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Nanoporous phenanthroline polymer locked Pd as highly efficient catalyst for Suzuki-Miyaura Coupling reaction at room temperature

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Because of the intrinsic advantages, Suzuki coupling reactions have been one of the most popular coupling reactions in organic synthesis, however developing a high-performance heterogeneous catalyst for Suzuki coupling reactions in aqueous media at low temperature (e.g. room temperature) is still a challenge. Herein, a heterogeneous catalyst with coordinated Pd as active site and a designed conjugated phenanthroline based porous polymer (CPP) as support was fabricated. Systematically investigation on CPP support by Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), Transmission electron microscopy (TEM), N_2 adsorption–desorption isotherm and Scanning electron microscopy (SEM) show that the derived CPP catalyst support owns a porous structure, moderately good surface area (141 m^2/g) and an excellent thermal stability. As a heterogeneous catalyst for the synthesis of biphenyl derivatives via Suzuki coupling, Pd/CPP achieves an excellent catalytic performance and recycling ability towards Suzuki reaction of various reactants at room temperature in ethanol-water medium.

KEYWORDS
Phenanthroline polymer, room temperature, Suzuki polycondensation reaction

1 | INTRODUCTION

The Suzuki-Miyaura coupling reaction is a widely used method for the construction of biphenyl compounds basic organic synthesis due to synthetic variations and functional group tolerance.[1–3] Homogeneous catalysts with excellent activity and products selectivity have been widely used in organic synthesis because of its uniform dispersion and small steric hindrance.[4–6] However, their shortage associated with recovery and reusability limits their industrial application.[1–6] To overcome these issues, the use of heterogeneous catalysts rather than homogeneous ones in Suzuki reactions is particularly fascinating as its improvement in reusability of the precious metal catalysts component.[7–10]

Recently, environmental awareness pressed us to produce chemical products and prompt the reaction processes in green reaction conditions and process.[11–14] It is estimated that about 80% of the useless chemical waste can be reduced from a reaction systems corresponds to the green solvent or procedure.[11–14] From secure, economic and ecological points of regard, the use of harmless water-based solvent in organic synthesis is a sensible choice. However, organic synthesis with water-based

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solvent usually needs high reaction temperature (usually >80 °C). In this regard, the design of a catalytic system using harmless solvent and mild conditions (room temperature and in air) would be a very promising and fascinating direction for exploiting greener and more secure Suzuki reactions.[14,15] Nowadays, many Suzuki-Miyaura coupling reactions can be conducted under very mild reaction conditions and in a short time,[15–21] among which various reusable heterogeneous catalysts have been exploited, including inorganic solid (silicate, agarose-alumina composite, CeO_2, iron oxide, TiO_2) and Merrifield resin supported catalysts.[15–34] But these inorganic solid supported usually suffers from poor stability due to the weak interaction between supports and active components.

Recent studies have demonstrated the feasibility of employing porous organic polymers (POPs) materials in adsorption,[35–37] gas storage,[38,39] and especially in heterogeneous catalysis[10,40–44] due to their high surface area, high stability and controllable skeletons. As in the case of other heterogeneous catalysts, POPs materials were designed and employed in catalysis mainly because their excellent stability to thermal treatments, organic and inorganic solvents and the incorporation of active metal components.[35] Except boron-containing COFs materials, the most well-known triazole,[45] imine[36,40,44] and hydrazine[44] based POPs materials are stable in water and organic solvents. Moreover, it has been well demonstrated that the heteroatoms (N,[10,46] O[47] and S[37]) in the skeletons of COFs, MOFs and other porous materials are feasible in anchoring different active metal ions.[46–48] The introduction of heteroatom is conducive to the recycling of catalysts and their industrial application.[46–48] However, there are only a very few reports available on the synthesis of organic polymer support and applications in Suzuki-Miyaura coupling reaction in water solvent at room temperature and in air atmosphere. Among all the polymer units, 1,10-phenanthroline has considerably strong coordinating ability toward metals ions, presumably due to its fixed and conjugated cis-chelating structure, which makes it an attractive ligand.[49] Consequently, 1,10-phenanthroline derivatives have widely synthesized into heterogeneous catalysts systems by immobilization,[50] loading[51] and integrated[46,52–54] method. To date, there are very few reports on phenanthroline based porous catalysts with covalently linked catalytic metal sites for heterogeneous catalysis.[46,55]

Herein, a heterogeneous catalyst with coordinated Pd as active site and a designed conjugated phenanthroline based porous polymer (CPP) as support was fabricated and the obtained Pd/CPP achieves an excellent catalytic performance and recycling ability towards Suzuki reaction of various reactants at room temperature in ethanol-water medium.

