

Cite this: *Green Chem.*, 2012, **14**, 930

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Graphite oxide as an efficient and durable metal-free catalyst for aerobic oxidative coupling of amines to imines†

Hai Huang, Jun Huang, Yong-Mei Liu,* He-Yong He, Yong Cao* and Kang-Nian Fan

Received 29th December 2011, Accepted 16th February 2012

DOI: 10.1039/c2gc16681j

Graphite oxide was found to be a highly efficient, reusable and cost-effective heterogeneous catalyst for the direct metal-free transformation of amines to afford the corresponding imines under mild and neat conditions with molecular oxygen as the terminal oxidant. This method is simple, economic and environmentally benign, resulting in practical advantages for the convenient synthesis of imines and their derivatives.

Catalytic oxidation of organic compounds using molecular oxygen (O₂) as the terminal oxidant has attracted an enormous amount of attention from the viewpoint of green sustainable chemistry.¹ In particular, considerable efforts have been devoted to the development of mild and efficient methods for the oxidation of alcohols to carbonyl products.² In contrast, the conversion of corresponding amines to imines by catalytic oxidation has remained largely undeveloped, despite great utility of imines in the synthesis of industrial materials, biologically active compounds and their intermediates, such as chiral amines,^{3a,b} hydroxylamines,^{3c-e} nitrones^{3f,g} and oxazolidines.^{3h,i} As an attractive alternative to the traditional amine-carbonyl condensation, catalytic amine oxidation can deliver direct synthesis of imines in a green and more efficient manner.^{4a} While a number of procedures^{4b-g} have been developed for such purposes, a persistent challenge is the control of reaction pathways to avoid undesired by-products, such as nitriles or aldehydes. Thus far, a range of transition-metal-based systems capable of efficient and selective oxidation of amines to imines has been reported.⁵ Despite their usefulness, many of these metal-mediated processes are not applicable in pharmaceutical or biotechnological applications due to toxicity concerns and separation problems. Therefore, the development of a simple, efficient and cost-effective process that can enable direct access to imines by metal-free amine oxidation utilizing O₂ as the sole oxidant is of high actual interest.

Graphene, a flat monolayer of carbon atoms arranged in a honeycomb network, has attracted tremendous attention owing to its outstanding electronic, optical, thermal, mechanical properties

and extremely high surface area.⁶ Until recently, the catalytic application of graphene and related carbon nanostructures has focused primarily on the use of these materials as supports for catalytically active transition metals.⁷ Very recently, Bielawski and co-workers has, however, shown that pristine graphite oxide (GO), a common precursor to graphene-like materials, can be directly used as an efficient catalyst which is capable of oxidizing a broad array of alcohols to their corresponding carbonyl compounds.^{8a} Following this seminal discovery, metal-free GO has emerged as a highly versatile material that can be applied to a variety of synthetic processes including alkyne hydration,^{8a} thiol oxidation,^{8c} C–H oxidation,^{8d} C–C^{8b} and carbon-heteroatom bond-forming^{8e} reactions. The unusual metal-free reactivity of GO has prompted us to investigate the possibilities offered by GO for direct transformation of amines by catalytic oxidation. Herein, we report the use of GO as a readily available, inexpensive, applicable, efficient and reusable catalyst for the direct synthesis of imines from amines under mild aerobic conditions. To the best of our knowledge, this is the first convenient metal-free catalytic process ever reported for an efficient imine synthesis from various amines using molecular oxygen as the oxidant under neat conditions.

