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FULL PAPER

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Novel palladium nanoparticles supported on β-cyclodextrin@graphene oxide as magnetically recyclable catalyst for Suzuki–Miyaura cross-coupling reaction with two different approaches in bio-based solvents

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A novel nanocatalyst was designed and prepared. Initially, the surface of magnetic graphene oxide (M-GO) was modified using thionyl chloride, tris(hydroxymethyl)aminomethane and acryloyl chloride as linkers which provide reactive C═C bonds for the polymerization of vinylic monomers. Separately, β-cyclodextrin (β-CD) was treated with acryloyl chloride to provide a modified β-CD. Then, in the presence methylenebisacrylamide as a cross-linker, monomers of modified β-CD and acrylamide were polymerized on the surface of the pre-prepared M-GO. Finally, palladium acetate and sodium borohydride were added to this composite to afford supported palladium nanoparticles. This fabricated nanocomposite was fully characterized using various techniques. The efficiency of this easily separable and reusable heterogeneous catalyst was successfully examined in Suzuki–Miyaura cross-coupling reactions of aryl halides and boronic acid as well as in modified Suzuki–Miyaura cross-coupling reactions of *N*-acylsuccinimides and boronic acid in green media. The results showed that the nanocatalyst was efficient in coupling reactions for direct formation of the corresponding biphenyl as well as benzophenone derivatives in green media based on bio-based solvents. In addition, the nanocatalyst was easily separable, using an external magnet, and could be reused several times without significant loss of activity under the optimum reaction conditions.

KEYWORDS
bio-based solvents, host–guest interaction, magnetic graphene oxide (M-GO), palladium nanoparticles, Suzuki–Miyaura cross-coupling reaction

1 | INTRODUCTION

Palladium-catalysed Suzuki–Miyaura cross-coupling reaction is one of the most powerful and versatile methods for the formation of C─C bonds.[1–11] It can be applied in the synthesis of a great variety of complex organic molecules, heterocyclic agrochemicals, pharmaceutical intermediates, drugs and precursors in the total synthesis of natural products.[12–15] In 2016, Weires *et al*. reported a modified nickel-catalysed Suzuki–Miyaura coupling of amides and boronic acid.[16] It was followed and supported by another report, showing the application of *N*-acylsuccinimides as twist-controlled, acyl-transfer reagents in Suzuki–Miyaura cross-coupling reaction via N─C amide bond activation.[17]

Cross-coupling reactions are frequently utilized for the synthesis of pharmaceuticals, agrochemicals and polymers. Although, homogeneous Pd-based catalyst systems often offer higher activities for these transformations,[18–20] they suffer from problems such as separation of catalyst from reaction mixture, catalyst recovery and catalyst reusability. These are serious drawbacks especially when expensive ligands and metal complexes are used in chemical industry. Thus, recent advances in 'green' reactions have focused on the design and synthesis of catalysts that are easily separable,[21–24] showing simplified product separation, presenting higher turnover frequencies (TOFs) and turnover numbers (TONs) and being used under the conditions required for sustainable green chemistry.[25] In this regard, a wide variety of alternative methods for heterogeneous Pd-catalysed Suzuki reactions have been introduced.[26] Significantly, for the preparation of various Pd species as heterogeneous catalysts, they have been immobilized onto poly(amido-amine) dendrimers,[27–30] polypyrrole,[31] polyvinylpyrrolidone,[32] poly(*p*-phenylene ethynylene),[33] polyaminoacetanilide composite,[34] Wang resin,[35] polystyrene–polyethylene glycol,[36] polystyrene–DVB,[37] polystyrene resin[38] and Merrifield resin,[39] each having its own merits and drawbacks. As a weakness, all of them have their catalytic active sites spread in all the regions of the resin, including the interior, and therefore it is difficult for the reagents to diffuse into the interior of the resin, thus the overall reaction rate is decreased.[38] For the improvement of the applicability of these Pd species, various polymers have been functionalized before being used as supports. Recently, many ongoing attempts have been focused on deposition of various nanoparticles on graphene oxide (GO) sheets due to the superior functionality[40–42] and excellent mechanical, electronic, optical and thermal properties.[43,44] GO has a unique atom-thick two-dimensional sheet structure consisting of hydrophilic oxygen functional groups such as epoxy bridges, carbonyl and hydroxyl groups. Such sheets can be chemically functionalized to provide graphene-based composites.

Designing water-soluble immobilized catalysts has received much attention in organic cross-coupling reactions. Popular strategies for the Suzuki–Miyaura reaction in water have been developed including addition of organic co-solvents,[45] being performed under microwave irradiation[46] and ultrasonic irradiation,[47] ligand-free methodology,[48] using surfactants[49] and the modification of the catalyst with water-soluble functional groups such as polyoxyethylene moieties[50] and sulfonate,[51] ammonium[52] and carboxylate groups.[53] Notably, conventional nanocatalysts show some drawbacks such as poor solubility of aryl halide in aqueous media and low capacity for increasing the efficiency of reaction. Recently, β-cyclodextrin (β-CD) as a hydrophilic molecule has attracted much attention of synthetic organic chemists. It is actually a cyclic oligosaccharide composed of seven α-D-glucopyranoside units linked together creating a cone shape with a hydrophobic inner cavity and a hydrophilic outer surface. This unique and particular structure makes it an ideal candidate for interaction with many organic compounds as guests, forming enclosure complexes via a stable host–guest relationship.[54–57] The applications of β-CD for organic synthesis as well as its importance as a phase transfer agent in catalysis have been well recognized.[58]

We are interested in the Suzuki–Miyaura cross-coupling reaction,[14,59] and also focused on Pd- and Pd nanoparticle-catalysed reactions, performing them under heterogeneous conditions[60,61] using β-CD[62–65] and have experience in activation of carbon heteroatoms catalysed by nickel.[66]

In addition to synthetic organic solvents, nature provides some materials such water as the most abundant and greenest solvent. Water as a green solvent and plentiful resource also shows admirable specificity and thus has been used in a plethora of chemical processes. Nowadays, an extensive investigation of the application of biomass-derived solvents is also underway.[67] Biomass feedstocks of plant and algal origin are green and readily accessible materials, and can be converted into fuels like ethanol, butanol, biodiesel and other hydrocarbon fuels. In this context, several biomass-derived solvents are industrially provided and are commercially available. They are ethanol, glycerol, ethyl lactate and cyrene. On the other hand, deep eutectic solvent (DES) systems based on choline chloride and glycerol or urea as green media have become available in recent years.[68] Choline chloride as a natural biocompatible compound is produced on large scale to provide chicken feed additive.

