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## Starch assisted Palladium(0) nanoparticles as *in situ* generated catalysts for room temperature Suzuki-Miyaura reaction in water

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Anindita Dewan\*, Pankaj Bharali, Utpal Bora and Ashim Jyoti Thakur

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**A simple and efficient methodology for the *in situ* generation of Pd-nanoparticles in presences of starch and NaOH at room temperature has been developed. It has been observed that starch played a dual role in controlling the reduction rate of metal ions and the aggregation process of metal atoms in solution. The *in-situ* generated Pd-nanoparticles show excellent catalytic activity in Suzuki-Miyaura cross coupling reaction of electronically diversified arylbromides and arylboronic acids in pure water at room temperature with low catalyst loading.**

### Introduction

Palladium-catalyzed Suzuki Miyaura cross-coupling is one of the vital methodologies for the synthesis of biaryls using aryl halides with arylboronic acids, and extensively used for the synthesis of important structural moieties such as polymers, agrochemicals, natural products and pharmaceutical intermediates.<sup>1</sup> The catalytic systems for these transformations composed of either Pd(0) or Pd(II) derivatives associated with suitable phosphine or nitrogen based ligands.<sup>2</sup> Although the palladium complexes of these ligands often show excellent catalytic activity, the main drawbacks are the availability, stability, and cost of the palladium complexes and related ligands. Additionally, due to the air and moisture sensitivity of these ligands, many of the reactions are performed in an inert atmosphere using hazardous organic solvents. However, from the green chemistry point of view, the uses of environmentally friendly solvent such as water<sup>3</sup>, ionic-liquids<sup>4</sup> or supercritical carbon dioxide<sup>5</sup> are favorable alternative to organic solvents in organic synthesis. In this respect, the development of catalyst in pure water seems particularly suitable for the Suzuki-Miyaura cross coupling reaction because of water soluble nature of arylboronic acids.<sup>6</sup> Recent developments into expansion of the Suzuki-Miyaura reaction have been focused on the use of palladium nanoparticles (PdNPs) as catalyst due to the unique properties arises at nanoscale.<sup>7</sup> Although

PdNPs often show excellent catalytic activity, however in majority of cases, synthesis of PdNPs requires high temperature, sonication and additional stabilizer, thereby making the process tedious and time consuming.<sup>8</sup> However, there are some reports of preparation of PdNPs under mild reaction condition. Consequently, there is growing interest to develop alternative green and eco-friendly routes for the synthesis of nanomaterials in single synthetic step with minimum chemical waste in environmentally friendly solvents. Recently, synthesis of PdNPs with controllable size and morphology have been reported via the reduction of palladium(II) salt using simple sugars and other biomass. Consequently, glucose<sup>9</sup> and silica-starch<sup>10</sup> derived PdNPs have been successfully applied in Suzuki reaction using isopropanol and DMF as solvent at high temperature using aryl iodides as coupling partner. Starch is one of the naturally occurring green biopolymers which is nontoxic, eatable and biodegradable. Now-a-days, the development of the green chemistry through organic reactions using environmentally benign solvents, biodegradable and non-toxic chemicals have become one of the most exciting researches. Keeping this in mind, we wish to explore starch assisted *in-situ* synthesis of PdNPs for C-C bond formation reaction with excellent yield in pure water at room temperature in a one pot tandem process. Emphasis has been given on *in-situ* generation of PdNPs, detail characterization and application in Suzuki-Miyaura coupling reaction of aryl bromides and phenylboronic acid in pure water at room temperature without using conventional ligand.

Our first aim was to generate PdNPs under aerobic conditions in water at room temperature and for that purpose Pd(OAc)<sub>2</sub> (0.001 g, 0.005 mmol) and NaCl (0.01 g, 0.17 mmol) were stirred in water (2 mL) for 15 min which resulted a clear orange coloured solution. To this orange coloured solution, starch (0.01 g) and NaOH (0.08 g, 2 mmol) were added and instantly the solution became decolourised indicating the formation PdNPs. The generation of PdNPs has been monitored by the UV/Vis absorption spectroscopy (Figure-1). In the UV/Vis spectroscopic experiment no absorption peak was observed for Pd(OAc)<sub>2</sub> in water, which may be due to poor solubility of Pd(OAc)<sub>2</sub> in pure water. However, after addition of NaCl, two absorption peaks at 225 and 275 nm were observed that could be assigned to the ligand-to-metal charge transfer band (LMCT).<sup>11</sup> It has been reported that addition of NaCl resulted formation of water soluble ate complex Na<sub>2</sub>Pd(OAc)<sub>2</sub>Cl<sub>2</sub>.<sup>6a</sup> However, no further changes of absorption peak in UV/Vis spectra was observed after addition of starch to the above solution

