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Mild and selective catalytic oxidation of organic substrates by a carbon nanotube-rhodium nanohybrid†

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A heterogeneous catalyst was assembled by stabilization of rhodium nanoparticles on carbon nanotubes. The nanohybrid was used for the catalytic aerobic oxidation of diverse substrates such as hydroquinones, hydroxylamines, silanes, hydrazines and thiols, at room temperature. The system proved very efficient on the investigated substrates and demonstrated high selectivity.

The selective oxidation of organic compounds under mild conditions is of practical importance in synthetic chemistry. In addition to classical stoichiometric processes, catalytic systems have been devised to perform oxidation reactions.[1] Further improvements in terms of sustainability were also achieved by supporting the catalysts, thus allowing their reclaim and reuse.[2] Among the various catalyst supports, nanostructured carbon allotropes, in particular carbon nanotubes (CNTs), have emerged as highly promising platforms that provide unique advantages such as chemical, thermal, and mechanical stability in liquid media, inertness, high specific surface area, and chemically tunable topography.[3] We previously reported supramolecular assemblies of metallic nanoparticles (*e.g.* Au, Pd, Ru) on carbon nanotubes. These assemblies afforded metal-coated CNTs that were subsequently used in the heterogeneous catalysis of various organic transformations.[4] In the course of our investigations we demonstrated that CNTs acted as synergistic support capable of enhancing the performances of the catalytic metal. With these critical features in mind, we sought to expand the scope of our nanohybrid systems by developing a catalyst that would promote a broad scope of oxidation reactions under mild and sustainable conditions. In the present article, we report the assembly and use of a CNT-supported rhodium catalyst (Fig. 1) for the selective oxidation of various substrates, including hydroquinones, silanes, hydroxylamines, hydrazines, and thiols.

The CNT-rhodium catalyst was assembled using a layer-by-layer approach according to a procedure adapted from our previous work.[4a] Briefly, carbon nanotubes were first sonicated in the presence of amphiphilic nitrilotriacetic-diyne (DANTA) surfactants in water, leading to the formation of supramolecular structures with a nanoring shape at the surface of the CNTs. While the hydrophobic portion of DANTA was adsorbed at the surface of the CNTs by van der Waals interactions, its hydrophilic head was oriented outward, at the interface with the aqueous medium. The rings were subsequently polymerized by UV irradiation which reinforced the cohesion of the assembly around the CNT. In a second step, a polycationic polymer (PDADMAC) layer was deposited on

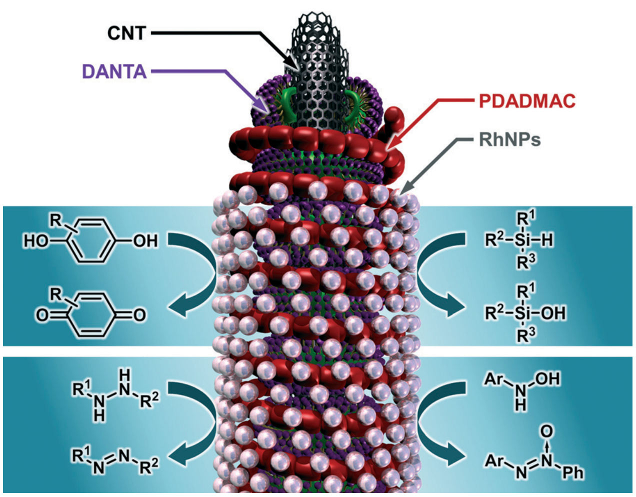

Fig. 1 Overview of the catalytic assembly and several oxidation processes studied in the present work.

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the primary coating and rhodium nanoparticles (RhNPs) were added to afford the final nanohybrid (RhCNT). Transmission electron microscopy (TEM) indicated that the RhNPs were of spherical shape, and size evaluation by statistical diameter measurement gave a mean particle diameter of *ca.* 2 nm (Fig. 2). The metal content of the aqueous RhCNT suspension was determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis which gave a Rh concentration of 5 mM.

With the rhodium-based nanohybrid in hands, we first investigated its potential in the aerobic oxidation of hydroquinones. The treatment of the latter compounds with cerium ammonium nitrate or chromium oxidants is a classical route to produce quinones.[5] Recent developments, exploiting milder conditions, have been reported by Kobayashi *et al.*[6] using polymer incarcerated noble metal particles, by the group of Bianco using carbon nanotube-supported silver nanoparticles with hydrogen peroxide,[7] and by our group using gold supported on CNTs in alkaline medium.[4c]

The rhodium-based catalytic system was set by working with 0.25 mol% of the RhCNT hybrid in a mixture of chloroform and water, under air (open flask), and at room temperature. These base-free conditions constitute an interesting improvement over our recently reported system using AuCNT/K_2CO_3.[4c] Under these conditions, hydroquinone **1a** was fully converted into *para*-quinone **2a** within 5 h (Table 1, entry 1).

