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Pd nanoparticles/graphene quantum dot supported on chitosan as a new catalyst for the reduction of nitroarenes to arylamines

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Abstract

A new heterogeneous catalyst was obtained by growing graphene quantum dots on chitosan and subsequent immobilization of Pd nanoparticles. The catalyst after characterization was used in the reduction of nitroarenes to the corresponding amines by $NaBH_4$ as a weak reducing agent of nitro compounds. The catalyst exhibited excellent catalytic activity and selectivity under mild reaction conditions in water as a green solvent during 1 h. Additionally, the catalyst can be reused for five consecutive runs without any significant decrease in its activity and selectivity.

Keywords Heterogeneous catalyst · Graphene quantum dot · Chitosan · Nitroarenes · Reduction

Introduction

Development of industrial processes soared concerns about the environmental safety. Nitro compounds are considered as one of the environmental pollutants, so their reduction to the safe amines is the project agenda for many researches [1, 2]. Arylamines have many useful applications as antioxidants, corrosion inhibitors, agrochemicals, photographic developers, and pharmaceuticals [3, 4]. Therefore, catalytic production of arylamines from nitroarenes is gained remarkable attention in the field of chemical industries. One of the key approaches is the utilization of nanomaterials such as metal nanoparticles in heterogeneous catalytic systems due to their advantages of easy separation, and capability of recovery and recycles [5]. Among various transition metal nanoparticles, palladium nanoparticles are able to be used for an array of catalytic goals [6] which its heterogeneous forms have been employed widely in the reduction of nitroaromatics [4].

Agglomeration of metal nanoparticles is a challenge for their successful application because of losing the surface area. Solid supports are important tools to prevent aggregation of the nanoparticles [7]. In recent years, a wide variety of supports have been extended for instance cellulose [8], SBA-15 [9], zeolite [10], and titania [11]. Biopolymers such as chitosan and cellulose are the leading support [12–14] due to their unique features such as physical and chemical versatility, ease of chemical or physical modification, biodegradability, and suitable sorption capacity [15]. Interests about chitosan as a support for the metal nanoparticles such as palladium nanoparticles have been progressively increased in recent years. Furthermore, the amine functional groups on the surface of chitosan play a key role for increasing metals loading on the polymer [16].

Graphene quantum dots (GQDs) have been extensively considered as a new class of promising organic nanomaterials due to their high stability, excellent biocompatibility, interesting surface area, and low-toxicity [17, 18]. While various nanosupports were introduced for Pd [19–22], GQDs demonstrated special activity to increase the catalytic performance of some transition metals such as Pd [4, 23]. In continuation of our research works about heterogeneous catalytic systems, herein we have investigated the preparation and catalytic activity of Pd/GQD-Chitosan nanocomposite. Successively, the catalytic activity of the presented catalytic system was evaluated through the reduction of nitroarenes to arylamines using sodium borohydride (NaBH₄) at ambient conditions.

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Experimental

Materials and methods

In this research, all of the chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Chitosan (80-90% deacetylated) with 2000 MW was obtained from Golden-shell Biochemical (Zhejiang, China). Citric acid as a starting material for the production of GODs was purchased from Sigma-Aldrich and used without further purification. Field emission scanning electron microscopy (FE-SEM) was carried out with a microscope of MIRA3TESCAN-XMU. Energydispersive X-ray spectroscopy (EDS) was performed with a scanning electron microscope of TSCAN Company, and the analytical instrumentation used for transformations of the catalyst was Fourier transform infrared spectrometer (FT-IR) using potassium bromide. Transition electron microscopy (TEM) micrographs were obtained with TEM Philips EM 208S. The elemental analysis was performed with an Elementar Analysensysteme GmbH VarioEL. Gas chromatographic (GC) measurements were carried out in Varian 3900 GC. The following conditions were used for all GC analyses: injector and detector temperature, 260 °C; initial temperature, 100 °C; temperature ramp, 3 °C/min; final temperature, 280 °C. Selectivity was calculated as follows: (peak area of the desired product/sum of the peak areas for desired and by-product) $\times 100$.

