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Selective Reduction of Nitroarenes Catalyzed by Sustainable and Reusable DNA-supported Nickel Nanoparticles in Water at Room Temperature

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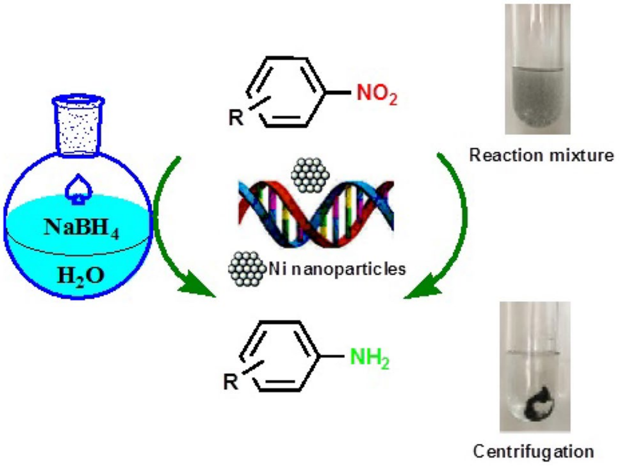
Abstract

In this research, a novel, biodegradable and environmentally friendly catalyst composed of nickel nanoparticles supported on DNA was prepared and fully characterized by Fourier transform infrared spectroscopy, high resolution transmission electron microscopy, energy-dispersive X-ray analysis, X-ray photoelectron spectroscopy, UV–vis spectroscopy, inductively coupled plasma optical emission spectroscopy, and elemental analysis. The catalyst exhibited remarkable catalytic activity and chemoselectivity for the reduction of various substituted nitroarenes with sodium borohydride ($NaBH_4$) as the source of inexpensive hydride in water at room temperature. High turnover frequency and selectivity were observed for the reduction of all tested substrates. Interestingly, the catalyst could be recovered conveniently for multiple recycling reactions with sustained activity. Furthermore, nearly no nickel species was leached out from the catalyst during the course of reaction, proving the true heterogeneity in the present catalytic protocol.

Graphical Abstract

The reduction of various nitroaromatic compounds into their corresponding amines is achieved by DNA supported nickel nanoparticles with the sodium borohydride as the reducing agent in water at room temperature.



Keywords DNA · Nickel nanoparticles · Heterogeneous catalysis · Reduction of nitroarenes

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Extended author information available on the last page of the article

1 Introduction

Aromatic nitro compounds are common organic pollutants, which are generated or released from the waste water of industries and agricultural waste [1, 2]. In contrast to these compounds, their reduction products, aromatic amines, are highly useful intermediates and building blocks in the preparation of pigments, dyes, pharmaceuticals, polymers, and agrochemicals [3–8]. Based on this fact, there has been considerable interest in the development of efficient and practical routes for the chemo-selective reduction of aromatic nitro compounds to give their corresponding amines. The traditional routes for this transformation usually involve the use of stochiometric reducing agents such as Fe/HCl, Zn, Sn, and sulfur compounds, which caused large amount of toxic waste and therefore hampering their widespread applications for numerous industrial processes [9, 10]. The catalytic hydrogenation route over transition metals along with a suitable hydrogen source such as hydrogen gas, sodium borohydride, hydrazine, etc presents a promising option to solve this problem as evidenced by the considerable increase efforts in this area [11, 12]. Several research studies have reported the use of different noble-metal catalysts like Pt, Pd, Au, Rh, and Ru for the reduction of nitro compounds because of their efficient catalytic activities [13–17]. However, the high cost and limited availability of these precious metals, turned researchers towards the Earth-abundant and much less expensive metals including Fe, Co,Cu, and Ni [18–22]. Among these metals, Ni is mostly used owing to its excellent catalytic activity and selective hydrogenation property.

Recently, metal nanoparticle-based (NPs) catalysts have attracted more and more attention due to their large surface areas and large number of exposed metal atoms, which increase the catalytic performance of metal NPs [23–25]. Nevertheless, metal NPs are prone to agglomerate because of the high surface energy and Van der Waals force, which inevitably reduces their catalytic activity [26, 27]. Another challenging issue for metal NPs is their separation and recycling from the reaction medium that restrict their applications in industrial-scale synthesis [28]. In order to circumvent these issues, great efforts in catalysis research have been devoted to stabilize the metal NPs on appropriate solid supports or stabilizing ligands [29–31]. In this context, various organic and inorganic supports such as polymers [32], metal oxides [33], mesoporous and amorphous silica [34, 35], carbon materials [36, 37], metal–organic framework (MOF) [38], and magnetic nanoparticles [39] have widely been used to stabilize the nickel nanoparticles (Ni NPs) and employed successfully as catalysts in the reduction of nitro compounds. Despite the interesting results that have been obtained, most of these supports are synthetic materials which need difficult and time-consuming efforts for their synthesis as well as surface functionalization to maintain high reactivity of catalyst. Accordingly, there is a strong need to develop naturally sourced catalysts for this transformation.

Over the past few decades, DNA-metal NPs hybrid materials have become of high interest in the field of heterogeneous catalysts. The unique features of natural DNA such as non toxicity, biodegradability, easy availability, renewability, good water dispersibility, and its high thermodynamic stability have made this molecule one of the most suitable support for metal NPs [40–42]. Up to now, many transition metals such as Pd, Au, Ag, and Pt have been immobilized on DNA to obtain catalysts in numerous catalytic reactions [43–46]. For example, in 2011, Wang et al. reported that Au NPs on DNA was effective catalyst for the synthesis of amide from alcohols and amines [46]. In 2012, the same group successfully synthesized Pd NPs on DNA which was active for the synthesis of imines from alcohols and amines or nitroarenes [43]. Another research group, Itoh et al., reported the preparation of hybrid Pd/DNA and its catalytic application in the hydrogenation and Suzuki–Miyaura coupling reactions [44]. Very recently, in 2017, Camacho's group showed that Pd NPs on DNA could act as an efficient catalyst for the Sonogashira coupling reaction [45].

