Facile synthesis of Fe@Pd nanowires and their catalytic activity in ligand-free C—N bond formation in water

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ABSTRACT

This work reports a facile synthesis of Fe@Pd nanowires. Ligand-free cross coupling reactions of arylboronic acids with various amines in aqueous medium proceed in very good to excellent yield with the use of Fe@Pd nanowires. Furthermore, the catalyst could be easily separated from the reaction mixture using a magnet and could be recycled several times without loss of catalytic activity.

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Amines are important intermediates in the chemical industry and for the manufacture of agrochemicals, pharmaceuticals, dyes, pigments, and rubber.[1] Transition metal catalyzed C—N bond formation by amination of aryl halides has been extensively explored.[2] This method involves the production of arylamines by coupling of aryl halides with various amines in the presence of stoichiometric amounts of transition metal ions. Earlier reported methods for the transition metal catalyzed amination of aryl halides suffered from drawbacks such as the use of expensive ligands and palladium and copper homogeneous catalysts, the environmental pollution caused by the utilization of organic solvents, low yields, high temperatures, long reaction times, harsh reaction conditions, poor availability or the need to prepare the ligands or catalysts, tedious work-ups, waste control, and the formation of side products.

Organic reactions in water have received considerable attention. Water is cheap, safe, non-combustible, non-explosive, and environmentally acceptable.[3] Only, a few C—N cross-coupling methods have been reported in the literature for the amination of aryl halides in water using various catalysts such as cyclopalladated ferrocenylimine complex, [(π-allyl)PdCl]₂, PS-PEG resin-supported palladium complexes.[4] Therefore, it is desirable to develop an efficient method for the synthesis of amines without the application of toxic organic solvents, expensive ligands, and homogeneous or expensive catalysts.

Metal nanoparticles have been used widely due to their unique electronic, optical, mechanical, magnetic, and chemical properties, which differ greatly from those of the bulk substances.[5] Palladium nanoparticles can be applied both in homogeneous and heterogeneous phases. Moreover, by using inexpensive and non corrosive heterogeneous catalysts, chemical transformations occur, especially for industrial processes, with higher efficiency and give better purities of the products, and offer easier work-up, which create economical and ecological advantages.[6] Among heterogeneous catalysts, magnetic nanoparticles have attracted much attention due to their unusual magnetic, physical and surface chemical and catalytic properties, high stability, and ease of recovery with an external magnet.[6c,d] In the present study, we report a simple, inexpensive, and two-step synthesis of Fe@Pd nanowires by arc discharge of Fe in deionized (DI) water and electroless deposition of palladium. The main advantage of the present method is the direct formation of Fe nanowires from discharge of iron electrodes in water.

Several methods are used for fabrication of Fe nanowires. They include epitaxy,[7a] chemical deposition,[7b] self-assembly[7c] and electrochemical methods.[7d] To the best of our knowledge, there are no reports on the fabrication of iron nanowires by the electrical arc discharge method. The early works on arc discharge method in liquids were based on the production of carbonaceous nanostructures such as MWCNTs, SWCNTs, SW-CNHs, and Nano onions.[8] In general, electrical arc discharge in water has the advantage in this

regard that it produces self-crystallized nanoparticles due to the high temperature caused by Joule heating. Moreover, compared with other techniques, electrical arc discharge in water is an attractive method because of the simplicity of the experimental set-up, the lack of complicated equipment, low impurity, and fewer production steps leading to a high-throughput and cost-effective procedure to generate high yields of nanoparticles.

Fe@Pd nanowires were fabricated in two-steps using a simple process. Fe nanowires of several micron lengths were synthesized through arc discharge of iron electrodes in DI water and then they were dispersed on glass substrates and dried in air. Palladium nanoparticles were overlaid on the surface of Fe nanowires via a simple drop-drying process by dropping $PdCl_2$ solution onto Fe nanowire films and drying them at room temperature. Figure 1 illustrates typical morphologies of Fe nanowires obtained at 5 A arc currents. In general Fe tends to form wire-like structures due to its lattice geometry. The presence of a high temperature region and DI water in the reactor leads to the formation of a temperature gradient and fast condensation process. In fact, rapid cooling of the products reduces the growth rate of the created nuclei and they do not have enough time to form wire-shape structures before stabilization. Hence, there are also shapes other than nanowires in our samples, which is due to fast condensation. Scanning electron microscopy images illustrate Fe nanowires with sizes ranging from 1 to less than 20 μm in length and about 100 nm in diameter. Figure 2 shows SEM micrographs of samples after Pd nanoparticle shell deposition. The Back scattering electron (BSE) mode permits having a contrast between elements with different atomic numbers. Hence, Pd particles appear as bright dots over the surface of Fe nanowires with average sizes of less than 30 nm.

