

# Magnetically recoverable catalytic Co–Co<sub>2</sub>B nanocomposites for the chemoselective reduction of aromatic nitro compounds†

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Magnetically recoverable and recyclable Co–Co<sub>2</sub>B nanocomposites are described for the catalytic and chemoselective reduction of nitroarenes using two different hydrogen sources, sodium borohydride and hydrazine hydrate. Both the systems display an interesting chemoselective reduction switch. The kinetics of reduction of nitroaromatics were studied for the first time and follow nitroreductase enzyme-like kinetics with exceedingly high  $K_{\text{cat}}$  ( $5.2 \times 10^4 \text{ s}^{-1}$ ) and  $K_{\text{cat}}/K_{\text{M}}$  ( $4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) values, reaching the state of catalytic perfection. The recyclability of the catalyst system was studied by magnetically recovering the nano composite catalyst.

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## Introduction

Aromatic amines are widely used as starting materials and intermediates for the manufacture of variety of chemicals such as dye stuffs, agrochemicals, pharmaceuticals, polymer surfactants, photographic rubber chemicals and chelating agents.<sup>1</sup> Reduction of the corresponding nitroaromatics is a common route followed for their preparation. A wide variety of methods have been documented and employed for the direct reduction of the nitro group to amine. Catalytic hydrogenation<sup>2</sup> employing molecular hydrogen and a metal catalyst is one of the most used methods in industrial processes where no side product except water is formed. The major drawback of catalytic hydrogenation is the difficulty in reducing selectively the nitro group in the presence of other functional groups. In such cases, stoichiometric reducing agents such as iron,<sup>3</sup> tin,<sup>4</sup> zinc in ammonium hydroxide,<sup>5</sup> or sodium hydrosulfite<sup>6</sup> are to be used. These processes produce large amounts of waste that is not environmentally sustainable in view of green chemistry perspectives. The successful approaches to address the problem of selectivity are the modification or tailoring<sup>7</sup> of the classical heterogeneous catalyst. The other drawback of catalytic hydrogenation is the price of the catalyst, the inflammability of the hydrogen gas, which needs to be used in excess under pressure and the high cost of the special

equipment. Nickel and cobalt boride catalysts also show good selectivity in the conversion of nitro to amine along with RANEY® Nickel and RANEY® cobalt.<sup>8</sup>

Metal nanoparticles, due to their quantum effect and high surface to volume ratio have generated tremendous interest in the field of organic synthesis, fuel cells and pollution treatment. Metal nanoparticles, due to their high Fermi potential can function as catalysts by lowering the reduction potential. Reduction of nitro to amine has been effected by metal nanoparticles<sup>9</sup> (Au, Ag, Pt, Pd, Ni and Cu) either directly or on a supported matrix. However, the recovery of noble metal nanoparticles for a stabilizer containing system is difficult. Use of magnetic nanoparticles has emerged as a promising alternative due to eliminating the requirements of either solvent swelling before or catalyst filtration after the reaction. However, most of the work relates to precious metals on magnetic materials, but, direct reduction using bio-relevant metals such as iron, copper and cobalt in its nanoform is rare. We were interested in using the bio-relevant metals in reduction studies without the use of flammable hydrogen gas. One of the ways was to look for an *in situ* hydrogen generating system. Recently, we have reported the facile hydrolysis of NaBH<sub>4</sub> for the controlled generation of hydrogen for PEMFC (proton energy membrane fuel cell) using Co–Co<sub>2</sub>B nanocomposites as the catalyst.<sup>10</sup> Herein, we report our findings on the novel reactivity of Co–Co<sub>2</sub>B nanocomposites for environmentally benign, cost effective and selective reduction of aromatic nitro compounds, oximes by sodium borohydride<sup>10</sup> and hydrazine hydrate<sup>11</sup> at ambient temperature and in greener solvents. The sodium borohydride system also reduces nitrile functionality while hydrazine hydrate does not, displaying an interesting chemoselective switch. The Co–Co<sub>2</sub>B nanocomposites follow nitroreductase enzyme-like

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kinetics in the reduction of nitroaromatics with exceedingly high  $K_{cat}$  ( $5.2 \times 10^4 \text{ s}^{-1}$ ) and  $K_{cat}/K_M$  ( $4.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ) values reaching the state of catalytic perfection. To our knowledge this is a first report of such novel kinetics of catalytic reduction of nitro compounds.

