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FULL PAPER

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A Bio-Inspired Magnetically Recoverable Palladium Nanocatalyst for the Ullmann Coupling reaction of Aryl halides and Arylboronic acids In Aqueous Media

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Abstract

Palladium nanoparticles supported on polydopamine-coated iron oxide nanoparticles (Pd/Fe_3O_4@PDA) were found to catalyze the Ullmann homocoupling of a wide variety of aryl halides, arylboronic acids and aryldiazonium salts in aqueous media in the presence of randomly methylated β-cyclodextrin (RM-β-CD). The synthesized nanoparticles were characterized by techniques such as TEM, SEM, EDX, XPS, ICP-AES and XRD. The synthesized catalyst can be easily recovered magnetically and reused up to five cycles without any significant loss of activity. This is the first report demonstrating the use of magnetically recoverable catalyst for Ullmann homocoupling reactions of aryl halides, arylboronic acids and aryldiazonium salts in water.

KEYWORDS

biomimetic catalysis, Cyclodextrins, Homocoupling, Polydopamine, water

1 | INTRODUCTION

In recent years, the aryl-aryl cross/homo-coupling reactions have emerged as one the most important synthetic transformations for the synthesis of symmetrical and unsymmetrical biaryls,[1–5] which are building blocks for the synthesis of a wide range of pharmaceuticals, medicinally important molecules, polymers, alkaloids, and other advanced materials.[6–8] In this context, over the decades, the Ullmann homocoupling of aryl halides and arylboronic acids has been widely utilized for the preparation of symmetrical biaryls. However, the use of stoichiometric amount of copper, high reaction temperature conditions renders these methods impractical for the synthesis of biaryls bearing thermosensitive functional groups.[9] Till date, substantial work has been introduced for the preparation of symmetrical biaryls with Pd,[10–17] Cu,[18–21] Ru,[22] Au,[23,24] Fe[25] and Ni-based catalysts[26] in catalytic amounts.[27–30] Yet, the development of new and efficient methods is of great interest and highly desirable[4,31] as most of these methods are homogeneous protocols and suffer from limited utility in practical processes because of challenges associated with catalyst non-reusability, products free of metal contaminations and requisite of ligands. Furthermore, these protocols are mainly demonstrated in organic solvents and very few are reported to work under aqueous conditions.[32] Hence, from a sustainable chemistry viewpoint, the development of heterogeneous based catalysts for Ullmann homocoupling protocols in a cheap and benign solvent media like water are highly desirable.

Although, the heterogeneous nanocatalysts regime of catalysts are categorically superior over the homogenous systems for most organic transformations, it is often difficult to isolate and separate them through filtration or centrifugation methods.[33,34] To overcome these issues, incorporation of recoverable magnetic nanoparticles (MNPs) as supports appear to be the most logical solution, which in addition also increases surface area of nanocatalysts. Among MNPs, Fe_3O_4-based magnetic

nanocatalysts are most preferred,[35–37] on account of their non-toxic nature and easy preparation methods.[38] Often, these iron oxide nanoparticles are fabricated with silica, dopamine, carbons and polymers, such capping plays a dual role of preventing the nanoparticle from aggregation and enhancing overall catalytic activity.[39–41] Polydopamine[42–44] is one such analogous and promising biomimetic polymeric material, which has high affinity for iron oxide surface and is easily prepared by self-polymerization of dopamine (the well-known neurotransmitter) at ambient conditions.

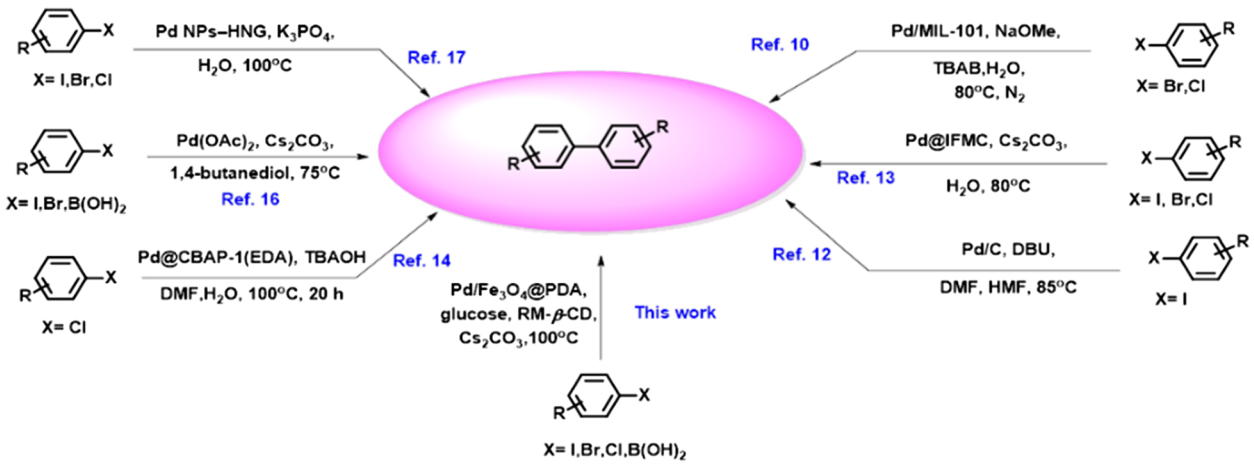
The other important aspect is solvent, as solvents[45–47] play a major role in the execution of processes in chemical industry, they have a profound impact on cost, safety and health issues. Henceforth, from green chemistry perspective, development of new methodologies in a benign solvent like water can be a promising alternative. However, the low solubility of various organic substrates in aqueous medium invalidates the preferences and makes it hard to channel the full utility. In such cases, the utilization of supramolecular based catalysts such as cyclodextrins (CDs)[48–50] that emulate the solubility issues and favor the reaction progress are necessary for achieving significant product conversions. Also owing to the unique properties such as host-guest inclusion complexes with various organic molecules, the use of hydrophobic cavity and hydrophilic exterior of CDs highly qualify them as benign mass transfer reagents, which has been widely explored over the past years for various reactions, such as oxidations, reductions, catalysis by CD-metal complex catalysis, biphasic reactions and epoxide ring opening[51–53]

