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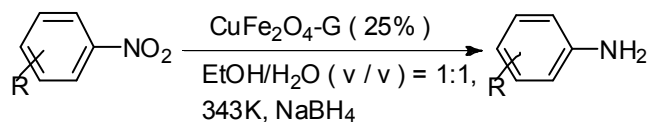
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Graphical Abstract:

Copper ferrite-graphene hybrid: a highly efficient magnetic catalyst for chemoselective reduction of nitroarenes

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In this paper, an inexpensive and magnetically recyclable copper ferrite-graphene hybrid nanocomposite was synthesized and used as an efficient catalyst for the reduction of nitroarenes for the first time.



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Copper ferrite-graphene hybrid: a highly efficient magnetic catalyst for chemoselective reduction of nitroarenes

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In this paper, a superparamagnetic copper ferrite-graphene hybrid nanocomposite ($\text{CuFe}_2\text{O}_4\text{-G}$) was synthesized by a hydrothermal method and used as an efficient catalyst for the reduction of nitroarenes for the first time. The method has been applied to a broad range of compounds with different properties. The $\text{CuFe}_2\text{O}_4\text{-G}$ catalyst can be readily recovered and reused at least five consecutive cycles without significant loss of its catalytic activity.

Introduction

Development of new catalytic transformations with easy separation and recyclability of the catalyst is an essential task in chemical synthesis. Aromatic amines are important starting materials and intermediates for the manufacture of a great variety of chemicals such as dyes, pesticides, herbicides, and agrochemicals.¹⁻³ They are generally synthesized by the chemical reduction of nitroarenes. Iron-compound,⁴ mixed metal compounds,⁵ transition metals (Cu, Ni)⁶ and noble metals (Pt, Pd, Au)⁷⁻⁹ are commonly employed as the catalyst for the reduction reaction. However, some of the methods employed have drawbacks, for example using expensive reagents, prolonged reaction time, using toxic and volatile solvent, unsatisfactory yield, etc. Hence, the development of an inexpensive, facile and effective method for the synthesis of aromatic amines is of high demand.

The copper ferrite, CuFe_2O_4 with a spinel structure, is one of the most important ferrites in powder form, has been widely applied in sensors, electronics and catalysts owing to its advantages of environmentally compatible, moisture insensitive, high dispersion, high reactivity and easy separation at an external magnet in recent years. Amini et al.¹⁰ investigated the low temperature CO oxidation over mesoporous CuFe_2O_4 nanopowders synthesized by a novel sol-gel method. Parella et al.¹¹ explored the catalytic application of CuFe_2O_4 nanoparticles for the Friedel-Crafts acylation. Feng et al.⁶ investigated the catalytic activity of CuFe_2O_4 nanoparticles for the reduction of 4-nitrophenol to 4-aminophenol with excess amount of NaBH_4 .

Graphene(G), discovered in 2004 by Geim and co-workers,¹² has enjoyed tremendous research interest in a wide range of fields over the past decades. Graphene-related nanomaterials exhibit a great application potential in catalysis¹³ thanks to their large specific surface area, easy modification, remarkable electrical conductivity, excellent adsorptivity, ultrathin thickness, superior structural flexibility, and high chemical and thermal stability. To

date, various kinds of catalysts, including TiO_2 ,¹⁴ SnO_2 ,¹⁵ ZnO ,¹⁶ Pt,^{17,18} Pt-Ru,¹⁹ Pt-Pd,²⁰ Pd²¹ and so on, have been supported on graphene-based templates for catalyzing different chemical transformations, energy conversion and photocatalytic reactions. Recently, superparamagnetic graphene- Fe_3O_4 nanocomposite (G- Fe_3O_4) was fabricated and used as an efficient catalyst for the reduction of nitroarenes with hydrazine hydrate as reductant, which is a toxic reagent.²² Copper ferrite-graphene hybrid was developed as an effective photocatalyst for the degradation of methylene blue under visible light irradiation, which also showed excellent electrochemical behaviors for use as the anode in lithium-ion batteries.²³ However, to our best knowledge, there has been no report yet about the use of copper ferrite-graphene ($\text{CuFe}_2\text{O}_4\text{-G}$) magnetic nanocomposite as catalyst for organic synthesis.

