

RESEARCH PAPER

Synthesis, Characterization and Catalytic Activity of Ligand Stabilized Palladium Nanoparticle: A Catalyst Compliment to the Heck Coupling Reaction

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ABSTRACT

The palladium metal is the most frequently used metal because of its excellent catalytic efficiency and most flexible varying oxidation state. So, we report that palladium nanoparticles (Pd NPs) stabilized by a ligand (*o*-vanilindiphenylethanedionedi-hydrazone, L) using reverse micelles method have been synthesized, while all particles are in spherical shape and ranging between 10 and 15 nm. This has been characterized by ¹H NMR, IR, UV, X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and scanning electron microscope (SEM) analyses. These nanoparticles were used as a catalyst for coupling reaction between aryl halides with terminal alkenes, Heck reaction, in the presence of potassium carbonate (K₂CO₃) as a base and NMP (N-Methyl-2-pyrrolidone) as a solvent. The present catalyst is an air and moisture stable and has significant catalytic activity in Heck cross-coupling reactions under operating conditions. Various aryl halides and terminal alkenes were coupled smoothly under air to afford the corresponding cross-coupled products in excellent yields.

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INTRODUCTION

Transition metal-catalyzed carbon-carbon bond forming reactions is widely employed methods of modern organic chemistry [1-3]. The use of catalytic method has been found a most interesting topic in the preparation of many natural products, materials science as well as agrochemical industry [4-7]. In this research topic, various metals are being employed in coupling reactions, however, in most cases, palladium metals are most frequently used because of their excellent catalytic efficiency and most flexible varying oxidation state [8-13]. In the last decade, synthesis of metal-nanoparticle (M-NPs) has attracted intensified attention, therefore, a maximum effort has been devoted to

the development of nanoparticles. The advantages of both nanocomposite and catalysis are the most interesting combination in heterogeneous and homogeneous catalysis.

The metal nanoparticles have exhibited very unusual and size-dependent properties like optical [14], magnetic [15, 16], electronic [17, 18], and chemical [19, 20] properties. The maximum efficiency showed by the nanoparticles depends on the size and shape. These nanoparticles exhibit superior properties than those of their bulk materials. They also show a high catalytic activity as heterogeneous catalysts [21, 22]. Particularly palladium metal is acquiring an interest due to its unique catalytic properties and high stability.

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Palladium nanoparticles have been extensively used as a catalyst for many organic reactions that are also catalyzed by organometallic palladium complexes such as olefin hydrogenation and carbon-carbon coupling reactions [23-32]. Although numerous phosphine-based ligands have been developed for organo-palladium compounds for their applications as catalysts for many organic reactions, these ligands have not been extensively utilized as stabilizing surfactants for palladium nanoparticles. There are few reports on the coordination chemistry of palladium nanoparticles [33-35]. For example, El-Sayed and co-workers investigated the effect of reagents and surfactants on the stability of palladium nanoparticles during Suzuki coupling reactions. Very recently, Chaudret [36] and Fujihara [37] groups reported on the asymmetric catalytic applications of chiral phosphine stabilized by palladium nanoparticles. For their extensive applications, synthesis of palladium nanoparticles stabilized by various ligands has become very important. In addition, comparative studies on the ligand coordination chemistry between metal nanoparticles and organometallic compounds

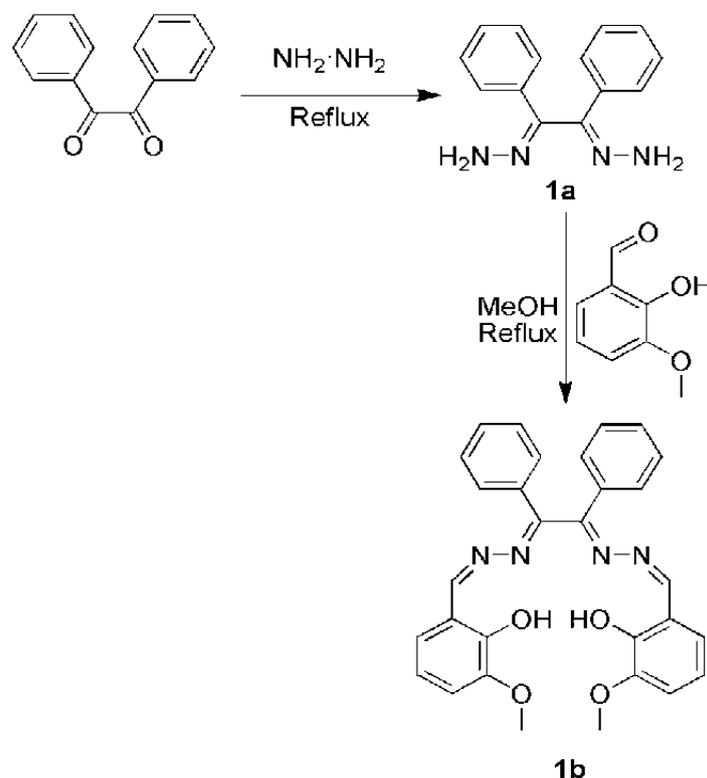
would provide useful information for the catalytic applications of palladium nanoparticles, because it is often very difficult to distinguish between homogeneous catalysis on molecular species and heterogeneous catalysis on metal nanoparticles [38-40]. Literature survey showed that no work has been published on polydentate ligand stabilized palladium nanoparticles, therefore, in our previous work, we reported ligand stabilized heterogeneous palladium nanocomposite for catalysing Heck reaction [41]. Here, as continuing our previous work, we study macro-cyclic ligand of diphenylethanedionedi-hydrazone to stabilize palladium nanoparticle and its application as a catalyst for Heck coupling reaction.

