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Graphical Abstract

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$$Ar^1X + Ar^2B(OH)_2 \longrightarrow \quad \longrightarrow Ar^1\text{-}Ar^2$$

$X = Cl, Br$

Fe$_3$O$_4$ NPs

Pd NPs

CODs

25 examples
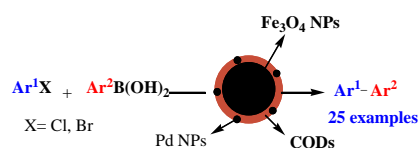
Green Synthesis of Carbon Quantum Dots from Vanillin for Modification of Magnetite Nanoparticles and Formation of Palladium Nanoparticles: Efficient Catalyst for Suzuki Reaction

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ARTICLE INFO

ABSTRACT

In this report we prepare carbon quantum dots (CQD) from vanillin as an ecofriendly and naturally abundant compound for modification of magnetic nanoparticles (CQD@Fe$_3$O$_4$ NPs). This new magnetic solid are used for complete reduction of PdCl$_2$ with formation of stabilized palladium nanoparticles (Pd@CQD@Fe$_3$O$_4$ NPs), which are characterized by SEM, TEM, EDX, solid UV, VSM, XPS, XRD, and N$_2$ adsorption–desorption analyses. These magnetic supported Pd NPs are efficient catalysts for the Suzuki-Miyaura cross-coupling reactions of aryl bromides at room temperature in aqueous ethanol and of aryl chlorides at 120 °C in PEG200 under low catalyst loading in air. The heterogeneous catalyst is recovered by an external magnet and reused for eight consecutive runs.

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1. Introduction

Palladium catalyzed cross-coupling reactions have become a key and potent tool in organic synthesis for the formation of carbon–carbon bonds.[1] Among them, the Suzuki-Miyaura reaction, which is the coupling between aryl, vinyl or alkyl halides or pseudo-halides and organoboron reagents is one of the advanced palladium catalyzed reactions for the formation of different types of compounds.[2] Traditionally, palladium pre-catalysts in the presence of toxic phosphine[3] or nitrogen ligands[4] are often employed for coupling reactions under homogeneous conditions. However, when compared to heterogeneous catalysts, homogeneous catalysts suffer from diminished catalytic activity during the reaction, lack of catalyst reusability, and difficulty for product purification. In the case of palladium, which is toxic and costly, recycling is very important from both economic and sustainable chemistry standpoints[5,6]

Nowadays, green chemistry objectives encourage chemists for design and preparation of new methodologies that reduce or eliminate the use or generation of hazardous substances. For this purpose, in recent years designing of new recyclable and heterogeneous catalysts with high efficiency and turnover number, low cost, and minimal leaching of toxic metals has received much attention.[7] In the past few decades, a wide range of efficient heterogeneous palladium catalysts using different solid supports have been reported for various Pd catalyzed organic reactions. However, usually separating of the heterogeneous catalyst from the reaction mixture by conventional methods such as simple filtration and centrifugation is not an easy task.[5,6] To address these challenges, many efforts have been made for using magnetic nanoparticles with unique properties such as easy isolation, high surface area and low toxicity as a promising support for palladium catalysts.[8] For this purpose, in recent years different methods and ligands have been reported for modification of magnetic nanoparticles and their relevant applications as Pd supports for various carbon-carbon bond formation reactions.[8]

Fluorescent carbon quantum dots (CQD) are an emerging class of carbon nanomaterials recently termed quasi-spherical nano carbons with sizes below 10 nm. These CQD are comprised of amorphous to nanocrystal line cores with predominantly graphitic or turbo static carbon (sp^2 carbon) or graphene and graphene oxide sheets fused by diamond-like sp^3 hybridized carbon insertions.[9] CQD have unique properties such as high solubility, photo-stability, fluorescence emission and they are considered as green, non-toxic, abundant, and inexpensive materials.[9] In recent years, different sources have been used for the preparation of CQD. However, recent emerging efforts have been paid for using inexpensive starting materials, such as chitosan,[10] orange peels[11] and cabbage[12] for the preparation of CQD. Recently, CQD obtained from clotted cream have been used for the synthesis of coated Pd nanoparticles (NPs) and used for Heck and Suzuki reactions.[13] Also, very recently, we have reported the preparation of CQD from citric acid and its using for modification of magnetic Fe_3O_4 nanoparticles and formation and stabilization of Pd NPs.[14]

Vanillin is a highly water soluble phenolic aldehyde, which occurs widely in plants, usually as a glycoside bound to sugar or as a precursor to vanillin bound to the large lignin molecule abundant in wood. Vanillin is widely used to introduce flavors in our food and free vanillin in the environment is not considered to represent any biohazard.[15]

In continuation of our interest in CQD and magnetic supported palladium catalysts,[16] now in this work we use for the first time vanillin as a cheap and naturally abundant compound for formation of CQD and its subsequent application for the modification of Fe_3O_4 NPs (CQD@Fe_3O_4). We envisaged that CQD generated from vanillin bearing formyl groups would facilitate the reduction of Pd(II) to Pd(0) and therefore the formation of Pd NPs to be used in carbon-carbon bond forming reactions. The CQD@Fe_3O_4 would be further used not only for the stabilization of Pd NPs but also for the easy recovery of this heterogeneous catalyst, which is referred to as Pd@CQD@Fe_3O_4 throughout this manuscript.

