Carbocatalytic Oxidative Dehydrogenative Couplings of þÿ(Hetero)Aryls by Oxidized Multi Walled Carbon N Liquid Phase

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# Carbocatalytic Oxidative Dehydrogenative Couplings of (Hetero)Aryls by Oxidized Multi-Walled Carbon Nanotubes in Liquid Phase

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Abstract: HNO$_3$-oxidized carbon nanotubes catalyze oxidative dehydrogenative (ODH) carbon-carbon bond formation between electron-rich (hetero)aryls with O$_2$ as a terminal oxidant. The recyclable carbocatalytic method provides a convenient and an operationally easy synthetic protocol for accessing various benzofused homodimers, biaryls, triphenylenes and related benzofused heteroaryls that are highly useful frameworks for material chemistry applications. Carbonyls/quinones are the catalytically active site of the carbocatalyst as indicated by model compounds and titration experiments. Further investigations of the reaction mechanism with a combination of experimental and DFT methods support the competing nature of acid-catalyzed and radical cationic ODHs, and indicate that both mechanisms operate with the current material.

At present, carbocatalytic gas-phase oxidative dehydrogenative (ODH) reactions of hydrocarbons are well established and numerous studies have identified carbonyl/quinoidic groups as active sites in various carbon materials.[1,2] Likewise, carbocatalyzed liquid-phase reactions have been recently undergoing fast developments.[3] Graphene oxide (GO),[4] one of the most highly oxidized forms of carbon, has been a popular choice as a carbocatalyst or in many cases as a stoichiometric oxidant (henceforth we call the latter as *carbon-mediated* reactions).[5] The GO contains carboxylic, anhydride, phenolic, and lactone groups mainly on edges, while epoxy and hydroxyl groups lie on the basal plane of the material. These and other oxygen containing functional groups, together with edges and defects on the carbon framework, can contribute to both the stoichiometric and the catalytic activity of GO and other carbon materials such as carbon nanotubes (CNT) or active carbons (AC).

Most of the published liquid-phase carbocatalytic or carbon-mediated reactions are functional group modifications: oxidations, reductions, or conversions based on acid-base chemistry. Meanwhile, reports on direct carbocatalytic (or carbon-mediated)
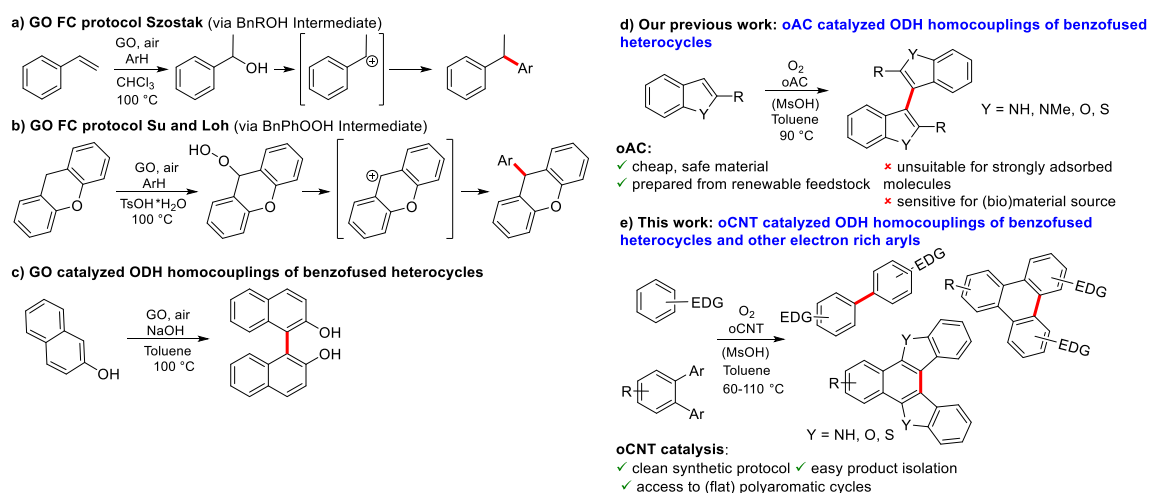
Scheme 1. Previous and current carbocatalyzed ODH C-C bond forming couplings

