Amine-Functionalized Graphene Oxide-Stabilized Pd Nanoparticles (Pd@APGO): A Novel and Efficient Catalyst for the Suzuki and Carbonylative Suzuki–Miyaura Coupling Reactions

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Supporting Information

ABSTRACT: Palladium nanoparticles (NPs) are decorated on the surface of an amine-functionalized graphene oxide (Pd@APGO) and characterized by using various analytical techniques. In this methodology, the surface of graphene oxide is modified using the amine functional groups which help stabilization and distribution of Pd NPs very well and increases the surface electron density of NPs by electron donating from amine groups. This developed catalyst shows a high catalytic activity toward the Suzuki coupling and carbonylative Suzuki–Miyaura coupling reactions at mild reaction conditions. The amine on the graphene oxide plays a very crucial role to stabilize and increase the electron density of Pd NPs and prevents the leaching of Pd metals. The Pd@APGO catalyst showed excellent catalytic activity (>90%) with a large range of substrates for both of the reactions and provides five recycle runs without the loss of its activity.

■ INTRODUCTION

In recent years, the use of nanocatalysts [nanoparticle (NPs)] has been a rapidly growing area because of their excellent efficiency and selectivity in catalysis.1–3 The inimitable properties and the enhanced performances of nanomaterials depend on their sizes, shapes, and supports. The combination of metal NPs with a proper support of choice gives a vast scope for the discovery of innovative and highly active catalysts which have industrial importance. Several systems have been established to immobilize palladium on a wide range of solid supports, such as microporous polymers,2–4 mesoporous silica,5–9 amorphous silica,10,11 magnetic material,5–12 and carbon nanofibers.13,14 However, a limited development of catalytic activity was found and recognized to the mass transfer control. Hence, there is a quick need to develop more efficient catalysts with proper support.

Among the various supports studied, the graphene oxide (GO) and functionalized GO get intense attention because of the unique structural and surface properties.15 Additionally, GO has the high surface area and the presence of abundant oxygen-containing functionalities such as phenolic, carboxylic which are tunable in nature.10–12 In particular, much attention has been focused on the amine-functionalized materials because the amines are well-recognized to stabilize metal NPs, avoid the aggregation of NPs without disturbing their appropriate properties, and are also anticipated to increase the catalytic activity of NPs.23–25 Recently, Bäckvall et al. immobilized Pd NPs on amine-functionalized aminopropyl (AmP)-functionalized siliceous mesocellular foam (Pd0-AmPMCF).26 This Pd0-AmPMCF catalyst shows high catalytic activities toward the Suzuki cross-couplings and hydrogenation of alkenes,27 in racemization of the amines,28 aerobic oxidation alcohols,28 and in selective transfer hydrogenation of nitroarenes to anilines.29 Jones and co-workers utilized amino polymer-silica composites containing amine functional group to support the Pd metal, and this material’s high catalytic activity toward the selective hydrogenation of alkenes.30 Very recently, Yang et al. synthesized amine-rich silica hollow nanospheres and utilized for the quinoline hydrogenation reaction.31

A wide variety of coupling reactions such as Heck,32 Suzuki,33 and Sonogashira34 reactions have been efficiently studied by the supported metal catalysts. Among them, the palladium-catalyzed cross-coupling reaction of aryl halides with aryl boronic acids is the most popular method for the construction of the unsymmetrical biaryls structures. Biaryls have attracted enormous interest because they are used as important units in...
molecular components, such as pharmaceuticals, natural products, herbicides, and in engineering materials, such as conducting polymers, molecular wires, and liquid crystals. Traditionally, for the Suzuki coupling reaction, homogeneous palladium/phosphine complexes have been utilized, which are generally toxic, unstable in moisture and air, rarely recoverable and expensive in nature. Still, Pd catalysts with phosphine-free heterogeneous Pd catalysts with green alternatives to the conventional homogeneous ones are needed.

By envisioning the high surface area and functional nature of GO, the property of amine functional group toward the stabilization and distribution of NPs offers an increased catalytic activity of metal NPs. Herein, by considering the electron-donating and coordination properties of amine to metal NPs, we synthesized, characterized Pd NPs on amine-functionalized GO and utilized for the Suzuki and carbon-ylative coupling reactions.

