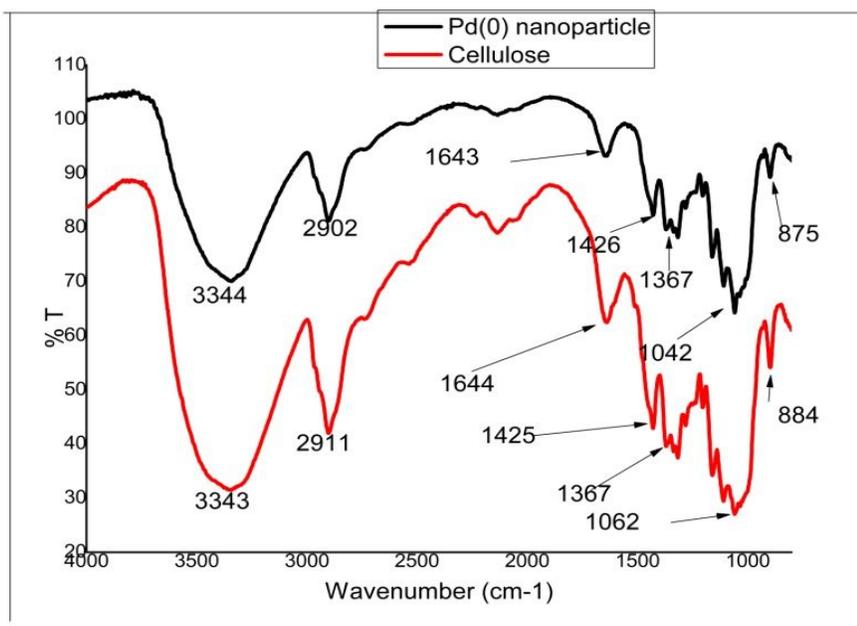


Fig. 3. FTIR spectra of pure cellulose and Pd(0)NPs@Cellulose.

Powder X-ray diffraction study (XRD) (Fig. 4) showed diffraction peaks at 2θ value of 17.1° , 19° and 23.65° corresponding to (101), (101) and (002) planes of cellulose. There were four peaks at 2θ value of 41.7° , 46.8° , 68.28° and 81.38° attributed to (111), (200), (220)

and (311) planes of Pd(0)NPs@Cellulose (Nadagouda *et al.*, 2012). The appearance of intense peak at 41.7° in comparison to the other peaks indicated the preferred growth direction of the nanocrystals.

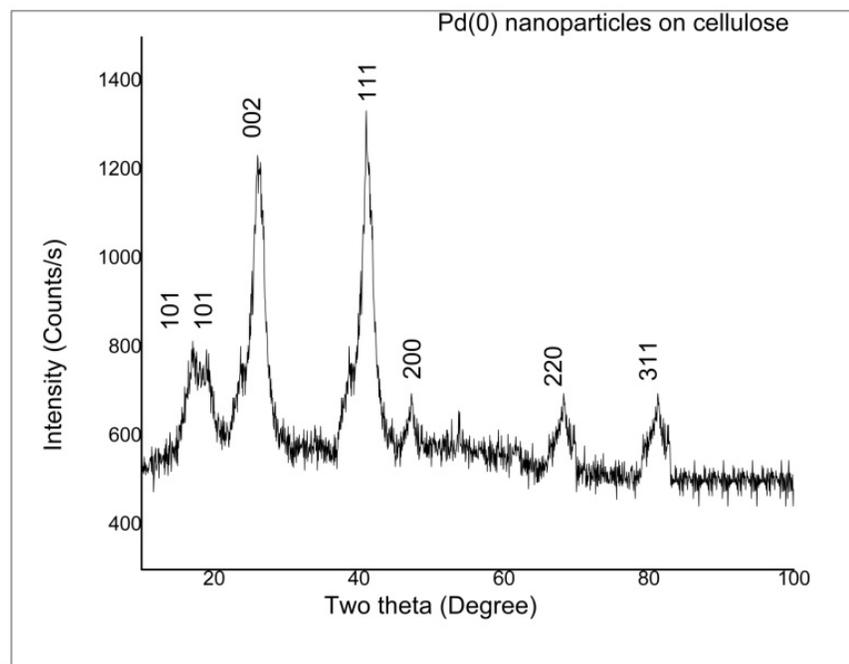


Fig. 4. Powder XRD pattern of Pd(0)NPs@Cellulose.

The morphology, size and size distribution pattern of the PdNps were investigated by HRTEM (Fig. 5A and B) which showed homogeneous particle size distribution in

the range of 20-40 nm with majority of particles being in the range of 18-22 nm.