In the present work, the catalytic activity of magnetic $\text{CuFe}_2\text{O}_4\text{-G}$ nanocomposite for the chemoselective reduction of nitroarenes was investigated using sodium borohydride as a hydrogen donor. The results demonstrate that the combination of CuFe_2O_4 with graphene results in a dramatic enhancement of the catalytic activity of CuFe_2O_4 .

Results and discussions

Material characterizations

X-ray powder diffraction analysis was used to identify the crystal structure of the $\text{CuFe}_2\text{O}_4\text{-G}$ (0.25) and CuFe_2O_4 . As shown in Fig. 1, except some Cu impurity peaks at 43.0° and 50.6° , all peaks were indexed to be CuFe_2O_4 (JCPDS 77-0010), in detail, the peaks at 30.5° , 35.2° , 57.0° , 62.8° and 74.1° are attributed to (220), (311), (511), (440) and (533) crystal planes of CuFe_2O_4 . While no typical diffraction peak of reduced graphene oxide was observed. It is speculated that the GO in the $\text{CuFe}_2\text{O}_4\text{-G}$ (0.25) heteroarchitecture was fully exfoliated due to the crystal growth of CuFe_2O_4 nanoparticles between the interlayer of GO sheets, which result in the low diffraction intensity of GO. The

formation of copper was identified based on the reported data (JCPDS 85-1326) at 43.0° and 50.6° . The reason of existence of metallic copper was that some of Cu^{2+} was reduced to copper metal in the formation process of CuFe_2O_4 due to the strong reducing capability of ethylene glycol ⁶.

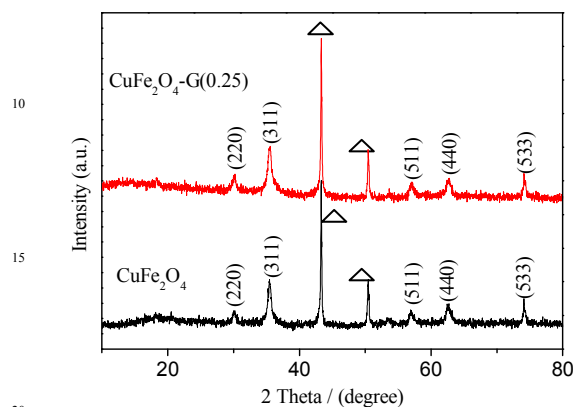


Fig. 1 XRD pattern of as-prepared $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$ and CuFe_2O_4 . Symbols (Δ) represent peaks of Cu.

Fig. 2 shows the SEM image of $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$. It can be seen that $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$ were composed of quasi-sphere particle with particle sizes of about 100 nm.

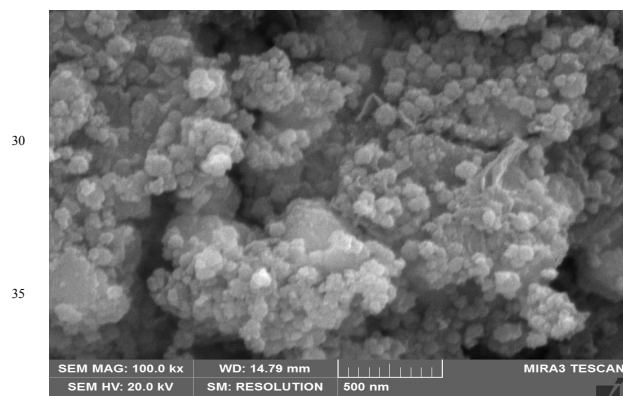


Fig. 2. SEM image of $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$.

The FTIR spectra were recorded to further testify the hybrid material. As shown in Fig. 3, the spectrum of GO is in good agreement with previous work.²⁴ The broad, intense band at 3250 cm^{-1} is assigned to the stretching of O-H. The peak at 1728 cm^{-1} corresponds to the stretching of the -C=O and -COOH groups on GO sheets. The peak at 1616 cm^{-1} (aromatic C=C) can be ascribed to the skeletal vibrations of unoxidized graphene domains. The C-O bond is associated with the band at 1047 cm^{-1} . From the FTIR spectrum of GO and $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$ samples, it can be clearly seen that the graphene oxide exhibits an obvious characteristic absorption peak at about 1728 cm^{-1} corresponds to the stretching of the -C=O and -COOH groups. However, it is can not be seen from the FTIR spectrum of $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$. It turned out that graphene oxide was reduced to graphene due to the strong reducing capability of ethylene glycol. From the FTIR spectrum of CuFe_2O_4 and $\text{CuFe}_2\text{O}_4\text{-G}$