2 | EXPERIMENTAL SECTION

2.1 | Synthesis

Porous phenanthroline based polymer catalyst was synthesized through Suzuki reaction. Firstly, 0.35 g tetrakis (triphenylphosphine) palladium (0.3 mmol), 0.51 g 3,8-dibromo-1,10-phenanthroline (1.5 mmol) and 0.46 g 1,3,5-phenyltriboronic acid tris-(pinacol) ester (1.0 mmol) building monomer were uniformly dispersed in 32.0 ml of 1,4-dioxane. Then, 8.0 ml 0.375 M solution of K_2CO_3 was added to the 1,4-dioxane dispersed solution for 5 min under vigorously ultrasonic treatment. Finally, the obtained homogeneous organic–inorganic mixture was vacuumed to remove residual oxygen and heated at 95 °C for 24 hr under nitrogen atmosphere. The resulting black precipitate was collected by filtration and thoroughly washed with 500 ml water to remove water-soluble substances and then washed by 300 ml ethanol to remove organic substances and then dried to obtain porous phenanthroline polymer (denoted as CPP, yield of 92.9%).

2.2 | Preparation of porous phenanthroline based polymer supported Pd catalyst

Phenanthroline based polymer supported Pd catalyst was prepared by simple loading method.[48] Briefly, CPP (1.5 g) material and palladium acetate (0.77 g) were refluxed in 40.0 ml acetonitrile at 55 °C for 4 hr. The solid was firstly filtered and washed repeatedly with about 100 ml acetonitrile to eliminate uncoordinated palladium (II) species by phenanthroline units in the support, then washed by dichloromethane in Soxhlet extractor for 24 hr to remove residual physisorbed Pd (II) ions. The washed product was dried in vacuum to give the tawny powders and the final obtained catalyst was denoted as Pd/CPP. The Pd content in Pd/CPP was measured to be 2.94% by flame atomic absorption spectrometry.

2.3 | Catalytic performance test of Pd/CPP catalyst for Suzuki reaction

Typically, aryl halides (0.5 mmol), phenylboronic acid or its derivatives (0.75 mmol), base (1.0 mmol) and Pd/CPP catalyst (10.0 mg, 0.55 mol % Pd) were added to 3.0 ml solvent. The reaction mixture was stirred at room temperature (25 °C) in air. After the reaction completely proceed (monitored by TLC), the mother solution was collected by centrifugation and the centrifuged deposit was washed and centrifuged with dichloromethane (5 ml) for third times. The organic solution was combined and washed with 15 ml water (3 times) to remove the remaining base. The organic crude products were then gathered under vacuum and further purified by column chromatography.

The recycle use performance test of the catalyst was conducted with bromobenzene and phenylboronic acid as the model substrate for the C-C coupling reaction. Concrete procedures are as follows: 0.5 mmol bromobenzene, 10 mg Pd catalyst (0.55 mol % Pd), 0.75 mmol phenylboronic acid and 1.0 mmol K_2CO_3 were dispersed in 3.0 ml ethanol/water mixed solvent and reacted for a certain of time. After each cycle procedure, the catalyst was recycled by centrifugation and washed by dichloromethane solvent and then reused directly without any other treatment. For characterization, the recycled catalyst was purified with 300 ml water initially and 300 ml dichloromethane subsequently, and dried at 80 °C under vacuum.

2.4 | Hot filtration test

To monitor whether the heterogeneous or homogeneous feature of Pd species were real effective species responsible for the catalytic performance, the heat filtration test was conducted according to the former reported method.[9]