carbon-carbon bond formations from non-functionalized substrates are still rare. Notably, Friedel-Crafts (FC) alkylations of styrenes and benzyl alcohols,[6] and xanthanes (Scheme 1b)[7] by GO in presence of air have been recently reported. From a strict mechanistic view, both reactions operate in a cascade manner: the GO catalyzed C-H oxygenation to C-OH or C-OOH is followed by an acid catalyzed carbocation formation leading eventually to FC-coupling with the aryl substrate. Moreover, analogic FC-protocol has been developed to activate allylic alcohols towards thiophene nucleophiles.[8] Also oxidative GO-mediated homocouplings of electron-rich aryls[9] and GO-catalyzed couplings of 2-naphtol derivates (Scheme 1c) have been described.[10]
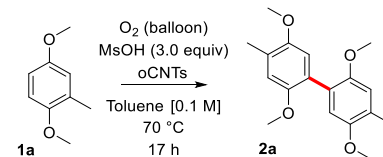
We have previously reported that oxidized active carbon (oAC) can catalyze the C-C bond-forming ODH reactions of indoles and analogues in the presence of O_2,[11] where experimental evidences point the reaction to proceed via radical mechanism by quinoidic oxygen centers.[12,13] Based on this, we envisioned that carbocatalysis could be used as a heterogeneous replacement for oxidative processes that are catalyzed or mediated by molecular quinones,[13,14] transition metals,[15] hypervalent iodines,[16] or nitrosoniums.[17] To that end, oxidized carbon nanotubes (oCNTs) would be the most suitable candidates as they offer significant advantages over oAC such as the high mechanical strength, better stability towards oxidation by O_2,[18] and fewer micropores susceptible to catalyst deactivation.[19] Still, we found only a few examples in the literature of liquid-phase carbocatalysis that utilize oCNTs such as the catalytic nitrobenzene reductions by Su and co-workers.[20] Here we report for the first time that oCNTs are highly efficient catalysts for forming C-C bonds oxidatively between two unfunctionalized positions of electron-rich aryls. Furthermore, easy setup, workup, and recyclability of oCNTs allow a facile replacement of traditional methods for these reactions with abundant carbon catalyst and oxygen, which is of high urgency with relation to current guidelines on sustainability of chemical processes and endangered elements.

We selected HNO_3-oxidized multi-walled (MW)CNTs out of the several reported materials[21] for catalysis testing as the oxidation procedure is well-studied including the spectroscopic and thermogravimetric analysis of produced functional groups on the MWCNTs.[22,23] For the test reaction of catalysis we selected dimerization of **1a** (Table 1) to **2a** as it is one of the prototypical ODH-reactions that has been studied with different oxidative systems such as DDQ/H+,[24] PIFA,[25] $MoCl_5$,[26] $NaNO_2$/H+,[27] electrolysis,[28] $FeCl_3$/SiO_2,[29] and MnO_2/BF_3□OEt_2.[30]

Using toluene as solvent, we screened several variables such as temperature, molarity, reaction time, loading of catalyst and the amount of MsOH additive (SI), which is known to increase oxidation potential of molecular quinones.[31] The temperature and the amount of catalyst affected the activity most from these variables. Finally, **2a** was obtained with 82% isolated yield.

Additional experiments with different conditions or catalysts were carried out to investigate the nature of the catalysis (Table 1). In the absence of MsOH or oCNT, reaction does not proceed (entries 2 and 3). The yield also drops to 16% when reaction is performed under Ar (entry 4). Similarly, reaction time reduction to 5 h lowers the yield to 36% (entry 11). In comparison with oCNTs, different oxidatively treated AC materials perform modestly with yields of 39% and 53% (entries 8 and 9) while a slightly better yield of 63% was received with untreated AC (entry 7). Also GO gave a relatively poor yield (entry 10). The related oxidation ability of AC has been previously associated to absorbed oxygen in AC that enables some stoichiometric activity in ODH couplings.[32] The HCl-treated CNTs provide a poor yield of 27% (entry 6). It has been shown that this treatment lowers overall oxygen content of MWCNTs.[22]

Table 1. Deviation to the standard reaction conditions

Entry:	Deviation from standard conditions	Yield [%]
1	None	83 (82)[a]
2	no MsOH	0
3	no oCNTs	0
4	Ar-atmosphere	16
5	CNTs instead of oCNTs	66
6	HCl-treated CNTs instead of oCNTs	27
7	Active carbon (AC) instead of oCNTs	63
8	Air oxidized AC instead of oCNTs	39
9	HNO_3-oxidized AC instead of oCNTs	53
10	GO instead of oCNTs	24
11	5 h reaction time	36
12	Anisole as solvent	9