(0.25) samples, the spectra show two main absorption corresponding to the stretching vibration of the tetrahedral and octahedral sites around 586 and 400 cm^{-1} , respectively. The observed values illustrate that the frequency bands appearing at 586 and 400 cm^{-1} are responsible for the formation of CuFe_2O_4 . The absorption band at 1596 cm^{-1} on spectrum referred to the vibration of remainder H_2O in the sample⁶.

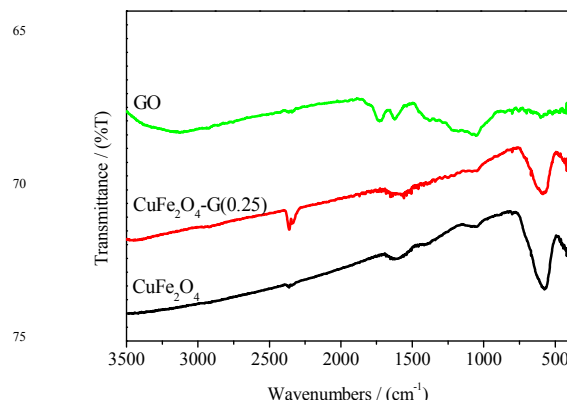


Fig. 3. FT-IR spectra of the GO, $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$ and CuFe_2O_4 .

Catalytic activity $\text{CuFe}_2\text{O}_4\text{-G}$

To obtain the optimal reaction conditions, the effect of type of catalyst and catalyst dosage on the reduction of *p*-nitrophenol were initially investigated (Table 1). As shown in Table 1, no product was obtained in the absence of the catalyst (Table 1, entry 1), indicating that the catalyst was necessary for the reaction. Only low yields of the product were obtained with either graphene, Fe_3O_4 or $\text{Fe}_3\text{O}_4\text{-graphene}$ (with 25 wt% graphene) as catalyst (Table 1, entries 2, 3, 4). While CuFe_2O_4 could catalyze the reduction of *p*-nitrophenol efficiently, 99% yield was obtained when the reaction was performed at 343 K for 16 min (Table 1, entry 5). The combination of CuFe_2O_4 with appropriate amount of graphene results in a dramatic enhancement of the catalytic activity of CuFe_2O_4 . The reaction time required to complete the reaction decreased with increasing the loading amount of graphene in $\text{CuFe}_2\text{O}_4\text{-G}$ until 25 wt% (Table 1, entries 7, 8, 9). Compare with CuFe_2O_4 catalyst, the reaction time could lower down to 9 min from 16 min with $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$ as the catalyst, which can be attributed to its unique heteroarchitecture, which provides the remarkable synergistic effect between the CuFe_2O_4 and the graphene sheets. The presence of graphene could enhance the adsorption of reactant molecules onto the catalytic sites of the $\text{CuFe}_2\text{O}_4\text{-G}$ through the $\pi\text{-}\pi$ stacking and/or electrostatic interaction. However, the catalytic activity of $\text{CuFe}_2\text{O}_4\text{-G}$ decreased when the content of graphene was increased to 35% (Table 1, entry 6). The large amount of graphene in $\text{CuFe}_2\text{O}_4\text{-G}$ might decrease the number of the catalytic sites, which resulted in the decreasing of the catalytic activity of $\text{CuFe}_2\text{O}_4\text{-G}(0.35)$. The above results also indicating that there is the most synergistic effect between CuFe_2O_4 and the graphene sheets. The reaction time could be further reduced with increasing the dosage of $\text{CuFe}_2\text{O}_4\text{-G}(0.25)$ (Table 1, entries 11,12). But a longer reaction time was required to complete the reaction with decreasing the reaction temperature from 343 K to 333 K (Table 1, entry 13).