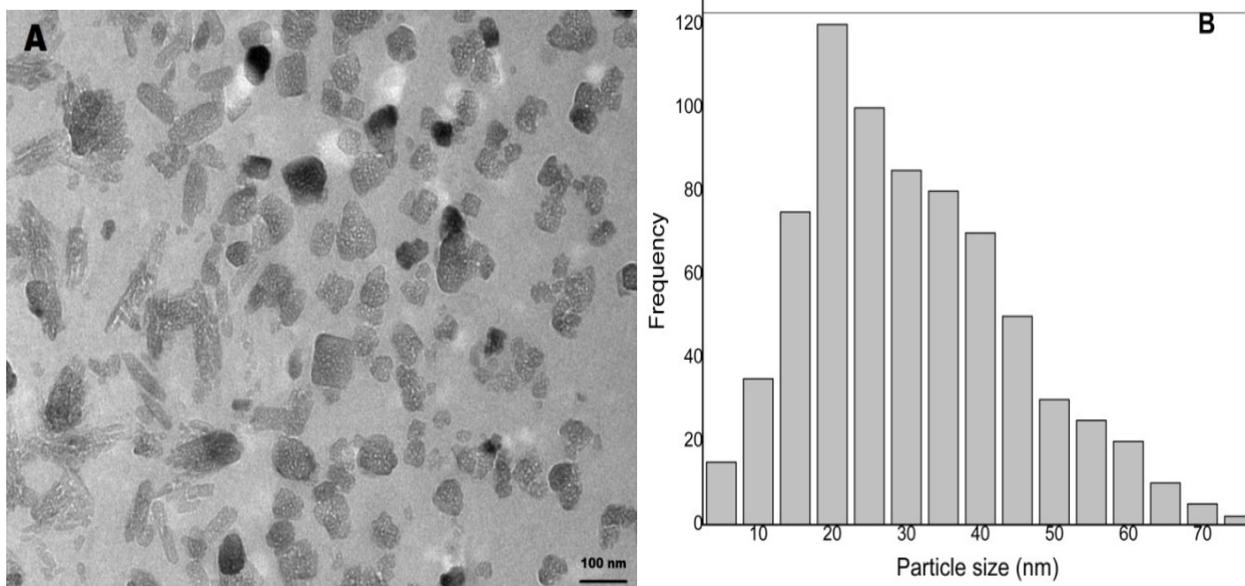


Fig. 5. (A) HRTEM image of Pd(0)NPs@Cellulose (B) particle size distribution of Pd(0)NPs@Cellulose nanoparticles. The particle size data is based on the image analysis of more than 500 particles.

The surface composition of the cellulose supported Pd nanoparticles has been analyzed by X-ray photoelectron spectroscopy. Figure 6A shows the characteristic XPS peaks of the Pd(0) 3d core level peaks of Pd(0)NPs@Cellulose catalyst. The spectrum demonstrated two peaks located at 336.32 eV and 341.53 eV could be assigned to the Pd⁰ 3d_{5/2} and Pd⁰ 3d_{3/2} spin-orbit components, respectively (Zhou *et al.*, 2012). Figure 6B and 6C show two XPS responses at 532.09 eV and 285.59 eV, corresponding to the O 1S_{1/2} and C1S_{1/2} core level binding energy respectively, which are present in the synthesized catalyst (Liu *et al.*, 2017). The ICP-AES analysis indicated 0.069 mmol Pd content per 10 mg of the catalyst.

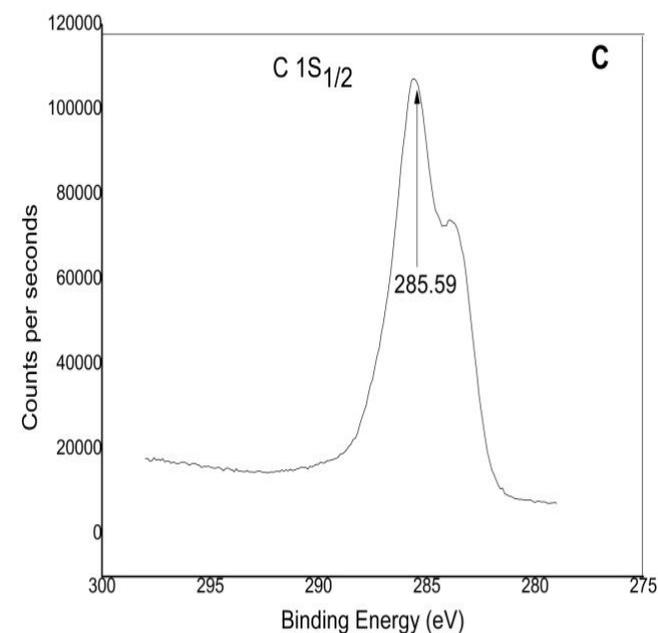
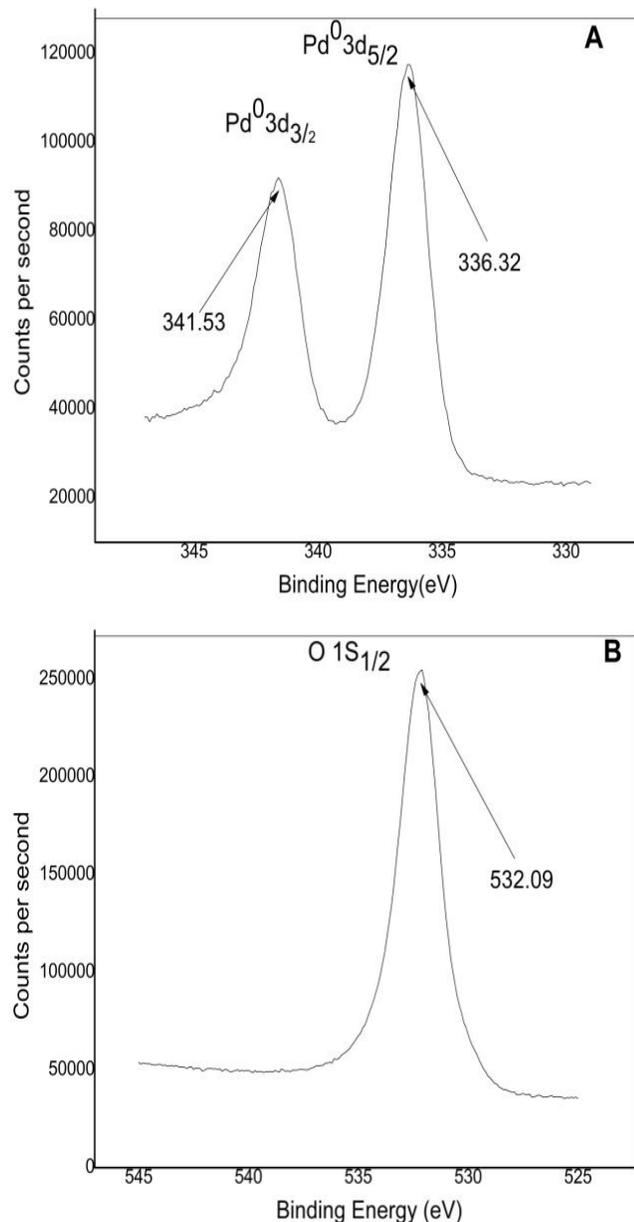