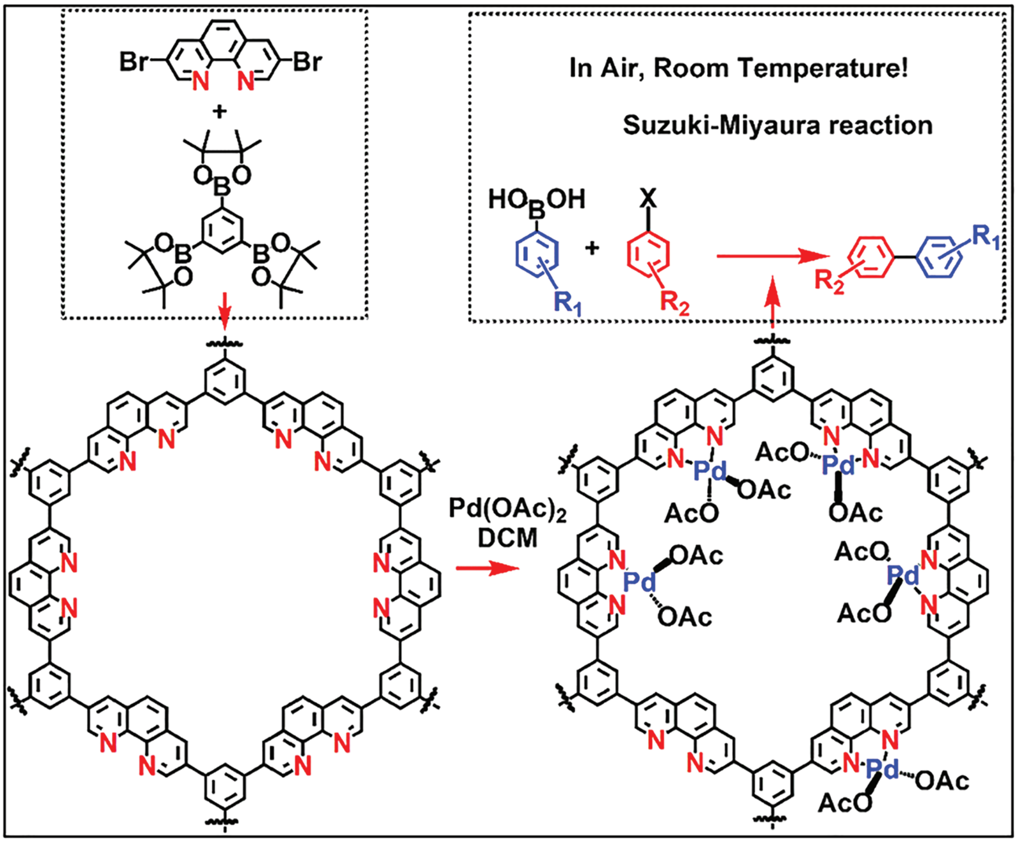
2.5 | Characterization

All reagents were commercially purchased and used without any further purification. The surface areas, pore size distributions of the support, pore volume and N_2 adsorption isotherms (77.3 K) were measured using Micromeritics ASAP 2020 M instrument. Before analysis, the samples were dried in vacuum oven and then degassed at 200 °C for 8 hr. FT-IR spectra were recorded on a Bruker VERTEX 70 FT-IR Spectrometer. TEM images were taken on a Tecnai G20 microscope (FEI Corp., Oregon, USA) instrument. Pd content data were obtained on Perkin Elmer AA-800 (Massachusetts, America). XRD patterns were recorded on an X'Pert PRO X-ray diffractometer with Cu Kα radiation. SEM images were obtained on a FEI Sirion 200 scanning electron microscope at 10.0 kV. XPS was performed in a VG multilab 2000 spectrometer, using an Mg-Al Ka X-ray source with the passing energy flow of 100 eV. The samples were degassed in a chamber at 5×10^{-10} mbar at room temperature. C1s transition was adjusted at 284.6 eV. Thermogravimetric (TGA) data were recorded on a PerkinElmer Diamond TG/DTA instrument.

3 | RESULTS AND DISCUSSION

3.1 | Catalyst characterization

As the Scheme 1 shown, phenanthroline based polymer CPP was synthesized by a simple Suzuki-Miyaura coupling reaction from 1,3,5-phenyltriboronic acid tris-(pinacol) ester and 3,8-dibromo-1,10-phenanthroline. The resulted CPP material is stable in common solvents such as water, ethanol, methanol, THF, dichloromethane, DMF, DMSO, acetone and trichloromethane, etc, which favors its application in heterogeneous catalysis as catalyst support. The FT-IR spectrum of 1,3,5-phenyltriboronic acid tris-(pinacol) ester, 3,8-dibromo-1,10-phenanthroline and the derived CPP polymer are shown in Figure 1. 1,3,5-phenyltriboronic acid tris-(pinacol) ester monomer shows a strong stretch at 2975–2845 cm^{-1} for methyl.[56] It can be seen that the peak around 3037 cm^{-1} emerged in the FT-IR spectra for both the raw material and the derived polymer, which can be attributed to the aromatic C-H stretching vibrations for all the compounds.[57] A broad absorption band at 3500–3280 cm^{-1} was observed in the FT-IR spectrum of resulting polymer, attributed to the existence of lattice or coordinated water in the polymer.[58] Compared with the adopted raw material of 1,3,5-phenyltriboronic acid tris-(pinacol) ester, the strong stretching peaks at 2975–2845 cm^{-1} for methyl disappeared, suggesting that the success of the polymerization of 1,3,5-phenyltriboronic acid tris-(pinacol) ester and 3,8-dibromo-1,10-phenanthroline. As shown in Figure 1, the peak at 1633 cm^{-1} is attributed to the stretching vibration peak of the C=N bond. Moreover, the distinct peak at 1401 belong to the deformation vibration of the benzene ring in aromatic skeleton of the polymer. The C=C and C=N bond infrared absorption peak confirmed the success of polymer syntheisis. After the loading of active metal, the stretching vibration peak of the C=N bond moves to 1584 cm^{-1}, which may be caused by the formation of a coordination bond between the N atom and the palladium ion. Furthermore, the solid state 13C CP/MAS NMR was further used to confirm the successful synthesis for phenanthroline based CPP polymer and its result was shown in Figure 2. The resonance peaks at 162.3, 145.1, and 124.7 ppm could be assigned to unsaturated aromatic carbons (C=N bond) in the phenanthroline units,[59] clearly indicating that the



