

Catalytic Oxidation of Silanes by Carbon Nanotube–Gold Nanohybrids**

Jubi John, Edmond Gravel, Agnès Hagège, Haiyan Li, Thierry Gacoin, and Eric Doris*

The selective oxidation of silanes has attracted wide interest as silanols are key synthons for the production of silicon-containing materials^[1] and nucleophilic partners in organometallic cross-coupling reactions.^[2] Silanes are classically converted into silanols using strong oxidizing agents such as osmium tetroxide,^[3] permanganate,^[4] ozone,^[5] peracids,^[6] or peroxides.^[7] However, under these reaction conditions, significant amounts of siloxanes and toxic by-products are formed. To overcome these drawbacks, catalytic systems involving water and oxygen have been recently devised. They offer the advantage of cleanly producing silanols along with hydrogen gas as the only by-product. While initial catalytic silane oxidation studies relied on homogeneous transition metals,^[8] heterogeneous catalytic systems have emerged as very promising alternatives.^[9,10] Indeed, the latter are more efficient (high conversion rate), recyclable, selective (little to no siloxane by-product formation), and usually operate under milder conditions.^[11] Amongst heterogeneous catalysts for silane oxidation, recent elegant examples include nanoporous gold by Asao, Yamamoto, and co-workers,^[9a] and hydroxyapatite-supported silver or gold nanoparticles by Kaneda and co-workers.^[10]

Herein we report an alternative strategy which has led to the discovery of the most efficient catalytic system to date for

silane oxidation. Our approach involves layer-by-layer (LBL) assembly of gold nanoparticles on carbon nanotubes (CNTs).^[12] Nanotubes provide high specific surface area and excellent nanoparticle (NP) dispersion. In addition, nanotubes are electronically active^[13] and stabilization of transient higher oxidation states of gold are anticipated by collaborative interactions with the metal.^[14] To the best of our knowledge, this is the first report on silane oxidation by CNT-supported catalysts.

The preparation of the CNT–gold nanohybrid (see the Supporting Information for details) started with aqueous self-assembly of amphiphilic nitrilotriacetic diyne lipids (DANTA) on multiwalled carbon nanotubes^[15] (Figure 1) to

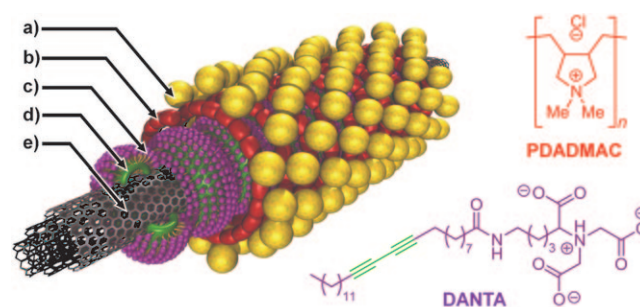


Figure 1. Schematic representation of the AuCNT nanohybrid: a) AuNP; b) PDADMAC layer; c) DANTA nanoring; d) polymerized region (green); e) multiwalled CNT.

yield a stable suspension. As previously described, DANTA self-organized as hemimicelles on the nanotube, thus giving rise to nanoring-like structures.^[16,17] While the hydrophobic portion of DANTA is adsorbed onto the CNTs through van der Waals interactions, its hydrophilic anionic head is oriented toward the aqueous phase.^[17a] To promote additional stability of the rings, the diyne motif incorporated in the lipophilic chain was photopolymerized by UV irradiation at 254 nm. Polymerization takes place within individual half-cylinders and reinforces cohesion of the assembly.^[18] After UV irradiation, the DANTA-decorated nanotubes became resistant to dialysis against water and to ethanol washes, thus indicating that the lipid assemblies were polymerized.^[16a] The second layer was thereafter deposited by stirring the suspended nanotubes with cationic poly(diallyldimethylammonium chloride) (PDADMAC) which adsorbed to the surface of the tube through electrostatic interactions with the primary anionic layer. The twice-coated CNTs were then recovered by centrifugation before a solution of freshly prepared colloidal gold nanoparticles (AuNPs) was added.^[19] The metallic NPs

