

COMMUNICATION

Depressing the hydrogenation and decomposition reaction in H₂O₂ synthesis by supporting gold-palladium nanoparticles on oxygen functionalized carbon nanofibers

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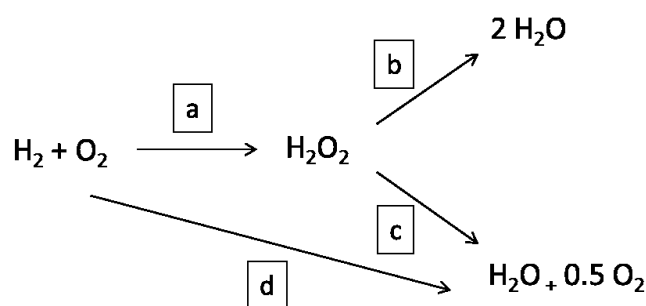
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In this work, we show that the introduction of acidic oxygen functionalities to the surface of carbon nanofibers serves to depress the hydrogenation and the decomposition of hydrogen peroxide during the direct synthesis of H₂O₂. Moreover, the presence of acidic groups enhances the H₂O₂ productivity in the case of supported AuPd nanoparticles.

Hydrogen peroxide is a high value commodity chemical, primarily used as a bleaching agent and an oxidant during the manufacture of caprolactam and propylene oxide.¹⁻³ The current synthetic process using substituted anthraquinones is only economic at a large scale. Moreover the transportation of H₂O₂ from the production site to the end point of use presents safety and cost-related issues. The direct synthesis of hydrogen peroxide from H₂ and O₂ performed on-site, would be a potential alternative. This process has attracted the attention of many researchers in the last century, and most studies have focused on supported palladium catalysts.⁴⁻⁷ The key problem of this process is related to selectivity, due to a number of side reactions forming H₂O, instead of H₂O₂, being observed as final product (Scheme 1).

High yields of H₂O₂ can be achieved by adding acid or halide promoters to the reaction medium, which suppress or limit the reactions forming water instead of hydrogen peroxide.⁸⁻¹⁰ We have shown that it is possible to switch off the hydrogenation and decomposition of H₂O₂ by pre-treating the activated carbon with HNO₃, thus increasing the acidity of the carbon surface.¹¹ Subsequently, similar results were obtained using acidic oxides as supports, such as SiO₂, Al-SBA-15, H-ZSM5.¹²⁻¹⁴ It was reported that the addition of Au to Pd increases the yield to hydrogen peroxide by limiting the hydrogenation and decomposition reaction (Scheme 1) even in the absence of halide and acids.^{10,15-20} When AuPd was prepared by

impregnation method (AuPd size 5-10 nm), Combining the effect of Au addition and the presence of acid pretreatment, a selectivity to H₂O₂ >98% was obtained.¹¹ However, in some cases, ultra-small nanoparticles (1-4 nm) prepared by sol immobilization, showed an increase of hydrogenation and decomposition activity when doping palladium with gold.^{21,22}



Scheme 1. Reaction pathways present in the direct production: a) H₂O₂ synthesis, b) hydrogenation, c) decomposition and d) combustion.

Carbon nanofibers (CNFs) have been chosen instead of activated carbon, due to the possibility of easily tuning the functionalities on the surface. Recently, CNFs have been shown to be a flexible support for Pd nanoparticles in the direct synthesis of hydrogen peroxide.^{20,23} In particular the introduction of nitrogen functionalities increased the Pd dispersion resulting in a higher H₂O₂ productivity compared to pristine CNFs.^{20,23} In this paper, the effect of acid functionalization of CNFs is investigated in depth. Particular attention has been dedicated to the characterization of the surface properties of the support. CNFs have been functionalized with oxygen groups to increase the acidity of the surface, and have subsequently been used as a support for Pd and AuPd nanoparticles. The effect of the acidic groups on depressing the undesired side reactions during the direct production of H₂O₂ has been evaluated.