<sup>a</sup> Department of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam, India, Pin 784028, E-mail: ani\_dewan@yahoo.co.in

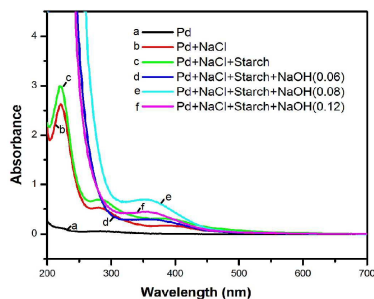
<sup>b</sup> Fax: +91(3712)267005/6; Tel: +91(03712)275067

<sup>c</sup> Address here.

† Footnotes relating to the title and/or authors should appear here.

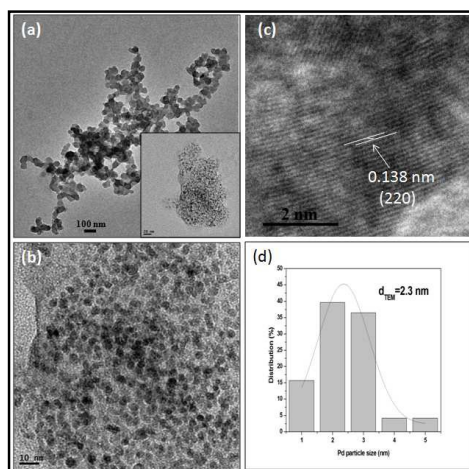
Electronic Supplementary Information (ESI) available: <sup>1</sup>H and <sup>13</sup>C NMR spectral data of products and Experimental Procedure. See DOI: 10.1039/x0xx00000x

containing  $\text{Pd}(\text{OAc})_2$  and NaCl. Interestingly, addition of NaOH to the above solution showed gradual decrease and finally disappearance of the absorption bands at 225 nm and 275 nm and appearance of a new absorption band at 350 nm. This absorption band could be ascribed to the LMCT band of mixed palladium (II) species, that is  $[\text{Pd}(\text{OAc})_2(\text{OH})_2]^{2-}$  and  $[\text{Pd}(\text{OAc})_3(\text{OH})]^{2-}$ . With the continuous addition of NaOH to the above solution, partial or complete ligand exchange of  $(\text{OAc})^-$  with  $(\text{OH})^-$  and form colloidal  $\text{Pd}(\text{OH})_2$  particles. The formation of Pd nanoparticles shown by TEM analysis results corresponds to such ligand exchange prior to the reduction with starch.<sup>11</sup>



**Figure 1:** UV/Vis absorption spectra of (a)  $\text{Pd}(\text{OAc})_2$  (0.001 g, 0.005 mmol), (b)  $\text{Pd}(\text{OAc})_2$  (0.001 g, 0.005 mmol) and NaCl (0.01 g, 0.17 mmol), (c) mixture of  $\text{Pd}(\text{OAc})_2$  (0.001 g, 0.005 mmol) and NaCl (0.01 g, 0.17 mmol), starch (0.01 g), and (d),(e), (f) are mixture of  $\text{Pd}(\text{OAc})_2$  (0.001 g, 0.005 mmol) and NaCl (0.01 g, 0.17 mmol), starch (0.01 g), with different amount of NaOH in 4 mL water.

The particle size and shape of the *in situ* generated PdNPs were further characterized by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) measurements (Figure 2). Figure 2(a) presents the global TEM image of *in-situ* generated PdNPs.



