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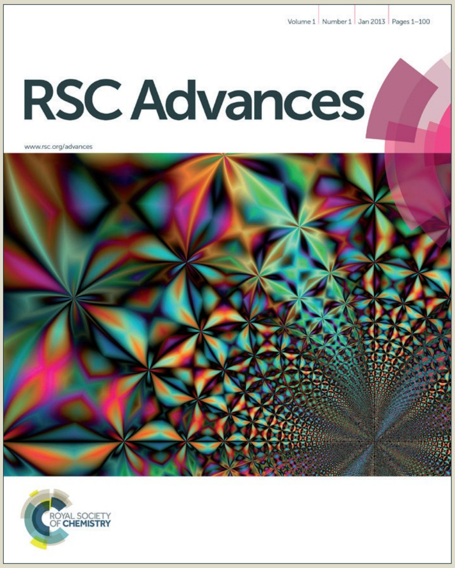

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Pd(0) supported on *N*-doped graphene quantum dots modified cellulose as an efficient catalyst for the green reduction of nitroaromatics

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A new efficient catalyst was introduced for the green reduction of nitroaromatics. The catalyst was obtained via modification of cellulose with *N*-doped graphene quantum dots and Pd nanoparticles. The new cellulose nanocomposite after characterization was applied as the catalyst in the reduction reaction of nitroaromatics using $NaBH_4$ at room temperature. Aromatic amines were obtained as the product of the reduction reaction during 2h. This reaction has the green reaction conditions such as mild reaction conditions, high yield, green solvent and recyclable catalyst. Also, the recovered catalyst is applicable in the reduction reaction for 6 times without significant decrease in activity.

Introduction

Reduction of organic nitro compounds is one of the most important reactions in the organic synthesis for the preparing of amines.[1] Aromatic amines have significant application in the preparation of dyes, antioxidants, pharmaceuticals, and agrochemicals.[2] Various approaches have been introduced for the reduction of aromatic nitro compounds using a hydrogen source such as alcohol, hydrazine hydrate, silane, and format.[3] Reduction of nitro groups with sodium borohydride ($NaBH_4$) in combination with metal nanoparticles represents an important catalytic system in modern preparative chemistry. The reduction of nitro compounds into amines using $NaBH_4$ under normal conditions[4] does not perform, instead, $NaBH_4$ in combination with a transition metal halide is able to reduce aromatic nitro compounds successfully.[5] $NaBH_4$, in protic moieties, reduces transition metal ions to give metal boride nanoparticles that allow the rapid reduction of nitro compounds into their corresponding amines.[6] Recently, some of the transition metals such as Pd and Au as the catalyst made a reduction of nitro compounds with good efficiency.[7] However, a great result in the reduction rate was obtained for bimetallic systems such as Pd-Ni, Pd-Cu and Pd-Ag.[8]

With increasing the importance of green chemistry in human life, heterogeneous catalysts have gained a special place in the catalyst research. Introduction of a large number of heterogeneous catalysts created a competition for the selecting a best heterogenized catalytic system for a reaction. High efficiency, non-toxicity, biocompatibility and recyclability are some of the challenging for heterogeneous catalysts. For affording the mentioned conditions various supports such as silica, cellulose, zeolite, alumina, titania and carbon nanotube were applied. Among the supports, cellulose has been attracted great attentions due to some advantages such as hydrophilicity, chirality, biodegradability and high functionality. In recent years wide investigations were performed on cellulose and its derivatives focusing on their biological, chemical, as well as mechanical properties. Cellulose and its derivatives can be used as a support since they are renewable, biodegradable and non-toxic.[9] Cellulose supported Cu(0) for Aza-Michael addition,[10] Pd(0) for Heck and Sonagashira couplings,[11] Cu(I)/Pd(0) for Click cyclization[12] and Co(II) for the oxidation reactions[13] are some example of cellulose supported catalysts.