Oxygen functionalities were introduced by treating the CNFs with HNO₃ at 353 K for 2 h, following the procedure previously reported.²⁵ This treatment allows removal of the residual

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amorphous carbon deriving from CNFs production.²³ The treatment did not significantly modify the textural properties such as surface area and pore size (Table S1). The textural properties of support and catalysts were reported in table The pristine and oxygen functionalized CNFs were used as support for Pd and AuPd nanoparticles generated in presence of polyvinyl alcohol (PVA) and sodium borohydride (NaBH₄).²⁶ XPS data were collected for the nanoparticles supported on the CNFs and the parent support materials. Fits to these data are summarized in Table 1 and Table S2. These data reveal a complex array of C-O functionalities that dominate the surface of the support materials (Table S2). The relative ratios of these surface functionalities (i.e. C-C, C-O, C=O, O=C-O, CO₃) remain similar on all the samples. The difference lies, as expected, in the higher amount of C=O for O-CNFs (Figure 1 and Table S2) and in the oxygen content at the surface, which increases from 7-9 % for the pristine CNFs to 17-20% for the functionalized O-CNFs (Table 1).

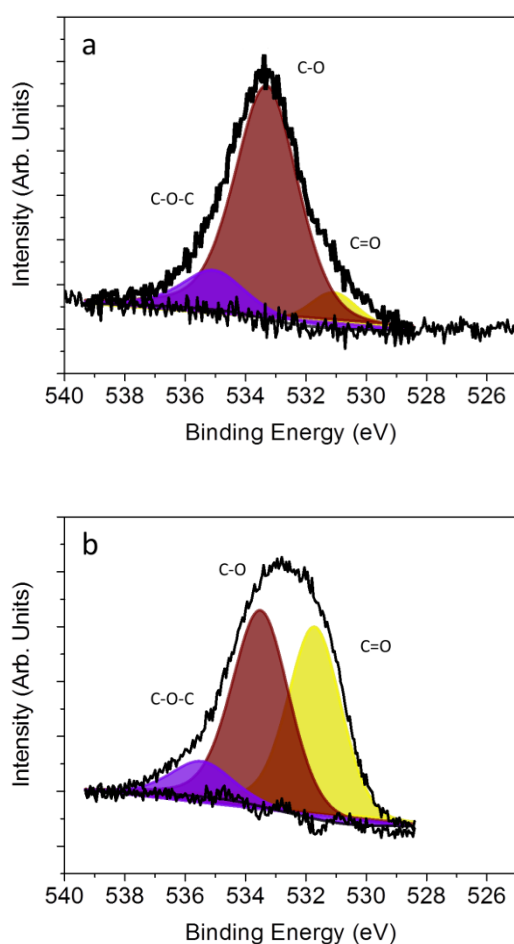


Figure 1 O1s XPS data collected for the a) CNFs and b) O-CNFs. XPS revealed significant differences in the spectra of the metal particles confined to the CNF and O-CNF samples. The Atomic percentage of Pd and AuPd species at the surface is 0.4% for the CNFs catalysts; in contrast only 0.1% of Pd and Au surface species are present for the O-CNF based catalysts. ICP analysis showed that in all cases the metal loading is 1 wt%. Therefore,

XPS results indicate that the metals are likely to be confined within the CNF pores, or trapped away from the surface, in particular in the case of O-CNFs. The introduction of oxygen species increases the hydrophilicity of the CNFs,²⁷ probably favouring the partial filling of the polar colloidal solution into the cavities of the CNFs. Unfortunately, due to the low signal of Au and Pd, in particular in the case of O-CNFs, it is not possible to determine the metal oxidation state reliably. Statistical analysis of particle size from STEM images showed a similar average nanoparticle diameter of 3-4 nm in all the materials (Table 1), with a narrow particle size distribution being observed for all the catalysts (Figure S1). Slightly smaller nanoparticles were obtained when metal nanoparticles were deposited on oxygen functionalized CNFs (table 1). Probably, the surface oxygen species act as anchoring point for the metal nanoparticles, limiting aggregation that may occur during the reduction step. Moreover, an inhomogeneous AuPd phase was obtained for pristine CNFs, along with the presence of alloyed nanoparticles and also segregated Au and Pd.²⁸ After the functionalization with nitric acid a cleaner surface was obtained²⁷ and as a consequence, AuPd alloyed nanoparticles were present.