Therefore, with such a view, in continuation to our interest in the development of metal supported on functionalized and polymer-coated iron oxides for various synthetic organic transformations[54,55] and designing of sustainable catalytic systems,[56–59] herein we demonstrate a biomimetic magnetically retrievable Pd/Fe_3O_4@PDA nanocatalyst for homo-coupling and cross-coupling reactions of arylboronic acids and aryl halides for construction of symmetrical-unsymmetrical biaryl compounds utilizing water as solvent. Scheme 1 outlines various palladium based catalytic approaches for homocoupling reactions.

2 | RESULTS AND DISCUSSION

Initially, the synthesis of the Pd/Fe_3O_4@PDA catalyst was carried out by an *in-situ* coating of Fe_3O_4 nanoparticles (50–100 nm) with polydopamine *via* self-polymerization of dopamine precursor in air under basic *p*H (8.4) conditions. In the subsequent step, palladium nanoparticles were immobilized on polymer-coated iron oxide nanoparticle. The as-made catalyst was further completely characterized by techniques such as TEM, SEM, XPS, XRD, and ICP-AES for establishing the structure and morphological changes.

The X-ray diffraction patterns of the obtained for $PdCl_2$, Fe_3O_4, Polydopamine (PDA), Fe_3O_4@PDA, native and recycled Pd/Fe_3O_4@PDA are presented in Figure S5 (refer to ESI). The characteristic diffraction peaks at 2θ of 30.2°, 35.5°, 37.3°, 43.3°, 53.8°, 57.2°, and 62.8° correspond to the diffraction of (220), (311), (222), (400), (422), (511), and (440) of the Fe_3O_4, which were indexed to Fe_3O_4 (JCPDS 65–3107). All these diffraction peaks match with the cubic structure of Fe_3O_4 (JCPDS 65–3107). Polydopamine being more amorphous structure did not show characteristic peaks. The fifth recycled Pd/Fe_3O_4@PDA catalyst spectra shows the same



SCHEME 1 Different Catalytic Approaches for Homocoupling Reactions

characteristic peaks as the native one, this evidently indicates that crystallography of the catalyst remains intact even after multiple cycles of usage.

To determine the surface morphology of the Pd/Fe_3O_4@PDA catalyst we performed the SEM and TEM analysis; for elemental composition and mapping EDX analysis was also carried out. In Figure S1 and S3 (ESI), SEM images show equal distribution of globular types layers stacked on each other, with a uniform particle distribution. The EDX analysis Figure S2 and S4 (ESI) suggest that about 6.81 wt% of palladium is supported on the Pd/Fe_3O_4@PDA catalyst. Further detailed study of surface morphology was investigated by using TEM analysis, Figure 1 and 2 shows a uniform polydopamine coating (10–100 nm) loaded with evenly distributed Pd nanoparticles of approximate size (2–5 nm).

The amount of Pd metal loaded on Fe_3O_4@PDA as revealed by ICP-AES analysis was found to be 6.92 wt%. The XPS survey spectrum of the native and recycled Pd/Fe_3O_4@PDA catalysts showed Pd 3d core level lines, the binding energy peak of Pd $3d_{5/2}$ and $3d_{3/2}$ in the fresh and five-time reused catalyst is found to be 335.31/340.51 eV and 335.6/340.6 (Figure 3 and 4), indicating that the loaded palladium is in its zero-oxidation state. The peaks at 338.7 eV and 343.4 eV in figure 4 can be assigned to Pd (II) species *i.e.* PdO which is in agreement with literature values.[60] The low intensities of these peaks in the spectra indicate that the major species present is Pd (0).

