Monodisperse palladium nanoparticles supported on chemically derived graphene: highly active and reusable nanocatalysts for Suzuki–Miyaura cross-coupling reactions

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Abstract: Addressed herein is the catalysis of monodisperse palladium nanoparticles (NPs) supported on chemically derived graphene (CDG) for the Suzuki–Miyaura cross-coupling of phenylboronic acid and various aryl halides. Monodisperse Pd NPs were synthesized by the solution phase reduction of palladium(II) acetylacetonate with morpholine borane complex in oleylamine and deposited on CDG via the liquid phase self-assembly method. Colloidal Pd NPs and CDG-Pd catalyst were characterized by TEM, XRD, SEM, and ICP-MS analyses. The CDG-Pd catalyst showed high activity in the Suzuki–Miyaura cross-couplings of different aryl halides including iodides, bromides, and even chlorides with phenylboronic acid under mild conditions. More importantly, the reusability experiments revealed that CDG-Pd catalyst was highly durable by almost maintaining its inherent activity after the 15th catalytic cycle.

Key words: Palladium nanoparticles, graphene, heterogeneous catalyst, Suzuki–Miyaura, cross-couplings

1. Introduction

Noble metals have received wide attention due to their exclusive applications in various fields, especially in catalysis.[1] Among the common noble metals studied for catalysis, palladium (Pd) has been a popular choice as catalyst for various chemical reactions,[2] and was highlighted by the 2010 Nobel Prize in Chemistry for carbon–carbon (C–C) coupling reactions in organic synthesis.[3] In this regard, considerable effort has been devoted to the preparation of highly active Pd catalysts to facilitate C–C coupling reactions to reach high reaction yields in short reaction times.[4] Among the Pd-catalyzed C–C coupling reactions, the Suzuki–Miyaura couplings, which include the cross-coupling reaction of aryl halides with aryl boronic acids,[5] are emerging as a preferred method for $C(sp^2)$–$C(sp^2)$ bond formation and have a wide range of applications.[6,7] In general, Suzuki–Miyaura coupling reactions are preferred as the key step in the total synthesis of natural products and polymer synthesis because of their favorable properties such as the use of commercially available starting materials, the requirement of relatively mild reaction conditions, the tolerance of a broad range of functionalities, and the possibility of using water as a solvent or co-solvent. Traditionally, these coupling reactions are carried out by homogeneous Pd catalysts in the presence of ligands such as phosphines,[8,9] carbenes,[10] amines,[11] or Schiff bases[12] and are performed generally in organic solvents. However, problems such as the use of expensive poisonous phosphine ligands and difficulty of separation and recovery of homogeneous catalysts make the heterogeneous catalysts more

attractive for coupling reactions due to both economic and environmental concerns. In this respect, colloidal or supported Pd nanoparticles (NPs) having particle size smaller than 10 nm have been used as efficient catalysts for C–C coupling reactions.[13,14]

Recently, a variety of transition metal NPs have been tested as catalyst for Suzuki–Miyaura coupling reactions,[15,16] because their high surface-to-volume ratio makes them very attractive as catalysts in chemical reactions over the other bulk ones.[17,18] However, NPs are kinetically unstable in solution and frequently aggregate to yield bulk metal, which reduces the catalytic activity and selectivity.[19] In order to obtain stable NPs, they must be stabilized by macromolecular organic ligands/polymers or immobilized on a high-surface area solid support materials such as activated carbon,[20,21] zeolites/molecular sieves,[15,22] metal oxides,[23] clays,[24] organic polymers,[18] mesoporous silica,[25] and apatites.[26] In addition to these commonly used support materials, our recent studies revealed that chemically derived graphene (CDG) is a unique host material for metal NPs to be used as catalysts in organic reactions in green solvents owing to its glorious physical and chemical properties such as having 2D structural graphitic layers that help to adsorb the aromatic component in the reactant mixture via $\pi-\pi$ interactions, pulling them in close range contact with the catalysts.[27]