SCHEME 1 Synthesis diagram towards the Pd-CPP catalyst for Suzuki-Miyaura Coupling Reaction

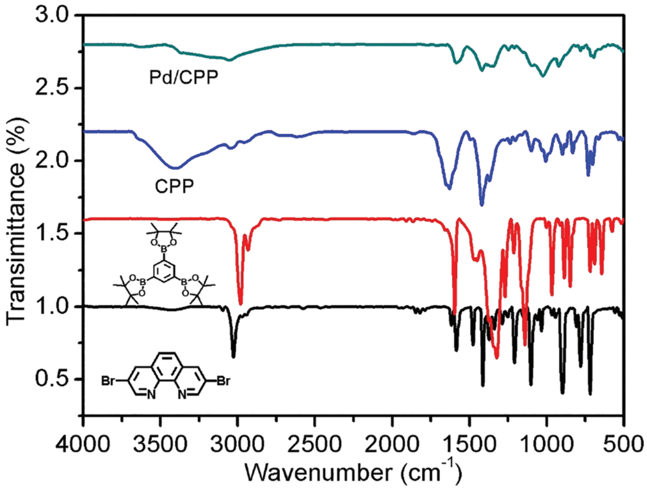


FIGURE 1 FT-IR spectra for the starting materials and the derived CPP

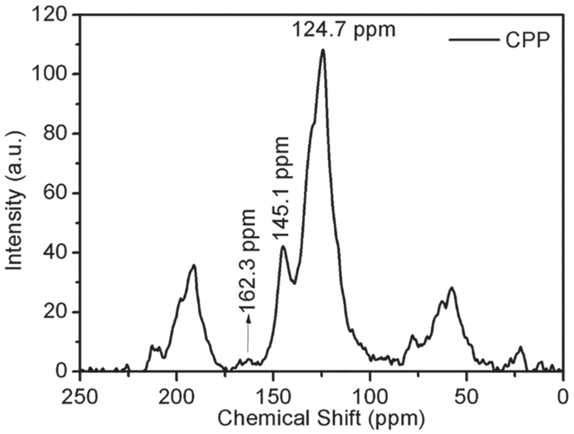


FIGURE 2 The 13C CP-MAS NMR spectroscopy of CPP polymer

phenanthroline monomers were integrated into the skeleton of the CPP polymer through the Pd catalyzed Suzuki-Miyaura condensation reaction. Obviously, both the 13C CP/MAS NMR and FT-IR results confirmed the successfully integration of the phenanthroline into the porous polymer.

The morphology and microstructure of CPP were observed through scanning electron microscope (SEM) and transmission electron microscope (TEM). SEM image of CPP in Figure 3a shows a lump-like morphology with honeycombed porous structure. The boundaries of the TEM image in Figure 3b show the layered arrangement of CPP polymer. Figure 3c shows the TEM image of Pd/CPP, which displays an analogous morphology to the original CPP, suggesting a good stability in organic solvent. The thermal stability of the solid CPP materials was studied by thermogravimetric analysis (TGA) under N_2