## Experimental section

### Chemicals and materials

Methanol,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , sodium borohydride and ammonium sulphate were purchased from Spectrochem, India. Ammonia-borane was synthesized from  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaBH}_4$  in 70–80% yields in 2–3 h of reaction time, using the procedure described by Ramachandran and Gagare.<sup>12a</sup> The purity of ammonia borane was confirmed by IR and  $^{11}\text{B}$  NMR spectroscopy (spectra shown in the ESI†).

### Characterization and sampling

$\text{Co-Co}_2\text{B}$  nanocomposites were prepared from anhydrous cobalt(II)chloride by reduction with ammonia borane in dried methanol without the use of any surfactants.<sup>10b,11</sup> These nanocomposites were characterized by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and surface area measurement.

### Synthesis of $\text{Co-Co}_2\text{B}$ nanocomposites

$\text{Co-Co}_2\text{B}$  nanocomposites were prepared by following the procedure given in the literature.<sup>13</sup> To a 3 mL methanol solution of anhydrous metal salt ( $\text{CoCl}_2$ , 20 mg) was added 1 mL of a methanol solution of ammonia borane (100 mg). Here, ammonia borane reduces  $\text{Co}^{2+}$  to  $\text{Co-Co}_2\text{B}$ . When  $\text{H}_2$  evolution ceased, black powder settled at the bottom of the test tube. The supernatant was syringed out and the nanopowder was washed several times with methanol. The as prepared nanocomposites were used, as such, for reduction studies.

### Sodium borohydride mediated reduction of nitroaromatics

To the freshly prepared and washed (with methanol) catalytic  $\text{Co-Co}_2\text{B}$  nanocomposites (prepared from 20 mg of anhydrous  $\text{CoCl}_2$ ), water and/or water/THF mixture (10 mL) was added. After about 5 min of magnetic stirring, the nitro compound (2 mmol) was added and then sodium borohydride (151 mg, 4 mmol) was charged in small portions. After completion of the reaction (monitored by tlc) the catalyst was magnetically separated. The remaining aqueous solution was then extracted with dichloromethane ( $3 \times 5 \text{ mL}$ ). The organic extract was concentrated under vacuo to provide the crude products. Further purification was effected by column chromatography using n-hexanes–ethyl acetate as an eluent. The pure compounds were then characterized by comparing (tlc, IR and  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR in some cases) with known compounds.

### Hydrazine mediated reduction of nitroaromatics

To a magnetically stirred mixture of the freshly prepared  $\text{Co-Co}_2\text{B}$  catalyst (prepared from 20 mg of anhydrous  $\text{CoCl}_2$ ) and the nitro compound (2 mmol) in methanol (2 mL), hydrazine hydrate (99%, 0.5 mL) was slowly added. After completion of

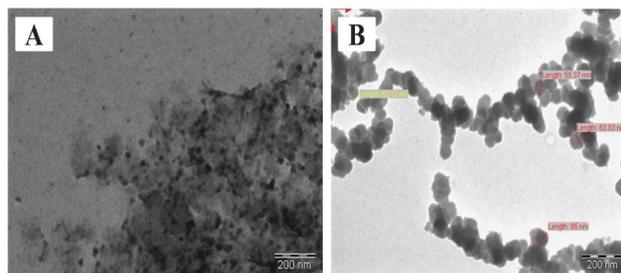


Fig. 1 TEM images of (A) the as prepared  $\text{Co-Co}_2\text{B}$  nanocomposites, and (B) the formation of assembled chain aggregates (scale bar shows 200 nm).

the reaction (monitored by tlc) the catalyst was magnetically separated. The catalyst was washed with methanol ( $2 \times 1 \text{ mL}$ ) and the combined washing on evaporation under reduced pressure gave the crude product. Further purification was effected by column chromatography using n-hexanes–ethyl acetate as an eluent.

