

# Nitro group reduction and Suzuki reaction catalysed by palladium supported on magnetic nanoparticles modified with carbon quantum dots generated from glycerol and urea

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Glycerol and urea were used as green and cheap sources of carbon quantum dots (CQD) for modifying  $\text{Fe}_3\text{O}_4$  nanoparticles (NPs). The obtained CQD@ $\text{Fe}_3\text{O}_4$  NPs were used for the stabilization of palladium species and the prepared catalyst, Pd@CQD@ $\text{Fe}_3\text{O}_4$ , was characterized using various techniques. This magnetic supported palladium was applied as an efficient catalyst for the reduction of aromatic nitro compounds to primary amines at room temperature using very low palladium loading (0.008 mol%) and also for the Suzuki–Miyaura cross-coupling reaction of aryl halides as well as challenging heteroaryl bromides and aryl diazonium salts with arylboronic acids and with potassium phenyltrifluoroborate. This magnetically recyclable catalyst was recovered and reused for seven consecutive runs in the reduction of 4-nitrotoluene to *p*-toluidine and for ten consecutive runs in the reaction of 4-iodoanisole with phenylboronic acid with small decrease of activity. The catalyst reused in the Suzuki reaction was characterized using transmission electron microscopy, vibrating sample magnetometry and X-ray photoelectron spectroscopy. Using experiments such as hot filtration and poisoning tests, it has been shown that the true catalyst works under homogeneous conditions according to the release–return pathway of active palladium species.

## KEYWORDS

carbon quantum dots, glycerol, magnetic, palladium, Suzuki

## 1 | INTRODUCTION

Nowadays environmental problems encourage chemists to design new reaction processes complemented with green chemistry objectives.<sup>[1]</sup> Along this line, recyclable heterogeneous catalysts play an important role in

decreasing or eliminating chemical wastes, particularly when large-scale operations or industrial scales are considered.<sup>[2]</sup> However, despite the extensive applications of heterogeneous catalysts in organic transformations, using simple methods such as filtration or centrifugation are not efficient and precise for the separation of

expensive and toxic metals such as palladium which have less than 5 ppm allowable limits in pharmaceuticals.<sup>[3,4]</sup> On the other hand, magnetic materials, due to their superparamagnetic behaviour and therefore ease of separation from reaction mixtures, large surface area to volume ratio and low toxicity, have been considered as promising supports for the stabilization of metal catalysts.<sup>[5]</sup>

Reduction of nitro compounds to the corresponding amines is a significant chemical reaction from industrial and academic standpoints. The resulting amines are valuable intermediates in the synthesis of various materials such as dyes, polymers, pesticides, antioxidants, drugs and agrochemicals. Various transition metals show good activities for the reduction of nitro compounds. However, palladium-catalysed nitro reductions offer high efficiency and selectivity for the formation of primary amines.<sup>[6]</sup> Also, among the vast number of reactions catalysed by palladium, the Suzuki–Miyaura reaction, which is the cross-coupling reaction between aryl, vinyl, or alkyl halides or pseudo-halides and organoboron reagents, could be considered one of the most important methods for the formation of different types of compounds, especially biphenyls.<sup>[7]</sup>

Concerning solid supports, carbon quantum dots (CQD) are a new class of carbon-derived nanomaterials with unique properties such as high solubility, photostability and fluorescence emission, being considered green, non-toxic, abundant and inexpensive materials.<sup>[8]</sup> In the past few years, CQD have been prepared using various green and cheap sources such as chitosan,<sup>[9]</sup> orange peels,<sup>[10]</sup> coffee grounds,<sup>[11]</sup> coriander leaves<sup>[12]</sup> and bloomed algae.<sup>[13]</sup> Recently, CQD were synthesized using glycerol as green solvent via a pyrolysis process and applied in cell imaging and drug release.<sup>[14]</sup> New applications of CQD were reported by Dey and co-workers as reducing agents for the synthesis of palladium nanoparticles (NPs) and their applications as efficient catalysts in Heck and Suzuki reactions.<sup>[15]</sup> Also, we recently reported the modification of magnetic NPs and magnesium oxide with CQD or graphene quantum dots and

their application for stabilization of Pd and Pd–Cu NPs in various cross-coupling reactions.<sup>[16]</sup> In continuation of our interest in CQD and magnetic palladium catalysts, herein, we report palladium supported on magnetic NPs of Fe<sub>3</sub>O<sub>4</sub> modified with nitrogen-doped CQD obtained from glycerol and urea as green and non-toxic sources. We envisaged that this material, Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs, could be used as a recyclable catalyst in the reduction of nitroarenes and in Suzuki–Miyaura reactions.