Motivated by the above reports, we envisioned that by using natural DNA as a support for Ni NPs, an active Ni catalyst for the reduction of nitroarenes would be prepared. To this end, herein, a nanocatalyst composed of Ni NPs on DNA was synthesized which efficiently promoted the transfer hydrogenation of nitroarenes into anilines using $NaBH_4$ as a hydrogen source in aqueous media. The prepared catalyst was stable enough to be recycled for at least five runs without appreciable loss of its catalytic activity. Moreover, the catalytic activity of this nano-catalyst was compared with other Ni-based catalysts. As far our awareness reach, this is the first time to prepare DNA-Ni NPs hybrid materials.

2 Experimental

2.1 Chemicals and Instruments

All chemicals were procured from Merck and Sigma–Aldrich chemical companies and used without any further refinement.

Fourier transform infrared (FT-IR) spectra were recorded in KBr matrices at room temperature with a Shimadzu FT-IR-8300 spectrophotometer. Elemental analyses on the samples were implemented using a 2400 series Perkin Elmer analyzer. The Ni content in the catalyst was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Varian Vista-Pro analyzer. Field emission scanning electron microscopy (Tescan Mira (II), operating at 15 kV) combined with an energy dispersive X-ray spectroscopy (EDX) was employed to investigate the elemental composition of the catalyst. High resolution transmission electron microscopy (TEM) images were obtained in a JEOL, JEM-2100F microscope operated at 200 kV. UV–vis studies were carried out on a Perkin-Elmer (LAMBDA 2) UV–vis spectrophotometer in water as the solvent. X-ray photoelectron spectroscopy (XPS) was carried out by a Thermo Scientific, ESCALAB 250Xi using Mg X-ray source. ^{1}H NMR spectra were recorded by using a Bruker Advance III 400 MHz NMR spectrometer using $CDCl_3$ or DMSO-d6 as the solvent and TMS as the internal standard. The reaction monitoring was accomplished by thin layer chromatograghy (TLC) on Merck silica gel 60 F_{254}. Columns chromatography was performed on columns of silica gel 60 (70–230 mesh).

2.2 Synthesis of NiNPs/DNA

$Ni(OAc)_2$ (0.1 mmol) was added to a solution of fish sperm DNA (10 mg) in methanol (3 mL). The mixture was stirred at room temperature for 24 h to ensure that Ni^{2+} ions thoroughly bound to DNA. Afterwards, 0.5 mmol of $NaBH_4$ was added to the mixture under nitrogen atmosphere to start the reduction reaction. After reduction, the mixture was left under vigorous stirring at room temperature for another 2 days under nitrogen atmosphere. After dilution with water, the resultant precipitate was separated by centrifugation, washed with water three times, and dried at room temperature.

2.3 General Procedure for the Reduction of Nitroarenes to Amines with NiNPs/DNA

In a typical experiment, 0.5 mmol of nitroarene and 0.002 g (2 mol%) NiNPs/DNA were added to 2 mL water and then stirred for 2–3 min for thoroughly mixing. Subsequently, 1 mmol of $NaBH_4$ was added to the reaction mixture under magnetic stirring at room temperature. The extent of the reaction was monitored by thin layer chromatography. Reproducibility of the results was checked by repeating the runs at least three times and was found to be within acceptable limits (±3%). When the reaction was completed, the reaction mixture was diluted with ethyl acetate and the catalyst was recovered by centrifugation. The combined organic fractions were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and n-hexane as the eluent, and the ratio of ethyl acetate and n-hexane was depended on the structure of the products. The structure of isolated products was verified by ^{1}H NMR.

2.4 Recyclability of Catalyst

The recyclability of NiNPs/DNA was examined by carrying out the reduction reaction of 4-chloronitrobenzene under the same reaction conditions as described above but with the magnification of 10 times. For each time, the catalyst was recovered by centrifugation after 3 h of reaction time. After this moment, the catalyst was washed with ethanol and water for several times to remove the inorganic and organic parts, and then dried in air. Afterwards, the catalyst was reused with a fresh charge of substrates and reagents for the next catalytic cycle under similar reaction conditions.

3 Results and Discussion

3.1 Synthesis and Characterization of Catalyst

The preparation of the catalyst was accomplished by using a very simple synthetic route which involved the treatment of inexpensive natural fish sperm DNA with $Ni(OAc)_2$ and $NaBH_4$ in methanol at room temperature for 72 h, without the use of additional stabilizing agents (Fig. 1). The black obtained solid catalyst was called NiNPs/DNA, and fully characterized with various techniques.

The Ni content in NiNPs/DNA as determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis, was 0.89 $mmolg^{-1}$. The contents of carbon and nitrogen in this sample were measured to be 33% and 12%, respectively, which were close to that calculated for DNA (C (34%)) and (N (14%)). Meanwhile, energy-dispersive X-ray (EDX) analysis was carried out to confirm the existence of all individual elements of DNA in NiNPs/DNA. As clearly observed, EDX spectrum of NiNPs/DNA (Fig. 2a) exhibited not only the presence of Ni but also the elements present in DNA such as C, O, P, Na, and N. Also, the field emission scanning electron microscopy (FE-SEM) image of NiNPs/DNA (Fig. 2b) showed that the surface morphology of NiNPs/DNA was uniform.