### Enzyme-like kinetics experiment

The nitrobenzene solution of 5–25 mg per 5 mL of 50% water/THF solvent was added to the previously prepared catalyst (1 mg). Then, sodium borohydride (10 mg) was added to this mixture and it was rapidly stirred mechanically in a 20 mL vial. A fixed quantity aliquot of this reaction mixture was removed as soon as possible after the addition of sodium borohydride, which was diluted further to 1 mL and absorbance was noted to obtain 0<sup>th</sup> reading. Similarly, this step was repeated for every 1 min interval till 5 min (absorbance near to zero).

## Results and discussion

The TEM image reveals the size of the nanocomposite to be in the range of 20–30 nm (Fig. 1). As the prepared  $\text{Co-Co}_2\text{B}$  nanocomposites are amorphous in nature, we annealed these nanocomposites at 350 °C for 12 h in nitrogen atmosphere and then the XRD was recorded. The XRD shows the peaks corresponding to metallic Co and  $\text{Co}_2\text{B}$  forms (Fig. S4 in ESI†). The surface area of the as prepared  $\text{Co-Co}_2\text{B}$  nanocomposites material was found to be  $89 \text{ m}^2 \text{ g}^{-1}$ .

Table 1 Reduction of *p*-nitrotoluene in different solvent systems using sodium borohydride<sup>a</sup>

Entry	Solvent system	Time (min)	Yield (%)
1	MeOH	60	42
2	EtOH	90	30
3	80% MeOH– $\text{H}_2\text{O}$	60	48
4	80% EtOH– $\text{H}_2\text{O}$	80	34
5	50% Dioxane– $\text{H}_2\text{O}$	45	51
6	50% THF– $\text{H}_2\text{O}$	20	82

<sup>a</sup> All the reactions were carried out with *p*-nitrotoluene (2 mmol),  $\text{Co-Co}_2\text{B}$  nanocomposites prepared from  $\text{CoCl}_2$  (20 mg) and  $\text{NaBH}_4$  (4 mmol) in different solvent systems (10 mL) at ambient temperature (26 °C).

**Table 2** Reduction of the nitro compounds by sodium borohydride using Co–Co<sub>2</sub>B nanocomposites in aqueous medium and by hydrazine hydrate in methanol<sup>a</sup>

Entry	Substrate	Product	NaBH <sub>4</sub>		N <sub>2</sub> H <sub>4</sub>	
			Time min	Yield %	Time min	Yield %
1			15	64	10	94
2			10	68	12	95
3			15	69	20	92
4			20	82	25	88
5			15	87	25	94
6			10	78	10	Q
7			15	75	10	76
8			20	65	10	70
9			15	80	10	85
10			15	86	15	92
11			20	90	15	Q
12			45	75	45	72
13			45	45	45	50 <sup>b</sup>
14			20	81	12	88
15			20	85	—	0
16			20	91	—	0

**Table 2** (Continued)

Entry	Substrate	Product	NaBH <sub>4</sub>		N <sub>2</sub> H <sub>4</sub>	
			Time min	Yield %	Time min	Yield %
17		—	—	0	—	0
18		—	—	0	—	0
19		—	—	0	—	0

<sup>a</sup> All the reactions were carried out with **1** (2 mmol), Co–Co<sub>2</sub>B nanocomposites prepared from CoCl<sub>2</sub> (20 mg) and an appropriate reducing agent at ambient temperature (26 °C). Q = quantitative.