2. Results and discussion

Preparations steps of Pd@CQD@Fe_3O_4 are summarized in scheme 1. Firstly, Fe_3O_4 NPs were prepared using the Massart procedure[17] from the reaction of $FeCl_3 \cdot 6H_2O$ and $FeCl_2 \cdot 4H_2O$ salts (Scheme 1).
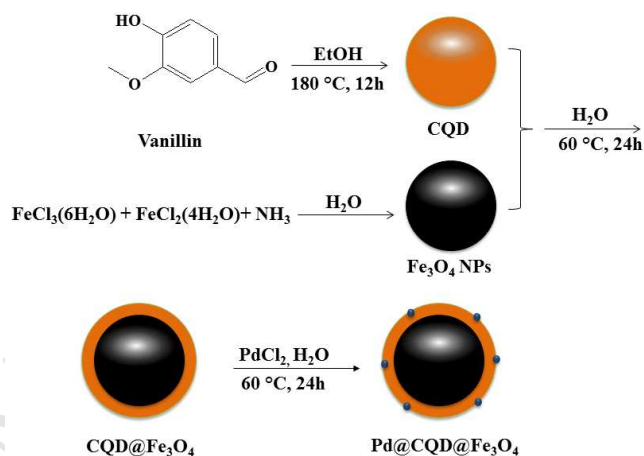
Scheme 1. The preparation steps toward the catalyst.

TEM image showed formation of magnetic nanoparticles in 15-20 nm average size (Fig. 1a). CQD were synthesized by heating an ethanol solution of vanillin in a Teflon autoclave at 180 °C for 12 h. Photoluminescence (PL) emission study of CQDs showed a broad emission centered at 413 nm in the emission spectrum with an excitation wavelength at 350 nm (Fig.1, ESI). Reaction of obtained CQD with magnetite NPs afforded CQD coated Fe_3O_4 NPs. Formation of CQD@Fe_3O_4 was proved by TEM image showing carbon shells around the Fe_3O_4 nanoparticles (Fig. 1b). Finally, Pd@CQD@Fe_3O_4 was obtained by treating of aqueous solution of $PdCl_2$ and CQD@Fe_3O_4 at 80 °C for 24 h. Loading of Pd on the Pd@CQD@Fe_3O_4 was determined using atomic absorption spectroscopy (AAS) analysis to be 0.14 mmolg^{-1}. TEM images of Pd@CQD@Fe_3O_4 showed the presence of small Pd NPs attached on surface of CQD@Fe_3O_4 (Fig. 1c). Also SEM images of the catalyst indicated the presence of dispersed and uniform particles (Fig. 1d).
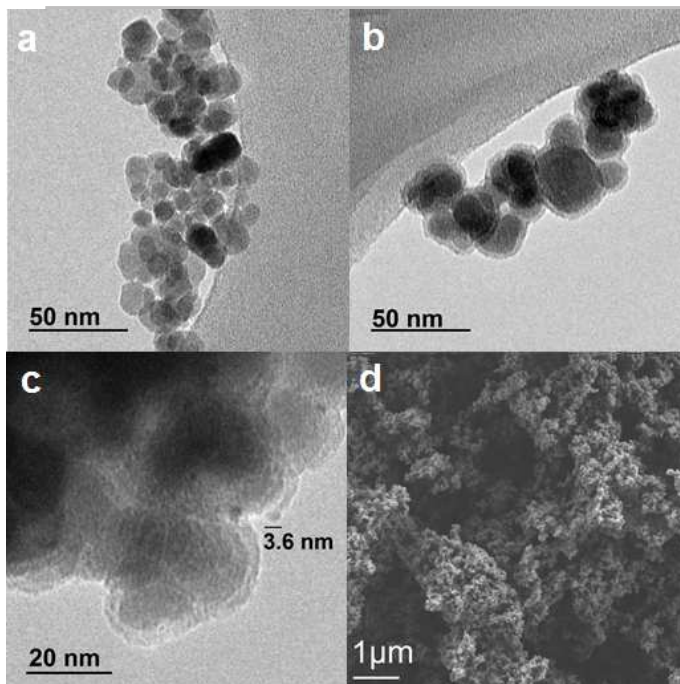
Fig. 1. TEM images of a) Fe₃O₄ NPs, b) CQD@ Fe₃O₄ NPs, c) Pd@CQD@ Fe₃O₄ NPs, and d) SEM image of Pd@CQD@ Fe₃O₄ NPs.

In order to find information about the oxidation state of palladium in the catalyst, a solid UV spectrum of catalyst and PdCl₂ as a source of Pd(II) species was studied (Fig. 2). Results indicated disappearing of a peak related to Pd(II) at 280 nm which confirms the reduction of Pd(II) to Pd(0).[18]
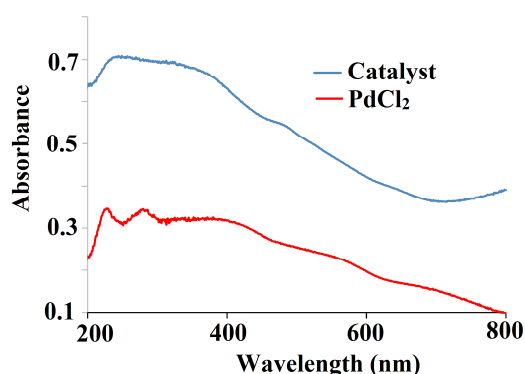

Fig. 2. Solid state UV-Vis spectra of the Pd@CQD@Fe₃O₄ NPs.