Figure 3a, b compare the FT-IR spectra of DNA with NiNPs/DNA. The DNA spectrum (Fig. 3a) showed symmetric and asymmetric PO_2^- stretching peaks at 1069 and 1232 cm^{-1}, respectively. Also, the band at 966 cm^{-1} was attributed to the P-O-C backbone stretching. In addition, the bands observed at 1400 to 1700 cm^{-1} for DNA could be corresponded to the C=C, C–N, and C=O functional groups present in the aromatic base pairs of DNA. Similarly to the spectrum of parent DNA, the FT-IR spectrum of NiNPs/DNA (Fig. 3b) exhibited these bands with greatly reduced intensity and significant changes in the position of them, which provided evidence for the interaction of Ni NPs with DNA. These results clearly confirmed the formation of NiNPs/DNA nanohybrid.

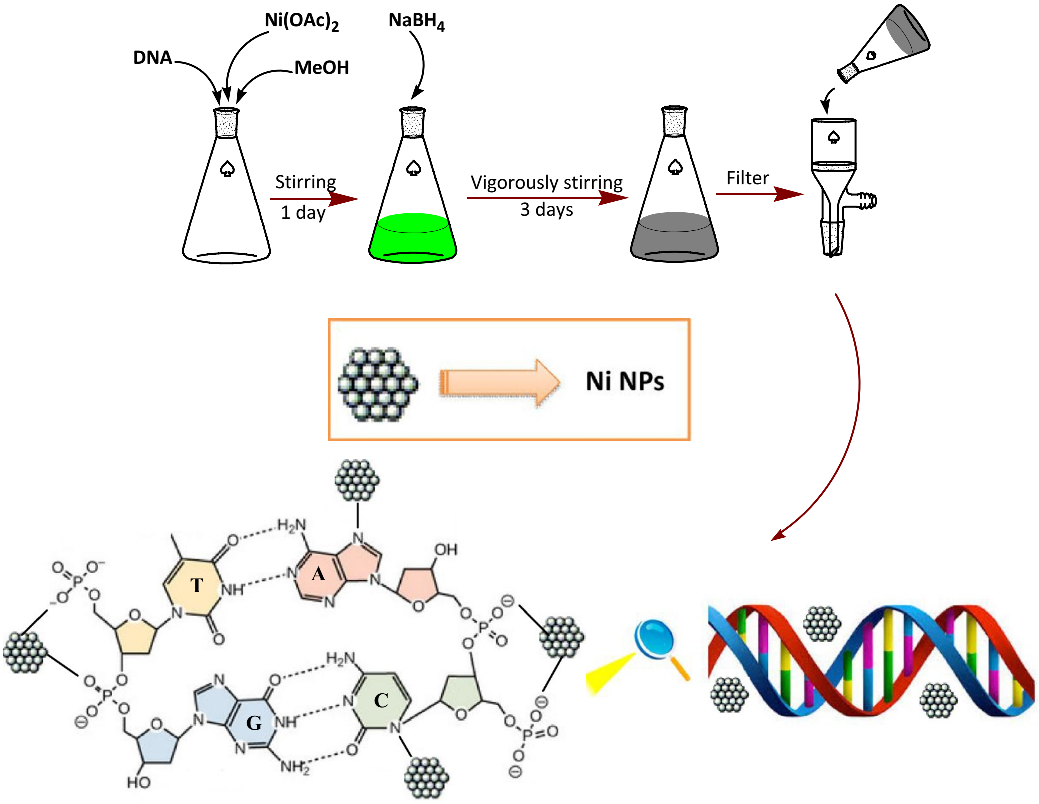


Fig. 1 Preparation of NiNPs/DNA

The formation of NiNPs/DNA nanohybrid was further confirmed by UV–vis spectroscopy. The UV–vis spectra of DNA, $Ni(OAc)_2$, and NiNPs/DNA were measured in water and are presented in Fig. 4. The spectrum of aqueous DNA solution exhibited a maximum at 263 nm, which was attributed to the absorption of aromatic base molecules in DNA structure. The absorption spectrum of aqueous $Ni(OAc)_2$ solution revealed an absorption peak at 394 nm with a shoulder at 218 nm due to the ligand to metal charge transfer (LMCT). As can be seen, the absorption peak due to DNA was found in the spectrum of NiNPs/DNA. However, the peak position of NiNPs/DNA sample was slightly shifted as compared to that of pure DNA solution. The reason behind this may be the interaction between DNA and Ni NPs. Furthermore, the absence of resonant peak above 300 nm proved the metallic nature of Ni NPs.

In order to investigate the elemental compositions and the oxidation state of Ni NPs in NiNPs/DNA, X-ray photoelectron spectroscopy (XPS) studies were carried out. In the XPS elemental survey scans of the surface of NiNPs/DNA (Fig. 5a) C, O, Na, P, N, Ni peaks was detected, which was in agreement with the EDX measurement. Figure 5b exhibits the enlarged XPS scan of Ni 2p. It can be seen that the Ni 2p spectrum was deconvoluted into three peaks. Two peaks at 853.4 and 860.8 eV were attributed to the Ni (0) $2p_{3/2}$ levels. The other peak located at 878.4 eV was related to the Ni (0) $2p_{1/2}$ level. The binding energies of these peaks were slightly higher than those of typical Ni (0) nanoparticles. This may be due to the interaction between DNA and Ni NPs. As the binding energy of Ni (II) did not appear in the XPS spectrum, it can be confirmed that the Ni (II) in NiNPs/DNA almost completely converted to metallic Ni NPs [47, 48].