[*] Dr. J. John, Dr. E. Gravel, Dr. E. Doris
 CEA, iBiTecS, Service de Chimie Bioorganique et de Marquage
 91191 Gif-sur-Yvette (France)
 E-mail: eric.doris@cea.fr

Dr. A. Hagège
 CEA, iBEB, Service de Biochimie et de Toxicologie Nucléaire
 30207 Bagnols-sur-Cèze (France)
 and
 CEA, iBEB, CNRS-UMR 6191
 13108 Saint Paul-les-Durance (France)

Dr. H. Li
 State Key Laboratory of Physical Chemistry for Solid Surfaces and
 National Engineering Laboratory for Green Chemical Productions of
 Alcohols, Ethers, and Esters, Department of Chemistry, College of
 Chemistry and Chemical Engineering, Xiamen University
 Xiamen 361005 (China)

Dr. T. Gacoin
 Laboratoire de Physique de la Matière Condensée, CNRS UMR
 7643, École Polytechnique
 91128 Palaiseau (France)

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were anchored by interaction with the polyammonium-covered nanotubes to ultimately afford the AuCNT nanohybrid assembly. Transmission electron microscopy (TEM) showed nanotubes decorated with a dense and uniform coating of monodisperse AuNPs. Size evaluation by statistical diameter measurement using selected images indicated a mean particle diameter of approximately 3 nm (Figure 2).

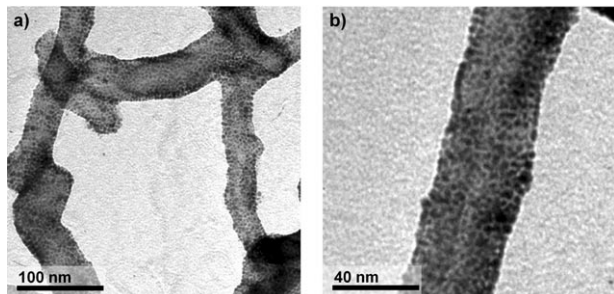


Figure 2. TEM images of AuCNT: a) Global view; b) Higher magnification.

The AuCNT nanohybrid was suspended in water and used as such in catalysis reactions. The gold concentration was measured by inductively coupled plasma mass spectrometry (ICP-MS; [Au] = 4 mM) and the metallic character was unambiguously established by X-ray photoelectron spectroscopy (XPS) analysis which showed characteristic Au 4f contributions (see the Supporting Information).

With the nanohybrid in hand, its application to silane oxidation was explored and dimethylphenylsilane (**1a**) was selected as a model substrate. Accordingly, treatment of **1a** with 0.1 mol% of the aqueous AuCNTs quantitatively afforded silanol **2a** after 45 minutes. The reaction was run in THF at room temperature under air. It is worth mentioning that no disiloxane by-product was detected by gas chromatography coupled to mass spectrometry (GC-MS). Involvement of the nanohybrid in the oxidation process was demonstrated by the following experiment: a standard oxidation reaction of **1a** was set up and, after 20 minutes, split into two equal portions. At this stage, GC analysis indicated 62% conversion into **2a**. The AuCNT catalyst was removed from one sample by centrifugation, whereas the second sample was left untouched. Both reactions were stirred for an additional 30 minutes. Whereas the reaction was complete in the nanohybrid-containing sample, no further conversion of **1a** into **2a** was detected in the absence of AuCNTs. These observations confirmed that oxidation of **1a** did occur at the surface of the nanohybrid which acts as a solid catalyst.

