

Pd immobilized on hybrid of magnetic graphene quantum dots and cyclodextrin decorated chitosan: An efficient hydrogenation catalyst

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ABSTRACT

Magnetic graphene quantum dots were prepared and incorporated in cyclodextrin decorated chitosan. The resulting hybrid was then palladated and characterized using TEM, BET, TGA, XRD, VSM, ICP and FTIR spectroscopy. Next, the catalytic activity of the prepared hybrid catalyst that benefits from the chemistry of both carbohydrates and magnetic graphene quantum dots was investigated for promoting hydrogenation reaction of nitroarenes in aqueous media under mild reaction condition. The study of the catalyst performance confirmed high catalytic activity and selectivity of the catalyst towards hydrogenation of the nitro group. Moreover, the catalyst could be magnetically separated from the reaction mixture and recycled up to ten reaction runs with a slight loss of the catalytic activity and Pd leaching. These results showed that the hybrid of magnetic graphene quantum dots and carbohydrates is an efficient catalyst support that can be potentially applied for the immobilization of nanoparticles to furnish heterogeneous catalysts for promoting the chemical transformations.

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1. Introduction

The use of carbohydrates as supports for the immobilization of catalysts witnessed growing attention [1–3]. Carbohydrates benefit from some advantages such as non-toxicity, biodegradability, diversity, availability, low costs, and biocompatibility. The presence of multi-functional groups on the backbone of carbohydrates allows the efficient stabilization of catalytic species and control of their leaching. This can lead to the formation of heterogeneous catalysts with high recyclability. On the other hand, the functionalities on the carbohydrates provides the opportunity for conjugation of other components to furnish carbohydrate-based hybrids/composites.

Chitosan, CS, is a biopolymer obtained from deacetylation of chitin [4–6]. CS not only possesses multi hydroxyl groups but also contains the primary amine group in its structure [7,8]. This unique feature of CS that facilitates covalent attachment of various groups on CS resulted in its wide-spread applications for catalytic purposes [9–13]. Cyclodextrin (CD), on the other hand, is a cone shape carbohydrate that has a unique capability for hosting the hydrophobic substrates in its hydrophobic inner space and shuffling them in the aqueous media due to the hydrophilic nature of its outer surface [14,15].

Graphene quantum dots (GQDs) are an emerging class of nano-scale carbon materials that benefit from outstanding properties such as photo-stability and non-toxicity, high biocompatibility and chemical inertness [16–21]. In recent years many research groups disclosed the utilities of GQDs for various applications such as material science, catalysis, bioimaging, biosensing and drug delivery [21–24].

Magnetic nanoparticles (MNPs) are attractive candidates for catalysis. Their fascinating properties such as low toxicity, high ratio of surface area to volume, facile preparation and low cost broaden their application for the development of magnetic catalysts [25–27]. In this line, the conjugation of MNPs with GQD received growing attention. It has been assumed that magnetization of GQDs can increase their functionalities and improve GQDs recovery and reuse [28].

Hydrogenation of nitroaromatics to the amine derivatives is an essential reaction in the chemical industry for the production of value-added products such as dyes, pesticides, antioxidants, pigments, pharmaceuticals etc. [29–31]. This reaction is mostly promoted using noble metal-based catalysts [32–34]. To render this chemical transformation economically and environmentally attractive, noble metals are immobilized on support to furnish heterogeneous and recyclable catalysts [35–37].

In continuation of our study on catalysts [38–40] and carbohydrate-based catalysts [41–43], in this article, we present a novel hybrid catalytic system that benefits from the chemistry of CD, CS GQDs. The

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catalyst was prepared through immobilization of magnetic GQDs on CD decorated CS followed by palladating. The formation of the catalyst was verified and then its catalytic performance (catalytic activity, selectivity, and recyclability) for the hydrogenation of nitroarenes in aqueous media has been examined.

2. Experimental

2.1. Materials and instruments

The reagents used for the preparation of the catalyst and examining its activity included CS, β -CD, H_2SO_4 , H_3PO_4 , KMnO_4 , H_2O_2 , HCl , $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH , CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$, NaBH_4 , $\text{Pd}(\text{OAc})_2$, *n*-hexane, ammonia, graphite powder, toluene, distilled water, nitrobenzene, 1-nitronaphthalene, 4-nitroacetophenone and ethyl acetate, all purchased from Sigma-Aldrich. The monitoring of hydrogenation reaction was performed by TLC method on commercial aluminum-backed plates of silica gel of 60 F254, visualized by applying ultraviolet light. FTIR spectra were recorded by employing PERKIN-ELMER-Spectrum 65 instrument. ICP analyses were carried out by using ICP analyzer (Varian, Vista-pro). VSM analyses were accomplished by vibrating

sample magnetometer (VSM, Lakeshore 7407, at room temperature). X-ray diffraction (XRD) patterns were obtained using a Siemens D5000 instrument. TEM images of the prepared catalyst were recorded by Philips CM30300Kv field emission transmission electron microscope. To record the thermogram of the catalyst, METTLER TOLEDO thermogravimetric analysis instrument with the heating rate was $10^\circ\text{C min}^{-1}$ under N_2 atmosphere was used. BELSORP Mini II apparatus was used for measuring the specific surface area of the catalyst. Pre-heating of the catalyst was carried out at 423 K for 3 h.