EXPERIMENTALS

Materials and methods

General Experiments

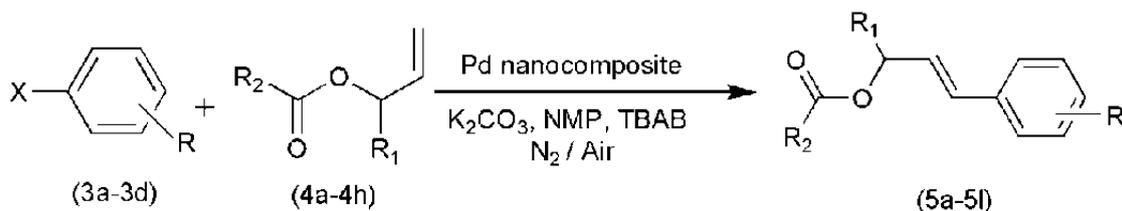
Benzyl, hydrazine hydrate, *o*-vanillin, cetyltrimethylammoniumbromide (CTAB), *n*-butanol, *iso*-octane, allyl acetates, aryl halides, HPLC grade chloroform, dichloromethane and palladium acetate were purchased from Sigma-Aldrich (INDIA). Himedia (INDIA), and Lobo Chemicals



Scheme 1: Synthesis of *o*-vanilindiphenylethanedionedi-hydrazone ligand



Scheme 2: Synthesis of Pd nano-composite (Pd NCs)



Scheme 3: Synthesis of 5a as a Heck reaction product

(INDIA) (commercially available from local sources) were used as received without further purification. Freshly distilled solvents were employed for all synthetic purposes. Spectroscopic grade solvents were employed for spectral works. All other chemicals were of AR grade. The progress of every coupling reaction was monitored by TLC. Yields refer to the isolated products after column chromatographic purification of compounds that have a purity of $\geq 95\%$. The products of Heck reactions were authenticated by matching spectroscopic data of the products obtained by us with those reported in the literature. ^1H and ^{13}C NMR spectra were recorded on a JNM-ECS-300 NMR spectrometer at 399.78 and 75.03 MHz, respectively, and Bruker Avance III, 400 MHz, 9.4 tesla magnet with chemical shifts reported in ppm relative to the residual deuterated solvent or the internal standard tetramethylsilane. Elemental analyses were carried out with a Perkin-Elmer 2400 Series II C, H, N analyzer. UV-Vis spectra were recorded on Varian Cary 5000. Melting points were determined in an electrically heated apparatus by taking the sample in a glass capillary sealed at one end.

Diphenylethanedionedi-hydrazone 1a.

10.5 g (50 mmol) of benzil was dissolved in 100 mL of ethylene glycol and 24.3 mL (500 mmol) of hydrazine hydrate was added to it. The resulting yellow solution was refluxed for 2 h and then it was left in the air. After 16 h a white microcrystalline compound 1a separated out which was filtered off and washed with water followed by diethyl ether. The compound was dried in air. Yield 8.9 g (75%); mp

144 °C. Anal. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_4$: C, 70.55; H, 5.93; N, 23.52 Found: C, 71.06; H, 5.76; N, 23.95%.

o-vanilindiphenylethanedionedi-hydrazone, (L)1b.