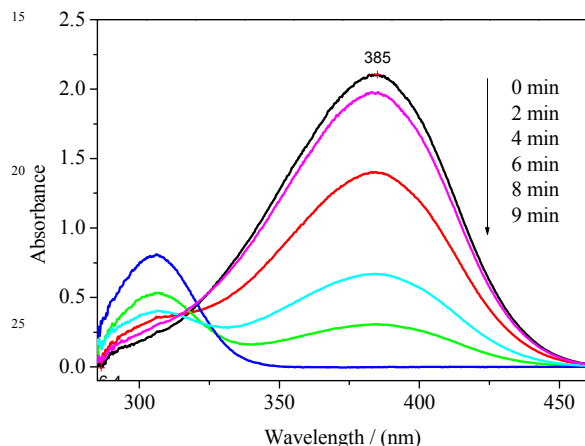
Table 1 Screening and control experiments for hydrogenation of *p*-nitrophenol.

$\text{HO}-\text{C}_6\text{H}_4-\text{NO}_2 \xrightarrow[\text{EtOH/H}_2\text{O (v/v) = 1:1, 343K, NaBH}_4]{\text{Catalyst}} \text{HO}-\text{C}_6\text{H}_4-\text{NH}_2$				
Entry	Catalyst	Catalyst (mg)	Time (min)	Yield (%)
1	-	20	500	-
2	G	20	500	trace
3	Fe ₃ O ₄	20	60	26
4	Fe ₃ O ₄ -G(0.25)	20	60	39
5	CuFe ₂ O ₄	20	16	99
6	CuFe ₂ O ₄ -G(0.35)	20	35	99
7	CuFe ₂ O ₄ -G(0.25)	20	9	99
8	CuFe ₂ O ₄ -G(0.15)	20	12	99
9	CuFe ₂ O ₄ -G(0.1)	20	14	99
10	CuFe ₂ O ₄ -G(0.25)	10	12	99
11	CuFe ₂ O ₄ -G(0.25)	30	4	99
12	CuFe ₂ O ₄ -G(0.25)	50	3	99
13	CuFe ₂ O ₄ -G(0.25)	20	40 ^a	99

Reaction condition: *p*-nitrophenol (1 mmol), solvent (10 mL, EtOH: water = 1:1), NaBH₄ (5 mmol), temperature (343 K).

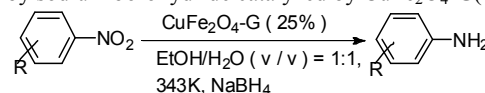
^a Temperature (333 K).

Fig. 4 showed the UV-vis absorption spectra of the reduction of *p*-nitroaniline by NaBH₄ at various reaction times in the presence of CuFe₂O₄-G (0.25). The observed peak at 385 nm for the *p*-nitroaniline shows a gradual decrease in intensity with time and a new peak appeared at 295 nm indicating the formation of *p*-phenylene diamine. The results indicated that CuFe₂O₄-G (0.25) exhibited considerably high activity for the reduction of nitroarenes with sodium borohydride as the hydrogen donor.

**Fig. 4.** Successive UV-vis absorption spectra of the reduction

of *p*-nitroaniline with NaBH₄ in the presence of CuFe₂O₄-G (0.25).

To show the generality of this model reaction, the reduction of a series of nitro aromatics was studied under the optimized reaction conditions. As shown in Table 2, aromatic nitro compounds containing various electrons donating (Table 2, entries 1-6) or electron-withdrawing groups (Table 2, entries 8) were converted to the corresponding amino aromatics in good yields and all the reactions could proceed smoothly. Moreover, the reduction was also successfully carried out on bulkier molecule such as 1- nitronaphthalene with high yield (Table 2, entry 7).

Table 2 Chemoselective reduction of nitro compounds into amines by sodium borohydride catalyzed by CuFe₂O₄-G(25%).

Entry	Carbonyl Compound	Product	NaBH ₄ (mmol)	Time (min)	Yield ^b (%)
1			5	9	99
2			5	4	99
3			5	10	96
4			5	30	95
5			5	45	92
6			5	10	99
7			5	20	91
8			6	30	93
9			5	30	92

Reaction condition: nitro compounds (1 mmol), solvent (10 mL, EtOH: water = 1:1), catalyst (20 mg), temperature (343 K).

The reusability and recycling of CuFe₂O₄-G(0.25) was also investigated. The catalyst was separated from the reaction mixture using an external magnet, washed with ethanol for three times, dried at 60°C in a vacuum oven for 2 h and reused in another reaction. The catalytic activity of CuFe₂O₄-G(0.25) did not show any significant decrease even after five runs.

