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Reduced graphene oxide as a recyclable catalyst for dehydrogenation of hydrazo compounds

Li-Sha Bai [a], Xiao-Min Gao [a], Xuan Zhang [a], Fei-Fei Sun [a,b], Ning Ma [a,b,*]

[a] Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

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ABSTRACT

Reduced graphene oxide served as a reusable and efficient carbocatalyst for aerobic oxidative dehydrogenation of hydrazo compounds. Azo compounds were obtained in high yields under mild reaction conditions.

Azo compounds have found important applications in industry and laboratory as organic dyes, pigments, indicators, food additives, radical initiators, and therapeutic agents.[1] The well known synthetic routes toward these compounds include azo coupling, Wallach rearrangement of azoxy compounds, coupling of primary arylamines with aromatic nitroso and nitro compounds, and reductive coupling of nitro aromatics.[2] Besides, azo derivatives have been obtained by oxidative dehydrogenation of *N*,*N*′-disubstituted hydrazines. The general methods to achieve this transformation involve the use of stoichiometric or excess oxidants, such as $Pb(CH_3CO_2)_4$, HgO, $FeCl_3$, *N*-bromosuccinimide in pyridine, and $NaNO_2$ in acetic anhydride.[3] However, these oxidative systems often generated wastes which were hard to recycle.

Catalytic oxidative dehydrogenations of arylhydrazines to azo compounds have been reported. Utilizing oxygen or H_2O_2 as clean oxidants, NH_4VO_3, $CuCl_2$, Co(II) complexes, and $TiCl_3$/HBr system were able to catalyze this transformation.[4a–c] Also, $FeSO_4$ acted as a catalyst using a mixture of $KClO_3$ and H_2SO_4 as oxidative system.[4d] Recently, Gozin et al. reported that $TiCl_3$/HBr system was a more efficient catalytic system than NH_4VO_3 with H_2O_2 as oxidant.[5] However, some drawbacks, such as toxicity and non-reusability of the catalyst as well as potential benzidine rearrangement which probably takes place under acid catalysis and leads to undesired suspect carcinogenic products, may exist in the above reactions.

Graphene (GP) and related carbon materials have attracted recurring attention in the past decade.[6] As a type of chemically prepared graphene, reduced graphene oxide (rGO) is obtained by reducing exfoliated graphite oxide (GO), which is the strongly oxidized product of graphite. The reducing agents involved in rGO preparation include hydrazine, H_2, $NaBH_4$, $NaHSO_3$, HI, etc. Among them, hydrazine is most commonly used.[7] Because of easy preparation, GO- and rGO-based carbon materials have been intensively investigated as robust and reusable catalysts.[8] GO showed catalytic activities to activate oxygen in dehydrogenation of alcohols to carbonyl compounds,[9a] oxidative coupling of amines to imines,[9b,c] and dehydrogenative aromatization of saturated nitrogen-containing heterocycles.[9d] Also, it has been reported as an acid catalyst in a variety of organic transformations by others and us.[10] In comparison to GO, rGO catalysis in organic conversions has been seldom investigated. Ma and co-workers disclosed the catalytic activity of rGO in reduction of nitrobenzene.[11a] Oxidative degradation of phenols and methylene blue in water by peroxymonosulfate has been described.[11b] More recently, we demonstrated that rGO could efficiently catalyze the synthesis of bis(aminothiocarbonyl)disulfides from secondary amines and CS_2 through aerobic oxidation.[11c] Herein, we propose a new rGO-catalyzed oxidative dehydrogenation of hydrazo compounds to their corresponding azo compounds.

In order to optimize the reaction conditions, we chose the oxidative dehydrogenation of hydrazobenzene (**1a**) as the model reaction. The employed rGO (rGO-1) was prepared by treating GO with hydrazine hydrate, which is the most common method

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* Corresponding author. Tel.: +86 22 27403475; fax: +86 22 27403475.
E-mail address: mntju@tju.edu.cn (N. Ma).

