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Catalytic Reduction of Aromatic Nitro Compounds in Aqueous Media using Silver Nanoparticles Embedded-Preyssler Functionalized Cellulose Biocomposite as a Green and Recoverable Catalyst

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Reduction reactions of aromatic nitro compounds to amines with high conversion and chemoselectivity have been achieved using a combination of catalytic quantities of silver nanoparticles embedded Preyssler-cellulose biocomposite (PC/AgNPs) with $NaBH_4$ under mild conditions and in an aqueous medium. The stabilization of silver nanoparticles on the surface of the Preyssler-functionalized cellulose biocomposite with more accessible active sites may be reliable for increased catalytic hydrogenation.

Keywords: Silver nanoparticles, Preyssler-cellulose biocomposite, Aromatic amines, Catalysis, Cellulose, Green chemistry.

INTRODUCTION

Aromatic and heterocyclic amines are frequently employed as raw materials, end products or intermediates in the organic synthesis of chemical industries, retaining great applications in various areas including pharmaceuticals, polymers, pesticides, medicines, dyes, cosmetics, pigments, *etc.* [1]. The amine functionality has a substantial role in drug design to predict and optimize the desired physico-chemical properties and bioactivity. Several drugs, agrochemicals and natural products comprise chiral amines serving as ligands in asymmetric catalysis [2]. Additionally, many harmful nitroaromatic compounds affecting serious environmental concerns, such as pollution of water resources through release of industrial wastewaters [3,4] can be converted into benign amino-aromatics. Amines are synthesized traditionally through the hydrogenation of nitro compounds, utilizing metal-base heterogeneous catalysts. Frequently, the reduction of nitro compounds that include competitive reducible functional groups often results in the formation of unwanted byproducts [5]. As a result, the reduction of nitro compounds that contain other reducible functional groups to the target amines efficiently and selectively still remains a big challenge. Accordingly, modification of structure of catalyst can result in increasing the selectivity, avoiding the undesirable side products and reducing the number of purification steps required and the waste of chemicals. In addition, creating highly recyclable catalysts in order to follow green chemistry principles is highly desirable.

Several low-cost nanostructured catalysts have been synthesized as suitable, eco-friendly and green choices for the reduction process of nitroaromatics [5-8] with great activities and selectivities under mild and benign reaction conditions. Recently, the synthesis of noble metal nanoparticles and their applications, particularly in catalysis, has gained much interest [9]. Among metal nanoparticles, silver nanoparticles (AgNPs) are of great interest because of their low-cost, powerful plasmonic effects and consequently, their outstanding catalytic activity [10-15]. Various range of applications of AgNPs in the field of catalysis, medical device coatings, antimicrobial, printable electronics, soaps, detergents, improvement of antimicrobial paper and drug delivery formulation have been reported [11]. The reduction of $AgNO_3$ using sodium borohydride ($NaBH_4$) as a reducing agent is considerably the most well-known method to prepare the monodispersive AgNPs with a size of less than 10 nm [16]. To develop environmentally benign processes in aqueous media without using volatile organic solvents, sodium borohydride ($NaBH_4$) is one favoured water-soluble reagent. In the reduction process of nitroaromatics to aromatic amines in the presence of $NaBH_4$ in aqueous media, electron transfer occurs from the electrons of BH_4^- to the nitroaromatic and

both of the species are absorbed on the surface of the catalyst [7]. All the compounds were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), field emission SEM (FESEM), transmission electron microscopy (TEM), scanning electron microscopy (SEM), infrared radiation (IR) and gas chromatography–mass spectrometry (GC-MS) to measure the proper transformation percentage and to ascertain the formation of reaction products [17-19]. Ultraviolet-visible spectroscopy (UV-vis) is an effective path to control the transformation procedure. 4-Nitrophenol has a common absorption peak at 317 nm. After the addition of aqueous $NaBH_4$ to 4-nitrophenol, 4-nitrophenolate ions are formed under alkaline conditions and a redshift of the maximum absorption peak happens instantly from 317 to 400 nm and the peaks at 400 nm are reduced over time [7].

Silver nanoparticles (AgNPs) are significant catalysts for several electron transfer chemical reactions [20-24], although the coagulation and aggregation properties of AgNPs, prevent employing the colloidal AgNPs directly as a catalyst [16]. The best method to overcome these difficulties, enhance the specific surface area and adsorption capability and increase the 'green' characteristics of the catalytic procedures is to develop new heterogeneous catalytic techniques based on green and biodegradable solid supports such as organic polymers, biopolymers and particularly, polysaccharide-supported catalysts with or without modification of the support [25,26]. Due to the specificity of cellulose towards attracting metal ions, several organic transformations *via* cellulose-based catalyst-coordinated metals such as palladium, ruthenium, platinum, copper, silver and nickel nanoparticles are reported in the literature [27-30].