In the next step, we tested the catalytic activity of the Fe@Pd nanowires for the amination of arylboronic acids under ligand-free conditions at room temperature (Scheme 1).

Initially, we employed *p*-anisidine and phenylboronic acid as model substrates for the development of optimized conditions. The reaction does not proceed in the absence of catalyst [Fe@Pd nanowires] (Table 1, entry 1). Also, no desired product was obtained in an identical reaction with iron nanoparticles (without Pd) (Table 1, entry 2). Several solvents such as toluene, 1,4-dioxane, and water were examined. According to the data given in Table 1, water was the most efficient solvent for this reaction (Table 1, entry 6). The reactivity of the catalyst in water in the presence of different bases was also investigated. Among the tested bases (Cs_2CO_3, K_2CO_3, Et_3N, $NaHCO_3$, and NaOAc), K_2CO_3 was found to be superior giving the highest yield of *N*-phenyl-4-methoxyani-

Figure 2. Typical SEM image of samples after deposition of Pd.
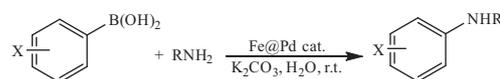
Scheme 1.

Table 1
Optimization of the reaction conditions for the amination reaction of phenylboronic acid with *p*-anisidine[a]

Entry	Cat. (mol %)	Base	Solvent	Yield[b] (%)
1	-	K_2CO_3	H_2O	0[c]
2	3.0	K_2CO_3	H_2O	0[d]
3	3.0	K_2CO_3	Toluene	48
4	3.0	K_2CO_3	1,4-Dioxane	44
5	3.0	K_2CO_3	1,4-Dioxane:H_2O (1:1)	60
6	3.0	K_2CO_3	H_2O	92
7	3.0	$NaHCO_3$	H_2O	11
8	3.0	NaOAc	H_2O	7
9	3.0	Cs_2CO_3	H_2O	45
10	3.0	Na_2CO_3	H_2O	57
11	3.0	Et_3N	H_2O	38
12	3.0	—	H_2O	0
13	1.5	K_2CO_3	H_2O	78
14	4.0	K_2CO_3	H_2O	91
15	3.0	K_2CO_3	H_2O	73[e]
16	3.0	K_2CO_3	H_2O	0[f]

[a] Reaction conditions: 1.0 equiv of phenylboronic acid, 1.0 equiv of *p*-anisidine, 2.0 equiv of base, and an aqueous suspension of Fe@Pd nanowires (0.3 mmol %), H_2O (10 mL), room temperature, 5 h.
[b] Isolated yield.
[c] The reaction was performed without the catalyst.
[d] The reaction was performed with iron nanoparticles (without Pd).
[e] The reaction was performed with $PdCl_2$.
[f] Reaction was performed under a nitrogen atmosphere.

Figure 1. Typical SEM image of Fe nanowires prepared at 5 A electrical arc currents.

line (Table 1, entry 6). In the absence of base, the reactions did not proceed even after a long reaction time (Table 1, entry 12). A decrease in the catalyst loading from 3.0 mol % to 1.5 mol % afforded the product in lower yield. No significant improvement in the yield was observed using higher amounts of the catalyst (Table 1, entry 14) and 3.0 mol % of the catalyst was found to be optimum. As shown in Table 1, when $PdCl_2$ was used as the catalyst the product was obtained in only moderate yield (Table 1, entry 15). It was found that a combination of [Fe@Pd nanowires] (3.0 mol %) and K_2CO_3 (2.0 equiv) in the presence of *p*-anisidine (1.0 equiv) and phenylboronic acid (1.0 equiv) in water (10 mL) was optimum for