In an attempt to ascribe catalyst efficiency for homocoupling reactions, initially, we started our investigation using 4-iodoanisole as a substrate with the combination of Pd/Fe_3O_4@PDA and randomly methylated (RM)-β-cyclodextrin as a mass transfer reagent, Na_2CO_3 as base, and glucose as a reductant under aqueous conditions at 100 °C. The reaction was allowed to proceed for 24 hr, the homocoupled product was obtained in 52% yield (Table 1, entry 1) with dehalogenated side products. With this preliminary result, next we screened various other bases (Table 1, entry 2–8), among which Cs_2CO_3 was found to be most effective to afford the product yield 92% and was continued for further study (Table 1, entry 8). The drastic decrease in homocoupled product was observed when the equivalents of base was reduced (Table 1, entry 9), which clearly shows the quantitative role of bases in typical coupling mechanism.[61] The reaction did not go to completion and afforded less yield when 0.15 mmol of glucose was used, this might be due to the inability in reducing metal further back to its lower oxidation state which is mainly responsible for catalytic cycle. On the other hand, more dehalogenated product was observed when an excess of glucose used, and its absence gave poor yields of desired product (Table 1, entries 10 and 11). The blank homocoupling reaction without use of any catalyst showed no progress (Table 1, entry 12). A decrease in the amount of Pd/Fe_3O_4@PDA catalyst resulted in lowering of product yield and no results was obtained under base-free conditions (Table 1, entries 13 and 19). Varying the stoichiometry and use of other cyclodextrin derivatives did not improve the product yield (Table 1, entries 14–18). A reaction without use of Cyclodextrin shows poor yield of homocoupled product (Table 1, entry 15). Cyclodextrin possess a distinguished hydrophilic outer surface and a hydrophobic inner cavity. The cavity is mainly accountable for the specific reversible binding of molecules (inclusion phenomenon) enhancing the interaction of reactant and catalyst, which is a driving force for reactions. Also, role of CD may also be to increases the solubility of the substrate.[62,63] This could be the explanation for improve in yield with the usage of Cyclodextrin in reaction. We performed a test with Fe_3O_4@PDA to understand the real catalyst, however no sign of homocoupled product observe which clearly shows role of Pd is important for reaction.

With the optimized reaction conditions in our hand, we studied the substrate scope by using various substituted aryl halides. Initially, iodobenzene was tried, as they are the model substrates and provide access to basic information to understand the electronic effect in

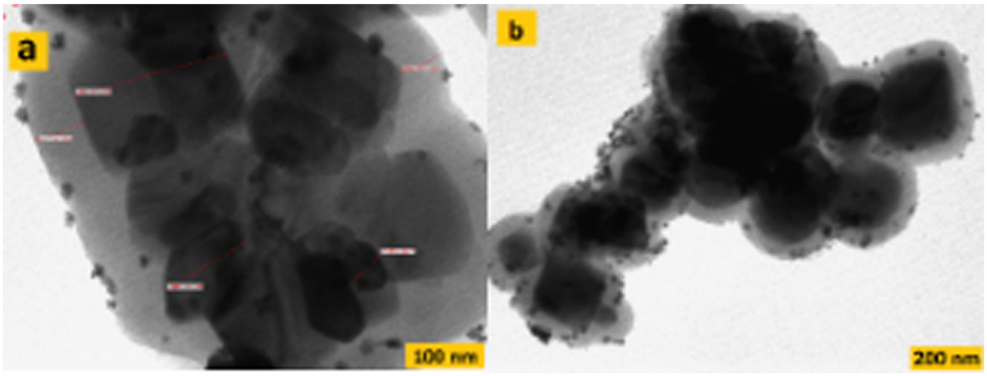


FIGURE 1 TEM images of native Pd/Fe_3O_4@PDA nanoparticles (a and b)

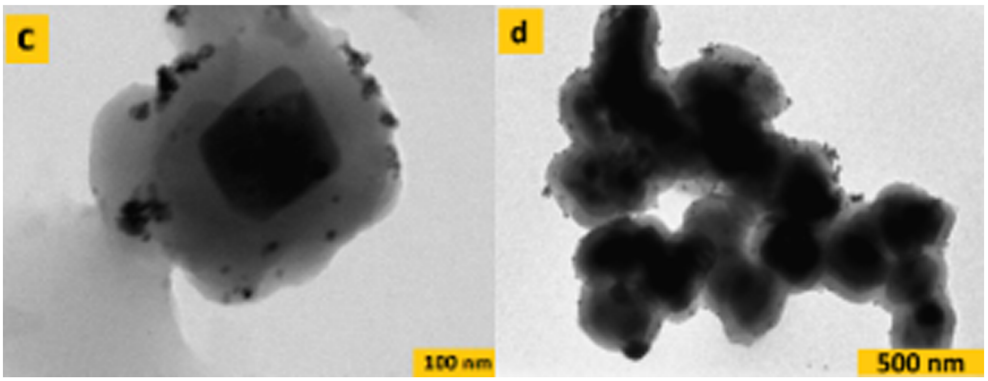


FIGURE 2 TEM images of recycled Pd/Fe_3O_4@PDA nanoparticles (c and d)

