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Graphene-Oxide-Catalyzed Cross-Dehydrogenative Coupling of Oxindoles with Arenes and Thiophenols

Hongru Wu[a], Chuntian Qiu[a], Zhaofei Zhang[a], Bing Zhang[a], Shaolong Zhang[a,b], Yangsen Xu[a], Hongwei Zhou[c], Chenliang Su[a]*, Kian Ping Loh[b]

[a] International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Engineering Technology Research Center for 2D Materials Information Functional Devices and Systems of Guangdong Province, Institute of Microscale Optoeletronics, Shenzhen University Shenzhen 518060, PR China

[b] Department of Chemistry, Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore

[c] College of Biological, Chemical Science and Engineering, Jiaxing University, 118 Jiahang Road, Jiaxing 314001, China

E-mail addresses: chmsuc@szu.edu.cn

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Abstract. Here, we explore the GO-catalyzed cross-dehydrogenative coupling of oxindoles with arenes and thiophenols for the rapid synthesis of 3-aryloxindoles and 3-sulfenylated oxindoles. Control experiments and small-molecule mimicking studies reveal that the acidic nature and quinone-type functionalities of GO are synergistically utilized for the coupling reaction. The reaction proceeds under simple and mild reaction conditions, exhibits good functional group tolerance, and can be easily scaled up to the gram level.

Keywords: Graphene Oxide; Cross-dehydrogenative coupling; Metal-free Catalysis; 3-sulfenylated oxindoles ; 3-aryloxindoles

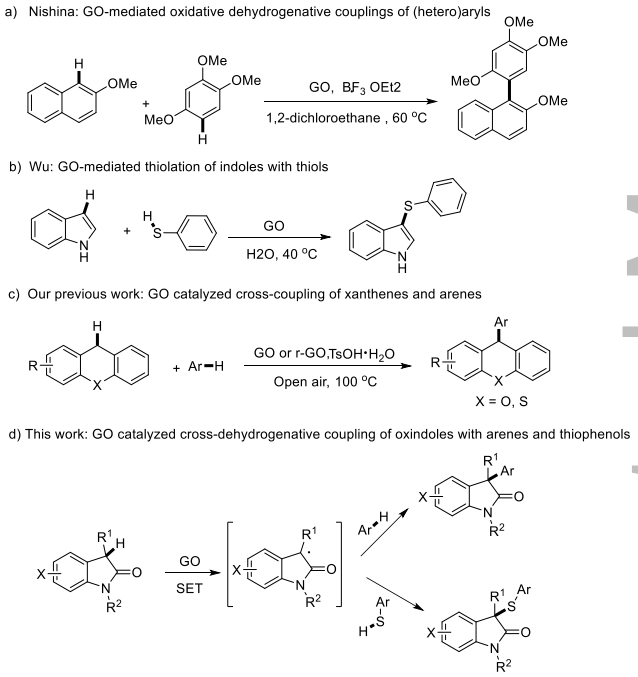

Figure 1. GO-mediated CDC reactions.

Graphene oxide (GO)-based materials have emerged as promising catalyts for liquid-phase organic reactions owing to their low-cost, production scalability (thousand tons-scale production) and rich chemical properties.[1] Endowed with rich oxygen functionalities and aromatic carbon scaffolds GO shows remarkable ability to catalyse a series of synthetic transformations [2], such as stoichiometric oxidations[3a-3e], solid acids-mediated reactions[3f-3g] and oxidations[3h-3i], C-C couplings[3j-3l] etc. The latter is currently a very active research area and the reactions are usually catalysed by precious metals. GO-based carbocatalyst are emerging as alternatives to precious metal resources that are dwindling in supply. Cross-dehydrogenative coupling (CDC) reactions, a means of constructing carbon–carbon bonds directly from two different C–H bonds with extremely high atom-economy, are very attractive targets of carbocatalysis, but rarely explored.[3i, 3l, 4] In 2016, Nishina and co-workers reported the first GO-mediated CDC reaction between two electron-rich arenes with GO and boron trifluoride diethyletherate ($BF_3{\cdot}OEt_2$), however GO was used as stoichiometric reagent and the reaction scopes were mainly limited to homocoupling (Figure 1a).[4a] Wu and co-workers sequentially developed the GO-mediated thiolation of indoles with thiols in water and presented a radical-based mechanism (Figure 1b).[4b] Recently, we had explored the carbocatalytic CH-CH type cross-