Cellulose-based composites are environmental friendly resources for sustainable development and a greener future because of the broad availability, biodegradability, biocompatibility, reinforcing abilities, low weight and low filler load requirements. Cellulose stabilizes AgNPs efficiently and effectively through powerful interactions as a result of having several hydroxyl and ether functional groups. During the preparation of catalyst, the cellulose can also control the size and shape of AgNPs formed in the porous structure and as a result it is an extraordinary supporting matrix for AgNPs. AgNPs on cellulose- and nanocellulose-based fillers or matrices to produce polymer biocomposites and functional polymeric components are valuable sustainable choices for green and eco-friendly composites [31,32].

Solid heteropolyacids (HPAs) are green polymeric materials, containing the early transition metal cations, M (generally W, Mo and V) and a central heteroatom, X (Si, P, Ge, *etc.*) [33-39]. Possessing high thermal stability, robust acidity and structural flexibility, HPAs are used extensively as homogeneous catalysts, heterogeneous catalysts, or heterogeneous surface catalysts in various chemical reactions. The Preyssler heteropolyanion, $[NaP_5W_{30}O_{110}]^{14-}$ with 14 acidic protons is an effective superacid solid catalyst that can be utilized both in homogeneous and heterogeneous phases. Recent studies have been extensively concentrated on the designing of organic-inorganic composites of HPAs and their applications in different reactions [33-39].

Herein, a successful effort to apply the silver nanoparticles embedded-Preyssler functionalized cellulose biocomposite (PC/AgNPs) as an eco-friendly and benign heterogeneous catalyst and reusable catalyst in the reduction of nitroarenes is reported. The stabilization of silver nanoparticles onto the functionalized microcrystalline cellulose/Preyssler heteropolyacid as a green, eco-friendly and benign nanobiocomposite heterogeneous catalyst with more accessible active sites made it reliable for increased catalytic hydrogenation achievements and was applied successfully in catalytic reduction of various nitroarenes in the presence of $NaBH_4$ under mild reaction conditions within very short times and in high or excellent yields. It is also found that PC/AgNPs exhibits advantages in terms of activity, stability, rapid separation and efficient recycling and has been also reported for the synthesis of biologically active 2-amino-4*H*-pyran and spirochromenes [35].

EXPERIMENTAL

All the chemical material and solvents such as acetonitrile (≥ 99%), ethanol (≥ 96%), dichloromethane (≥ 99%), N,N-dimethylformamide (DMF, ≥ 99.8%) and 25 % ammonia solution (NH_4OH) were used with high purity from Merck. The required chemicals such as sodium borohydride ($NaBH_4$, 98%) and nitroaromatic derivations were purchased from Sigma-Aldrich, USA. Electrothermal 9200 apparatus was used to determine the melting point of products. Bruker Tensor 27 FT-IR spectrometer (400-4000 cm^{-1}) was used to detect absorbance bands of organic products using a KBr disk. All products were already known and the obtained analytical results (melting points and FTIR spectra) were in good agreement with the literature data.

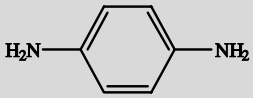
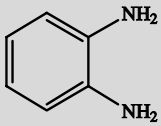
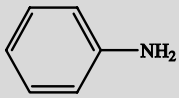
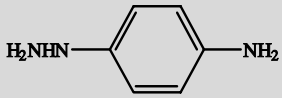
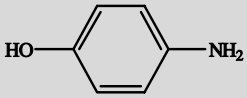
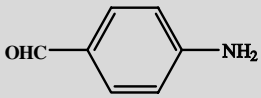
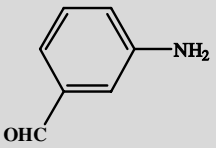
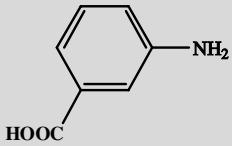
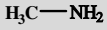
General procedure: To a round bottomed flask containing nitro compound (1 mmol) and 5 mL H_2O, 0.03 g PC/AgNPs catalyst was added and the mixture was vigorously stirred at room temperature. Then, $NaBH_4$ (0.076 g, 2 mmol) was added to the suspension and the reaction temperature was raised to 60 ºC. After completion of the reaction (monitored by TLC using *n*-hexane:ethyl acetate 9:1), CH_2Cl_2 (3 × 8 mL) was added to the mixture, the catalyst was separated with simple filtration and the hydrogenated product was obtained after evaporation of solvent (Table-1).