Diphenylethanedionedi-hydrazone 1a (6.00 g, 0.03 mol), and *o*-vanillin (9.13g, 0.06 mol) in absolute methanol (60 mL) was refluxed for 4 h, and allowed to cool to the room temperature. The precipitate formed was filtered off. The filtrate still contained the product which was collected by reducing the volume of the filtrate to dryness. The synthesized crude compound was obtained in the form of a yellow solid 1b (Scheme 1) (5.10 g, 85%), M.P >350 °C; IR (KBr, cm^{-1}) 3009 (br), 2832 (br), 1602 (s), 1452 (s), 1378 (w), 1252 (s), 1077 (w), ^1H NMR (CDCl_3 , 400 MHz) 11.10 (2H s, OH), 8.77 (2H, s, -CH), 7.90-7.88 (4H, d, H-Arbenzil), 7.44-7.35 (6H, m, H-Ar benzyl), 6.91-6.72 (6H, m, H-Ar *o*-vanilin) and 3.80 (6H, s, O-Me);

Synthesis of nano palladium composition (Pd NCs) 2a.

Two micro-emulsion systems (I and II) were prepared for the synthesis of palladium nanocomposite consisting of CTAB as surfactant and acetate as co-anion using reverse micelle method. The micro-emulsion I, containing cetyltrimethylammoniumbromide (CTAB) as the surfactant, *n*-butanol as the co-surfactant, isooctane as the hydrocarbon phase, conductivity water and 0.417 mmol of the ligand (L). Similarly, the micro-emulsion II was prepared which contained the same constituents as micro emulsion I except that ligand (L), however, it had 0.417 mmol of a Pd(OAc)_2 . The weight fractions of the various

constituents utilized in these micro-emulsions are: 16.66% of CTAB, 17.70% of n-butanol, 57.4% of isooctane, and 8.1% of the aqueous phase. The two micro emulsions were mixed together very slowly and stirred overnight using a magnetic stirrer, as reported [62]. The pale-red precipitate so-obtained was separated from the apolar solvent and the surfactant by centrifuging and was thoroughly washed with HPLC grade chloroform. The compound so-obtained was then air dried and used without any further purification (Scheme 2). Yield: 160 mg, (60%).

(5.10 g, 85 %), M.P >350 °C; IR (KBr, cm^{-1}) 3009 (br), 2832 (br), 1602 (s), 1452 (s), 1378 (w), 1252 (s), 1077 (w), ^1H NMR (CDCl_3 , 400 MHz) 11.29 (2H s, OH), 8.59 (2H, s, -CH), 7.90-7.88 (4H, d, H-Ar benzil), 7.41-7.36 (6H, m, H-Ar benzyl), 6.91-6.79 (6H, m, H-Ar *o*-vanilin) and 3.60 (6H, s,

O-Me); and 3.54 (6H, s, CH_3 , Acetate ion). Solid state UV-Vis: λ_{max} (nm, log): 425 (0.25).

General procedure for Heck reaction 5a.

To the mixture of K_2CO_3 (138.25mg 1.0 mmol), nano palladium (6.8 mg, 0.1 mmol), TBAB (161.18mg 0.5 mmol) and NMP (5 mL) was added aryl halide 3a (78 mg, 0.5 mmol) and allyl acetate 4a (100 mg, 1.0 mmol, 2.0 eq.) subsequently. The reaction mixture was vigorously stirred under air or N_2 atmosphere at 120 °C for an appropriate time (see Table 1) till the reaction became complete, and progress of the reaction was monitored by TLC (Scheme 2). After cooling to room temperature and concentrating in a vacuum, it was centrifuged and filtered. The precipitate was washed three times using dichloromethane (5 mL x 3 times). The extracted solutions were combined and