Fig. 6. (A) 3d core-level XPS of the catalyst, Pd(0)NPs@Cellulose (B) 1S core-level XPS oxygen (C) 1S core-level XPS carbon.

Catalytic activity of Pd(0)NPs@Cellulose under microwave heating

The catalytic activity of Pd(0)NPs@Cellulose have been studied in the Suzuki-Miyaura and Heck cross-coupling reactions under microwave heating (Tohidi *et al.*, 2018). The Suzuki reaction was initially started by employing 2-bromobenzaldehyde (0.5 mmol) and phenylboronic acid (0.75 mmol) as model substrates in order to investigate the reaction conditions. At first, we have performed the reaction with different amounts of the catalyst 5, 10, 15, 20 mg, and even in the absence of the catalyst. It was seen that 15 mg of catalyst is very effective for necessary conversion (Table 1, entry 3). No product was formed in the absence of catalyst (Table 1, entry 6). While the reaction was allowed to proceed with PdCl₂ as catalyst only 30 % product could be obtained from the reaction mixture (Table 1, entry 5), distinctly revealed the vital role of Pd(0)NPs@Cellulose in the reaction. On decreasing the amount of catalyst from 20 mg to 5 mg the yield decreases to 90% (Table 1, entry 1), however increasing the amount of catalyst loading (15 mg to 20 mg) did not alter the yield. Therefore, the minimum amount of catalyst loading was found to be 15 mg of Pd(0)NPs@Cellulose for necessary conversions.

Different solvents like C₂H₅OH, H₂O, i-PrOH, CH₃OH, CH₃CN and dimethylsulfoxide (DMSO) as well as different bases like K₂CO₃, NaOH, Et₃N, NaOAc and Cs₂CO₃ were also tested in order to obtain the optimum reaction conditions. The best result was obtained by using water as a solvent and 2 eq. of K₂CO₃ (Table 1, entry 3). No product is obtained in the absence of base (Table 1,

entry 14). The reaction was also performed with 1.5 and 2.5 eq. of K_2CO_3 , which gave 88 and 98% yields, respectively (entries 12 and 13). Therefore, we performed further reactions taking 2 eq. of K_2CO_3 . Similarly, the optimum temperature and time for this reaction was found to be $80^\circ C$ and 10 min. Based on the above observations it

was evident that a combination of 0.5 mmol of 2-bromobenzaldehyde, 0.75 mmol of phenylboronic acid, 15 mg of catalyst, 2 eq. of K_2CO_3 and 5 ml of water under microwave heating at $80^\circ C$ was sufficient to get an excellent product yield.

Table 1. Optimization of reaction conditions for the Suzuki coupling reaction of 2-bromobenzaldehyde with phenylboronic acid^a.

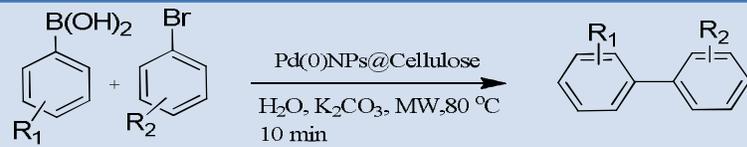
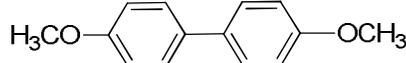
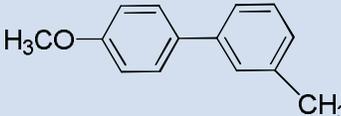
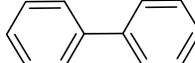
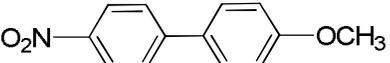
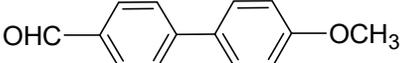
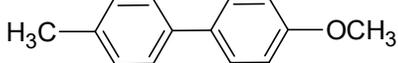
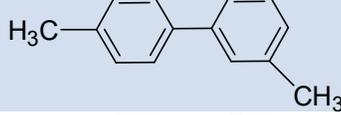
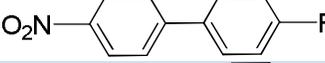
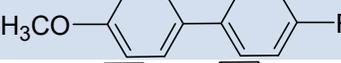
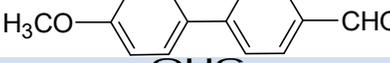
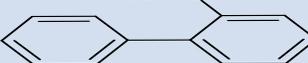
Entry	Catalyst (Amount in mg)	Solvent	Base (eq.)	Time (min)	Temperature ($^\circ C$)	Yield ^b (%)
1	Pd(0)NPs@Cellulose (5)	H ₂ O	K ₂ CO ₃ (2)	10	80	90
2	Pd(0)NPs@Cellulose (10)	H ₂ O	K ₂ CO ₃ (2)	10	80	95
3	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	10	80	98
4	Pd(0)NPs@Cellulose (20)	H ₂ O	K ₂ CO ₃ (2)	10	80	98
5	PdCl ₂ (15)	H ₂ O	K ₂ CO ₃ (2)	10	80	30
6	-----	H ₂ O	K ₂ CO ₃ (2)	10	80	--
7	Pd(0)NPs@Cellulose (15)	C ₂ H ₅ OH	K ₂ CO ₃ (2)	10	80	67
8	Pd(0)NPs@Cellulose (15)	ⁱ PrOH	K ₂ CO ₃ (2)	10	80	70
9	Pd(0)NPs@Cellulose (15)	CH ₃ CN	K ₂ CO ₃ (2)	10	80	85
10	Pd(0)NPs@Cellulose (15)	CH ₃ OH	K ₂ CO ₃ (2)	10	80	71
11	Pd(0)NPs@Cellulose (15)	DMSO	K ₂ CO ₃ (2)	10	80	60
12	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (1.5)	10	80	88
13	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2.5)	10	80	98
14	Pd(0)NPs@Cellulose (15)	H ₂ O	---		80	---
15	Pd(0)NPs@Cellulose (15)	H ₂ O	NaOH	10	80	85
16	Pd(0)NPs@Cellulose (15)	H ₂ O	Et ₃ N	10	80	82
17	Pd(0)NPs@Cellulose (15)	H ₂ O	NaOAc	10	80	76
18	Pd(0)NPs@Cellulose (15)	H ₂ O	Cs ₂ CO ₃	10	80	70
19	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	10	100	98
20	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	10	50	60