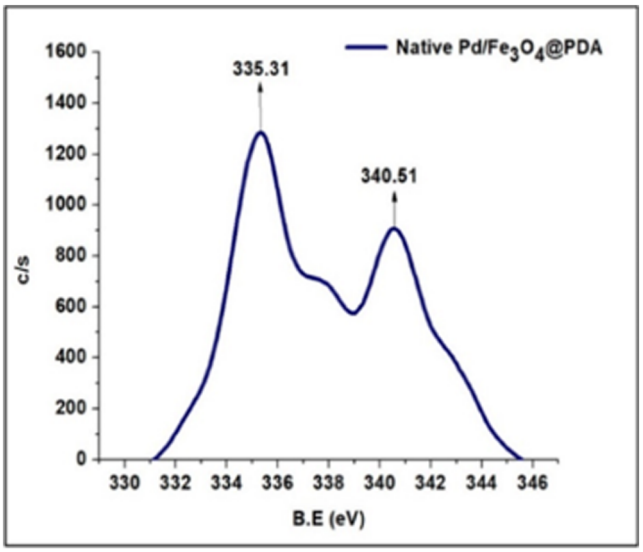


FIGURE 3 XPS analysis of Pd in native Pd/Fe_3O_4@PDA

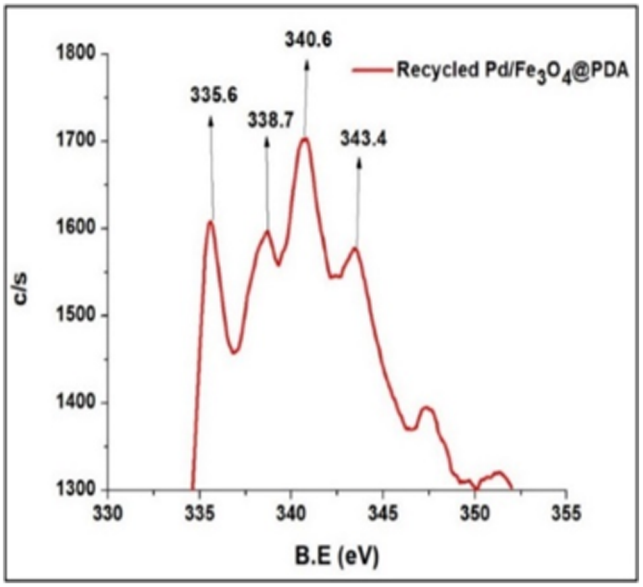
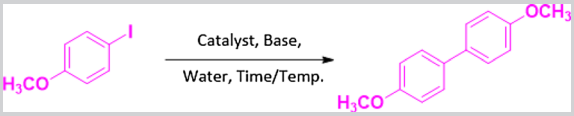


FIGURE 4 XPS analysis of recycled Pd/Fe_3O_4@PDA

TABLE 1 Optimization of reaction conditions[a]



Entry	Base	Reductant	Cyclodextrin	Yield [%][b]
1	Na_2CO_3	Glucose	RM-β-CD	52
2	K_2CO_3	Glucose	RM-β-CD	64
3	KOH	Glucose	RM-β-CD	24
4	NaOMe	Glucose	RM-β-CD	72
5	Et_3N	Glucose	RM-β-CD	39
7	Pyridine	Glucose	RM-β-CD	32
8	**Cs_2CO_3**	**Glucose**	**RM-β-CD**	**92**
9	Cs_2CO_3	Glucose	RM-β-CD	57[c]
10	Cs_2CO_3	Glucose	RM-β-CD	62[d], 71[e]
11	Cs_2CO_3	--	RM-β-CD	26
12	Cs_2CO_3	Glucose	RM-β-CD	NR[f]
13	Cs_2CO_3	Glucose	RM-β-CD	68[g]
14	Cs_2CO_3	Glucose	RM-β-CD[h]	74
15	Cs_2CO_3	Glucose	--	19
16	Cs_2CO_3	Glucose	β-CD	61
17	Cs_2CO_3	Glucose	α-CD	27
18	Cs_2CO_3	Glucose	γ-CD	32
19	--	Glucose	RM-β-CD	NR
20	Cs_2CO_3	Glucose	γ-CD	32[i]
21	Cs_2CO_3	Glucose	RM-β-CD	NR[j]

[a]Reaction conditions: Pd/Fe3O4@PDA (50 mg), 4-iodoanisole (1 mmol), base (1.0 mmol), glucose (0.25 mmol), RM-β-CD (100 mg) and solvent (4 ml), [b]Isolated yield, [c]0.5 mmol of Cs_2CO_3, [d]0.15 mmol of glucose, [e]0.5 mmol of glucose, [f]without catalyst, [g]Catalyst 25 mg, [h]50 mg of RM-β-CD, [i]Pd/C as catalyst, [j]Fe_3O_4@PDA as catalyst, RM = Randomly methylated

any coupling mechanism. All halobenzenes *viz.* bromo and chlorobenzenes homocoupled effectively, to afford the corresponding biphenyl products in good to excellent yields (Table 2). A variety of substituted aryl halide bearing functional groups, such as -OCH_3, -CH_3, -F, -NO_2 and -CN were tolerated to afford the products in moderate to excellent yields (Table 2, 2a-2 h, 92–68%).