## RESULTS AND DISCUSSION

### Characterization of Catalyst

The overall synthetic procedure of Pd@AP-GO (see the Experimental Section and the Supporting Information for a detailed procedure) is shown below (Figure 1). The as-synthesized Pd@APGO catalyst was characterized by using various analytical techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The SEM images of the synthesized Pd@APGO catalyst showed the well-organized distribution of Pd NPs on the surface of the amine-functionalized GO (Figure 2). The surface of GO with amine functional group helps for the stabilization of NPs. When only GO was used instead of the amine-functionalized ones for the deposition of Pd NPs, the agglomerated distribution of Pd NPs on the surface of GO was found (Supporting Information S1). Then, the synthesized material was characterized by using TEM analysis, which showed that the spherical Pd NPs are well-distributed on the surface of the amine-functionalized GO. The average particle size of Pd NPs ranges from 4 to 10 nm (Figure 3). The particle size distribution was calculated, and it was observed that the maximum particle sizes were 7 nm, mainly 8 and 9 nm (Supporting Information S2). Next, XPS was performed to measure the elemental composition. The overall XPS spectrum shows the presence of all of the expected elements such as C, N, O, Si, and Pd (Figure 4a). The Pd0 state of the Pd metal was further confirmed by the XPS peak at 334.55 eV (Figure 4b).

Figure 1. Schematic presentation of Pd@AP-GO catalyst.

Figure 2. SEM images of the synthesized Pd@APGO catalyst (a,b).

Figure 3. (a,b) TEM images of showing the presence of Pd NPs on the surface of APGO and (c,d) closure view of NPs showing small NPs.

Figure 4. (a) Overall XPS spectral survey and (b) XPS analysis of Pd in Pd@APGO catalyst.
Application of Pd@APGO for the Suzuki Coupling Reaction. The prepared Pd@APGO catalyst was then investigated for the carbon–carbon bond formation reactions. The Suzuki cross-coupling reaction was selected, as it is one of the central reactions from a viewpoint of its versatile applications. For an effective cross-coupling, the use of basic conditions is effective. The iodobenzene and phenylboronic acids were utilized for the optimization of reaction conditions (Table 1). Initially, we have studied the effect of various solvents (Table 1, entries 7–11). Whereas the use of organic bases such as Et3N and DABCO also provides good to moderate yields of biaryls (Table 1, entries 12–21). Next, for the comparative study, the Pd NPs supported on the bare GO (Pd@GO) were also tested for the coupling reaction, and it was found that Pd@GO exhibited a lower activity (72%) than the Pd@APGO catalyst. This indicates that the presence of amine functional groups along with other groups help to increase the activity of Pd NPs by electron donation. The catalytic activity of Pd@APGO was compared with reported Pd0-AmPMCF (which utilizes MW), and it was found that the Pd@APGO shows comparable activity and utilizes lower temperature (Table 1, entry 19–20). Additionally, the catalytic activity of Pd@APGO was compared with the recently reported, highly active ASNTs@Pd, and it was found that the Pd@APGO shows similar activity (Table 1, entry 21).44

After the optimization of reaction conditions in hand, we have further extended the catalytic activity of the Pd@APGO for the substrate scope of biaryls (Table 2). The use of iodobenzene provides an excellent yield of biphenyl; then, the use of the reaction was investigated; it was found that by decreasing the reaction temperature below 80 °C, the yield of biaryls decreased (Table 1, entries 14–16). To investigate the catalytic activity of the catalyst because of the presence of amine functional groups, the Pd@APGO(a) catalyst was synthesized (Supporting Information S3b). By decreasing the percentage of amine up to half level, a decreased yield of biaryls was noted (Table 1, entry 17). Next, a comparative study of the developed Pd@APGO catalyst with other catalysts was done (Table 1, entry 18–21). Next, for the comparative study, the Pd NPs supported on the bare GO (Pd@GO) were also tested for the coupling reaction, and it was found that Pd@GO exhibited a lower activity (72%) than the Pd@APGO catalyst. This indicates that the presence of amine functional groups along with other groups help to increase the activity of Pd NPs by electron donation. The catalytic activity of Pd@APGO was compared with reported Pd0-AmPMCF (which utilizes MW), and it was found that the Pd@APGO shows comparable activity and utilizes lower temperature (Table 1, entry 19–20). Additionally, the catalytic activity of Pd@APGO was compared with the recently reported, highly active ASNTs@Pd, and it was found that the Pd@APGO shows similar activity (Table 1, entry 21).44