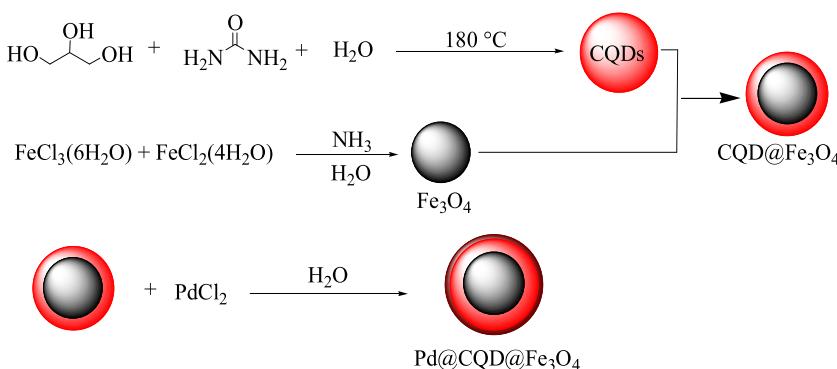
## 2 | RESULTS AND DISCUSSION

Synthetic steps for the preparation of the catalyst are summarized in Scheme 1. The corresponding CQD were obtained by heating glycerol and urea in a Teflon autoclave at 180 °C. Photoluminescence emission study of the prepared CQD showed a broad emission centred at 430 nm with an excitation wavelength at 350 nm (Figure 1), which is a characteristic sign for the formation of CQD.<sup>[7]</sup> In the case of CQD@Fe<sub>3</sub>O<sub>4</sub> NPs, aqueous solution of the prepared CQD was mixed with prepared Fe<sub>3</sub>O<sub>4</sub> NPs<sup>[17]</sup> at 80 °C for 48 h. In the final step, an aqueous solution of CQD@Fe<sub>3</sub>O<sub>4</sub> NPs was treated with a sonication-assisted solution of PdCl<sub>2</sub> under vigorous stirring, and the final solid Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs were obtained with a Pd content of 0.08 mmol g<sup>-1</sup> determined using atomic absorption spectroscopy.

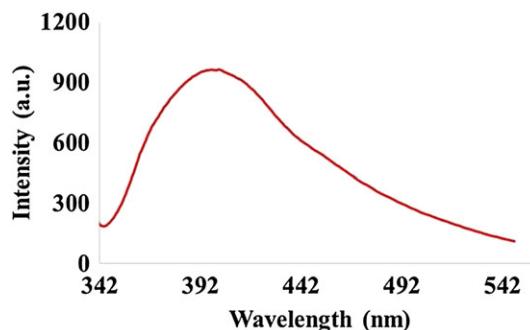
Transmission electron microscopy (TEM) images of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> at different magnifications show that the sample has uniform particles of 15–20 nm. Despite that Pd species are not visible in TEM images, a very thin layer of CQD shell is detectable around the magnetic NPs (Figure 2).

Also, scanning electron microscopy (SEM) images show the presence of highly monodispersed and uniform magnetic NPs (Figure 3).

The corresponding energy-dispersive X-ray spectroscopy (EDS) mapping images of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> indicated the presence of C, N, Fe and Pd in the structure (Figure 4).



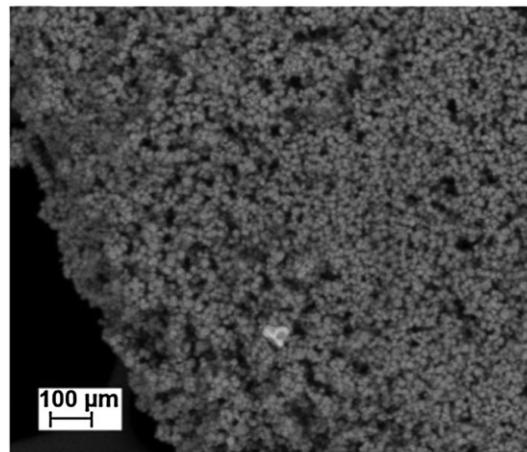
**SCHEME 1** Steps for the preparation of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs



**FIGURE 1** Fluorescence spectrum of CQD prepared from glycerol and urea

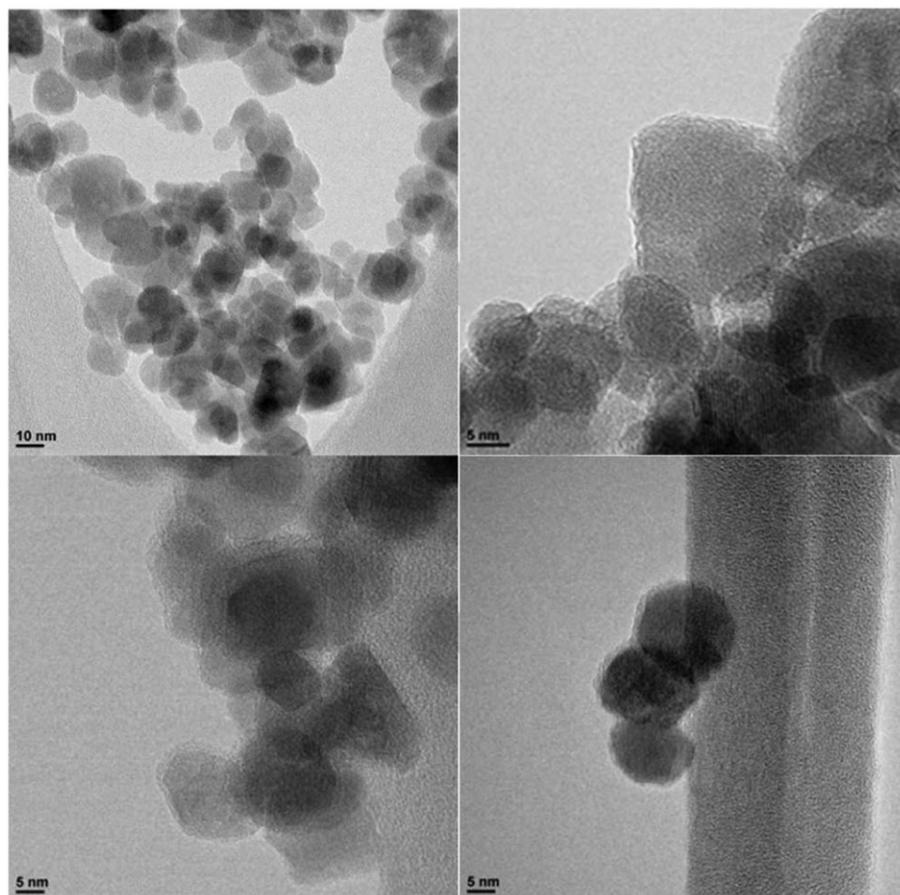
Further insight into the surface composition of the Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs was obtained from X-ray photoelectron spectroscopy (XPS). High-resolution XPS of the obtained materials in the C 1 s region confirmed the presence of carbon from the appearance of four peaks at 284.58, 285.3, 286.02 and 288.80 eV corresponding to C—C/C=C, C—N, C—O and C=O forms of carbon, respectively (Figure 5).<sup>[18]</sup>

