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LETTER

One-pot electrochemical synthesis of palladium nanoparticles and their application in the Suzuki reaction†

Krishna M. Deshmukh,[a] Ziyauddin S. Qureshi,[a] Kushal D. Bhatte,[a] K. A. Venkatesan,[b] T. G. Srinivasan,[b] P. R. Vasudeva Rao[b] and Bhalchandra M. Bhanage*[a]

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A novel potential controllable, template free, electrodeposition/synthesis of palladium nanoparticles on an electrode surface as well as in the bulk electrolyte using ionic liquid as an electrolyte cum stabilizer is reported for the first time. The present method of preparation of palladium nanoparticles is advantageous as it eliminates the requirement of additional stabilizers or capping agents. The prepared palladium nanoparticles are characterized by different techniques such as TEM, SEM, EDAX and XPS analyses. These nanoparticles exhibited high catalytic activity for the Suzuki coupling reaction of unactivated halides in aqueous media with high TON.

Palladium nanoparticles (PdNPs) synthesis has gained considerable interest in the last few decades due to their potential applications in catalysis, photonics, electronics, and biomedical sensing.[1] Because of their large number of applications in different fields, the controlled synthesis of PdNPs with well-defined shape and size has its special importance. Most of the previous approaches required the use of organic or capping agents, such as 15-membered triolefinic macrocycles,[2] dendrimers,[3] and surfactants,[4] which helps to prevent the agglomeration of metal nanoparticles. Even though it has potential for various applications as described above, the conventional chemical reduction process has a major limitation of contamination due to partial incorporation of reducing agents or capping agents (*e.g.* hydrogen or boron). The protecting agents used in most of these processes have strong coordination affinity to surface atoms of metal nanoparticles limiting their catalytic applications *e.g.*, thiols that often inhibit catalytic activity.[5] The alternative method for palladium nanoparticles synthesis involving chemical vapour deposition has a drawback of requirement of specialized equipments and scale up issues.

Recently, Ionic Liquids (ILs) have been used as green electrolytes for electrochemical synthesis and the stabilization of various metal nanoparticles in ILs is possible without any additives.[6] Stabilization of nanoparticles in ILs may be due to the weak anionic or cationic interactions with nanoparticle surfaces.[7]

Dupont *et al.* reported the stabilization of metal nanoparticles in ionic liquids through a solvation force formed due to the ionic liquid structure at the solid–liquid interface.[8] Later Atkin *et al.* studied that the IL structure in the vicinity of solid nanoparticles produces solvation forces that are sufficient to prevent aggregation and this was confirmed using AFM analysis.[9]

Electrochemical methods have several advantages in terms of quickness, ease of operation, cost effectiveness and energy efficiency. In spite of such attractive features little attention has been paid towards the use of electrochemical methods for PdNPs synthesis.[10] Reetz and Helbig were the first to describe an electrochemical procedure for the formation of palladium and nickel nanoparticle colloids and in their method a metal sheet is anodically dissolved. The intermediate metal salt formed is reduced at the cathode, to provide metallic particles which are stabilized by tetraalkyl ammonium salts along with co-electrolyte acetonitrile/tetrahydrofuran.[11] More recently, Cha *et al.* reported the synthesis of PdNPs by means of anodic dissolution of palladium metal foil using *N*-butyl-*N*-methylmorpholinium as an electrolyte and acetonitrile which acts as a supporting electrolyte cum stabilizer.[12] Endres *et al.* reported nanocrystalline electrodeposition of Al, Fe, and an Al–Mn alloy as well as nanocrystalline Pd from a Lewis basic ionic liquid with or without nicotinic acid as an organic additive.[13] These reported methods utilize organic solvents, with requirement of surfactants or stabilizers, and hence development of a clean and neat process for PdNPs synthesis is desirable.