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| entry | solvent base | T (°C) | yield (%) |
|-------|-------------|--------|-----------|
| 1     | toluene K2CO3 | 80     | 71        |
| 2     | dioxane K2CO3 | 80     | 68        |
| 3     | THF K2CO3    | 80     | 70        |
| 4     | CH3CN K2CO3  | 80     | 73        |
| 5     | water K2CO3  | 80     | 22        |
| 6     | ethanol K2CO3| 80     | 80        |
| 7     | water/toluene K2CO3 | 80 | 45        |
| 8     | water/EtOH K2CO3 | 80 | 96        |
| 9     | water/EtOH Na2CO3 | 80 | 90        |
| 10    | water/EtOH Cs2CO3 | 80 | 94        |
| 11    | water/EtOH NaOAc | 80 | 78        |
| 12    | water/EtOH Et3N | 80 | 73        |
| 13    | water/EtOH DABCO | 80 | 70        |
| 14    | water/EtOH K2CO3 | 60 | 90        |
| 15    | water/EtOH K2CO3 | 40 | 82        |
| 16    | water/EtOH K2CO3 | 30 | 75        |
| 17    | water/EtOH K2CO3 | 80 | 80        |
| 18    | water/EtOH K2CO3 | 80 | 70        |
| 19    | water/EtOH K2CO3 | 90 | 99        |
| 20    | water/EtOH K2CO3 | 90 | 26        |
| 21    | EtOH K2CO3   | 80     | 96.1      |

*Reaction conditions: iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (1.5 mmol), Pd@APGO (5 mg), and solvent (5 mL, 1:1 water/EtOH). Determined by GC, all reactions were carried out for 6 h. 4Pd@AP-GO(a). 4Pd@GO catalyst used. 4Pd0-AmPMCF, MW 15 min (ref 27). 4Pd0-AmPMCF 15 min (ref 27). 4ASNTs@Pd (ref 44).
bromobenzene and chlorobenzene as cheap aryl halides were also tested and it was found that as compared to the iodobenzene, bromobenzene provides a good yield, whereas chlorobenzene provides a moderate yield (Table 2, entry 1). Then, the phenylboronic acids comprising electron-withdrawing groups such as fluoro, chloro, and bromo were studied, and it was observed that all are well-tolerant under optimized reaction conditions and provide good to excellent yield of biaryls (Table 2, entries 2–4).

Next, the phenylboronic acids with electron-donating substituents such as methoxy and phenoxo at the ortho position were also tested, and they were also found to be reactive and provides the excellent yield (Table 2, entries 5–6). Then, the electron-donating group of phenylboronic acids at the meta position such as methyl, methoxy, and phenyl group also provides excellent yield of biaryls (Table 2, entries 7–9). Next, alkyl halides containing electron withdrawing groups such as fluoro, nitro, and carboxylic acids were tested, and it was found that they also provided an excellent yield of coupled products (Table 2, entries 10–12). Notably, the strong electron-withdrawing group similar to 4-nitrochlorobenzene was also well-tolerant and provides good yield. Then, the alkyl halides containing methoxy and phenoxo group also provided good yield (Table 2, entries 13–14). The electronically withdrawing substrate similar to 1-(3-iodophenyl)ethanone also provided a good yield of the coupled product (Table 2, entry 15).

