Green Chemistry

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View Article Online
DOI: 10.1039/C6GC00222F

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ARTICLE

High Graphite N Content in Nitrogen-Doped Graphene as an Efficient Metal-free Catalyst for Reduction of Nitroarenes in Water

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Four kinds of nitrogen-doped graphene (NG) as metal-free catalysts are synthesized by a one-step hydrothermal reaction and thermal treatment using graphene oxide and urea as precursors. It is found that the reduction of nitroarenes can be catalyzed by using low NG loading and small amount of $NaBH_4$ in water with high yield. The type of nitrogen species in NG shows an important effect on the reduction reaction. The NG catalyst containing the most graphite N shows the highest catalytic activity during reduction of nitroarenes, which demonstrates that the graphite N of NG displays a key role in impelling this reaction. The reaction mechanism is proved by GC-MS experiment, and DFT calculation reveal the reason for the graphite N shows better catalytic activity. It is worth to note that no dehalogenation phenomenon occurs during reduction process for halogen substituted nitroarenes in contrast to conventional metal catalysts. In addition, the NG catalyst can be simply recycled and efficiently used for eight consecutive runs with no significant decrease in activity.

Introduction

The catalytic reduction of nitroarenes to the corresponding amine is considerable in organic synthesis because it is one of the atomic efficiency methods to produce intermediates or the key precursors of pharmaceuticals, polymers, pesticides, explosives, fibers, dyes and cosmetics.[1] For their importance, a plentiful of metal catalysts, including Pd, Au, Cu, Fe, Ni, Sm, Ag, and Zn to catalyze reduction of nitroarenes have been developed.[2-7] Unfortunately, some metal-based catalysts suffer from low tolerant toward substituted nitroarenes, leading to undesired byproducts and difficult purification. Therefore, bimetallic nanoparticle catalysts are developed for reduction of nitroarenes to enhance the reaction activity and selectivity due to its synergistic effects.[8,9] Recently, metal-free catalysts, such as carbon materials, have attracted more and more attention for catalysis of organic molecule transformation reactions, due to its cheap, stable, biocompatible, environment-friendly and readily available properties.[10-12]

As one of the most remarkable carbon materials, graphene, consisting of a single or few layers of graphite, acts as a scaffold which attracts encouraging attention due to its excellent physical, chemical and mechanical properties.[13-15] Moreover, it is well known that doping nitrogen heteroatoms is an efficient way to tailor its electric properties and expand its applications, such as biosensors, transparent counter electrodes, electrochemical sensors, supercapacitor electrodes and catalysts.[16-20] Therefore, numerous methods have been explored to synthesize nitrogen-doped graphene, including direct synthesis: CVD, solvothermal, arc-discharge approach in the presence of C, N-containing precursors;[21-24] and postsynthesis treatment: thermal and plasma treatment of synthesized graphene or graphene oxide in an N-containing environment.[25-27]

In the field of catalysis, the graphene-based materials are found to catalyze various types of organic molecule transformation, such as oxidation reaction, reduction reaction, ring opening reaction and Michael addition.[28,29] The reduction of nitroarenes to the corresponding amine is considerable in organic synthesis because the amine is the key intermediates of pharmaceuticals, polymers, pesticides, explosives, fibers, dyes and cosmetics.[30] Although, the carbon materials, such as N-doped carbons, reduced graphene oxide and NG have been used as catalysts for reduction of 4-nitrophenol, the high loading of catalyst and large amount of reductant are needed.[31-34]

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[‡] Electronic supplementary information (ESI) available: DFT calculation detail, spectroscopic data (^{1}H NMR) of products.

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DOI: 10.1039/C6GC00222F

Therefore, the development of highly effective and handle-convenient catalysts, less toxic solvent, low temperature and high selective reaction system for reduction nitroarenes reaction is still highly desirable.

In this work, we prepared high graphite N content of nitrogen-doped few-layered graphene materials by a one-pot hydrothermal method. It is found that the reduction of aromatic nitro compounds could be triggered by a small amount of NaBH4 and low loading of high graphite N content NG in water at room temperature. The catalyst show good tolerance to variety of different functional groups, and various kinds of substituted nitroarenes could be reduced with excellent yields and high selectivity. More importantly, the proportion of doped nitrogen species could significantly affect the NG catalytic behavior, which are demonstrated by the DFT calculation. The reaction intermediates are studied by GC-MS experiment, and the reaction mechanism is proposed according to the GS-MS results. Moreover, the catalyst is very stable and easily recycled, which could be recycled for eight times without dramatic decline in catalytic activity.