Herein, we report a novel, one stroke potential controllable, electrochemical method for the synthesis of PdNPs in the electrolyte as well as on the working electrode. Here ionic liquid plays a role of an electrolyte cum stabilizer. The catalytic activity of PdNPs was studied for the Suzuki–Miyaura coupling reaction of unactivated aryl halides using water as a benign reaction media.

Recent studies revealed that if there is any common anion present between metal salt and ionic liquid, there is drastic increase in the solubility of the metal salt in ionic liquid.[14] Considering these observations we have conducted the electrodeposition of palladium metal from a 1-butyl-3-methylimidazolium acetate IL ([BMim][OAc]), which has a common anion with a

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[a] *Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai-19, India. E-mail: bm.bhanage@ictmumbai.edu.in; Fax: +91-22-24145614; Tel: +91-22-33611111*
[b] *Fuel Chemistry Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603102, India*

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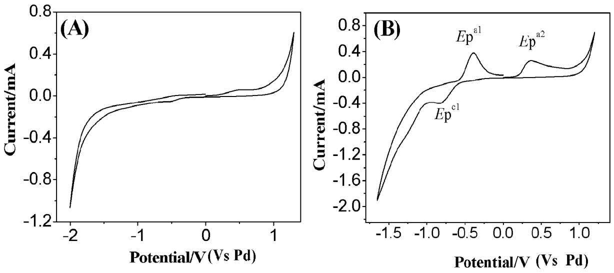


Fig. 1 The cyclic voltammograms of [BMim][OAc] (A) and a 50 mM solution of palladium acetate in [BMim][OAc] (B).

metal precursor $Pd(OAc)_2$ responsible for the dissolution of metal. The presence of a common acetate anion leads to increase in solubility of the metal salt in IL. We observed that at a certain potential, deposition of metallic PdNPs took place at the working electrode as well as the formation PdNPs was observed in the bulk electrolyte. We further investigated the effect of various process parameters on the morphology of formed nanoparticles.

A prominent reduction wave (Ep^{c1}) observed at −0.91 V (*vs.* Pd) is due to the reduction of Pd(II) to Pd(0)[15] and a couple of oxidation waves (Ep^{a1} and Ep^{a2}) at −0.38 V and 0.33 V may be due to the oxidation of Pd (Fig. 1).[16]

Controlled potential electrolysis of a solution of palladium(II) acetate (50 mM) in [BMim][OAc] was carried out at three different potentials (−0.8 V, −1.6 V, −2.4 V *vs.* Pd) using an aluminium plate (1 cm × 1 cm) as a cathode. When we applied a low potential (−0.8 V), it was observed that the palladium particles tend to get deposited on the electrode surface itself. The deposition of palladium on the electrode surface was confirmed by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS). A micrograph of the electrodeposit showed a pure metallic Pd(0) deposit (Fig. 2A and B). This was further confirmed by the X-ray Photoelectron Spectroscopy (XPS) analysis, which gives a doublet with binding energies of 335.5 eV (Pd $3d_{5/2}$) and 340.7 eV (Pd $3d_{3/2}$) (Fig. S1, ESI†). This shows presence of Pd(0).[17]

However, it was interesting to observe that the formation of palladium nanoparticles in the bulk electrolyte took place when the applied high potential was lowered to −2.4 V, which was significantly lower as compared to that at the onset of palladium deposition.

Formation of PdNPs in the bulk electrolyte is well supported by the X-ray diffraction (XRD) analysis, which revealed the characteristic diffraction patterns corresponding to the (111), (200) and (220) reflections, respectively, for the face centered cubic (fcc) phase of metallic palladium (JCPDS card no. 5-681). The average crystallite size was 5.93 ± 1 nm, calculated by the Scherer equation, which is in good agreement with results obtained from Transmission Electron Microscopy (TEM) analysis (Fig. S2, ESI†). At the same time palladium deposition was not observed at the working electrode, which was also confirmed by SEM-EDS analysis (Fig. 2C and D). When we applied an intermediate potential (−1.6 V) (Fig. 3A), we found the deposition of metallic palladium on the electrode as well as the formation of PdNPs in the bulk electrolyte. The XPS spectrum of the palladium formed in the bulk shows two peaks, one at a lower binding energy of 334.5 eV (Pd $3d_{5/2}$) and another at 339.8 eV (Pd $3d_{3/2}$), which confirms the formation of nanoparticles (Fig. 3B).