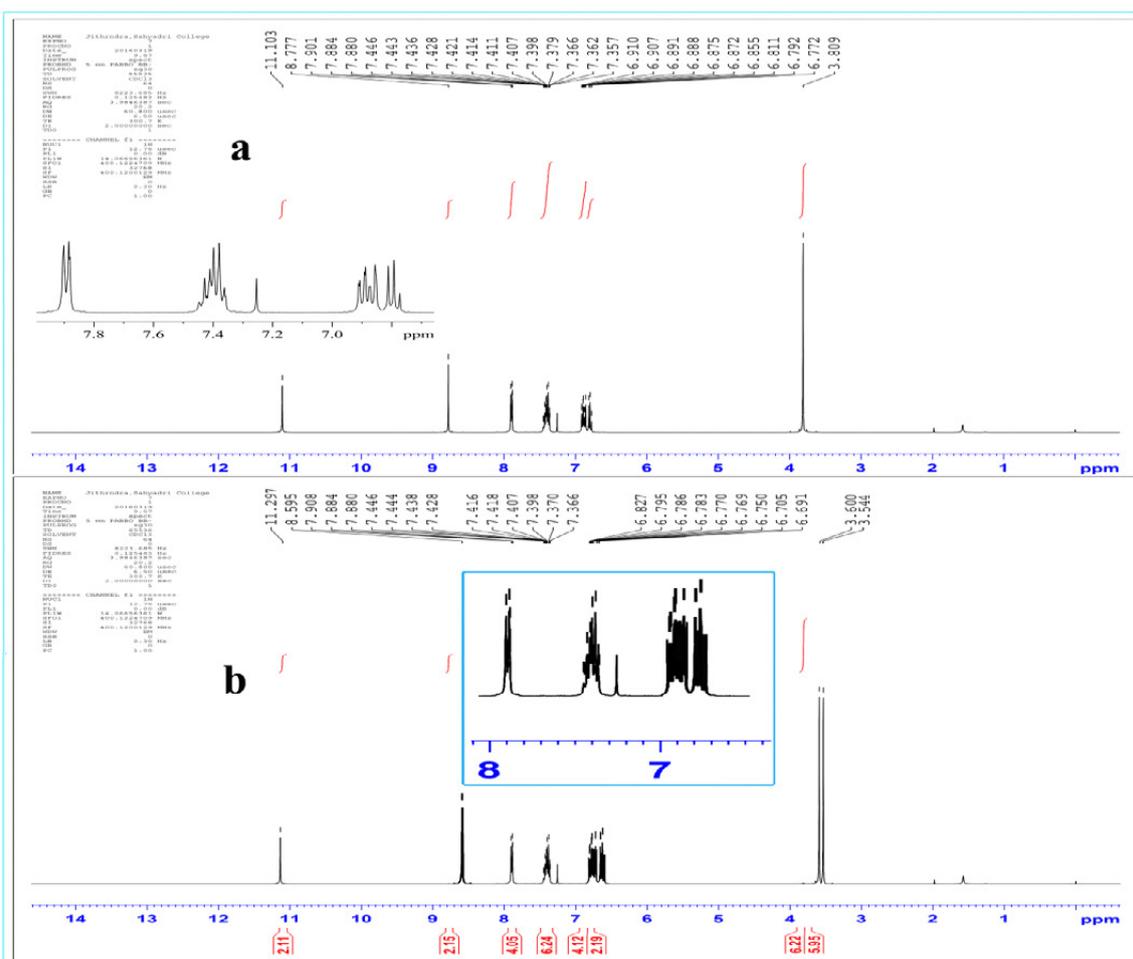


Fig. 1: Comparison of ^1H NMR spectrum of ligand (a) and ligand capped Pd NCs (b)

washed with water for about three times. The crude product was purified by chromatography on a short silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford 80 mg (91%) of crude product 3aa. The precipitate was further washed sufficiently with distilled water and HPLC grade chloroform then dried, and the palladium nanoparticles were recovered. The same catalyst was reused four times for Heck coupling reaction. ^1H NMR (CDCl_3 , 399.7 MHz): δ = 7.41-7.24 (m, 5 H), 6.68 (d, J = 15.6 Hz, 1 H), 6.34 (dt, J = 15.6, 6.3 Hz, 1 H), 4.74 (d, J = 6.3 Hz, 2 H), 2.10 (s, 3 H). ^{13}C NMR (CDCl_3 , 75.4 MHz): δ = 170.9, 136.2, 134.2, 128.6, 128.1, 126.6, 123.1, 65.0, 20.8.

RESULTS AND DISCUSSION

Characterization of palladium nanocomposition

The ligand was synthesized by previously reported method with slight modification of the reactant and reaction conditions, by Schiff base reaction with benzildihydrazine and *o*-vanillin, the structure was confirmed by FT-IR, and ^1H NMR. The ligand is then used for the synthesis of palladium nanoparticle. In this work, palladium metal was stabilized using organic moiety with acetate ion as

a co-anion forming stable nanocomposite or nano coordination compound. The ^1H NMR spectrum of the free ligand showed signals at 11.10 ppm for -OH proton; while a singlet at azomethine proton appears at 8.79 ppm and aromatic ring protons signals are in the range of 8.00 to 6.85 ppm. In the ^1H NMR spectrum of the synthesized nanocomposite, using CH_3COO^- as co-anion, signals are observed with the loss of splitting (Fig. 1). Some ^1H signals are found to be a downfield shift as compared to the uncoordinated ligand signals. Azomethine proton at 8.59 ppm instead of 8.79 ppm and methyl proton are found at 3.60 ppm compared to 3.80 ppm with loss of splitting, while only aromatic protons show a very slight shift in the position. Some peaks show downfield shifting with slight broadening at azomethine proton, hydroxyl proton, methoxy proton signals and aromatic proton signals, indicative of a little paramagnetic environment which confirm the existence of palladium nanoparticles.