Experimental

General information

All the chemicals are used as received without further purification: aromatic nitro compounds (Aladdin industrial corporation); urea (Sinopharm Chemical Reagent Beijing Co., Ltd); graphite powder (200 mesh), silica gel (Alfa Aesar, Johnson Matthey Company); $KMnO_4$, H_3PO_4, H_2SO_4, H_2O_2, NaOH, ethanol, acetic ether, hydrochloric acid (Beijing Chemical Works). The morphology and the size of the NG samples were characterized by transmission electron microscopy (TEM, FEI, F20) combined with an energy dispersive X-ray spectroscopy (EDS) at an acceleration voltage of 200 kV. X-ray diffraction (XRD, Bruker D8 Advance Germany) was applied to characterize the crystal structure of the hybrid materials, and the data was collected on a Shimadzu XD-3A diffractometer using Cu Kα radiation. The X-ray photoelectron spectroscopy (XPS, Thermo Fisher K-Alpha American with an Al Ka X-ray source) was used to measure the elemental composition of samples. The H-nuclear magnetic resonance (^{1}H-NMR) was recorded on the JNM-LA300FT-NMR (300 MHz, 400 MHz) for checking the final product. The reaction intermediates were analyzed by using a BRUKER SCION TQ GC-MS.

Synthesis of Graphene Oxide

Graphene oxide (GO) was synthesized from graphite powder according to a modified Hummer's method.[35] Typically, graphite powder (0.5 g) and $KMnO_4$ (3 g) were initially put into a round-bottom flask. Then a mixture of concentrated H_2SO_4/H_3PO_4 (60 mL: 6.6 mL) was added. The mixture was stirred at 50 °C for 12 h. After cooling down to room temperature, the mixture was transferred into an ice bath (~40 mL). 30% H_2O_2 (~2.5 mL) was added drop wise with stirring for 0.5 h. The mixture was centrifuged (4000 r/min, 5 min) to separate solid from liquid. The yellow solid was washed with HCl (1 mol/L) one time and deionized water four times to remove oxidant agents. Then the remaining solution was dialyzed for one week to eliminate excess ions. The obtained graphite oxide was dispersed in water and subsequently ultrasonicated (120 W, 40 kHz) for 2 h. The final product was obtained by freeze dried.

Synthesis of NG sheets and reduction of GO

Four kinds of NG catalysts were prepared by a one-step hydrothermal reaction of graphene oxide with urea and thermal treatment.[36] Typically, 50 mg GO together with 1.5 g urea (1:300), was diluted in 35 ml deionized water under sonication for 1 h. The solution was sealed in 50 ml Teflon-lined autoclave and maintained at 180 ^{o}C for 12 h. The black solids (N-doped graphene sheets) were filtered then separated into four sections: the first section was washed with hydrochloric acid (1 mol/L) one time and distilled water four times to remove the excess urea. The collected sample was freeze dried overnight for further use, denoted as NG-1. The other three NG catalysts are obtained by thermal treatment of the samples at 700 ^{o}C, 800 ^{o}C and 900 ^{o}C for 4 hours with Ar continuously flowing, denoted as NG-700, NG-800 and NG-900, respectively. The thermal treated samples are prepared by directly filtrated without being washed after hydrothermal treatment of the GO and urea. Afterwards they were washed with deionized water several times and freeze dried overnight. For comparison, reduced graphene oxide (rGO) was synthesized similarly by hydrothermal method in 180 ^{o}C for 12 h, following by washing with deionized water and freeze-drying overnight.

Catalytic reduction of nitroarenes

In a typical catalysis reaction, 2 mg NG-1 was mixed with 0.5 mmol p-nitrchlorobenzene (40 mg) and 1 ml water, then stirred for 1-2 min for thoroughly mixing. 10 equiv. of $NaBH_4$ (2.5 mmol/mL) 2mL was added dropwise into the above solution under magnetic stirring at room temperature. The reaction was monitored by thin layer chromatography (TLC). After the reaction, the crude product was isolated by extracting four times by ethyl acetate. The aqueous phase with NG catalyst was washed with water and alcohol twice, respectively. It was centrifuged (3100 rpm, 3 min) for separation each time, and dried at 60 ^{o}C for the next cycles. The organic phase was purified by two methods. Workup A, the saturated hydrochloric ethyl acetate solution was added to the organic phase, and a white precipitate (the aminehydrochloride) was formed immediately. The hydrochloride was removed by filtration, and washed with ether to give the yield. Workup B, the organic phase was concentrated, and the residue was purified by a column chromatography (petroleum ether/ethyl acetate mixture) to give the isolated yield. With the isolated product yield in hand, the structure of products was identified by ^{1}H NMR.