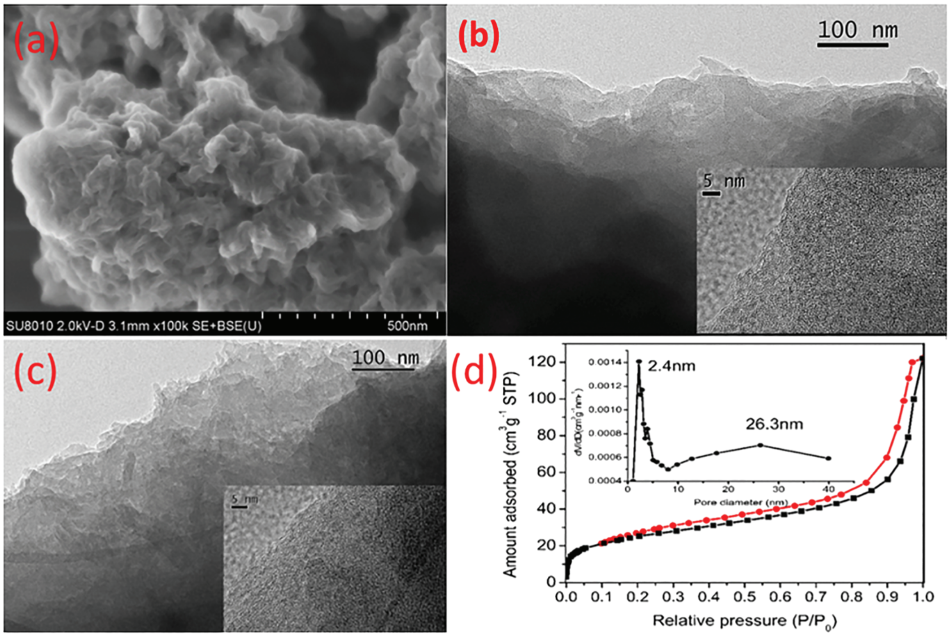


FIGURE 3 (a) FE-SEM image of CPP; (b) TEM image of CPP; (c) TEM image of Pd/CPP; (d) nitrogen sorption isotherms and the pore size distribution curve (inset)

atmosphere. The obtained thermal plots for CPP polymer material was as shown in Figure S1 in supporting information (SI). The weight loss at 450 °C was just 10%, suggesting that the obtained porous polymer shows a good thermal stability. Wide angle X-ray diffraction was used to study the crystalline structure of CPP polymer. XRD pattern for CPP material in Figure S2 exhibits a board peak at 2θ value of 23.5° with no other characteristic diffraction peak, implying the amorphous nature of the phenanthroline based polymer. Compared with the XRD of the CPP material, there is only one board characteristic peak at 23.5° in the XRD spectrum, indicating that the structure of the catalyst is also amorphous.

The textural properties of the derived CPP polymer are very critical parameters for heterogeneous catalysts and analyzed by N_2 sorption analysis. The nitrogen sorption isotherms of CPP, as shown in Figure 3d, exhibit a IV type isotherms with a sharp uptake of nitrogen gas when relative pressure (P/P_0) under 0.001, indicating the existence of microporous structure. Additionally, an obvious rise from the middle to the high relative pressure ($P/P_0 = 0.8–1.0$) means the existence of macropores in the polymer architecture. The pore size distribution curve, as shown in Figure 3d inset, also verified the coexistence of primary micropore, meso- and macro-pore, which may resulted from piled pore and the intrinsic porosity.[60] The BET surface area of CPP was calculated to be 141 m^2/g.

X-ray photoelectron spectroscopy (XPS) measurement was performed to further analysis the state of Pd species in Pd/CPP catalyst. As shown in Figure 4, the XPS spectra of the fresh Pd/CPP exhibits two peaks around the binding energy (B.E.) of 337.6 eV and 342.8 eV, revealing that Pd species in the CPP were present in +2 oxidation state rather than in metallic state.[9,10] Moreover, the binding energy for +2 state Pd in Pd/CPP catalyst shifted 0.6 eV to nether more value in contrast to that of 338.4 eV for Pd element in Pd $(OAc)_2$. This negative shift suggests the strong coordination interaction of active Pd ions with the N atoms in the CPP polymer: electrons gravitate toward Pd ions, which increases the electron density of Pd ions and makes the +2 state Pd ions minor electron-deficient, which is agrees well with XPS experiment results of N species.[10]

3.2 | Catalytic performance for Suzuki-Miyaura coupling reaction

The palladium-catalyzed Suzuki reaction is a powerful means to construct C-C bond in organic synthesis. The

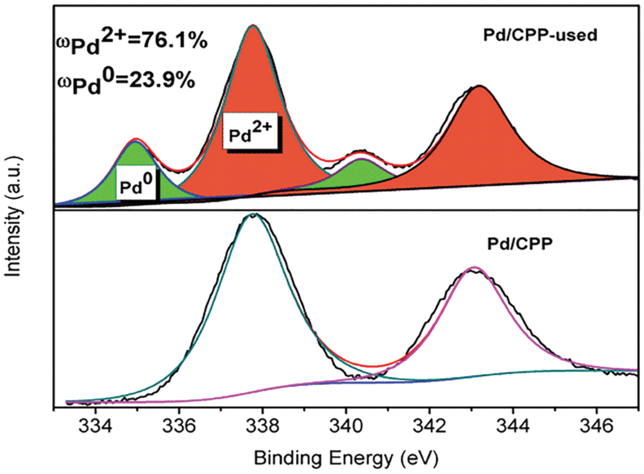


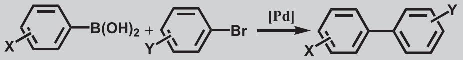
FIGURE 4 XPS spectra of fresh Pd/CPP and the used Pd/CPP catalysts