<sup>b</sup> Yield after chromatographic purification.

The experimental procedure for the reduction of nitro to amine using Co–Co<sub>2</sub>B nanocomposites is very simple. Initially, the reduction of nitrobenzene **1a** was examined in ethanol. We could observe the reduction taking place (silica TLC plates), however, the reduction could not go to completion even after prolonging the reaction or adding an excess of sodium borohydride. Next we examined methanol, methanol–water (1 : 1) and ethanol–water (4 : 1) systems without being able to get complete reduction. When the reaction was carried out in water, to our surprise complete reduction took place. Reactions in water as a medium are ones of paramount interest in the research community.

After the initial success, we evaluated the system for other nitroarene compounds. *o*-Nitrotoluene and *m*-nitrotoluene could be successfully reduced, however for solid *p*-nitrotoluene complete reduction could not be observed due to solubility problems. Hence, different aqueous systems were tried and THF–water (1 : 1) could give a maximum yield in a short time (entry 6, Table 1), so this protocol was used for the reduction of all solid nitro compounds (Table 2). A variety of substituted aromatic nitro compounds were reduced successfully to the corresponding amines. 4-Chloronitrobenzene **1e** and 4-iodonitrobenzene **1f** were easily reduced to the respective halo anilines **2e**, **2f** without any dehalogenation, which is often a problem when other procedures of reduction are employed. 4-Nitrobenzoic acid **1g** was made soluble in water by adding a small quantity of Na<sub>2</sub>CO<sub>3</sub> to yield a soluble salt of 4-nitrobenzoic acid, which was further reduced to 4-aminobenzoic acid **2g** without affecting the carboxylic acid group. The methyl ester in **1h** remained intact during the reduction process of the corresponding nitrobenzene. Similarly, nitrophenol **1i** could be reduced to aminophenol **2i** in a water system using sodium borohydride. Nitrophenols are the major organic pollutants found in waste waters from industrial and agricultural origins. Hence, our method of employing Co–Co<sub>2</sub>B nanocomposites in combination with sodium borohydride in a water system can

**Table 3** Comparison of the reduction of substituted nitro aromatics with other functionalities and possible reduction products

Entry	Substrate	Product	NaBH <sub>4</sub>			N <sub>2</sub> H <sub>4</sub>		
			P <sup>a</sup>	T <sup>b</sup>	C <sup>c</sup>	P <sup>a</sup>	T <sup>b</sup>	C <sup>c</sup>
1			2r	10	90	2p	5	95
						(2p : 2q = 92 : 8) <sup>d</sup>		
2			2t	12	93	2s	10	74
						(2s : 2t = 2 : 1) <sup>d</sup>		
3			2v	5	96	2w	25	90
4			<sup>e</sup>	—	—	2y	5	70

<sup>a</sup> Product. <sup>b</sup> Time. <sup>c</sup> Yield. <sup>d</sup> Ratio given is based on <sup>1</sup>H NMR spectra, <sup>e</sup> Not attempted.

be a potential alternative for waste water treatment. In the case of *m*-dinitrobenzene **1j**, direct formation of diamine **2j** was observed. The reduction of 1-(benzyloxy)-4-nitrobenzene **1k** quantitatively resulted in 4-(benzyloxy)aniline **2k** in just few minutes without any hydrogenolysis product. The nitro groups on the homoaromatic systems, such as in **1l** and **1m**, were also reduced successfully. Further, these reduction processes were also tried on functionalities such as oximes, nitriles and aliphatic nitro compounds. The oximes benzaldehyde **1n** and benzonitrile **1o** were smoothly reduced to benzyl amines **2n** and **2o**, respectively. Benzyl cyanide **1p** was reduced to homobenzyl amine **2p**. Methyl benzoate **1q**, (nitromethyl)benzene **1r** and 2-nitropropane **1s** remained unaffected. The reduction of 1-(allyloxy)-4-nitrobenzene **1t** yielded 4-propoxynitrobenzene **2r** along with starting material in a 9 : 1 ratio.