Results and discussion

DOI: 10.1039/C6GC00222F

Four kinds of NG catalysts have been prepared by a one-step hydrothermal reaction of graphene oxide with urea and thermal treatment. The morphologies of the resultant NG and GO are characterized by SEM and TEM images, as shown in Fig. 1. The NG nanosheets showed a typical crumpled surface with random stacking, which is possibly attributed to the defective structure formed upon exfoliation and the presence of foreign nitrogen atoms. The high-resolution TEM image further indicates that these nanosheets consist of 3-10 layers. The interlayer distance is averagely ~0.37 nm, as shown in Figs. 1b2-e2, similar to the interlayer distance of graphite (~0.34 nm).[17] It can be seen from SEM image that compared with the silk veil-like morphology of GO, partially aggregated and crinkled structure seen in Figs. 1b-e was obtained at the end of doped graphene sheets of NG-1, which is in accordance with previous report that the GO layers would be refabricated when they were thermal treated and influenced by the heteroatom doping process.[37]

Further insights of the structural properties of NG are obtained from XRD characterization, as shown in Fig. 2a. The key indicator of GO is centered at 10.6°, being indexed to (001) plane, corresponding to a 0.83 nm interlayer space, demonstrating the insert of oxygen-containing functional group to form the graphene oxide. In the case of NG, the peak at 10.6° disappears and a small peak at 26.5° index to (002) plane of graphite emerged after hydrothermal and thermal process. These results indicate that the well-ordered graphene with 0.34 nm spacing has been recovered after reduction process. The four types of NG catalysts show no significant difference, which demonstrates that the different temperature has no significant influence on nitrogen-doped graphene crystalline form. However, with elevated temperature, the peak is shifted to a slightly higher 2θ degree, implying a better elimination of surface functional groups and that nitrogen atoms have been successfully doped into the graphitic system.[11, 38]

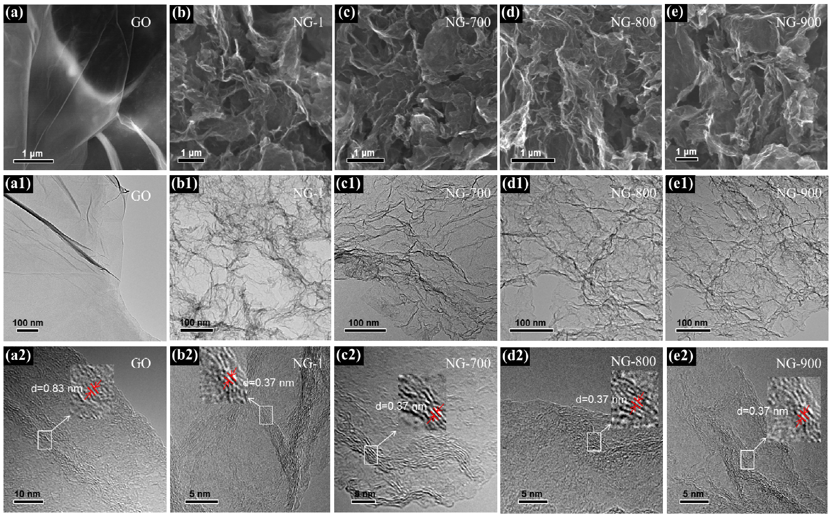

Fig. 1 SEM images of GO (a), NG-1 (b), NG-700 (c), NG-800 (d), NG-900 (e); TEM images of GO (a1), NG-1 (b1), NG-700 (c1), NG-800 (d1), NG-900 (e1); HRTEM images of GO (a2), NG-1 (b2), NG-700 (c2), NG-800 (d2), NG-900 (e2).

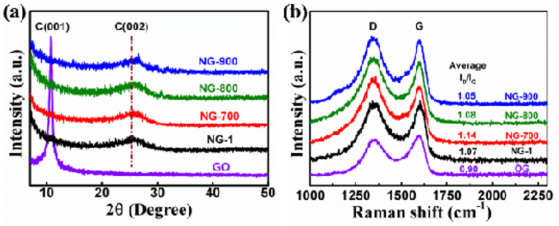

Fig. 2 (a) XRD patterns of GO and NG samples. (b) Raman spectra of GO and NG samples.

Raman spectroscopy is an important tool for identifying the structure of graphene to distinguish the interaction between molecules, the number of layer and doping status of graphite. The Raman spectra of GO and NG are displayed in Fig. 2b. The G band (~1599 cm^{-1}) is commonly observed for all graphitic structures due to the E_{2g} vibrational mode present in the sp2 bonded graphitic carbon and the D band (~1344 cm^{-1}) is associated with disordered samples or graphene edges.[39] It is well known that the integrated intensity ratio of D band versus G band (I_D/I_G) is a significant parameter of reflecting the defect and disorder level in the graphitic carbon layers.[40] The I_D/I_G values of GO, NG-1, NG-700, NG-800, NG-900 are 0.90, 1.07, 1.14, 1.08 and 1.05, respectively, indicating that more defective sites have been created through the incorporation of nitrogen atoms into the carbon network. Moreover, the I_D/I_G value of NG shows decrease with the temperature increasing, which may be due to the fact that NG is partial reduced by decrease of nitrogen atom under high temperature.[41]

The element analysis of the NG samples has been further characterized by XPS (Fig. 3a). There exist three peaks in the XPS spectrum, corresponding to C1s, O1s and N1s at about 285.08, 399.08 and 532.10 eV, respectively. The content of oxygen in each sample is 10.17%, 7.16%, 6.33% and 4.23%,