In this work, we report the catalytic performance of monodisperse Pd NPs assembled on CDG in Suzuki–Miyaura C–C coupling reactions of arylboronic acid with various aryl halides (Ar-X, X: Cl, Br, or I) in DMF/water (v/v = 1/9) mixture under relatively mild reaction conditions. By using a modified version of oleylamine-mediated synthesis protocol comprising the reduction of palladium(II) acetylacetonate with morpholine borane (MB) in oleylamine (OAm) 5 nm Pd NPs were prepared.[28] The colloidal Pd NPs were deposited on CDG via a liquid phase self-assembly method. Colloidal Pd NPs and CDG-Pd catalyst were characterized by transmission electron microscope (TEM) and X-ray diffraction methods. CDG-Pd catalyst was directly tested as catalyst in the Suzuki–Miyaura coupling reactions of various Ar-X (X: Cl, Br, or I) and phenylboronic acid and found to be efficient by yielding the respective coupling products reaching up to 97%. Moreover, CDG-Pd catalyst was a highly durable catalyst in the Suzuki–Miyaura coupling reactions by providing fifteen recycles with no observable Pd leaching and negligible loss in activity.

2. Results and discussion

2.1. Synthesis and characterization of monodisperse Pd NPs and chemically derived graphene supported Pd NPs

Monodisperse 5 nm Pd NPs were synthesized by using a modified version of the oleylamine-mediated synthesis protocol comprising the solution phase reduction of Pd(acac)$_2$ with MB in OAm at 70 °C. This is different from the previous report by Sun's group where the borane *tert*-butylamine complex (BBA) was used as a reducing agent to prepare Pd NPs in OAm.[28] In the current recipe, MB was found to be better for controlling the reducing kinetics of Pd(acac)$_2$ because it is a milder reducing agent than BBA. Figure 1A shows the representative TEM image of the colloidal Pd NPs taken from their hexane dispersion. As clearly seen from the TEM image and the associated particle size histogram (Figure 1B), these NPs have uniform size distribution with an average size of 5 nm and a standard deviation in diameter less than 10%, indicating monodispersity. The X-ray diffraction of the Pd NPs depicted in Figure 1C shows a typical pattern for a face centered cubic (fcc) crystal structure of Pd (JCPDS card no. 01-071-3757) and the broad (111) peak observed at $2\theta = 39.8°$ indicates that each NP has small crystalline size.
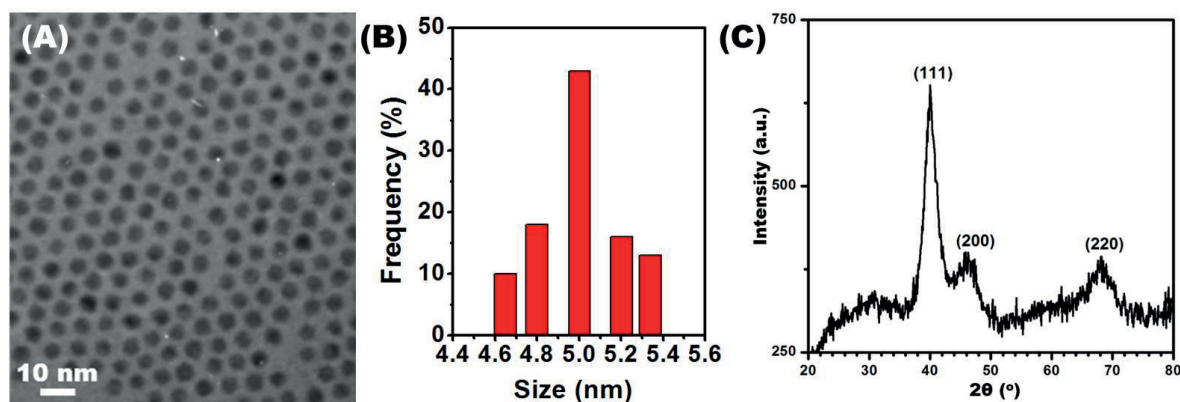
Figure 1. (A) A representative TEM image, (B) TEM image associated particle size histogram, (C) the XRD pattern of colloidal Pd NPs taken from their hexane dispersion.