[a] Isolated yield
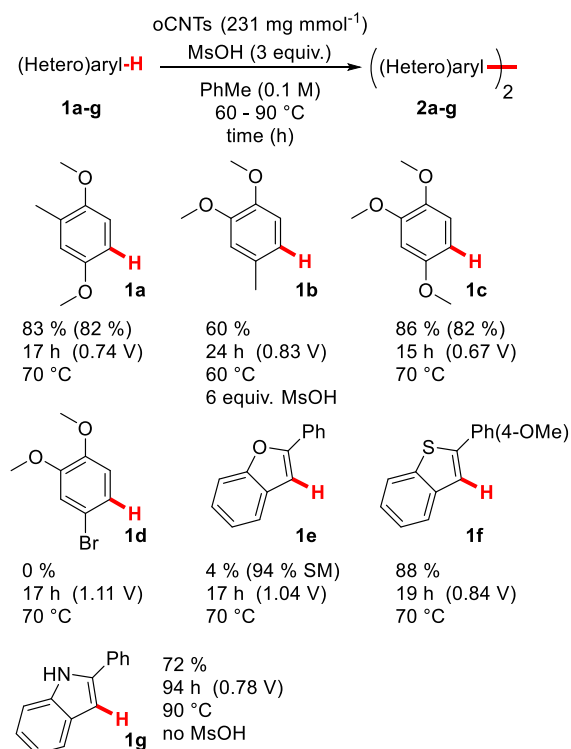
Scheme 2. Intermolecular coupling scope (V vs. Fc).

Next, we explored different intermolecular couplings of (hetero)arenes (Scheme 2). The coupling product **2c** was obtained in a high 86% yield after 15 h at 60 °C, and **2b** was obtained in a 62% yield after 24 h at 70 °C. These yields

correlated well with the oxidation potentials of the substrates. We found out the oxidation potential limit for substrate to be reactive is *ca.* 1.1 V (Fc): this is best seen by comparing two borderline substrates, **1d** and **1e**, with oxidation potentials of 1.11 V and 1.05 V, respectively. **1d** was not reactive, while 5% yield of coupling product of **1e** was obtained. The lower oxidation potentials of arenes **1a-c** (0.67 – 0.83 V) seem to favor the couplings. In accordance, the low oxidation potentials of heteroarenes **1f** and **1g** (0.84 V and 0.78 V, respectively) are in agreement with their facile conversion to **2f** and **2g** (without MsOH) with 88% and 72% yields, respectively.

Likewise, oCNTs can catalyze several intramolecular cyclodehydrogenations with slightly modified reaction conditions (Scheme 3). Cyclization of **3a** to **4a** proceeds with an excellent 91% yield, while **3b** was converted to **4b** with an 88% yield. Interestingly, **3c** required a very long reaction time and after 6 days, 29% yield was obtained together with 60% of unreacted starting material. To our pleasure, **4d**, which has been indicated as potential substructure for p-type organic semiconductors[33] and promising framework for optoelectonic applications,[34] was obtained in an 84% yield. Similarly, **4f**, substructure found in molecules with interesting chiroptical properties for *e.g.* spintronic devices,[35] was obtained in 82% yield. Also, **4e** could be obtained in 21% yield. This framework has been used in a host-material for C_{60}-fullerenes.[36]