**Figure 2:** (a) TEM, (b) & (c) HRTEM images of PdNPs and (d) PdNPs distribution.

It could be observed from the TEM image that PdNPs preferentially crystallize in spherical shape. Closer view of the TEM image at higher resolution demarcate that very fine spherical nanoparticles of Pd are homogeneously distributed (inset of Figure 2(a)). A

representative HRTEM image as shown in Figure 2(b) reveals that nearly monodisperse spherical PdNPs with an average particle size of  $\sim 2\text{--}3$  nm were obtained. The PdNPs so observed could be rapidly obtained within  $\approx 5$  min by using starch as soluble polymer which reduces  $\text{Na}_2\text{Pd}(\text{OAc})_2\text{Cl}_2$  in presence of NaOH (2 mmol, 0.08g). Figure 2(c) confirms the presence of crystal plans with the lattice 'd' spacing of 0.138 nm which corresponds to the (220) plane of Pd NPs. The distribution of the *in-situ* generated Pd NPs (from Figure 2(b)) was analyzed using Gaussian fits and the resultant data were plotted in histograms in Figure 2(d). It could be ascertained from the figure that more than 80% of the PdNPs lie in the size range of 1–3 nm and the mean particle diameter was about 2.3 nm.

**Table 1:** Optimization of reaction conditions

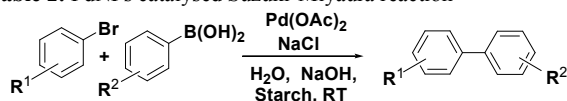
Entry	$\text{Pd}(\text{OAc})_2$ (mmol)	Starch (g)	Base (g)	Time (h)	Yield (%) <sup>c</sup>
1	0.005	0.22	NaOH (0.08)	6	70
2	0.005	0.01	NaOH (0.08)	3	98
3	0.005	0.02	NaOH (0.08)	3	98
4	0.005	-	NaOH (0.08)	6	20
5 <sup>b</sup>	0.005	0.01	NaOH (0.08)	6	40
6	0.005	0.01	NaOH (0.06)	6	50
7	0.005	0.01	NaOH (0.12)	6	40
8	0.0025	0.01	NaOH (0.08)	6	50
9	-	0.03	NaOH (0.08)	6	Nil
10 <sup>d</sup>	0.005	0.02	NaOH (0.08)	6	60
11	0.005	0.01	$\text{K}_2\text{CO}_3$	6	70
12	0.005	0.01	$\text{Na}_2\text{CO}_3$	6	65
13	0.005	0.01	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	6	50
14	0.005	0.01	$\text{NaHCO}_3$	6	70
15	0.005	0.01	$\text{CH}_3\text{COONa}$	6	80
16	0.005	0.01	-	6	-

<sup>a</sup>Reaction Conditions: 4-methoxybromobenzene (1 mmol), phenylboronic acid (1.2 mmol), NaCl (0.17 mmol), water (4 mL), R.T. (25 °C), in air. <sup>b</sup>in absence of NaCl, <sup>c</sup> Isolated yield; <sup>d</sup>glucose was used in place of starch.

It is worth to mention that the system exhibit excellent catalytic activity for coupling of unreactive aryl bromide with phenylboronic acid in pure water at room temperature. The efficiency of this *in-situ* generated Pd(0) NPs as catalyst was evaluated in the coupling reaction of 4-methoxybromobenzene (1 mmol) and phenylboronic acid (1.2 mmol) as the model substrates. The results are summarized in the table 1. It is also well known from literature that below certain minimum concentration of starch, agglomeration of PdNPs takes place which affects the rate of reaction. At starch concentrations of 0.01 g and 0.02 g, no agglomeration occurs so we get very good results of the reaction (Table 1, entries 2 and 3). In our reaction system, NaOH plays crucial role as pH maintainer as well as a base. To investigate this effect we have also screened different concentrations of NaOH and the reaction was found to be most effective with NaOH (0.08 g, 2