The scope of the AuCNT-catalyzed oxidation was then investigated on a panel of silanes (Table 1). First, sterically exposed triethylsilane (**1b**) was quantitatively oxidized to the corresponding silanol **2b** in 15 minutes. The reaction proceeded cleanly with no disiloxane formation. Next, oxidation of two reputedly challenging substrates (**1c** and **1d**) was examined. Whereas the oxidation of the hindered triisopropylsilane (**1c**) has been reported to be problematic and

Table 1: AuCNT-catalyzed oxidation of various substrates.^[a]

RSi(R') ₂ H + n H ₂ O		AuCNTs, air		RSi(R') ₂ OH + n H ₂	
1a-j		THF, RT, t		2a-j	
Entry	Silane	1	t [min]	2	(Yield [%]) ^[b]
1	PhSi(Me) ₂ H	1a	45	2a	(98)
2	(Et) ₃ SiH	1b	15	2b	(99) ^[c]
3	(iPr) ₃ SiH	1c	60	2c	(93)
4	(Ph) ₃ SiH	1d	180	2d	(98)
5	(Ph) ₂ SiH ₂	1e	30	2e	(99)
6	PhSiH ₃	1f	90	2f	(97)
7	p(MeO)C ₆ H ₄ C≡CSi(Me) ₂ H	1g	240	2g	(96)
8	MeSi(Ph) ₂ H	1h	120	2h	(96)
9	BnSi(Me) ₂ H	1i	45	2i	(94)
10	HSi(Me) ₂ C ₆ H ₄ Si(Me) ₂ H	1j	180	2j	(96)

[a] Reaction conditions: silane (0.2 mmol), AuCNT (0.1 mol%) suspended in water, THF (2 mL). [b] Yield of isolated product. [c] Yield determined by GC analysis of the reaction mixture using dodecane as an internal standard.

require either extensive reaction times^[10c] or high catalyst loading,^[9a] in our hands, it was smoothly converted into silanol **2c** after 1 hour using only 0.1 mol% of catalyst. Oxidation of deactivated triphenylsilane (**1d**) afforded triphenylsilanol (**2d**) in excellent yield; this is in contrast to the previously reported supported-gold catalyst.^[10c] Moreover, diphenylsilane (**1e**) and phenylsilane (**1f**), which contain, respectively, two and three Si–H bonds to be oxidized, were also quantitatively transformed into the corresponding diphenylsilanediol (**2e**) and phenylsilanetriol (**2f**). In addition, acetylene-containing silane **1g** was selectively converted into its silanol counterpart **2g** without any concurrent oxidation. The AuCNT nanohybrid also permitted the efficient conversion of diphenylmethylsilane (**1h**) and benzyldimethylsilane (**1i**) into the corresponding silanols **2h** and **2i**. Finally, 1,4-bis(dimethylsilyl)benzene (**1j**) was doubly oxidized into **2j** in excellent yield. Again, no disiloxane condensation by-products were detected for the above examples.

To assess recyclability of AuCNTs, multiple dimethylphenylsilane (**1a**) oxidation cycles were carried out. The supported catalyst was recovered after each experiment by simple centrifugation and reused after washing with THF. Reuse experiments proceeded with neither significant loss of catalytic activity nor selectivity, even after five consecutive runs (Table 2). After the fifth run, TEM analysis showed no major alteration of the nanohybrid morphology despite slight particle aggregation that resulted in some bare nanotube areas (see the Figure S7 in the Supporting Information).

In addition to recyclability, higher efficacy of the nanohybrid was demonstrated by comparison of its oxidation performances to those of both colloidal AuNPs and gold salts. Silane **1a** was thus reacted with various gold sources at two different loadings (0.1 or 0.01 mol%). While the nanohybrid catalyst showed equally high efficiency in the two experiments (Table 3, entries 1 and 2), 0.01 mol% of colloidal AuNPs failed to catalyze the oxidation of **1a** (entry 4). The same holds true for tetrachloroauric acid which provided only traces of the oxidized silane **2a**, regardless of the catalyst

Table 2: Recycling experiments of AuCNT catalyst.^[a]

PhSi(Me) ₂ H + H ₂ O		AuCNTs, air	PhSi(Me) ₂ OH + H ₂	
1a		THF, RT	2a	
Entry	Catalyst		Yield of 2a [%] ^[b]	
1	fresh		98	
2	recycle 1		99	
3	recycle 2		97	
4	recycle 3		98	
5	recycle 4		96	

[a] Reaction conditions: silane (0.2 mmol), AuCNT (0.1 mol%) suspended in water, THF (2 mL), 45 min. [b] Yield of isolated product.