2.2. Catalyst preparation

2.2.1. Synthesis of graphene oxide sheets

Using natural graphitic powder, graphene oxide was prepared using Hummers' method with slight modification [44]. Briefly, graphitic powder (1 g) was dispersed in a 9:1 mixture of $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ and stirred for 30 min. Afterward, KMnO_4 (6 g) was added slowly and the mixture was heated up to 50°C . After agitating for 24 h, the mixture was cooled to ambient temperature, and deionized water (200 mL) was added. The resulting suspension was then treated with H_2O_2 (5 mL, 30%). In the next step, the mixture was washed with HCl (1 M) twice, centrifuged

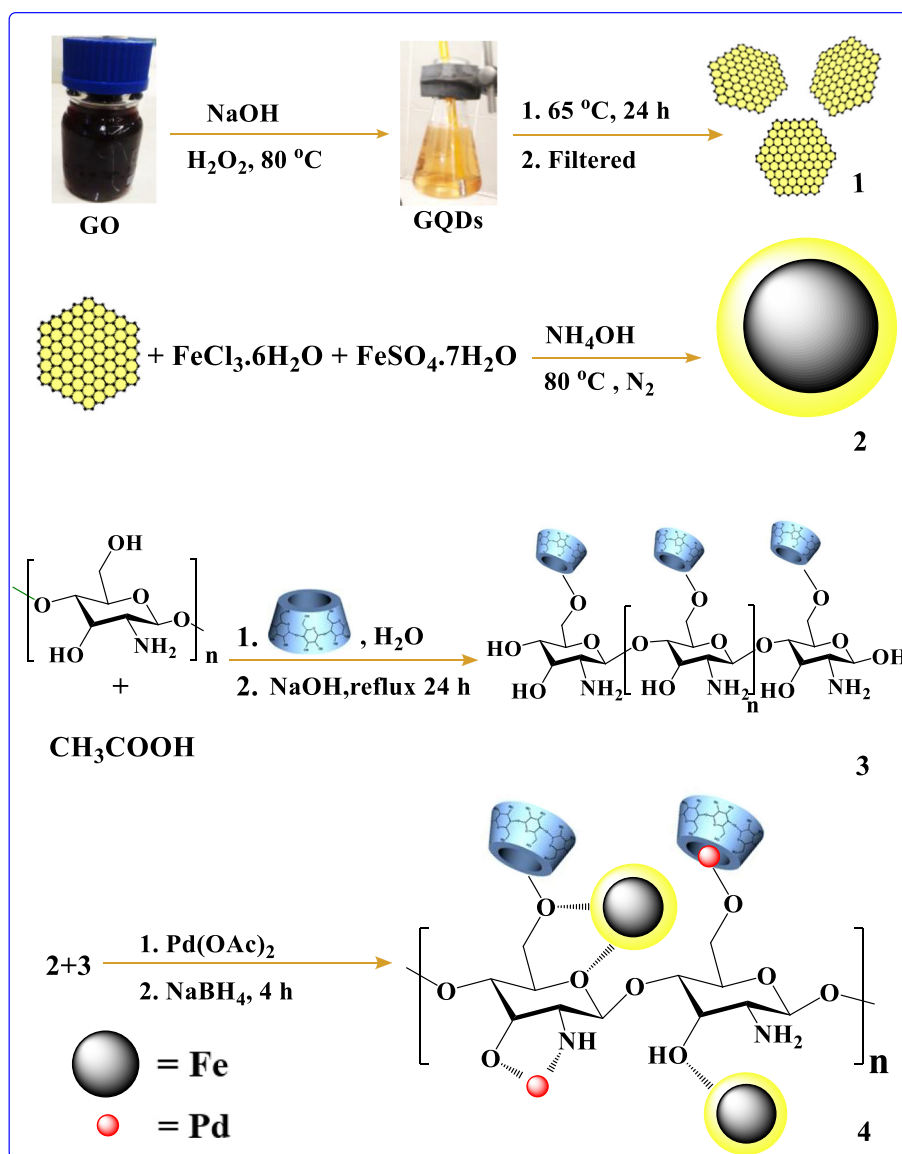


Fig. 1. A schematic view for the preparation of Pd@CS-CD-MGQDs.

and its pH has been adjusted to 6. Finally, the obtained solid was dispersed in deionized water (100 mL) and sonicated for 1 h.