Stimulated by the facts and concerns mentioned above, herein, we report the design, preparation and characterization of M-GO/(AM-MBA-β-CD@Pd) (M-GO, magnetic GO; AM, acrylamide; MBA, methylenebisacrylamide) nanocomposite and its application as an efficient and recyclable catalyst for the Suzuki–Miyaura cross-coupling reactions of aryl halides with boronic acids as well as for modified Suzuki–Miyaura cross-coupling reactions of *N*-acylsuccinimides and boronic acid in green media (Figure 1 and Scheme 1).

2 | EXPERIMENTAL

2.1 | Reagents and materials

Graphite powder, potassium persulfate, acrylamide, methylenebisacrylamide, azobisisobutyronitrile, $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, H_2SO_4 (98%), HNO_3 (65%) and NH_4OH (28%) were purchased from Merck. $Pd(OAc)_2$, boronic

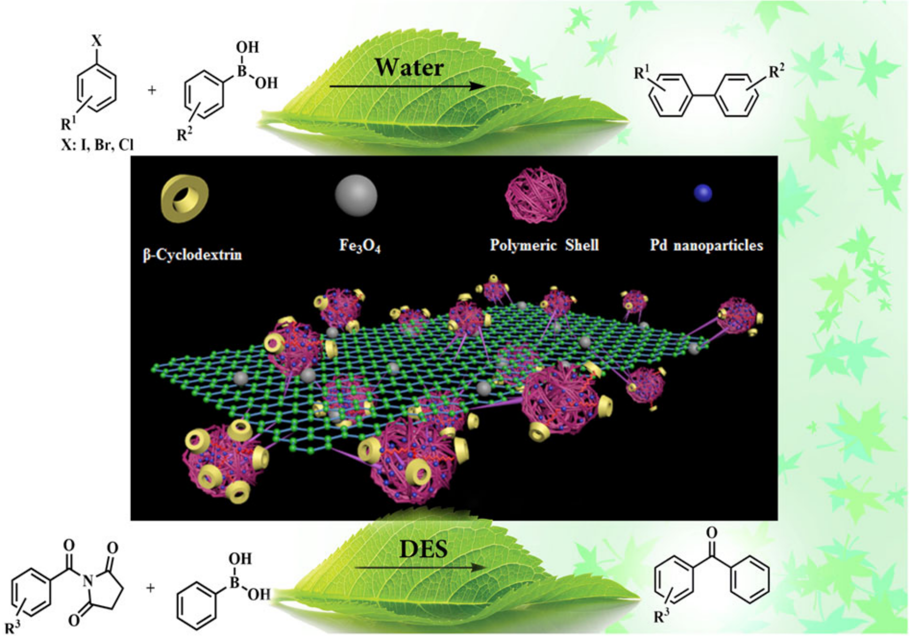


FIGURE 1 Schematic of M-GO/(AM-MBA-β-CD@Pd) nanocomposite

acids, variously substituted aryl halides and β-CD were purchased from Sigma-Aldrich. All employed solvents, initially, were dried using standard processes and freshly distilled prior to use.

2.2 | Instrumentation

Fourier transform infrared (FT-IR) spectra were recorded using a BOMEM MB series spectrometer in the form of KBr pellets over the range 400–4000 cm^{-1}. For determination of Pd loaded on the nanocomposite, a Shimadzu model AA-680 atomic absorption spectrometer with air–acetylene flame atomizer and hollow cathode lamp was used. A scanning electron microscopy (SEM) instrument (Philips XL-30) was used for investigation of surface morphological features and size of the nanocatalyst. In order to obtain more quantitative data of the surface of the nanocatalyst, a transmission electron microscopy (TEM) instrument (Philips CM-30) was employed. The progress of the cross-coupling reactions was monitored using GC with a Shimadzu instrument. The crystalline phases of the nanocatalyst were investigated using X-ray diffraction (XRD) measurements (diffraction angle (2θ) from 10° to 80° with a Siemens D5000 X-ray diffractometer). The magnetic properties of the synthesized nanocomposite were analysed using vibrating sample magnetometry (VSM) with a DC magnetometer (1.5 T, $I_{max} = 150$ A, $P \leq 9$ kW) at room temperature.