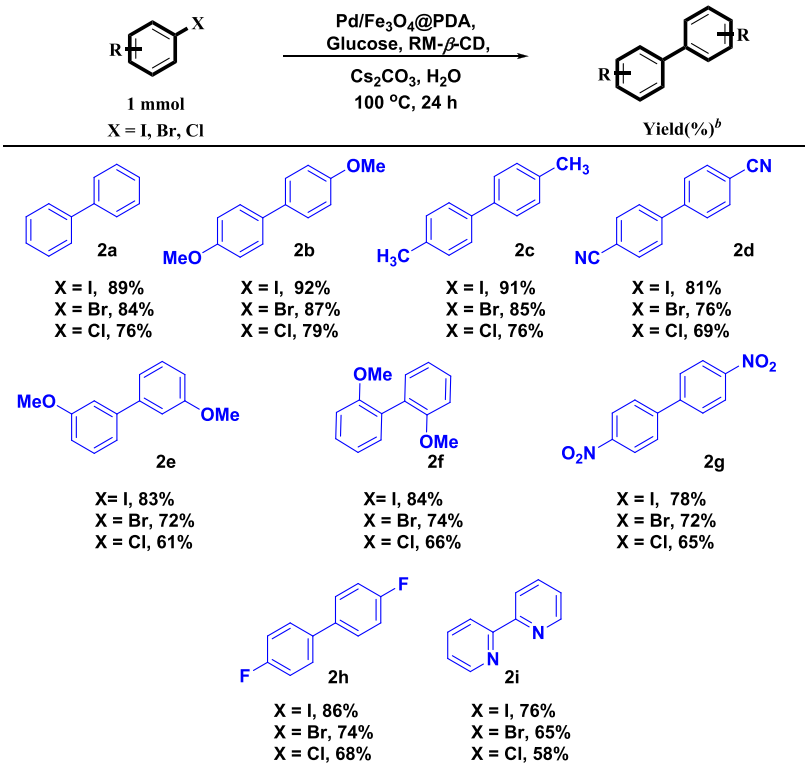
The electron-donating group attached on the phenyl moiety furnished the products in good yield compared to their electron withdrawing counterparts (Table 2, 2b and 2f). The Ullmann reaction of bromoarene and chloroarene bearing electron-withdrawing substituent afforded dehalogenated by-product (Table 2, 2d, 2 g and 2 h). Additionally, the products/reactants containing cyano which are susceptible to undergo hydrolysis and oxidation did not show any formation of hydrolyzed (or) oxidized products (Table 2, 2d). The *ortho*-substituted halide substrates showed slightly lower conversion, might be due to steric hindrance (Table 2, 2f). Presence of -OCH_3 group at meta position to a small degree acts as a deactivator for oxidative addition reactions (Table 2, 2e).

Heterocyclic halides which are challenging substrates in coupling reactions also afforded moderate yields of product (Table 2, 2i). The Ullmann coupling of the aryl chlorides wasn't that promising, due to the sluggish reactivity of C-Cl bond. The results as summarized in Table 2, clearly shows that the coupling reaction proceeds *via* oxidative insertion of aryl halide to metal, which followed the general trend of aryl iodide > aryl bromide > aryl chloride.

Having completed the homocoupling reactions, we further extended the study to explore the versatility of the catalyst we further tested it for cross-coupling reactions of two different aryl halides. The cross-coupling of aryl halides is interesting and less explored owing to several issues pertaining to selectivity if formation of cross-coupled products. Therefore, with such a view, we choose 4-iodoanisole and 4-iodotoluene to check for the efficiency of the developed catalyst (Table 3).

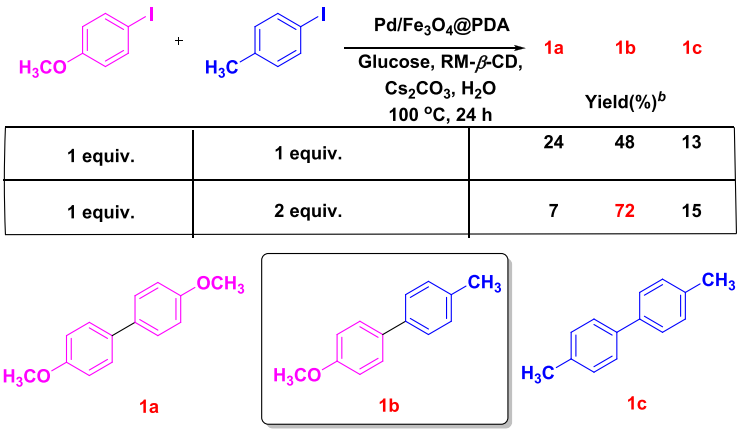
Interestingly, the cross-coupled product in case of these substrates was found to be 48% when one equivalent of the coupling partners each. The later was improved to 72% when one of the coupling partner

TABLE 2 Ullmann coupling of various aryl halides using Pd/Fe_3O_4@PDA[a]



[a]Reaction conditions: Pd/Fe_3O_4@PDA (50 mg), aryl halide (1 mmol), base (1.0 mmol), glucose (0.25 mmol), RM-β-CD (100 mg) and solvent (4 ml), aryl bromide and chloride at 120 °C, RM = Randomly methylated. [b]Isolated Yield.