Table 3: Comparison of various Au sources in the oxidation of **1a**.^[a]

PhSi(Me) ₂ H + H ₂ O		Catalyst, air	PhSi(Me) ₂ OH + H ₂	
1a		THF, RT	2a	
Entry	Catalyst	Loading [mol%] ^[b]	Yield of 2a [%] ^[b]	
1	AuCNT	0.1	100	
2	AuCNT	0.01	91	
3	AuNP colloid	0.1	90	
4	AuNP colloid	0.01	trace	
5	HAuCl ₄	0.1	< 2	
6	HAuCl ₄	0.01	trace	

[a] Reaction conditions: silane (0.2 mmol), catalyst (0.1 or 0.01 mol%) suspended in water, THF (2 mL), 1 h. [b] Yield determined by GC analysis of the reaction mixture using dodecane as an internal standard.

loading (entries 5 and 6). These results suggest that AuNPs are the active species and that the nanotubes are not an inert support. In fact, CNTs are likely to synergistically assist silane oxidation by stabilizing transient higher oxidation states of gold through a charge-transfer process.^[13a]

As shown above, the AuCNT nanohybrid can promote fast oxidation of silanes with as little as 0.01 mol% loading, which is unprecedented. To compare its catalytic efficacy with already reported systems, turnover numbers (TONs) and frequencies (TOFs) of the nanohybrid were measured on the commonly studied silanes **1a** and **1b**.^[20] The oxidation of **1a** was catalyzed with 0.001 mol% of the AuCNTs to reach a striking TON of 72000 and TOF of 12000 h⁻¹. In the case of **1b**, a TON of 18000 was obtained after 1 hour (TOF = 18000 h⁻¹) when using 0.005 mol% of the nanohybrid. To the best of our knowledge, these values are the highest ever reported for any silane oxidation catalyst, and are approximately two orders of magnitude superior to those of other supported nanoparticle systems (see the Supporting Information for a detailed comparison).

To confirm that both water and oxygen are needed in the AuCNT-catalyzed oxidation (as previously reported for analogous systems),^[10] two test reactions were run with silane **1a**. Experiment A was carried out under oxygen-free conditions in the presence of water, whereas experiment B was run under oxygen gas but in anhydrous conditions. Both reactions failed to deliver silanol **2a** after 1 hour at room temperature (0.1 mol% Au loading). As anticipated, when oxygen was bubbled through the mixture of experiment A, and water was added to the mixture of experiment B, silane

oxidation started immediately and was complete in less than 1 hour. The origin of the oxygen atom incorporated into the silanols was assessed using ¹⁸O-labeled water in the catalyzed oxidation of **1a**. This reaction led quantitatively to the formation of PhSi(Me)₂¹⁸OH, thus designating water as the oxygen source, which is consistent with the observed H₂ evolution. Recent reports on the mechanism of gold-catalyzed oxidation of alcohols suggest that O₂ activates water which, in turn, oxidizes the substrate at the surface of gold.^[21] A similar activation could likely be operative in the case of silanes.

To conclude, we have reported the first nanotube-based hybrid system for the oxidation of silanes. The reusable catalytic system could easily oxidize both alkyl and aryl silanes in high yields, under mild conditions, and with no siloxane by-product. The nanohybrid compares most favorably to any other catalytic system in terms of overall efficacy and turnover values.

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