^aReaction conditions: 2-bromobenzaldehyde (0.5 mmol), phenylboronic acid (0.75 mmol), Pd(0)NPs@Cellulose (15 mg), K_2CO_3 (2 eq.), H₂O (5mL), $80^\circ C$. ^bIsolated yield.

After investigating the effects of different parameters, we next examined the versatility of our catalyst using different substituted arylbromides and arylboronic acids. From the results given in Table 2, it is seen that the arylbromides with both electron-donating and

electron-withdrawing groups undergo coupling reaction with arylboronic acid effectively to give products in excellent yields (90-98%). In addition, the present protocol is also useful in the case of heteroaryl halide with 4-fluoroboronic acid (Table 2, entries 12 and 13).

Table 2. Suzuki coupling reaction of substituted phenylboronic and various arylbromides under microwave heating^a.

				
Entry	R ₁	R ₂	Product	Yield (%) ^b
1	4-OCH ₃	H		97
2	4-OCH ₃	4-OCH ₃		98
3	4-OCH ₃	3-CH ₃		97
4	H	H		95
5	4-NO ₂	H		91
6	4-NO ₂	4-OCH ₃		94
7	4-CHO	H		93
8	4-CHO	4-OCH ₃		95
9	4-COCH ₃	4-OCH ₃		92
10	4-CH ₃	4-OCH ₃		95
11	4-CH ₃	3-CH ₃		96
12	4-NO ₂	4-F		93
13	4-OCH ₃	4-F		94
14	4-OCH ₃	4-CHO		95
15	H	2-CHO		94

^aReaction conditions: arylbromide (0.5 mmol), arylboronic acid (0.75 mmol), Pd(0)NPs@Cellulose (15 mg), K₂CO₃ (2 eq.), H₂O (5mL), 80°C. ^bIsolated yield.

In order to expand the scope of our catalyst we have conducted the Heck reaction using this catalyst. The Heck reaction needed 10-15 min for effective completion. For optimization of the reaction conditions we have performed a model reaction between iodobenzene (0.5 mmol) and methyl acrylate (1.0 mmol) (Table 3). From Table 3 it was evident that a combination of 0.5 mmol of iodobenzene, 1.0 mmol of methyl acrylate, 20 mg of

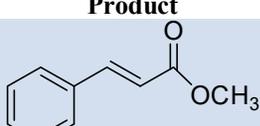
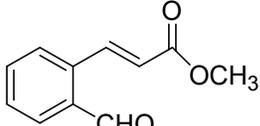
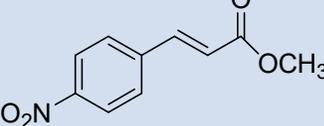
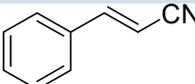
catalyst, 2 eq. of K_2CO_3 and 5 ml of water under microwave heating at $80^\circ C$ was sufficient to get an excellent product yield. Nevertheless of the substituents exhibit in arylbenzenes and alkenes (Table 4), the catalyst successfully catalyzed the Heck coupling reactions with magnificent yields in aqueous media under microwave conditions.

Table 3. Optimization of reaction conditions for the Heck reaction of iodobenzene with methyl acrylate^a.