Concerning the catalytic active site, we have previously observed a correlation between the catalytic activity of the oAC and the amount of carbonyl groups in it.[12] In order to trace whether oCNTs behave similarly, the catalyst was treated with phenyl hydrazine (PH) to selectively block the carbonyl/quinone groups of oCNTs.[37] When PH-oCNTs were used as catalyst, yields of **2a** and **4a** dropped to 0%. Furthermore, when oCNTs were replaced with tetracene, anthraquinone or 9,10-phenanthrenequinone, yields received were 0%, 3%, and 21% of **2a**, respectively (Figure 1, top). Recently, these compounds have been used as model compounds for zig-zag edges and carbonyls/quinones.[7,38] These experiments indicate that carbonyls/quinones are the catalytically active sites. The presence of C=O groups (0.74% at) as well as O=C-O (5.55% at) and C-OH groups (3.84% at) were confirmed with XPS surface analysis of oCNT (Figure 1, bottom). Also no metals were detected on the surface in the same XPS survey. The EDX-analysis, however, showed that CNT-materials contain ca. 1 wt% of embedded Co and Mo that could not be removed by HCl or HNO_3 treatments (SI). Similar abundance of these metal impurities were found in ICP-OES analysis of untreated CNTs, HCl-washed CNTs and oCNTs. Importantly, both HCl and HNO_3 treatments decrease the amount of the metallic impurities whereas HCl treatment decreases and HNO_3 treatment increases the yield of the test reaction. With ICP-MS, we also detected low quantities of potentially catalytic metals such as Ni (<1000 ppm), Cu (<200 ppm), Pd (<0.4 ppm), while the lowest amounts were found for oCNT (Table S2, SI). Notably, the strong correlation between the catalytic activity and quinoidic groups is clear based on several experiments, i.e., XPS, model compound study, C=O blocking experiment, catalytic studies with other carbon materials, and electrochemistry.
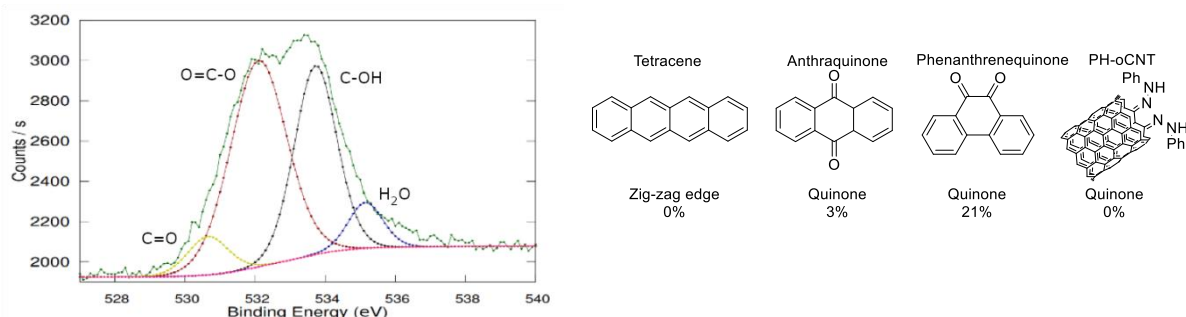

Figure 1. Top: Yields of **2a** received with model compounds and PH-titrated oCNTs. Bottom: O1s XPS of oCNT.

Two previously discussed intramolecular mechanisms were studied computationally for *o*-terphenyls **3a–c** in Scheme 3:[14,31,39] acid-catalyzed mechanism operating *via* arenium ion (**B-D**, Figure 2), and mechanism operating via radical cation (**E-F**, Figure 2). We do not consider the widely accepted gas-phase quinoidic hydrogen atom abstraction ODH-mechanism[40] to be important in our acidic conditions. To understand how different quinoidic groups with varying electronic properties affect the mechanism, we studied two catalysts that were experimentally tested with the intermolecular reaction: 9,10-phenanthrenequinone (PhQ, Figures 1 and 2) and anthraquinone (AQ, Figures 1 and S4). Protonated catalyst, PhQ, oxidizes the substrates exergonically (**E**) and reversibly, and the radical cation (**E**) present the free energy minimum for the reactions, see Figure 2. The formed radical cation can cyclize directly to form the C-C bond with activation free energies of 24.7, 25.5, and 38.8 kcal/mol in Figure 2, for **3a**, **3b**, and **3c**, respectively. While the barriers for **3a** and **3b** are in accordance with the experimental yields: 91% and 88%, respectively, the activation free energy for radical cationic C-C bond formation for **3c** is considered too high. The acid-catalysed C-C bond formation, however, is lower in energy and thus obtained activation free energy for **3c** is 34.1 kcal/mol, while the radical cationic mechanism is still operative with **3a** (24.7 kcal/mol) and **3b** (25.5 kcal/mol). Therefore, we consider that substrates with activated nucleophilic bond-forming carbon, *i.e.*, **3a** and **3b**, react *via* radical cationic mechanism, while for **3c** the arenium cation mechanism is prevalent. Furthermore, depending on the proton affinity and redox potentials of the oxidant, the oxidation (**E**) can become endergonic (AQ in Figure S4) and favour arenium cation mechanism for all **3a–c**, or even more exergonic and drive the reaction *via* radical cationic C-C bond formation also with **3c**, see *ortho*-benzoquinone in Figure S4. The shift in operative mechanism is thus not only