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to prepare rGO. It was characterized by FT-IR, XRD, XPS, TG, and TEM. FT-IR spectra of GO and rGO-1 are shown in Figure 1. For GO, the following characteristic peaks were observed: 3347 cm^{-1} for hydroxyl O—H, 1726 cm^{-1} for carbonyl C=O, 1619 cm^{-1} for aromatic C=C, 1411 cm^{-1} for carboxyl C—O, 1223 cm^{-1} for epoxy C—O, and 1053 cm^{-1} for C—O. This indicates that GO contains abundant oxygen-containing functional groups. After reduction by hydrazine hydrate, the peaks associated to oxygen-functional groups decreased significantly, and the peak at 1726 cm^{-1} for carbonyl C=O totally disappeared. The peak at 1619 cm^{-1} moved to 1555 cm^{-1}, indicating formation of aromatic C = C groups.

Figure 2 shows the X-ray diffraction (XRD) patterns of GO and rGO-1. For GO, a sharp diffraction peak displays at 11.8°, corresponding to an interlayer *d*-spacing of 0.749 nm as the oxygen-functional groups located on the graphene sheet. After being reduced by hydrazine hydrate, no sharp peaks were observed, indicating that most of the oxygen-containing groups were removed during the reduction process. XPS analysis showed that rGO-1 had a C/O ratio of 7.0, which was much greater than that of GO (1.2). This also supported the removal of most of the oxygen-containing groups.

TG analysis of rGO-1 is shown in Supplementary data. There was no apparent mass loss at around 200 °C, indicating that little amount of oxygen-functional groups remained after reduction of GO. The morphology of rGO-1 was observed by TEM (see Supplementary data). TEM image showed large aggregated or spread graphene sheets with numerous wrinkles.

As reaction temperature was raised from 10 °C to 30 °C, the reaction time was reduced and the yield of azobenzene (**2a**) increased (entries 1–3, Table 1). However, when the temperature changed from 30 °C to 40 °C, the yield of **2a** decreased (entry 4, Table 1). Furthermore, the amount of catalyst was changed. The yield of **2a** reached to 97% satisfactorily when the loading of rGO-1 was 10 wt % (entries 5–8, Table 1). Subsequently, different solvents were screened (entries 9–13, Table 1). The results demonstrated that ethanol, acetone, and acetonitrile could serve as the solvent but ethanol was the best choice. Meanwhile, the reaction was carried out under nitrogen atmosphere. The yield of **2a** was fairly poor, which indicated that oxygen in air could be the final oxidant (entry 14, Table 1). In addition, other rGOs were prepared in the presence of $NaBH_4$, $NaHSO_3$, and hot water, which were marked as rGO-2, rGO-3, and rGO-4, respectively. Their catalytic activities were much lower than that of rGO-1 (entries 15–17, Table 1). While graphite power was not able to catalyze this transformation (entry 18, Table 1). The reaction was sluggish in the absence of rGO-1 (entry 19, Table 1). Thus, the optimum reaction conditions were found as 10 wt% of rGO-1, 30 °C, EtOH as solvent, and under open-air.

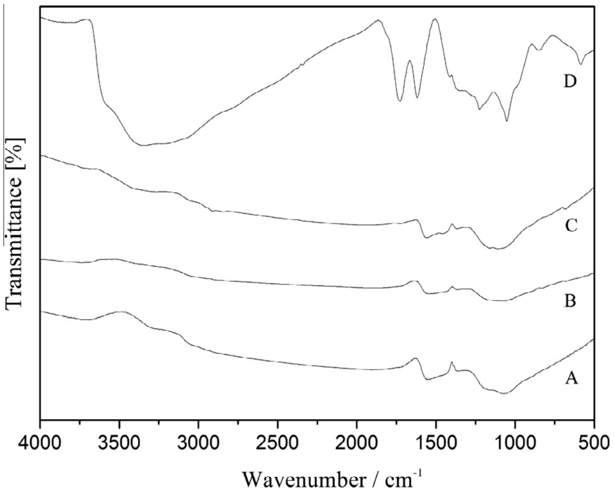

Figure 1. FT-IR of pristine rGO-1, (A) rGO-1 after being used one time, (B) rGO-1 after being used five times, (C) and GO (D).