One of the advantages of using heterogeneous catalysis is the possibility to recycle the catalyst, thus reducing the cost and environmental impact of the process. To investigate this key feature, five successive oxidations of **1a** were performed with the same RhCNT sample which was recovered by centrifugation after each cycle and reused in the next reaction. No significant decrease of the catalytic activity was observed throughout the different oxidation cycles as quinone **2a** was produced in nearly constant yields (94–96%, Table S1†).

To explore the scope of the process, several other 1,4-hydroquinones were treated under the above conditions. Among these, electron-rich trimethyl-substituted **1b** as well as 1,4-dihydroxynaphthalene **1c** were readily converted to the corresponding 1,4-quinones (entries 2 and 3) in 99 and 98% yields, respectively. On the other hand, chlorinated hydroquinone **1d** was only partially converted into the corresponding quinone **2d** after 5 h‡ (60% yield, entry 4) and electron-deficient acetyl-substituted hydroquinone **1e** could not be oxidized, even upon prolonged exposure to the RhCNT catalyst (entry 5). As an example of the oxidation of 1,2-hydroquinones, the transformation of *tert*-butyl-substituted catechol (**1f**) into the corresponding *ortho*-quinone was efficiently carried out, but required 15 h of reaction to afford a satisfactory yield of product (97% yield, entry 6).

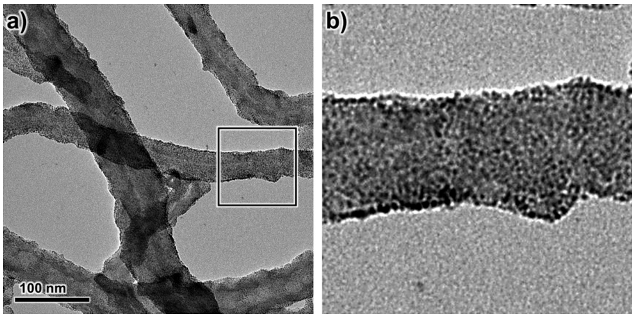
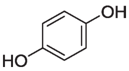
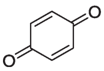
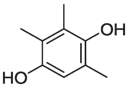
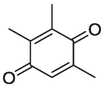
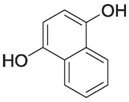
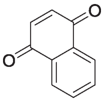
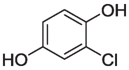
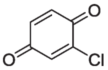
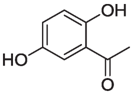
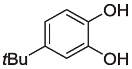
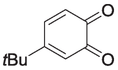


Fig. 2 a) TEM image of the RhCNT hybrid and b) 400% magnification of the boxed area.

Table 1 Scope of the RhCNT-catalyzed oxidation of hydroquinones[a]

Entry	Substrate	1	Product	2	Yield[b]
1		**1a**		**2a**	96%
2		**1b**		**2b**	99%
3		**1c**		**2c**	98%
4		**1d**		**2d**	60%
5		**1e**	—	**2e**	NR[c]
6[d]		**1f**		**2f**	97%

[a] Conditions: **1** (0.2 mmol), RhCNT (0.25 mol%, 100 μL of a 5 mM aqueous suspension), $CHCl_3/H_2O$ 3 : 1 (1 mL), room temp., open flask (air), 5 h. [b] Isolated yields. [c] No reaction. [d] After 15 h of reaction.

It should be noted that the transformation proceeds with low amounts of RhCNT hybrid at room temperature and requires neither base nor added oxidant species. Thanks to these features, the system stands out as one of the most convenient catalysts described so far for the oxidation of hydroquinones.

We next turned our attention to the aerobic oxidation of silanes. The latter are classically converted to silanols using strong oxidizing agents (*e.g.* osmium tetroxide, permanganate, ozone, peracids, or peroxides)[8] but catalytic systems combining water and oxygen have been devised in recent years. Amongst the heterogeneous catalysts for silane oxidation,[9] several noble metal-based systems, such as nanoporous gold,[9a] carbon-supported palladium nanoparticles,[9g] and AuCNT[4a] have been reported but, to the best of our knowledge, rhodium-based systems have not been described so far.