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Table 1. The peak positions and relative atomic ratios of N species for NG-1, NG-700, NG-800 and NG-900 samples based on XPS analysis[a]

	Pyridinic N		Pyrrolic N		Graphitic N		Pyridinic N-oxide		
Catalyst	BE (eV)	Ratio (%)	BE (eV)	Ratio (%)	BE (eV)	Ratio (%)	BE (eV)	Ratio (%)	Total N ratio (%)
N-1	398.4	1.27	399.4	2.71	400.3	4.26	402.6	0.59	8.83
N-700	398.5	3.04	399.5	2.40	400.7	1.39	402.1	1.36	8.03
N-800	398.5	2.46	399.8	0.56	400.6	2.03	401.8	1.90	6.94
N-900	398.1	0.98	399.3	1.17	401.2	1.05	404.3	0.40	3.60

[a] Hydrogen is not taken into account for the calculation.

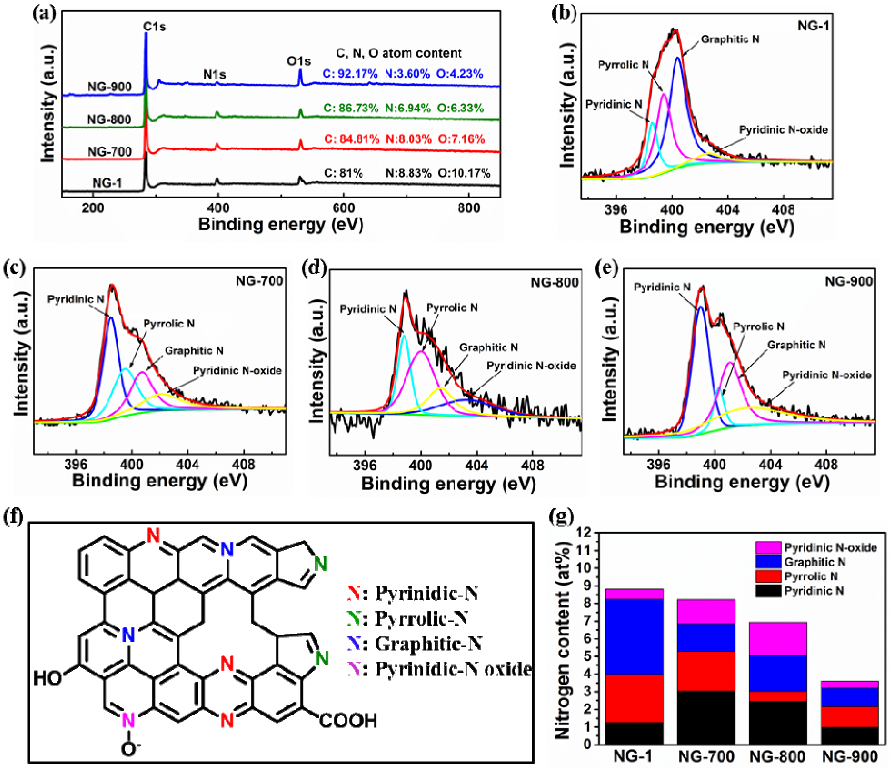
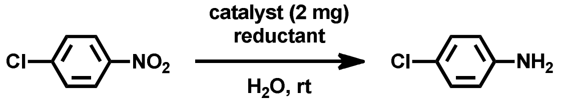


Fig. 3 XPS survey of NG samples (a). N scans of NG-1 (b), NG-700 (c), NG-800 (d), NG-900 (e). Configuration of four types of N species (f). Nitrogen content of each type of N species in different samples (g).

and the contents of N element in NG-1, NG-700, NG-800, NG-900 are 8.83%, 8.03%, 6.94%, 3.60%, respectively, as seen in Fig. 3a and Table 1. The high resolution N1s XPS spectrum of NG shown in Figs. 3b-e demonstrates that the binding energy around 398, 399, 401 and 402 eV is attributed to pyridinic N, pyrrolic N, graphitic N and pyridinic N-oxide, respectively.[36] Pyrrolic and pyridinic N are always located at the margin of graphene, bonded with carbon atoms, forming five-membered ring and six membered ring. Graphitic N substitutes carbon atoms inside the graphene sheet, and it can be found at either the edge or the center of graphene framework. Pyridinic N-oxide bonded to two carbon atoms and one oxygen atom, which is also located at the edges of graphene plane (Fig. 3f).[42] Moreover, the analysis of the N1s peak provides the relative atomic ratios of each type of N species are summarized in Table 1 and Fig. 3g. For NG-1, the main type nitrogen is graphitic N, which occupies 48% of total N atoms. As for the annealing samples, the large amount of urea can react with NG-1, which can be used to explain the decrease in graphitic N after thermal treatment. As for why hydrothermal treatment of the NG-1 and urea can decrease the graphitic N content is unclear. It can be seen that, with elevated annealing temperature from