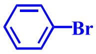
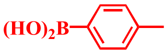
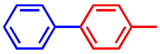
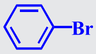
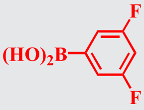
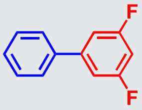
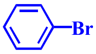
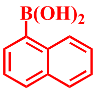
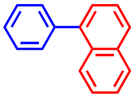
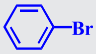
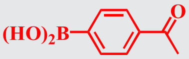
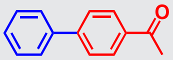
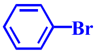
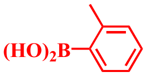
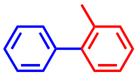
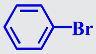
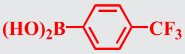
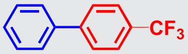
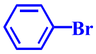
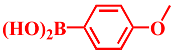
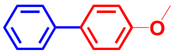
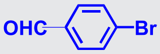
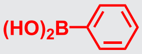
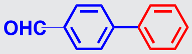
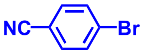
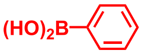
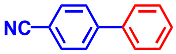
catalytic performance of the Pd/CPP catalyst in heterogeneous Suzuki reaction was systematically investigated. Firstly, bromobenzene was chosen as model substrate to optimize the reaction conditions. The Suzuki reactions were examined on Pd/CPP catalyst using $K_3PO_4 \cdot 3H_2O$ as a base in air atmosphere and at room temperature (25 °C), and various solvents were used (Table S1, entries 1–12 in supporting information). Noticeably, Pd/CPPs worked more efficiently when using a green solvent of ethanol and water ($V_{ethanol}:V_{water} = 1:1$) than other common solvents, attributed to the presence of hydroxyl group in alcohol molecule, which endows it a hydrogen bond donor, and thus facilitates the C-Br bond dissociation of halides and boost the coupling reaction.[61] The influence of the bases on the catalytic property of the present heterogeneous reactive system was also investigated with the ethanol and water ($V_{ethanol}:V_{water} = 1:1$) as solvent. As shown in Table S1, it can be found that K_2CO_3 worked the best performance compared with $K_3PO_4 \cdot 3H_2O$, CH_3COOK, KOH, Na_2CO_3, $Na_3PO_4 \cdot 12H_2O$ and NaOH (Table S1, entries 13–18). To rule out the catalytic action of the light, the Suzuki reaction also carried out in the dark. It was found that there is no significant difference in catalytic performance compared with the catalytic reaction in the light with all other things being equal (Table S1, entries 19). Without the component of Pd, the pure CPP polymer showed no conversion of the bromobenzene raw material, conforming that the catalytic activity stems from the active component of Pd (Table S1, entries 20). As showed in Table S1, the yield of the target reaction product was very low catalyzed by Pd $(OAc)_2$ and 1,10-Phenanthroline coordinated Pd $(OAc)_2$, indicating that the CPP polymer as scaffold plays an important role in catalytic process (Table S1, entries 21 and 22). The superior catalytic performance of Pd/CPP to Pd $(OAc)_2$ and 1,10-Phenanthroline coordinated Pd $(OAc)_2$ may be attributed to the strong coordinating ability of the CPP support toward metals ions and the rich porosity, in which, the former enables a highly uniform dispersion of Pd, while, the later provide a unique confined space for the substrate molecule and the catalytically active sites. To judge whether the heterogeneous Pd/CPP catalyst or the dissolved homogeneous Pd species were the actual active component responsible for the Suzuki reaction, the hot filtration experiment was tested.[62] When 92.9% of bromobenzene is converted into biphenyl in 20 mins at room temperature and in air, the catalyst in the reaction system was filtered and then the filtrate was heated to react continuously for another 2 hr under the previous reaction conditions. After hot filtration, the yield of the target product is 92.7%, showing no further conversion of the raw materials without the participation of Pd/CPP. The hot filtration test indicates that the heterogeneous Pd/CPP is the effective catalytic component instead of homogeneous leaked Pd^{2+} ions (Table S1, entries 23).