Also, the presence of Pd in the structure was proved using XPS by studying the binding energy range of 335–342 eV related to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>. These results

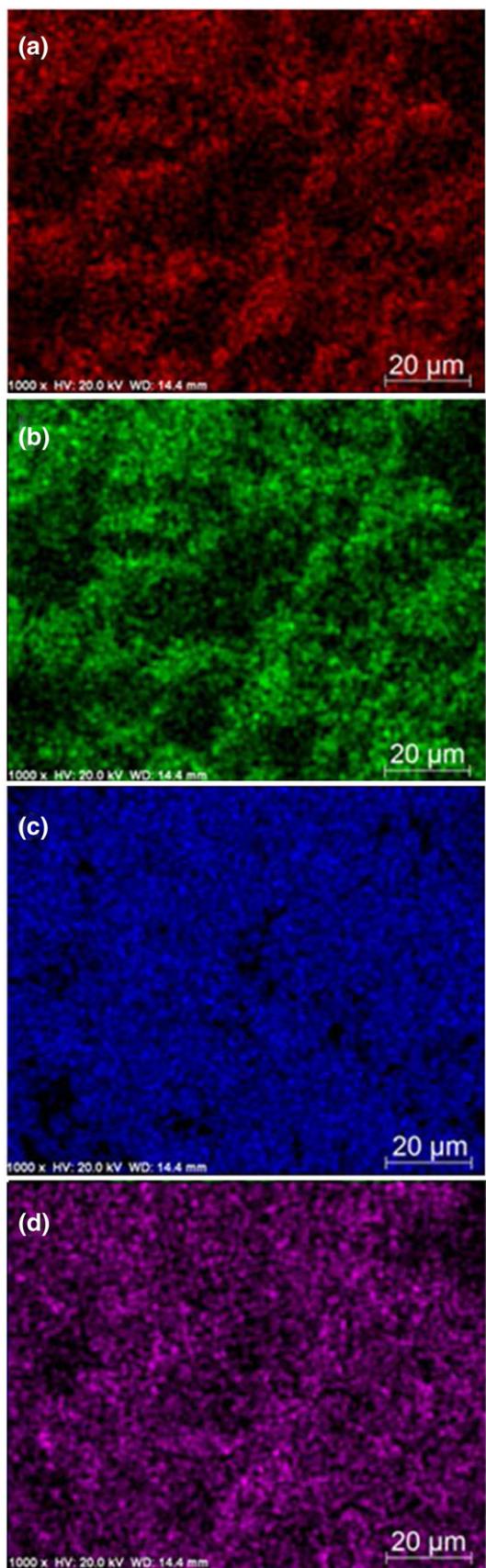


**FIGURE 3** SEM image of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs

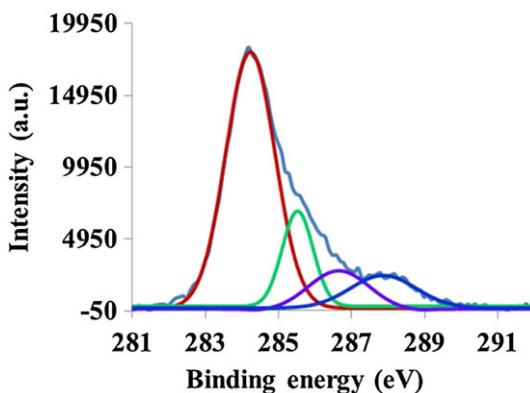
showed the presence of two peaks at 335.6 and 340.8 eV related to Pd(0) and peaks at 338 and 343 eV related to Pd(II) species.<sup>[19,20]</sup> As can be seen in Figure 6, Pd is mainly in metallic state proving the noteworthy ability of CQD for reducing Pd(II) to Pd(0). The mechanism of the metal reduction is not clear for us. However, it is believed that the various hydroxyl and carboxyl



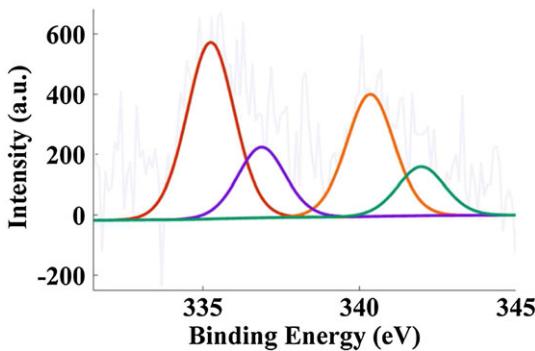
**FIGURE 2** TEM images of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs at different magnifications



**FIGURE 4** EDS mapping images of (a) C, (b) N, (c) Fe and (d) Pd.



**FIGURE 5** XPS spectrum of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs in C 1 s region



**FIGURE 6** XPS spectrum of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs in Pd 3d region

functionalized groups on the CQD surface can act as reducing agents and produce metal NPs.<sup>[15,21]</sup>

Powder X-ray diffraction (XRD) study of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> showed peaks at  $2\theta$  values of  $40.2^\circ$ ,  $46.7^\circ$  and  $68.2^\circ$  related to (111), (200) and (220) planes of Pd(0) and  $2\theta$  values of  $30.1^\circ$ ,  $35.5^\circ$ ,  $43.1^\circ$ ,  $53.4^\circ$ ,  $57.0^\circ$  and  $62.6^\circ$  corresponding to (210), (311), (400), (422), (511) and (440) planes of Fe<sub>3</sub>O<sub>4</sub> (Figure 7).<sup>[22]</sup>

The superparamagnetic property of the catalyst was confirmed from the magnetization curve ( $74 \text{ emu g}^{-1}$ ), showing zero coercivity and remanence on the magnetization loop and absence of hysteresis loop (Figure 8).