700 °C to 800 °C, the contents of the pyridinic and the pyrrolic N show a decrease, and the graphitic N shows an increase with enhancing the temperature.[43] It is probably due to its thermal stability at high temperature. When annealing temperature increased from 800 °C to 900 °C, the graphitic N of NG-900 are decreased compared with that of NG-800. However, the ratio of the graphitic N in total N content does not decrease. This result may be due to the N species which have been directly removed from the graphene sheet, leading to the decrease of the total N content.[37] The phenomenon for the first increase and then decrease of the graphitic N with increasing the temperature is also previously reported.[44] It is worth to note that the graphitic N content in NG-1 is obviously larger than those in NG-700, NG-800 and NG-900, which indicates the hydrothermal treatment can probably form dominant stable graphitic N.

Table 2. Evaluation of reaction conditions for the reduction of 4-chloronitrobenzene[a]



Entry	Catalyst	reductant	Time	Yield[b]
1	NG-1[c]	$NaBH_4$	12	90
2	NG-1	$NaBH_4$	3	98
3	NG-1	$NH_2NH_2 \cdot H_2O$	4	73
4	NG-1	H_2	24	no reaction
5	NG-1	$OHCH_2CH_2OH$	24	no reaction
6	NG-1	$PhMe_2SiH$	24	36
7	NG-700	$NaBH_4$	12	53
8	NG-800	$NaBH_4$	12	70
9	NG-900	$NaBH_4$	12	42
10	NG-800[d]	$NaBH_4$	6	97
11	NG-900[e]	$NaBH_4$	6	95
12	GO	$NaBH_4$	24	37
13	rGO	$NaBH_4$	24	64
14	no catalyst	$NaBH_4$	24	no reaction
15	C_3N_4	$NaBH_4$	24	trace
16	Isoquinoline	$NaBH_4$	24	trace

[a] Standard reactions conditions: 0.5 mmol 4-chloronitrobenzene, 2 mg of catalyst, 3 mL H_2O, 5 mmol (10 equiv.) reductant under room temperature. [b] Isolated Yield. [c] 1 mg of catalyst was used. [d] 2.5 mg NG-800 was used. [e] 4.9 mg NG-900 was used.

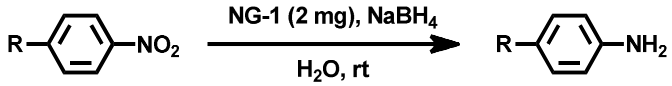
The NG catalyst is used to catalyze the hydrogenation of nitroarenes. Reductants and catalysts were preliminary investigated on the hydrogenation of 4-chloronitrobenzene for the formation of 4-chloroaniline at room temperature in water, and the results were summarized in Table 2. To our great delight, when using 1 mg NG-1 catalyst to catalyze the hydrogenation 0.5 mmol of 4-chloronitrobenzene with 5 mmol $NaBH_4$ in H_2O, 90% yield of 4-chloroaniline is obtained in 12 h (entry 1). The hydrogenation of 4-chloronitrobenzene proceeds completely by using 2mg NG-1 (entry 2). Among various kinds of reductants, the weak reductive reductants, such as hydrazine hydrate, hydrogen, ethylene glycol, phenyldimethylsilane, exhibit lower reactivity compare to that of $NaBH_4$ (entries 3-6). Although the amount of N atom in NG-700 catalyst is similar to the case of NG-1, the content of graphite N in NG-700 is lower than that in NG-1, resulting in low yield of 4-chloroaniline (entry 7). It is interesting to note that the NG-800 catalyst with lower content of N atom shows better activity than NG-700 (entry 8), properly due to the higher graphite N content in NG-800 than the case of NG-700. Among all the NG catalysts, the NG-900 catalyst shows a lower reactivity, however, the yield of 4-chloroaniline is not reduce dramatically compare to the case using NG-700 as catalyst (entry 9). These results indicate that graphite N in NG catalysts is critical for impelling the reaction rather than the amount of N atom in NG catalysts. In order to identify our prediction, the amounts of NG-800 and NG-900 catalysts are further increased to equal the N-containing of NG-1, producing 4-chloroaniline in 97% and 95% yields for 6 h (entries 10 and 11). The difference of activity is due to the different amount of graphite N in each catalyst sample. Moreover, for the purpose of comparison, a series of control experiments, such as without catalyst, using GO, rGO, C_3N_4 and isoquinoline as catalysts have been performed. The results indicate that GO and rGO show a lower reactivity, producing 4-chloroaniline in 37 % and 64% (entries 12 and 13), demonstrating that O atom contributes little to the catalytic reduction reaction. In the cases of using of C_3N_4, isoquinoline or without catalyst, the reaction does not proceed (entries 14-16). On the other hand, the high catalytic activity of NG is not caused by the defect sites on the surface of NG due to the fact that the catalyst NG-700 with the largest defective sites (Fig. 2b) is not the best catalyst. These results strongly demonstrate that the NG catalyst is indispensable for hydrogenation of nitroarenes.