No selectivity was obtained for the reduction of *p*-nitroacetophenone **1u**, which resulted in 1-(4-aminophenyl)-ethanol **2t** as the only reduced product. As expected, 2-nitrobenzaldehyde **1v** was completely reduced to 2-(aminophenyl)methanol **2v** (Table 3).

Hydrazine hydrate is known to be used as a hydrogen source in metal catalysed reduction. We also investigated hydrazine hydrate with the Co-Co<sub>2</sub>B nanocomposites for the reduction of aromatic nitro compounds. For all the liquid aromatic nitro compounds the corresponding amines could be obtained easily in water. However, for a better work-up procedure methanol was used as the solvent and for methanol insoluble compounds a methanol-THF combination was used. For most of the nitro compounds the reduction pattern remained the same as that of the sodium borohydride system.

However, aromatic nitrile and other functional groups remained unaffected by the hydrazine hydrate system displaying an interesting chemoselective switch in few systems. In the case of the reduction of 1-(allyloxy)-4-nitrobenzene **1t**, 4-(allyloxy)aniline **2p** was obtained as a major product along with 4-propoxyaniline **2q** in a 98 : 2 ratio (based on  $^1\text{H NMR}$ ). *p*-Nitroacetophenone **1u** gave 1-(4-aminophenyl)ethanone **2s** and 4-(1-hydrazonoethyl)aniline **2u** in a 2 : 1 ratio. 2-Nitrobenzaldehyde **1v** gave a hydrazine adduct of 2-amino-benzaldehyde **2w**. Finally, a remarkable selectivity was achieved for the reduction of 4-nitrobenzonitrile **1w** with hydrazine that resulted in the reduction of only the nitro group giving product **2y**. The chemoselectivity switch displayed using both the systems is revealed in Table 3.

In the literature,<sup>14</sup> a  $\text{CoCl}_2/\text{NaBH}_4$  (2 : 10) mixture is reported for the reduction of aromatic nitro compounds. In order to check whether our protocol is similar to this reported method, we attempted reduction using a catalytic amount of  $\text{CoCl}_2$ . However, in none of the cases tried could we observe complete reduction of the nitro compounds, unless more than stoichiometric amount of  $\text{CoCl}_2$  was added. Also, the CoB formed *in situ*<sup>14b</sup> was found to be difficult to separate magnetically. We also separately prepared CoB and then used this for reduction studies. In both the cases, i.e.  $\text{NaBH}_4$  and  $\text{N}_2\text{H}_4$ , we were able to achieve reduction but again more than a stoichiometric amount of CoB was required followed by an acid–base workup procedure.

This indicates that the Co– $\text{Co}_2\text{B}$  nanocomposites are more robust and efficient in the reduction of nitro compounds than CoB. Also, the present procedure efficiently reduces aromatic nitro compounds without the use of any promoter. In the view of sustainable chemistry, a good catalyst can be recycled a number of times for a particular reaction. Excellent recyclability can be achieved by the use of magnetic nanoparticles, which have been successfully demonstrated as efficient catalysts and catalyst supports in a plethora of reactions.<sup>15</sup>

In the present case, Co– $\text{Co}_2\text{B}$  showed magnetic attractability (Fig. 2) and this enabled us to recycle the catalyst for several catalytic cycles in the reduction of nitrobenzene (Fig. 3). The leaching test carried out by AAS analysis confirmed that no remnant  $\text{Co}^{2+}$  ions could be detected in



Fig. 2 Magnetic attractability of the Co– $\text{Co}_2\text{B}$  nanocomposites toward the external magnet.