2.2.2. Synthesis of graphene quantum dot (GQD)

GQDs were prepared according to a typical method [45]. In brief, H_2O_2 (30%, 40 mL) was added to graphene oxide stock solution (5 mL, 5 mg/mL). The mixture was then heated up to 65 °C. Subsequently, ammonia (25–28%, 10 mL) was introduced to the mixture in a dropwise manner. After heating for 24 h, the GQDs were filtered.

2.2.3. Synthesis of magnetic graphene quantum dots, MGQDs

Briefly, GQDs solution (160 mL) was sonicated for 30 min. Subsequently, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1.942 g) was added to GQDs solution and the mixture was stirred under nitrogen flow at room temperature. Then, the reaction temperature was raised to 80 °C and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1.082 g) was added. After stirring for 30 min, ammonia solution was introduced slowly to adjust the pH to 10. After stirring for 30 min, MGQDs were separated by using an external magnet, washed with distilled water several times and dried at 100 °C overnight [46].

2.2.4. Decoration of chitosan with cyclodextrin: preparation of CS-CD

A suspension of chitosan (2 g) in 0.1 M acetic acid solution (100 mL) was subjected to ultrasonic irradiation of power 120 W for 25 min to afford a homogenous colloidal solution. Meanwhile, CD (1 g) was dissolved in distilled water (100 mL). Afterward, the two mixtures were mixed together and NaOH solution was added in a dropwise manner to adjust the pH to 10. Subsequently, the mixture was refluxed overnight. Upon completion of the reaction, the product was filtered and washed several times with distilled water and ethanol. Finally, the CS-CD solid was dried in an oven at 100 °C overnight.

2.2.5. Immobilization of MGQD on CS-CD

CS-CD solid (0.5 g) was dispersed in 50 mL distilled water with ultrasonic irradiation for 15 min. Then, the mixture was stirred. Meanwhile, MGQD (0.05 g) was dissolved in distilled water (50 mL) and slowly added to the CS-CD suspension. Subsequently, the resulting mixture was stirred at ambient temperature for 12 h. Afterward, the solid, CS-CD-MGQDs, was filtered and dried at 100 °C overnight.

2.2.6. Immobilization of Pd NPs on the CS-CD-MGQDs

For the immobilizing of palladium nanoparticles on CS-CD-MGQDs, CS-CD-MGQDs (0.6 g) was suspended in ethanol (50 mL) by sonication for 30 min. Then, a solution of $\text{Pd}(\text{OAc})_2$ (0.015 g) in distilled water (10 mL) was gradually added to the suspension, and the mixture was then stirred at ambient temperature for two hours. Then, a solution of NaBH_4 in distilled water (10 mL, 0.2 N) was introduced to the aforementioned suspension and the mixture was stirred for two hours. Finally, the obtained solid, Pd@CS-CD-MGQDs, was filtered and dried overnight. Using ICP analysis the content of Pd in the catalyst was calculated to be 0.02 mmol g^{-1} . The schematic procedure of the synthesis of the catalyst is presented in Fig. 1.

2.3. A typical procedure for the hydrogenation reaction

Typically, 1 mmol of nitro compound (nitrobenzene, 1-nitronaphthalene or 4-nitroacetophenon), the catalyst (6 mg) and deionized water (5 mL) were put into the reactor and stirred at 50 °C under H_2 atmosphere (1 bar). The progress of the reaction was monitored by TLC. At the end of the reaction, the catalyst was simply filtered, washed with ethanol and dried at 100 °C overnight. The yield of the reaction was measured by GC.

3. Result and discussion

3.1. Catalyst characterization

In Fig. 2 the TEM image of Pd@CS-CD-MGQDs is depicted. As shown, CS-CD can be seen as a fine sheet. On CS-CD two types of particles can be seen. The larger dark spots on CS-CD can represent MGQDs. As shown, similar to magnetic nanoparticles, MGQDs are packed together to form small aggregates. Apart from MGQDs, very fine spots can also be detected on CS-CD that can be assigned to Pd nanoparticles.

To confirm the formation of MGQDs and Pd@CS-CD-MGQDs, their XRD patterns have been recorded. As shown in Fig. 3A, MGQDs exhibited the characteristic bands of magnetic nanoparticles at $2\theta = 30.9^\circ$, 35.8° , 43.5° , 54.0° , 57.4° , 63.1° and 75° (JCPDS card no. 39-1346) [47,48]. In the XRD pattern of Pd@CS-CD-MGQDs, the characteristic bands of MGQDs can be observed, confirming that upon immobilization of MGQD on CS-CD, it preserved its structure. Apart from the MGQDs bands, the broad band at $2\theta = 20^\circ$ can be observed that is assigned to the amorphous CS-CD. Notably, in the XRD pattern of Pd@CS-CD-MGQDs the representative bands of Pd nanoparticles were not detected. This issue can be assigned to the low Pd loading as well as their high dispersion on the support [49].