The advancement of nanoscience and technology is indebted discovery of various new nanomaterials for versatile applications utilizing their size and shape dependent properties. Quantum dots (QDs) are one of the nanomaterials well known for their variation of bandgap with size. Conventional QDs such as PbS, and CdSe are extremely hazardous for processing, and there are also innumerable challenges for disposal and recycling.[14] Organic quantum dots such as graphene quantum dots (GQDs) don't have the limitations of conventional QDs. GQDs with tunable emissions are considered to be an important nanomaterials due to the superiority in resistance to photobleaching, low toxicity, excellent biocompatibility, low cost, and abundance of raw materials in nature.[15] They have been demonstrated potential applications on optical bioimaging probes,[16] theranostic agent,[17] detection probes,[18] light-emitting diode materials,[19] and efficient visible light-active photocatalysts[20] and so on.

Doping of GQDs with hetero atoms (such as B, N, S, and F) is also an effective method to tune the optical and electrical properties of GQDs.[21] Among the dopants, N is interesting for the electronic modification due to its comparable size with carbon. From our point of view as a catalyst designer,

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existence of N can be assist to homogeneous distribution of metal nanoparticles on the GQDs. However, *N*-GQDs can be good support for the metal nanoparticles such as Pd(0) generated in situ for the catalytic propos. Also, due to efficient activity of graphene as a support in the reduction reaction, it was expected that *N*-GQDs will be an efficient support for Pd(0) in the catalytic reduction of nitro compounds. For possibility of the *N*-GQDs recycling, cellulose as a green support chemically modified with *N*-GQDs, then Pd(0) nanoparticles was deposited on the modified support to give PdNPs@Cell-*N*-GQD. PdNPs@Cell-*N*-GQD was investigated in the reduction of nitroaromatics as a heterogeneous recoverable catalyst using $NaBH_4$ as a reductant agent (Scheme 1).

N-GQD was synthesized from citric acid and ethylenediamine in H_2O as the solvent in autoclave.[22] For preparation of the PdNPs@Cell-*N*-GQD, the carboxylic acid group of *N*-GQD was activated with *N*,*N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) and then reacted with cellulose to give Cell-*N*-GQD. To achieve homogeneous distribution of Pd(II) on the Cell-*N*-GQD, they were stirred at room temperature for 24 h. Then, Pd(II) was reduced to Pd NPs with $NaBH_4$ to give PdNPs@Cell-*N*-GQD (Scheme 2).

The catalyst was characterized with FT-IR, UV-Vis spectroscopy, Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Diffraction pattern (XRD), Thermal Gravimetric Analysis (TGA), Flame Atomic Absorption Spectroscopy (FAAS) and Transmission Electron Microscopy (TEM). The FT-IR spectra for cellulose, *N*-GQDs, Cell-*N*-GQD and PdNPs@Cell-*N*-GQD were prepared (Figure 1). Absorption bands at 2856 cm^{-1} for C-H band and 1577 cm^{-1} for C=O are characteristic peaks of *N*-GQDs which observed in the FT-IR spectrum of Cell-*N*-GQD, and approved the modification of cellulose with *N*-GQD.

One of the important behaviors of the *N*-GQDs is the photoluminescence (PL) activity. The PL activity of prepared *N*-GQD was studied in excitation wavelengths 350, 370, 390, 400, 410, 430 and 450 nms with strongest peak at about 400 nm. Also, the PL peaks of *N*-GQD shift to longer wavelengths with increasing the excitation wavelength (Figure 2). PL activity of *N*-GQD was quenched in Cell-*N*-GQD which approved the bonding of *N*-GQD to cellulose.

EDS is a common method for approve the metal loading on the support. The EDS analysis showed that Pd nanoparticles were loaded on the Cell-*N*-GQD surface (Figure 3). The amount of Pd loading on the support was determined to be 0.14 mmol per 1g PdNPs@Cell-*N*-GQD with FAAS.