RESULTS AND DISCUSSION

Silver nanoparticles embedded-Preyssler functionalized cellulose biocomposite (PC/AgNPs) catalyst was characterized by SEM, TEM, FT-IR, UV-visible techniques as reported by Saneinezhad *et al*. [35]. UV-visible results show the absorption band at 440 nm and the colour change of the reaction medium from yellow to deep brown at pH 12.5 with the addition of aqueous silver nitrate. Scanning electron microscope analysis (SEM) reveals the strong immobilization of Preyssler on functionalized cellulose with high surface density and the favourable binding of the metal ions from aqueous $AgNO_3$ solution with Preyssler anion owning highly distributed charged surfaces (Fig. 1).

The transmission electron microscopy (TEM) image of AgNPs generated by Preyssler-cellulose (PC) nanobiocom-

TABLE-1
REDUCTION OF AROMATIC NITRO COMPOUNDS IN THE PRESENCE OF PC/AgNPs AND $NaBH_4$

Entry	Product	Time (min)	Yield (%)	m.p. (°C) Obs.	m.p. (°C) Lit. [6]
1		40	98	141-144	145-147
2		35	97	101-104	102-104
3		45	98	Liquid	Liquid
4		65	90	Oil	Oil
5		65	92	186-188	186-190
6		40	98	79	77-79
7		45	97	29-31	28-30
8		110	92	182	187-189
9		50	95	Liquid	Liquid

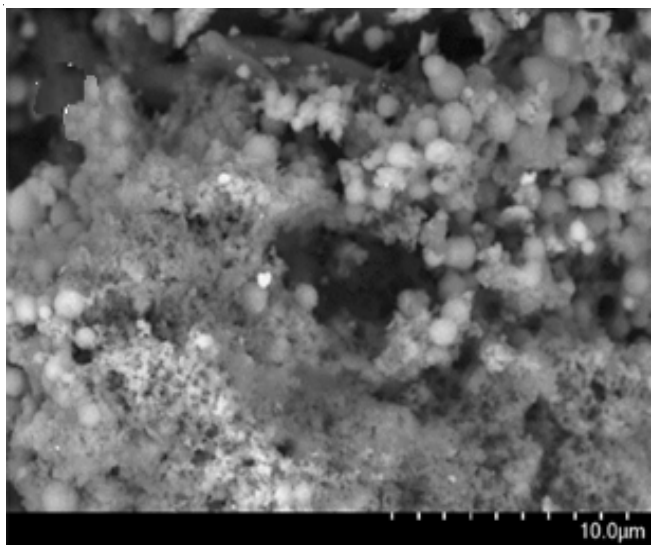


Fig. 1. SEM image of PC AgNPs (pH = 12.5, PC = 1 g, temperature = 80 °C, $AgNO_3$ = 6 mM) {Reprinted with permission [Ref. 35]}

posite revealed the spherical shape of AgNPs with a size of 50 nm at the 1% wt. loading of Preyssler (Fig. 2).

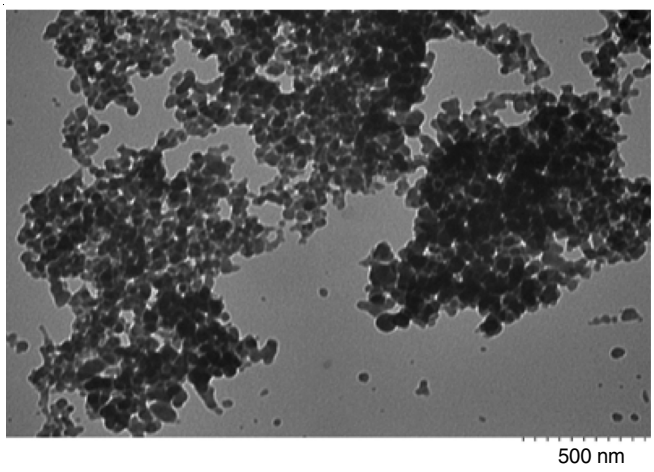
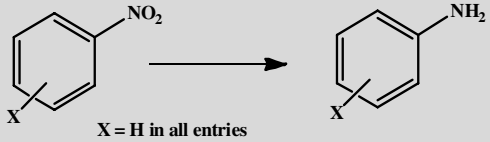