Furthermore, oxidation state of palladium in Pd@CQD@Fe₃O₄ was investigated using X-ray photoelectron spectroscopy (XPS). Results showed two intensive doublet peaks at 335.6 and 340.8 eV in Pd 3d region which are assigned to the Pd(0) species (Figure 3). These results indicated that the palladium is in reduced form, confirming the capability of CQD@Fe₃O₄ for efficient reduction of Pd(II) to Pd(0) nanoparticles.[3f, 16a, 19] This reduction only took place partially in the case of citric acid derived CQD.[14]
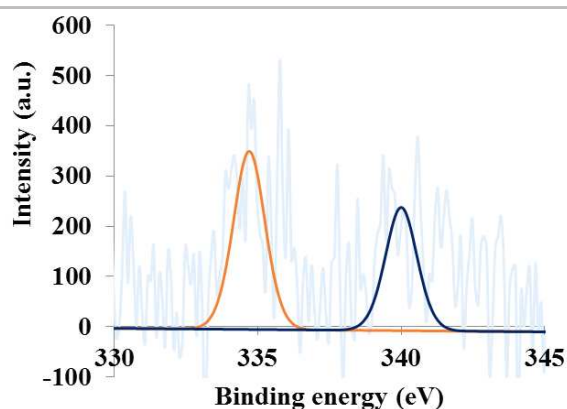

Fig. 3. XPS spectrum of the Pd@CQD@Fe₃O₄ NPs in Pd 3d region.

XPS analysis confirmed the presence of carbon in the structure of Pd@CQD@Fe₃O₄ NPs with related peaks to C1s at 284.8 eV corresponding to C=C, 286.4 eV for C-O, and 288.6 eV for C=O forms of carbon (Fig. 4).[20]
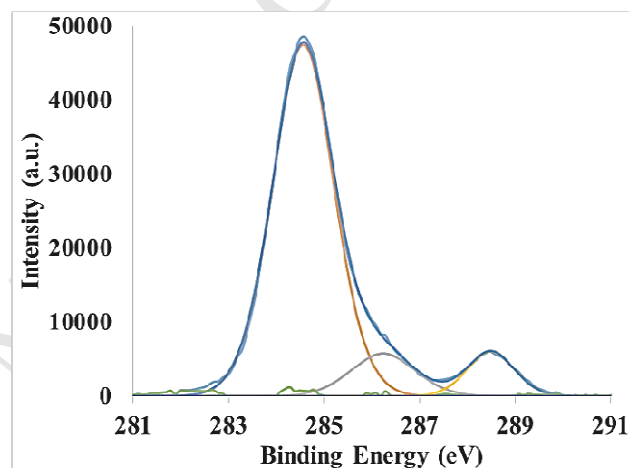

Fig. 4. XPS spectrum of the Pd@CQD@Fe₃O₄ NPs in C 1s region.

The superparamagnetic performance of the catalyst was confirmed using a magnetization curve showing Zero coercivity and remanence on the magnetization loop and absence of hysteresis loop (Fig. 5).
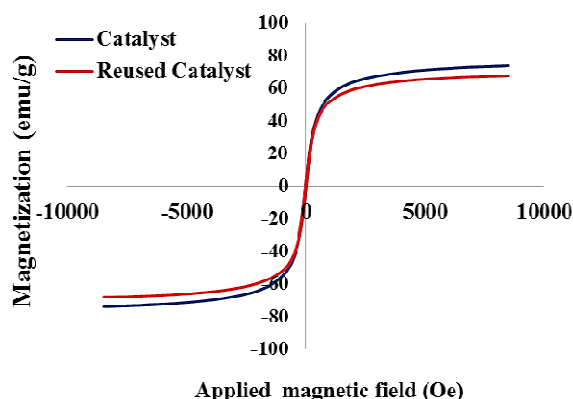

Fig. 5. Magnetization curves of Pd@CQD@Fe₃O₄ NPs and reused catalyst after the 3rd run.

The nitrogen adsorption–desorption isotherms for Pd@CQD@Fe₃O₄ NPs showed type-IV isotherms with a H3

hysteresis loop according to the IUPAC classification (Fig. 6). Also, the Brunauer–Emmett–Teller (BET) surface areas for Pd@CQD@Fe$_3$O$_4$ NPS was determined to be 90 m^{2}g^{-1}.
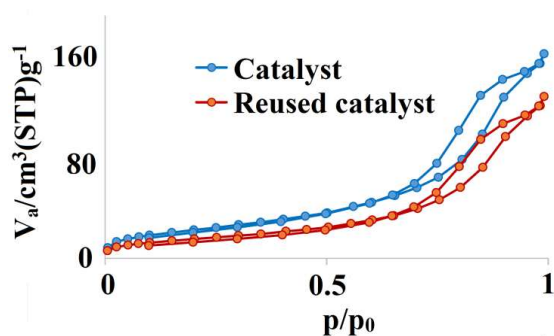
case the Pd loading was lower (0.1 mol% instead of 0.22 mol%) confirming the better efficiency of this new catalyst.

Fig. 6. The nitrogen adsorption-desorption isotherm of the Pd@CQD@Fe$_3$O$_4$ NPs and reused catalyst after the 3rd run.

X-ray powder diffraction (XRD) of sample showed diffracted peaks observed at 2theta value of 30.1°, 35.5°, 43.1°, 53.4°, 57.0°and 62.6° correspond to (210), (311), (400), (422), (511), and (440) plans of Fe$_3$O$_4$ and also related diffraction peaks of Pd(0) corresponding to (111), (200) and (220) plans are detected at 40.2°, 46.7° and 68.2° (Fig. 7).