XRD pattern of PdNPs@Cell-*N*-GQD exhibits the diffraction peaks of (101), (002) and (040) for cellulose, and (111), (200) and (220) for Pd (Figure 4). The diffraction peak of the *N*-GQDs was overlapped with cellulose (002).

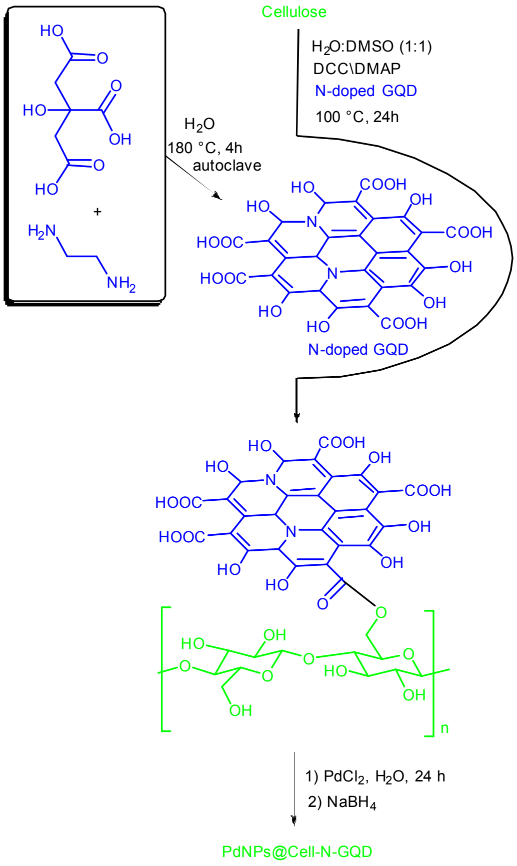
TGA which applied for the study of thermal behavior of materials evidenced PdNPs@Cell-*N*-GQD starts to decomposition above 209 °C in air which it's a good thermal stability for a catalyst. Also, other mass loss was observed at 231 °C for PdNPs@Cell-*N*-GQD (Figure 5).

The TEM image of the catalyst indicates the *N*-GQDs was deposited on the cellulose with the particle size between 4-9 nm (Figure 6a). Also, deposition of PdNPs was successfully performed on the cellulose with the particle size between 25-35 nm (Figure 6b).

Scheme 1. Reduction of nitroaromatics with PdNPs@Cell-*N*-GQD

$$Ar{-}NO_2 \xrightarrow[NaBH_4]{PdNPs@Cell\text{-}N\text{-}GQD} Ar{-}NH_2$$

Scheme 2. Synthesis of PdNPs@Cell-*N*-GQD



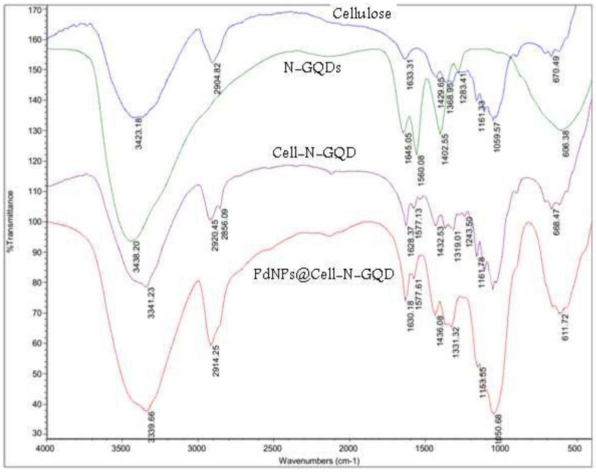


Figure 1. FT-IR spectra for cellulose, *N*-GQD, Cell-*N*-GQD and PdNPs@Cell-*N*-GQD