To obtain the distribution and size of Ni NPs on DNA surface, NiNPs/DNA was characterized by high resolution transmission electron microscopy (HRTEM). Figure 6 depicts the HRTEM images of NiNPs/DNA. Near spherical nanoparticles that were uniformly distributed on DNA surface could be observed in the HRTEM images. The average size of nanoparticles was in the range of 3–4 nm. This result also suggested that the presence of the aromatic nucleobases on DNA backbone facilitated dispersion of Ni NPs along DNA strand through chelating effect.

3.2 Catalytic Reduction of Nitroarenes

After the successful preparation and characterization of NiNPs/DNA, its catalytic activity was evaluated in the reduction of nitroarenes. To find the optimum reaction conditions, the effect of different reaction parameters including reducing reagent, solvent, temperature, and the amount of

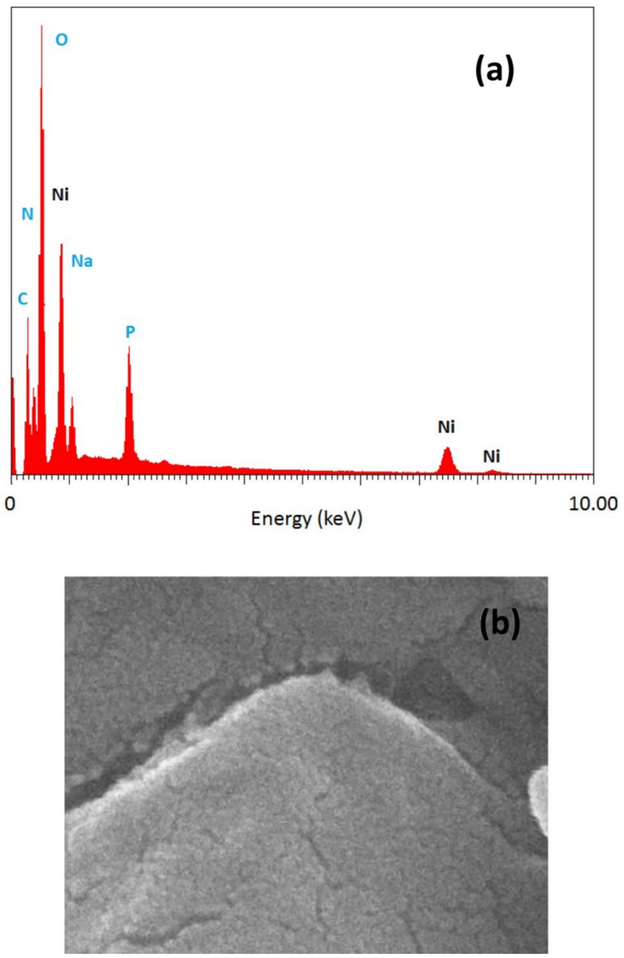


Fig. 2 EDX spectrum (**a**) and FE-SEM image (**b**) of NiNPs/DNA

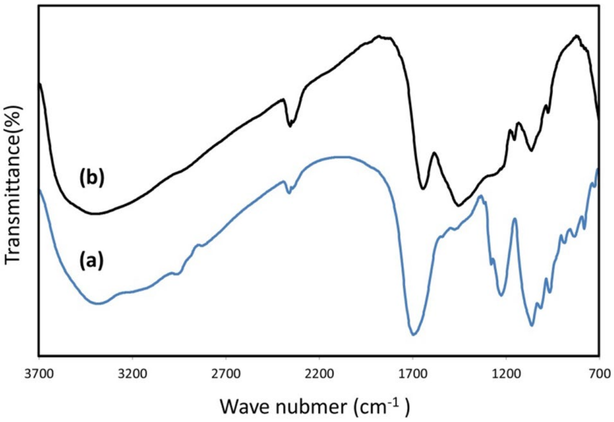


Fig. 3 FT-IR spectrum of DNA (**a**) and NiNPs/DNA (**b**)

catalyst was examined in the reduction of 4-chloronitrobenzene as the model substrate (Table 1). Firstly, to assess the effect of the solvent on the reaction in the presence of $NaBH_4$ as a hydrogen source, different solvents such as water, toluene, MeOH, EtOH, DMSO, and DMF were used. When toluene was used as the reaction solvent, only low yield was achieved (entry 1). Utilizing the aprotic solvents such as DMF and DMSO as the reaction solvent provided moderate yields (entries 2,3). However a significant increase in yield was observed when protic polar solvents like water, MeOH, and EtOH were used as the reaction solvent (entries