mmol.) concentration (Table 1, entry 2 vs 6 and 7). The best condition for the formation of biaryl was obtained when reaction was carried out at room temperature in pure water in presence of Pd(OAc)<sub>2</sub>, (0.001 g, 0.005 mmol), NaCl (0.01 g, 0.17 mmol), starch (0.01 g) and NaOH (0.08 g, 2 mmol) (Table 1, entry 2). Interestingly, further lowering of Pd(OAc)<sub>2</sub> loading to 0.0025 mmol afforded a significant decrease in yield to 50% and without Pd(OAc)<sub>2</sub>, starch and NaCl themselves could not catalyze the reaction (Table 1, entries 9, 4 and 5). Again, use of glucose instead of starch gave significantly lower yield of cross coupled product (Table 1, entry 10). Moreover, since the Suzuki-Miyaura reaction has been influenced by the nature of base, therefore we have studied the impact of different bases (2 mmol) on cross-coupling reaction and nano particles formation using 4-methoxybromobenzene and phenylboronic acid as the model substrates (Table 1, entries 11-16). The results evidently show that base is essential for the coupling reactions since no coupling product was obtained without base (Table 1, entry 16). Besides NaOH, the reaction can tolerate other inorganic bases such as K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O, NaHCO<sub>3</sub>, and CH<sub>3</sub>COONa although significant difference in yields were observed (Table 1, entry 11-15). The alkali metal hydroxides provides highest yield (Table 2, entry 2).

**Table 2:** PdNPs catalysed Suzuki-Miyaura reaction



Entry	R <sup>1</sup>	R <sup>2</sup>	Time(h)	Yield (%) <sup>c</sup>
1	H	H	4	98
2	H	OCH <sub>3</sub>	4	95
3	H	Cl	5	95
4	4-OCH <sub>3</sub>	H	3	98
5	4-OCH <sub>3</sub>	OCH <sub>3</sub>	3	95
6	4-OCH <sub>3</sub>	Cl	3	95
7	2-OCH <sub>3</sub>	H	4	98
8	4-CH <sub>3</sub>	H	3	95
9	4-CH <sub>3</sub>	OCH <sub>3</sub>	3	95
10	4-CH <sub>3</sub>	t-Butyl	5	90
11	4-CH <sub>3</sub>	Cl	5	95
12	4-NO <sub>2</sub>	t-Butyl	5	95 <sup>b</sup>
13	4-NO <sub>2</sub>	H	8	98 <sup>b</sup>
14	4-NO <sub>2</sub>	OCH <sub>3</sub>	8	85 <sup>b</sup>
15	4-NO <sub>2</sub>	Cl	8	80 <sup>b</sup>
16	4-CHO	H	8	90 <sup>b</sup>
17	4-CHO	OCH <sub>3</sub>	8	90 <sup>b</sup>
18	4-CHO	Cl	8	85 <sup>b</sup>
19	4-COCH <sub>3</sub>	H	8	90 <sup>b</sup>
20	4-COCH <sub>3</sub>	OCH <sub>3</sub>	8	90 <sup>b</sup>
21	4-COCH <sub>3</sub>	Cl	8	85 <sup>b</sup>

<sup>a</sup>Reaction Conditions: aryl bromide (1 mmol), arylboronic acid (1.2 mmol), Pd(OAc)<sub>2</sub> (0.005 mmol), NaCl (0.17 mmol), Starch (0.01 g), NaOH (2 mmol), water (4 mL), R.T (25 °C), in air. <sup>b</sup> EtOH (0.25 mL) was used as co-solvent for solubility. <sup>c</sup> Isolated yield.

To evaluate the scope and limitations of the current procedure, reactions of a wide array of electronically diverse aryl

bromides with arylboronic acids were examined using the above optimised reaction conditions (Table 1, entry 2). The results are summarized in Table 2. It can be seen from the Table 2 that the cross-couplings of aryl bromides with the arylboronic acids bearing either electron-withdrawing or electron-donating functional groups were carried out smoothly by the *in-situ* generated Pd(0) nano species. The coupling reactions of arylbromides containing electron-donating groups (Table 3, entries 4-11) proceeded more efficiently than those of arylbromides containing electron-withdrawing groups (Table 3, entries 12-21), while the arylbromides with an electron-withdrawing substituents such as nitro, aldehyde, acetophenone groups needed a longer reaction time for completion may be due to their solubility problem. To overcome this solubility issue we have added about 0.25 mL ethanol for these particular substrates (Table 3, entries 12-21). However, if we used more than this specific amount of ethanol, some sticky substances solid out and reaction yield became very poor. Interestingly, an electron-donating group in the *ortho* position of an arylbromide such as 2-MeO (Table 3, entry 7) also showed good reactivity. The effect of the different substituents of an arylboronic acid on the Suzuki coupling reaction was also studied (Table 2) and no such significant difference was observed in the yield and reaction time.