The GO was prepared from natural graphite powder using a modified Hummers method.⁹ To ensure complete removal of the residual metallic impurities, the resulting GO suspension was extensively dialyzed for 5 days. Based on an inductively coupled plasma mass spectrometry (ICP-MS) analysis, the Mn content in the GO thus obtained was found to be lower than 30 ppb. The other metals like Fe, Co, Cu, Pb, *etc.* were below the detection limit. The chemical nature and structural morphology of the final GO material was then thoroughly characterized by a range of spectroscopic methods including transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) analysis. The TEM image showed that the GO nanosheets have a thickness of several layers (Fig. 1a). The XRD pattern of GO displayed a well-defined peak at $2\theta = 11.6^\circ$ (Fig. 1b), which corresponds to an interplanar distance of *ca.* 0.76 nm. The characteristic *d*₀₀₂ reflection of graphite at 26.6° could not be observed, which gave evidence that complete oxidation was achieved.¹⁰ The FTIR measurements showed several intense, broad absorption features centered at 3400, 1726, 1577, 1227 and 1061 cm⁻¹, confirming the presence of carboxyl-, hydroxyl- and epoxy-based functional groups on the GO surface (Fig. S1 in ESI†). The presence of a high abundance of oxygen-

Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, P.R. China. E-mail: yongcao@fudan.edu.cn; Fax: (+86-21) 65643774

†Electronic supplementary information (ESI) available: Experimental section, FTIR, XPS and temporal reaction profiles data. See DOI: 10.1039/c2gc16681j

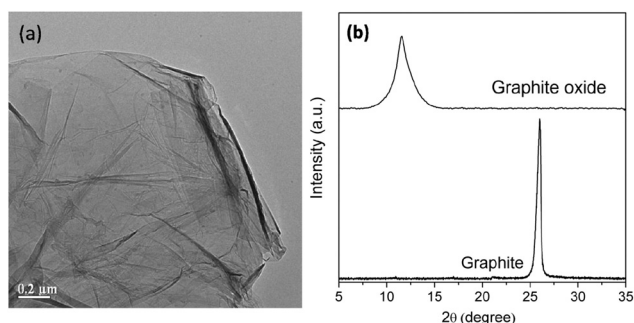
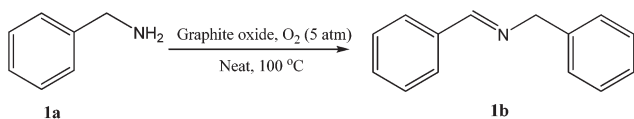


Fig. 1 (a) TEM image of graphite oxide powders. (b) X-Ray diffraction patterns pristine graphite and graphite oxide.



Scheme 1 Oxidation of benzylamine (**1a**) to *N*-benzylidene benzylamine (**1b**) catalyzed by GO.

Table 1 Oxidation of benzylamine (**1a**) into *N*-benzylidene benzylamine (**1b**) under various conditions^a

Entry	Catalyst	Loading [wt%]	Con. ^b [%]	Yield [%]
1	GO	50	99	98
2 ^c	GO	50	92	90
3 ^d	GO	50	n.r.	—
4 ^e	GO	50	40	38
5 ^f	GO	50	30	27
6	GO	20	71	70
7	GO	100	99	97
8	GO	200	99	96
9	No catalyst	—	2.5	2.5
10	NG	50	5	5
11	AC	50	12	12
12	MWCNTs	50	10	9.5
13	RGO	50	27	25
14	Au/TiO ₂ ^g	50	75	61 ^h

^a Reaction conditions: **1a** (5 mmol), 5 atm O₂, 100 °C, 4 h, n.r. = no reaction. ^b Conversion of **1a** to **1b**, as determined by GC with anisole as an external reference. ^c After five runs. ^d 5 atm N₂. ^e 1 atm O₂. ^f 80 °C, 5 h. ^g Au/TiO₂ (type A, lot no. Au/TiO₂ no. 02-1) were supplied by the World Gold Council (WGC). ^h The sole by-product was benzaldehyde.

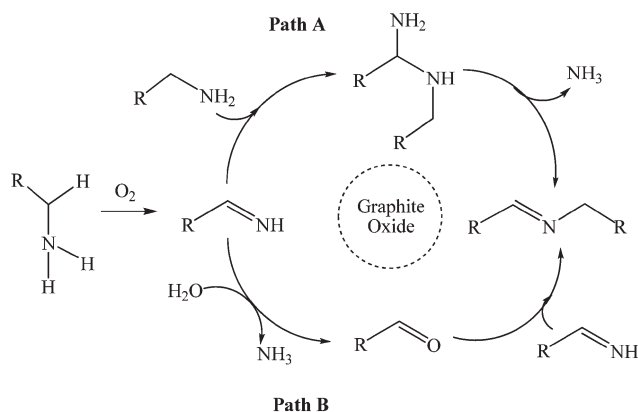
containing functional groups on the GO surface was further confirmed by XPS analysis, which showed a pronounced shoulder on the higher binding energy tail of the C 1s peak (Fig. S2 in ESI†).