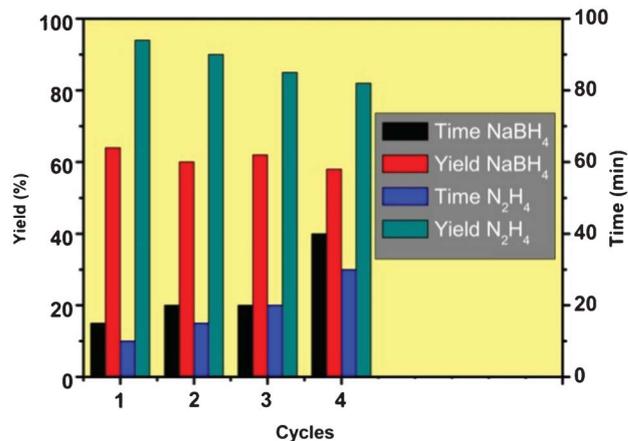


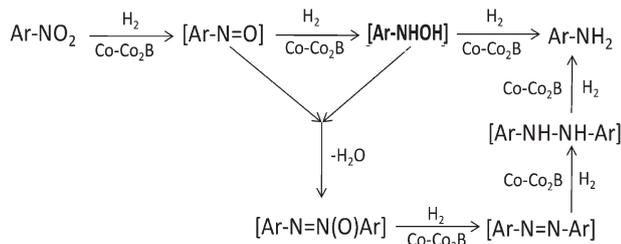
Fig. 3 Recyclability of the catalyst for the reduction of nitrobenzene using sodium borohydride and hydrazine mediated reactions.

the products after the magnetic separation. Interestingly, it was possible to isolate the azobenzene as an intermediate involved in the reduction process during the later cycles in the case of the hydrazine mediated reaction. It appears that the accumulation of azobenzene occurs when the catalyst is not active enough for further transformation (Fig. S11 and S19, ESI†). We also found the appearance of peaks in the LCMS accounting for the 1-hydroxy-1,2-di(naphthalen-1-yl)diazene, corresponding to the azoxy intermediate and naphthalen-1-amine (**2l**) during the reduction of 1-nitronaphthalene (**1l**) (Fig. S20, ESI†).

To shed some light on the mechanism of the reduction pathway, the reaction was also monitored by UV-vis spectroscopy. The spectrum recorded after an interval of a few minutes of reaction shows absorbance at 235 nm and 287 nm, typical of aniline, along with absorbance at 259 nm for nitrobenzene. We did not find any absorbance at 307 nm for the formation of nitrosobenzene (285 nm & 307 nm). We also could not confirm the formation of phenylhydroxylamine (233 nm)<sup>16</sup> as an intermediate due to the interference of the absorption of aniline in the same region (Fig. S21, ESI†). When we studied the reduction of nitrosobenzene over Co– $\text{Co}_2\text{B}$  nanocomposites using sodium borohydride we did observe the formation of azobenzene as an intermediate (324 nm) along with aniline, whereas in the case of the hydrazine mediated reduction, no azobenzene was detected.

The reduction probably takes place on the active surface of the Co– $\text{Co}_2\text{B}$  nanocomposites by the liberated hydrogen formed upon solvolysis of sodium borohydride<sup>12</sup> or by the oxidation of the hydrazine hydrate. A general mechanistic pathway is shown in Fig. 4. Nitrobenzene reduction over Co– $\text{Co}_2\text{B}$  nanocomposites was also followed by IR spectroscopy (Fig. S22, ESI†) but not much information could be revealed.

Interestingly, we observed an unusual formation of assembled chain aggregates of Co– $\text{Co}_2\text{B}$  nanocomposites with the growth of particles upon reductive usage (Fig. 1B). The reason for the formation of chain aggregates is unclear at this



**Fig. 4** The general mechanistic pathway of reduction of nitro compounds by direct and condensation route.

moment. A detailed investigation has to be addressed in this respect, which may stimulate and attract further interest in this area. The chain assembly of magnetic nanoparticles may be useful in the field of electronics and may find application in various nanoelectronic devices. Our nitro reduction procedures may be potentially considered for the preparation of assembled nano-structured chain aggregates in aqueous media through a chemical route.