Colloidal Pd NPs were deposited on CDG via a solution-phase self-assembly method including the sonication of hexane dispersion of Pd NPs and ethanol solution of CDG for 2 h at room temperature. Figure 2 shows a representative TEM image of CDG-Pd catalyst prepared by the solution phase self-assembly process. The image and the associated particle size histogram (the inset in Figure 2) reveal that the Pd NPs are almost uniformly deposited on the CDG nanosheets by preserving their initial size and morphology. The morphology and microstructure of Pd NPs as well as its support (CDG) were investigated by scanning electron microscope (SEM) and a representative SEM image is shown in Figure 3. The thin layered structure of CDG nanosheets with an irregular shape and topology were clearly seen in the SEM image, and the spherical Pd NPs are almost uniformly distributed over the CDG nanosheets.
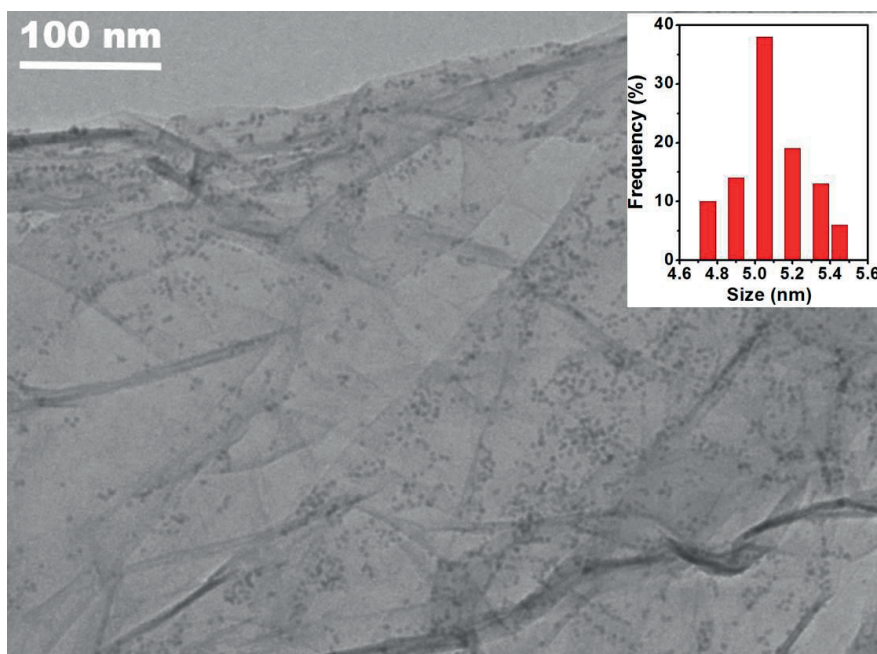

Figure 2. A representative TEM image for the Pd NPs supported on CDG (CDG-Pd). The inset shows the associated particle size histogram for the Pd NPs supported on CDG.
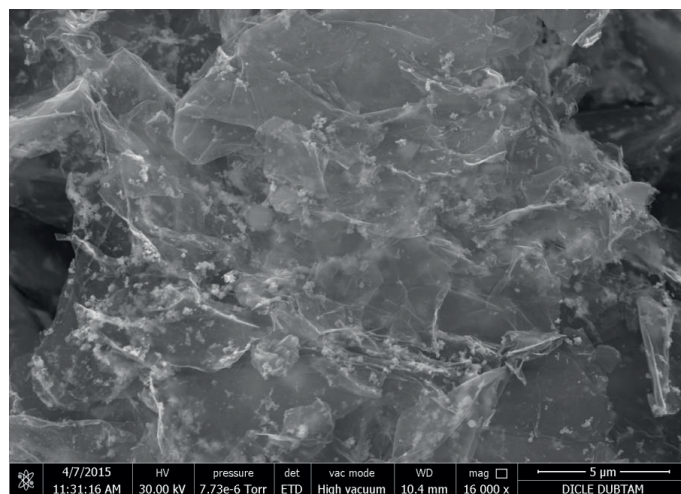
Figure 3. A representative SEM image of CDG-Pd catalysts.