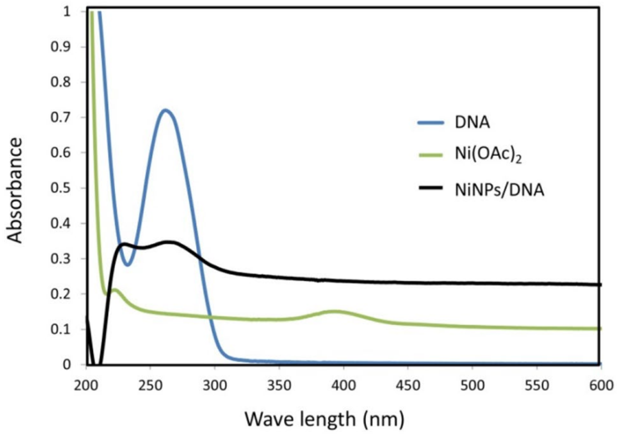


Fig. 4 UV–vis spectra of DNA, $Ni(OAc)_2$ and NiNPs/DNA in water

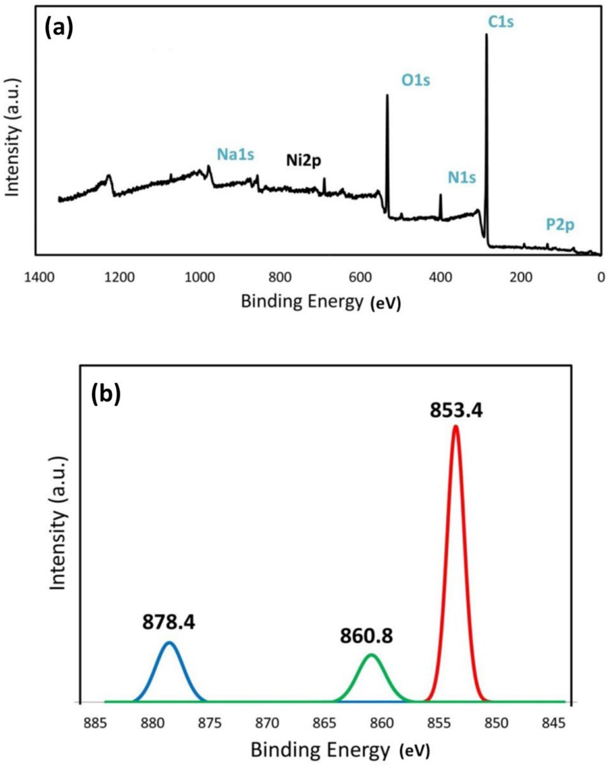


Fig. 5 XPS survey spectrum of NiNPs/DNA (**a**), the high-resolution XPS spectrum of the Ni 2p region (**b**)

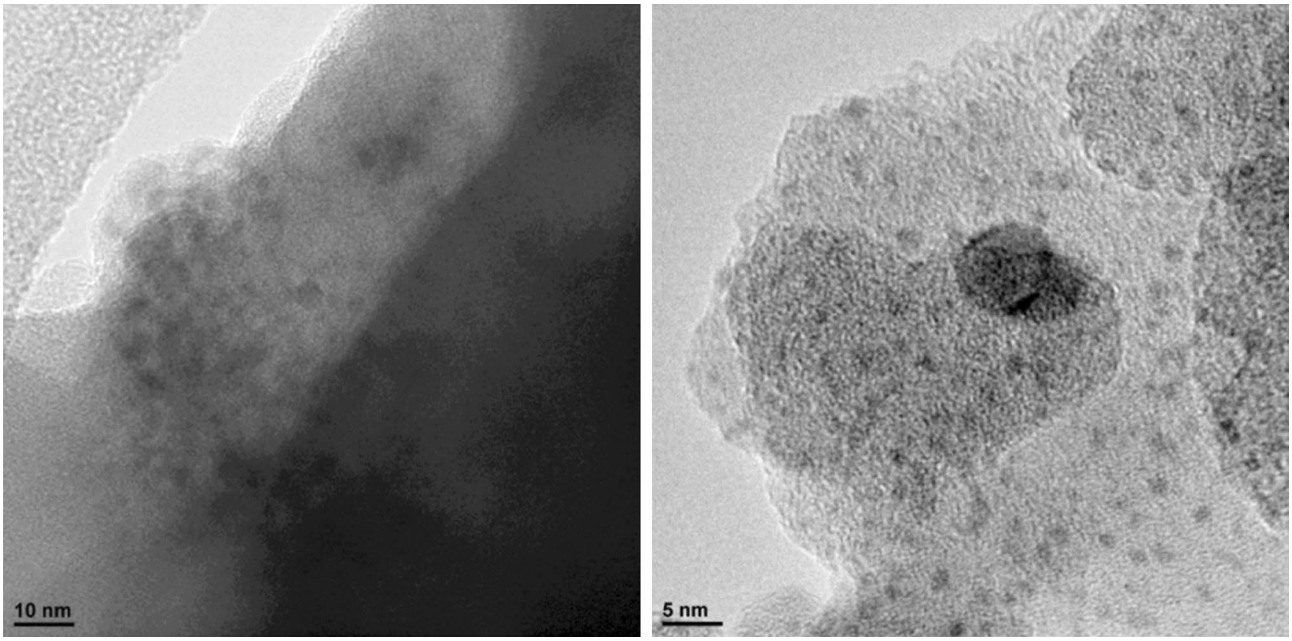


Fig. 6 HRTEM images of NiNPs/DNA

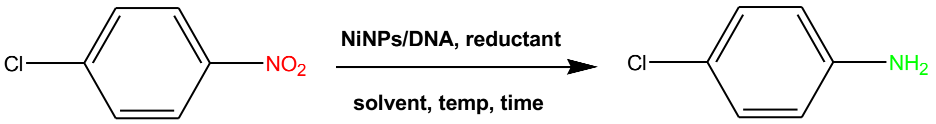
4–6). Among these solvents, water was chosen as the optimum solvent since it is cheap, readily available, nontoxic, noncorrosive, and nonflammable [49, 50]. Next, to improve the observed scope in water, the reaction was carried out in the presence of other reducing agents such as ammonium formate, acetic acid, ethylene glycol, hydrazine hydrate, and formic acid (entries 7–11). As can be seen from the data in Table 1, these hydrogen sources showed lower activity compared to that of $NaBH_4$. The effect of reaction temperature on the catalytic activity of NiNPs/DNA was also studied in the model reaction. It was found that increasing the temperature to 50 °C did not improve the product yield (entry 12). Finally, we turned our attention to optimize the amount of catalyst and 2 mol% of catalyst was recognized as optimum (entries 13,14). Additionally, in the absence of catalyst, no reduction of 4-chloronitrobenzene to 4-chloroaniline was observed, demonstrating that NiNPs/DNA catalyst is necessary for the reaction (entry 15). From the above discussions, it could be seen that the best yield was afforded in the reduction of 4-chloronitrobenzene by using $NaBH_4$ as hydrogen source in water as a green solvent at room temperature for 3 h.