Preparation of the Pd/GQD-Chitosan support

In the experimental procedure, 0.3 g of the *N*, *N'*- dicyclohexylcarbodiimide (DCC) and 0.05 g of the *N*, *N'*dimethylaminopyridine (DMAP), 1 g chitosan, and 0.1 g citric acid were added into a round bottom flask containing 10 mL DMSO:H₂O (1:1) and the mixture was stirred at 90 °C for 3 h. Then, 20 mL acetone was added to the mixture and the precipitate was filtered out, washed with acetone (2×10 mL), and dried in an oven at 60 °C. A beaker contains 1 g citric acid, and 1 g citric acid-chitosan was heated in a furnace at 150 °C for 1 h. After that, 10 ml H₂O was added to the mixture and the precipitate was filtered out, washed with acetone (2×10 mL), and dried in an oven at 60 °C.

In order to prepare Pd/GQD-Chitosan, 0.05 g of PdCl₂ was gradually added into the 0.5 g obtained GQDs-Chitosan in 10 mL distilled water under continuous stirring. The reduction of Pd(II) to Pd(0) was performed by the addition of NaBH₄ solution (0.8 g in 5 mL H₂O). After 2 h, the product was separated by centrifuging at 12,000 rpm, washing with H₂O (2×5 mL), and drying at 70 °C.

Typical procedure for the catalytic reduction of nitroarenes in the presence of the Pd/ GQD-Chitosan

In a typical procedure, 1 mmol nitrobenzene as precursor, 0.6 mmol NaBH₄, 5 mL H₂O, and 0.2 g Pd/GQD-Chitosan as catalyst were mixed at room temperature for 1 h. The reaction progress was followed with thin layer chromatography (TLC). On completion, the catalyst was separated through filtering, washed with acetone, and reused for consecutive runs (Scheme 1).

Results and discussion

Chitosan has a lot of amine functionalities susceptible for modification by electrophiles. In this regard, chitosan was reacted with citric acid under activation with DCC/DMAP to give citric acid-chitosan. Since one of the most important approaches for the synthesis of GQD is based on citric acid self-condensation reaction [24], the loaded citric acid on the chitosan commenced condensation reaction with unattached citric acids to yield GQDs on chitosan. Finally, Pd nanoparticles were deposited on the modified chitosan by the chemical reduction of Pd(II) (Scheme 2).

Characterization of Pd/GQD-Ch catalyst

FT-IR spectroscopy was employed to approve the modifications of chitosan toward the synthesis of Pd/GQD-Chitosan (Fig. 1). Chitosan citric acid demonstrated an absorption peak at 1694 cm⁻¹ for carbonyl groups and a new vibration mode at 3331 cm⁻¹ for OH groups of citric acid. With the transformation of citric acids to GQDs, the peak at 1694 cm⁻¹ was disappeared and a new peak was observed at 1706 cm⁻¹ which attributed to the removing carbonyls of citric acids and formation of new carbonyls on GQDs. In addition, the OH peak at 3331 cm⁻¹ did not observe in the GQD-chitosan spectrum confirming the transformation. Pd deposition of the GQD-chitosan had no significant changes on the GQD-chitosan spectrum, as expected.

The EDS analysis was employed to obtain an elemental analysis of the nanocomposite structure. These results indicated that Pd has been successfully anchored



Scheme 1 Reduction of nitroarenes to arylamine on the surface of the Pd/GQD-Chitosan catalyst

Scheme 2 Preparation procedure of Pd/GQD-Ch catalyst

Transmittance (%)

4000



Fig. 1 FT-IR spectra of preparation of chitosan, chitosan citric acid, GQD-chitosan, and PdNPs/GQDs-Chitosan

Wavenumber (cm-1)

to the nanocomposite (Fig. 2). ICP-MS analysis showed 0.31 mmol Pd per 1 g of the catalyst.

XRD also is a potent analysis instrument to reveal the composite structures. The analysis was used to investigate the catalyst structure which showed some peaks related to chitosan, GQD, and Pd nanoparticles (Fig. 3).



Fig. 2 EDS spectra of the Pd/GQD-Chitosan catalyst

SEM image of Pd/GQD-Chitosan was provided for the observation of the nanocomposite's surface. Although the image indicated the polymer particles of chitosan, elucidation of GQD and PdNPs needs TEM micrographs (Fig. 4).