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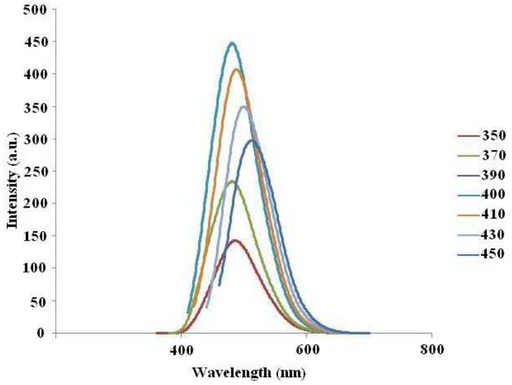

Figure 2. The PL of *N*-GQD

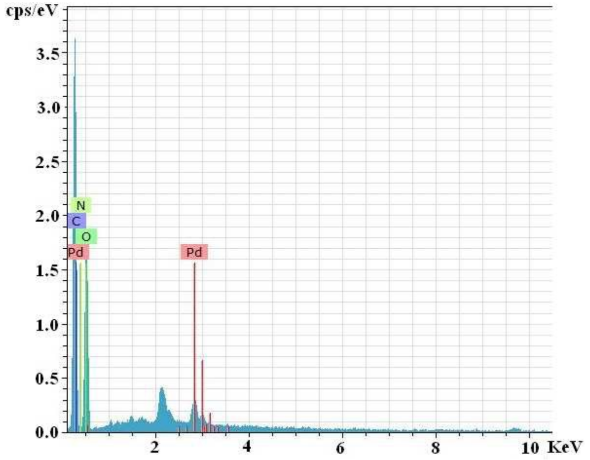

Figure 3. The EDS analysis of PdNPs@Cell-*N*-GQD

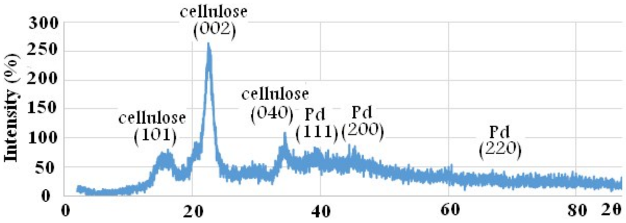

Figure 4. The XRD pattern of PdNPs@Cell-N-GQD

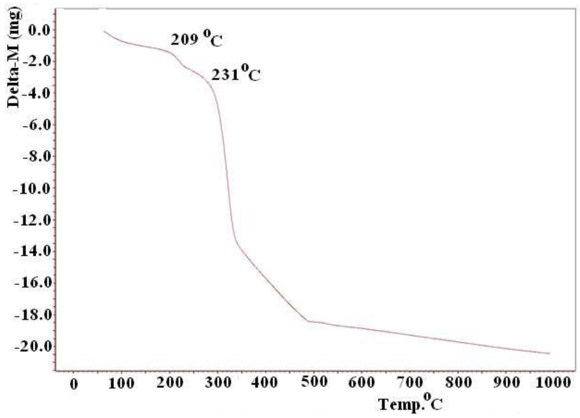

Figure 5. The TGA of PdNPs@Cell-*N*-GQD in air

The catalytic activity of PdNPs@Cell-*N*-GQD was evaluated in the reduction of nitroaromatics. So, the reduction of nitrobenzene (**1a**) (1 mmol) with $NaBH_4$ was investigated for the optimization of reaction conditions. It was found that 0.56 mol% Pd (Table 1, entries 1-3) with 1 mmol of $NaBH_4$ (2eq) in H_2O (Table 1, entries 5-9) at room temperature is the best reaction conditions for the reduction of nitrobenzene. The catalyst was separated via filtration and after removing of the solvent, the product was purified using column chromatography with ethylacetate:*n*-hexane solvent. The ^1H NMR study show that the reduction of nitrobenzene proceeded to give aniline (**2a**). Aniline was produced as the sole product with 95% yield during 2h without any byproduct. The reaction yield was decreased in the low amounts of catalyst. The reaction did not perform in the absence of $NaBH_4$, and gave low yield in low amount of $NaBH_4$ (Table 1, entry 4). After screening a variety of solvents, H_2O was determined to be the best solvents. Also, the reaction did not perform without the catalyst (Table 1, Entry 10).