The ligand showed characteristic IR bands at 1602 cm^{-1} is C=N stretching frequencies, 1252 cm^{-1} and 1077 cm^{-1} are assigned to O- CH_3 stretching frequencies (Fig. 2). A broad and sharp IR band at 3009 and

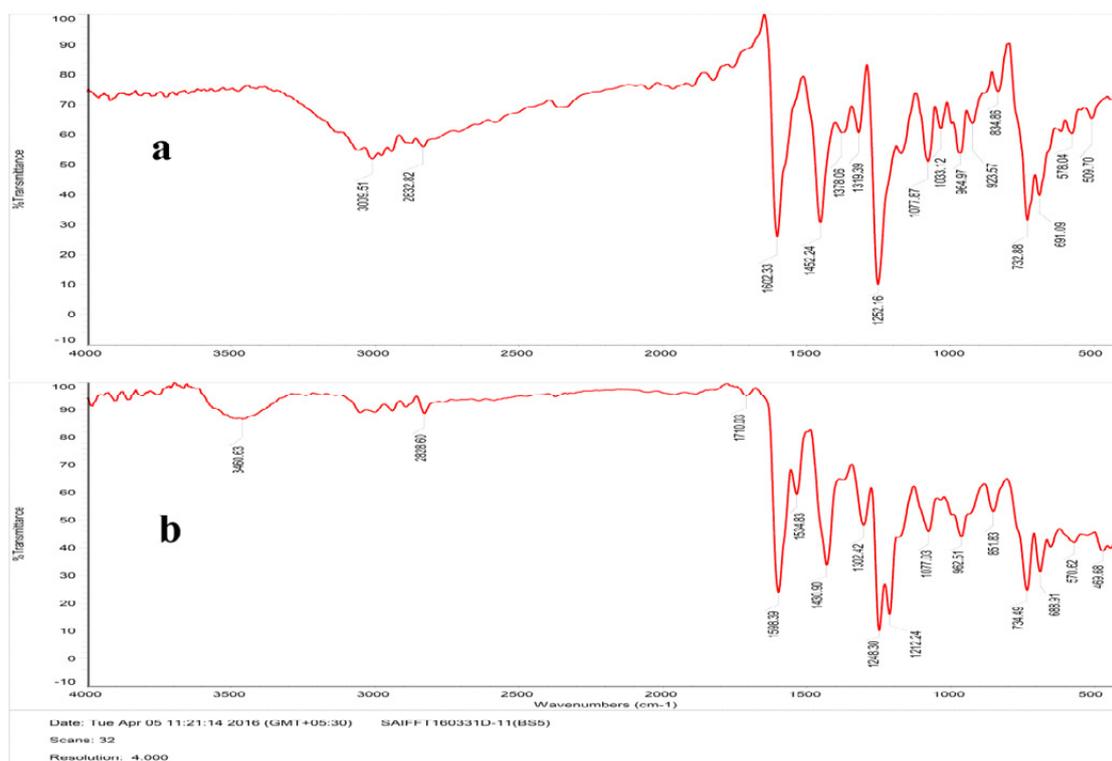


Fig. 2: FT-IR Spectrum of ligand and Pd NCs.

2832 cm^{-1} are due to aromatic -CH group and stretching of -CH₃ group, respectively. Hydrogen of -OH group is involved in hydrogen bonding with adjacent methoxy group, hence, its corresponding band was not appeared in the uncoordinated ligand. In palladium nanocomposite IR spectrum, the -OH group mainly appeared at 3046 cm^{-1} . The strong C=N bands and -O-Me bands are shifted to 1598 cm^{-1} and 1248 cm^{-1} , respectively. It is interesting to note that in Pd NCs OH band and

C-O-C bands are weak and shifted to higher energy region. The presence of acetate anions in the Pd NCs is confirmed by the presence of strong IR band at 1212 cm^{-1} (-COO⁻). The IR data clearly indicate that the palladium ions are completely bound to the ligand in the nanocomposite [64].

LPd(OAc)₂ (nanocomposite with OAc as the co-anion) show polydispersity. The solid-state electronic spectrum of the TPA ligand, (Fig. 3), shows two strong bands in the region 176-220 nm which are assigned to the π - π^* transition, a characteristic band of the terephthalic acid group. A broad but less intense d-d band observed in the region 430 nm is the characteristic band due to the presence of Pd (II) ion, which is coordinated to the TPA ligand [66]. The low energy d-d transition suggests approximately square planar geometry for palladium (II) nanocomposite. The square planar structure of LPd(OAc)₂ capped by the terephthalic acid group could provide suitable anchoring sites on the nano surface.