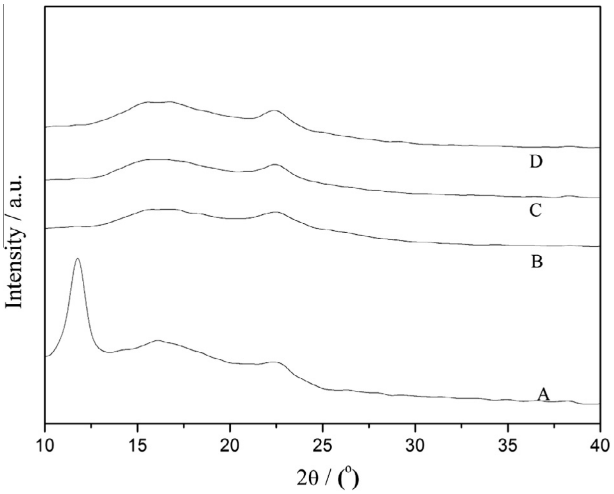

Figure 2. XRD patterns of GO, (A) pristine rGO-1, (B) rGO-1 after being used one time, (C) and rGO-1 after being used five times (D).

The dehydrogenations of various hydrazo compounds (**1b**–**k**) were examined and the results are summarized in Table 2. For the substrates having electron-donating groups, the reactions took place readily to give the corresponding azo products in good to excellent yields (entries 1–2, 4–8). Changing rGO loading to 5 wt % and 2 wt % led to extension of the reaction time and decrease of the yields (see Supplementary data, Table 1S). Symmetric substrates in the reaction were prepared by the reductive coupling of the corresponding nitro compounds. Among them, 3,3′-dimethyl hydrazobenzene was difficult to isolate, so its ethanol solution was directly used without purification and the yield of **2c** was based on *m*-nitrotoluene. In the cases of hydrazo compounds having an electron-withdrawing group, the oxidative dehydrogenation proceeded more slowly (entries 9 and 10). Extension of reaction time did not result in the increase of yields. Changing rGO loading to 5 wt% resulted in a poor yield of **1i** even for a long reaction time under reflux (see Supplementary data, Table 1S).

After dehydrogenation reaction of hydrazobenzene (**1a**), rGO-1 was recovered by filtering the solid out, washing thoroughly with ethanol, and drying. Then it was reused in the reaction. At sixth run, no obvious loss of catalytic activity was observed (Table 3). There was no significant change in IR spectra (Figure 1) and TG curves (see Supplementary data) of rGOs before first run, after first run, and after fifth run.

At this stage it is hard to propose a detailed mechanism of this reaction. Recently, Loh et al. reported that unpaired electrons in the holes and at the edges of ba-GO sheets could activate O_2 to form $O_2^{\cdot -}$ and led to aerobic oxidative coupling of benzylamines.[9c] The ba-GO in their research was prepared by treatment of GO with base and acid sequentially. Without regard to the carboxyls at the edges, the structure of basal plane of ba-GO was very similar with that of rGO.[12] Enlightened by their mechanism study, we envisage that rGO might activate O_2 to form $O_2^{\cdot -}$ similarly, then hydrazo compound **1** was oxidized by $O_2^{\cdot -}$ to produce azo compound **2** and H_2O_2 (Scheme 1). Meanwhile, an electron was released and transferred back to rGO, then rGO structure with unpaired electrons was recovered. However, pristine GO has less unpaired electrons at the edges of its sheets,[9c] so it showed lower catalytic activity than rGO (entries 3 vs 18, Table 1).

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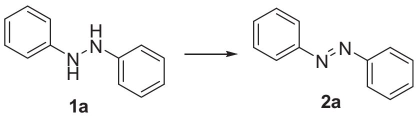
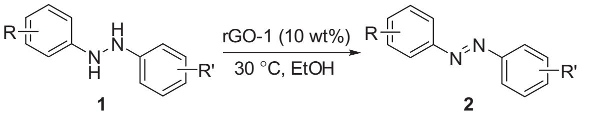
Table 1
Dehydrogenation of hydrazobenzene[a]