Dimethylphenylsilane (**3a**) was selected as a model substrate but it failed to react under the reaction conditions that were used for the oxidization of hydroquinones. Nevertheless,

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‡ Increasing the reaction time led to some degradation products.

replacing the binary solvent mixture ($CHCl_3$/water) with THF permitted to afford silanol **4a** in 96% yield within 2 h (Table 2, entry 1) upon treatment of **3a** with 0.25 mol% of aqueous RhCNT. It is worth mentioning that no disiloxane by-product was detected by gas chromatography coupled to mass spectrometry (GC-MS).

The recyclability of the catalyst for this process was tested over five consecutive cycles (as described above). The conversion remained as efficient throughout the experiment, with yields of **4a** ranging from 93 to 96% (Table S2†), with no need to increase the reaction time.

The scope of the RhCNT-catalyzed oxidation was then investigated on a panel of silanes. To validate the high activity of the system, the oxidation of two admittedly challenging substrates (**3b** and **3c**) was undertaken. The oxidation of deactivated triphenylsilane (**3b**) afforded triphenylsilanol (**4b**) in excellent yield (entry 2) in contrast to previously reported supported catalyst. The complete oxidation of hindered triisopropylsilane (**3c**) into silanol **4c** was also achieved (entry 3) even though it required more time than other substrates. As another example, diphenylsilane (**3d**), which contains two Si–H bonds to be oxidized, was quantitatively transformed to the corresponding diphenylsilanediol **4d** (entry 4). Finally, benzyldimethyl silane **3e** was also selectively converted to its silanol counterpart **4e** (entry 5) despite the formation of trace amounts of condensation by-products (<5% of disiloxane).

We then investigated the RhCNT-mediated oxidation of hydroxylamines through which we expected the formation of the corresponding nitroso derivatives.[10] The nanohybrid-catalyzed oxidation of *tert*-butyl hydroxylamine **5a** in $CHCl_3/H_2O$ afforded the nitroso compound **6a** in nearly quantitative yield (Table 3, entry 1). The reaction of *N*-cyclohexylhydroxylamine **5b** also cleanly produced nitrosocyclohexane **6b** in 93% yield (entry 2). It is to be noted that no isomerization of nitrosocyclohexane **6b** into the corresponding cyclohexanone oxime was detected, despite the fact that tautomerization is classically observed with substrates bearing a Cα-proton.

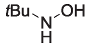
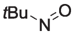
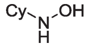
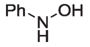
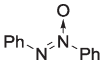
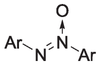
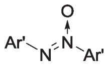
While the reaction of aliphatic substrates satisfactorily provided access to nitroso compounds in high yields, aromatic hydroxylamines behaved differently. For example, in the case of phenylhydroxylamine **5c**, a dimeric product was obtained in the form of an azoxy derivative **6c** (entry 3). The mechanism behind the conversion observed in entry 3 may follow an initial path somehow similar to that of aliphatic substrates where the starting phenylhydroxylamine **5c** is slowly oxidized into the corresponding nitroso derivative **5c′** (Scheme 1).[11] As **5c′** accumulates, its condensation with unreacted phenylhydroxylamine **5c** affords azoxy derivative **6c** after elimination of water. The same comments hold true for aromatic substrates bearing either electron-withdrawing or electron-donating substituents such as 4-cyanophenylhydroxylamine **5d** (entry 4) and 4-methoxyphenylhydroxylamine **5e** (entry 5) which led to the clean formation of the corresponding azoxy dimers **6d** (95% yield) and **6e** (89% yield), respectively. Recycling of the catalyst using phenylhydroxylamine **5c** as substrate showed no significant decrease in yields of **6c** (Table S3†).

Table 2 Scope of the RhCNT-catalyzed oxidation of silanes[a]

Entry	Substrate	3	Product	4	Yield[b]
1	$PhSi(Me)_2H$	**3a**	$PhSi(Me)_2OH$	**4a**	96%
2	Ph_3SiH	**3b**	Ph_3SiOH	**4b**	95%
3[c]	iPr_3SiH	**3c**	iPr_3SiOH	**4c**	92%
4	Ph_2SiH_2	**3d**	$Ph_2Si(OH)_2$	**4d**	92%
5	$BnSi(Me)_2H$	**3e**	$BnSi(Me)_2OH$	**4e**	93%

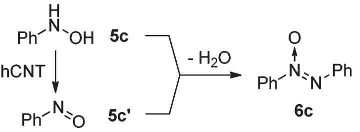
[a] Conditions: 3 (0.2 mmol), RhCNT (0.25 mol%, 100 μL of a 5 mM aqueous suspension), THF (1 mL), room temperature, open flask (air), 2 h. [b] Isolated yields. [c] After 12 h of reaction.