2.2.1 | Synthesis of M-GO/(AM-MBA-β-CD@Pd) nanocomposite

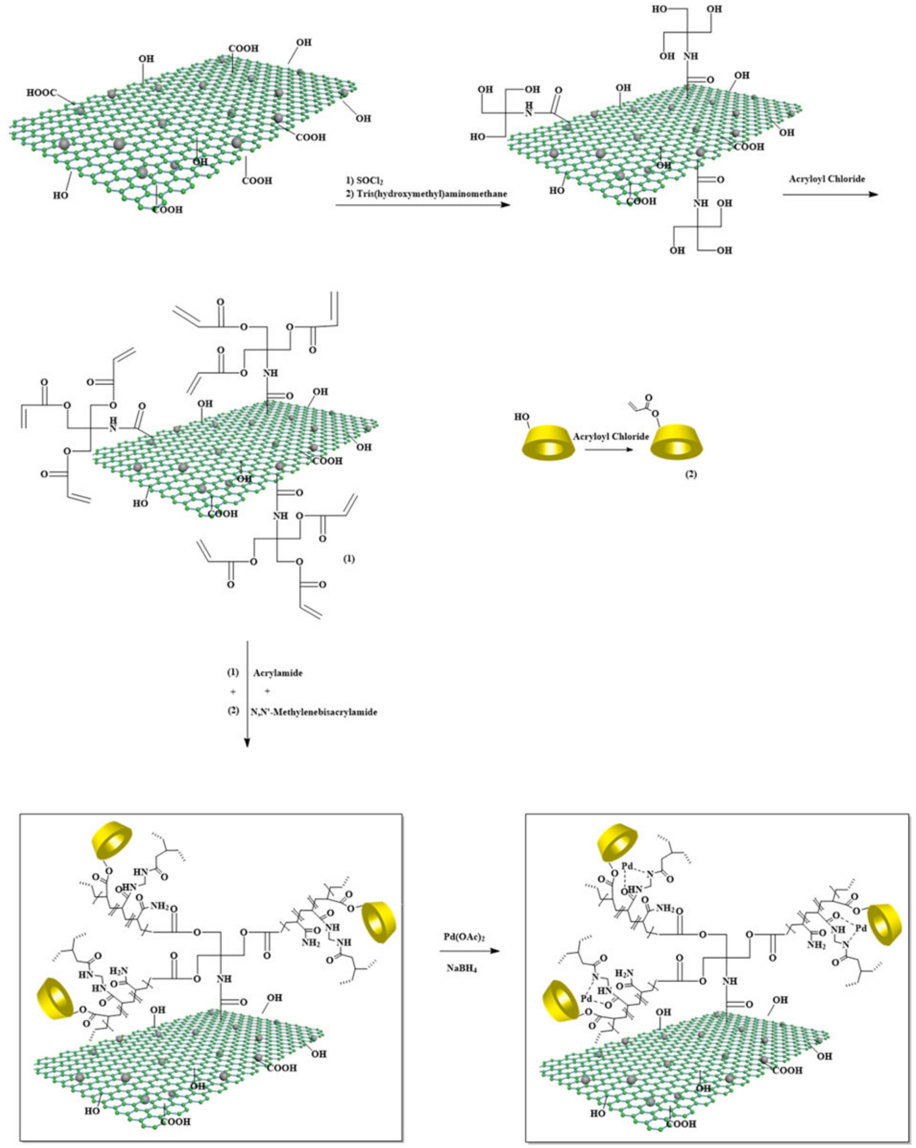
The detailed synthesis of the M-GO/(AM-MBA-β-CD@Pd) nanocomposite is described step by step in the supporting information. GO sheets were prepared via a modified Hummers method.[69]

2.3 | Preparation of DES

A choline chloride-based DES was prepared according to a procedure reported in the literature.[70] Accordingly, choline chloride with urea, ethylene glycol and glycerol were mixed and heated at 80°C until the formation of a liquid. The obtained DES was used without any further purification.

2.4 | Suzuki–Miyaura reaction catalysed by M-GO/(AM-MBA-β-CD@Pd) nanocomposite: general procedure

In a typical experiment, an appropriate aryl halide (1 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (3 mmol), GO/(AM-MBA-β-CD@Pd) nanocomposite (0.008–0.1 mol%) and water (6 ml) were placed in a 50 ml round-bottom flask. The reaction mixture was stirred for various times (2–5 h) and at various temperatures (40–80°C) depending on each particular substrate. Upon completion of the reaction (monitored by GC), the



SCHEME 1 Synthesis route of M-GO/(AM-MBA-β-CD@Pd) nanocomposite

mixture was cooled to ambient temperature (25°C). Then, the solution was diluted with distilled water–ethyl acetate and the catalyst was separated from the reaction mixture using a magnet bar. The filtrate was extracted with ethyl acetate, and the organic phase was separated, dried over MgSO4, left for a while and then filtered off. The organic solvent was evaporated to dryness under reduced pressure to give a crude material. The residue was purified by column chromatography (ethyl acetate–*n*-hexane) to give the pure corresponding product. All compounds were known and identified by comparison of their physical and spectroscopic data with those of authentic samples, which were found to be identical.

2.5 | Synthesis of benzophenones from reaction of *N*-acylsuccinimides and boronic acid: general procedure

An appropriate *N*-acylsuccinimide (**1**; 0.5 mmol), synthesized according to a previously reported procedure,[71] and 0.6 mmol of phenylboronic acid **2** were added to a 10 ml round-bottom flask fitted with a magnetic stirrer containing a suspension of catalyst (0.03 mol%) in 2 ml of DES (choline chloride–glycerol, 1:2). The resultant mixture was vigorously stirred at 90°C for 5 h. The progress of the reaction was monitored by TLC (ethyl acetate–*n*-hexane). After completion of the reaction, the mixture was cooled to room temperature. Then, water

(5 ml) was added to this mixture, the nanocatalyst was separated using an external magnet and then ethyl acetate was added (5 ml). The residue was purified by column chromatography (ethyl acetate–*n*-hexane) to afford the pure corresponding products **3a–f**.

3 | RESULTS AND DISCUSSION

3.1 | Characterization

3.1.1 | FT-IR spectroscopic analysis

FT-IR analysis was successfully applied to investigate the presence of functional groups in the synthesized compounds. The FT-IR spectrum of GO (Figure 2a) exhibited the main absorption bands at 1721, 1618 and 3400 cm^{-1} that are assigned to C═O stretching vibration, C═C of aromatic ring and —OH groups of GO, respectively. According to Figure 2b (spectrum of M-GO), the band at 553 cm^{-1} is attributed to Fe—O stretching vibration. After modification of M-GO with tris(hydroxymethyl) aminomethane (Figure 2c), the appearance of the band at around 1695 cm^{-1} is due to the amide carbonyl vibration. In the spectrum of acrylate-modified GO (Figure 2d), the C═O stretching band at around 1731 cm^{-1} and the C—O stretching band at 1200 cm^{-1} are characteristic for ester bonds, indicating the successful linkage of acryloyl chloride to the surface of amine-modified M-GO. The spectrum of vinyl-modified β-CD (Figure 2e) exhibited peaks at 1731 and 1029 cm^{-1} which were assigned the C═O and C—O stretching bands, respectively. Appearance of these bands confirmed the successful linkage of acryloyl chloride to β-CD. The spectrum of the final polymeric nanocomposite (Figure 2f) showed bands at 1639 and 3300 cm^{-1} which can be assigned to CONH_2 and NH groups, respectively.