Having established the essential nature of the GO material, the conversion of benzylamine (**1a**) was chosen as a model to explore the feasibility of the proposed reaction (Scheme 1). In a preliminary experiment, neat **1a** was heated to 100 °C in the presence of 50 wt% GO for 4 h under 5 atm O₂ (Table 1). To our delight, the corresponding imine, *N*-benzylidene benzylamine (**1b**), can be obtained in an excellent yield of ca. 98% (Table 1, entry 1). Of yet further interest is that the GO sample was stable and can be easily reused in next reaction without an appreciable loss in either activity or selectivity between the first and fifth

runs (Table 1, entries 1 and 2).¹¹ Compared to previously reported oxidative self-coupling of amines using metal catalysts (e.g., high surface area iron-based metal–organic frameworks; MOFs),^{4g} appreciably less time was required (4 h *versus* several days) to achieve quantitative reaction using GO under similar temperatures and catalyst loadings. Subsequent experiments performed at 80 °C or with lower oxygen pressures under otherwise identical reaction conditions showed that the reaction rate was significantly decreased (Table 1, entries 3–5). Furthermore, it was found that variations in the GO loadings (ranging from 20–200 wt%) had a significant effect on the isolated yield of the imine product (Table 1, entries 6–8). While 20 wt% GO afforded 70% of the target product (Table 1, entry 6), increasing the loading to 50 wt% GO was found to be sufficient to drive the oxidation reaction to quantitative conversion (Table 1, entry 1).

The high efficiency of GO for the direct transformation of neat **1a** with O₂ relative to other pure carbon nanostructures was shown clearly (Table 1). For example, the use of natural flake graphite (NG), activated carbon (AC), multi-walled nanotubes (MWCNTs) or hydrazine-reduced GO (RGO) in place of GO results in only very poor yields of the imine product (Table 1, entries 10–13). Moreover, it is important to note that aerobic oxidation of **1a** to corresponding **1b**, in absence of catalyst, can only deliver a very low conversion (Table 1, entry 9), and with GO as the catalyst the reaction does not proceed in the absence of oxygen (Table 1, entry 3). These experiments clearly demonstrate the indispensable role of GO in facilitating the selective oxidation of **1a** to **1b** in the presence of oxygen. At this point, it should also be stressed here that the solventless conditions tested in this study are essentially different from precedents reported with gold catalysts that require organic solvents.^{5a–d} For the sake of straightforward comparison with an earlier study,^{5a} an additional test using gold nanoparticles supported on TiO₂ (Au/TiO₂), which is among the best gold catalysts reported for this aerobic oxidation, was performed under our solventless conditions. In this case, conversion of 75% of **1a** to **1b** with 81% selectivity was attained (Table 1, entry 14). This relatively low selectivity of **1b** with Au/TiO₂ as compared to that with GO may be attributed to the occurrence of undesired reactions arising by the oxidative cleavage of imine product under oxygen atmosphere.

Given the observed high activity and selectivity, it is of interest to clarify the catalytic origin of the present GO–amine oxidation system. In line with the broad literature documenting metal-free carbocatalysis using molecular O₂ as the oxidant,^{8d,e,12} a facile oxidative dehydrogenation of the reactant molecules by highly functionalized GO could be the key factor for achieving efficient amine oxidation under mild conditions. On the other hand, it is known that the oxidation of primary amines can proceed by two different oxidative dehydrogenation routes (Scheme 2) both involve the formation of a RCH=NH intermediate.^{5c} In path **A**, this intermediate is attacked by a second molecule of the primary amine to give an aminal which loses NH₃ to give the coupled imine product RCH=NCH₂R. In path **B**, the initially formed imine reacts with trace amounts of H₂O to give the aldehyde RCH=O, which subsequently reacts with a second molecule of the amine to give the final imine product. In the GO-catalyzed solventless reaction described herein, a phenomenon worthy of note is the transient formation of notable amount of aldehyde at