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couplings of xanthenes with arenes. Both GO and highly-reduced GO showed high reactivity for this CDC reaction and furnished the coupling products in good yields. Mechanistic studies suggest that quinone-type functionalities as well as the zigzag edges in GO materials are the catalytic active sites (Figure 1c). [3i]

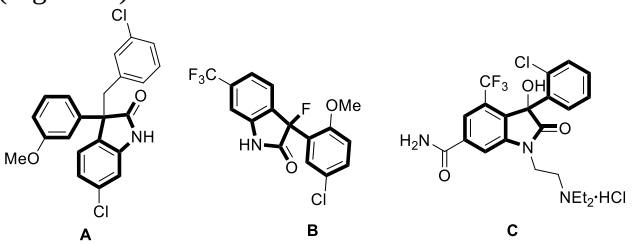
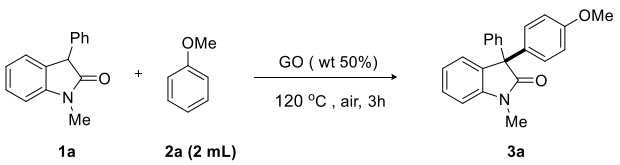


Figure 2. Representative bioactive compounds and pharmaceutical molecules with 3-arylation 2-oxindole skeleton: A (an anticancer agent), B (a neuroprotective agent), C (a potent growth hormone secretagogue).

3-Aryloxindoles and their derivatives are ubiquitous in natural products as well as pharmaceutical molecules (Figure 2).[5] The existing strategies generally rely on utilizing pre-functionalized substrates, transition metal catalysts or operationally tedious procedures.[6] Herein, we devise a sustainable and metal-free strategy for the construction of 3-aryloxindoles via the most direct and efficient CDC coupling of oxindoles with arenes using low-cost and commercial available GO as the carbocatalyst. Control experiments and small-molecule mimicking studies reveal that that acidic groups and quinone-type functionalities in GO are synergistically utilized for activating the oxindoles, which allows the sequential Friedel-Crafts-type reaction with electron-rich arenes. To broaden the classes of CDC reactions catalyzed by GO, we have also examined the carbocatalytic cross-coupling of oxindoles with thiophenols to directly construct 3-sulfenylated oxindoles for the first time,[7] with good to excellent yields via radical-induced coupling reactions.

First, *N*-methyl-3-phenyl-2-oxindole (**1a**) and anisole (**2a**) were reacted in the presence of various graphene-related materials, as shown in Table 1. No product was observed when the reaction was conducted at 120 °C in the absence of GO (entry 1). The coupling product (**3a**) was formed in 91% yield when using 50 wt% of GO (entry 2). However, b-GO (base-treated GO, entry 3), r-GO (highly-reduced GO, entry 4) and other carbonaceous materials, such as graphite (entry 5) and active carbon (entry 6) that possess much fewer oxygen functionalities, showed no catalytic activity. These results suggest that oxygen functional groups on the GO surface play vital roles in this cross-coupling system. Further studies revealed that the amount of GO had great impact on the yield of **3a** (entry 7-8). The influence of metal impurities in GO was excluded (see Figure S1 in the Supporting Information). Finally, the optimal conditions were identified by performing the reaction with 0.2 mmol of **1a**, 50 wt% of GO in 2 mL anisole at 120 °C for 3 h.