In the next step, the magnetic properties of MGQDs and Pd@CS-CD-MGQDs were measured by recording their magnetization curves. As shown in Fig. 3B, the magnetic saturation (M_s) value of Pd@CS-CD-MGQDs was 15.0 emu g^{-1} , while this value for MGQDs was 42.6 emu g^{-1} . This result confirmed that MGQDs showed the high magnetic property. Moreover, it can be seen that upon MGQDs immobilization on CS-CD, the magnetic property decreased dramatically. This observation is due to the non-magnetic property of CS-CD. Notably, although the magnetic saturation of Pd@CS-CD-MGQDs is relatively low, the catalyst could be magnetically separated from the mixture of the reaction.

In Fig. 4, the FTIR spectra of GQDs, CS-CD, MGQDs and Pd@CS-CD-MGQDs are illustrated. The FTIR spectrum of GQDs showed the band at 3419 cm^{-1} that is representative of $-\text{OH}$ group, 2924 cm^{-1} that is indicative of $-\text{C}-\text{H}$ functionality, 1627 cm^{-1} that is related to $-\text{C}=\text{C}$ group and 1101 cm^{-1} that is due to $-\text{C}-\text{O}$ functionality. This analysis confirmed that GQDs are abundant with functional groups. The FTIR spectrum of MGQDs is similar to that of GQDs and exhibited all characteristic bands of GQDs, indicating the fact that GQD did not collapse upon

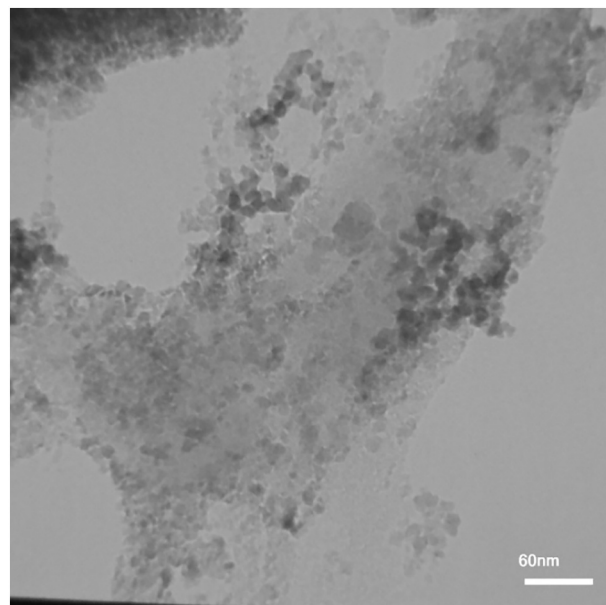


Fig. 2. TEM image of the catalyst.