Table 1 Main characteristic of CNFs based catalysts

Catalyst	Average MNPs diameter (nm)	Surface composition (%)		
		O	Pd	Au
CNFs	-	7.8	-	-
O-CNFs	-	18.3	-	-
1% Pd/CNFs	3.6	9.2	0.4	-
1% Pd/O-CNFs	3.2	20.2	0.1	-
1% AuPd/CNFs	4.1	7.6	0.2	0.4
1% AuPd/O-CNFs	3.7	17.1	N.D.	0.1

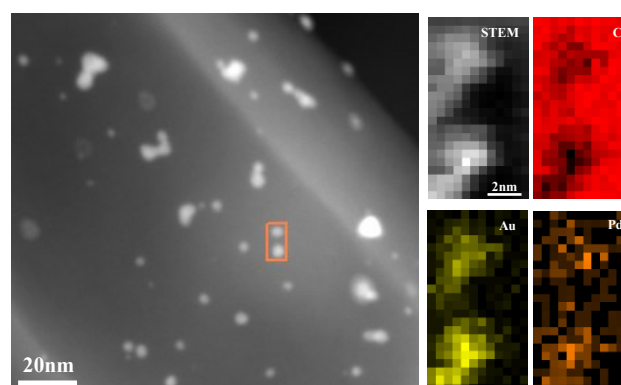


Figure 2 Overview STEM image of 1% AuPd/O-CNFs and the corresponding elemental maps obtained from STEM-EDX spectrum imaging in the area marked with box.

Fig. 2 shows an overview STEM image of AuPd/O-CNFs and the composition maps obtained from STEM-EDX spectrum imaging. In an area within the box marked in Figure 2. Au and Pd maps show the homogenous distribution of both metals in the two particles, indicating the formation of alloyed nanoparticles. As a representative example, the atomic Au-Pd ratio calculated from the lower particle in the spectrum imaging is 7.8:2.2. The catalytic tests were performed using a stainless steel autoclave under reaction conditions optimized in previous studies for AuPd catalysts.¹¹ To investigate the effect of acid functionalization on the hydrogenation and decomposition reactions, bare supports and supported metal catalysts were first tested (Table 2)

Table 2 Activity of CNFs based catalysts

Catalyst ^a	Productivity ^b [Mol H ₂ O ₂ kg _{cat} ⁻¹ h ⁻¹]	Hydrogenation ^c [Mol H ₂ O ₂ kg _{cat} ⁻¹ h ⁻¹]	Decomposition ^d [Mol H ₂ O ₂ kg _{cat} ⁻¹ h ⁻¹]
CNFs	5	60	198
O-CNFs	5	39	48
1% Pd/CNFs	21	472	77
1% Pd/O-CNFs	6	95	65
1% AuPd/CNFs	12	316	196
1% AuPd/O-CNFs	18	17	135

^a For AuPd catalysts, Au:Pd ratio is 6:4 mol:mol

^b Hydrogen peroxide synthesis conditions: 5% H₂/CO₂ (2.9 MPa) and 25% O₂/CO₂ (1.1 MPa), 8.5 g of solvent (2.9 g of water, 5.6 g of MeOH), 0.01 g catalyst, 2 °C, 1200 rpm, 30 min.

^c Hydrogen peroxide hydrogenation reaction conditions: 2.9 MPa 5% H₂/CO₂, 8.5 g of solvent (2.22 g of H₂O, 5.6 g of MeOH, and 0.68 g of 50% H₂O₂), 0.01 g of catalyst, 2 °C, 1200 rpm, 30 min)

^d Hydrogen peroxide decomposition reaction conditions: MPa of 25% O₂/CO₂, 8.5 g of solvent (2.22 g of H₂O, 5.6 g of MeOH and 0.68 g of 50% H₂O₂), 0.01 g of catalyst, 2 °C, 1200 rpm, 30 min.