Table 1. The dehydrogenative arylation of **1a** with **2a**[a)]



Entry	Catalyst	Catalyst amount (wt%)	Yield (%)[b)]
1	-	-	0
2	GO	50	91
3	b-GO	50	0
4	r-GO	50	0
5	Graphite	50	0
6	Active carbon	50	0
7	GO	40	78
8	GO	30	62

a) The reaction of **1**a (0.2 mmol) in the presence of the catalyst in anisole (2 mL) at 120 °C for 3h under an air atmosphere. b) Yield was determined by ^{1}HNMR with 1,3,5-trimethoxybenzene as an internal standard substance.

Under the optimized conditions, the reaction scope was explored with various substituted 2-oxindoles (Scheme 1). Unsubstituted 2-oxindolegaves the corresponding products **3b** in 76% yield. Using *N*-methyl-2-oxindole (R_2 = H) (**1c**) as the substrate, multi-steps cross-coupling of **1c** with anisole gave the di-substituted product **3c** in 67% yield. When R_2 was 4-CH_3Ph, the reaction furnished the corresponding product in a slightly lower yield (**3d**, 66%). A diverse set of substituted *N*-methyl-3-benzyl-2-oxindoles were all smoothly coupled with anisole, affording the corresponding products **3e**-**3h** in good to excellent yields (73~92%). Next, the region-selective cross-coupling reactions were examined with a variety of electron-rich arenes **2**. It is noteworthy that the reactions showed extremely high region-selectivity to produce one regioisomer product in good yields (**3j**–**3l**). Hydroxy groups, which hardly survived in traditional approaches, were well-tolerated to give the coupling products **3m-n** in moderate to good yields. This protocol was also applicable to heterocyclic aromatic compounds, producing the products **3o**–**3p** in a range of 47-67% yields. When using toluene or chlorobenzene as arene substrates, no coupling products were observed, which was consistent with the nature of Friedel–Crafts-type reactions.[6n, 8] Interestingly, the carbocatalytic CH-CH coupling strategy could be successfully extended to α-arylation of deoxybenzoins (**3q**-**3s**) in acceptable yields, making this carbocatalytic CDC strategy much more appealing.

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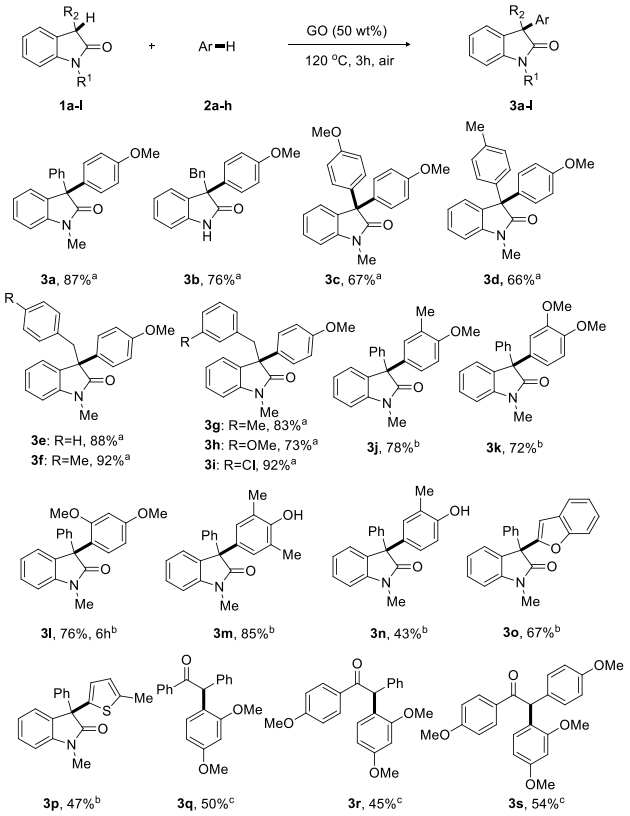
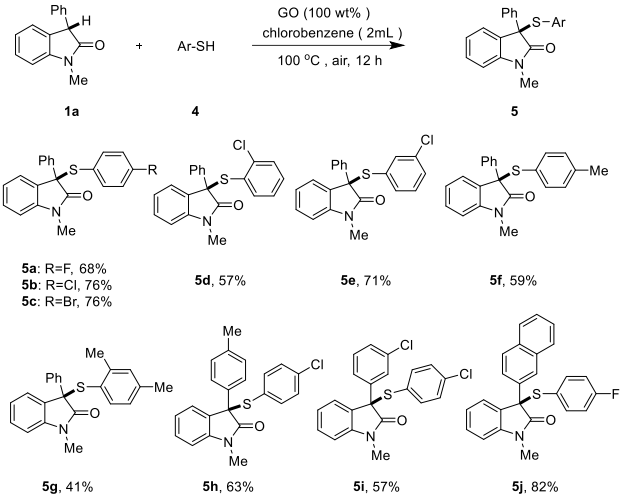