After acquiring the optimal reaction conditions, the couplings of various other aryl bromides derivatives with phenylboronic acid were then proceeded at room temperature (25 °C) in air with ethanol-water as solvent. The reactions of bromobenzene with different arylboronic acids derivatives were also conducted under the same mild reaction conditions (shown in Table 1, entries 1–8). As shown in Table 1, the electron-donating substituents on the arylboronic acid can reacted smoothly and yield their corresponding products with high conversion and selectivity, while electron-withdrawing groups substituted arylboronic acid derivatives exhibited lower yield than electron-donating groups substituted ones under the same reaction conditions. Aryl bromides of various electronic characters also reacted smoothly with unsubstituted phenylboronic acid substrates at 25 °C in air atmosphere within 1 h (Table 1, entries 9–13). Electron-deficient aryl bromides generally exhibited better catalytic performance than electron-rich ones.[9] To extend the testing scope of substrates, the catalytic performance of Pd/CPP catalyst in Suzuki reaction of chlorlbenzene and 4-Chlorotoluene was further tested. The heterogeneous catalyst produced their corresponding biphenyls with excellent activity with halide/Pd ratio at 0.55 mol % at 80 °C within 5 hr, (Table 1, entries 14–16). Motivated by the exciting results of Pd/CPP catalyst in Suzuki reactions of aryl bromides and phenylboronic acids under mild reaction conditions, the catalytic reaction towards the coupling of phenylboronic acid and benzyl chloride were also examined. The catalyst acquired 71.2% yield of diphenylmethane within 5 hr, which demonstrates that Pd/CPP catalyst has high activity (Table 1, entries 17).[63,64]

The Pd based catalyst catalyzed Suzuki reaction has been widely used in homogeneous media for the versatile construction of C-C bouds.[65–71] However, their practical application is still limited due to the difficulty in reusability.[9] In addition, high reaction temperature, inert gas protection and environment unfriendly solvent is usually inevitable. Developing an efficient and recyclable Pd based heterogeneous catalysts is thus a hopeful solution. One of the main advantages of the heterogeneous catalyst is the separation and the recycling of the catalyst.[5] To study the recycling performance of the Pd/CPP catalyst in the present Suzuki reaction, the reaction of phenylboronic acid and bromobenzene at 25 °C in air and in ethanol-water mixed medium was selected. After recycled for five runs, the result (Figure 5) shows that there is no obvious change in catalytic activity in the first three runs. However, the catalytic activity of the solid Pd/CPP

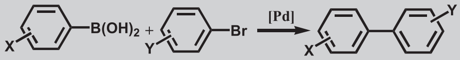
TABLE 1 Effect of aryl halides and aryl boronic acid on Suzuki-Miyaura reaction over Pd/CPP [a] catalyst

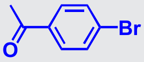
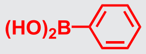
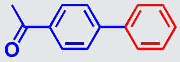
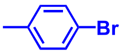
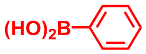
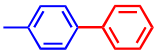
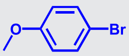
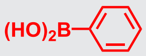
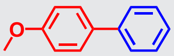
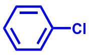
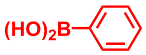
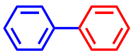
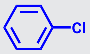
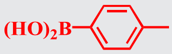
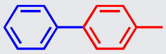
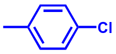
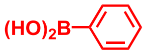
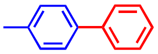
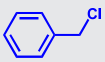
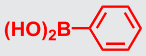
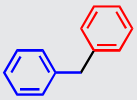


Entry	Substrate 1	Substrate 2	Product	*t* (h)	Yield (%)[b]
1				1	99
2				1	93
3				2	98
4				2	97
5				1	99
6				1	95
7				1	99
8				1	99
9				1	98

(Continues)

TABLE 1 (Continued)



Entry	Substrate 1	Substrate 2	Product	*t* (h)	Yield (%)[b]
10				1	97
11				1	93
12				1	99
13[c]				5	94
14[c]				5	98
15[c]				5	82
16[c]				1.0	93

[a] 0.55 mol % Pd, 0.5 mmol of aryl halide, 0.75 mmol of arylboronic acid, 1.5 mmol of $K_3PO_4.3H_2O$, 3 ml solvent (v (EtOH): v(H_2O) = (3:2)), 25 °C, In Air

[b] Isolated yield.

[c] 80 °C, In N_2 atmosphere.

catalyst reduced slightly in the last two recycle test. To ascertain the deactivation cause of catalyst, the content of Pd in Pd/CPP catalyst after five runs was determined to be 2.94% by atomic absorption spectroscopy (AAS) analysis (vs 2.94% Pd in the fresh Pd/CPP catalyst), which indicates an excellent stability of the Pd/CPP catalyst during the coupling reaction. In addition, the TEM image (Figure S3) of the catalyst after the fifth run showed that metallic Pd nanoparticles with uniform size of 5 nm (Figure S4) generated in reused catalyst, indicating that partial Pd^{2+} ions were reduced into the metallic Pd nanoparticles during the coupling reactions. The pore parameter of used catalysts analyzed by N_2 sorption analysis and the result was shown in Figure S5. The sharp uptake of nitrogen gas at relative pressure (P/P_0) under 0.001 disappeared after reuse, impling the micropores in the Pd/CPP catalyst was disappeared. Furthermore, the BET surface area of reused Pd/CPP catalyst decreased from 141 m^2/g (Pd/CPP) to 101 m^2/g, which may be caused by the blockage of microporous by active metal. Part