The formation of palladium nanoparticles was confirmed by PXRD diffractogram, (Fig. 4). All peaks of palladium were observed in the diffractogram of 2 θ value range 10–80°, indicating

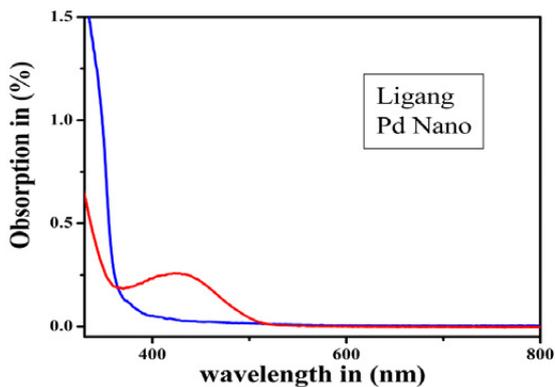


Fig. 3: Comparison of electronic spectra of ligand and Pd NCs

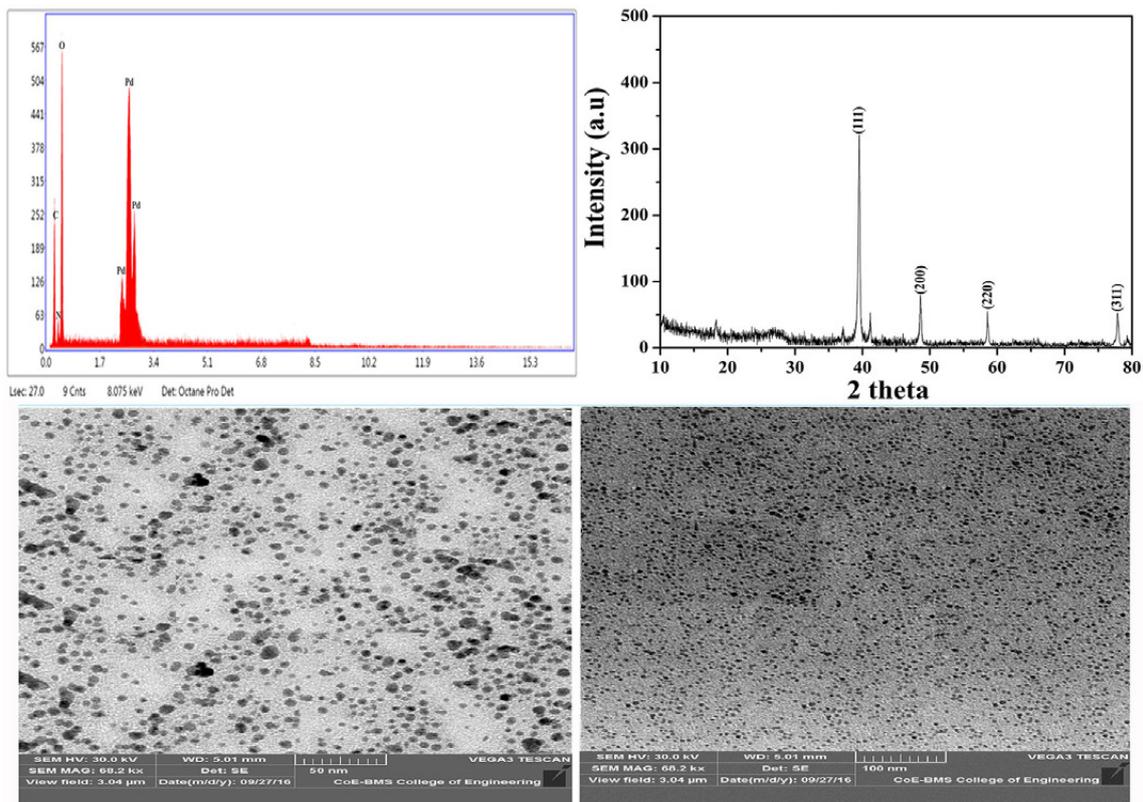


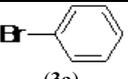
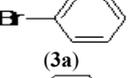
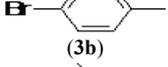
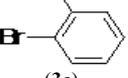
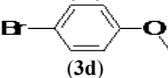
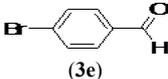
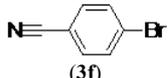
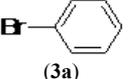
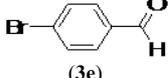
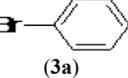
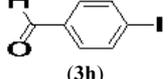
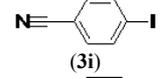
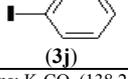
Fig. 4: EDX spectrum, PXRD spectrum and SEM images of Pd NCs.

the crystalline nature of palladium nanoparticles. The X-ray reflections were indexed to the fcc structure of palladium nanocomposite and the diffraction peaks observed 2θ values at 40° , 48° , 59° and 78° respectively representing the (111), (200), (220) and (311) Bragg's reflection and match with literature JCPDS standard card (#05-0681) and confirmed the formation of palladium nanoparticles with halo shape fcc crystal structure, which is also consistent with the earlier reports.