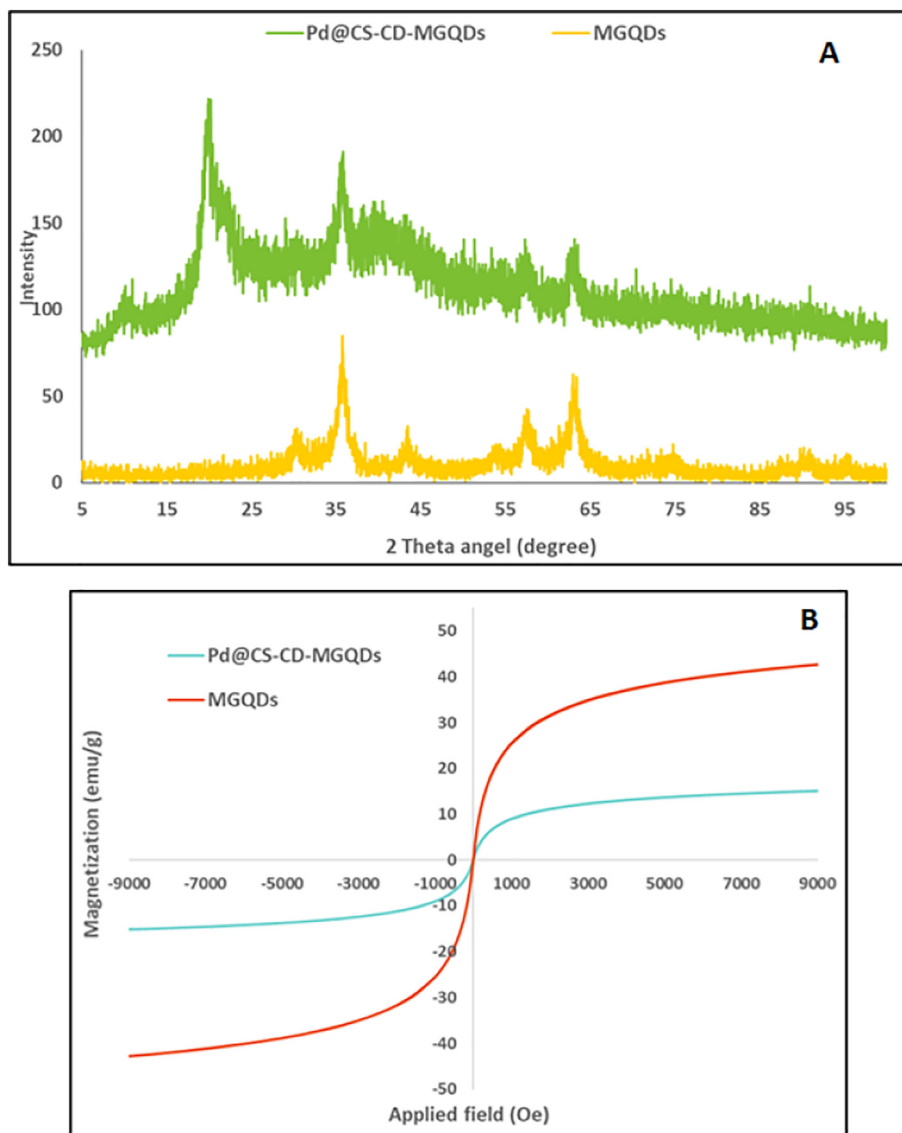


Fig. 3. A: XRD patterns of MGQDs and Pd@CS-CD-MGQDs, B: VSM analyses of MGQDs and Pd@CS-CD-MGQDs.

magnetization. The FTIR spectrum of CS-CD showed the characteristic bands at 2961 cm^{-1} ($-\text{CH}_2$), 3438 cm^{-1} ($-\text{OH}$) and 1652 cm^{-1} . In the FTIR spectrum of the final catalyst, the characteristic bands of MGQDs can be observed. Notably, the characteristic bands of CS-CD are overlapped with those of MGQDs. Hence, to confirm the successful immobilization of MGQDs on CS-CD other analyses have been carried out.

Using BET technique, the specific surface area of the catalyst was estimated to be $4.79\text{ m}^2\text{g}^{-1}$.

In Fig. 4B the TGA thermogram of Pd@CS-CD-MGQDs is depicted. The thermogram of the catalyst is very similar to that of CS [41] and showed the weight loss stages for loss of water (below 200°C), degradation of CS-CD ($\sim 300^\circ\text{C}$) and decomposition of GQD. Using TGA data, the content of CS-CD and GQD were estimated to be ~ 37 and 8.2 wt\% .

3.2. Catalytic activity

To start the study of the catalytic activity of the catalyst, a model hydrogenation reaction, hydrogenation of nitrobenzene was selected. Then, to achieve the highest reaction yield of the desired product, the reaction condition was optimized. As tabulated in Table 1, the optimum values of the reaction variables (solvent, temperature and catalyst

loading) were obtained by using the “One factor at the time” method. In more detail, to optimize one factor, others have been kept unchanged and only the effect of that factor was studied. As shown, investigation of the effect of the reaction solvent confirmed that water was the best solvent. Considering the environmentally benign nature of water, this result was very promising. The study of the effect of the reaction temperature confirmed that an increase of the reaction temperature from ambient temperature to 50°C , improves the yield of the product. Regarding the effect of the catalyst loading, it was found that 0.5 mol\% Pd@CS-CD-MGQDs was the optimum catalyst amount.

In the next step, it was studied whether Pd@CS-CD-MGQDs could catalyze a reaction of steric substrates such as 1-nitronaphthalene that is poorly soluble in aqueous media. The result, Table 2, showed that Pd@CS-CD-MGQDs could promote the reaction of sterically demanding catalyst to afford the product in high yield. However, the reaction yield for 1-nitronaphthalene was lower than that of nitrobenzene. This observation can be attributed to the large size of 1-nitronaphthalene that hinders its efficient encapsulation in CD cavity. In the following, the selectivity of Pd@CS-CD-MGQDs towards hydrogenation of nitro group was examined by 4-nitroacetophenone. The result, Table 2, confirmed that Pd@CS-CD-MGQDs was highly selective and only promoted hydrogenation of nitro functionality, but not carbonyl group to afford 4-amino