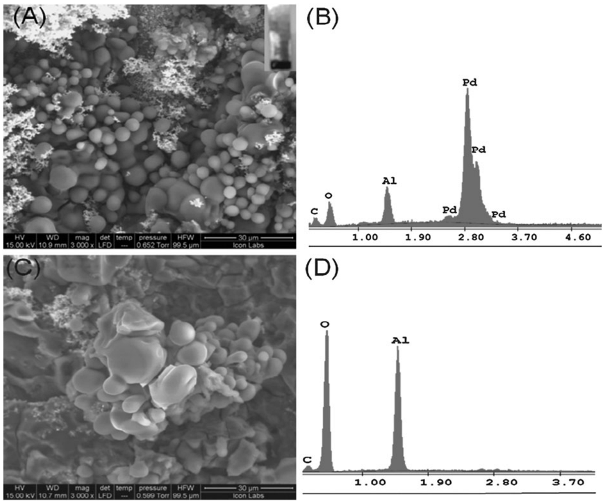


Fig. 2 SEM and EDS images of the Pd deposit at a potential of −0.8 V, electrolysis time 2500 s (A, B). Inset: Pd-deposit. The deposit at a potential of −2.4 V, electrolysis time 2500 s (C, D).

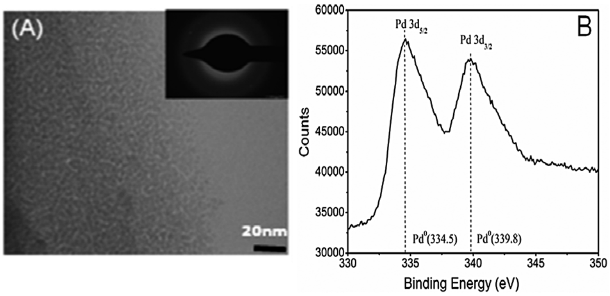


Fig. 3 (A) The TEM image of PdNPs deposited from bulk electrolyte at an applied potential of −1.6 V along with the diffraction pattern of palladium (inset figure) and (B) XPS spectra of the nanoparticle from bulk synthesized at an applied potential of −1.6 V, electrolysis time 1000 s.

Studies at different potentials exhibited that palladium tends to deposit at the working electrode at low potential (−0.8 V) while at higher potential (−2.4 V) it tends to get stabilized in the electrolyte. Whereas at an intermediate potential (−1.6 V) one can achieve both the goals simultaneously (Fig. S3, ESI†). It is obvious that when electrolysis is carried out at high negative potential, like −2.4 V, the bulk electrolyte undergoes decomposition. Since palladium is only 50 mM as compared to the electrolyte (∼5 M), the electrode is covered only with ionic liquid and no space seems to be available for electrodeposition of palladium on the electrode. As a result, the palladium deposit falls down rather than adhering to the working electrode. This is not possible at −0.8 V since palladium only is reduced and the IL is intact; but it also happens at −1.6 V because the onset of decomposition of the electrolyte occurs below −1.5 V (Fig. 1).