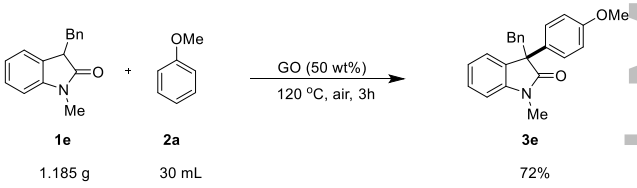
Scheme 1. General reaction conditions: oxindoles (0.2 mmol) and 50 wt % of GO in anisole (2 mL) at 120 °C for 3h under an air atmosphere, b) oxindoles (0.2 mmol), aromatic substrates (0.6 mmol) and 50 wt % of GO in 1,2-dichlorobenzene (2 mL) at 100℃ for 5h. c) deoxybenzoins (0.2 mmol), aromatic substrates (0.6 mmol) and 100 wt % of GO in dichloroethane (2 mL) at 85℃ for 10 h. d isolated yields.

3-Thio-substituted oxindoles and their derivatives are important in bioactive molecules as well as natural products.[9-13] Traditional methods for synthesis these include the direct sulfenylation of oxindoles with sulfenylating agents, such as N-thioimides[12] and disulfides[13], or nucleophilic substitution of prefunctionalized oxindoles such as 3-hydroxy-oxindoles by acid-catalyst.[11] The direct cross-dehydrogenative-coupling of oxindoles and thiophenols for the construction of 3-sulfenylated oxindoles is highly desired but still unexplored.[7] To this end, we turned our attention to the CDC reactions of oxindoles with thiophenols using the GO carbocatalyst. Under the established conditions (see scheme 2), thiophenols bearing electron-withdrawing substituents such as F, Cl, Br furnished the desired products in 57-76% yields (**5a-5e**). Thiophenols with electron-donating substituents gave the products in 41-59% yields (**5f-5g**). A series of substituted oxindoles were also comparable with the synthesis conditions, producing the coupling products in good yields (**5h-5j**).



Scheme 2. General reaction conditions: oxindoles (0.2 mmol), thiophenols (0.6 mmol) and 100 wt % of GO in PhCl (2 mL) at 100℃ for 12h under an air atmosphere, all yields refer to isolated products based on oxindoles.

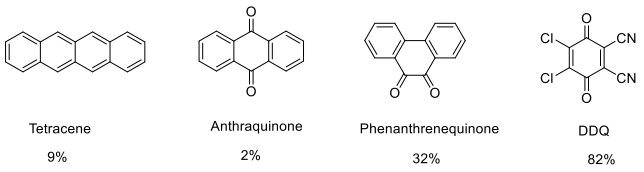
Carbocatalysis using GO materials could be easily scaled up as they are low-cost and abundantly available. Herein, arylation of 3-substituted oxindoles, a chosen model reaction, was scaled up to the gram level by using GO (0.59 g, 50 wt%), **1e** (1.185 g, 5 mmol) and anisole as the substrate, successfully furnished the desired product **3e** in 72% yield.