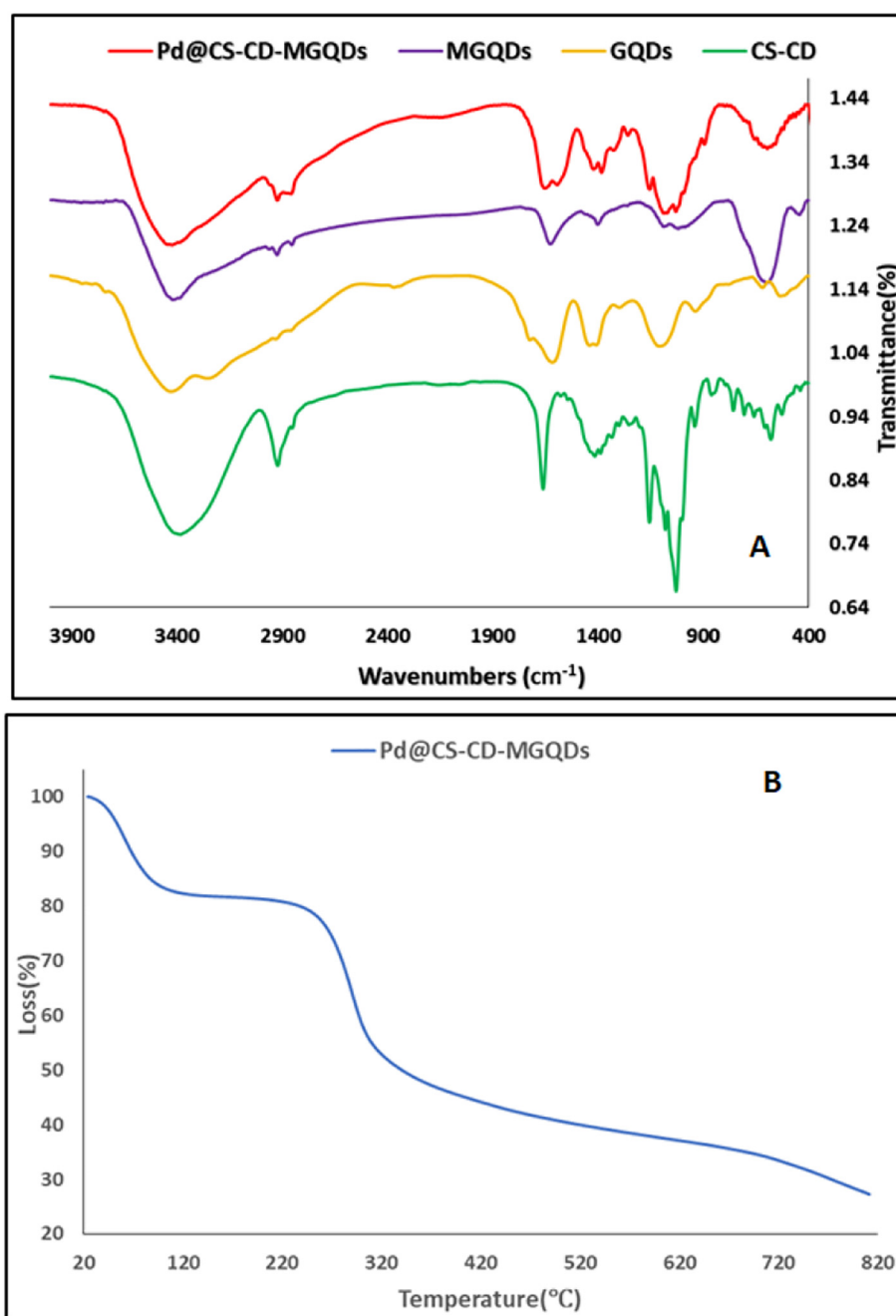


Fig. 4. A: FTIR spectra of CS-CD, GQDs, MGQDs, and Pd@CS-CD-MGQDs, B: thermogram of Pd@CS-CD-MGQDs.

acetophenone as a sole product. Next, hydrogenation of nitrobenzene derivatives with electron donating and electron withdrawing functionalities was carried out to confirm the generality of the protocol. As tabulated in Table 2, reagents with different electronic properties could tolerate the hydrogenation reaction to furnish the corresponding amines. However, the results confirmed that the presence of electron donating groups led to the lower yield of the reaction.

The aim of this work was studying the performance of the hybrid of carbohydrates and magnetic carbon dots as a catalyst support. To this purpose, Pd nanoparticles were immobilized on CS-CD-MGQDs and the catalytic activity of the resulting catalyst was investigated for hydrogenation of nitroarenes as a model chemical reaction. Motivated by the high activity of the catalyst, it was also studied whether the catalytic activity of Pd@CS-CD-MGQDs is comparable with previously reported catalysts for this reaction. In Table 3, the catalytic performance of Pd@CS-CD-MGQDs is compared with some of the previously reported catalysts

used for the hydrogenation of nitroarenes. As can be seen in Table 3, the hydrogenation of nitroarenes has been performed using various catalysts. The results showed that Pd@CS-CD-MGQDs exhibited high catalytic activity that is higher or comparative (slightly lower) to the tabulated catalysts. Regarding the reaction condition, it can be observed that hydrogenation of nitrobenzene can be achieved in the presence of both hydrogen and chemical reducing agents such as NaBH₄. Although the use of chemical reducing agents is efficient, mostly, they are toxic or expensive. On the other hand, the protocols in which hydrogen gas with low pressure has been required are safer and more economically attractive. Moreover, performing the hydrogenation reaction in water as environmentally benign solvent is more appealing than use of toxic solvents. Regarding the reaction time, it can be seen that Pd@CS-CD-MGQDs can promote the model reaction in relatively short reaction time that is comparable or lower than some of the reported procedures. As shown, using different catalysts, the model reaction has been

Table 1

Optimization of the conditions in the nitrobenzene hydrogenation reaction.