Entry	Catalyst (Amount in mg)	Solvent	Base (eq.)	Time (min)	Temperature ($^\circ C$)	Yield ^b (%)
1	Pd(0)NPs@Cellulose (10)	H ₂ O	K ₂ CO ₃ (2)	15	80	80
2	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	15	80	85
3	Pd(0)NPs@Cellulose (20)	H ₂ O	K ₂ CO ₃ (2)	15	80	90
4	PdCl ₂ (20)	H ₂ O	K ₂ CO ₃ (2)	15	80	30
5	-----	H ₂ O	K ₂ CO ₃ (2)	15	80	--
6	Pd(0)NPs@Cellulose (15)	C ₂ H ₅ OH	K ₂ CO ₃ (2)	15	80	65
7	Pd(0)NPs@Cellulose (15)	CH ₃ CN	K ₂ CO ₃ (2)	15	80	80
8	Pd(0)NPs@Cellulose (15)	CH ₃ OH	K ₂ CO ₃ (2)	15	80	61
9	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (1.5)	15	80	78
10	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2.5)	15	80	90
11	Pd(0)NPs@Cellulose (15)	H ₂ O	---		80	---
12	Pd(0)NPs@Cellulose (15)	H ₂ O	NaOH	15	80	80
13	Pd(0)NPs@Cellulose (15)	H ₂ O	NaOAc	15	80	70
14	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	10	80	78
15	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	15	100	90
16	Pd(0)NPs@Cellulose (15)	H ₂ O	K ₂ CO ₃ (2)	15	50	60

^aReaction conditions: arylhalides (0.5 mmol), alkene (0.75 mmol), Pd(0) NPs@Cellulose (20 mg), K₂CO₃(2 eq.), H₂O (5 mL), $80^\circ C$, Time : 15 min, microwave. ^bIsolated yield.

Table 4. Heck reaction of aryl halides and olefins under microwave heating catalyzed by Pd(0)NPs@Cellulose^a.

Entry	R	Y	Product	Yield (%) ^b
1	H	COOCH ₃		90
2	2-CHO	COOCH ₃		88
3	4-NO ₂	COOCH ₃		86
4	H	CN		85

^aReaction conditions: arylhalides (0.5 mmol), alkene (0.75 mmol), Pd(0) NPs@Cellulose (20 mg), K₂CO₃(2 eq.), H₂O (5 mL), 80 °C, Time : 15 min, microwave. ^bIsolated yield.

Leaching and Reusability of Pd(0)NPs@Cellulose Hot filtration Test

The heterogeneity of Pd(0)NPs@Cellulose catalyst was confirmed by ICP-AES analysis and hot filtration test by using 2-bromobenzaldehyde and phenylboronic acid as coupling partners under similar conditions. The catalyst was filtered off after 3 min and found 20% conversion (GCMS). Then the reaction was allowed to run for

another 15 min without catalyst and % conversion showed constancy at 20%, indicating non-leaching of Pd into the solution and affirmed heterogeneity of this catalytic system (Fig. 7). A parallel reaction without filtration exhibited 98% conversion. The Pd content in the filtrate was determined by ICP-AES analysis, and found to be below detection limit.

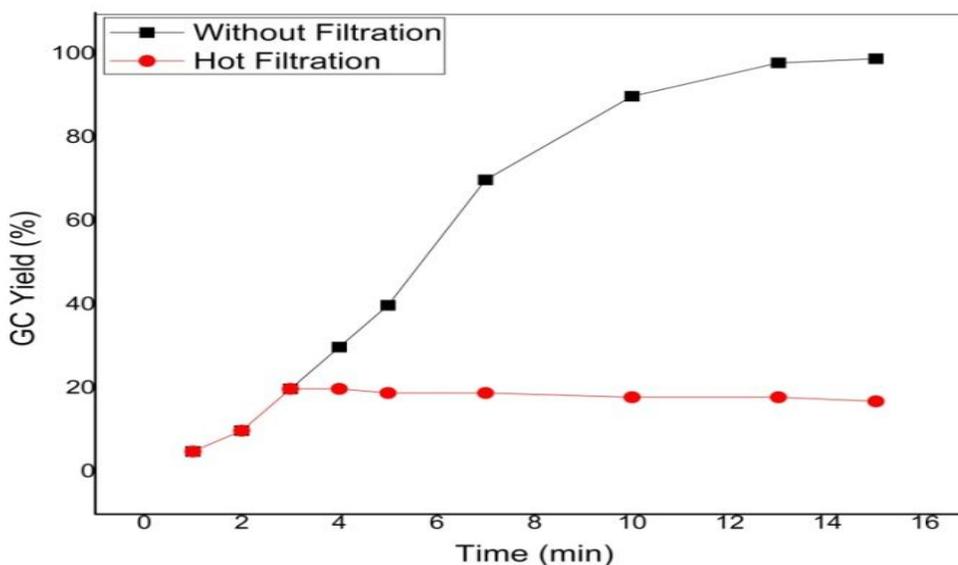


Fig. 7. Activity of the catalyst for the reaction between phenylboronic acid and 2-bromobenzaldehyde with hot filtration and without filtration.

Reusability

The reusability of the catalyst is of significant importance to evaluate catalyst efficacy. It was checked by using Suzuki reaction between phenylboronic acid and 2-bromobenzaldehyde under optimized conditions. After completion of the reaction it was separated by filtration, washed with water and acetone, followed by vacuum

drying. The catalyst can then be reused in a new coupling reaction. It was interesting to observe that the catalyst can be reused up to 10 cycles without major loss of yield of product (Fig. 8). The recovered catalyst after 5th and 10th cycles was investigated by powder XRD and TEM analysis and found to be intact after consecutive cycles (Fig. 9).