The nano-composite was further characterized by energy-dispersive spectrometry (EDX, Fig. 4), showing that palladium metal atom is covered with organic species and also revealed that the hollow spheres of Pd NCs composed of the minor amount of carbon, oxygen and nitrogen which came from the organic ligand and CTAB, respectively.

The Fig. 4(a, b) shows the typical SEM image of Pd NCs. It confirms that the palladium nanoparticles have irregular spherical shapes. In

Table 1: Pd NCs catalyzed Heck reaction of allyl acetate 4a with different aryl halides 3a-3j.

Entry	3a	4a	Catalyst	Temp($^\circ$ C)	Time (h)		Yield of 5a (%) ^b	
					Air	N ₂	Air	N ₂
1		(4a)	-	120	8	8	-	-
2		(4a)	Pd NCs	120	8	5	92 (5a)	94
3		(4a)	Pd NCs	120	8	6	91 (5b)	92
4		(4a)	Pd NCs	120	7	5	84 (5c)	88
5		(4a)	Pd NCs	120	7	7	72 (5d)	81
6		(4a)	Pd NCs	120	8	5	88 (5e)	89
7		(4a)	Pd NCs	120	8	5	91 (5f)	93
8		(4b)	Pd NCs	120	8	7	55 (5g)	61
9		(4c)	Pd NCs	120	8	6	78 (5h)	81
10		(4d)	Pd NCs	120	8	8	53 (5i)	54
11		(4a)	Pd NCs	120	6	5	91 (5j)	91
12		(4a)	Pd NCs	120	7	5	91 (5k)	93
13		(4a)	Pd NCs	120	6	5	92 (5l)	94

^aReaction conditions: K₂CO₃ (138.25mg 1.0 mmol), nano palladium (6.8 mg, 0.1 mmol), TBAB (161.18mg 0.5 mmol) and NMP (5 mL) was added 3a (61 mg, 0.5 mmol) and 4a (100 mg, 1.0 mmol, 2.0 eq.) at 120 $^\circ$ C under N₂ and air. ^bisolated yield.

the image the pale colored regions in the central parts, in contrast to the dark spot, implies a spherical structure. The unchanged contrast difference between the center and edge in the SEM image of one sphere is obtained when the sample grid is rotated by different degrees, further support for their spherical structure. The average diameter of the spherical structure is about 5 nm. The overall result of palladium nanocomposite showed that benzildihydrazine ligand serves as a good capping agent and provides good stability at nano-sized palladium metal atom.

Heck coupling reaction of aryl halide and allyl acetate

The catalytic activity of Pd nanocomposite has been investigated by Heck coupling reaction. The Heck cross-coupling reaction was found to be highly dependent on the nature of the solvent. As reported in the literature, polar aprotic solvents tend to give the best results for the Heck coupling reaction. The effect of the temperature and type of the reaction on the yield of the final product were also investigated. We employed several solvents in the Heck model reaction. Among evaluated polar and non-polar solvents, N-Methyl-2-pyrrolidone (NMP) was found to be the most productive solvent among the tested polar and nonpolar solvents. The most productive solvent (Table 2, entry 1) which is consistent with the previous report. The solvents such as MeOH, EtOH, AcOH and dioxane produced a moderate conversion, (Table 2). Toluene a non-polar solvent yielded a very poor conversion (Table 2, entry 7).

The effect of a base on the catalytic performance of this system was investigated by taking the model reaction in different bases. Among the several organic and inorganic bases, potassium carbonate

(K_2CO_3) was found to be the most effective base; it has the highest conversion rate, therefore, it was chosen as the preferred base for the reactions (Table 3, entry 1). The inorganic bases were less effective and afforded moderate yield for the coupled products (Table 3). The low conversion was achieved when a base, triethylamine (Et_3N) was used (Table 3, entry 3). This may be due in part to blocking of free coordination sites on the palladium center.[47,48]

Further, the studies carried out to find the influence of the different amounts of catalyst, which in turn, vary the product yield. The results indicate that 0.5 mmol/L catalyst offered below 50% yield and a very small quantity of the catalyst say 0.001mmol/L produces a moderately good yield. Therefore, it is concluded that intermediate quantity says about 0.01 mmol/L loading of the catalyst may lead to the high product yield. Reactions occur under N_2 atmosphere as well as air, but typically high yield was observed under N_2 atmosphere than air. The amount of variation in