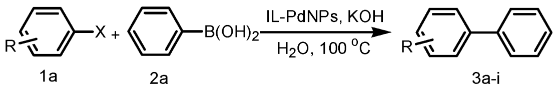
To understand the formation of PdNPs in the electrolyte bath, we have studied the electrolytic system comprised of palladium(II) chloride in 1-butyl-3-methylimidazolium chloride

[BMim][Cl]. In this system formation of PdNPs was not observed as reported in the literature.[15c,18] This indicates that the stabilization and formation of particles is highly dependent on the choice of the anion, here the acetate anion is acting as a stabilizer or capping agent. Earlier, Endres *et al.* reported that the electrodeposition of Al and of Ta is strongly influenced by ionic liquids. In [$Py_{1,4}$]TFSA, Al is obtained as a nanomaterial whereas in [EMIm]TFSA, a microcrystalline material is obtained. Ta was deposited from [$Py_{1,4}$]TFSA, whereas from [EMIm]TFSA only non-stoichiometric TaF_x was obtained. These consequences were explained on the basis of interfacial solvation layers.[19] The other factors which govern the size and shape of the palladium nanoparticle such as effect of concentration and electrolysis time were also studied (Fig. S4 and S5, ESI†).

Catalytic activity of isolated PdNPs was tested for the Suzuki–Miyaura coupling reaction with a very low loading of PdNPs in water as reaction media. Initially, the reaction of iodobenzene with phenylboronic acid was studied as a model reaction and the role of various bases like KOH (97%), K_2CO_3 (87%), and triethylamine (48%), and solvents like toluene (60%), 1,4-dioxane (72%), and water (97%) was investigated. It was observed that the reaction was more favourable using KOH as a base and environmentally benign water as a solvent with a high TON number of up to 9.7×10^2.

The efficiency of the present system was further extended for the coupling of various aryl halides with different steric and electronic properties with phenylboronic acid (Table 1). Phenylboronic acid was found to couple smoothly with iodobenzene providing an excellent yield (97%) of the desired product. Encouraged by these results we focused our attention on less reactive aryl bromides and chlorides. Electron donating groups such as methoxy and withdrawing groups such as nitro were well tolerated under the present catalytic system (entries 2–5). Sterically hindered bromonaphthalene and benzyl bromide react efficiently providing 81% and 60% yield of the desired product respectively (entries 6 and 7). Heterocyclic aryl halides like 2-bromopyridine were also found to react smoothly under the present conditions (entry 8). Aryl chlorides fail to carry out the reaction under present conditions; this is due to high C–Cl bond strength and their unwillingness to undergo oxidative addition.

Table 1 Suzuki reaction of aryl/heteroaryl halide catalyzed by IL-PdNPs in aqueous media[a]



Entry	Aryl/heteroaryl halide (**1a**)	Product (**3a–i**)	Time/h	Yield[b] (%)
1	Iodobenzene	**3a**	1	97, 78[c]
2	4-Iodoanisole	**3b**	2	91
3	1-Iodo-4-nitrobenzene	**3c**	1	98
4	4-Bromoanisole	**3d**	7	87
5	3-Bromoacetophenone	**3e**	5	90
6	1-Bromomethylbenzene	**3f**	15	60
7	1-Bromonaphthalene	**3g**	12	81
8	2-Bromopyridine	**3h**	15	52
9	Chlorobenzene	**3i**	18	64[d]

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), KOH (2 mmol), IL-PdNPs (0.001 mmol), water (2 mL), temp., 100 °C. [b] Isolated yields. [c] Pd/C. [d] Tetrabutyl ammonium bromide (TBAB) (1 mmol).

In an attempt to improve reaction conversion of aryl chlorides, a phase transfer agent like tetrabutylammonium bromide (TBAB) was added, which enhanced the yield significantly (entry 9) with prolonged reaction time. Presumably, here TBAB plays a role of PTC and stabilizer for the nanocatalyst.[20]

Moreover, the catalyst efficiency of PdNPs was compared with the present heterogeneous catalyst Pd/C under the present reaction conditions. It was found that Pd/C gives 78% yield of the desired product as compared to the PdNPs that give 97% yield. The enhancement of the yields may be due to the excellent dispersion of PdNPs in water.[21] To study a greener and economical aspect of the present protocol, catalytic activity was investigated for five consecutive recycles for a model substrate iodobenzene and phenylboronic acid under optimized reaction conditions. The PdNPs were effectively recycled up to five cycles. The TEM image of the recycled PdNPs shows that the catalyst was stable enough (Fig. S6, ESI†) and could be used for the further consecutive recycles.