Table 2
Amination of different arylboronic acids using Fe@Pd nanowires as the catalyst
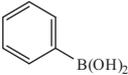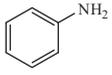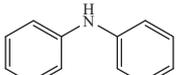
Entry	Arylboronic acid	Amine	Product	Yield[a] (%)
1				95
2				92
3				94 (94, 93, 93, 91)[b]
4				88
5				83
6				79
7				90
8				92
9				91
10				75
11				77
12				78
13				78
14				88
15				92
16				90
17				94
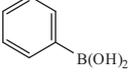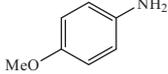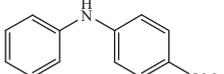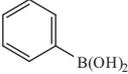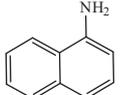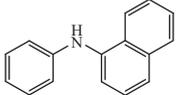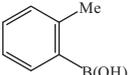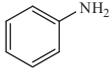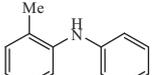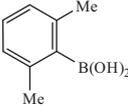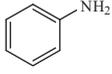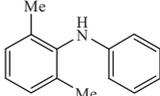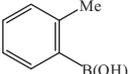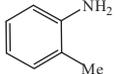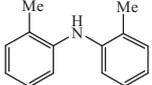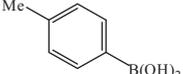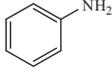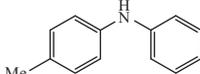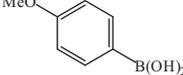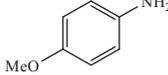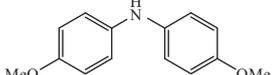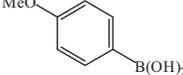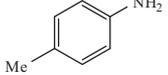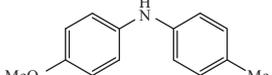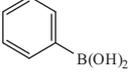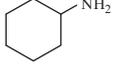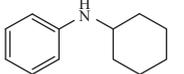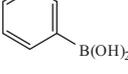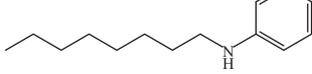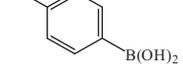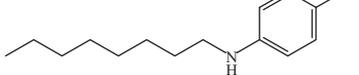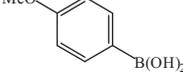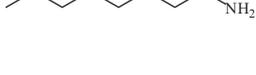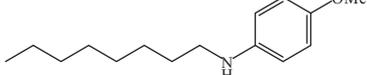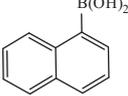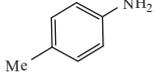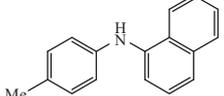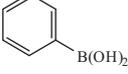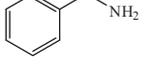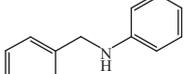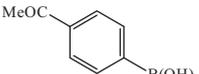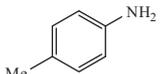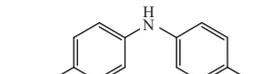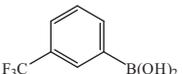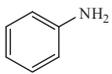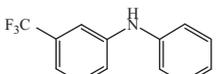
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Table 2 (continued)

Entry	Arylboronic acid	Amine	Product	Yield[a] (%)
18				92
19				78
20				74
21				73

[a] Yields after work-up.

[b] The yields from four subsequent runs using the same recovered catalyst.

a fast and efficient reaction (Table 1, entry 6). No desired product was observed in the absence of air (under a nitrogen atmosphere; Table 1, entry 16), which indicated that an oxidative process was involved in the formation of the product.

After determining the optimized conditions, we next investigated the scope of the magnetic catalyst for the C—N cross-coupling reaction of a diverse range of arylboronic acids containing both electron-releasing and electron-withdrawing groups with various amines (Table 2). This newly developed Fe@Pd-catalyzed amination protocol was also applied to aliphatic and heterocyclic amines (Table 2, entries 10–13, 18 and 19–21). In all cases, this protocol afforded the desired products in good to excellent yields. As shown in Table 2, reactions of *ortho*-substituted arylboronic acids with amines afforded good yields (entries 4–6). An *ortho*-substituent on aniline could also promote this reaction (entry 6). 1-Naphthylboronic acid gave the corresponding adduct in good yield (entry 14).