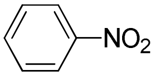
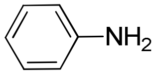
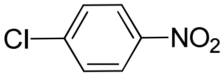
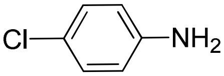
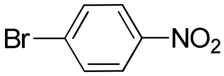
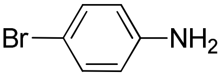
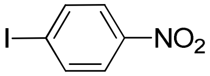
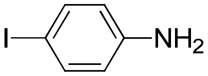
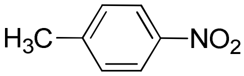
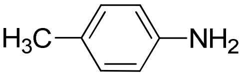
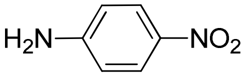
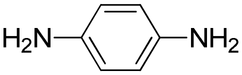
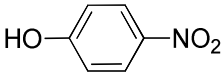
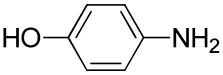
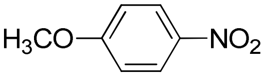
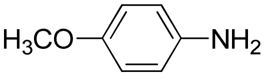
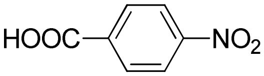
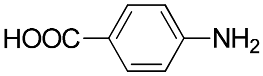
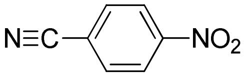
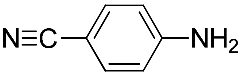
Moreover, we have further extended the NG-1 catalyst to various nitroarenes to examine the generality of the reaction. The scope and limitations of NG-1 catalyzed reduction of nitroarenes into amines by $NaBH_4$ in water are summarized in Table 3. For nitrobenzene, the aniline is formed in 85% yield (entry 1). It is noteworthy that chloro, bromo and iodo-substituted nitroarenes are reduced without undergoing any dehalogenation, affording the corresponding products in high yields (entries 2-4). The reactions of substrates bearing an electron-donating group at R produce the corresponding products in excellent yields (entries 5-7). Substrate 4-nitroanisole with a strong electro-donating group afforded the desired products in moderate yield by using 20 equiv. $NaBH_4$ (entry 8). In addition, electro-withdrawing groups, such as carboxyl and cyano functionalities in nitroarenes remain intact by using the NG catalyst, indicating a highly chemoselective process (entries 9 and 10).

The recyclability of NG-1 has been evaluated by using 4-chloronitrobenzene as test substrate. After completion of the reaction, the catalyst was filtered from the reaction and washed by H_2O for next run. This process is repeated for eight cycles, giving all cycles with excellent yields when prolonging the reaction time to 6 hours (Fig. 4).

A probably reaction mechanism for NG catalyst with high catalytic activity during the reduction of 4-chloronitrobenzene has been proposed in Fig. 5. NG plays the positive role to improve the catalytic activity, which is ascribed to the carbon atoms next to the doped N atoms on NG surface can be activated. Moreover, the absorption of reactants on the surface of NG is a critical step for catalyzing the reactions.[20] First BH_4^- ions can be adsorbed on the surface of NG catalyst in solution. Meanwhile, nitroarenes are also adsorbed onto the NG surface and this process is reversible (adsorption accompanied by desorption). Once both the substrates are chemisorbed onto the NG surface there is a hydrogen transfer to the nitroarenes. To obtain the reaction pathway involved in NG-catalyzed reduction reactions, the intermediate state has been analyzed by the GC-MS, as shown in Fig. S1 in which the hydroxylamine, hydrazine and diazene oxide three intermediates have been detected. Therefore, the reaction mechanism may be concluded that the aromatic nitro compound is reduced to the nitroso compound and then to the corresponding hydroxylamine. Then, one molecule of the nitroso compound and a molecule of the hydroxylamine yield the azoxy compound, which is reduced in a series of consecutive steps to the azo, hydrazo and aniline compounds, as shown in the condensation route of Fig. S2. However, we cannot exclude the reaction proceeded in the direct route of Fig. S2.[45] To investigate the influence of the doped N atoms, the configurations of four kinds of nitrogen-doped graphene together with the adsorbed nitrobenzene (as a representative of nitroarene) were optimized by DFT. The most stable four kinds of representative structures are shown in Fig. 6. The computational details are described in supporting information. According to the Fig. 6, it is found that the parallel adsorption with an AB stacking structure is more stable than vertical adsorption due to the lower adsorption energy. Furthermore, compared to these four NG catalysts, the graphitic NG exhibits the lowest adsorption energy and the longest N-O bonds, indicating the highest catalytic activity, which is in good agreement with the experimental observations. This good performance is attributed to the weak conjugation and higher positive charge density on the neighbour carbon atoms, activated by the doped N atoms, being consistent with the other theoretical results.[20]

Table 3. Catalytic reduction of nitroarenes into amines by NaBH4 catalyzed by NG-1[a]



Entry	Reactant	Product	T (h)	Yield[b] (%)
1			3	85
2			3	98
3			5	90
4			15	82
5			8	95
6			6	93
7			2	93
8[c]			9	80
9[c]			6	85
10[c]			15	63

[a] Standard reactions Conditions: 0.5 mmol nitroarene, 2 mg of NG-1, 3 mL H_2O, 5 mmol (10 equiv.) $NaBH_4$ under room temperature. [b] Isolated yield. [c] 10 mmol $NaBH_4$ was used.