In summary, for the first time we have successfully demonstrated a potential, controllable, one stroke electrochemical method for synthesis of PdNPs using ionic liquid as an electrolyte cum stabilizer. Furthermore, PdNPs were successfully applied as catalysts in the Suzuki coupling reaction of several unactivated aryl/heteroaryl halides in environmentally benign water as a solvent with effective recyclability.

Experimental section

Materials and methods

All commercial reagents and solvents were used directly as purchased without further purification. Palladium acetate was purchased from Parekh Platinum Ltd (PPL) Mumbai, India, in its highest purity available and was used as it is. Optimized yields were based on GC (Perkin-Elmer, Clarus 400) analysis by the external standard method. All the products are known, and representative products were characterized by ^{1}H NMR (Varian, 300 MHz) and ^{13}C NMR (Varian, 75 MHz) spectroscopy. The ionic liquid 1-butyl-3-methylimidazolium acetate [Bmim][OAc] was prepared using the reported method available in the literature.[22] Purity of the ionic liquids prepared was checked using ^{1}H NMR, ^{13}C NMR and IR analyses.

Scanning electron microscopy (SEM) analysis (FEI, Quanta 200) was carried out to study the surface morphology. The morphology of prepared nanoparticles (Phillips Model CM 200, operating voltage 200 kV) was studied using a transmission electron microscope (TEM). X-Ray diffraction (XRD) measurements were carried out on a Rigaku X-ray diffractometer with a Cu Kα (Kα = 1.5405 Å) radiation source operating at 40 kV. X-Ray photoelectron spectroscopic (XPS) measurements were carried out on a VG Micro Tech ESCA 3000 instrument at a pressure of $> 1 \times 10^{-9}$ Torr (pass energy of 50 eV, electron take off angle 60° and the overall resolution was ~0.1 eV).

Procedure for electrodeposition/synthesis of palladium nanoparticles

In a typical process, in a flat bottom beaker 50 mM solution of palladium acetate in 1-butyl-3-methyl imidazolium acetate

[Bmim][OAc] was prepared by dissolving the required quantity of palladium acetate in [Bmim][OAc], which was then placed in an electrolytic cell maintained at a temperature of 80 °C under a nitrogen atmosphere. The electrolysis study was conducted on an aluminium (1 cm × 1 cm) plate, with a platinum rod acting as a counter electrode and a palladium wire acting as a quasi-reference electrode. After electrolysis electrodeposits on the aluminium plate were washed extensively with acetone and de-ionized water before subjecting them to surface morphology analysis. The mother electrolyte which contains nanoparticles was first extensively washed with de-ionized water and subjected to centrifugation to separate out metal particles. It was observed that at higher negative potential (−2.4 V) decomposition of ionic liquids leads to the color change to dark brown.

Experimental procedure for the Suzuki coupling reaction

A 10 mL tube was filled with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), KOH (2.0 mol), IL-PdNPs (0.001 mmol) in water (3 mL) and was properly sealed. The reaction mixture was heated at 100 °C for a desired time and was cooled to room temperature on completion of the reaction. Aryl halide conversion as well as product formation was monitored by gas chromatography. The product was extracted in ethyl acetate (3 × 5 mL) and evaporated on a rota vac. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh; PE–EtOAc, 95 : 05) to afford the desired product. The structures of the obtained products were confirmed by ^{1}H NMR and ^{13}C NMR analyses.