TABLE 3 Optimization of cross-coupling reaction in aryl halide[a]



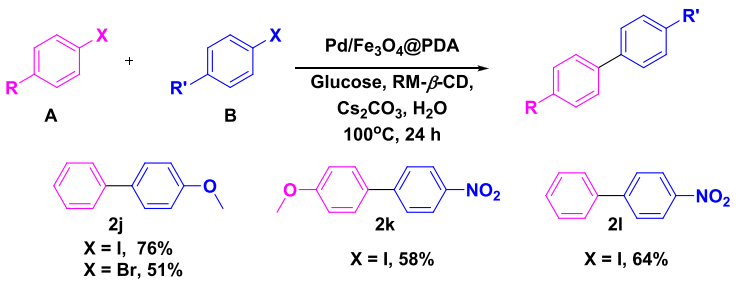
[a]Reaction conditions: Pd/Fe_3O_4@PDA (50 mg), 4-iodoanisole (0.5 mmol), 4-iodotoluene (0.5/1.0 mmol), base (1.0 mmol), glucose (0.25 mmol), RM-β-CD (100 mg) and solvent (4 ml). RM = Randomly methylated. [b]Isolated Yield

4-iodotoluene was employed 2 equivalents. Other substrates with different substituent such as nitro were also tested for conversion but afforded the cross-coupled products in only moderate yields (Table 4, 2 k and 2 l).

Having completed the substrate scope of the homocoupling and cross-coupling of aryl halides, we further extended the study for alternate organic substrates such as arylboronic acids and aryldiazonium salts. We started our investigation using arylboronic acids as a model substrate, under the optimized reaction conditions. The best result was obtained with water as the solvent, RM-β- CD as phase transfer reagent, 50 mg of (6.92 wt%) Pd/Fe_3O_4@PDA of catalyst, K_2CO_3 as base at room temperature under air atmosphere. Interestingly, we were able to homocouple several arylboronic acids bearing various functional groups such as methoxy, methyl, fluoro and ester to afford products in good to excellent yields (Table 5, 2a, 2b, 2c, 2 h, 2 m and 2n). Moreover, poor yields were observed with the nitro-substituted arylboronic acid, this could be due to the influence of substituents on the transition state formed during the progress of the reaction (Table 5, 2 g).

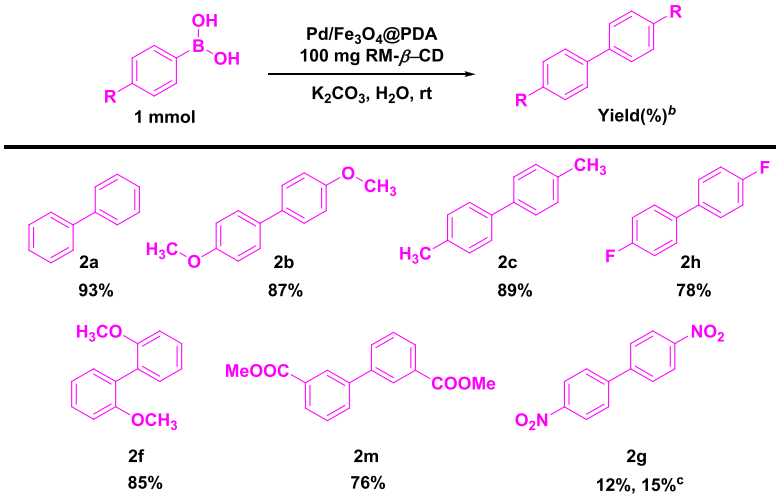
Unlike homocoupling, the cross-coupling of arylboronic acids furnished product in low yield (Table 6), also the electron withdrawing counterpart did not give satisfactory result similar to aryl halide cross-coupling reactions (Table 6, 2 k and 2 l). Following this, looking at popularity of aryldiazonium salts as an electrophile in various organic transformations, we also decided to test it for homocoupling reactions (Table 7). Unfortunately, the catalyst showed very poor activity toward 4-methoxy and 4-nitro diazonium salts. We could only

TABLE 4 Ullmann cross-coupling of various aryl halides using Pd/Fe_3O_4@PDA[a]



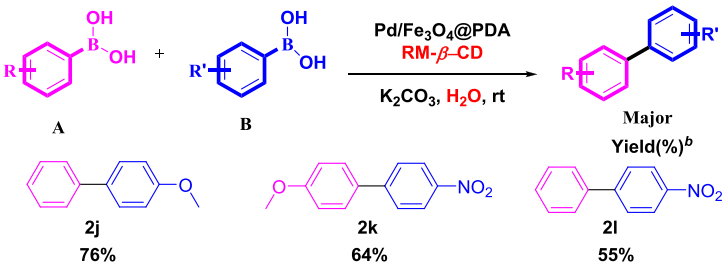
[a]Reaction conditions: Pd/Fe_3O_4@PDA (50 mg), aryl halide A (0.5 mmol), aryl halide B (1.0 mmol), base (1.0 mmol), glucose (0.25 mmol), RM-β-CD (100 mg) and solvent (4 ml), aryl bromide at 120 °C, RM = Randomly methylated. [b]Isolated Yield.