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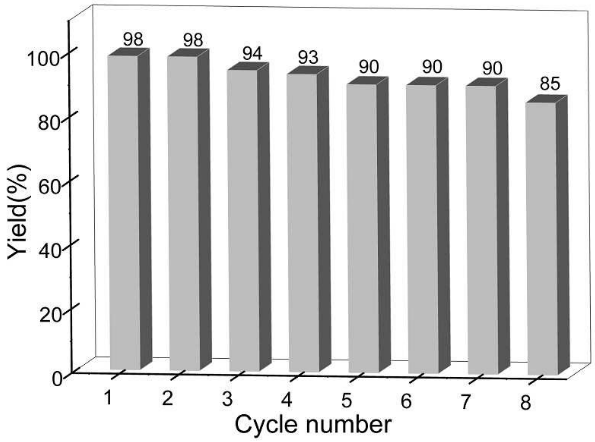

Fig. 4 The catalyst reusability for the reduction of 4-chloronitrobenzene.

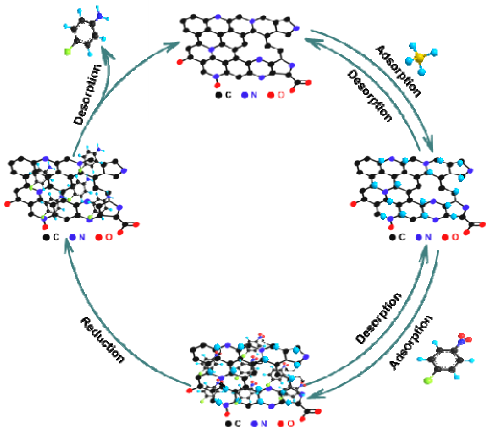

Fig. 5 A possible reaction mechanism for the reduction of 4-chloronitrobenzene catalyzed by the NG-1 catalyst and sodium borohydride.

