

Cu nanoparticles: a highly efficient non-noble metal catalyst for rapid reduction of nitro compounds to amines with NaBH_4 in water

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Abstract The purely aqueous-phase reduction of a wide range of nitro compounds to the corresponding amines has been carried out with NaBH_4 in the presence of inexpensive Cu nanoparticles as catalyst. The reactions were taken place in water (80 °C) within 4–15 min to give amines in high to excellent yields.

Keywords Amines · Cu NPs · NaBH_4 · Nitro compounds · Reduction

Introduction

Structurally diverse arylamines constitute major building blocks, and they are used extensively as key intermediates for the preparation of pharmaceuticals, drugs, dyes, pigments, and agrochemicals [1–4]. Generally, reduction of nitro compounds represents a straightforward and versatile method for the preparation of amines [5–8]. The literature review shows that though many synthetic routes have been reported for such achievement, however, the development of simple procedures, which utilize inexpensive and more efficient catalysts, is the subject of interest and still is demanded.

Recently, much attention has been devoted to the metal nanoparticles catalysts that exhibited high catalytic activities because of their extremely small dimensions and huge special surfaces. In this context, some procedures involving hydrogenation of nitrobenzenes into arylamines catalyzed

by Pt nanoparticles supported on mesoporus/nanofibers carbon [9–11], polymer-stabilized Ru colloidal catalysts [12], Au nanoparticles on TiO_2 [13–15], and Rh supported on highly porous ionic copolymer [16] have been reported. In spite of high catalytic activity and selectivity achieved by noble metal catalysts, their high cost is a major limitation. Therefore, substitution of inexpensive non-noble metals catalysts with the precious noble metals, such as Pt, Pd, and so on, is highly desirable.

Copper is a cheaper alternative to various noble metals with a range of potential applications in the field of nanoscience and nanotechnology [17, 18]. It is an important industrial material due to its novel physiochemical properties. In the field of electronics, Cu is the most common metal, since it has excellent electrical conductivity as well as low cost [19]. In recent years, Cu nanoparticles (Cu NPs) have attracted considerable attention in various catalytic reactions, such as low-temperature oxidation of carbon monoxide [20], oxidation of alcohols [21], C–C and C–heteroatom bond formations [22], three-component coupling reactions [23], and hydrogenation of azides [24].

Herein, we wish to report a new application for inexpensive non-noble metal Cu NPs for rapid and green reduction of nitro compounds to amines using NaBH_4 in water as an easily available and eco-friendly safe solvent (Scheme 1).

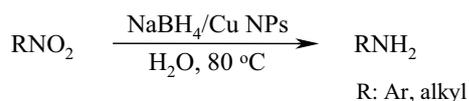
Results and discussion

Synthesis and characterizations of Cu NPs

Copper nanoparticles were prepared through the reduction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with NaBH_4 under N_2 atmosphere. Characterization of Cu NPs was then carried out by X-ray diffraction (Fig. 1) and FT-IR spectroscopy (Fig. 2) followed by a

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Scheme 1 Reduction of nitro compounds with $\text{NaBH}_4/\text{Cu NPs}$