Observing the remarkable activity of Co-Co<sub>2</sub>B nanocomposites in the reduction of aromatic nitro compounds, it was thought worthwhile to investigate the kinetics of the reduction reaction. The detailed kinetics of reduction of *p*-nitrophenol (PNP) in water was studied using sodium borohydride as the reductant. As the reduction was carried out in the presence of sodium borohydride (basic pH), the peak due to the absorbance of PNP at  $\lambda_{\max} = 317$  nm shifted bathochromically to  $\lambda_{\max} = 400$  nm, corresponding to the formation of the *p*-nitrophenolate ion. After a few minutes of addition of sodium borohydride to the aqueous reaction mixture containing the nanocatalyst and PNP, the peak at 400 nm disappeared and a new peak started appearing at  $\lambda_{\max} = 290$  nm, which is ascribed to the formation of the corresponding amino compound. In contrast to other reports on the reduction of nitro compounds using Pt, Pd and Ag nanocatalysts,<sup>17</sup> it is noteworthy to mention that the reduction reaction initiated instantaneously without any induction time. The decrease in the absorbance of *p*-nitrophenolate was monitored at different time intervals (Fig. 5A). This decrease in absorbance was found

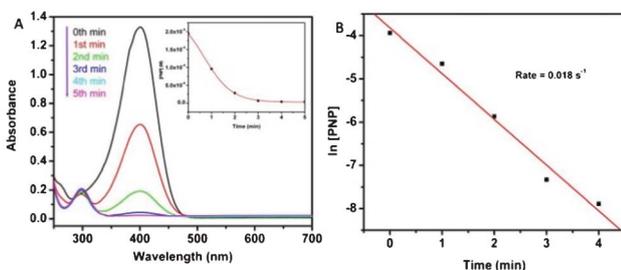
to be rapid, which is consistent with the high activity of the present nanocatalyst.

In comparison to the concentration of PNP and nanocatalyst, the concentration of sodium borohydride was high, and, therefore, it is assumed that the rate of the reaction is merely dependent on the concentration of PNP and follows first order kinetics (see eqn (1)).<sup>18a</sup>

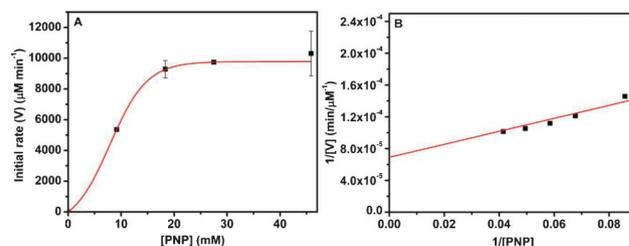
$$dC_{\text{PNP}}/dt = -K_{\text{app}}C_{\text{PNP}} \quad (1)$$

The apparent rate constant ( $K_{\text{app}}$ ) in this case was found to be  $0.018 \text{ s}^{-1}$ , which is calculated from the eqn (1) and slope of the plot of  $\ln[\text{PNP}]$  versus time (Fig. 5B). This  $K_{\text{app}}$  is significantly higher than those reported very recently for Au nanoparticles stabilized on nanocrystalline magnesium oxide, Ag nanodendrites and Ag nanoparticles.<sup>18</sup>