Scheme 2 Possible mechanisms for the GO-catalyzed aerobic oxidation of primary amines to imines according to ref. 5c.

the initial stage of the reaction (Fig. S3a in ESI†).¹³ Considering the hygroscopic nature of GO, it is likely that a reasonable amount of water occluded in the GO nanosheets could play a key role in facilitating the target product formation. This is further supported by the fact that a deliberate introduction of a substantial amount of H₂O can greatly accelerate the reaction (Fig. S3b in ESI†). Therefore, it seems that the present GO-mediated amine oxidation may occur mainly through path **B**.

Based on these results the scope and limitations of GO-catalyzed amine oxidation were explored, using 5 atm oxygen pressure at 100 °C. As revealed in Table 2, various structurally diverse benzylamines, regardless of the presence of electron-donating or electron-withdrawing functionalities, could be directly coupled to give the corresponding imines in excellent yields. The reaction rate depended qualitatively on the Hammett constant of the substituent (see Fig. S4 in ESI†),¹⁴ with the oxidation being favored by the presence of electron-donating substituents (Table 2, entries 2, 3, and 6, 7). Moreover, higher reaction rates for the *para*-substituted benzylamines relative to the *meta* and *ortho* isomers reveal the presence of a steric effect (Table 2, entries 3–5). It is noteworthy that halo-substituted benzylamines performed well, leading to halo-substituted imine compounds (Table 2, entries 6, 7), which could be used for further transformations along with the imine functionality.¹⁵ Furthermore, heterocyclic amines containing nitrogen and sulfur atoms, which usually poison most metal catalysts,^{4b,16} could also be converted into the corresponding imines in excellent yields (Table 2, entries 8 and 9). Note that the oxidation of both pyridyl- and thiophene-methylamine appeared much more efficient than that of their phenyl counterparts. However, under similar conditions, the oxidation of aromatic amines lacking a hydrogen atom at the α -carbon position, such as aniline, did not proceed at all (Table 2, entry 10).

To further investigate the catalytic ability of the present GO system, we next applied this system to the selective oxidation of secondary amines. As exemplified in the entries 11–14 of Table 2, a number of secondary amines could be selectively oxidized to their corresponding imines with high to excellent yields. One aspect that deserves mention is that, compared to the case with benzylamines as described above, a much longer reaction time is required to complete the reaction of these secondary

Table 2 Oxidation of amines to imines catalyzed by GO^a

Entry	Substrate	Time [h]	Con. ^b [%]	Yield ^c [%]
1		4	99	98(91)
2		3.5	99	97
3		3	99	98(92)
4		3	91	88
5		3	84	80
6		5	95	89
7		6	96	88
8		2	97	96(90)
9		2	93	88
10		4	n.r.	—
11		8	98	88(81)
12		8	95	83
13		8	97	75
14		5	97	95(90)
15		4	n.r.	—
16		4	n.r.	—

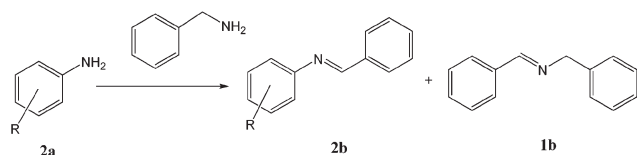
^a Reaction conditions: amine (5 mmol), 50 wt% loading GO, 5 atm O₂, 100 °C, n.r. = no reaction. ^b Conversion of amine to the corresponding imine, as determined by GC with anisole as external reference. ^c Numbers in parenthesis refer to yields of isolated products.

amines. These results are again indicative of the presence of a steric effect. In the case of dibenzylamine, a comparably low selectivity to **1b** (ca. 90%) for the imine was observed (Table 2, entry 11), with the main by-product being benzaldehyde; the formation of which was ascribed to the oxidative cleavage of the C=N bond.¹⁷ The same phenomenon also occurred in the case of *N*-benzylaniline, with by-products of benzaldehyde and aniline being formed (Table 2, entry 13). On the other hand, 1,2,3,4-tetrahydroisoquinoline was quantitatively dehydrogenated to 3,4-dihydroisoquinoline (Table 2, entry 14). Attempts were also made to oxidize simple aliphatic amines such as piperidine and *n*-hexylamine, but they were unsuccessful (Table 2, entries 15, 16).