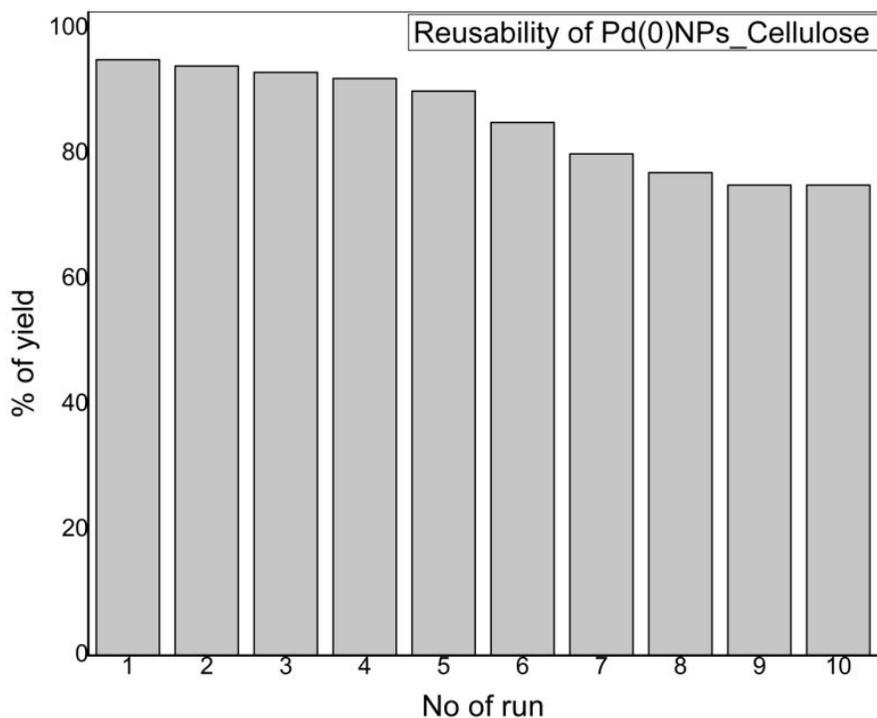


Fig. 8. Recycling activity of Pd(0)NPs@Cellulose catalyst in water.

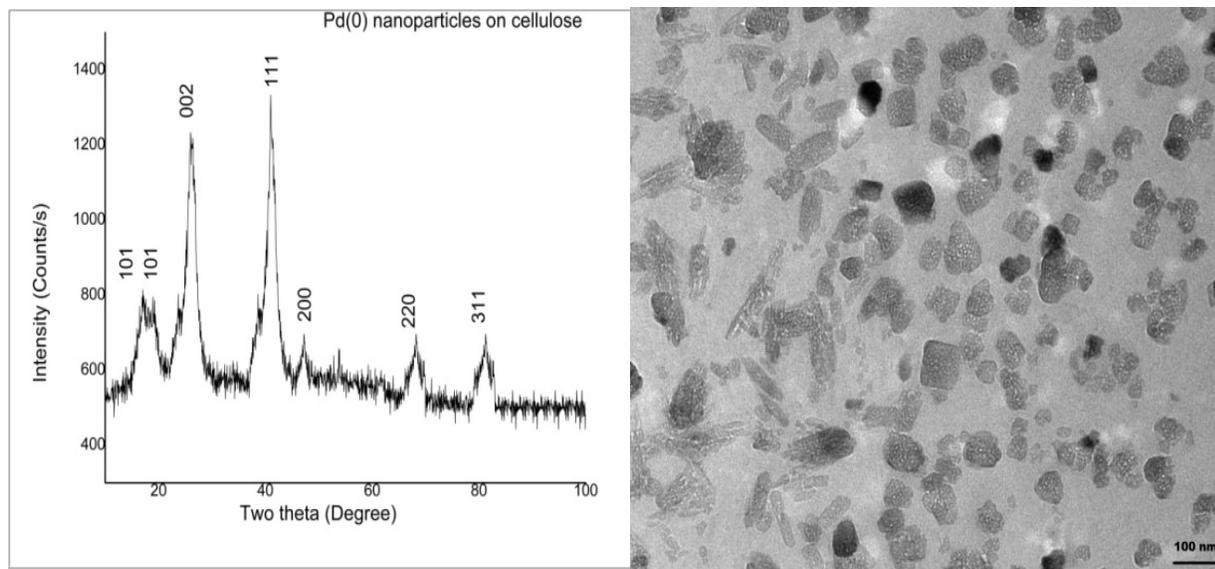


Fig. 9. Powder XRD pattern and HRTEM image of recovered catalyst.

CONCLUSION

The synthesis of Pd(0)NPs@Cellulose using the heartwood extract of *A. lakoocha* Roxb is a green biogenic approach. We have depicted a novel approach for the isolation of active bio-reductant 'resveratrol' from the heartwood extract of *A. lakoocha* Roxb. This benign protocol for the synthesis of Pd NPs provides thermo and air-stable crystalline PdNPs without using harmful reducing agents, ligands, solid waste disposals, etc. The presence of 0.103mmol of Pd per 15 mg of the catalyst, Pd(0)NPs@Cellulose conferred excellent catalytic activity for Suzuki as well as Heck coupling reactions in water. The added advantage of the catalyst is of easy preparation and separability, ten times reusability, supporting its sustainability.