For the investigation of Pd NPs and N-GQDs effects on the reaction, the reduction reaction of nitrobenzene was studied using PdNPs@Cellulose. Interestingly, the reduction reaction was performed using PdNPs@Cellulose with aniline as the sole product in 67% yield during 3h. Since PdNPs@Cell-*N*-GQD afforded high yield in short time, these results show the high activity of Pd in the presence of *N*-GQD in the nitroaromatic reduction reaction. Also, cellulose as a support reduced the PdNPs aggregation and increased surface area.

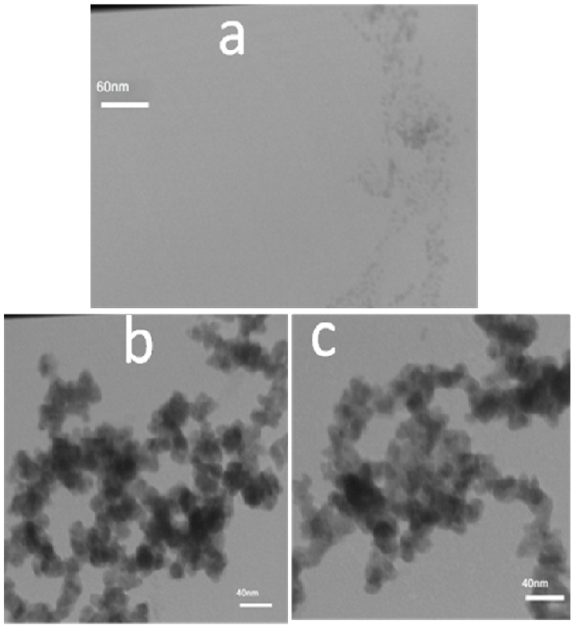

Figure 6. The TEM images of Cell-*N*-GQD (a), PdNPs@Cell-*N*-GQD before use (b) and PdNPs@Cell-*N*-GQD after use

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Table 1. Optimization of the reaction conditions for reduction of nitrobenzene[a]

Entry	(Pd mol%)	Solvent	Yield (%)[b]
1	0.43	H_2O	81
2	0.56	H_2O	95
3	0.71	H_2O	96
4[c]	0.56	H_2O	71
5	0.56	EtOH	60
6	0.56	EtOH:H_2O (1:1)	93
7	0.56	MeCN	0
8	0.56	MeOH	57
9	0.56	CH_2Cl_2	0
10	-	H_2O	0

[a]Reaction conditions: nitrobenzene (2 mmol), $NaBH_4$ (1 mmol), solvent (5 mL), room temperature, 2h. [b] Isolated yield. [c] $NaBH_4$ (1 mmol).

Table 2. The reduction of various nitroaromatics using PdNPs@Cell-*N*-GQD and $NaBH_4$

Entry	R	solvent	Yield (%)[b]
1	Ph	H_2O	95
2[c]	*p*-HOOC-Ph	H_2O	91
3[c]	*o*-HOOC-Ph	H_2O	90
4[c]	*p*-O_2N-Ph	H_2O/EtOH	88[d]
5	*p*-H_2N-Ph	H_2O/EtOH	91
6	*p*-H_3C-Ph	H_2O/EtOH	94
7	*o*-H_3C-Ph	H_2O/EtOH	92
8	*m*-H_3C-Ph	H_2O/EtOH	93
9[c]	*m*-O_2N-Ph	H_2O/EtOH	86[e]
10	naphtyl	H_2O/EtOH	90
11[c]	*o*-O_2N-Ph	H_2O/EtOH	89[f]
12	*o*-HO-Ph	H_2O/EtOH	93
13	*m*-HO-Ph	H_2O/EtOH	94
14	2,3-dimethyl-Ph	H_2O/EtOH	93
15	2,6-dimethyl-Ph	H_2O/EtOH	90

[a]Reaction conditions: nitroaromatic 1 (1 mmol), $NaBH_4$ (1 mmol), PdNPs@Cell-N-GQD (0.05 g), solvent (5 mL), room temperature, 2h. [b]Isolated yield. [c]$NaBH_4$ (2 mmol).[d]R´=*p*-H_2N-Ph. [e]R´=*m*-H_2N-Ph. [f]R´=*o*-H_2N-Ph.