Experimental

Materials and instrumentation

Ferric trichloride hexahydrate (FeCl₃·6H₂O), copper sulfate

pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium borohydride (NaBH_4), glycol, sodium hydroxide (NaOH), ethanol were all obtained from Chengxin Chemical Reagents Company (Baoding, China). Nitroaromatics were purchased from Aladdin Reagent Limited

Company. The water used throughout the work was double-distilled on a SZ-93 automatic double-distiller from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China). IR spectra (cm^{-1}) were measured with a WQF-510 spectrometer. UV-vis absorption spectra were measured with a UV-vis spectrometer (UV-3600, Shimadzu). The size and morphology of the catalyst were observed by scanning electron microscopy (SEM) using a Hitachi S4800 field emission electron microscope operated at 30 kV. The XRD patterns of the samples were recorded with a Rigaku D/max 2500 X-ray diffractometer using Cu $K\alpha$ radiation (40 kV, 150 mA) in the range $2\theta = 10^\circ$ – 80° . ^1H NMR (400 MHz) spectra were obtained with a Bruker AVANCE 400 spectrometer ($\text{DMSO}-d_6$) using TMS as an internal standard.

Synthesis of CuFe_2O_4 -graphene heteroarchitecture

Graphite oxide (GO) was prepared according to the procedure reported by us.^{25,26} CuFe_2O_4 -graphene heteroarchitectures with differing graphene content (10, 15, 25, 35 wt%) were synthesized by a modified hydrothermal method reported in the literature.

A typical experiment procedure for the synthesis of CuFe_2O_4 -graphene heteroarchitecture with 25 wt % graphene content is as follows: 40 mg of GO was dispersed into 30 mL of ethylene glycol with sonication for 12 h. 0.1675 g (0.67 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.3618 g (1.34 mmol) of FeCl_3 were added to 10 mL of ethylene glycol and sonicated for 1 h. The above two solutions were then mixed together and stirred for 30 min. After that, the mixture was adjusted to pH of 8 with 6 mol L^{-1} NaOH aqueous solution and stirred for 30 min, yielding a stable bottlegreen homogeneous emulsion. The resulting mixture was transferred into a 70 mL Teflon-lined stainless steel autoclave and heated to 180°C for 24 h under autogenous pressure. After the reaction mixture was cooled down to room temperature, the precipitate was filtered, washed with distilled water and ethanol, and dried in a vacuum oven at 30°C for 12 h. The product was labeled as CuFe_2O_4 -G (0.25). For comparison, the same method was used to synthesize CuFe_2O_4 without adding GO.

Reduction reactions of nitroarenes

In a 25 mL round bottom flask, nitroarenes (1.0 mmol, 1 eq.) was dissolved in a mixture of 10 mL H_2O - EtOH (1:1, v/v). Then, sodium borohydride (5.0 mmol, 5 eq.) and CuFe_2O_4 -G (0.25) (20 mg) were added. The mixture was stirred at 70°C for an appropriate time depending upon the nature of the substrate. Upon completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and the catalyst was separated by a magnet for recycling tests. The reaction mixture was extracted with ether (3×10 mL). The organic phase were combined together and dried over anhydrous MgSO_4 . The solvent was evaporated under vacuum. The pure products were obtained by silica-gel column chromatography using petroleum ether: ethylacetate (4:1) as the eluent. The products were identified by IR and ^1H NMR.

Conclusions

In conclusion, an inexpensive and magnetically recyclable catalyst, CuFe_2O_4 -G (0.25), was synthesized by a hydrothermal method. CuFe_2O_4 -G (0.25) was used as an efficient catalyst for the reduction of nitroarenes. The results demonstrate that the combination of CuFe_2O_4 with graphene results in a dramatic enhancement of the catalytic activity of CuFe_2O_4 , which can be attributed to the remarkable synergistic effect between the CuFe_2O_4 and the graphene sheets. The CuFe_2O_4 -G (0.25) catalyst can be readily isolated from the reaction mixture using an external magnet due to its superparamagnetism and it can be reused at least five consecutive cycles without significant loss of its catalytic activity. We believe that this method is important addition to known procedures for reduction of aromatic nitro compounds either on a lab as well as on larger scale.

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Notes and references

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20