After having established the optimal reaction conditions, the scope and limitations of NiNPs/DNA was examined in the reduction of various nitroarenes. The results are summmarized in Table 2. As seen in Table 2, an excellent aniline yield of > 99% was obtained when nitrobenzene was employed as the starting material (entry 1). Substrates with non-reducible groups like OCH_3, CH_3, OH, and NH_2 at the ortho or para positions, were successfully reduced in high yields (entries 2–8). This proved that the steric character of substrates had no obvious effect on this catalytic system. Interestingly, halogen (I, Br, Cl, F)-substituted nitroarenes were selectively reduced to their corresponding halo anilines with no observable dehalogenation (entries 9–12). Also, the most challenging reducible functional groups such as CN, $COCH_3$, and COOH were well-tolerated and remained intact during the reduction process (entries 13–15), giving the corresponding aryl amines as the sole products, respectively. These results clearly confirm the excellent chemoselectivity of this catalytic protocol. Further, NiNPs/DNA exhibited high catalytic activity for the reduction of arenes containing more than one nitro group such as 1,2-dinitrobenzene and 1,4-dinitrobenzene (entries 16,17). The reduction of hetrocyclic nitroarene was also carried out; 3-aminopyridine, which is important building block for the synthesis of a variety of agrochemicals and pharmaceuticals, was obtained in high yield (entry 18). Finally, another relevant example to show the scope of the present protocol, is the highly efficient reduction of bulkier molecules. In these cases, NiNPs/DNA exhibited low catalytic activity and longer reaction times were necessary to achieve high yields (entries 19–23). This may be due to the solubility problem in water and steric hindrance effect of these molecules.

3.3 Catalyst Leaching and Recycling

For heterogeneous catalytic systems, an important issue to be seriously addressed is the possibility of active metal leaching into the reaction solution during the catalytic

Table 1 Optimization of reaction parameters for the reduction of 4-chloronitrobenzene



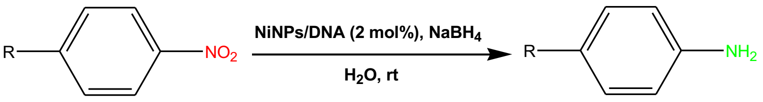
Entry	Catalyst (mol%)	Reductant	Solvent	Temp (°C)	Time (h)	Yield (%)[a]
1	2	$NaBH_4$	toluene	r.t	3	15
2	2	$NaBH_4$	DMF	r.t	3	60
3	2	$NaBH_4$	DMSO	r.t	3	67
4	2	$NaBH_4$	water	r.t	3	96
5	2	$NaBH_4$	MeOH	r.t	3	92
6	2	$NaBH_4$	EtOH	r.t	3	97
7	2	$HCOONH_4$	water	r.t	24	NR
8	2	CH_3COOH	water	r.t	10	5
9	2	$HOCH_2CH_2OH$	water	r.t	24	NR
10	2	N_2H_4	water	r.t	10	38
11	2	HCOOH	water	r.t	10	53
12	2	$NaBH_4$	water	50	3	98
13	1	$NaBH_4$	water	r.t	5	94
14	4	$NaBH_4$	water	r.t	3	96
15	None	$NaBH_4$	water	r.t	24	10

Typical conditions: 4-chloronitrobenzene (0.5 mmol), reductant (1 mmol), water (2 mL)

[a] Isolated yield after chromatography

reaction. It is known that these leached metals can catalyze the reaction, so the reaction will not perform under real heterogeneous catalysis conditions. Thus, in order to ascertain the heterogeneous nature of NiNPs/DNA and to confirm that no Ni species was leached from the catalyst into the solvent during the reaction, a filtration experiment was done for the reduction reaction of 4-chloronitrobenzene under optimized conditions. After the reaction has performed for 1 h with the conversion of 58%, the catalyst was filtered out from the reaction system and the filtrate was allowed to react further for an additional 12 h. The resulting conversion was only 61% after this time, demonstrating that the reaction was almost halted by the separation of the catalyst and there is no Ni species in the solution for fruitful conversion. It can