2.2. Catalysis of monodisperse Pd NPs supported on chemically derived graphene (CDG-Pd) for the Suzuki–Miyaura cross-coupling reactions

The performance of CDG-Pd catalyst was studied in the Suzuki–Miyaura C–C coupling reactions of phenylboronic acid with various aryl halides including chlorides, iodides, and bromides. We firstly tested the catalytic activity of the CDG-Pd catalyst for the coupling of $p-$ bromoacetophenone with phenylboronic acid under aerobic conditions. It is noteworthy that the control experiments showed that the coupling reaction did not occur in the absence of the catalyst. Next, we studied the effect of the reaction conditions by conducting a series of optimization experiments with different solvents (water, dioxane, or DMF, as sole solvent or in DMF/water (8:2, 5:5, 1:9, respectively) mixture), bases (K_2CO_3, K_3PO_4, Cs_2CO_3, K^tBuO, NaOH), and temperature (25, 60, and 100 °C). Each catalytic reaction was carried out three times to examine reproducibility and the results are summarized in Table 1. The efficiency of the CDG-Pd catalyst was found to be dependent on the nature of the solvent, base, and temperature. For instance, there was no conversion of $p-$ bromoacetophenone when DMF, dioxane, or water was used as the sole solvent (Table 1, entries 1, 12, 15) at room temperature. We found that conversion of $p-$ bromoacetophenone to corresponding biaryl product reached up to 89% in the presence of K_3PO_4 within 24 h in water at 100 °C (Table 1, entry 6), while the conversion of $p-$ bromoacetophenone was negligible in DMF or dioxane as sole solvent at 110 °C (Table 1, entries 14, 17). The effect of base on the efficiency of CDG-Pd catalyst in the coupling reactions was also studied by testing several bases including K_3PO_4, K_2CO_3, Cs_2CO_3, K^tBuO, and NaOH. The CDG-Pd catalyst provided almost quantitative conversion to corresponding biaryl products in the presence of all tested bases (Table 1, entries 22–26), but the best result was obtained by K_3PO_4 within 20 min (Table 1, entry 22) in DMF/water (1:9) solvent system at 100 °C. Upon examining the results of optimization experiments, it was found that the best results in terms of yields and reaction times were obtained by using K_3PO_4 as a base in DMF/water (1:9) mixture at 100 °C within 20 min reaction times (Table 1, entry 22). It is noteworthy that the use of water is key to perform the reactions under reflux conditions (Table 1) and, moreover, the use of water as solvent instead of organic solvent is advantageous in the green chemistry context.[29,30]

It is well known that the reactivity of aryl chlorides towards Suzuki–Miyaura coupling reactions is lower than that of bromides or iodides under the same reaction conditions, which is due to the high dissociation

Table 1. Screening of reaction parameters for Suzuki–Miyaura cross-coupling reaction catalyzed by CDG-Pd catalyst.
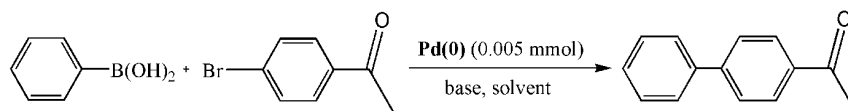
| Entry	Base	Solvent	T (°C)	Time	Conv.(%)^a
1	K_2CO_3	water	rt	24 h	-
2	K_2CO_3	water	60	24 h	73
3	K_2CO_3	water	100	24 h	87
4	K_3PO_4	water	rt	24 h	-
5	K_3PO_4	water	60	24 h	75
6	K_3PO_4	water	100	24 h	89
7	Cs_2CO_3	water	rt	24 h	-
8	Cs_2CO_3	water	60	24 h	84
9	Cs_2CO_3	water	100	24 h	83
10	K^tBuO	water	100	24 h	86
11	NaOH	water	100	24 h	84
12	K_3PO_4	DMF	rt	24 h	-
13	K_3PO_4	DMF	60	24 h	35
14	K_3PO_4	DMF	110	24 h	65
15	K_3PO_4	Dioxane	rt	24 h	-
16	K_3PO_4	Dioxane	60	24 h	-
17	K_3PO_4	Dioxane	110	24 h	< 10
18	K_3PO_4	DMF/water (8:2)	110	5 h	98
19	K_3PO_4	DMF/water (5:5)	110	3 h	95
20	K_3PO_4	DMF/water (1:9)	rt	24 h	-
21	K_3PO_4	DMF/water (1:9)	60	24 h	93
22	K_3PO_4	DMF/water (1:9)	100	20 min	97
23	K_2CO_3	DMF/water (1:9)	100	30 min	96
24	Cs_2CO_3	DMF/water (1:9)	100	30 min	99
25	K^tBuO	DMF/water (1:9)	100	30 min	97
26	NaOH	DMF/water (1:9)	100	30 min	94
27 ^{b}	K_3PO_4	DMF/water (1:9)	rt	24 h	-
28 ^{b}	K_3PO_4	DMF	110	24 h	-
29 ^{b}	K_3PO_4	water	100	24 h	-
30 ^{b}	K_3PO_4	DMF/water (1:9)	100	24 h	62