Encouraged by excellent yields of the oxidative self-coupling of benzylamines, an effort was initiated to explore the feasibility of using the GO-mediated protocol to produce asymmetrically substituted imines by the oxidative cross condensation of benzylamines and amines lacking hydrogen atoms at the α -carbon (Scheme 3). In a preliminary experiment, the reaction was carried with equimolar amount of **1a** and aniline, the former amine was completely oxidized to form a mixture of imines, namely **1b** and *N*-benzylidene aniline (**2b**) in 72 and 24% yield, respectively (Table 3, entry 1). Formation of **2b** corresponds to the dehydrative coupling of benzaldehyde, the proper and most reasonable reaction according to the literature, with aniline.¹⁸ Meanwhile, the lack of aniline oxidation favored the preferential trapping of benzylamine in residual aniline. To optimize the reaction further, the reaction was carried out in the presence of four equivalents of aniline. In this case, the selectivity towards the target asymmetric *N*-benzylidene aniline increased remarkably with minimal self-condensation of **1a** (Table 3, entry 2). By using this newly established procedure, a variety of anilines¹⁹ bearing electron-withdrawing and electron-donating substituents can be converted into the corresponding benzylidene anilines in excellent yields under neat conditions as depicted in Table 3.

Finally, to further expand the variety of asymmetrically substituted imines that can be obtained through the GO-mediated procedure, we have carried out analogous experiments with different simple aliphatic amines such as piperidine and *n*-hexylamine, and the results are summarized in entries 7 and 8 of Table 3. In all cases, high yields of the corresponding benzylidene alkylamines are obtained with GO, a result indicating that the proposed methodology is applicable for the production of a wide diversity of asymmetrically substituted imines.

In summary, we have demonstrated a simple, efficient and eco-friendly protocol for the direct synthesis of useful imines from amines *via* a facile GO-mediated metal-free catalysis procedure, which proceeds under mild and neutral conditions with molecular O₂ without using any cosolvent. Both symmetrical,



Scheme 3 Oxidative cross condensation of benzylamines and primary amines lacking hydrogen atoms at the α -carbon.

Table 3 Oxidative cross coupling of benzylamine (**1a**) with anilines or aliphatic amines (**2a**)^a

Entry	Amine (2a)	Time [h]	Con. ^b [%]	Yield [%]	
				2b	1b
1 ^c		4	97	23	74
2		4	98	89	9
3		4	97	90	7
4		4	99	95	5
5		4	99	94	6
6		5	99	84	16
7		6	99	92	8
8		6	99	88	12
9		8	99	91	9

^a Reaction conditions: **1a** (1 mmol), **2a** (4 mmol), 50 wt% loading GO (base on **1a** + **2a**), 5 atm O₂, 100 °C. ^b Conversion based on **1a**. Numbers in parenthesis refer the present of 5 ml toluene for the amine (**2a**) is solid. ^c **1a** (1 mmol), **2a** (1 mmol), 50 wt% loading GO (base on **1a** + **2a**).

asymmetrical and cyclic imines can be conveniently prepared by this method. The clean and mild synthetic procedure described herein is expected to contribute to its utilization for the development of sustainable products and processes.

This work was financially supported by the National Natural Science Foundation of China (20873026, 20803012 and 2107-3042), New Century Excellent Talents in the University of China (NCET-09-0305), the State Key Basic Research Program of PRC (2009CB623506), and Science & Technology Commission of Shanghai Municipality (08DZ2270500).

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