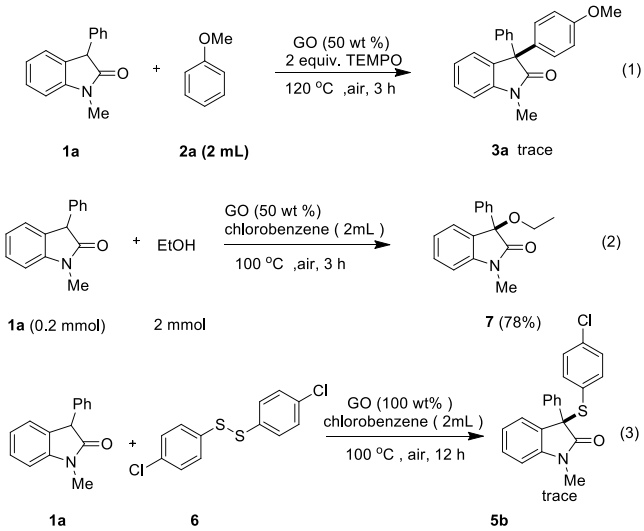
Scheme 3. Gram-scale reaction of arylation of 3-substituted oxindoles.

To probe the origin of GO's catalytic activity in the arylation of 3-substituted oxindoles, the surface-functionalities of GO was fine tuned.[1h] First, r-GO, where most of the oxygen functionalities were removed by high-temperature annealing (800 °C),[3i] showed no reactivity, indicating the importance of oxygen-functionalities. We next utilized the small molecule analogues to mimic the active-domain in GO to repeat the catalytic behavior of GO in such CDC coupling. $TsOH{\cdot}H_2O$ (*p*-Toluenesulfonic acid monohydrate) herein was used to mimic the acidic nature of GO; tetracene, anthraquinone, 9,10-phenanthrenequinone and DDQ (2,3-Dichloro-5,6-dicyano benzoquinone) were used respectively to mimic other active sites. As shown in Table 2, tetracene, anthraquinone, 9,10-phenanthrenequinone and DDQ (2,3-dichloro-5,6-dicyano benzoquinone), gave 9%, 2%, 32% and 82% yields, respectively (see scheme 4). As expected, either DDQ or $TsOH{\cdot}H_2O$

alone showed no reactivity (Table 2, entries 5-6). These experiments indicate that the acidic groups and quinone-type functionalities in GO worked synergistically in promoting the CDC couplings. Our further study also confirm that hydroxyl and epoxide oxygen-functionalities inevitably lost during the heating process may not have contributed to the catalytic pathways, but could be benefit to the reaction as an oxidant (See Figure S3, Table S2).



Scheme 4. Evaluation of small molecular analogue mimics. Reaction conditions: oxindoles (0.2 mmol), $TsOH{\cdot}H_2O$ (0.2 mmol) and small molecular (0.5 mmol) in anisole (2 mL) at 120 °C for 3h under an air atmosphere. Yield was determined by ^{1}HNMR with 1,3,5-trimethoxybenzene as an internal standard substance.



Scheme 5. Control experiment.

To investigate the reaction pathway, a radical inhibition experiment was conducted using TEMPO (2,2,6,6-tetramethyl piperidinooxy) as blocker (Scheme 5).[14] As expected, no desired product was detected, confirming that the catalysis proceeds via a radical reaction pathway. The radical intermediate could be further oxidized to the cation species which was trapped by alcohol, which indicated the existence of cation species under the reaction condition. (eq 2). [15] In addition, when using bis(4-chlorophenyl) disulfide **6** instead of thiophenol, no desired product **5b** could be observed, indicating that **6** is not the intermediate (eq 3).[4]