**Catalyst showed excellent recyclability up to phenylboronic acid and aryl iodide. Notably, the Pd@APGO reaction condition for the Suzuki coupling reaction of a catalyst was investigated for the recyclability by using a standard iodopyridine, 2-iodothiophene, and 3-iodo-1-

**Carbonylative Coupling Reactions.** After the successful application of Pd@APGO for the Suzuki coupling reaction, the Pd@APGO catalyst then further utilized for the carbonylative Suzuki–Miyaura coupling reaction to synthesize biaryl ketones. The biaryl ketones are very important structural scaffolds found in a wide variety of the molecules. Among the various methods reported for the synthesis of biaryl ketones, carbonylative Suzuki–Miyaura coupling by using carbon monoxide (CO) as the C1 source is considered as the most prominent method because of the wide functional group tolerance. Number of homogeneous and heterogeneous palladium-based catalysts are well-documented in literature. By considering the high activity of synthesized Pd@APGO catalyst for the synthesis of biaryls, we applied for the synthesis of biaryl ketones by using CO, aryl halides, and aryl boronic acids. Initially, CO (2 bar), aryl iodide c (1 mmol), phenylboronic acid b (1.2 mmol), Pd@APGO (5 mg), anisole (10 mL), and K2CO3 (1.5 mmol) were utilized for the synthesis of biaryl ketones at 80 °C. The Pd@APGO catalyst provides an excellent yield of biaryl ketones up to 93% (Table 3, 16). Next, the substrate scope was studied by using the Pd@APGO catalyst. Various electron-donating phenylboronic acids such as methyl and methoxy were tested and a very good yield of the carbonylated product was noted (Table 3, 17, 18, and 19). Then, electron-withdrawing functional groups on boronic acids such as nitrile and nitro were tested for the carbonylative coupling reaction, and it was found that they also provided good yields of functionalized biaryl ketones (Table 3, 20 and 21). Interestingly, aryl iodides containing heterocycles were tested for the coupling reactions to synthesize the heterocyclic aromatic ketones such as 2-imidopyridine, 2-imidophenone, and 3-iodo-1H-indole, and the good yield was noted (Table 3, 22, 23 and 24).

**Recyclability of the Catalyst.** The developed Pd@APGO catalyst was investigated for the recyclability by using a standard reaction condition for the Suzuki coupling reaction of a phenylboronic acid and aryl iodide. Notably, the Pd@APGO catalyst showed excellent recyclability up to five recycle runs with negligible loss in its activity (Figure 5). To investigate the structural morphology after fifth recycles, the Pd@APGO catalyst again were characterized by using SEM analysis; no structural changes occurred after recyclability (Figure 6).

**CONCLUSIONS**

In conclusion, we have developed Pd@APGO as a highly active catalyst for the synthesis of biaryls and biaryl ketones from the Suzuki and carbonylative Suzuki–Miyaura coupling reactions. Similar to the reported methods, it was found that the presence of amine groups on the surface of GO stabilizes Pd NPs and accelerates the reactivity of Pd NPs by electron donation of amine groups. A wide range of substrates of biaryls and biaryl ketones with heterocyclic rings are affordable by using the developed catalyst. High surface area and various functional groups on GO (hydroxyl and amine) avoids the leaching of Pd NPs. The synthesized Pd@APGO catalyst was well-charac-

**Table 3. Pd@APGO Catalyzed Synthesis Biaryl Ketones**

| Reaction Conditions | Yield (%) |
|--------------------|-----------|
| **HO-B** | | **CO** |
| | | **Pd@APGO** |
| | | **K2CO3, Anisole** |
| | | **80 °C, 8 h** |
| **16/93%** | | **17/91%** |
| **19/75%** | | **20/85%** |
| **22/40%** | | **23/48%** |
| **24/65%** | |

“Reaction conditions: aryl iodide (1 mmol), aryl boronic acid (1.2 mmol), CO (2 bar), K2CO3 (1.5 mmol), Pd@APGO (5 mg), and anisole (10 mL) at 80 °C for 8 h. Determined by GC.”