Table 3. Successive trials by using recoverable PdNPs@Cell-*N*-GQD for the reduction reaction of nitrobenzene[a]

Trial	Catalyst amount (g)	Yield (%)[b]
1	0.04	95
2	0.04	95
3	0.04	94
4	0.04	94
5	0.04	94
6	0.04	94

[a]Reaction conditions: nitrobenzene (1 mmol), $NaBH_4$ (1 mmol), H_2O (5 mL), r.t., 2h. [b]Isolated yield

For more investigation of the PdNPs@Cell-*N*-GQD activity, the reaction was examined for various electron withdrawing and electron donating substituted nitroaromatics and dinitroaromatics. For most of the nitroaromatics H_2O:EtOH (1:1) was applied as the solvent since the reduction reaction in H_2O gave lower yields. The reduction reaction successfully afforded aniline derivatives in high yields. Dinitroaromatics gave the corresponding diamine in the reduction reaction (Table 2, entries 4, 9 and 11). For nitro carboxylic acids the reaction gave corresponding amino carboxylic acid which shows carboxylic acid is stable versus reduction with $NaBH_4$ in the presence of PdNPs@Cell-*N*-GQD.

Potential Pd leaching into the reaction mixture was also analyzed with FAAS analysis. For this purpose, sample was taken through a syringe filter during the heterogeneous reduction reaction of nitrobenzene, the solvent was evaporated, and the residue was dissolved in HNO_3. The analysis of these samples with FAAS showed that the Pd concentration in the reaction solution was less than the detection limit. This result indicates that virtually no Pd leaches from the surface into the solution. Also, did not observe any changes in the FT-IR spectrum of the catalyst recovered from the reaction (Figure 7). The TEM image of the catalyst after the reaction shows that no aggregation was happened for PdNPs (Figure 6c).

Recyclability of the PdNPS@Cell-N-GQD was examined in the reduction of nitrobenzene. After carrying out the reaction, the catalyst was separated via filtration, washed with EtOH (2 × 5 mL) and reused. An only minor decrease in the reaction yield was observed after six repetitive cycles for the reaction (Table 3).

Finally, a comparison study was performed for the obtained results with some recent reports about reduction of nitrobenzene as a sample. Most important factors for this reaction are yield, solvent, temperature and reaction duration. As can be seen from Table 4, various catalysts were used for the reduction of nitrobenzene which in all of them high yields obtained. So, the challenge of this reaction is the gentling of the reaction conditions not increasing the yield. A comparison of PdNPs@Cell-*N*-GQD with other catalysts of Table 4 for the reduction of nitrobenzene shows that very good conditions resulted with PdNPs@Cell-*N*-GQD. H_2O as the solvent at room temperature in 2h is a convenient reaction conditions for the reduction of nitrobenzene with PdNPs@Cell-*N*-GQD. Also, the catalyst has other advantages commonly for most of heterogeneous catalysts including easy separation and recyclability. PdNPs@Cell-*N*-GQD has another advantage compared to some heterogeneous catalysts including easy preparation of the catalyst.