Next, we studied the reusability of this heterogeneous Fe@Pd catalyst in C—N coupling reactions (Table 2). After completion of the reaction, the catalyst was recovered by the application of an external magnet, then washed with ethyl acetate, and dried in a hot air oven at 100 °C for 2 h. The recovered catalyst was reused under similar conditions for the next run, and the catalytic behavior of the Fe@Pd nanowires was found to be unaltered over five consecutive cycles (Table 2, entry 3).

A general catalytic cycle for this reaction is presented in Scheme 2. This reaction allows aryl carbon—nitrogen bond formation via the oxidative coupling of arylboronic acids with —NH containing compounds in air.
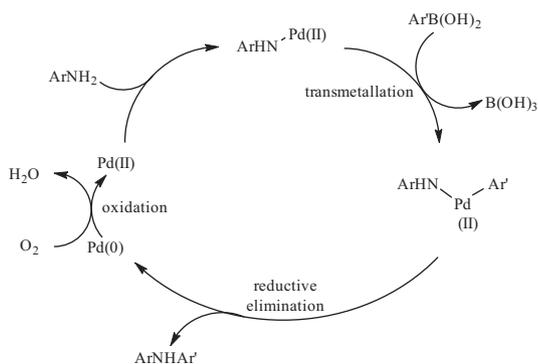
In summary, we have successfully synthesized Fe@Pd nanowires through a facile procedure. The catalyst exhibited good activities in ligand-free cross coupling reactions of arylboronic acids with amines in aqueous medium. Furthermore the Fe@Pd nanowires could be easily separated by a magnet, and could be recycled several times without loss of the catalytic activity. Further investigations on the application of this system on other catalytically synthetic reactions are in progress.

Preparation of Fe@Pd nanowires

Fe nanowires were prepared using a system consisting of two main parts: a high current DC power supply and a reactor including an anode, cathode, and a micrometer, which moves the anode in contact with the cathode. In this method, an 8 V DC voltage and 5 A current are applied between two metallic iron electrodes; it was found that the voltage dropped to 5 V during arcing but the current remained constant. Both the anode and cathode were made of Fe, wire-shaped, 2 mm in diameter and of 99.99% purity. Initially, we brought the two electrodes into contact, leading to a small contact cross section and thus to a high current density. As more Fe was ablated from the anode, the plasma expands, pushing the liquid away, and a gaseous bubble forms. Melted species can react with the plasma and then condense into the liquid. In order to extract the dispersed wires, the solution was evaporated at a pressure of 10^{-1} Torr and centrifuged several times and then dispersed on a glass substrate. Deposition of Pd on the surface of Fe nanowires was accomplished via a simple drop-drying process by dropping PdCl$_2$ solution onto Fe nanowire films and drying them at room temperature. This solution was prepared by ultrasonically solving 0.02 g of PdCl$_2$ powder (5 N), 99.9 mL DI water and 0.1 mL HCl. After Pd deposition, samples were washed with DI water several times and then dried in air.

Preparation of diphenylamine; typical procedure

To a stirred solution of phenylboronic acid (1.0 mmol), aniline (1.0 mmol), and K$_2$CO$_3$ (2.0 mmol) in deionized H$_2$O (10 mL) at room temperature was added an aqueous suspension of Fe@Pd nanowires (3.0 mol % in 3 mL of H$_2$O). The mixture was stirred at room temperature for 5 h. After completion of the reaction (as monitored by TLC), 2 M HCl was added and the catalyst was separated by applying an external magnet. The catalyst was washed with EtOAc. The mixture was extracted with EtOAc (2 × 20 mL), dried, and concentrated. The residue was subjected to gel permeation chromatography to afford pure product. Mp 51–53 °C (lit.[9a]

Scheme 2. Proposed mechanism for the Pd-catalyzed oxidative amination of arylboronic acids.

52–53 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ_H = 7.26–7.20 (m, 4H), 7.08–7.04 (m, 4H), 6.93 (t, J = 7.4 Hz, 2H), 5.74 (1H, s). All the products are known compounds and the spectral data and melting points were identical to those reported in the literature.[9]

Acknowledgements

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