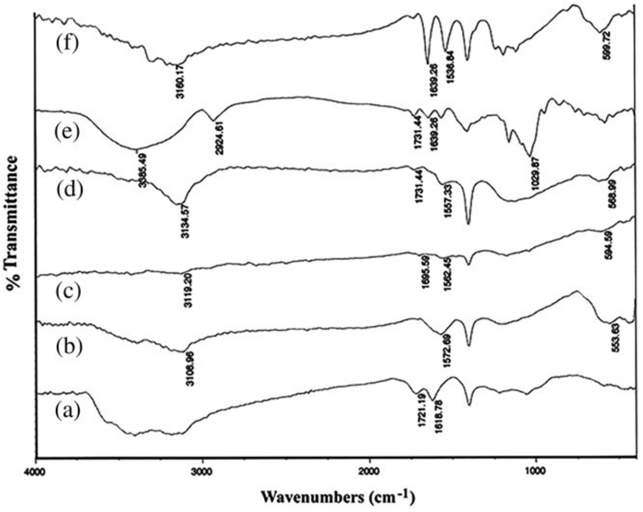


FIGURE 2 FT-IR spectra of (a) GO, (b) M-GO, (c) amine group-modified GO, (d) vinyl group-modified GO, (e), acrylated β-CD and (f) M-GO/(AM-MBA-β-CD@Pd) nanocomposite

3.1.2 | NMR spectroscopic analysis

Functionalized β-CD was used as a monomer in the structure of the catalyst. This applied monomer shows a dual role (inclusion of complex and providing hydrophilic properties). The functionalized β-CD monomer was produced using acryloyl chloride, in which one of the primary —OH groups of β-CD was reacted with the carbonyl group of acryloyl chloride. The NMR analysis of the product illustrated the functionalization of β-CD (Figure 1 in supporting information).

3.1.3 | XRD analysis

XRD patterns of prepared GO, M-GO and the M-GO/(AM-MBA-β-CD) nanocomposite are depicted in Figure 3. The sharp characteristic GO peak at around 10.6° is attributed to the (002) plane of GO sheets and another peak at 42.2° corresponds to the (001) reflection plane of GO.[72–74] In comparison with the pattern of pure graphite which is dominated by an intense peak at $2\theta = 26.48°$ corresponding to reflection in (002) planes of well-ordered graphene layers, a graphene peak (26.4°) can be attributed to a very small concentration of non-oxidized graphene.[75] According to the type of sample holder, the peak at $2\theta = 63°$ is attributed to the duplex stainless steel of the analytical apparatus[76] (Figure 3a). Interestingly, the XRD pattern of the M-GO hybrid indicated the presence of a similar crystalline structure of pure Fe_3O_4 at $2\theta = 30.22°$, 35.59°, 43.29°, 53.69° and 62.81° which indicated the structure of Fe_3O_4

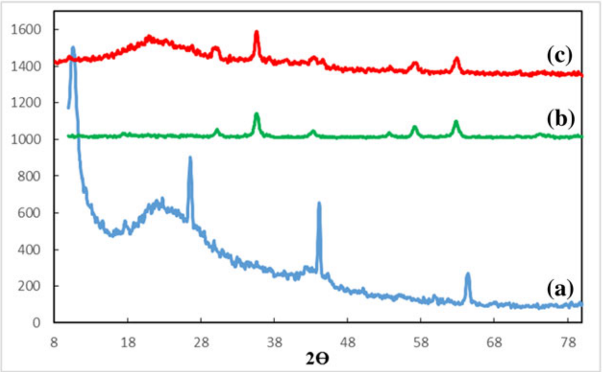


FIGURE 3 XRD patterns of (a) GO, (b) M-GO and (c) M-GO/(AM-MBA-β-CD) nanocomposite

nanoparticles (Figure 3b). Nevertheless, the diffraction peak ($2\theta \sim 10.8°$) of GO totally disappeared in the pattern of the M-GO hybrid, which most probably is due to the exfoliation/distortion of GO bundles, when they are ground with Fe_3O_4.[77] The XRD pattern of the M-GO/(AM-MBA-β-CD) nanocomposite showed a broad diffraction peak at $2\theta = 10–28°$ assigned to the scattering of amorphous polymeric skeleton (Figure 3c).

3.1.4 | SEM and TEM images

The morphologies of GO sheets and the final nanocomposite are demonstrated in Figure 4A,B. The SEM image of GO shows a homogeneous and smooth coating layer with a size of several micrometres (Figure 4A). In comparison to GO, the SEM image of the M-GO/(AM-MBA-β-CD@Pd) nanocomposite (Figure 4B) shows spherical polymeric particles on the surface of GO sheet. The results confirmed the successful polymerization of monomers as a shell on M-GO sheet. The distribution of Pd nanoparticles onto the surface of M-GO was characterized by cross-sectional TEM imaging of the final nanocomposite (Figure 4C,D). According to the TEM images, round-shaped structures of the Pd nanoparticles are clearly observed, indicating that Pd nanoparticles were successfully loaded onto the surface of M-GO/(AM-MBA-β-CD). The high density of polymeric backbones prevents the agglomeration of Pd nanoparticles on the GO sheets.