Based on these findings, a plausible mechanism is proposed in Figure 3. First, the inherent surface acidity of GO activates the oxindole substrate **1a** so that it tautomerizes to its enol form,[6n,16] which is easily oxidized to the corresponding radical **A'** via a single-electron-transfer (SET).[16] Then, radical **A'** is oxidized to the cation species **B'** by GO. The sequential Friedel-Craft-type coupling of intermediate **B'** with anisole (**2a**) provides 3-aryloxindoles **3a** via intermediate **C'**. Single-electron-transfer (SET) oxidation of thiophenol promoted by GO gives a sulfur radical **6**, which undergoes a radical-induced coupling with intermediate **B'** to afford the 3-sulfenylated oxindoles **5** .[6n,8]

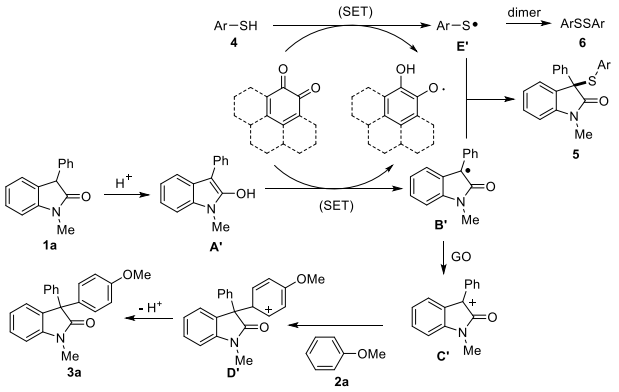


Figure 3. Plausible reaction mechanism.

In summary, we have developed GO-catalyzed cross-dehydrogenative coupling of oxindoles with arenes and thiophenols for the rapid construction of 3-aryloxindoles and 3-sulfenylated oxindoles via a metal-free and sustainable process. The acidic nature of GO as well as its quinone-type functionalities work synergistically in promoting the CDC couplings. This metal-free strategy has a broad substrate scope with high atom economy and affords several advantages, such as being metal-free, and good scalability. This study suggests that GO materials are expected to lead to the discovery of new organic transformations.

Experimental Section

General procedure for the CDC coupling of oxindole with anisole: A mixture of 3-substituted-2-oxindole (0.2 mmol) and 50 wt % of GO in anisole (2 mL) were stirred at 120 °C for 3h under an air atmosphere. The mixture was cooled to room temperature, and the anisole was removed under reduced pressure. The residue was purified by flash column chromatography eluted with ethyl acetate/petroleum ether to afford the desired product (**3a**-**3i**).

General procedure for the CDC coupling of oxindole with activated arenes: A mixture of oxindoles (0.2 mmol), aromatic substrates (0.6 mmol) and 50 wt % of GO in 1,2-dichlorobenzene (2 mL) were stirred at 100℃ for 5h. The mixture was cooled to room temperature, and the residue was purified by flash column chromatography eluted with ethyl acetate/petroleum ether to afford the desired product (**3j**-**3p**).

General procedure for the CDC coupling of deoxybenzoins with activated arenes: A mixture of deoxybenzoins (0.2 mmol), aromatic substrates (0.6 mmol) and 100 wt % of GO in dichloroethane (2 mL) were

stirred at 85℃ for 10h.The mixture was cooled to room temperature, and the residue was purified by flash column chromatography eluted with ethyl acetate/ petroleum ether to afford the desired product (**3q-3s**).

General procedure for the CDC coupling of oxindole with thiophenols: A mixture of oxindoles (0.2 mmol), thiophenols (0.6 mmol) and 50 wt % of GO in PhCl (2 mL) at 100℃ for 12h under an air atmosphere. The mixture was cooled to room temperature, and the residue was purified by flash column chromatography eluted with ethyl acetate/petroleum ether to afford the desired product (**5a-5j**).

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Graphene-Oxide-Catalyzed Cross-Dehydrogenative Coupling of Oxindoles with Arenes and Thiophenols

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Hongru Wu[a], Chuntian Qiu[a], Zhaofei Zhang[a], Bing Zhang[a], Shaolong Zhang[a,b], Yangsen Xu[a], Hongwei Zhou[c], Chenliang Su[a]*, Kian Ping Loh[b]