The nitrogen adsorption–desorption isotherms for Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs were of type IV with H3 hysteresis loop according to the IUPAC classification, and the Brunauer–Emmett–Teller surface areas of  $71 \text{ m}^2 \text{ g}^{-1}$  (Figure S1, supporting information). The pore size distribution of the catalyst was calculated from adsorption branch of the isotherm using the Barrett–Joyner–Halenda method. A relatively narrow pore size distribution at a mean value of  $r_p = 1.64 \text{ nm}$  and pore volume of  $v_p = 0.45 \text{ cm}^3 \text{ g}^{-1}$  for the catalyst indicate appropriate size distribution (Figure S2, supporting information).

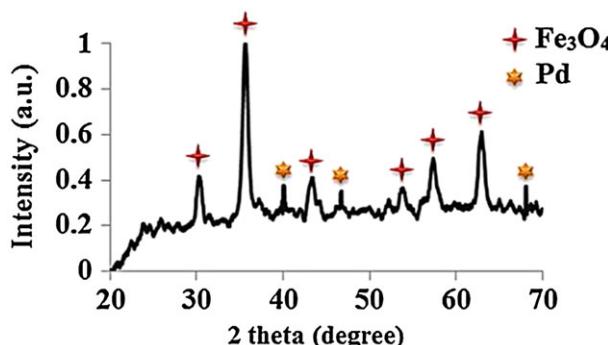


FIGURE 7 XRD pattern of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs

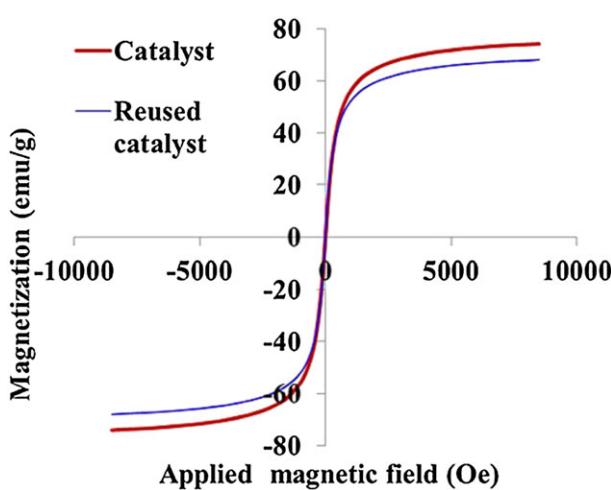


FIGURE 8 Magnetization curves of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs and of reused catalyst after third run.

Thermogravimetric analysis of the Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs showed one weight loss in the range 25–100 °C which is related to physisorbed water and solvents and a second main weight loss between 250 and 340 °C, which is related to the decomposition of CQD. This result confirmed the thermal stability and negligible leaching of the structure up to 250 °C (Figure 9).

The catalytic properties of the Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs were first assessed in the reduction of aromatic nitro compounds. We focused our initial investigation on the effect of various types of reducing agents and palladium amount on the reduction of nitrobenzene as a model reaction in aqueous ethanol (Table 1). Results indicated that using NaBH<sub>4</sub> as source of hydrogen and 0.1 mol% Pd at room temperature, the reaction proceed well and 100% conversion of nitrobenzene to aniline was obtained (Table 1, entry 1). Therefore, we used a smaller amount of Pd (0.002–0.008 mol%) at room temperature (Table 1, entries 2–5). Results of this study showed excellent conversion to desired product using 0.008 mol% of Pd catalyst during 2 h (Table 1, entry 5). Using other hydrogen sources under

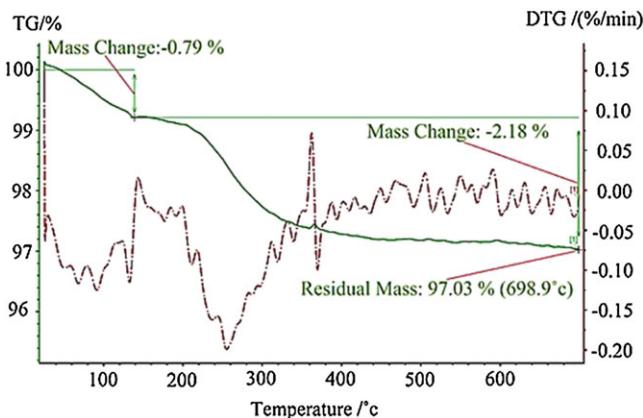


FIGURE 9 Thermogravimetric analysis of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs

different reaction conditions gave lower yields for the reaction (Table 1, entries 6–12). Thus, we selected NaBH<sub>4</sub> as a source of hydrogen and 0.008 mol% of Pd loading at room temperature as the optimized reaction conditions. It is worth mentioning that NaBH<sub>4</sub> is a mild and efficient reducing agent for the reduction of nitro group<sup>[23]</sup> and the model reaction in the absence of Pd catalyst failed to proceed (Table 1, entry 13).

Next, the scope and limitations of this reductive methodology using a series of nitroarenes were examined (Table 2). The results indicated that the reduction of aromatic nitro compounds containing electron-donating groups such as Me, —OMe and —NH<sub>2</sub> (Table 2, entries 2–5) as well as nitroarenes having electron-withdrawing groups such as —NO<sub>2</sub>, F, —COMe and Br proceeded well and afforded the corresponding amines in high to excellent yields (Table 2, entries 6–10). Also, reactions of nitroarenes containing *o*-substituents proceed effectively and gave amines in high to excellent yields (Table 2, entries 11–14). Finally the reduction of 2,6-dimethylnitrobenzene, as a highly sterically hindered nitroarene, took place giving the corresponding amine in high 91% yield after 24 h (Table 2, entry 15).