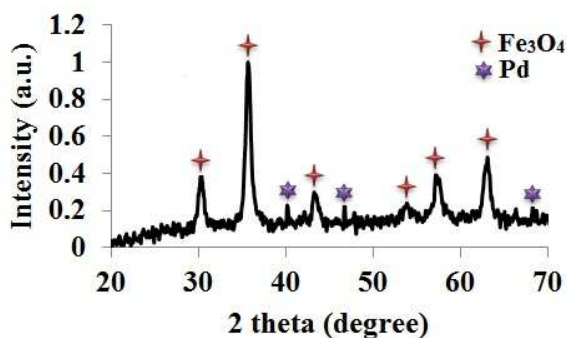**Fig. 7.** XRD pattern of the Pd@CQD@Fe$_3$O$_4$.

The catalytic activity of the prepared Pd@CQD@Fe$_3$O$_4$ NPs was evaluated in the Suzuki–Miyaura cross-coupling reaction. For this purpose, the reaction of 4-bromoanisol with phenylboronic acid was select as the model reaction. Initially, the reaction was studied in water and the effect of different bases such as K$_2$CO$_3$, NaOAc, Et$_3$N and K$_3$PO$_4$ at 30 °C was studied (Table 1, entries 1-4). Results indicated the formation of product in low to moderate yields. However, using NaOAc and K$_2$CO$_3$ in EtOH as the solvent afforded 4-methoxybiphenyl in 72% and 83% yield, respectively (Table 1, entries 5 and 6). In continue, equal mixture of H$_2$O:EtOH was selected as solvent and effect of different bases and catalyst loading were studied (Table 1, entries 7-14). Results indicated that using K$_2$CO$_3$ in aqueous ethanol (1:1), the reaction took place almost quantitatively in 24 h using 0.1 mol% of catalyst at 30 °C (Table 1, entry 7). By lowering the catalyst amount to 0.05 and 0.02 mol%, reactions yields decreased to 70% and 18%, respectively (Table 1, entries 8 and 9). Using other bases such as DABCO, K$_3$PO$_4$, Et$_3$N, and NaOAc in aqueous ethanol (1:1) at 30 °C gave lower yields than K$_2$CO$_3$ for this reaction (Table 1, entries 10-14). Other solvents such as CH$_3$CN, THF and toluene gave very poor results (Table 1, entries 15-17). These reaction conditions (Table 1, entry 7) are similar to the ones used with citric acid derived CQD.[14] However, in this

Table 1. Optimization of the reaction conditions for the reaction of 4-bromoanisol and phenylboronic acid catalyzed by Pd@CQD@Fe$_3$O$_4$ NPs.[a]
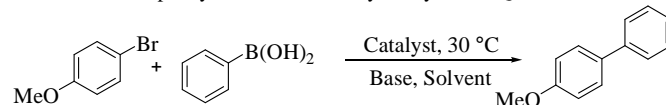
Entry	Pd (mol%)	Base	Solvent	Yield(%)[b]
1	0.1	K$_2$CO$_3$	H$_2$O	49
2	0.1	NaOAc	H$_2$O	34
3	0.1	Et$_3$N	H$_2$O	65
4	0.1	K$_3$PO$_4$	H$_2$O	57
5	0.1	NaOAc	EtOH	72
6	0.1	K$_2$CO$_3$	EtOH	83
7	0.1	K$_2$CO$_3$	H$_2$O:EtOH	100
8	0.05	K$_2$CO$_3$	H$_2$O:EtOH	70
9	0.02	K$_2$CO$_3$	H$_2$O:EtOH	18
10	0.1	NaOAc	H$_2$O:EtOH	22
11	0.1	Et$_3$N	H$_2$O:EtOH	84
12	0.1	DABCO	H$_2$O:EtOH	58
13	0.1	K$_3$PO$_4$	H$_2$O:EtOH	83
14	0.1	NaOH	H$_2$O:EtOH	10
15	0.1	K$_2$CO$_3$	CH$_3$CN	11
16	0.1	K$_2$CO$_3$	THF	4
17	0.1	K$_2$CO$_3$	Toluene	2

[a] Reaction conditions: 4-bromoanisol (0.5 mmol), base (0.75 mmol), solvent (2 mL).
[b] GC yields.

With the optimized reaction conditions in hand, substrate scope of the Suzuki-Miyaura cross-coupling reaction for structurally different aryl halides and arylboronic acids was examined (Table 2). Results of Table 2 indicated that for the aryl bromides having electron-donating groups such as –OH, OMe as well as bromobenzene and aryl bromides containing electron-withdrawing groups such as –CHO, -Cl, -CN, and –NO$_2$ reactions proceed efficiently and gave the corresponding biphenyls in high isolated yields (Table 2, entries 1-8).

Reactions of challenging heterocyclic aryl bromides such as 5-bromopyrimidine and 5-bromoindole with phenylboronic acid were also proceed very well and desired coupling products were obtained in 84-93% yields at room temperature (Table 2, entries 9 and 10). We have also studied the scope of the reaction with different substituted arylboronic acids such as 3,5-difluorophenyl, 3-nitrophenyl, 2-naphthyl, 4-methoxyphenyl and 4-chlorophenyl with aryl bromides, which proceeded efficiently and biphenyl products were obtained in high to excellent yields (Table 2, 11-20).