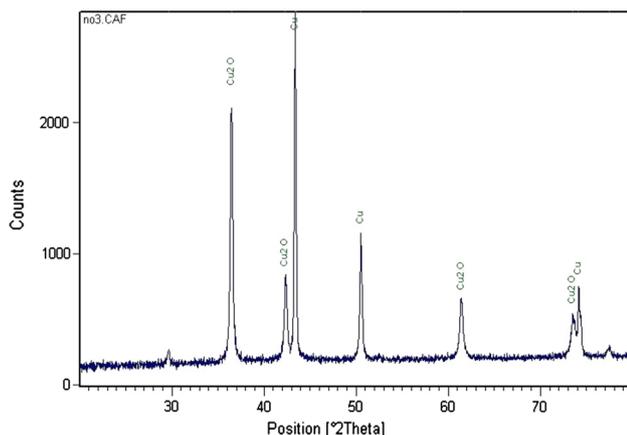
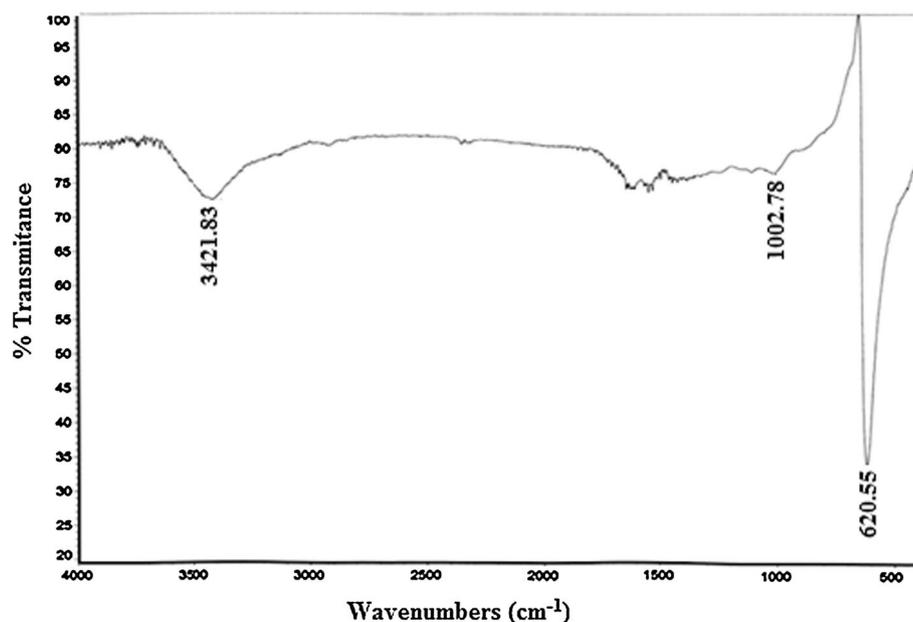


Fig. 1 XRD spectrum of Cu NPs

comparison with authentic ones [25–27]. In XRD spectrum, the diffraction peaks at $2\theta = 43.31$ and 50.51 are attributed to metallic Cu. However, additional peaks belonged to Cu_2O are also observable in the spectrum. Contamination of Cu NPs with Cu_2O is a common and is not controllable during the collection of NPs. This is due to the oxidation of metallic Cu with air oxygen and is prepared on the surface of Cu NPs. FT-IR spectrum of the prepared Cu NPs is also in good agreement with the reported data in the literature.

Fig. 2 FT-IR spectrum of Cu NPs



The morphology and size distribution of the prepared Cu NPs were investigated by scanning electron microscopy (SEM) (Fig. 3). The left image shows that the surface of NPs has too much porosity leading to high surface area. The SEM analysis also exhibited that the size of Cu NPs varies from 42 to 47 nm (right image).

Reduction of nitro compounds with $\text{NaBH}_4/\text{Cu NPs}$

Nowadays in organic synthesis, increasing attention is being focused on green chemistry using environmentally benign reagents and conditions, specially using aqueous solvents, which often lead to clean and eco-friendly protocols through the simplified workups and offsetting the costs. Aprotic dipolar solvents with high boiling points are expensive and are difficult to remove from the reaction mixtures. Thus, using water as an ecologically safe solvent is practically more concerned.

Aligned to the outlined strategies and to investigate the catalytic activity of Cu NPs, we performed the reduction of nitrobenzene as a model compound with NaBH_4 in the presence and absence of copper nanoparticles under different reaction conditions. In addition, H_2O was used as an easily available and eco-friendly solvent (Table 1, entries 1–7).

Observation of the results showed that the reduction of nitrobenzene with NaBH_4 or Cu NPs alone did not any efficient (entries 1 and 2). However, the influence of Cu NPs on reducing capability of NaBH_4 was noteworthy (entry 3). Further examinations resulted that using the molar equivalents of 2:0.15 for $\text{NaBH}_4/\text{Cu NPs}$ under oil bath conditions (80°C) performed the reduction of nitrobenzene with 95 % conversion (entry 5). We also found that the addition type