In an attempt to extend the application of this catalyst, Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> was used in the Suzuki–Miyaura cross-coupling reaction of aryl halides. In order to study the optimized reaction conditions, 4-bromoanisole was allowed to react with phenylboronic acid and the effects of various factors such as solvent and base were considered. Results of this study indicated that using equal mixture of ethanol and water as a solvent, *t*-BuOK as a base and 0.3 mol% of Pd catalyst gave the desired product in 92% yield (Table 3, entry 4).

Using the optimized reaction conditions, the Suzuki reaction of structurally different aryl halides with various arylboron compounds was studied. Reactions of aryl bromides containing electron-withdrawing groups such as 4-NO<sub>2</sub>, 4-CN, 4-Cl, 4-COCH<sub>3</sub>, 4-CHO and 3-CHO with

**TABLE 1** Optimization of reaction conditions for reduction of nitrobenzene<sup>a</sup>

Entry	H donor	Temp. (°C)	Time (h)	Catalyst (mol%)	Yield (%) <sup>b</sup>
1	NaBH <sub>4</sub>	r.t.	2	0.1	100
2	NaBH <sub>4</sub>	r.t.	2	0.002	10
3	NaBH <sub>4</sub>	r.t.	24	0.002	64
4	NaBH <sub>4</sub>	r.t.	24	0.004	91
5	NaBH <sub>4</sub>	r.t.	2	0.008	97
6	NH <sub>4</sub> HCO <sub>2</sub>	90	24	0.008	7
7	NH <sub>4</sub> HCO <sub>2</sub>	r.t.	24	0.1	3
8	N <sub>2</sub> H <sub>4</sub>	r.t.	24	0.008	2
9	N <sub>2</sub> H <sub>4</sub>	r.t.	24	0.1	2
10	HCO <sub>2</sub> H	r.t.	24	0.008	1
11	Glycerol	r.t.	24	0.008	1
12	i-PrOH	r.t.	24	0.008	0
13	NaBH <sub>4</sub>	r.t.	24	—	0

<sup>a</sup>Reaction conditions: nitrobenzene (0.5 mmol), H donor (2 eq.), catalyst and solvent (2 mL).

<sup>b</sup>GC yields using normalization method.

phenylboronic acid proceeded efficiently and the desired biphenyls were obtained in high to excellent yields (Table 4, entries 1–6). Also, reactions of less reactive aryl bromides containing electron-donating groups such as —OH and —OMe as well as bromobenzene and 1-bromonaphthalene proceeded efficiently and afforded biphenyls in high to excellent yields (Table 4, entries 7–10). Reactions of challenging 2-bromopyridine and 5-bromopyrimidine as heterocyclic compounds proceeded efficiently without poisoning and deactivation of the catalyst by heteroatoms and afforded products in 82–90% isolated yields (Table 4, entries 11 and 12). Furthermore, reactions of aryl bromides with other arylboronic acids and potassium phenyltrifluoroborate gave products in high to excellent yields (Table 4, entries 13–21). Reactions of aryl chlorides under the optimized reaction conditions were sluggish; therefore different reaction conditions were studied. It has been found that using PEG200 and NaOH at 120 °C are the most effective conditions for the Suzuki reaction of aryl chlorides (Table 4, entries 22–25). In addition, reactions of aryl iodides with arylboronic acids under optimized reaction conditions proceeded very efficiently and afforded coupling products in excellent yields in less than 4 h (Table 4, entries 26–28).

Arendiazonium salts are alternative substrates to aryl halides in various Pd-catalysed coupling reactions<sup>[24]</sup> and can be easily prepared from commercially available anilines. In order to show the potential activity of the catalyst under investigation, we studied the Suzuki reaction of different aryl diazonium tetrafluoroborates

with phenylboronic acid under the optimized reaction conditions. Results of this study showed formation of desired products in high to excellent yields using either electron-donating or electron-withdrawing substituents in the aryl diazonium salt (Table 4, entries 29–33).

In order to study the recycling properties of the catalyst, reduction of 4-nitrotoluene under optimized reaction conditions was studied. After completion of the reaction, the catalyst was separated using an external magnet and, after washing with diethyl ether and drying, it was used in another reaction run. Results showed that this catalyst can be recovered and reused for seven consecutive runs without significant decrease in activity (Figure 10). Also, the recyclability of the catalyst was studied in the Suzuki reaction of 4-iodoanisole with phenylboronic acid under the optimized reaction conditions. Also in this case, the catalyst can be easily recycled, using an external magnet (Figure S3, supporting information), during ten consecutive runs with very small decrease in catalytic activity (Figure 10).

TEM images of the reused catalyst after ten runs showed that the structure was preserved and also the presence of the CQD shell (Figure 11). Leaching of Pd and Fe from the catalyst after ten runs was found to be 16 and 0.2%, respectively. These results confirm the strong ability of CQD for protection of Fe<sub>3</sub>O<sub>4</sub> NPs and preventing their leaching and aggregation during the recycling processes. However, XPS study of reused catalyst after the third run showed that all palladium species are excited in reduced Pd(0) form (Figure 12). Study of the

**TABLE 2** Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs-catalysed reduction of nitroarenes using NaBH<sub>4</sub> as a hydrogen source in aqueous ethanol at room temperature<sup>a</sup>

Entry	Substrate	Product	Yield (%) <sup>b</sup>	Time (h)
				Catalyst (0.008 mol%)
1			97	2
2			87 (100)	2 (4)
3			86 (100)	2 (4)
4			93	4
5			90 (100)	4 (12)
6			99	2
7			98	4
8			97	8
9			97	5
10			96	4
11			95	4
12			91	4
13			98	6
14			96	2

(Continues)

TABLE 2 (Continued)

Entry	Substrate	Product	Yield (%) <sup>b</sup>	Time (h)
15			91	24

<sup>a</sup>Reaction conditions: nitroarene (0.5 mmol), catalyst (0.008 mol% Pd), NaBH<sub>4</sub> (2 eq.), H<sub>2</sub>O-EtOH (5:1, 2 ml) at room temperature under argon atmosphere.