Reaction conditions: ^{a}p-bromoacetophenone, 1.0 mmol; phenylboronic acid, 1.5 mmol; Solvent, 10.0 mL; base, 2 mmol; CDG-Pd catalysts (0.005 mmol Pd determined by ICP-MS), open air atmosphere. ^{b}p-chloroacetophenone.

energy of Ph-Cl: 96 kcal/mol compared to the ones for Ph-Br: 81 kcal/mol or Ph-I: 65 kcal/mol that leads to reluctance by aryl chlorides to oxidatively add to Pd(0) centers, a critical initial step in Pd-catalyzed coupling reactions.[16,31−34] In this respect, we also tested the catalysis of CDG-Pd catalyst in the Suzuki–Miyaura coupling reaction of $p-$chloroacetophenone with phenylboronic acid in DMF/water (v/v = 1/9) solvent system. Although $p-$chloroacetophenone was found to be less reactive compared to the aryl iodides or bromides (Table 1, entry 27), the CDG-Pd catalyst provided the highest conversion of 62% in the presence of K_3PO_4 within 24 h in DMF/water (v/v = 1/9) solvent system at 100 °C (Table 1, Entry 30). In another test reaction, the use of water or DMF as the sole solvent did not provide improved conversion (Table 1, entries 28, 29).

Next, the catalytic efficiency of CDG-Pd catalyst having 11.76 wt % Pd loading determined by ICP-MS

with different substrates bearing either electron-donating or electron-withdrawing substituents ($p-$bromoacetophenone, $p-$bromobenzaldehyde, $p-$bromobenzo nitril, $p-$chlorobenzo nitril, 1-bromo-4-nitrobenzene, $p-$bromobenzene, $p-$iodobenzene, $p-$bromoacetophenone, and $p-$bromotoluene) was screened under the optimized conditions and the results are given in Table 2. As can clearly be seen, all the corresponding biphenyls were obtained in high yields reaching up to 98%. Of the nine different aryl halides used in the Suzuki coupling with phenylboronic acid, the ones with electron-withdrawing substituents gave the highest yield with TOF values (Table 2 entries 1–4). The coupling reactions of $p-$chlorobenzonitril with phenylboronic acid were also tested; the highest conversion reached up to 68% under optimized conditions within 15 h (Table 2, entry 5), which is very important for the practical utilization of the catalytic Suzuki–Miyaura coupling reactions. We also tested the catalysis of CDG-Pd in the Suzuki–Miyaura coupling of phenyliodide with phenylboronic acid in the presence of K_3PO_4, which yielded 96% coupling product in 10 min (Table 2, entry 7).