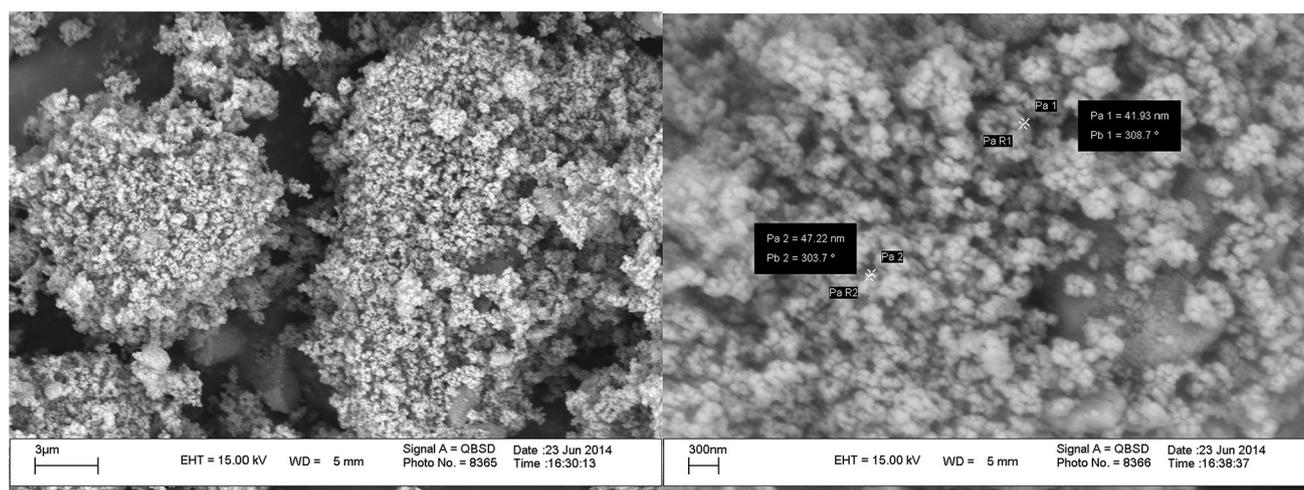


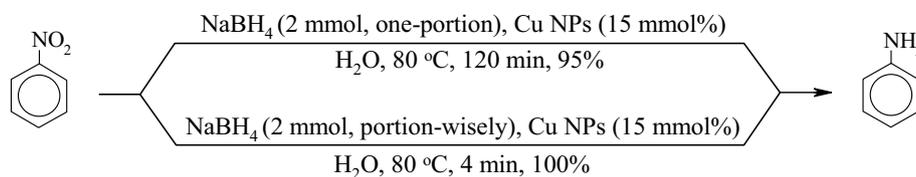
Fig. 3 SEM images of Cu NPs

Table 1 Optimization experiments for reduction of nitrobenzene to aniline with $\text{NaBH}_4/\text{Cu NPs}$ system

Entry	NaBH_4 (mmol)	Cu (mmol)	Solvent (2 mL)	Condition	Time (min)	Conversion (%)
1	2	–	H_2O	Oil bath (80 °C)	120	0
2	–	0.15	H_2O	Oil bath (80 °C)	120	5
3	2	0.15	H_2O	rt	120	45
4	2	0.15	H_2O	Oil bath (60 °C)	120	75
5	2	0.15	H_2O	Oil bath (80 °C)	120	95
6	2	0.1	H_2O	Oil bath (80 °C)	120	85
7 ^a	2	0.15	H_2O	Oil bath (80 °C)	4	100

^a NaBH_4 was added portion wisely

Scheme 2 Reduction of nitrobenzene with $\text{NaBH}_4/\text{Cu NPs}$



of NaBH_4 to the reaction mixture in one-portion or portion wisely extremely influenced the rate of reduction. It means that when 2 molar equivalents of NaBH_4 in one-portion were added to the reaction mixture, we got the maximum efficiency of 95 % within 120 min. In contrast, the portion wisely addition of NaBH_4 (2 molar equivalents) dramatically completed the reaction within 4 min (Table 1, entry 7; Scheme 2). Therefore, the conditions mentioned in entry 7 were selected as optimum reaction conditions.

The scope and generality of this synthetic protocol was then studied through the reduction of structurally different aromatic nitro compounds under the optimized conditions (Table 2). The summarized results in Table 2 show that the reduction of nitroarenes having electron-releasing or withdrawing functionalities was carried out successfully using 2

molar equivalents of NaBH_4 and 15 mmol % Cu NPs within 4–15 min (H_2O , 80 °C) (entries 1–12). Molecules with the complexity of nitro and carbonyl groups did not show any selectivity, and both of functional groups were reduced with the same reactivity. This fact was shown with the reduction of nitrobenzaldehydes and nitroacetophenones to the corresponding amino alcohols (entries 9–14). It is notable that the complete reduction of nitroacetophenones required higher molar equivalents of NaBH_4 and Cu NPs. Further examinations resulted that the present method was also efficient for the reduction of dinitroarenes to the corresponding phenylenediamines using 3:0.2 molar equivalents of $\text{NaBH}_4/\text{Cu NPs}$ in H_2O at 80 °C (entries 15, 16). We also found that the reduction of heterocyclic nitro compounds, such as 3-nitropyridine and 2-nitrothiophene with