Reactions of less reactive aryl chlorides were studied under optimized reaction conditions. However, reactions proceed sluggish and very poor results were obtained. Therefore, we examined different reaction conditions such as different temperatures, solvents and bases for the reactions of aryl chlorides (Table 1, SI). Results indicated that reactions of 4-
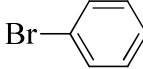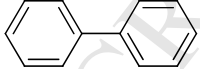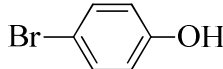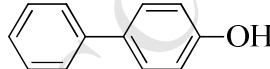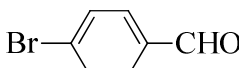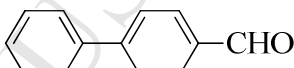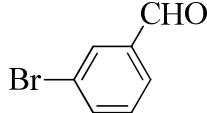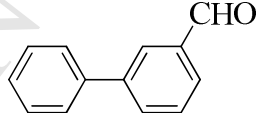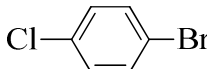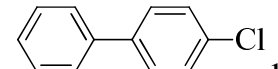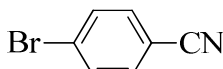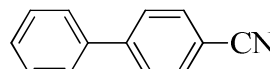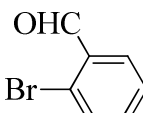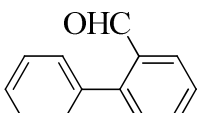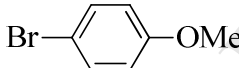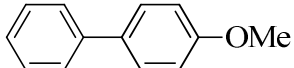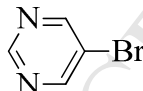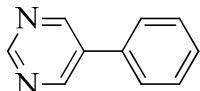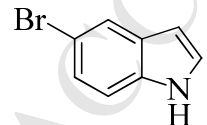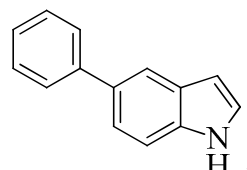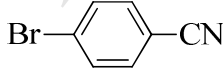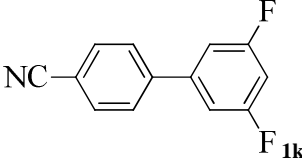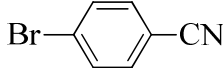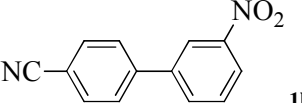
chlorobenzaldehyde, 4-chlorobenzonitrile ~~ACCEPTED MANUSCRIPT~~ and 4-chloronitrobenzene in mixture of H_2O:EtOH using K_2CO_3, t-BuOK and NaOH at 95 °C gave low to moderate yields (Table 1, SI, entries 1-9). By changing solvent to xylene and increasing reaction temperature to 120 °C, yields of reactions were improved (Table 1, ESI, entries 10-18). However, best yields were obtained using PEG200 as solvent and K_2CO_3 as a base at 120 °C (Table 1, SI, entries 19, 22 and 25). Using these new optimized reaction conditions, cross-couplings of activated aryl chlorides with 4-methoxyphenyl- and phenylboronic acids were also studied giving the corresponding products in good yields (Table 2, entries 21-23).
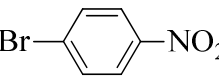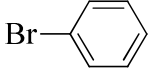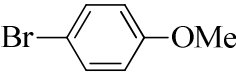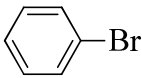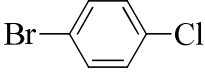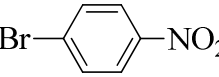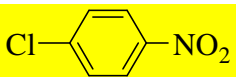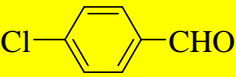
Table 2. The reactions of structurally different aryl chlorides and bromides with arylboronic acids in the presence of the catalyst Pd@CQD@Fe$_3$O$_4$ NPs.[a]

$$Ar^1X + Ar^2B(OH)_2 \xrightarrow[\text{K}_2\text{CO}_3, \text{H}_2\text{O:EtOH or PEG}]{\text{Catalyst, 30-120 °C}} Ar^1-Ar^2$$

X= Br, Cl

Entry	Ar^{1}X	Ar^2	Time (h)	Product	Yield (%)[b]
1	Br—C$_6$H$_5$	Ph	10	**1a**	94
2	Br—C$_6$H$_4$—OH	Ph	10	**1b**	93
3	Br—C$_6$H$_4$—CHO	Ph	2	**1c**	93
4	Br—C$_6$H$_4$—CHO (meta)	Ph	7	**1d**	83
5	Cl—C$_6$H$_4$—Br	Ph	1	**1e**	94
6	Br—C$_6$H$_4$—CN	Ph	0.5	**1f**	91
7	Br—C$_6$H$_4$—CHO (ortho)	Ph	2	**1g**	94
8	Br—C$_6$H$_4$—OMe	Ph	24	**1h**	90
9	pyrimidinyl-Br	Ph	17	**1i**	84
10	indolyl-Br	Ph	24	**1j**	93
11	Br—C$_6$H$_4$—CN	3,5-difluorophenyl	4	**1k**	92
12	Br—C$_6$H$_4$—CN	3-nitrophenyl	36	**1l**	95