**Figure 5. Recyclability of the Pd@APGO catalyst.**

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General Procedure for the Suzuki Coupling Reaction. In a stainless-steel autoclave containing an automatic stirrer (100 mL), aryl iodide (1 mmol), aryl boronic acid (1.2 mmol), K$_2$CO$_3$ (1.5 mmol) containing anisole (10 mL), and 5 mg Pd@APGO were added and then flushed with CO twice. At the room temperature, the autoclave was pressurized with CO gas. After completion of the reaction, the autoclave was cooled to the room temperature, and the pressure of the CO gas was carefully released. Then, the reaction mixture was centrifuged for 15 min at 10 000 rpm, and Pd@APGO was separated from the reaction mixture. To afford a pure product, the synthesized substrates were purified by column chromatography (silica gel, 100–200 mesh size), with petroleum ether-ethyl acetate as the eluent. The products were confirmed by GC−MS and $^1$H and $^{13}$C NMR spectroscopic analysis. The same procedure was utilized for the recycling of the Pd@APGO catalyst.

**EXPERIMENTAL SECTION**

### General

All chemicals were purchased from diverse commercial sources and were used without further purification. The reaction was monitored by gas chromatography−mass spectrometry (GC−MS) and thin layer chromatography using Merck silica gel 60 F254 plates. The GC−MS-QP 2010 instrument (Rtx-17, 30 m $\times$ 25 mm i.d., the film thickness ($d_f$) = 0.25 μm (column flow 2 mL min$^{-1}$, 100−240 °C at 10 °C min$^{-1}$ rise) was used for the mass analysis of the products. Graphite (45 mm) was purchased from Wako Chemicals. Products were purified by column chromatography on 100−200 mesh silica gel. The $^1$H NMR spectra were recorded on 500 MHz spectrometers in CDCl$_3$ using tetramethylsilane (TMS) as an internal standard. The $^{13}$C NMR spectra were recorded on 125 MHz spectrometers in CDCl$_3$. Chemical shifts were reported in parts per million (δ) relative to TMS as an internal standard, and the $J$ (coupling constant) values were reported in Hz. The products were confirmed by GC−MS and $^1$H and $^{13}$C NMR spectroscopic analysis.

#### Synthetic Procedure of the Pd@APGO Catalyst

The GO is synthesized by using a modified Hummers method and then functionalized with an amine by using our previously reported method$^{21}$ (see Supporting Information S2 and for the synthesis of Pd@APGO(a), see Supporting Information S3b). The Pd@GOIL was prepared by using the general impregnation−reduction system. Typically, in 5 mL of deionized water, about 500 mg of AP-GO was dispersed under ultrasound. Then, the desired amount of PdCl$_2$ aqueous solution (0.016 g mL$^{-1}$) was added into the round-bottom flask. Then, the mixture was kept for an ultrasound treatment for 10 min, and a freshly prepared aqueous solution of NaBH$_4$ (9 mg mL$^{-1}$) was added slowly. Then, the reaction mixture was stirred for 30 min. Again, the ultrasound treatment was performed for 25 min; the resulting reaction mixture was filtered and the black powder product was washed several times under vacuum by using deionized water and EtOH. Then, the obtained reaction mixture was dried at 60 °C for 6 h. The presence of 5 wt % of Pd metal on the surface of APGO was confirmed by using inductively coupled plasma-atomic emission spectroscopy analysis.

#### General Procedure for the Suzuki Coupling Reaction

In a typical procedure, the in-reaction vial aryl halides (1.0 mmol), boronic acids (1.2 mmol), K$_2$CO$_3$ (1.5 mmol), Pd@APGO (5 mg), and water/ethanol (5 mL) as a solvent were taken. The reaction mixture was continuously stirred for 6 h at the desired temperature. Then, by adding 5 mL of EtOAc as a solvent in the reaction mixture, the catalyst and the product were separated by using centrifugation for 15 min at 10 000 rpm. To afford a pure product, the synthesized substrates were purified by column chromatography (silica gel, 100−200 mesh size), with petroleum ether-ethyl acetate as the eluent. The products were confirmed by GC−MS and $^1$H and $^{13}$C NMR spectroscopic analysis. The same procedure was utilized for the recycling of the Pd@APGO catalyst.

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