Characterization data

1-Butyl-3-methylimidazolium acetate [Bmim][OAc]. δ_H (300 MHz, $CDCl_3$): 10.05 (1H, s), 7.45 (1H, s), 7.36 (1H, t, J = 4.5 Hz), 4.29 (2H, t, J = 7.8 Hz), 4.05 (3H, s), 2.00 (3H, s), 1.86 (2H, m), 1.37 (2H, m), 0.95 (3H, t, J = 7.5 Hz) ppm; δ_C (75 MHz, $CDCl_3$) δ: 175.29, 136.89, 123.48, 121.75, 49.29, 36.10, 31.75, 22.06, 19.07, 13.10 ppm; IR (neat): 3142, 2961, 2874, 1711, 1571, 1465, 1383 1248, 1172, 1008, 878 cm^{-1}.

Biphenyl (Table 1, entry 1). δ_H (300 MHz, $CDCl_3$): 7.58 (4H, t, J = 7.8 Hz), 7.43 (4H, t, J = 7.2 Hz), 7.35 (2H, d, J = 7.2 Hz) ppm; δ_C ($CDCl_3$ 75 MHz): 141.28, 128.82, 127.30, 127.22 ppm.

4-Methoxylbiphenyl (Table 1, entry 2). δ_H (300 MHz, $CDCl_3$): 7.51–7.56 (4H, m), 7.41 (2H, t, J = 7.2 Hz), 7.3 (1H, t, J = 7.2 Hz), 6.98 (2H, d, J = 8.7 Hz), 3.85 (3H, s) ppm; δ_C ($CDCl_3$ 75 MHz): 159.21, 140.89, 133.83, 128.79, 128.21, 126.79, 126.72, 114.30, 55.39 ppm.

4-Nitrobiphenyl (Table 1, entry 3). δ_H (300 MHz, $CDCl_3$): 8.30 (2H, d, J = 9.0 Hz), 7.73 (2H, d, J = 8.4 Hz), 7.64 (2H, d, J = 8.4 Hz), 7.42–7.53 (3H, m) ppm; δ_C ($CDCl_3$ 75 MHz): 147.56, 147.04, 138.69, 129.12, 128.89, 127.74, 127.34, 124.04 ppm.

3-Acetylbiphenyl (Table 1, entry 5). δ_H (300 MHz, $CDCl_3$): 8.04 (1H, t, J = 1.2 Hz), 7.91 (1H, dt, J = 7.8 Hz, 1.8 Hz), 7.77 (1H, dt, J = 7.5 Hz, 1.2 Hz), 7.23–7.62 (6H, m), 2.64 (3H, s) ppm; δ_C ($CDCl_3$, 75 MHz): 198.10, 141.73, 140.19, 137.65, 131.65, 129.07,128.95, 127.21, 26.79 ppm.

1,1′-Methanediyldibenzene (Table 1, entry 6). δ_H (300 MHz, $CDCl_3$): 7.16–7.30 (10H, m), 3.97 (2H, s) ppm; δ_C ($CDCl_3$, 75 MHz): 141.16, 128.99, 128.51, 126.12, 41.99 ppm.

1-Phenylnaphthalene (Table 1, entry 7). δ_H (300 MHz, $CDCl_3$): 7.80–7.90 (3H, m), 7.36–7.51 (9H, m) ppm; δ_C ($CDCl_3$, 75 MHz): 140.82, 140.32, 133.86, 131.68, 130.14, 128.81, 128.31, 127.70, 127.29, 126.99, 126.76, 126.08, 125.83, 125.44 ppm.

2-Phenylpyridine (Table 1, entry 8). δ_H (300 MHz, $CDCl_3$): 8.66 (1H, d, J = 4.8 Hz), 7.95–7.99 (2H, m), 7.67 (2H, dd, J = 0.9 Hz, 3.3 Hz), 7.37–7.48 (3H, m), 7.16 (1H, qr) ppm; δ_C ($CDCl_3$, 75 MHz): 157.06, 149.41, 139.07, 136.56, 128.76, 128.53, 126.70, 121.95, 120.29 ppm.

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