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REFERENCES

- Azarian, A., Nasrollahzadeh, M., Sajadi, SM. and Rostami-Vartooni, A. 2015. Palladium nanoparticles supported on copper oxide as an efficient and recyclable catalyst for carbon(sp²)-carbon(sp²) cross-coupling reaction. *Mater. Res. Bull.* 68:150-154.
- Baran, NY., Baran, T. and Menten, A. 2018. Production of novel palladium nanocatalyst stabilized with sustainable chitosan/cellulose composite and its catalytic performance in Suzuki-Miyaura coupling reactions. *Carbohydr. Polym.* 181:596-604.
- Baruah, D., Das, RN., Hazarika, S. and Konwar, D. 2015. Biogenic synthesis of cellulose supported Pd(0) nanoparticles using heartwood extract of *Artocarpus lakoocha* Roxb- A green, efficient and versatile catalyst for Suzuki and Heck coupling in water under microwave heating. *Catal. Commun.* 72:73-80.
- Basavegowda, N., Mishra, K. and Lee, YR. 2015. Ultrasonic-assisted green synthesis of palladium nanoparticles and their nanocatalytic application in multicomponent reaction. *New J Chem.* 39:972-978.
- Borah, HJ., Singhal, R. and Hazarika, S. 2017. *Artocarpus lakoocha* Roxb.: An Untapped Bioresource of Resveratrol from North East India, its Extractive Separation and Antioxidant Activity. *Ind. Crops Prod.* 95:75-82.
- Byrappa, K., Ohara, S. and Adschiri, T. 2008. Nanoparticles synthesis using supercritical fluid technology – towards biomedical applications. *Adv. Drug Delivery Rev.* 60:299-327.
- Campelo, JM. Luna, D., Luque, R., Marinas, JM. and Romero, AA. 2009. Sustainable Preparation of Supported Metal Nanoparticles and their Applications in Catalysis. *Chem. Sus. Chem.* 2:18-45.
- Chen, F., Huang, M. and Li, Y. 2014. Synthesis of a Novel Cellulose Microencapsulated Palladium Nanoparticle and Its Catalytic Activities in Suzuki-Miyaura and Mizoroki-Heck Reactions. *Ind. Engin. Chem. Res.* 53:8339-8345.
- Coccia, F., Tonucci, L., Bosco, D., Bressan, M. and d'Alessandro, N. 2012. One-pot synthesis of lignin-stabilised platinum and palladium nanoparticles and their catalytic behaviour in oxidation and reduction reactions. *Green Chem.* 14:1073-1078.
- De Rivera, FG., Angurell, I., Rossell, MD., Erni, R., Llorca, J., Divins, NJ., Muller, G., Seco, M. and Rossell, O. 2013. A General Approach To Fabricate Fe₃O₄ Nanoparticles Decorated with Pd, Au, and Rh: Magnetically Recoverable and Reusable Catalysts for Suzuki C-C Cross-Coupling Reactions, Hydrogenation, and Sequential Reactions. *Chem. Eur. J.* 19:11963-11976.
- Dhakshinamoorthy, A., Asiric, AM. and Garcia, H. 2015. Metal-organic frameworks catalyzed C-C and C-heteroatom coupling reactions. *Chem Soc Rev.* 44:1922-1948.
- Habibi, Y. 2014. Key advances in the chemical modification of nanocelluloses. *Chem. Soc. Rev.* 43:1519-1543.
- Iravani, S. 2011. Green synthesis of metal nanoparticles using plants. *Green Chem.* 13:2638-2650.
- Issaabadi, Z., Nasrollahzadeh, M. and Sajadi, SM. 2018. Green synthesis of Pd/Fe₃O₄ nanocomposite using *Hibiscus tiliaceus* L. extract and its application for reductive catalysis of Cr(VI) and nitro compounds. *Sep. Purif. Technol.* 197:253-273.
- Kalidindi, SB. and Jagirdar, BR. 2012. Nanocatalysis and Prospects of Green Chemistry. *Chem Sus Chem.* 5:65-75.
- Khan, M., Khan, M., Kuniyil, M., Adil, SF., Warthan, AA., Alkhatlan, HZ., Tremel, W., Tahir, MN. and Siddiqui, MRH. 2014. Dalton Trans. Biogenic synthesis of palladium nanoparticles using *Pulicaria glutinosa* extract and their catalytic activity towards the Suzuki coupling reaction. 43:9026-9031.