Table 2. The Suzuki–Miyaura cross-coupling reactions of aryl halides with phenylboronic acid catalyzed by CDG-Pd catalyst.
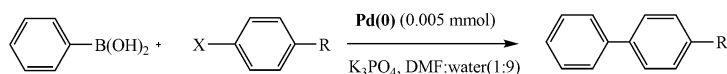
Entry	R	X	Product	Time (min)	Conv. (%)	TOF (h^{-1})
1	CH$_3$C(O)-	Br		20	97	582
2	CH(O)-	Br		20	92	562
3	-CN	Br		20	94	564
4	-NO$_2$	Br		20	98	588
5	-CN	Cl		15 h	68	10
6	-H	Br		30	91	364
7	-H	I		10	96	1162
8	CH$_3$O-	Br		120	85	86
9	CH$_3$-	Br		120	83	84

Reaction conditions: 1.0 mmol of p-R-C$_6$H$_4$X (aryl halide), 1.5 mmol of phenylboronic acid, 2.0 mmol base, CDG-Pd catalysts (0.005 mmol Pd determined by ICP-MS), DMF-Water (1:9), 100 °C; open air atmosphere; base; K$_3$PO$_4$. Purity of compounds was checked by NMR and yields are based on arylhalides. All reactions were monitored by GC; TOF = (mol product/mol Cat) × h^{-1}.

Finally, for the recycling experiment of CDG-Pd catalyst in Suzuki–Miyaura coupling reactions, the coupling of $p-$bromobenzaldehyde with phenylboronic acid was used as the test reaction in the presence of 0.005 mmol Pd that contained CDG-Pd catalyst under the optimized conditions. Figure 4 shows the catalytic run versus conversion % graph for the 15 consecutive catalytic runs. As can be clearly seen, CDG-Pd catalyst maintains 82% of its initial catalytic activity at the end of the fifteenth cycle of Suzuki–Miyaura coupling reactions. This result indicates that CDG-Pd catalyst is a highly durable catalyst that could be recycled in many successive runs without significant loss of initial activity for Suzuki–Miyaura cross-coupling reactions under the optimized conditions. A slight decrease was observed in the catalytic activity of CDG-Pd catalyst during the nine consecutive runs, which might be due to the passivation of the surface of NPs by boron-containing side products.[15,35−38]
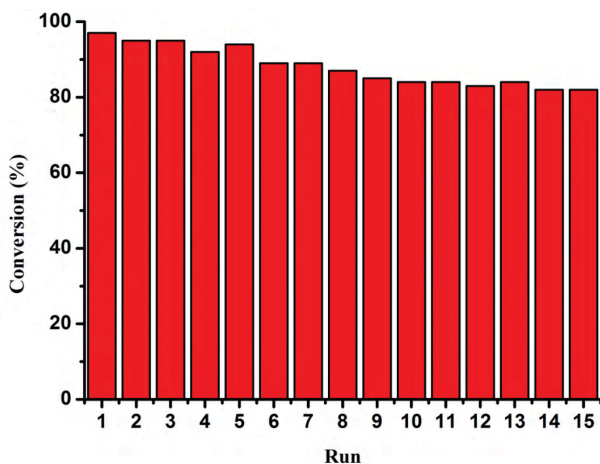

Figure 4. A recyclability test for CDG-Pd catalysts in the Suzuki–Miyaura cross-coupling reaction of $p-$bromoacetophenone with phenylboronic acid in DMF/water (1:9) solvent system under optimized reaction conditions.

In summary, we have successfully demonstrated that monodisperse Pd NPs supported on CDG were highly active catalysts in the Suzuki–Miyaura cross-coupling reactions of phenylboronic acid with aryl halides, even aryl chlorides, under moderate conditions. The CDG-Pd catalyst was also stable and could be recycled for the cross-coupling reactions, providing 82% conversion after the 15th successive run without noticeable leaching of Pd. The CDG-Pd catalyst reported herein combines both the efficiency of a homogeneous Pd catalyst and the durability of a heterogeneous catalyst, and we think that it will be a promising catalyst candidate for various Pd-based catalytic applications.

3. Experimental

3.1. Materials

Oleylamine (OAm, $>$70%), palladium(II) acetylacetonate (Pd(acac)$_2$, 99%), morpholine borane complex (MB, 95%), hexanes (99%), all the chemicals used for the synthesis of chemically derived graphene except natural graphite flakes (KMnO$_4$, H$_2$O$_2$ (30%), NaNO$_3$, H$_2$SO$_4$ (98%), dimethylformamide (DMF)), and all the chemical used in the Suzuki–Miyaura coupling reactions were purchased from Sigma-Aldrich and used as received. Natural graphite flakes (average particle size 325 mesh) were purchased from ABCR GmbH & Co. and used without any further treatment. Deionized water was purified by water purification system (Milli-Q System).