O-CNFs catalysts showed an evident beneficial effect in reducing the decomposition and hydrogenation reaction. For hydrogenation reaction this is more evident for metal supported on CNFs with a decreasing of activity from 472 to 95 mol H₂O₂ kg_{cat}⁻¹h⁻¹ observed for Pd/CNFs and Pd/O-CNFs, respectively, and from 316 to 17 mol H₂O₂ kg_{cat}⁻¹h⁻¹ for AuPd/CNFs and AuPd/O-CNFs, respectively (Table 2). For bare supports the beneficial effect of the acid treatment is less evident (60 to 39 mol H₂O₂ kg_{cat}⁻¹h⁻¹ for CNFs and O-CNFs, respectively). For the decomposition reaction the positive effect of the acid treatment is more evident for bare supports, with a decrease in rate from 198 to 48 mol H₂O₂ kg_{cat}⁻¹h⁻¹ being

observed for CNFs and O-CNFs, respectively (Table 2). For the supported metal catalysts a decreasing from 77 to 65 mol H₂O₂ kg_{cat}⁻¹h⁻¹ for Pd/CNFs and Pd/O-CNFs, respectively and from 196 to 135 mol H₂O₂ kg_{cat}⁻¹h⁻¹ for AuPd/CNFs and AuPd/O-CNFs, respectively was obtained (Table 2). Comparing monometallic Pd and bimetallic AuPd it appears evident that the introduction of Au decreases the activity of the hydrogenation reaction but increases the decomposition rate regardless the support used (Table 2).

In term of productivity, the addition of Au to Pd increases the amount of H₂O₂ when supported on O-CNFs (Table 2), as reported by previous studies,^{11,18} whereas for AuPd supported on CNFs the opposite trend was observed. The difference could be attributed to the different morphology of the AuPd catalysts. Indeed the synergistic effect with Au addition to Pd has been observed only when a pure AuPd alloy phase, without segregation of Au and Pd, was obtained, as for AuPd/O-CNFs.⁷ It should be also noted that the capacity of O-CNFs to depress the side reaction compared to pristine CNFs has a beneficial effect on the total H₂O₂ productivity only for AuPd nanoparticles (Table 2). Indeed the productivity for the monometallic Pd decreases from 21 mol H₂O₂ kg_{cat}⁻¹h⁻¹ for Pd/CNFs to 6 mol H₂O₂ kg_{cat}⁻¹h⁻¹ for Pd/O-CNFs. These results can be explained by the lower accessibility of Pd sites for Pd/O-CNFs compared to Pd/CNFs or by the formation of a less reactive PdO phase in presence of a large amount of oxygen species on the support surface (Table 1). Unfortunately Pd oxidation state cannot be confirmed by XPS due to the low intensity of Pd signal for Pd/O-CNFs. For AuPd, the higher activity of a homogeneous alloy compared to a mixture of inhomogeneous alloy phases and segregated metals overcomes the lower accessibility of the active sites in AuPd/O-CNFs compared to AuPd/CNFs.

Herein we showed that the introduction of acidic oxygen functionalities on the surface of CNFs is beneficial in depressing the undesired side reaction occurring during the direct synthesis of H₂ and O₂. In particular, the possibility to easily tune the amount and the nature of the functionalities on the surface of CNFs makes these materials appealing for this reaction. AuPd/CNFs catalysts showed a good activity compared to AuPd supported on other carbon materials (microporous and mesoporous carbons) reported in the literature (Table S3) even a direct comparison is very difficult due to the different experimental reaction conditions used. It has been also shown that the addition of Au to Pd has a beneficial effect on the productivity of H₂O₂ only when a AuPd alloy, without any segregation of the two metals, is obtained.

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