Table 2: Optimization of the solvent

Entry	Solvent	Yield ^c
1	NMP ^b	92, 94 ^b
2	MeCN ^b	85, 89 ^b
3	Acetone	80
4	MeOH	Trace
5	Ethanol	>20
6	Dioxane	>20
7	Toluene	60
8	MeOH/H ₂ O (6:4) ^b	58, >30 ^b
9	EtOH/H ₂ O (6:4) ^b	68, >50 ^b
10	DMF	80
11	DMSO	80

^aReaction conditions: K_2CO_3 (138.25mg 1.0 mmol, 2.0 eq.) nano palladium (6.8 mg, 0.1mmol), TBAB (161.18mg 0.5 mmol) and solvent (5 mL) was added bromobenzene 4a (61 mg, 0.5 mmol) and allyl acetate 3a (100 mg, 1.0 mmol, 2.0 eq) at 120 °C under N_2 . ^bUnder N_2 and air. ^cisolated yield.

Table 3: Optimization of the base with selective solvent

Entry	Solvent	Base	Yield ^c
1	NMP	K_2CO_3 ^b	92, 94 ^b
2	NMP	CH_3COONa ^b	80, 63 ^b
3	NMP	NEt_3 ^b	>20
4	NMP	$NaHCO_3$ ^b	61, 60
5	NMP	KOH ^b	67, >30 ^b
6	NMP	$NaOH$ ^b	60, >30 ^b
7	MeCN	K_2CO_3	>30
8	Acetone	K_2CO_3	65
9	MeCN	CH_3COONa	72
10	Acetone	CH_3COONa	63

^aReaction conditions: Base (138.25mg 1.0 mmol, 2.0 eq.) nano palladium (6.8 mg, 0.1mmol), TBAB (161.18mg 0.5 mmol) and Solvent (5 mL) was added bromobenzene 4a (61 mg, 0.5 mmol) and allyl acetate 3a (100 mg, 1.0 mmol, 2.0 eq.) at 120 °C under N_2 . ^bUnder N_2 and air. ^cisolated yield.

yield is 10 to 20 % for most of the reactions. Now with optimized reaction conditions, the scope of allyl acetate has been investigated with different aryl halides employing 2% mol of Pd NCs in NMP at 120 °C under N₂ atmosphere and the results are collected in Table 1.

The scope of the reaction was subsequently explored using various allyl acetate (4a-4d) with appropriate aryl halides (3a-3j), the excellent isolated yield of arylation product (5a-5l) was obtained with 2% mol of palladium nanocomposite in about 5 to 8hr. Substituted aryl halides with electron-withdrawing substituents worked equally well as those with electron-donating substituents, giving arylation product like 5a, 5b, 5f (Table 1). In particular, *p*-methyl bromobenzene 4b, 4-bromobenzonitrile 4f with allyl acetate resulted in higher yield of the product 5b and 5f, respectively (Table 1). The reaction of *o*-methyl bromobenzene 4c with terminal alkene gives quite less yield under optimized condition; the reason for this is the steric factor which restricts the reaction. The aryl iodides found to be more reactive than the corresponding aryl bromides and the reaction appeared to be suggesting with aryl chloride in the present Pd-catalyzed reaction. The reductive coupling reaction with aryl iodides was completed in 6h and produced higher yield with just 2 mol % of the Pd nanocomposite catalyst. Thus, *m*-corbanyliodobenzene 3g reacted with allyl acetate 4a forming 5j with 91% yield. Similarly, 3-iodobenzonitrile 3h reacted with allyl acetate 4a to afford the substituted aryl product 5k in excellent yield. Without substituted aryl iodide, which has no other substitutions, gave highest 94% yield under the similar condition. An extremely efficient reactions were observed in the case of 4b, 4e and 4f producing their corresponding products 5b, 5e and 5f being obtained in high yield after 6h, 5h and 5h respectively (92%, 89%, 93% yield entries). The overall reactions indicate that palladium nanocomposite is an efficient catalyst for Heck coupling reaction and also it exhibits a wide range of functional group tolerance for the catalytic activity.

CONCLUSION

In summary, we report the synthesis of palladium nanoparticle which is stabilized by a ligand. This product showed highly effective catalytic character in Heck reactions. It is demonstrated that the ligand serves as a capping

agent for stabilization and also ligand was completely wrapping a palladium metal in nano size as well as serving as a stabilizer for keeping the Pd nanocomposite from particle coalescence *via* a weak coordination bond between ligand and metal nanoparticles. This catalyst was successfully employed as a catalyst for Heck cross-coupling reactions. The catalyst is more efficient with respect to the loading of catalyst, the yield of the Heck reaction product and a wider range of functional group tolerance. The main advantages of the present catalyst are the easy synthesis, phosphine free conditions as well as convenient handling due to insensitivity to air and moisture which allows the reactions to be conducted in the non-dry solvent under air.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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