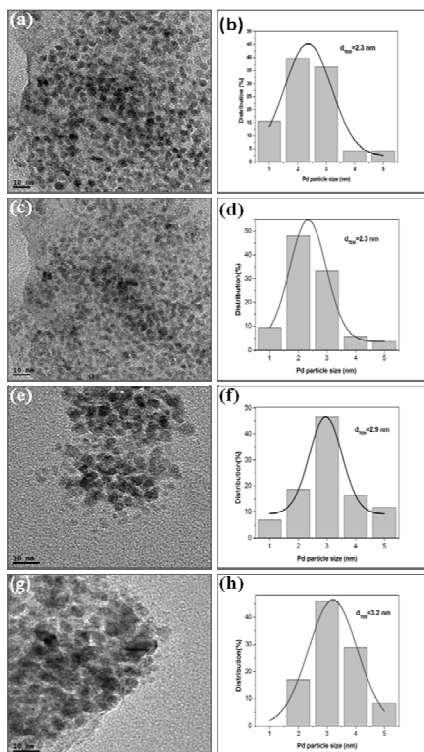
**Table 3:** Reusability test of starch derived *in-situ* generated PdNPs in Suzuki-Miyaura reaction

Recycle number	1	2	3	4
Yield (%)	98	92	87	55

Next, to examine the reusability of the *in-situ* Pd-nanocatalyst in Suzuki reaction, a series of four consecutive runs were carried out using 4-methoxybromobenzene (1 mmol) with and phenylboronic acid (1.2 mmol) as the model substrates in pure water at room temperature (Table 3). At the end of the each reaction, the aqueous layer with Pd nano-catalyst was reused for a new batch. As shown in Table 3, cycle 1 to cycle 3 gave excellent yields. After the third cycle, the yield decreases sharply, which is due to decrease in the activity of the catalyst. Here, we have examined the stability of the PdNPs employing HRTEM imaging before and after catalyzing the Suzuki reaction. Figure 3(a) shows HRTEM image of the *in-situ* generated PdNPs before the Suzuki reaction. The corresponding particle distribution is presented in Figure 3(b) (Figures 3(a) and 3(b) are identical to Figure 2(b) and 2(d), respectively; included in this figure for better comparison). Figure 3(c) and 3(d) present HRTEM images of the PdNPs after the first cycle and its corresponding particle size distribution. There were no changes of size distributions of the NPs before and after the first cycle (comparing Figures 3(b) and 3(d)). The HRTEM image of the NPs and their corresponding particle size distribution after the second and third cycle are shown in Figures 3(e), (f), and 3(g), (h), respectively. It could be ascertained from figure that the average sizes of the nanopalladium after the second and third cycle were 2.9 nm and 3.2 nm respectively. In principle, the catalytic activity of nano-catalyst was determined by the size of the NPs. The catalytic activity of smaller size NPs is more effective. We could see that both the widths and centres of the size distributions of the NPs increase after second and third cycle and that the size distribution shifts towards large size. Thus, the catalysts loose some catalytic activity and increased the



recycle time. After third cycles, the catalytic activity decreased sharply. Actually after every reaction cycle the starch molecules are moved away from the surface of PdNPs and aggregation of PdNPs takes place and consequently the size of the nanoparticles became larger. Additionally we have carried out ICP analysis of the crude and silica gel-purified products of the reaction of 1-bromo-4-nitrobenzene and phenylboronic acid. The results of the analysis have been found to be 1.84 and 1.64 ppb respectively, which confirms negligible contamination of Pd with the product.



**Figure 3:** TEM and HRTEM images of PdNPs (a) before the reaction, (c) after first cycle, (e) after second cycle, (g) after third cycle and (b), (d), (f) and (h) are their corresponding particle size distribution.

## Conclusions

In conclusion, we have developed a simple and effective methodology for the *in-situ* generation of PdNPs in the presence of starch and NaOH at room temperature. We identified the dual role played by starch in controlling the reduction rate of metal ions and the aggregation process of metal atoms in solution. The amount of starch and base used are very critical for the generation of NPs and their catalytic activity. The *in-situ* generated PdNPs show excellent catalytic activity in Suzuki-Miyaura cross-coupling reaction of electronically diversified aryl bromides and arylboronic acids in water at room temperature with low catalyst loading.

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