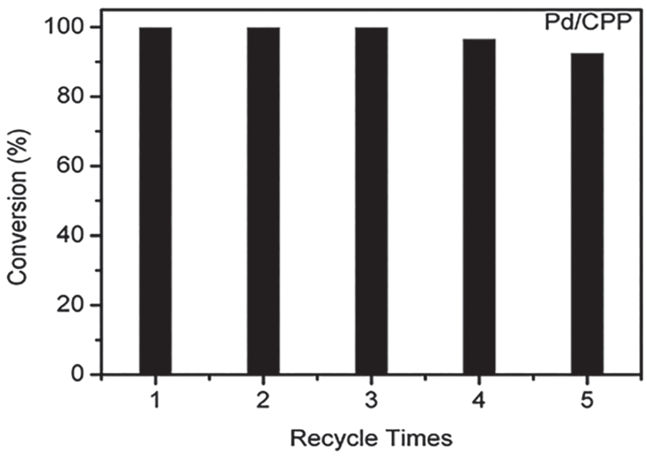


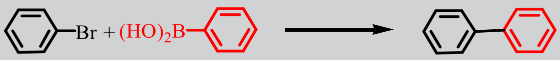
FIGURE 5 Recycle use performance of Pd/CPP catalyst for Suzuki-Miyaura reaction

Pd ions was reduced into Pd nanoparticles during the Suzuki-couling reaction process. The resulted Pd nanoparticles was highly dispersed in the structure of the catalyst, which may blocked the micropores and reduced the special surface area. The XPS results further verified that about 23.9 at % Pd^{2+} ions were reduced into the metallic Pd nanoparticles (Figure 4). Therefore, the loss of active specie of Pd^{2+} into Pd nanoparticles maybe account for the reduction in the catalytic activity during recycling use. As the Table 2 shown, the TOF value in the literatures were between 11 and 802 h^{-1} with similar reaction conditions, however, the TOF of this work was 1037 h^{-1}, indicating that the catalyst has exhibited very excellent catalytic properties for the coupling of bromobenzene and phenylboronic acid.

4 | CONCLUSION

In summary, for the first time, a phenanthroline based polymer materials (CPP) was synthesized by simple Suzuki-Miyaura coupling reaction. After anchoring of Pd $(OAc)_2$ into CPP polymer skeleton, the derived Pd/CPP catalyst exhibits a superior catalytic activity towards Suzuki reaction, in which the Pd/CPP catalyst can build C-C bonds by a board scope of the reactants at room temperature, in ethanol-water medium and in air with an excellent yield and recycling catalytic performance due to the strong coordinating ability of the CPP support toward metals ions and the rich porosity, enabling a highly uniform dispersion of Pd and providing a unique confined space for the substrate molecule and the catalytically active sites. It is believed that the phenanthroline based CPP scaffold could act as a stable, robust and versatile supports and host a variety of metal ions or nanoparticles for catalyzing a wide scope of reactions. Moreover, the presented strategy in designing phenanthroline based polymer loaded Pd catalyst for Suzuki reaction under very mild conditions may provide an alternative route to develop new green, efficient and recyclable catalytic systems for C-H activation, Buchwald-Hartwig amination and Hydrogen Evolution.

TABLE 2 Activity comparison of Pd catalyst in the SM reaction of bromobenzene in our research and references



Entry	Catalyst	Time(h)	Yield(%)	TOF(h^{-1})
1[16]	Pd@Al_2O_3-agarose	2	95	280
2[17]	Pd/CeO_2	3	89	11
3[18]	Pd@Cdots@Fe_3O_4	2	98	223
4[19]	Fe@FexOy/Pd	4	95	48
5[22]	Fe_3O_4/Ethyl-CN/Pd	1	96	124
6[25]	Fe_3O_4/Py/Pd (0.02)	0.66	98	132
7[30]	Fe_3O_4@TA/Pd	3	96	320
8[32]	L-arginine/$PdCl_2$ (1)	1	96	112
9[70]	PdNPs@[Bmim]Lac	4	94	24
10[26]	SBA-15/1,3-DCG/Pd	1	98	802
11[27]	Pd@PS-Met	4	96	240
12	Pd/CPP	1	95	1037

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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