It should be mentioned that, for the first time, we observed the change in concentration of PNP has an effect on the initial rate ( $V$ ) of the reaction. Hence, we investigated the steady state kinetics of the reduction of PNP by sodium borohydride in the presence of a catalytic amount of Co-Co<sub>2</sub>B nanocomposites. At a relatively low concentration of PNP there is a linear increase in  $V$ , whereas at the higher concentration of PNP there is smaller increment in  $V$ , which remains unaffected upon a further increase in the concentration of PNP (Fig. 6A). A typical Michaelis-Menten curve is obtained, as is the case for any enzyme catalyzed reaction. Fig. 6B shows the Lineweaver-Burk plot or double reciprocal plot of the initial velocity versus PNP concentration. Various parameters were then calculated from this plot, which are tabulated in Table 4. The  $K_{\text{M}}$  value is high, indicating that there is sufficient binding affinity of the nanocatalyst towards the PNP substrate, and which is also a result of a surprisingly high  $K_{\text{cat}}$  value of  $5.2 \times 10^4 \text{ s}^{-1}$ . A large value of  $K_{\text{cat}}$  renders the rapid catalytic event. Further, the catalyst efficiency  $K_{\text{cat}}/K_{\text{M}}$ , which is also a measure of substrate specificity in this case, is very high, reaching the state of catalytic perfection, as is the case in enzyme fumarase with  $K_{\text{cat}}/K_{\text{M}} = 2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>19</sup> Fascinatingly, these data suggest that the Co-Co<sub>2</sub>B nanocomposites have nitroreductase enzyme-like activity, where nitroreductase is reported to reduce nitrobenzene using NADH or NADPH as coenzymes.<sup>16</sup>



**Fig. 5** (A) Decrease in absorbance of PNP during the reaction. The inset in A also shows the corresponding time variance decrease in the concentration of PNP. (B) Plot of  $\ln[\text{PNP}]$  versus time, corresponding to the plot A.



**Fig. 6** (A) Steady state kinetics of the reduction reaction. (B) Lineweaver-Burk plot corresponding to plot A.

**Table 4** Kinetic parameters of Co–Co<sub>2</sub>B nanocomposites in the reduction of the PNP substrate using sodium borohydride as a cosubstrate<sup>a</sup>

$E$ (M)	$K_M$ (mM)	$V_{max}$ ( $\mu\text{M min}^{-1}$ )	$K_{cat}$ ( $\text{s}^{-1}$ )	$K_{cat}/K_M$ ( $\text{M}^{-1} \text{s}^{-1}$ )
$2.3 \times 10^{-11}$	11.83	14 468	$5.2 \times 10^4$	$4.4 \times 10^6$

<sup>a</sup>  $[E]$  is the nanoparticle molar concentration of Co–Co<sub>2</sub>B nanocomposites,<sup>20</sup>  $K_M$  is the Michaelis constant,  $V_{max}$  is the maximal reaction velocity,  $K_{cat}$  is the catalytic constant, where  $K_{cat} = V_{max}/[E]$  and  $K_{cat}/K_M$  is the catalyst efficiency.

## Conclusion

In conclusion, we have developed a cost effective, efficient reduction procedure to convert an aromatic nitro group to amine using simple first row transition metal Co–Co<sub>2</sub>B nanocomposites. The reaction proceeds under mild and ambient conditions employing sodium borohydride in aqueous medium or employing hydrazine, without affecting other functionalities such as acid, halo, hydroxyl, ester, and benzyloxy groups. The catalyst is also useful in the reduction of an oxime group. In addition to the reduction of the aromatic nitro group, the sodium borohydride system also reduces nitrile functionality, which is not observed in the hydrazine system, leading to chemoselectivity. Another interesting chemoselectivity was observed during the reduction studies of 4-allyloxy nitrobenzene. The sodium borohydride system resulted in the selective reduction of the double bond, while the hydrazine system selectively reduced the nitro group witnessing a chemoselective switch of the hydrogen source for the present reduction protocol. The rapid reduction of nitrophenol using aqueous sodium borohydride may find application in developing a waste water treatment process to get rid of nitrophenols from industrial and agricultural waste. The added feature of the present method is the ease of separation of the nanocatalyst after use by an external magnet and the recyclability of the catalyst for several cycles without apparent leaching. We have also shown for the first time that the nanocatalyst follows nitroreductase enzyme-like kinetics with a very high  $K_{cat}/K_M$  value, approaching the state of catalytic perfection.

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