3.1.5 | X-ray photoelectron spectroscopy (XPS)

XPS was applied to investigate the electronic state of Pd species that exist within the catalyst. As shown in Figure 2 in the supporting information, the binding energies of Pd 3d in the catalyst were 335.48 and 340.94 eV which are ascribed to Pd^0 $3d_{5/2}$ and $3d_{3/2}$, respectively.[78,79]

3.1.6 | VSM analysis

The magnetic properties of the final nanocomposite were investigated using VSM. According to Figure 3 in the supporting information, the magnetization curves are symmetric and pass through the origin. These observations showed no remanence and coercivity, indicating the supermagnetic behaviour of the nanocatalyst. The value of magnetic saturation (M_s) is around 10 emu g^{-1}, far less than that of pure Fe_3O_4 due to the presence of the polymeric shell on the surface of M-GO sheets.

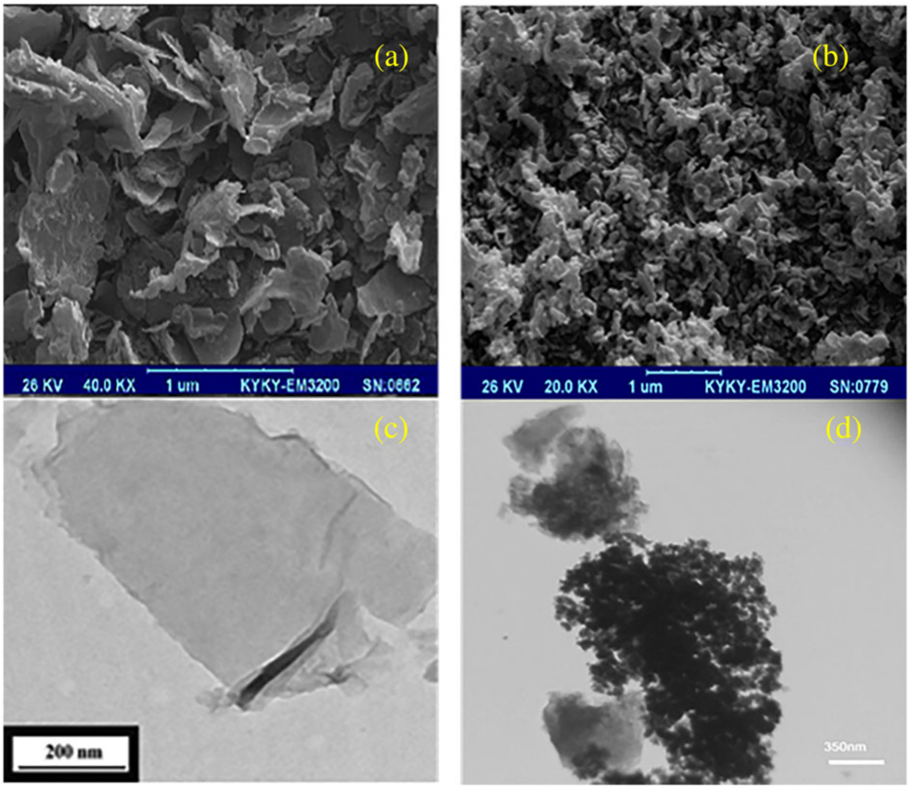


FIGURE 4 SEM images of (a) GO and (b) M-GO/(AM-MBA-β-CD@Pd) nanocomposite. TEM images of (c) GO and (d) M-GO/(AM-MBA-β-CD@Pd) nanocomposite

However, this magnetic property of the nanocomposite was sufficient for efficient magnetic separation (collected in less than 60 s using an external magnetic field).

3.2 | Catalytic performance of final magnetic nanocomposite

Pd nanoparticles immobilized onto polymers have been extensively employed in various cross-coupling reactions.[80,81] Nonetheless, there are just a few reports of the utilization of magnetically separable nanoparticles stabilized by hydrophilic polymers for catalysed cross-coupling reactions under eco-friendly conditions.[82–84]

In this work we examined the catalytic activity of our novel and easily separable M-GO/(AM-MBA-β-CD@Pd) nanocomposite in Suzuki–Miyaura cross-coupling reactions under eco-friendly conditions. The flexibility in surface functionalities, large surface area to volume ratio and superior mechanical performance of the M-GO/(AM-MBA-β-CD@Pd) nanocomposite had a great impact on the amount of catalyst loaded and decreased the required reaction time significantly. The heterogeneous Suzuki–Miyaura cross-coupling process has been generally investigated using aryl iodides as reactive substrates, which are rather expensive. Utilization of aryl bromides as substrate instead of aryl iodides in Suzuki–Miyaura cross-coupling reactions is more desirable from an economic point of view for large-scale synthesis. Meanwhile, activation of aryl chlorides as reactants is extremely challenging because of the higher bond strength of aryl moiety with chloride. Thus, Suzuki–Miyaura cross-coupling reactions of aryl chlorides with an appropriate boronic acid partner often need to be performed under harsh reaction conditions. Here, water plays a dual role, as a medium and co-catalyst due to its high surface tension and hydrophobic nature.[85] The hydrophobic effect emphasizes the tendency of nonpolar molecules or their surfaces to aggregate in water. According to Breslow, for the hydrophobic effect in water, the substrates are forced to form aggregates in order to decrease the exposed organic surface area.[86] When a salt or polar molecules is dissolved or dispersed in water, the hydrophobic effect is increased.

In this research, at first, we successfully examined the Suzuki–Miyaura cross-coupling reaction of bromobenzene with phenylboronic acid in the presence of our novel designed, prepared and fully characterized Pd-based nanocatalyst in water as a green solvent as a model reaction (Table 1). The use of water as the solvent provides excellent interaction between the heterogeneous stabilized Pd nanocomposite and hydrophilic (boronic acid) and hydrophobic (aryl halide) species which consequently resulted in an increase in the yield and rate of the cross-coupling reaction. The amount of catalyst used and time of the reaction are two significant parameters which were carefully studied in this work. The best conversion occurred in the above-mentioned model reaction when the substrate was reacted in the presence of 0.01 mol% of catalyst in 3 h, providing the corresponding biphenyl in satisfactory yield (Table 1).