Fig. 2. TEM image of AgNPs {Reprinted with permission [Ref. 35]}

Catalytic performance of Preyssler-functionalized cellulose/AgNPs biocomposite: To optimize the reaction conditions and evaluate the catalytic performance of PC/AgNPs, nitrobenzene was selected as a model reaction. In the presence of $NaBH_4$ and 0.03 g catalyst in water at room temperature,

nitrobenzene gave aniline in 55% yields after 55 min (Table-2, entry 8). Next, the temperature was changed to improve the yield of the model reaction and the reaction proceeds in an excellent yield (98%) at 60 ºC in H_2O using 0.03 g catalyst after 40 min (Table-2, entry 7). The reaction under alcoholic reaction conditions was completed within a similar time as the aqueous reaction system, but in a lesser yield. To improve the progress of this reduction reaction, the effect of several solvents including CH_3CN, CH_2Cl_2, EtOH, DMF and water with 0.03 g of catalyst was optimized. However, no satisfactory yield was observed using CH_3CN or DMF (each 15 %) and only trace amounts of product were observed using a non-polar solvent like CH_2Cl_2. Furthermore, it was observed that under these conditions, the reaction required longer times (50-55 min) to afford comparable yields (Table-2, entries 1, 2, 3). When the reaction was accomplished under aqueous conditions, a high yield of the reduction product was obtained in a short time (Table-2, entry 7, 9, 10). The sufficient amount of catalyst for the completion of reduction was optimized for 0.03 g. It was found that the reaction provided a slightly lower yield when accomplished with 0.02 g of catalyst than with 0.03 g in water and the yield was also not affected by the increasing quantity of catalyst loaded to 0.4 g in water (Table-2, entries 7, 9, 10).

TABLE-2
OPTIMIZATION CONDITIONS FOR REDUCTION OF NITROAROMATIC COMPOUNDS



X = H in all entries

Entry	Catalyst amount (g)	Solvent	Temp. (°C)	Time (min)	Yield (%)
1	0.03	CH_3CN	60	50	15
2	0.03	CH_2Cl_2	Reflux	55	Trace
3	0.03	DMF	60	50	15
4	0.03	EtOH	60	40	75
5	0.03	H_2O	Reflux	40	80
6	0.03	H_2O	80	45	75
7	0.03	H_2O	60	40	98
8	0.03	H_2O	r.t.	55	55
9	0.02	H_2O	60	40	92
10	0.04	H_2O	60	40	98

Thus, the optimized reaction condition was selected to evaluate the generality of this catalyst application with several electron-rich and -deficient substrates. It was gratifying to observe that PC/AgNPs nanoparticles-embedded-Preyssler functionalized cellulose biocomposite catalyst can efficiently catalyze the reduction of all of the tested nitro compounds to deliver the corresponding amines under mild reaction conditions in good to excellent yields (Table-1).

Reusability studies: To evaluate the reusability of PC/AgNPs in the model reaction, the catalyst was separated by the completion of each cycle, rinsed with EtOH, dried and reused in the next cycle. Results demonstrate that up to 6 runs, recycling the catalyst, shows no significant loss of catalytic activity (Fig. 3).

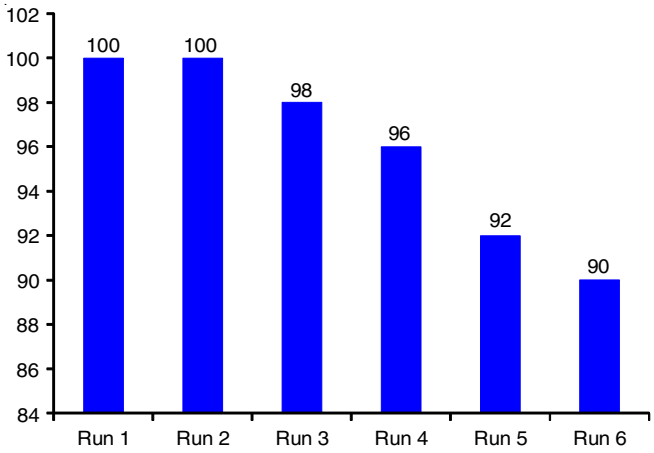


Fig. 3. Reusability test of the PC/AgNPs for model reaction

Conclusion

In conclusion, the above-mentioned research has opened a gateway to an environmental-friendly and powerful strategy for the reduction of nitro compounds using an eco-friendly, benign and green silver nanobiocomposite heterogeneous catalyst. Reduction of nitro compounds using silver nanoparticles-embedded Preyssler-functionalized cellulose (PC/AgNPs) nanobiocomposite catalyst in the presence of $NaBH_4$ were accomplished in an aqueous solution. The amount of catalyst, different solvents and temperature were also screened. The catalysts show a high activity and selectivity towards a reduction reaction at small catalyst concentrations. Under the optimal conditions, several nitro compound derivatives were examined and the results show that the reactions were efficiently catalyzed under mild reaction conditions and the reduction occurred in good to excellent yields. The work-up protocol was simple and the catalyst was easily recovered and reused in the next run.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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