Entry	Catalyst	Catalyst loading (wt %)	T (°C)	Solvent	Time (h)	Yield[b] (%)
1	rGO-1	10	10	EtOH	8	95
2	rGO-1	10	20	EtOH	2.5	92
3	rGO-1	10	30	EtOH	2.5	97
4	rGO-1	10	40	EtOH	2.5	93
5	rGO-1	1	30	EtOH	5	65
6	rGO-1	2	30	EtOH	10	92
7	rGO-1	5	30	EtOH	5.5	93
8	rGO-1	10	30	EtOH	3	98
9	rGO-1	10	30	CH_3COCH_3	4	95
10	rGO-1	10	30	CH_3CN	4	96
11	rGO-1	10	30	THF	10	94
12	rGO-1	10	30	MeOH	10	86
13	rGO-1	10	30	CH_2Cl_2	10	83
14	rGO-1	10	30	EtOH	5	21[c]
15	rGO-2	10	30	EtOH	10	75
16	rGO-3	10	30	EtOH	10	78
17	rGO-4	10	30	EtOH	10	77
18	GO	10	30	EtOH	10	51
19	Graphite	10	30	EtOH	10	13
20	None		30	EtOH	10	13

[a] Reacted in an open vessel.
[b] Isolated yield.
[c] Under N_2 atmosphere.

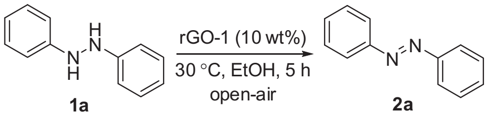
Table 2
Dehydrogenation of various hydrazo compounds[a]



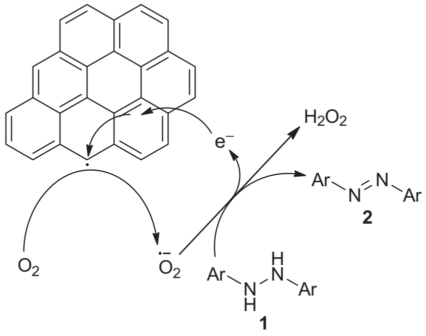
Entry	Substrate (**1**)	Time (h)	Product (**2**)	Yield[b] (%)
1	**1a** (R = R′ = H)	3	**2a**	98
2	**1b** (R = R′ = *o*-Me)	3	**2b**	97
3	**1c** (R = R′ = *m*-Me)	3	**2c**	69[c]
4	**1d** (R = R′ = *p*-Me)	2	**2d**	95
5	**1e** (R = *p*-OMe, R′ = H)	2.5	**2e**	92
6	**1f** (R = *p*-OCH$_2$Ph, R′ = H)	2	**2f**	90
7	**1g** (R = *p*-OEt, R′ = *p*-Me)	2.5	**2g**	89
8	**1h** (R = *p*-OCH$_2$Ph, R′ = *p*-Me)	3.5	**2h**	89
9	**1i** (R = R′ = *o*-Cl)	6	**2i**	60[d]
10	**1j** (R = R′ = *p*-Cl)	4.5	**2j**	81
11	**1k** (R = *p*-OCH$_2$Ph, R′ = *p*-Cl)	2.5	**2k**	98

[a] Reacted in an open vessel.
[b] Isolated yield.
[c] Yield is based on *m*-nitrotoluene.
[d] Reflux for 6 h.

Table 3
Reuse of rGO



Run	1	2	3	4	5	6
Isolated yield (%)	98	97	98	92	99	95



Scheme 1. Possible catalytic function of rGO.

In conclusion, we have found an efficient and facile method to prepare aromatic azo compounds from their corresponding hydrazo compounds under mild conditions. As an easily available carbocatalyst involved in this oxidative dehydrogenation, rGO can be easily recovered and reused at least five times without any loss of catalytic activity. Another feature of this protocol is that air acts as the oxidant. Further investigations on reaction mechanism and other rGO-catalyzed dehydrogenative reactions are ongoing in our laboratory.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.06.097.

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12. In Loh's report, b-GO was obtained by treating GO with NaOH solution (0.1 M) under reflux for 1 h. It has been demonstrated that treatment of GO with hot NaOH solution led to the formation of rGO (Fan, X.; Peng, W.; Li, Y.; Li, X.; Wang, S.; Zhang, G.; Zhang, F. *Adv. Mater.* **2008**, *20*, 4490–4493). So the structures of rGO-1 and b-GO are very similar, which was also demonstrated through IR and XRD analysis by us (see Supplementary Data). Loh et al. then treated b-GO with HCl solution to get ba-GO. This acid treatment process could recover the carboxyl groups at the edges of b-GO sheet, but the structure of basal plane of b-GO was not affected greatly. Due to the similar basal plane structures of rGO and ba-GO, we think they could activate O_2 by a similar unpaired electron pattern.

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