Table 3 Scope of the RhCNT-catalyzed oxidation of hydroxylamines[a]

Entry	Substrate	5	Product	6	Yield[b]
1		**5a**		**6a**	99%
2		**5b**		**6b**	93%
3		**5c**		**6c**	93%
4	$p(CN)C_6H_4N(H)OH$	**5d**		**6d**[c]	95%
5	$p(MeO)C_6H_4N(H)OH$	**5e**		**6e**[d]	89%

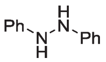
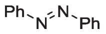
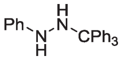
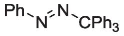
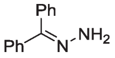
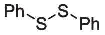
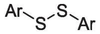
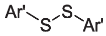
[a] Conditions: 5 (0.2 mmol), RhCNT (0.25 mol%, 100 μL of a 5 mM aqueous suspension), $CHCl_3/H_2O$ 3 : 1 (1 mL), room temperature, open flask (air), 12 h. [b] Isolated yields. [c] Ar = $p(CN)C_6H_4$. [d] Ar′ = $p(MeO)C_6H_4$.

Finally, the aerobic oxidation of hydrazines into their corresponding azo derivatives[12] and that of thiols into disulfides were explored. The reaction of 1,2-diphenylhydrazine **7a** (Table 4, entry 1) cleanly afforded, after 12 h of reaction in $CHCl_3/H_2O$, 1,2-diphenyldiazene **8a** in 92% yield. Similarly, 1-phenyl-2-tritylhydrazine **7b** reacted smoothly to give 1-phenyl-2-trityldiazene **8b** in 88% yield (entry 2). However, diphenylmethylene hydrazine **7c** did not react under our reaction conditions and remained unaffected (entry 3). On the other hand, thiophenol **7d** was converted into the corresponding disulfide **8d** within 12 h of reaction and in 96% yield (entry 4). Substituted thiophenol derivatives were also readily oxidized regardless of electronic deficiency (**7e**, entry 5) or enrichment (**7f**, entry 6). It is to be noted that the reaction is not operative with aliphatic thiols (*e.g.*



Scheme 1 Postulated mechanism for the formation of azoxy compounds.

Table 4 Scope of the RhCNT-catalyzed oxidation of hydrazines and thiols[a]

Entry	Substrate	7	Product	8	Yield[b]
1		7a		8a	92%
2		7b		8b	88%
3		7c	—	—	NR[c]
4	PhSH	7d		8d	96%
5	$p(NO_2)C_6H_4SH$	7e		8e[d]	97%
6	$p(tBu)C_6H_4SH$	7f		8f[e]	98%

[a] Conditions: 7 (0.2 mmol), RhCNT (0.25 mol%, 100 μL of a 5 mM aqueous suspension), $CHCl_3/H_2O$ 3 : 1 (1 mL), room temperature, open flask (air), 12 h. [b] Isolated yields. [c] No reaction. [d] Ar = $p(NO_2)C_6H_4$. [e] Ar′ = $p(tBu)C_6H_4$.

1-dodecanethiol). Again, recycling of the RhCNT catalyst (with 1,2-diphenylhydrazine **7a**) led to no significant decrease in yields (of **8a**) over five successive cycles (Table S4†).

Conclusions

The carbon nanotube-rhodium nanohybrid was found to be an efficient catalytic system to perform mild and selective oxidations of various substrates which include hydroquinones, hydroxylamines, silanes, hydrazines, and thiols. The nanohybrid can be readily recycled and it operates under mild conditions as reactions were conducted at room temperature, with low catalytic loading (0.25 mol%). The system proved very efficient on the investigated substrates and demonstrated high selectivity. The results obtained in the context of this study thus compare favorably to previous reports in terms of scope and overall efficiency.

Acknowledgements

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Notes and references

1 See, for example: (*a*) J. Muzart, *Chem. Rev.*, 1992, **92**, 113; (*b*) S. E. Allen, R. R. Walvoord, R. Padilla-Salinas and M. C. Kozlowski, *Chem. Rev.*, 2013, **113**, 6234; (*c*) P. Gamez, P. G. Aubel, W. L. Driessen and J. Reedijk, *Chem. Soc. Rev.*, 2001, **30**, 376; (*d*) V. Sridharan and J. C. Menendez, *Chem. Rev.*, 2010, **110**, 3805.

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