3.2. Characterization methods

Samples for TEM analyses were prepared by depositing a single drop of sonicated Pd NPs or CDG-Pd dispersed in hexane or ethanol, respectively, on amorphous carbon coated copper grids. TEM images were taken on a FEI Tecnai G^2 Spirit BiO(TWIN) at 120 kV. X-ray diffraction (XRD) patterns were obtained by a Rigaku Miniflex diffractometer with Cu Kα radiation (30 kV, 15 mA, $\lambda = 1.54051$ Å) over a 2θ range from $10°$ to $90°$ at room temperature. The palladium content of the CDG-Pd catalyst was determined by an Agilent 7700X inductively coupled plasma mass spectroscope (ICP-MS) after the powdered sample was completely dissolved in aqua regia (v/v (HNO$_3$/HCl)= 1:3).

GC analyses were performed on a Shimadzu GC2010 Plus instrument equipped with a capillary column (5% biphenyl, 95% dimethylsiloxane). The GC parameters used for the product analysis in our one of previous studies[39] were applied to product analysis performed in the current study.

3.3. Synthesis of chemically derived graphene (CDG)

CDG was prepared using our well-established two-step procedure the details of which were given in one of our recent publications[27] and the detailed characterization of CDG was reported by our publication elsewhere.[40]

3.4. Synthesis of monodisperse Pd NPs and supporting them on CDG

Monodisperse Pd NPs were prepared using a modified version of the oleylamine mediated synthesis reported by Sun and his co-worker.[28] In a typical synthesis of 5 nm Pd NPs, palladium(II) acetylacetonate (0.328 mmol, 0.1 g) was mixed with OAm (10 mL) and the mixture was heated to 90 °C under N$_2$ protection to form a homogeneous solution. Next, morpholine borane complex (2 mmol, 0.2 g) dissolved in 3 mL of OAm was injected into the resulted solution described above at 90 °C. The mixture solution was further heated to 120 °C at a heating rate of 5 °C min^{-1} and kept at this temperature for 30 min. The product was precipitated out with ethanol followed by centrifugation. This process was repeated twice and the final NPs were dispersed in hexane for the catalysis.

A solution-phase self-assembly method was used to deposit Pd NPs on CDG via sonicating the mixture of hexane dispersion of Pd NPs and ethanol solution of CDG. Briefly, 10 mg of Pd NPs dispersed in 10 mL of hexane was added to 20 mL of ethanol solution of CDG (1 mg mL^{-1}), and the mixture was sonicated for 2 h. The product was then separated from the solvents via centrifugation (8000 rpm, 12 min) and washed with ethanol twice before it was dried under vacuum.

3.5. General procedure for the Suzuki–Miyaura cross-coupling reactions

The details of the procedure used for the catalytic Suzuki–Miyaura cross-coupling reactions and the methods for product analysis can be found in our recent publications.[16,39]

3.6. Recycling of CDG-Pd catalyst in Suzuki–Miyaura cross-coupling reactions

To determine the recyclability of the CDG-Pd catalyst in Suzuki–Miyaura cross-coupling reactions, the coupling reaction between $p-$bromoacetophenone and phenylboronic acid in the presence of the CDG-Pd catalyst (0.005 mmol Pd) was performed 15 times. After the completion of the first cycle, a new batch of substrates (1 mmol p-bromoacetophenone, 1.5 mmol phenylboronic acid, and 2.0 mmol K$_3$PO$_4$) was added to start the second cycle of the catalytic coupling reaction and the mixture was stirred for another 20 min to complete the second

cycle. A similar procedure was followed for up to 15 cycles of the coupling reaction. For the calculation of product yield, an assumption was made that all of the p-bromoacetophenone was consumed because it is the limiting reactant.

Acknowledgments

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