TABLE 5 Ullmann coupling of various arylboronic acids using Pd/Fe_3O_4@PDA[a]



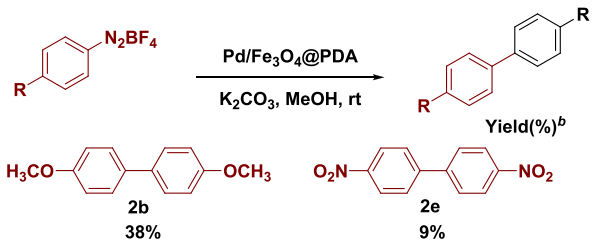
[a]Reaction conditions: Pd/Fe_3O_4@PDA (50 mg), arylboronic acid (1.0 mmol), base (1.0 mmol), RM-β-CD (100 mg) and solvent (4 ml) under air atmosphere. RM = Randomly methylated. [b]Isolated yield. [c]at 60 °C.

TABLE 6 Ullmann cross-coupling of various arylboronic acids using Pd/Fe_3O_4@PDA[a]



[a]Reaction conditions: Pd/Fe_3O_4@PDA (50 mg), arylboronic acid A (0.5 mmol), arylboronic acid B (1.0 mmol), base (1.0 mmol), RM-β-CD (100 mg) and solvent (4 ml) under air atmosphere. RM = Randomly methylated. [b]Isolated yield.

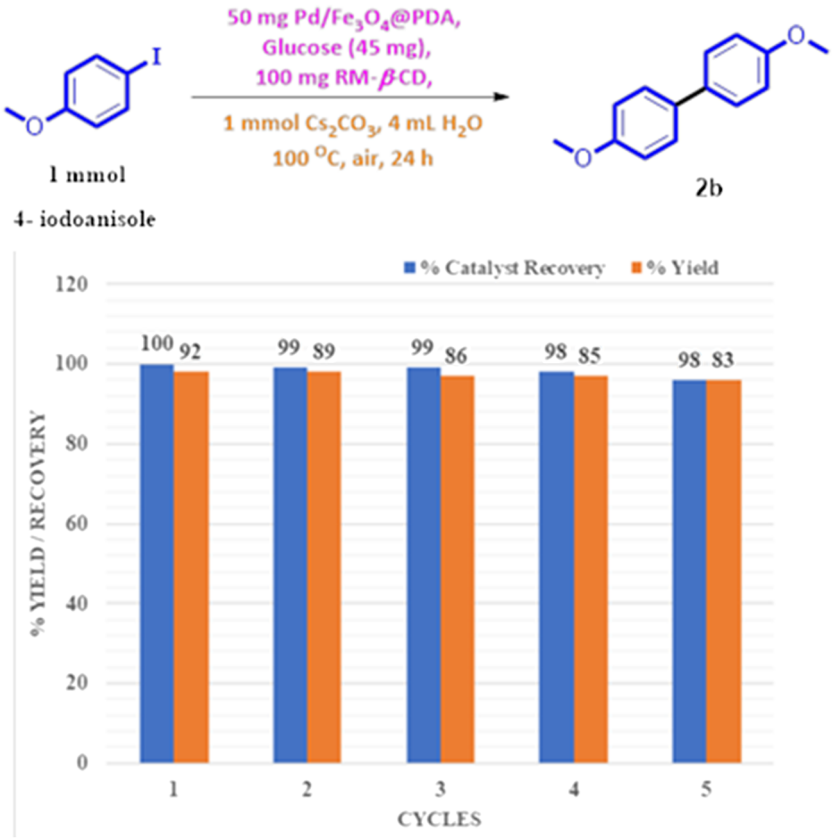
TABLE 7 Ullmann homocoupling of various aryldiazonium salts using Pd/Fe_3O_4@PDA[a]



[a]Reaction conditions: Pd/Fe_3O_4@PDA (50 mg), aryldiazonium salt (1 mmol), methanol (3 ml) under air atmosphere. [b]Isolated yield.

get 38% yield in case of former whereas the later having electron withdrawing substituent gave 90% yields of the desired homocoupled product (Table 7, 2b and 2 g).