Table 2 presents the corresponding biaryls as coupled products, obtained from the reaction of variously substituted boronic acids with a variety of aryl halides. As is evident, iodobenzene, 4-iodotoluene and 4-iodoanisole gave the corresponding biaryls in the presence of 0.008 mol% catalyst in only 2 h (Table 2, entries

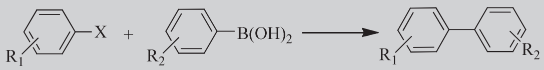
TABLE 1 Optimization of reaction conditions for Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid catalysed by M-GO/(AM-MBA-β-CD@Pd) nanocomposite[a]

Entry	Amount of catalyst (mol%)	Temp. (°C)	Solvent	Time (h)	Conversion (%)[b]
1	0.1	80	H_2O	8	100
3	0.05	80	H_2O	8	100
4	0.05	80	H_2O	6	100
5	0.05	70	H_2O	5	100
6	0.05	70	H_2O	3	100
7	0.02	70	H_2O	3	100
8	0.02	50	H_2O	3	100
9	**0.01**	**50**	$\mathbf{H_2O}$	**3**	**100**
10	0.008	50	H_2O	3	96
11	0.01	40	H_2O	3	98

[a] Reaction conditions: phenylboronic acid (1.2 mmol), bromobenzene (1 mmol), K_2CO_3 (3 mmol), M-GO/(AM-MBA-β-CD@Pd) nanocomposite as catalyst, H_2O (6 ml).

[b] Calculated by GC.

TABLE 2 Suzuki–Miyaura reaction of various aryl halides with arylboronic acids catalysed by M-GO/(AM-MBA-β-CD@Pd) nanocomposite[a]



Entry	R_1	R_2	X	Amount of catalyst (mol%)	Time (h)	Temperature (°C)	Conversion (%)[b]	TOF	TON
1	H	H	I	0.008	2	40	100	6125	12 250
2	4-Me	H	I	0.008	2	40	100	6125	12 250
3	4-OMe	H	I	0.008	2	40	100	6125	12 250
4	H	H	Br	0.01	3	50	97	3033	9 099
5	4-NO_2	H	Br	0.01	3	50	98	3066	9 198
6	4-Me	H	Br	0.01	3	50	95	3000	9 000
7	H	H	Cl	0.01	3	50	NR	—	—
8	H	H	Cl	0.1	5	60	67	120	600
9	4-Me	H	Cl	0.1	5	60	62	116	580
10	4-NO_2	H	Cl	0.1	5	60	70	126	630
11	H	Me	I	0.008	2	40	98	5750	11 500
12	4-Me	Me	I	0.008	2	40	97	5687	11 374
13	4-OMe	Me	I	0.008	2	40	96	5625	11 250
14	H	Me	Br	0.01	3	50	95	2966	8 898
15	4-Me	Me	Br	0.01	3	50	94	2933	8 799
16	H	Me	Cl	0.1	5	80	58	100	500
17	4-Me	Me	Cl	0.1	5	80	50	84	420
18	4-OMe	Me	Cl	0.1	5	80	45	80	400

[a] Reaction conditions: arylboronic acid (1.2 mmol), aryl halide (1 mmol), K_2CO_3 (2–3 mmol), M-GO/(AM-MBA-CD@Pd) nanocomposite as catalyst, H_2O (6 ml).

[b] Calculated by GC.

1–3). To establish the general substrate scope, variously substituted aryl bromides were used. Aryl bromides bearing electron-donating and electron-withdrawing groups gave the corresponding biaryls in excellent yields in the presence of 0.01 mol% catalyst in only 3 h (Table 2, entries 4–6). The prepared catalyst efficiently catalysed the Suzuki cross-coupling reactions of aryl iodides and aryl bromides. It has been shown that the Suzuki reaction does not proceed smoothly when aryl chlorides are used, these being commonly less reactive than aryl iodides and aryl bromides in the Suzuki–Miyaura cross-coupling reaction since a C—Cl bond is stronger than both C—Br and C—I bonds. Thus, longer reaction times, more active catalyst or higher catalyst loading are required. In fact, aryl chlorides are more accessible and are commercially less expensive than their bromo and iodo counterparts. Thus, employing aryl chlorides in Suzuki–Miyaura cross-coupling reactions in at the pilot and even bench scale is more desirable. Encouraged by the preparation of an efficient Pd-based nanocatalyst which fruitfully catalysed the Suzuki–Miyaura cross-coupling reaction, we selected a model reaction involving chlorobenzene and phenylboronic acid and reacted them in the presence of 0.01 mol% of our catalyst in water. This reaction proceeded sluggishly, giving the products after 5 h, but a significant amount of starting materials remained unreacted in the reaction mixture. Delightfully, by increasing the amount of catalyst loading to 0.1 mol% and extending the reaction time to 5 h at 60°C, our model reaction completed, giving rise to the corresponding product in satisfactory yield (entry 8). Encouraged by this result, the Suzuki–Miyaura cross-coupling reactions of aryl chlorides with various boronic acids were performed under identical reaction conditions, leading to the formation of the corresponding products (entries 9–10, 16–18). Furthermore, 4-tolylboronic acid was reacted with various aryl halides under the same reaction conditions to afford the corresponding products (entries 11–18). All products were known and identified by comparison of their physical data (melting points) and spectral data (^{1}H NMR and FT-IR spectra) with those of authentic samples and found to be identical.