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Entry	ArX	ArB(OH)₂	Time (h)	Product	Yield (%)
13	Br—⬡—CN	2-naphthyl	24	naphthyl—⬡—CN **1m**	70
14	Br—⬡—NO₂	3-nitrophenyl	36	O₂N—⬡—⬡—NO₂ **1n**	92
15	Br—⬡	4-metoxyphenyl	3	⬡—⬡—OMe **1i**	88
16	Br—⬡—CN	4-chlorophenyl	3	NC—⬡—⬡—Cl **1o**	94
17	Br—⬡—OMe	4-metoxyphenyl	4	MeO—⬡—⬡—OMe **1p**	92
18	⬡—Br	4-chlorophenyl	3	⬡—⬡—Cl **1e**	83
19	Br—⬡—Cl	4-chlorophenyl	3	Cl—⬡—⬡—Cl **1q**	93
20	Br—⬡—NO₂	4-metoxyphenyl	3	O₂N—⬡—⬡—OMe **1r**	94
21	Cl—⬡—NO₂	4-metoxyphenyl	15	O₂N—⬡—⬡—OMe **1r**	91[b,c]
22	Cl—⬡—CN	Ph	15	⬡—⬡—CN **1f**	80[b,c]
23	Cl—⬡—CHO	Ph	15	⬡—⬡—CHO **1c**	81[b,c]

[a] Reaction conditions: ArBr (0.5 mmol), ArB(OH)₂ (0.75 mmol), K₂CO₃ (0.75 mmol), EtOH:H₂O (2 mL, 1:1), catalyst (3.6 mg containing 0.1 mol% Pd).
[b] Isolated yields.
[c] Reaction conditions: ArCl (0.5 mmol), ArB(OH)₂ (0.75 mmol), K₂CO₃ (0.75 mmol), PEG200 (2 mL), catalyst (3.6 mg containing 0.1 mol% Pd) at 120 °C.

Finally recycling of the Pd@CQD@Fe₃O₄ NPs was studied using the reaction of 4-bromobenzonitrile and phenylboronic acid under optimized reaction conditions. Results of this study by GC indicated that the catalyst recycled for 8 consecutive runs with 12% decrease in activity until run 8 and 27% decrease until run 9 (Fig. 8). It is worth mentioning that leaching of Pd after the 3 run was determined to be 2.3%, slightly higher than in the case of citric acid CQD.[14]

TEM and SEM (Fig. 9) images of reused catalyst confirmed that catalyst preserves its structure during the reactions with small increase in Pd NPs size.
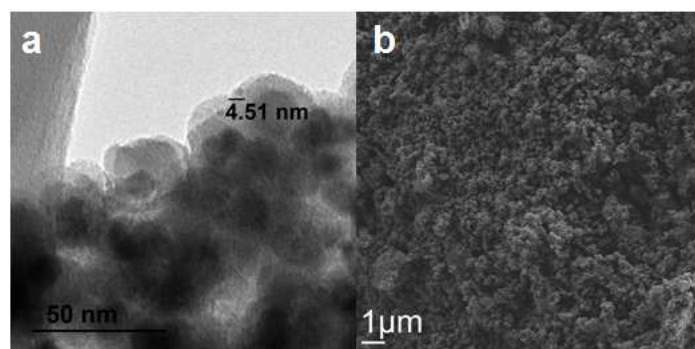
Fig.9. a) TEM image and b) SEM image of reused catalyst after the 3rd

XPS analysis of the reused catalyst showed that Pd is completely in its reduced form showing related doublet peaks at 335.6 and 340.8 eV (Fig. 10). Furthermore, VSM analysis of the reused catalyst showed a small decrease in magnetization value and preserve of superparamagnetic property of material (Fig. 5). These results are further confirmed by nitrogen adsorption–desorption isotherm of reused catalyst which is similar to the fresh catalyst (Fig. 6).

Fig. 8. Recycling of the catalyst for the reaction of 4-bromobenzonitrile with phenylboronic acid at room temperature catalyzed by Pd@CQD@Fe₃O₄ NPs (yields were determined by GC).

Fig. 10. XPS spectrum of the reused catalyst Pd@CQD@Fe$_3$O$_4$ NPs after the 3rd run.

3. Conclusions

In conclusion, the prepared CQD using vanillin as a new cheap and naturally abundant compound, used for modification of Fe$_3$O$_4$ NPs gave CQD@Fe$_3$O$_4$ NPs, which was able to reduce completely Pd(II) to Pd(0) in a greater extent than the previous described cit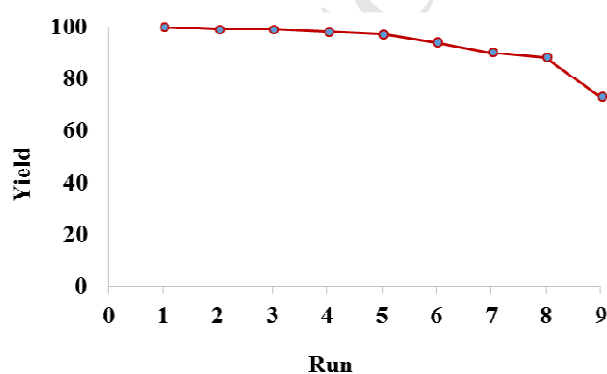ric acid derived CQD. This modified CQD@Fe$_3$O$_4$ NPs was used for stabilization of Pd NPs and the obtained solid was applied as an efficient and magnetically separable heterogeneous catalyst for the Suzuki-Miyaura reaction of aryl and heteroaryl bromides at room temperature in aqueous ethanol and aryl chlorides at 120 °C in PEG 200. The loading of Pd was much lower than in the already described CQD composite Pd Nps. This catalyst was recycled up to eight times with small decrease in its activity and the fresh and recovered catalysts can be characterized by spectroscopic and microscopic techniques.