TEM micrographs were prepared for screening Pd and GQD nanoparticles. Low focused TEM image of Pd/ GQD-Chitosan showed shadows on the polymer backbone



Fig. 3 XRD pattern of Pd/GQD-Chitosan



Fig.4 SEM image of Pd/GQD-Chitosan nanocomposite (the scale bar = $100 \ \mu m$)

(Fig. 5a) which more focusing on the shadows (Fig. 5b) revealed a well-ordered structure of GQD deposited on the polymer. Also, the dispersion of Pd NPs on the composite was confirmed with a TEM image with the maximum particle size between 6 and 8 nm (Fig. 5c).

Thermal Gravimetric Analysis (TGA) was performed on Pd/GQD-Chitosan and was compared with chitosan's TGA curve (Fig. 6). The TGA curve of Pd/GQD-Chitosan revealed that the catalyst is stable at temperatures below 258 °C. This range of temperature is convenient for catalyst stability giving an opportunity to use the catalyst in relatively high temperatures. In the meantime, Pd/GQD-Chitosan demonstrated a little decrease in the decomposition temperature compared to chitosan which obviously confirms the Pd catalytic activity on the degradation of chitosan.



Fig. 5 TEM micrographs of Pd/GQD-Chitosan (the scale bar for a 100 nm, b 50 nm and c 50 nm)



Fig. 6 TGA analyses of chitosan (a) and Pd/GQD-Chitosan (b)

Reduction of nitroarenes

The catalytic activity of the generated Pd/GQD-Chitosan composite was evaluated in the reduction of nitroarenes. For that, preliminary optimization was performed on the nitrobenzene reduction as the model substrate. The specified time to complete the reduction reaction was determined in the production of aniline at mild conditions using TLC. The reduction of 1 mmol nitrobenzene needs 0.062 mmol Pd in the presence of NaBH₄ (0.6 mmol) in H₂O (5 mL) at room temperature to give aniline with 99% GC conversion during 1 h. The reaction yield was declined in low catalyst amounts and the reaction duration did not decrease using an excess catalyst (Table 1). Then, the effect of the solvent on the reduction reaction was investigated. In this regard, aniline was evaluated as the sole product and its yield was determined to be 99% in the presence of water (entry 1) and 96% in the presence of water/ethanol with a 1:1 ratio (entry 2) as solvents. The use of organic solvents for the reaction including ethanol (entry 3), methanol (entry 4), acetonitrile (entry 5), and dichloromethane (entry 6) did not afford high yields. Moreover, NaBH₄ amounts were optimized with a minimum of 0.6 mmol for obtaining a higher yield.

For the development of the catalyst application, the reduction of nitrobenzene derivatives was also studied (Table 2). Nitro compounds were converted to the corresponding amines in high yields. The existence of various substitutes for nitroarenes affected the performance of the catalyst. Also, some of the substrates need EtOH: H_2O (1:1) as the solvent.

The effects of the catalyst ingredients were investigated on the reaction yield of nitrobenzene reduction. The reduction reaction in the presence of GQD-chitosan did not afford any product and Pd-chitosan gave aniline as the product with

Table 1 Selective reduction of nitrobenzene as a model substrate

Entry	Catalyst (mol %)	Solvent	Time (h)	Yield (%) ^a
1	0.032	H ₂ O	1	81
2	0.062	H_2O	1	99
3	0.062	H_2O	0.75	84
4	0.062	MeOH	1	45
5	0.062	MeCN	1	32
6	0.062	CH ₂ Cl ₂	1	0
7	0.062	EtOH	1	51
8	0.062	H ₂ O:EtOH (1:1)	1	96
9 ^b	0.062	H ₂ O	1	87

Reaction conditions: nitrobenzene (1 mmol), NaBH_4 (0.6 mmol), solvent (5 mL), rt

^aGC yield

^bNaBH₄ (0.5 mmol)

a 63% yield. While GQD cannot carry out the reduction reaction directly, it improves the catalytic activity of Pd significantly which can be found from 99% conversion of the reaction in the presence of PdNPs/GQD-Chitosan [4, 23] (Table 3).

Recyclability of Pd/GQD-Chitosan was investigated in the reduction of nitrobenzene. The results demonstrated that the catalyst could be utilized for the next batch after the separation of catalyst in the first run from the reaction medium. It is worthy that the catalytic activity of the obtained nanocomposite was surprisingly high and the loss of activity in the recycled catalyst was found to be negligible (Fig. 7).