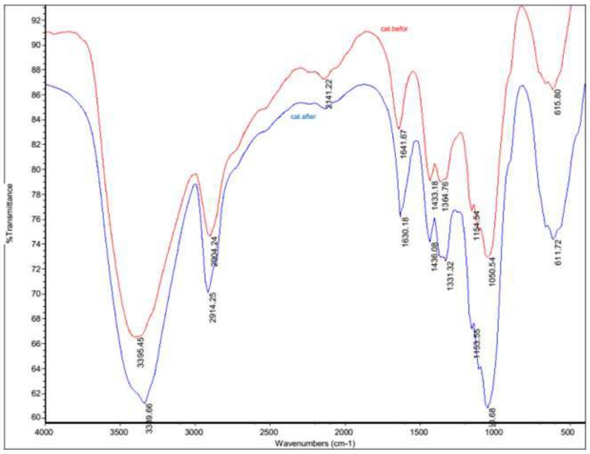

Figure 7. FT-IR spectra of PdNPs@Cell-*N*-GQD

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Table 4. Comparison of the results for reduction of nitrobenzene to aniline.

Entry	Catalyst	[Ref.]	Solvent	Time (h)	Temp. (°C)	Yield (%)
1	Pd-gCN	23	EtOH	4	70	99 (G)
2	zinc powder/chelating ethers	24	Ether/H_2O	9	70	90 (I)
3	Co-Mo_2C/AC	25	EtOH	2	80	100
4	Ni–B	26	H_2O/EtOH	8	r.t.	99.6
5	Zinc phthalocyaninein PEG-400	3g	EtOH	8	100	99 (G)
6	Fe_3O_4/ *β*-alanine-acrylamide-Ni	2	H_2O	5	room	98 (I)
7	PdNPs@Cell-N-GQD	-	H_2O	2	room	95

Conclusions

A new cellulose supported *N*-GQDs and PdNPs was synthesized. Pd NPs has great activity in the vicinity of *N*-GQDs for the reduction of nitroaromatics. Cellulose as a support afforded the recyclability of the catalyst. The catalyst was applied in the reduction of nitroaromatics to corresponding amines selectively in high yields. The reduction reaction was performed with $NaBH_4$ in H_2O or H_2O:EtOH (1:1) as the solvents at room temperature in 2h. Various nitrobenzenes and dinitrobenzenes were reduced to the corresponding amine in good yields. Mild reaction conditions and green solvent of this reaction in combination with recyclability of the catalyst make the presented method an interesting approach compared to most of the reports.

Experimental

Preparation of PdNPs@Cell-*N*-GQD

N-GQD was synthesized from citric acid and ethylenediamine in H_2O in autoclave at 180 °C during 4 h.[22] For preparation of the PdNPs@Cell-*N*-GQD, *N*-GQD (0.3 g) was dissolved in 40 mL H_2O:DMSO (1:1) and then, cellulose (2 g) was added to the solution. *N*,*N′*-Dicyclohexylcarbodiimide (0.2 g) and 4-dimethylaminopyridine (0.03 g) were added to the mixture and the mixture was stirred at 100 °C. After 24 h, the reaction mixture was filtered off and the residue washed with H2O (3 × 10 mL) and acetone (3 × 5 mL) to give Cell-*N*-GQD. Cell-*N*-GQD (2 g) was dispersed in H_2O (20 mL), and $PdCl_2$ (0.04 g) added to the mixture under stirring. Stirring was continued for 24 h and then, 10 mL solution of $NaBH_4$ (0.01g) was added dropwise during 2 h. Finally, PdNPs@Cell-*N*-GQD was filtered off, washed with H_2O (3 × 10 mL) and dried in oven (70 °C).

Typical procedure for the reduction of nitrobenzene

Nitrobenzene (0.12 g, 1.00 mmol) was added to a round-bottomed flask containing colloidal of PdNPs@Cell-*N*-GQD (0.04 g) in H_2O (5 mL) at room temperature. 5 mL of $NaBH_4$ solution (0.6 mmol) was added dropwise to the reaction vessel during 0.5 h. After 1.5 h, PdNPs@Cell-*N*-GQD was separated with filtration and washed with acetone (2 × 5 mL). The filtrate solvent was evaporated under vacuum and the product purified with column chromatography with n-hexane:ethylacetate (4:1).

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