4. Experimental section

4.1. *Synthesis of CQD from vanillin as carbon source*

Vanillin (0.9 g, 5.9 mmol) was dissolved in ethanol (90 mL) and the mixture was transferred to an autoclave and heated at 180 °C for 12 h. The autoclave was cooled to room temperature and the obtained material was centrifuged at 10000 rpm for 10 min to remove larger particles.

4.2. *Synthesis of CQD@Fe$_3$O$_4$*

Freshly prepared Fe$_3$O$_4$ nanoparticles[17] (0.5 g) were sonicated in water (5 mL) for 15 min. Then, 7 mL of the CQD suspension was added to the flask containing the magnetic nanoparticles. The mixture was mechanically stirred for 24 h at 60 °C. Resulting carbon quantum dots modified Fe$_3$O$_4$ was subjected to magnetic separation and the obtained material was washed with deionized water (3×20 mL) and ethanol (3×20 mL) and dried under vacuum.

3.3.3. Synthesis of Pd@CQD@Fe$_3$O$_4$ NPs

CQD@Fe$_3$O$_4$ (500 mg) was sonicated in water (10 mL) for 30 min at room temperature. In another flask PdCl$_2$ (60 mg, 0.33 mmol) dissolved in water (5 mL). The resulting solution was added to the flask containing CQD@Fe$_3$O$_4$ and the mixture was mechanically stirred for 24 h at 60 °C under reflux. Then, the solid was separated magnetically, washed with water (3×20 mL) and ethanol (3×20 mL) and dried in an oven at 60 °C.

4.3. *General Procedure for calculating of loading of Pd*

First, palladium solutions were prepared with known concentrations of 2, 4, 6, 8 and 10 ppm. The calibration curve was plotted according the absorption intensities of standard solution which recorded by atomic absorption spectrometry. Next, 5 mg of catalyst was dissolved in 5 mL of HCl and HNO$_3$ (ratio 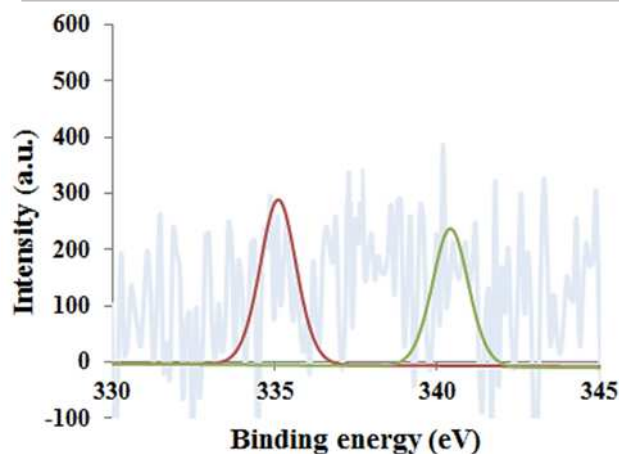of HCl/HNO$_3$ = 3:1 in volume) and was mechanically stirred for 24 h. Finally, the solution diluted with distilled water in volume of 25 mL and the absorption intensity of catalyst was recorded. The amount of palladium was determined according calibration plot to be 0.14 mmolg^{-1}.

4.4. *General Procedure for the Suzuki-Miyaura coupling reaction*

Aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), K$_2$CO$_3$ (104 mg, 0.75 mmol), catalyst (3.6 mg, containing 0.1 mol% Pd) and EtOH:H$_2$O (2 mL, 1:1), were added to a 5 mL flask, and the mixture was stirred mechanically at 30 ºC. The progress of the reaction was monitored by GC. After completion of the reaction, the crude product was extracted using ethyl acetate. The pure products were obtained by column chromatography on silica gel using hexane and ethyl acetate as eluent.

5. Characterizations of products

5.1. 1,1'-biphenyl (**1a**):[21]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.65-7.67 (m, 4H), 7.48-7.52 (m, 4H), 7.39-7.43 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 141.28, 128.80, 127.30, 127.21.

5.2. [1,1'-biphenyl]-4-ol (**1b**):[21]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.57-7.59 (m, 2H), 7.51-7.55 (m, 2H), 7.43-7.47 (m, 2H), 7.33-7.37 (m, 1H), 6.93-6.97 (m, 2H), 4.79 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 155.06, 140.77, 134.08, 128.76, 128.44, 126.76, 126.75, 115.67.

5.3. [1,1'-biphenyl]-4-carbaldehyde (**1c**):[21]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 10.10 (s, 1H), 7.98-8.01 (m, 2H), 7.78-7.81 (m, 2H), 7.66-7.69 (m, 2H), 7.51-7.54 (m, 2H), 7.44-7.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm):192.01, 147.24, 139.75, 135.20, 130.32, 129.05, 128.51, 127.73, 127.41.

5.4. [1,1'-biphenyl]-3-carbaldehyde (**1d**):[21]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 10.13 (s, 1H), 8.14-8.15 (m, 1H), 7.89-7.92 (m, 2H), 7.63-7.73 (m, 3H), 7.50-7.54 (m, 2H), 7.42-7.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm): 192.39, 142.20, 139.72, 136.93, 133.11, 129.53, 129.04, 128.67, 128.24, 128.05, 127.18.