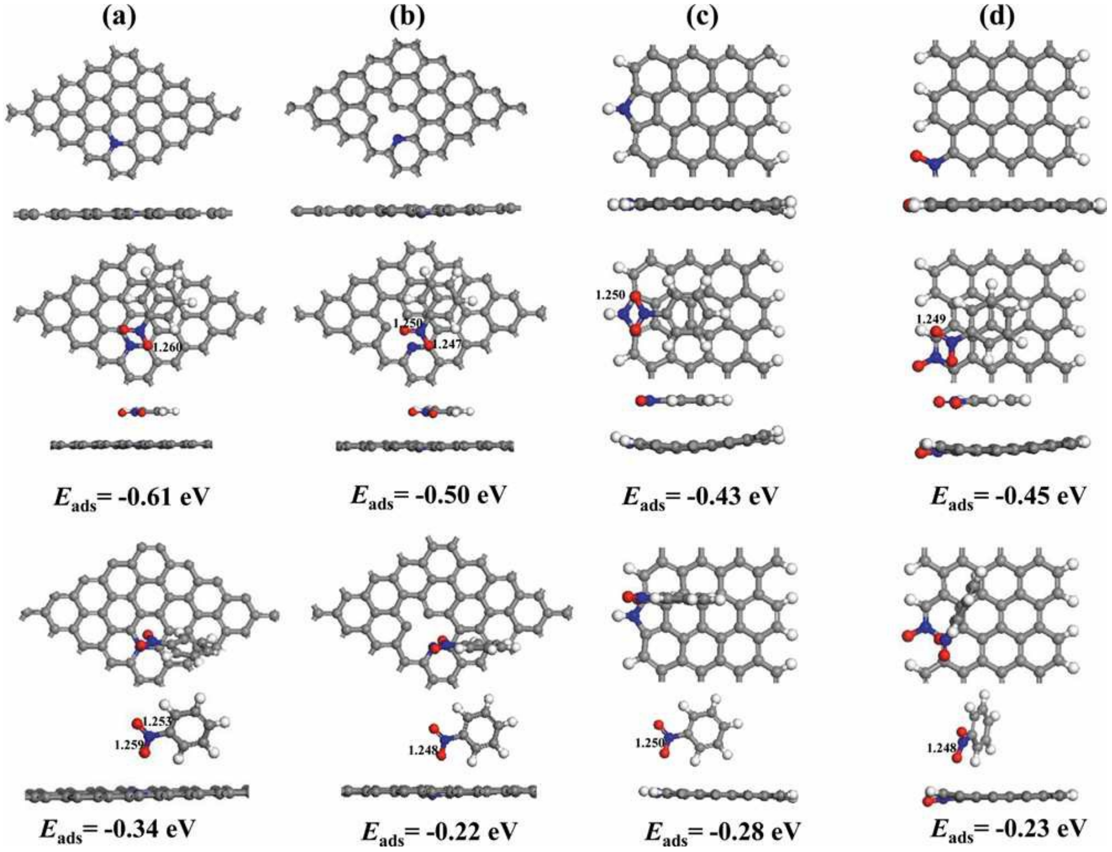

Fig. 6 The structures of nitroarenes adsorbed on NG: adsorbed at the (a) graphitic N, (b) pyridinic N, (c) pyrrolic N, and (d) pyridinic N-oxide. The gray, blue, red and white balls stand for C, N, O and H atoms, respectively. Both parallel adsorption and vertical adsorption were calculated.

Conclusions

In conclusion, we have synthesized four kinds of NG catalysts by a one-step hydrothermal reaction of graphene oxide with urea and thermal treatment. The NG-1 catalyst shows high catalytic performance during the reduction of nitroarenes in water by a small amount of $NaBH_4$ in water. Our results reveal that different type of N-doping in NG significantly affect the catalytic activity, and graphite N is the key determinant for impelling the reaction. Moreover, the NG-1 catalyst displays remarkable activity toward reduction of halogen substituted nitroarenes without undergoing any dehalogenation, affording the corresponding products in high yields. We have succeeded to detect the reaction intermediate by using the GC-MS measurement, and proposed the reaction mechanism. It is worth mentioning, DFT calculations reveal that N species decorated

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into graphene matrix, especially the quaternary ones exhibits the lowest adsorption energy and the longest N-O bonds, indicating the highest catalytic activity. The catalyst can be simply and efficiently used for eight consecutive runs without significant loss of activity. Further work is in progress to extend carbon catalysis for other organic molecule transformation reactions.

Acknowledgements

This work was supported by National Natural Science Foundation of China (Nos. 21202203, 21576289 and 21322609), Science Foundation Research Funds Provided to New Recruitments of China University of Petroleum, Beijing (No. YJRC-2013-31), Science Foundation of China University of Petroleum, Beijing (No. 2462015YQ0306, 2462014QZDX01), Thousand Talents Program and National High-tech R&D Program of China (863 Program, No. 2015AA034603). The authors thank National Natural Science Foundation of China for financial support (Grant Nos: 21203174), Natural Science Foundation of Jilin Province (No.20130522141JH, 20150101012JC). We are grateful to Computing Center of Jilin Province and Computing Center of Jilin University for essential support.

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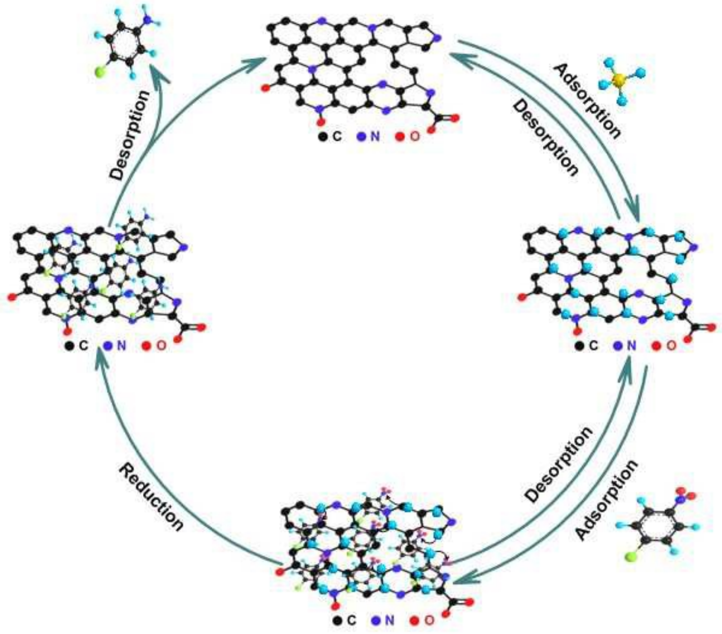
A graphic abstract



Four kinds of nitrogen-doped graphene (NG) as metal-free catalysts are synthesized by a one-step hydrothermal reaction and thermal treatment using graphene oxide and urea as precursors. It is found that the reduction of nitroarenes can be catalyzed by using low NG loading and small amount of $NaBH_4$ in water with high yield. The type of nitrogen species in NG shows an important effect on the reduction reaction. The NG catalyst containing the most graphite N shows the highest catalytic activity during reduction of nitroarenes, which demonstrates that the graphite N of NG displays a key role in impelling this reaction. It is worth to note that no dehalogenation phenomenon occurs during reduction process for halogen substituted nitroarenes in contrast to conventional metal catalysts. In addition, the NG catalyst can be simply recycled and efficiently used for eight consecutive runs with no significant decrease in activity.