Encouraged by the results, confirming the high activity and diversity of the novel M-GO/(AM-MBA-β-CD@Pd) nanocomposite in the expeditious synthesis of biphenyl derivatives in water as a user-friendly solvent, we decided to examine its catalytic activity in the synthesis of benzophenone derivatives (Figure 5) through cross-coupling reaction of *N*-acylsuccinimides as versatile acyl-transfer reagents and phenylboronic acids (modified Suzuki–Miyaura cross-coupling reaction). In general, an amide is not very reactive since its bonds are comparatively strong. However, some amides have emerged as promising precursors for achieving highly selective amide cross-coupling reactions, leading to the direct access to benzophenone derivatives, as reported previously.[17,87] Inspired by this breakthrough, we investigated the catalytic efficiency of the novel M-GO/(AM-MBA-β-CD@Pd) nanocomposite for N-C bond cleavage to yield benzophenones via modified Suzuki–Miyaura coupling reaction. Interestingly, we found that the M-GO/(AM-MBA-β-CD@Pd) nanocomposite acted as a robust and effective catalyst not only in the efficient and facile synthesis of biphenyls via Suzuki–Miyaura cross-coupling reactions, but it also plays a significant catalytic role in the direct synthesis of benzophenones in DES as neoteric medium in our model reaction involving *N*-acylsuccinimides and phenylboronic acid to give the corresponding benzophenone. In order to optimize the reaction conditions, we investigated the effect of various media such as water, ethanol, tetrahydrofuran and CH_3CN as well as three other types of DES systems based on choline chloride as hydrogen bond acceptor and urea, ethylene glycol and glycerol as hydrogen bond donor. The required amount of catalyst and reaction time for the synthesis of benzophenones from the reaction of *N*-acylsuccinimides and phenylboronic acid were also optimized. As evident from Table 3, higher yield of product was obtained and shorter reaction time required when using 0.03 mol% M-GO/(AM-MBA-β-CD@Pd) nanocomposite in choline chloride and glycerol mixture at 90°C (Table 3, entry 10). Electron-withdrawing groups such as nitro group on *N*-acylsuccinimides showed increased yields in comparison to electron-donating groups. These results prompted us to establish our novel catalyst in a synthetic methodology leading to the straightforward

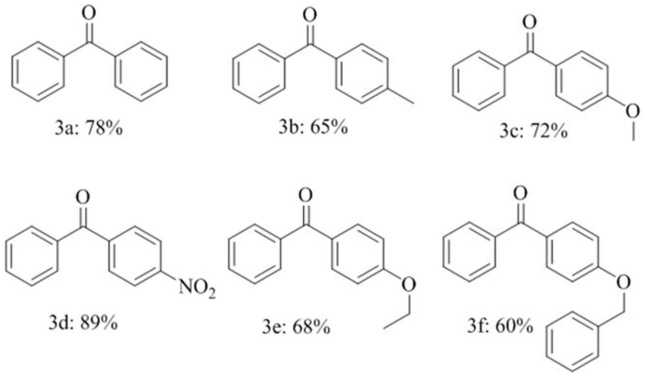
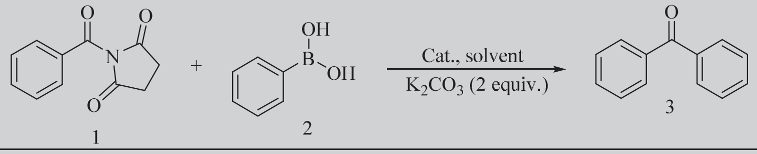


FIGURE 5 Structure and isolated yields of products

TABLE 3 Optimization of reaction conditions for synthesis of benzophenones[a]



Entry	Solvent[b]	Time (h)	Amount of catalyst (mol%)	Temp. (°C)	Yield (%)[c]
1	Water	6	0.03	100	0
2	EtOH	6	0.03	78	Trace
3	Water–EtOH	6	0.03	80	Trace
4	Tetrahydrofuran	6	0.03	60	32
5	CH_3CN	6	0.03	80	20
6	ChCl–urea	6	0.03	90	65
7	ChCl–ethylene glycol	6	0.03	90	52
8	ChCl–glycerol	6	0.03	90	78
9	ChCl–glycerol	6	0.02	90	64
10	ChCl–glycerol	5	0.03	90	78
11	ChCl–glycerol	4	0.03	90	72
12	ChCl–glycerol	4	0.03	75	60

[a] Reaction conditions: 1 (0.5 mmol), 2 (0.6 mmol), K_2CO_3 (1 mmol).

[b] ChCl, choline chloride.

[c] Isolated yield.

synthesis of benzophenones under milder reaction conditions. TON and TOF for compound **3d** were also determined to be 2966 and 593, respectively. Using DES as medium in this catalytic system, in addition to the benefits of the philosophy of green chemistry, leads to products and can also participate in subsequent reactions. Next, the versatility of the nanocatalyst for amide acyl N—C bond cross-coupling process to achieve diverse benzophenones using several reactants was demonstrated and the results are shown in Figure 5. All the reactants have been applied successfully in this cross-coupling reaction in DES with appropriate yields.

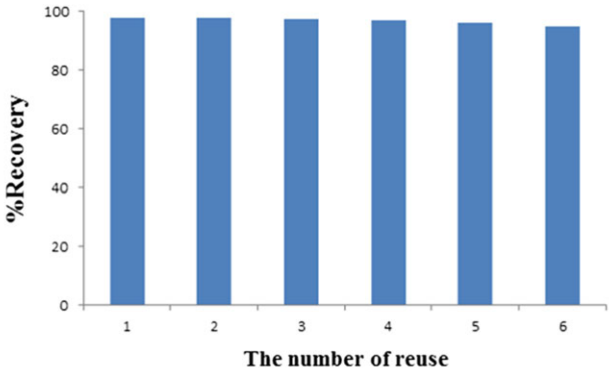


FIGURE 6 Reusability of M-GO/(AM-MBA-β-CD@Pd) nanocomposite catalyst in Suzuki–Miyaura reaction of bromobenzene with phenylboronic acid

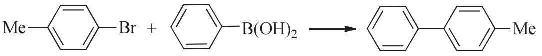
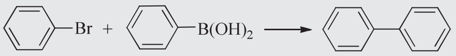
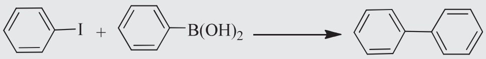
3.3 | Leaching

Another catalytic experiment was further conducted to estimate the impact of Pd leaching. For this purpose, a certain amount of the novel catalyst was dispersed in water (as solvent) in the presence of K_2CO_3. The mixture was stirred for a particular time and then filtered off to achieve a transparent solution. In the next step, in accordance with our model reaction, Suzuki–Miyaura coupling substrates, namely phenylboronic acid and bromobenzene, were introduced to the clean supernatant obtained as described above and this mixture was heated to 80°C under stirring. We did not observe the formation of biphenyl even after 5 h, indicating that the coupling reaction is catalysed by heterogeneous catalysis and is not a homogeneous type with leaching of Pd.