dependent on the substrate but also on the nature of the quinoidic groups of the oCNT. Moreover, we observed aromatic proton-deuterium exchange during the coupling of **1a** to **2a** under acidic conditions in d_{12}-toluene (SI), which is in accordance with the reversibly nature of the oxidation and the protonation.
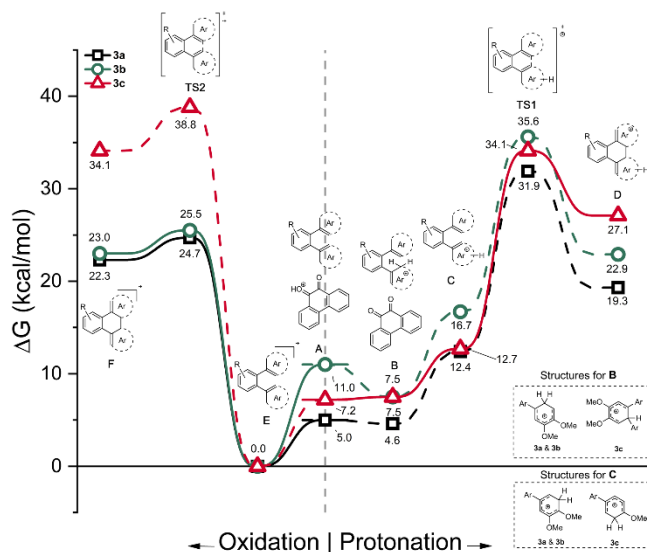

Figure 2. Energy profiles with phenanthrenequinonium cation for oxidation induced (to left) and acid-catalyzed (to right) C-C bond formation for **3a** (black square), **3b** (green circle), and **3c** (red triangle). Favored pathway is presented with solid line. See SI for full details.

Recyclability of the carbocatalyst was tested on a cyclodehydrogenation of **3a** to **4a** with ~230 mg of catalyst. In the first step, yield of 81% of **4a** was obtained after 13 h. In the second cycle, yield of 73% was recorded. However, in this case, reaction time had to be increased to 1 d for a full conversion. The 3rd, 4th and 5th cycle gave 72%, 77% and 75% yields after 1 d, respectively, confirming the good recyclability of the catalyst. The XPS analysis of catalyst after five cycles shows an increase of oxygen content, specifically in the abundance of C-O groups (3.8% to 12.2%), but also in reduced amounts of C=O groups (0.74% to 0.18%, SI). This could be interpreted as wearing of active sites of oCNT. However, for a great part, the C-O content increase can be explained by the absorption of some starting material / product (**3a/4a**) on oCNTs that is also observed by a mass increase of the recycled catalyst. Correspondingly, some C-O group can arise from reduction of C=O (quinone to hydroquinone conversion), which is expected to be reversible under reaction conditions.

To further elucidate the acid additive effects on the redox behaviour of oCNTs, we measured cyclic voltammograms (CV) from differently functionalized CNTs in various H_2SO_4 concentrations (Figure 3 and SI). The CV recorded for untreated CNT is very close to those previously reported in the literature.[41] The oxidative treatment increases the overall current densities. Electrochemical response in 100 – 400 mV (vs. SCE) potential region has been associated to the *o*-quinones in graphite electrode materials.[42] Notably, upon an increase of the acid concentration, a gradual shift of reduction peak potentials are observed in both regions *i.e.* protons participate in the oCNT redox process (See further discussion in SI).
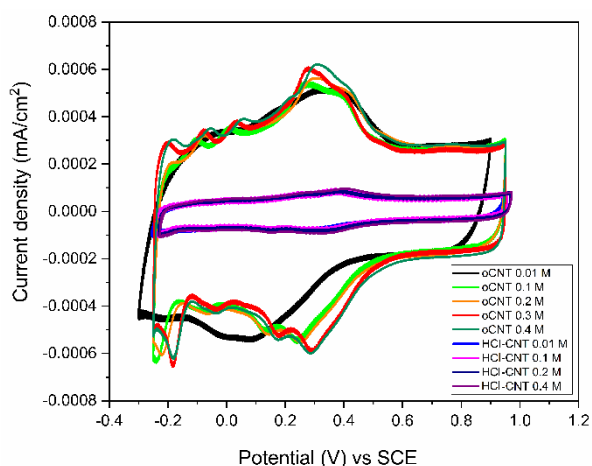

Figure 3. CV of HCl treated CNT and oCNT measured in various H_2SO_4 concentrations. Scan rate: 50 mV/s.

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In conclusion, we have devised oCNT catalysis for a diverse set of electron rich substrates to complete ODH C-C coupling reactions utilizing O_2 as a terminal oxidant. To our knowledge, this is the first example of a C-C coupling by CNT catalysis. The catalyst can be used in the synthesis of several important frameworks for materials chemistry and it displays recyclability. Catalytic activity is associated to the presence of quinoidic oxygens and is improved by MsOH additive. We anticipate that the development of oCNT-materials with better oxidative powers facilitate the discovery of new carbocatalytic reactions.

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TOC

Catalysis with carbon material: HNO_3-oxidized carbon nanotubes catalyze oxidative dehydrogenative (ODH) carbon-carbon bond formation between electron-rich (hetero)aryls with O_2 as a terminal oxidant.