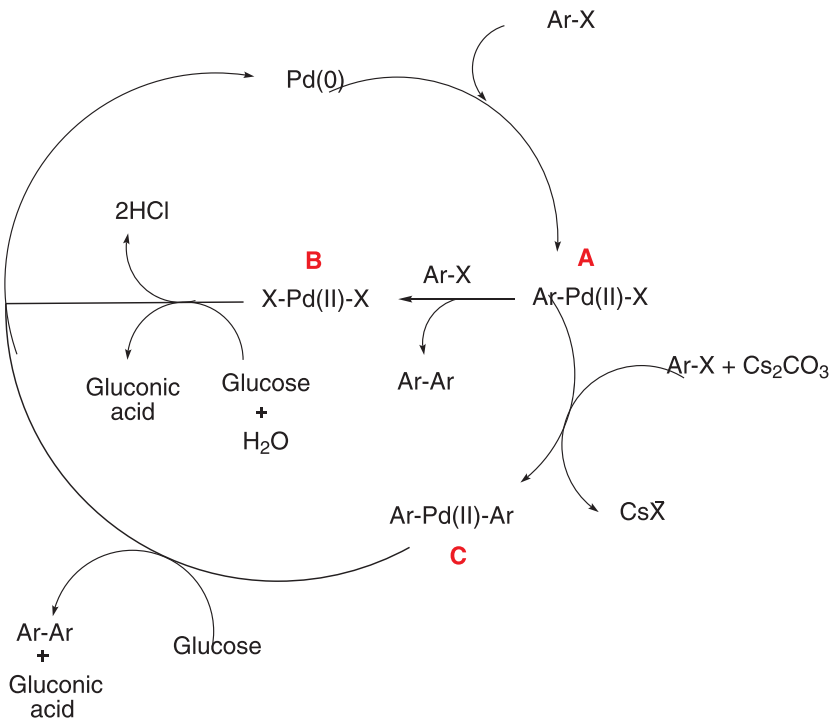
Separation, Recovery and Recycling of the catalyst is most important in sustainable organic transformation, which is typically accomplished by traditional and tedious methods of filtration or centrifugation with reduced efficiency. In our catalytic system, due to the magnetic nature of nano-Fe_3O_4, catalyst was recovered easily using an external laboratory magnet and the coupled product is extracted from aqueous layer using ethyl acetate. The same catalyst was used for next five cycles (Scheme 2). Although, the yields of coupled product were slightly decreasing in the further next



SCHEME 2 Recyclability of Pd/Fe_3O_4@PDA nanocatalyst

cycles, still we obtained good yield even after five-time use of the catalyst. Catalyst recovery was excellent with 98% amount of catalyst recovered after five cycles.

Thereafter, we examined the leaching of palladium metal from the support, which is one of the major concerns in heterogeneous catalysis. This case was investigated by removing the catalyst from the reaction mixture after the first and fifth cycle, subjecting the solution to ICP analysis. The Pd leaching was found to be negligible 1.4 and 7.2 ppm respectively. To study in detail about



SCHEME 3 Plausible Mechanistic Pathway

the heterogeneity of the catalyst, we did a hot filtration test. For this, the homo-coupling reaction between 4-iodoanisole was allowed for the initial 2 hr, which accomplished the desired coupled product in 58% yield, subsequently Pd/Fe_3O_4@PDA catalyst was separated magnetically. The collected filtrate was then taken in another flask and reaction continued at 100 °C for next 24 hr, which showed no increase in the coupled product yield. Another hot filtration test was performed under the same optimized conditions (reaction conversion after 2 hr ~ 57%) wherein the catalyst was separated by centrifugation (3000 rpm) and filtrated solution was continued for reaction to take place. This also showed no further increase in coupled product yield the and hence confirm catalyst's heterogeneous property.

A plausible reaction mechanism for the Ullmann type homocoupling of aryl halide catalyzed by the Pd/Fe_3O_4@PDA was proposed in Scheme 3. The first step involves the reactant-CD inclusion complex interaction with the Pd NPs. Followed by oxidative addition of Pd (0) onto aryl halide produces arylpalladium halide intermediate (A). Here onwards the reaction may go through two pathway, Path 1 involve the addition of the another equivalent of aryl halide to the intermediate A under the basic medium which results into the formation of diarylpalladium complex (C) with subsequent liberation of halide ions, followed by the elimination of Ullmann products facilitated by glucose molecules thus regeneating the Pd (0) species. Aternatively, the reaction may traverse through Path by the reaction of aryl halide with the intermediate A, forming the Ullmann products and Pd (II)X_2. The Pd (II) X_2 so formed may get reduced by glucose to complete the cycle. During the reduction process, glucose gets oxidized to gluconic acid.[57] Moreover, any chance of formation of acidic species from the halide ion remnants is not possible under the basic aqueous conditions.

3 | CONCLUSIONS

In summary, we developed a bio-inspired magnetically recoverable palladium nanocatalyst Pd/Fe_3O_4@PDA and characterized it by several spectroscopic techniques to explain the structure and morphology. It showed excellent catalytic efficiency in homocoupling reaction of aryl halides and arylboronic acids under aqueous medium for a wide range of substrates. Also, it displayed good catalytic activity in cross-coupling reaction among two different aryl halides but was inactive for aryl chlorides, also homocoupling reactions in case of substrates like arylboronic acids and aryldiazonium salts underwent smoothly at room temperature using water as solvent. The yields of the products in all transformations were found to be good to excellent. Furthermore, catalyst could be easily recovered using a magnet, recycled and reused up to five cycles. Use of RM-β-CD was found to increase the yields of coupled products and hence improved the catalyst performance in water.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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