Table 2 Reduction of various nitroarenes in the presence of NiNPs/DNA catalyst



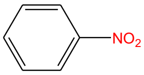
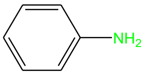
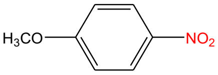
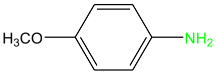
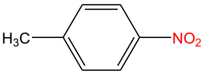
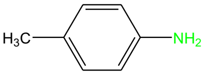
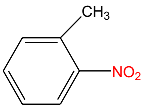
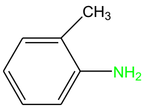
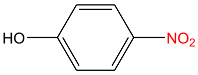
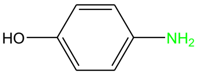
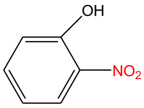
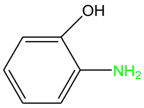
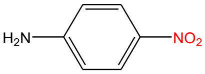
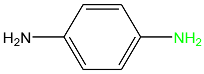
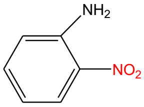
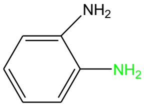
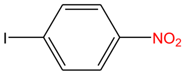
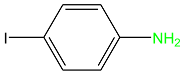
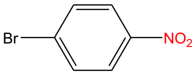
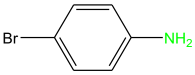
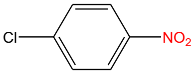
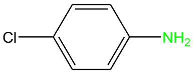
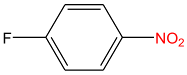
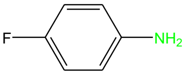
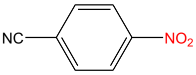
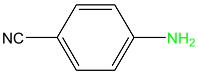
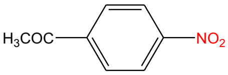
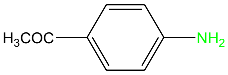
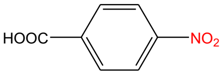
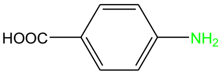
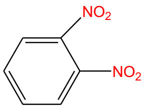
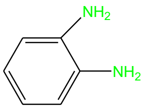
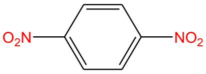
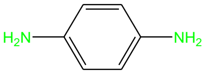
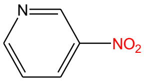
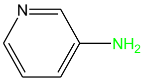
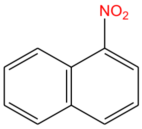
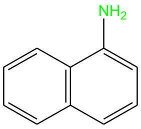
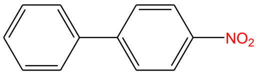
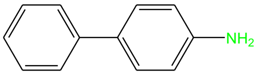
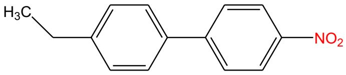
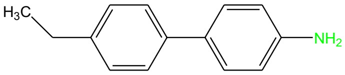
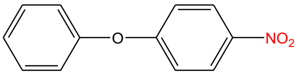
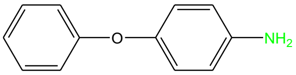
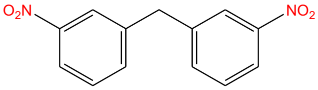
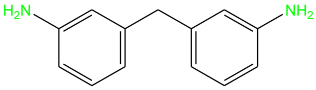
Entry	Reactant	product	Time (h)	Yield (%)[b]
1			2	>99
2			2	97
3			2.5	95
4			2.5	92
5			2	89
6			2	93
7			3	>99
8			3	95
9			3	89
10			3	92

Table 2 (continued)

Entry	Reactant	product	Time (h)	Yield (%)^{b}
11			3	96
12			3	>99
13			2	95
14			2	98
15			1.5	97
16			2	84
17			2	91
18			1.5	97
19			4	95
20			4	91
21			4	88
22			5	85
23			5	78

Reaction conditions: Reactant (0.5 mmol), $NaBH_4$ (1 mmol) in water (2 mL)

[a] Isolated yield after chromatography

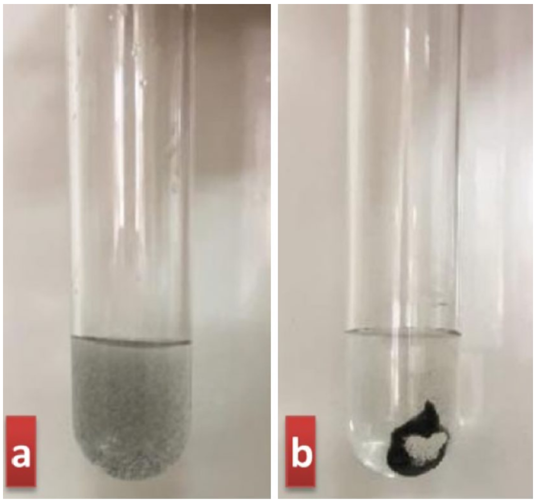


Fig. 7 Pictures showing the reaction medium before (**a**) and after (**b**) centrifugation

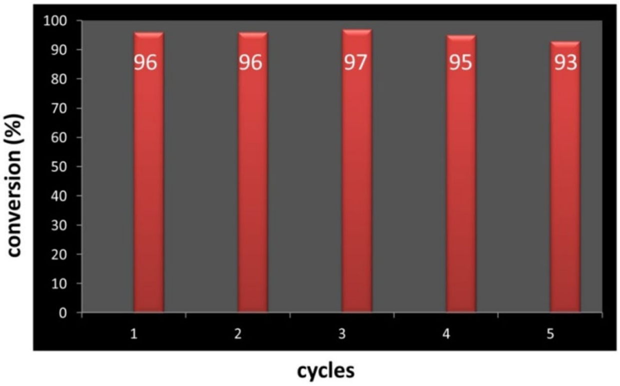


Fig. 8 Recycling of NiNPs/DNA in the reduction of 4-chloronitrobenzene

thus be concluded that there is a strong interaction between the Ni NPs and DNA and NiNPs/DNA is an outstanding heterogeneous catalyst.

Another important issue concerning the use of a heterogeneous catalyst is its recyclability and stability. To clarify this issue, the recycling experiments of NiNPs/DNA catalyst were carried out in the reduction of 4-chloronitrobenzene. After each catalytic reduction cycle, the catalyst was simply recovered by centrifugation (Fig. 7), washed, dried and then immediately reused in subsequent cycles. As evident from Fig. 8, the catalyst could be recycled and reused five times without obvious deterioration of its catalytic activity. These results collectively confirm the high stability and recyclability of NiNPs/DNA catalyst.

3.4 A comparison Between Catalytic Activity of NiNPs/DNA in the Reduction of Nitrobenzene Related to Other Reported Ni-Catalysts

Table 3 exhibits the comparative data of catalytic activity of the present catalyst with other previously reported Ni-based heterogeneous catalysts for the reduction of nitrobenzene to aniline. From Table 3, it is appeared that NiNPs/DNA showed superior results in terms of yield and reaction time compared with the other catalytic systems. Though high yields were also achieved in some of them, some organic solvents were used as reaction medium or large quantities of the catalyst or relatively high temperature was required. Therefore, a simple preparation of NiNPs/DNA with high catalytic performance in a green solvent, namely water, was presented in our work.