3.4 | Hot filtration test

Furthermore, hot filtration test was performed to investigate whether the reaction proceeded in a heterogeneous

TABLE 4 Comparison results of cross-coupling reaction using M-GO/(AM-MBA-β-CD@Pd) nanocomposite as catalyst with previously reported results

Entry	Catalyst (Pd loading, mol%)	Reaction conditions	Time (h)	Yield (%) or conversion (%)	Ref.
					
1	Poly(NIPAM-*co*-4-VP)-Pd (1)	K_2CO_3, H_2O, 60°C	5	95	[88]
2	GO-NH_2-Pd(II) (1)	K_2CO_3, EtOH–H_2O, 60°C	4	71	[89]
5	Pd@MIL-101 (0.15)	K_2CO_3, EtOH–H_2O, 25°C	6	92	[90]
6	N-doped NPC-Pd (0.2)	K_2CO_3, EtOH–H_2O, 25°C	1	95	[91]
7	N-doped PC-900-Pd (0.2)	K_2CO_3, EtOH–H_2O, 25°C	1.5	91	[92]
8	M-GO/(AM-MBA-β-CD@Pd) nanocomposite (0.01)	K_2CO_3, H_2O, 50°C	3	90	This work
					
9	MOF-5-NPC-900-Pd (0.1)	K_2CO_3, EtOH–H_2O, 25°C	1	98.6	[93]
10	GO-NH_2-Pd (II) (1)	K_2CO_3, EtOH–H_2O, 60°C	4	73	[89]
11	Pd/Fe_3O_4/G (0.3)	EtOH–H_2O, 25°C	45 min	100 conversion	[94]
12	Pd–Co_3O_4/G (1)	EtOH–H_2O, 120°C	10 min	100 conversion	[95]
13	M-GO/(AM-MBA-β-CD@Pd) nanocomposite (0.01)	K_2CO_3, H_2O, 50°C	3	91	This work
					
14	Pd/CuO (1)	K_2CO_3, EtOH–H_2O, 150°C	10 min	90	[96]
15	M-GO/(AM-MBA-β-CD@Pd) nanocomposite (0.008)	K_2CO_3, EtOH–H_2O, 40°C	4	98	This work

or homogeneous fashion. In a typical experiment, our novel Pd-based catalyst (0.01 mol%), bromobenzene (1 mmol), phenylboronic acid (1.2 mmol) and K_2CO_3 (3 mmol) were taken in water in a round-bottomed flask and stirred at 50°C for 1 h (conversion at 42%). At this stage, the catalyst was separated using a magnet and the experiment was continued for another 2 h. However, no further progress in the reaction was observed even after a prolonged reaction time (monitored by GC). Furthermore, atomic absorption spectroscopic analysis did not show any Pd leaching in this stage. This means that no Pd nanoparticles were leached into the reaction mixture and the catalytic activity of the novel catalyst mainly depended on the Pd complex.

3.5 | Reusability and stability of nanocatalyst

The reusability of the nanocatalyst in the Suzuki–Miyaura reaction was also investigated by performing the model reaction. Bromobenzene and phenylboronic acid were reacted under the already determined optimized reaction conditions. In each cycle, 3 ml of aqueous solution containing reagents and the catalyst was added into a 50 ml round-bottomed flask at optimal temperature. After completion of the reaction, the nanocatalyst was separated from the mixture using an external magnetic bar, washed with water, dried at room temperature and reused for the next cycle in the same reaction. As shown in Figure 6, the nanocatalyst could be reused at least six times without any appreciable loss in its activity in the Suzuki–Miyaura cross-coupling reaction. The remaining amount of Pd after the sixth cycle was decreased by 0.250 mmol g^{-1} to 0.235 mmol g^{-1}as determined using atomic absorption spectroscopic analysis (6% leaching).

3.6 | Comparison

To evaluate the efficiency of the M-GO/(AM-MBA-β-CD@Pd) nanocomposite, its catalytic activity was compared to those reported in previous literature. As evident from Table 4, the M-GO/(AM-MBA-β-CD@Pd) nanocomposite is a superior nanocatalyst in terms of using green conditions, reaction time and also isolated yield.[88–96]

4 | CONCLUSIONS

Our investigations demonstrate that the immobilization of Pd nanoparticles on M-GO/(AM-MBA-β-CD) nanocomposite produces a well-defined and superior catalyst for Suzuki–Miyaura cross-coupling reactions in water as well as bio-based solvents such as DESs based on choline chloride and glycerol. The novel nanocatalyst with polymer shell due to sharing an electron pair of N and O atoms of AM and MBA was developed in which Pd nanoparticles have a better chance of interaction in aqueous media. On the other hand, β-CD provides suitable interaction with aryl halides and *N*-acylsuccinimides as guests generating inclusion complexes via stable host–guest interactions. This prototype catalyst demonstrated an encouraging level of catalytic activity in the Suzuki–Miyaura cross-coupling reactions of aryl halides including challenging aryl chlorides. More importantly, it uniquely activates the amide N—C bond for facile cleavage in green media to give benzophenones in high yields. This catalyst can be easily separated using a magnetic field and can be reused for six runs without significant loss of activity under optimum reaction conditions. The separated and reused catalyst needs no pre-activation for being used in a subsequent run. The catalyst also showed high TOFs and TONs as two important green chemistry metrics.

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