Table 2 Reduction of nitro compounds with NaBH₄/Cu NPs system

Entry	Substrate	Product	Molar ratio Subs./NaBH ₄ /Cu	Time (min)	Yield (%) ^a
1			1:2:0.15	4	91
2			1:2:0.15	5	93
3			1:2:0.15	4	93
4			1:2:0.15	4	91
5			1:2:0.15	5	96
6			1:2:0.15	4	95
7			1:2:0.15	5	93
8			1:2:0.2	12	93
9			1:2:0.15	5	97
10			1:2:0.15	4	92
11			1:2:0.15	15	91
12			1:2:0.15	5	92
13			1:2.5:0.2	8	94
14			1:2.5:0.2	15	92
15			1:3:0.2	12	95
16			1:3:0.2	10	93
17			1:2:0.15	10	92
18			1:2:0.15	8	90
19	1-Nitrohexane	1-Hexylamine	1:2:0.15	5	89
20	2-Nitroheptane	2-Aminoheptane	1:2:0.15	7	91

All reactions were carried out in H₂O (2 mL, 80 °C)^a Yields refer to isolated pure products

NaBH₄/Cu NPs system (2:0.15), was carried out perfectly within 8–10 min to afford the corresponding heteroamines in 90–92 % yields (entries 17, 18). Reducing capability of NaBH₄/Cu NPs system toward aliphatic nitro compounds was also studied by the reduction of 1-nitrohexane and 2-nitroheptane at the optimized reaction conditions. The results showed that as aromatic and heterocyclic nitro compounds, this protocol was also efficient, and the corresponding aliphatic amines were obtained efficiently within 5–7 min (entries 19, 20).

Conclusions

In summary, we have shown that NaBH₄ in the presence of Cu NPs efficiently reduces verities of nitro compounds to the corresponding amines. Reduction reactions were carried out in water with the molar equivalents of 2–3 for NaBH₄ and 0.15–0.2 for Cu NPs under oil bath conditions (80 °C). The product amines were obtained in high to excellent yields within 4–15 min. High yields, easy work-up procedure, the cheapness and availability of the reagents, ability of aromatic, heterocyclic and aliphatic nitro compounds toward reduction, and the benefits of using water as a green solvent are the significant advantages that make this protocol a synthetically useful addition to the present methodologies.

Experimental

General

All reagents and substrates were purchased from commercial sources with high quality, and they were used without further purification. FT-IR and ¹H, ¹³C NMR spectra were recorded on Thermo Nicolet Nexus 670 and Bruker Avance spectrometers (300 MHz). The products are known, and they were characterized by their ¹H, ¹³C NMR, and FT-IR spectra followed by comparison with authentic data [28]. TLC was applied for the purity determination of substrates, products, and the reaction monitoring over silica gel 60 F₂₅₄ aluminum sheet.

Preparation of Cu NPs [25, 26]

In a two-neck round-bottom flask (250 mL) equipped with a magnetic stirrer and a dropping funnel, NaBH₄ (0.151 g, 4 mmol) was added. The flask was then purged with N₂ and continued to stand under its atmosphere. The dropping funnel was charged with aqueous solution of CuCl₂·2H₂O (0.01 M, 200 mL) and was added to the flask within 45 s. By the reaction of NaBH₄ with light green CuCl₂·2H₂O solution, a yellow–brown and then a brown–black

gelatinous precipitate together of gas evolution was prepared. The reaction was completed within 2 min. The resulted precipitate was filtered and washed with distilled water (3 × 20 mL) and acetone (20 mL) followed by drying in vacuo to afford Cu NPs in 89 % yield (size of NPs: 42–47 nm).

A typical procedure for reduction of nitrobenzene to aniline with NaBH₄/Cu NPs system

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a mixture of nitrobenzene (0.123 g, 1 mmol) and H₂O (2 mL) was prepared. Cu NPs (0.0095 g, 15 mmol %) was then added, and the mixture was stirred for 3 min at 80 °C. Afterward, NaBH₄ (0.076 g, 2 mmol) was added portion wisely (two portions) with the interval of 2 min, and the resulting mixture was continued to stirring at 80 °C. TLC monitored the progress of the reaction (*n*-hexane/EtOAc: 5/2). After completion of the reaction, Cu NPs was separated by filtration, and the mixture was extracted with EtOAc (2 × 5 mL). The organic layer was then dried over anhydrous Na₂SO₄. Evaporation of the solvent affords the pure liquid aniline in 91 % yield (0.085 g, Table 2, entry 1).

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