Entry	Catalyst (mol%)	Solvent	Temperature (°C)	Time(h)	Yield(%)
1	0.5	H ₂ O	r.t	1	90
3	0.5	H ₂ O	70	1	85
5	0.5	H ₂ O	50	1	97
6	0.7	H ₂ O	50	1	97
3	0.3	H ₂ O	50	1	80
9	0.5	EtOH	50	1	80
10	0.5	Toluene	50	1	30
11	0.5	EtOH/H ₂ O(2:1)	50	1	70
12	0.5	EtOH/H ₂ O(1:1)	50	1	85
13	0.5	EtOH/H ₂ O(1:2)	50	1	90

Table 2Hydrogenation of nitro compounds by Pd@CS-CD-MGQDs.^a

Entry	Substrate	Time (h)	Yield (%)
1	Nitrobenzene	1	97
2	1-Nitronaphthalene	1.5	80
3	4-Nitroacetophenone	1.5	90
4	4-Nitroaniline	3	83
5	1-Bromo-2-nitrobenzene	3	89
6	1-Chloro-2-nitrobenzene	3	90
7	2-Nitrotoluene	3	80

^a Reaction conditions; substrate (1 mmol), H₂O (5 ml), catalyst (0.5 mol%), H₂ gas (1 atm), 50 °C, agitation (800 rpm).

performed at different temperature ranging from room temperature to 60 °C. From the results tabulated in Table 3 it can be concluded that Pd@CS-CD-MGQDs showed high catalytic performance that is comparable to some of the most efficient catalysts. Notably, use of biocompatible and available polysaccharides (CS and CD) for the fabrication of Pd@CS-CD-MGQDs as well as the magnetic feature of the catalyst that can improve the recovery and recyclability of the catalyst render Pd@CS-CD-MGQDs a promising catalyst.

3.3. Catalyst recyclability

In the final step, the recyclability of Pd@CS-CD-MGQDs was examined. For the recyclability test, the model hydrogenation reaction under the optimum hydrogenation condition (discussed in Result and discussion) was performed using the recycled Pd@CS-CD-MGQDs. In more detail, after the first reaction run, the catalyst was recovered, washed and dried and applied for promoting the next reaction run.

Table 3

The comparison of the catalytic activity of Pd@CS-CD-MGQDs for the hydrogenation of nitrobenzene with that of some of the catalysts in the literature.

Entry	Catalyst	Time	Solvent	Temperature (°C)	Reducing agent	Yield (%)	Ref.
1	Pd@CS-CD-MGQDs (0.5 mol%)	1 h	H ₂ O	50	H ₂ /1 atm	97	This work
2	Pd@Hal-biochar ^a (0.03 mol%)	1 h	H ₂ O	r.t.	H ₂ /1 atm	75	[50]
3	Pd/PPh ₃ @FDU-12 (8.33 × 10 ⁻⁴ mmol Pd)	1 h	EtOH	40	H ₂ /10 bar	99	[51]
4	PdCu/graphene (2 mol% Pd)	1.5 h	H ₂ O/EtOH	50	NaBH ₄	98	[52]
5	Pd@Hal-pDA-NPC ^b (1 mol%)	2 h	H ₂ O	50	H ₂ /1 atm	92	[53]
6	APSNP ^c (1 mol%)	2 h	EtOH	r.t.	H ₂ /40 atm	100	[54]
7	Pd@Hal-Hydrogel + cyclodextrin (2 wt%)	2 h	H ₂ O	50	H ₂ /1 atm	95	[55]
8	Pd@Hal/di-urea ^d (1.5 wt%)	1 h	H ₂ O	50	H ₂ /1 atm	100	[56]
9	Pd@Hal-CIL ^e (1 wt%)	1 h	H ₂ O	r.t.	H ₂ /1 atm	100	[57]
10	Pd@CNT-P ^f (3 wt%)	2 h	H ₂ O	60	H ₂ /1 atm	100	[58]
11	Pd@Hal-CCD ^g (1 wt%)	1.5 h	H ₂ O	r.t.	H ₂ /1 atm	100	[59]
12	PdNP(0.5%)/Al ₂ O ₃ (0.3 g)	3 h	THF	r.t.	H ₂ /1 atm	100	[60]
13	Pd@HTMC ^h	1 h	H ₂ O	50	H ₂ /1 atm	100	[61]
14	Pd/graphene	1.5 h	H ₂ O/EtOH	50	NaBH ₄	91	[52]
15	PdCu/C (2 mol% Pd)	1.5 h	H ₂ O/EtOH	50	NaBH ₄	85	[52]