<sup>b</sup>GC yield.

TABLE 3 Optimization of reaction conditions of 4-bromoanisole and phenylboronic acid catalysed by Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs<sup>a</sup>

Entry	Catalyst (mol% Pd)	Base	Solvent	Yield (%) <sup>b</sup>
1	0.3	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O-EtOH	53
2	0.3	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O-CH <sub>3</sub> CN	10
3	0.3	NaOH	H <sub>2</sub> O-EtOH	49
4	0.3	t-BuOK	H <sub>2</sub> O-EtOH	92
5	0.2	t-BuOK	H <sub>2</sub> O-EtOH	71
6	0.1	t-BuOK	H <sub>2</sub> O-EtOH	53
7	0.01	t-BuOK	H <sub>2</sub> O-EtOH	7
8	0.3	t-BuOK	H <sub>2</sub> O-EtOH	15 <sup>c</sup>
9	0.3	t-BuOK	EtOH	63
10	0.3	t-BuOK	H <sub>2</sub> O	72
11	0.3	NaOH	H <sub>2</sub> O	53
12	0.3	NaOH	EtOH	70
11	0.3	NaOH	H <sub>2</sub> O-EtOH	41

<sup>a</sup>Reaction conditions: 4-bromoanisole (0.5 mmol), phenylboronic acid (0.75 mmol), base (0.75 mmol), catalyst and solvent (2 ml).

<sup>b</sup>GC yields using normalization method.

<sup>c</sup>Reaction performed at 50 °C.

magnetization curve of reused catalyst showed that the catalyst preserved its superparamagnetic properties with very small decrease of magnetization (Figure 8). Also, the nitrogen adsorption-desorption isotherms for Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs showed preservation of the structure with isotherms similar to that of the fresh catalyst (Figure S4, supporting information). In addition, these results indicated  $v_p = 0.30 \text{ cm}^3 \text{ g}^{-1}$  and  $r_p = 4.61 \text{ nm}$  for the recycled catalyst which may be due to damage of walls of pores during the washing and recycling of the catalyst (Figure S5, supporting information).

To understand whether the catalyst works via a heterogeneous pathway, or proceeds using leached Pd, we used the hot filtration test for the reaction of 4-

bromobenzaldehyde with phenylboronic acid under the optimized reaction conditions. During this test, the catalyst was stirred in the reaction solvent (H<sub>2</sub>O-EtOH) for 30 min at 60 °C. Then, the catalyst was removed by filtration and 4-bromobenzaldehyde, phenylboronic acid and t-BuOK were added and the resulting mixture was allowed to react. After 2 h, GC analysis of reaction showed the formation of 25% of the desired coupling product and 75% of 4-bromobenzaldehyde. It should be noted that a positive hot filtration test is interpreted as proof for homogeneous catalysis, whereas a negative hot filtration test does not necessarily indicate the emergence of heterogeneous catalysis due to the possibility of fast deactivation or redeposition of soluble active species. Furthermore, using

**TABLE 4** Reactions of structurally different aryl halides and aryldiazonium tetrafluoroborates with arylboronic acids and potassium phenyl trifluoroborate in the presence of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs catalyst<sup>a</sup>

Entry	Ar <sup>1</sup>	Ar <sup>2</sup> BR	Time (h)	Product	Yield (%) <sup>b</sup>	Catalyst (0.3 mol%)
						t-BuOK, EtOH:H <sub>2</sub> O (1:1)
X=Cl, Br, I, N <sub>2</sub> <sup>+</sup> BF <sub>4</sub> <sup>-</sup>						60–120 °C
R=(OH) <sub>2</sub> , F <sub>3</sub> K						
1		PhB(OH) <sub>2</sub>	2		94	
2		PhB(OH) <sub>2</sub>	2		100 <sup>c</sup>	
3		PhB(OH) <sub>2</sub>	12		80	
4		PhB(OH) <sub>2</sub>	2		99 <sup>c</sup>	
5		PhB(OH) <sub>2</sub>	2		94	
6		PhB(OH) <sub>2</sub>	12		85	
7		PhB(OH) <sub>2</sub>	12		88	
8		PhB(OH) <sub>2</sub>	12		99 <sup>c</sup>	
9		PhB(OH) <sub>2</sub>	24		96	
10		PhB(OH) <sub>2</sub>	24		77	
11		PhB(OH) <sub>2</sub>	24		90	
12		PhB(OH) <sub>2</sub>	24		82	
13		MeO--B(OH) <sub>2</sub>	24		95	
14		Cl--B(OH) <sub>2</sub>	3		100 <sup>c</sup>	

(Continues)

TABLE 4 (Continued)

Entry	Ar <sup>1</sup>	Ar <sup>2</sup> BR	Catalyst (0.3 mol%)	Ar <sup>1</sup> -Ar <sup>2</sup>	Time (h)	Product	Yield (%) <sup>b</sup>
15					4		93
16					24		93
17					24		92
18		PhBF <sub>3</sub> K			4		93
19		PhBF <sub>3</sub> K			4		94
20		PhBF <sub>3</sub> K			12		80
21		PhBF <sub>3</sub> K			9		83
22		PhB(OH) <sub>2</sub>			24		86 <sup>d</sup>
23		PhB(OH) <sub>2</sub>			24		95 <sup>d</sup>
24		PhB(OH) <sub>2</sub>			24		75 <sup>d</sup>
25		PhB(OH) <sub>2</sub>			24		91 <sup>c,d</sup>
26		PhB(OH) <sub>2</sub>			1		95
27		PhB(OH) <sub>2</sub>			4		100 <sup>c</sup>
28		PhB(OH) <sub>2</sub>			4		95