3.5 Plausible Mechanism for the Reduction of Nitrobenzene

According to the above results and available literature data [2, 36], a plausible reaction mechanism has been proposed for the NiNPs/DNA-catalyzed reduction of nitrobenzene using $NaBH_4$ as hydrogen source in aqueous medium, and is shown schematically in Fig. 9. At first, a B-H bond cleavage takes place in a rate-determining step to afford the Ni-H species [step 1]. Secondly, nitrobenzene is adsorbed on the surface of NiNPs/DNA catalyst. Then, hydride transfer occurs from such high reactive species to nitro group of nitrobenzene to generate nitroso compound, followed by the fast reduction to hydroxylamine [step 3 and 4]. Finally, the

Table 3 Comparison of the catalytic activity of NiNPs/DNA with other reported Ni-catalysts in the reduction of nitrobenzene

Entry	Catalyst (mol%)	Solvent	Reductant	Temp (°C)	Time (h)	Yield (%)	Ref
1	NiNPs/DNA (2)	H_2O	$NaBH_4$	25	2	> 99	[This work]
2	Ni/Trisimidazolium (2)	THF	$NH_2NH_2.H_2O$	66	2	97	[51]
3	Fe_3O_4_Ni (8.85)	Glycerol	Glycerol	80	3	94	[39]
4	Ni/NGr (5)	THF/H_2O	H_2	110	8	98	[52]
5	Fe_3O_4@PAMAM/Ni(0)-PEG (2)	H_2O	$NaBH_4$	40	2	91	[48]
6	Ni-PAMAM PVA/SBA-15 (10)	H_2O	$NaBH_4$	25	0.16	98	[53]
7	NiNPs/PVP (20)	H_2O	$N_2H_4.H_2O$	25	1.25	99	[54]

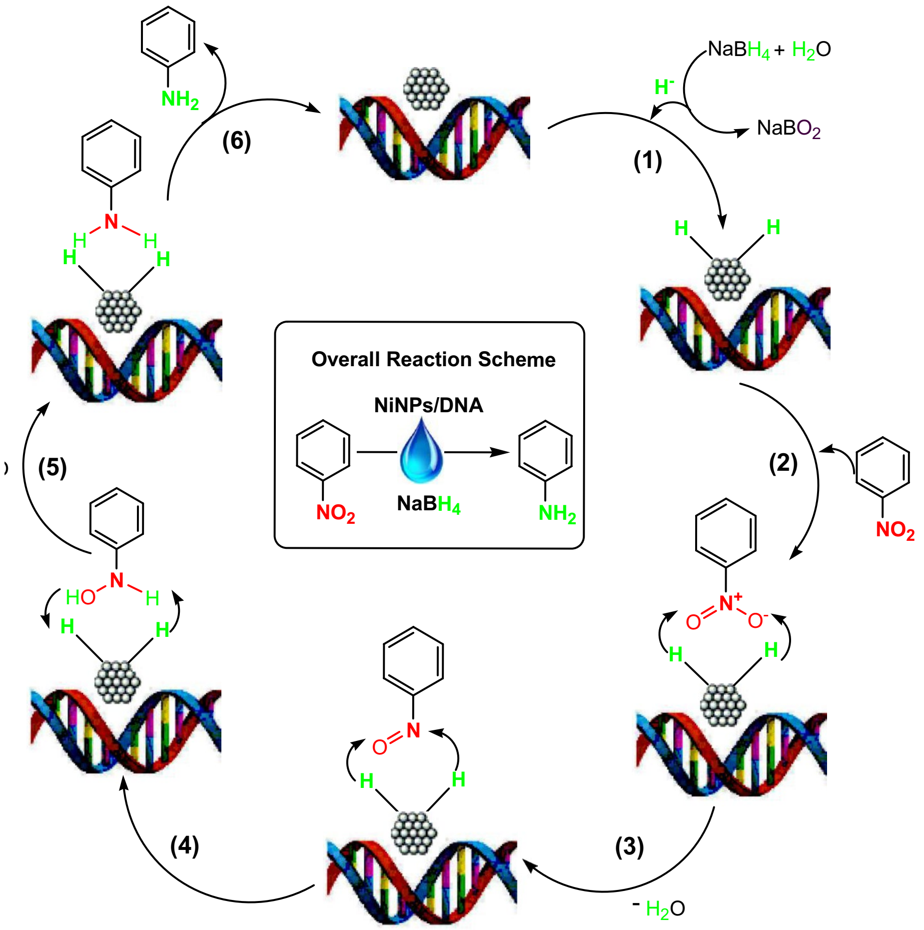


Fig. 9 Plausible reaction mechanism for the reduction of nitrobenzene catalyzed by NiNPs/DNA and $NaBH_4$

hydroxylamine is further reduced into aniline [step 5] and desorbed from the surface [step 6]. It is noteworthy that, during whole progress of the reduction of nitrobenzene, none of these intermediates were detected by TLC and only the final product (aniline) was detected. This can be deduced that these intermediates were converted into aniline very rapidly, hence it is difficult to follow them [13, 55].

4 Conclusions

In conclusion, we have reported the facile synthesis of DNA-based nickel nanoparticles and their application as a novel catalyst in the selective reduction of nitroarenes under mild and heterogeneous conditions. Diverse functionalized nitroarenes could be transformed to the corresponding aromatic amines in good to excellent yields. Notably, selective reduction of the nitro group was observed in the presence of other potentially reducible moieties including halogens, ketone, carboxylic acid, and nitrile. Moreover, the catalyst was very stable and could be simply recycled at least five times without considerable deactivation. The combination of several advantages exhibited by this nanocatalyst such as eco-friendly nature, facile synthesis, low cost, high catalytic performance, mild reaction condition, stability and convenient recovery, demonstrates that the catalyst should be considered as a viable alternative in reduction reactions on efficiency, environmental and economical grounds.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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