5.5. 4-chloro-1,1'-biphenyl (**1e**):[21]

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 7.58-7.64 (m, 2H), 7.54-7.58 (m, 2H), 7.41-7.50 (m, 4H), 7.37-7.40 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm):140.02, 139.71, 133.80, 133.40, 128.92, 128.90, 128.42, 127.61, 127.01.

5.6. [1,1'-biphenyl]-4-carbonitrile (**1f**):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.75-7.78 (m, 2H), 7.71-7.74 (m, 2H), 7.61-7.71 (m, 2H), 7.50-7.55 (m, 2H), 7.44-7.50 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 145.70, 139.20, 132.64, 129.15, 128.70, 127.77, 127.27, 119.00, 110.93.

5.7. [1,1'-biphenyl]-2-carbaldehyde (1g):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.02 (s, 1H), 8.06-8.08 (m, 1H), 7.66-7.70 (m, 1H), 7.48-7.56 (m, 5H), 7.40-7.47 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):192.55, 146.02, 137.77, 133.73, 133.61, 130.81, 130.14, 128.46, 128.15, 127.81, 127.59.

5.8. 4-methoxy-1,1'-biphenyl (1h):[21]

¹HNMR (400 MHz, CDCl₃) δ(ppm): 7.56-7.62 (m, 4H), 7.45-7.49 (m, 2H), 7.33-7.37 (m, 1H), 7.01-7.05 (m, 2H), 3.90 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):159.17, 140.86, 133.81, 128.76, 128.19, 126.77, 126.69, 114.23, 55.38.

5.9. 5-phenylpyrimidine (1i):[21]

¹HNMR (400 MHz, CDCl₃) δ(ppm): 9.25 (s, 1H), 9.0 (s, 2H), 7.63-7.51 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 157.15, 154.92, 134.51, 134.11, 129.52, 129.17, 127.05.

5.10. 5-phenyl-1H-indole (1j):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (s, 1H), 7.93 (s, 1H), 7.71-7.73 (m, 2H), 7.49-7.54 (m, 4H), 7.38-7.40 (m, 1H), 7.32-7.36 (m, 1H), 6.66-7.68 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):142.59, 135.34, 133.47, 128.70, 128.43, 127.45, 126.37, 124.90, 121.97, 119.31, 111.29, 103.07.

5.11. 3',5'-difluoro-[1,1'-biphenyl]-4-carbonitrile (1k):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.78-7.80 (m, 2H), 7.67-7.70 (m, 2H), 7.11-7.17 (m, 2H), 6.88-6.93 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):164.74, 164.62, 162.27, 162.14, 143.24, 143.21, 143.19, 142.48, 142.39, 142.29, 132.86, 127.75, 118.51, 112.25, 110.42, 110.35, 110.23, 110.16, 104.23, 103.98, 103.73.

5.12. 3'-nitro-[1,1'-biphenyl]-4-carbonitrile (1l):

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.49-8.50 (m, 1H), 8.31-8.34 (m, 1H), 7.95-7.97 (m, 1H), 7.83-7.85 (m, 2H), 7.76-7.79 (m, 2H), 7.70-7.74 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.86, 143.03, 140.84, 133.11, 133.00, 130.25, 127.92, 123.37, 122.18, 118.43, 112.43.

5.13. 4-(naphthalen-2-yl)benzonitrile (1m):[22]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.09 (br, 1H), 7.98-8.00 (m, 1H), 7.91-7.97 (m, 2H), 7.84-7.86 (m, 2H), 7.79-7.81 (m, 2H), 7.73-7.76 (m, 1H), 7.56-7.61 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):145.63, 136.45, 133.51, 133.16, 132.69, 128.98, 128.42, 127.99, 127.76, 126.82, 126.79, 126.59, 124.90, 119.02, 110.94.

5.14. 3,4'-dinitro-1,1'-biphenyl (1n):[23]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.53-8.54 (m, 1H), 8.39-8.42 (m, 2H), 8.33-8.34 (m, 1H), 7.98-8.02(m, 1H), 7.82-7.85 (m, 2H), 7.72-7.76 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.88, 147.93, 144.87, 140.47, 133.23, 130.29, 128.13, 124.48, 123.59, 122.33.

5.15. 4'-chloro-[1,1'-biphenyl]-4-carbonitrile (1o):[24]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.75-7.77 (m, 1H), 7.67-7.69 (m, 1H), 7.54-7.57(m, 1H), 7.46-7.50 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 144.40, 137.60, 134.98, 132.74, 129.36, 128.51, 127.61, 118.81, 111.29.

5.16. 4,4'-dimethoxy-1,1'-biphenyl (1p):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.50-7.52 (m, 4H), 6.98-7.01 (m, 4H), 3.88 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):158.70, 133.50, 127.76, 114.17, 55.38.

5.17. 4,4'-dichloro-1,1'-biphenyl (1q):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.50-7.53 (m, 4H), 7.43-7.46 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):138.45, 133.77, 129.07, 128.24.

5.18. 4-methoxy-4'-nitro-1,1'-biphenyl (1r):[21]

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.30 (d, *J*=8.4, 2H), 7.73 (d, *J*=8.8, 2H), 7.62 (d, J=8.8, 2H), 7.06 (d, *J*=8.8, 2H), 3.91(s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm):160.45, 147.24, 131.10, 128.61, 128.60, 127.11, 124.18, 114.63, 55.46.

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