(Continues)

**TABLE 4** (Continued)

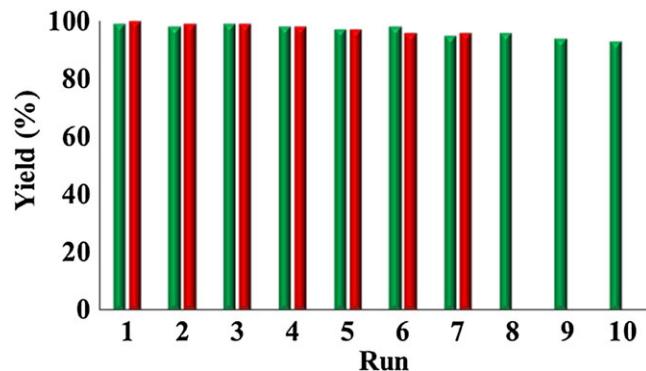
Entry	Ar <sup>1</sup>	Ar <sup>2</sup> BR	Catalyst (0.3 mol%)	Ar <sup>1</sup> -Ar <sup>2</sup>		
				t-BuOK, EtOH:H <sub>2</sub> O (1:1)	60-120 °C	
29		PhB(OH) <sub>2</sub>		3		91
30		MeO-C <sub>6</sub> H <sub>4</sub> -B(OH) <sub>2</sub>		3		97
31		PhB(OH) <sub>2</sub>		3		90
32		PhB(OH) <sub>2</sub>		3		88
33		PhB(OH) <sub>2</sub>		1		96

<sup>a</sup>Reaction conditions: Ar<sup>1</sup>X (0.5 mmol), Ar<sup>2</sup>BR (0.75 mmol), t-BuOK (0.75 mmol), EtOH-H<sub>2</sub>O (2 ml, 1:1), catalyst Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs (0.3 mol% Pd) at 60 °C.

<sup>b</sup>Isolated yield.

<sup>c</sup>GC yield.

<sup>d</sup>Reaction conditions: ArCl (0.5 mmol), PhB(OH)<sub>2</sub> (0.75 mmol), NaOH (0.75 mmol), PEG200 (2 ml), catalyst Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs (0.3 mol% Pd) at 120 °C.

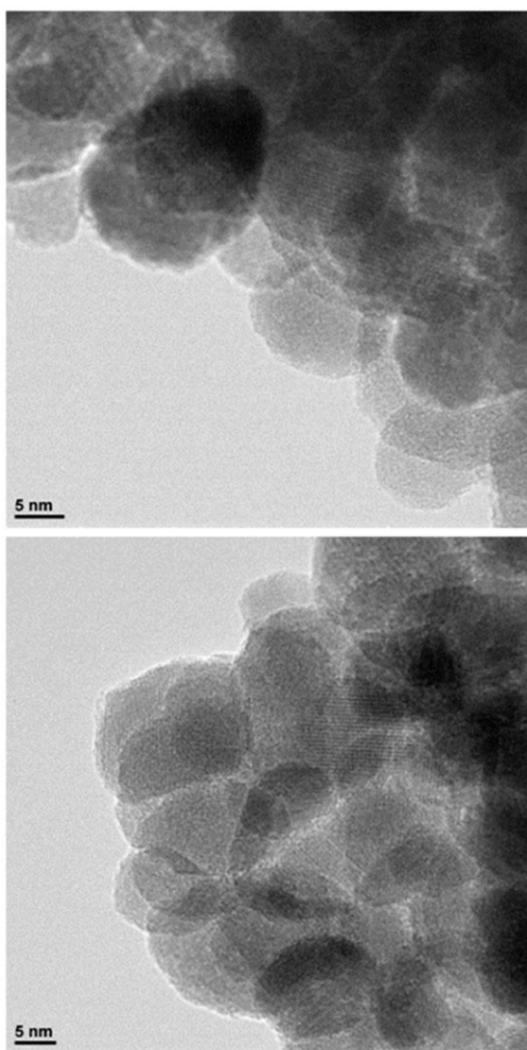


**FIGURE 10** Recycling of Pd@CQD@Fe<sub>3</sub>O<sub>4</sub> NPs catalyst in the reduction of 4-nitrotoluene (red) and Suzuki reaction of 4-iodoanisole with phenylboronic acid (green)

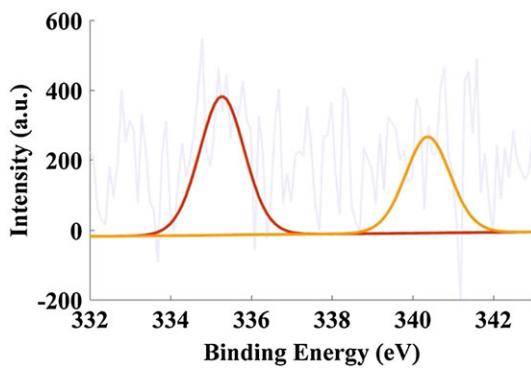
solely hot filtration test for detection of heterogeneous versus homogeneous catalysis is not sufficient and further experiments are needed for finding the nature of the catalyst.<sup>[25]</sup> In order to gain more insight into the behaviour of the catalyst in the reaction, we added polyvinylpyridine (PVPy; 2% cross-linked) as an efficient poisoning agent for soluble palladium species to the reaction mixture of 4-bromobenzaldehyde with phenylboronic acid in a molar ratio of 100:1 (PVPy:Pd). Very interestingly, results

showed that the reaction was quenched without formation of product and starting material was intact. Also, addition of SH@Fe<sub>3</sub>O<sub>4</sub>, obtained from modification of Fe<sub>3</sub>O<sub>4</sub> NPs with 3-mercaptopropyltrimethoxysilane, showed complete suppression of activity.<sup>[25]</sup> Another method for detection of homogeneous systems versus heterogeneous ones is an inverse relationship between the active Pd concentration and the conversion in homogeneous mechanisms. To investigate the effect of Pd concentration, reaction of 4-bromobenzaldehyde with phenylboronic acid using 0.3, 1 and 2 mol% was studied. Results showed the formation of products in 92, 90 and 78% yields, respectively. This reduction of reactivity with higher percentage of Pd catalyst is attributed to the formation of inactive Pd clusters from leached soluble Pd species.<sup>[26]</sup>