- Khazaei, A., Khazaei, M., Nasrollahzadeh, M. and Tahsili, MR. 2017. Highly efficient reusable Pd nanoparticles based on eggshell: Green synthesis, characterization and their application in catalytic reduction of variety of organic dyes and ligand-free oxidative hydroxylation of phenylboronic acid at room temperature. *Tetrahedron*. 73:1-11.
- Khodadadi, B., Bordbar, M. and Nasrollahzadeh, M. 2017. Green Synthesis of Pd Nanoparticles at Apricot Kernel Shell Substrate Using *Salvia Hydrangea* Extract: Catalytic Activity for Reduction of Organic Dyes. *J. Colloid Interf. Sci.* 490:1-25.
- Kumar, A., Negi, YS., Choudhary, V. and Bhardwaj, NK. 2014. Characterization of Cellulose Nanocrystals Produced by Acid-Hydrolysis from Sugarcane Bagasse as Agro-Waste. *J. Mater. Phys. Chem.* 2:1-8.
- Leadbeater, NE. 2005. Fast, easy, clean chemistry by using water as a solvent and microwave heating: the Suzuki coupling as an illustration. *Chem. Commun.* 2881-2902.
- Liu, S., Li, J., Jurca, T., Stair, PC., Lohr, TL. and Marks, TJ. 2017. Efficient carbon-supported heterogeneous molybdenum-dioxo catalyst for chemoselective reductive carbonyl coupling. *Catal. Sci. Technol.* 7:2262-2267.
- Lu, Z., Jasinski, JB., Handa, S. and Hammond, GB. 2018. Recyclable cellulose-palladium nanoparticles for clean cross-coupling chemistry, *Org. Biomol. Chem.* 16:2748-2753.
- Maham, MM., Nasrollahzadeh, M., Sajadi, S. and Kohsari, I. 2018. Biosynthesis, characterization and catalytic activity of the Pd/bentonite nanocomposite for base- and ligand-free oxidative hydroxylation of phenylboronic acid and reduction of Chromium (VI) and nitro compounds. *Micropor. Mesopor. Mater.* 271:128-154.
- Maryami, M., Nasrollahzadeh, M., Mehdipour, E. and Sajadi, SM. 2017. Green synthesis of the Pd/perlite nanocomposite using *Euphorbia neriiifolia* L. leaf extract and evaluation of its catalytic activity. *Sep. Purif. Technol.* 184:298-323.
- Mochochoko, T., Oluwafemi, OS., Jumbam, DN. and Songca, SP. 2013. Green synthesis of silver nanoparticles using cellulose extracted from an aquatic weed; water hyacinth. *Carbohydr. Polym.* 98:290-294.
- Nadagouda, MN., Desai, I., Cruza, C. and Yang, DJ. 2012. Novel Pd based catalyst for the removal of organic and emerging contaminants. *RSC Adv.* 2:7540-7548.
- Nasrollahzadeh, M. and Banaci, A. 2015. Hybrid Au/Pd nanoparticles as reusable catalysts for Heck coupling reactions in water under aerobic conditions. *Tetrahedron Lett.* 56:500-503.
- Nasrollahzadeh, M. and Sajadi, SM. 2016. Green synthesis of Pd nanoparticles mediated by *Euphorbia thymifolia* L. leaf extract: Catalytic activity for cyanation of aryl iodides under ligand-free conditions. *J. Colloid Interf. Sci.* 469:191-195.
- Nasrollahzadeh, M., Sajadi, SM. and Maham, M. 2015. Green synthesis of palladium nanoparticles using *Hippophae rhamnoides* Linn leaf extract and their catalytic activity for the Suzuki–Miyaura coupling in water. *J. Mol. Cat. A Chem.* 396:297-303.
- Otari, SV., Patil, RM., Waghmare, SR., Ghosha, SJ. and Pawar, SH. 2013. A novel microbial synthesis of catalytically active Ag–alginate biohydrogel and its antimicrobial activity. *Dalton Trans.* 42:9966-9975.
- Patel, K., Kapoor, S., Dave, DP. and Mukherjee, T. 2005. Synthesis of Pt, Pd, Pt/Ag and Pd/Ag nanoparticles by microwave-polyol method. *J. Chem. Sci.* 117:311-316.
- Peralta-Videa, JR., Zhao, L., Lopez-Moreno, ML., Rosa, G., Hong, J. and Gardea Torresdey, JL. 2011. Nanomaterials and the environment: A review for the biennium 2008–2010. *J. Hazard. Mater.* 186:1-15.
- Raveendran, P., Fu, J. and Wallen, SL. 2003. Completely Green Synthesis and Stabilization of Metal Nanoparticles. *J. Am. Chem. Soc.* 125:13940-13941.
- Sajjadi, M., Nasrollahzadeh, M., Maham, M., Sajadi, SM. and Barzinjy, AA. 2018. Biosynthesis of the palladium/sodium borosilicate nanocomposite using *Euphorbia milii* extract and evaluation of its catalytic activity in the reduction of chromium (VI), nitro compounds and organic dyes. *Mater. Res. Bull.* 102:24-50.
- Sajadi, S., Nasrollahzadeh, M., Rostami-Vartooni, MA. and Khalaj, M. 2015. Green synthesis of Pd/Fe₃O₄ nanoparticles using *Euphorbia condylocarpa*, *M. bieb* root extract and their catalytic applications as magnetically recoverable and stable recyclable catalysts for the phosphine-free Sonogashira and Suzuki coupling reactions. *J Mol. Cat. A Chem.* 396:1-31.
- Tohidi, MM., Nasrollahzadeh, M., Issaabadi, Z. and Sajadi, SM. 2018. Recent Progress in Application of Graphene Supported Metal Nanoparticles in C–C and C–X Coupling Reactions. *Chem. Rec.* 18:165-229.

Varma, RS. 2012. Greener approach to nanomaterials and their sustainable Applications. *Curr. Opin. Chem. Eng.* 1:123-128.

Wu, X., Lu, C., Zhang, W., Yuan, G., Xiong, R. and Zhang, X. 2013. A novel reagentless approach for synthesizing cellulose nanocrystal-supported palladium nanoparticles with enhanced catalytic performance. *J Mater Chem A.* 1:8645-8653.

Wu, XC., Xu, L. and Zhu, JJ. 2008. Green preparation and catalytic application of Pd nanoparticles. *Nanotechnology.* 19:305603-305609.

Xu, Y., Zhang, L. and Cui, Y. 2008. Catalytic Performance of Cellulose Supported Palladium Complex for Heck Reaction in Water. *J. Appl. Polym. Sci.* 110:2996-3000.

Zhou, P., Wang, H., Yang, J., Tang, J., Sun, D. and Tang, W. 2012. Bio-supported palladium nanoparticles as a phosphine-free catalyst for the Suzuki reaction in water. *RSC Adv.* 2:1759-1761.

Zhu, H., Du, ML., Zou, M., Xu, C. and Fu, YQ. 2012. Green synthesis of Au nanoparticles immobilized on halloysite nanotubes for surface-enhanced Raman scattering substrates. *Dalton Trans.* 41:10465-10471.

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