^a Hybrid of halloysite and char.^b Pd nanoparticles immobilized on the poly-dopamine decorated Hal nanotubes hybridized with N-doped porous carbon monolayer.^c Activated palladium sucrose nanoparticles.^d Halloysite clay decorated with ligand.^e Halloysite decorated with ionic liquid derived carbon.^f Pd on the CNT decorated with cyclodextrin containing polymer.^g Halloysite decorated with cyclodextrin derived carbon sphere.^h Pd immobilized on halloysite decorated with cyclodextrin modified melamine-based polymer.

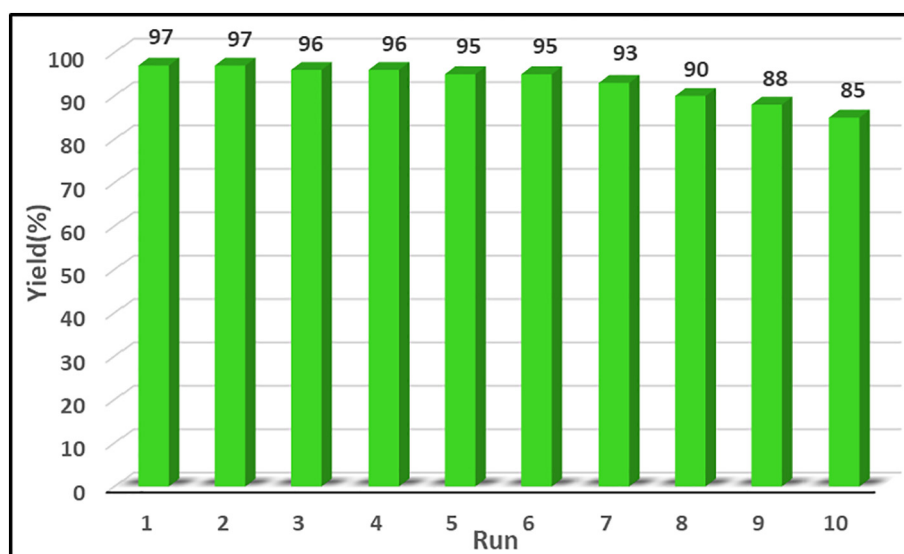


Fig. 5. The results of the recycling experiment of the catalyst for the model reaction under optimum reaction condition.

This cycle was repeated for ten runs of reaction and the yield of aniline for each cycle was measured. The results, Fig. 5, confirmed the high catalytic activity of Pd@CS-CD-MGQDs. As shown, the catalyst maintained its activity for the second run and only a slight loss of the activity was observed. To study the leaching of Pd upon recycling, the reused catalyst after ten reaction runs was subjected to ICP analysis. Measurement of Pd content of the recycled catalyst confirmed that recycling did not induce significant Pd leaching and the recycled catalyst preserved 94 wt% of its initial Pd loading.

4. Conclusion

With the aim of developing a heterogeneous catalyst that benefits from the chemistry carbohydrates that are abundant biological compounds and magnetic carbon dots, Pd@CS-CD-MGQDs, is designed and synthesized through a multi-step procedure. First, GQDs were prepared and magnetized to furnish MGQD. Meanwhile, CS was decorated with CD. In the next step, MGQDs have been incorporated into CS-CD and the resulting hybrid system was palladated. To study the catalytic activity of Pd@CS-CD-MGQDs, hydrogenation of nitroarenes in the aqueous media was targeted as a model reaction. It was found that Pd@CS-CD-MGQDs could promote the reaction under mild reaction condition to afford the corresponding amines in high yields. Moreover, the catalyst was selective towards hydrogenation of nitro functional group. On the other hand, the magnetic feature of the catalyst facilitated its recovery by using an external magnet. The recycling tests confirmed high recyclability of the catalyst up to ten reaction runs with slight Pd leaching and loss of the catalytic activity. These features of Pd@CS-CD-MGQDs render it a promising carbohydrate based catalyst with comparable performance to some of the previously reported catalysts.

CRedit authorship contribution statement

Mahsa Esmailzadeh: Visualization, Writing original draft, Formal analysis. **Samahe Sadjadi:** Funding acquisition, Methodology, Supervision, Writing - original draft, Writing - review and editing. **Zeinab Salehi:** Funding acquisition, Methodology, Supervision.

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Declaration of competing interest

The authors declare no conflict of interest.

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