From the results of experiments discussed above, we conclude that when using this catalyst, reactions proceed via a release-return Pd(0) system in which leached active Pd(0) species catalysed the reaction and transfer of Pd between solvent and support is responsible for its recycling.<sup>[27]</sup> These results are similar to those obtained by Arai and co-workers in which when a homogeneous Pd catalyst was used in the presence of additional support, the Pd species deposited on the support after the completion of the reaction.<sup>[28]</sup>



**FIGURE 11** TEM images of reused catalyst after tenth run for the reaction of 4-iodoanisole with phenylboronic acid



**FIGURE 12** XPS spectrum of reused Pd catalyst in 3d region for the reaction of 4-iodoanisole with phenylboronic acid after third run

### 3 | CONCLUSIONS

In this work we prepared  $\text{Fe}_3\text{O}_4$  NPs modified with CQD obtained from glycerol and urea as cheap and green starting materials. The new magnetic compound can

reduce Pd(II) to Pd(0) and the obtained  $\text{Pd}@\text{CQD}@\text{Fe}_3\text{O}_4$  NPs catalyst showed high activity in the selective reduction of nitroarenes and the Suzuki cross-coupling reaction. This magnetically recyclable catalyst was reused for several times in both reactions without significant loss of activity, and the fresh and recovered catalysts were characterized using various techniques. The true nature of the catalyst in Suzuki reaction was also determined using different tests to be a homogeneous system.

## 4 | EXPERIMENTAL

### 4.1 | Synthesis of $\text{Fe}_3\text{O}_4$ NPs

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (16 mmol, 4.32 g) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (8 mmol, 1.59 g) were dissolved in deionized water (150 ml) under argon atmosphere and vigorous mechanical stirring. Then, aqueous ammonia (25%, 13 ml) was added slowly under argon atmosphere and the resulting mixture was stirred at 80 °C for 4 h. The black magnetic precipitates were separated using an external magnet and washed several times with deionized water and ethanol and dried in a vacuum oven at 60 °C for 24 h to afford black magnetic NPs.

### 4.2 | Synthesis of $\text{CQD}@\text{Fe}_3\text{O}_4$

The CQD used in our experiments were synthesized by carbonization of glycerol and urea. A solution of glycerol (12.5 ml) and urea (1 g) in distilled water (10 ml) was stirred at room temperature for 10 min and the resulting mixture was heated in a Teflon autoclave at 180 °C for 4 h. Then, the mixture was cooled to room temperature and the obtained material was centrifuged at 10 000 rpm for 10 min to remove larger particles. After centrifugation the viscous oil was transferred to a 25 ml flask containing  $\text{Fe}_3\text{O}_4$  NPs (500 mg in 10 ml of water) and the mixture sonicated for 15 min. Then, this mixture was stirred using a mechanical stirrer at 80 °C for 48 h. Resulting  $\text{CQD}@\text{Fe}_3\text{O}_4$  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.

### 4.3 | Synthesis of $\text{Pd}@\text{CQD}@\text{Fe}_3\text{O}_4$

In a 50 ml flask,  $\text{CQD}@\text{Fe}_3\text{O}_4$  (1 g) was sonicated in water (7 ml) for 10 min. In another batch,  $\text{PdCl}_2$  (20 mg, 0.11 mmol) was sonicated and dissolved in water (3 ml) and the resulting solution was added slowly to the flask containing  $\text{CQD}@\text{Fe}_3\text{O}_4$  under argon atmosphere and the mixture stirred at 60 °C for 24 h. Then, the resultant solids were collected using a magnet, followed by washing

with water ( $2 \times 10$  ml) and EtOH ( $2 \times 10$  ml) and dried under vacuum at  $70^\circ\text{C}$ .

#### 4.4 | General procedure for catalytic reduction of nitro compounds

Nitroarene (0.5 mmol),  $\text{NaBH}_4$  (2 eq.), catalyst (0.008 mol% Pd) and water–ethanol (5:1, 2 ml) were added to a 5 ml flask and stirred for appropriate reaction time at room temperature. Progress of the reactions was monitored by GC analysis. After completion of the reaction, crude product was extracted with ethyl acetate ( $3 \times 5$  ml) and purified using column or plate chromatography.

#### 4.5 | General procedure for Suzuki–Miyaura reaction

Aryl halide or arenediazonium salt (0.5 mmol), arylborane compound (0.75 mmol), base (0.75 mmol),  $\text{Pd@CQD@Fe}_3\text{O}_4$  NPs catalyst (0.3 mol% Pd) and solvent (2 ml of aqueous ethanol or PEG 200) were added to a 5 ml flask, and the mixture was stirred mechanically at appropriate temperature ( $60\text{--}120^\circ\text{C}$ ). The progress of the reaction was monitored by GC or TLC. After completion of the reaction, the crude product was extracted using ethyl acetate or dichloromethane. The pure products were obtained by column or TLC plate chromatography on silica gel.

#### 4.6 | Typical recycling procedure for reaction of 4-Iodanisole with Phenylboronic acid

After completion of the reaction which was monitored by GC analysis, the catalyst was separated using an external magnet. Then, the separated catalyst was washed with diethyl ether and after drying was used in another run of the reaction. This process was repeated for ten consecutive runs. A similar process was applied for the recycling of the catalyst in the reduction reaction.

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