In addition, the FT-IR spectrum of the recycled catalyst was prepared and compared to the spectrum of an unused catalyst (Fig. 8). The spectra comparison evinced that the catalyst structure did not change during the reaction.

A hot filtration test was performed on the catalyst. For that, the catalyst was removed from the nitrobenzene reaction mixture after 20 min and the progress of the reaction was monitored by GC. It is observed that the reaction completely was quenched after removing the catalyst which confirms performing the reaction heterogeneously (Table 4). In the meantime, a leaching study was carried out on the solution by ICP-MS analysis which the result showed very low leaching, 0.2 μ g/L, of Pd in the solution.

The proposed mechanism for the reduction of nitro compounds by the catalyst was shown in Scheme 3. The mechanism includes activation of nitro by Pd NPs to give I which under the nucleophilic attack of hydride ion afforded intermediate II. Intermediate II by the reaction with a H_2O and a hydride ion produced amine and Pd oxide. The prepared Pd oxide under the reaction with hydride ion can yield Pd to retain the catalytic cycle. The role of GQD in this reaction is assisting to the stability of the produced Pd intermediates because of extensive electronic system on its structure which can distribute the charge of intermediates on its structure and help to their stability.

Conclusions

Herein, we have developed an active and effective catalytic system based on chitosan as a green support for the selective reduction of nitroarenes to arylamines in mild condition with significant yields. Chemoselectivity of the catalyst toward ortho, meta, and para isomers of the products was also investigated about the reduction of some nitrobenzene derivatives. By considering the reusability of the catalyst, no meaningful loss of yield was observed during its application for five consecutive runs. Finally, arylamines were successfully synthesized during the reduction of nitroarenes in a mild condition using water as a green solvent at room temperature. Table 2Selective reduction ofnitrobenzene derivatives withPdNPs/GQDs-Chitosan

Entry	Substrate	Product	Solvent	Yield $(\%)^a$
1	NO ₂	NH ₂	H ₂ O	99
2	NO ₂	CI NH2	H_2O	98
3		NH ₂	H ₂ O	96
4	NO ₂	NH ₂	H ₂ O	97
5	NO ₂	NH ₂	H ₂ O	98
6 ^b		NH ₂ NH ₂	H ₂ O:EtOH (1:1)	74
7 ^b		NH ₂	H ₂ O:EtOH (1:1)	77
8 ^b		H ₂ NH ₂	H ₂ O:EtOH (1:1)	78
9	NO ₂	NH ₂	H ₂ O	98
10	NO ₂	NH ₂	H ₂ O	98
11	O ₂ N NH ₂	H ₂ N NH ₂	H ₂ O:EtOH (1:1)	66
12	O ₂ N NH ₂	H ₂ N NH ₂	H ₂ O:EtOH (1:1)	62
13	OH NO ₂	OH NH ₂	H ₂ O:EtOH (1:1)	65
14	O ₂ N OH	H ₂ N OH	H ₂ O:EtOH (1:1)	68
15	NO ₂ OH	NH ₂ OH	H ₂ O:EtOH (1:1)	81
16	O ₂ N OH	H ₂ N OH	H ₂ O:EtOH (1:1)	79

Reaction conditions: nitrobenzene (1 mmol), NaBH₄ (0.6 mmol), solvent (5 mL), rt ^aGC yield ^bNaBH₄ (1.0 mmol)



Fig. 7 Recycling of the Pd/GQD-Chitosan catalyst for the reduction of nitroarenes to arylamines



Fig.8 FT-IR spectra of Pd/GQD-Chitosan (**a**), and the recovered Pd/GQD-Chitosan (**b**)

Table 3 Investigation of the catalyst ingredients

Entry	Catalyst	Yield (%) ^a
1	PdNPs/GQD-Chitosan	99
2	GQD-Chitosan	0
3	PdNPs-Chitosan	63

Reaction conditions: nitrobenzene (1 mmol), NaBH_4 (0.6 mmol), solvent (5 mL), rt

^aGC yield

Table 4Hot filtration test forthe reduction of nitrobenzene byPd/GQD-Chitosan

Entry	Time (min)	Yield (%)	
1	20	47	
2	30	48	
3	60	48	

Reaction conditions: nitrobenzene (1 mmol), NaBH₄ (0.6 mmol), solvent (5 mL), rt ^aGC yield



Scheme 3 Mechanism of the nitro's reduction by the catalyst

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