

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

Supporting Information

1. Experimental

1.1. Catalyst preparation

1.1.1 Carbon nanofibers functionalization

Commercial CNFs were supplied from Applied Science. CNFs consists of tubular fibers with an average diameter of 80 nm and a specific surface area of 40 m²/g. The oxygen-containing carbon nanofibers were obtained by treating the pristine CNFs with HNO₃ using the following procedure. A solution of CNFs in HNO₃ concentrate (10 g of CNF per liter of HNO₃) was kept at 353 K for 2 h under continuous stirring, then rinsed with distilled water, and finally dried at 373 K for several hours. The oxygen functionalized CNFs was labeled as O-CNFs.

1.1.2 Pd catalyst preparation

Solid Na₂PdCl₄•2H₂O (Aldrich, 99.99% purity) (0.189 mmol) and PVA (87–89% hydrolysed (M.W. 13,000–23,000) from Aldrich) (1%wt) solution (Pd/PVA 1/0.5 wt%) were added to 100 mL of H₂O. After 5 min, NaBH₄ (purity >96% from Fluka) (0.1 M) solution (Pd/NaBH₄ 1/8 mol/mol)

was added to the brown solution under vigorous magnetic stirring. Within a few minutes of sol generation, the colloid was immobilized by adding the support under vigorous stirring. The amount of support was calculated as having a total final metal loading of 1 wt.%. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors) to remove PVA, and products deriving from the synthesis (Na, Cl) and dried at 80 °C for 4 h.

1.1.3 AuPd catalyst preparation

NaAuCl₄·2H₂O (Aldrich, 99.99% purity) (0.074 mmol) was dissolved in 70 mL of H₂O and PVA (1% w/w) was added (Au/PVA 1/0.5 wt%). The yellow solution was stirred for 3 min and 0.1 M NaBH₄ (Au/NaBH₄ 1/4 mol/mol) was added under vigorous magnetic stirring. Within a few minutes of sol generation, the gold sol was immobilized by adding the support under vigorous stirring. The amount of support was calculated as having a gold loading of 0.73% wt. After 2 h the slurry was filtered, the catalyst washed thoroughly with distilled water (neutral mother liquors). The Au/CNFs was then dispersed in 70 ml of water; Na₂PdCl₄ (0.051 mmol) and PVA (1%wt) solution (Pd/PVA 1/0.5 wt%) were added. H₂ was bubbled (50 mL/min) under atmospheric pressure and room temperature for 2 h. After additional 18 h, the slurry was filtered, the catalyst thoroughly washed with distilled water. The total metal loading was 1%wt.

1.3. Catalyst testing

Catalyst testing was performed using a stainless steel autoclave (Parr Instruments) with a nominal volume of 100 ml and a maximum working pressure of 17.4 MPa. The autoclave was equipped with an overhead stirrer (0–2000 rpm) and provision for measurement of temperature and pressure. For the standard reaction conditions we have employed previously, the autoclave was charged with the catalyst (10 mg), solvent (5.6 g MeOH and 2.9 g H₂O, both HPLC grade), purged three times with 5% H₂/CO₂ (0.7 MPa) and then filled with 5% H₂/CO₂ and 25% O₂/CO₂ to give a hydrogen to oxygen ratio of 1:2 at a total pressure of 4.0 MPa. Stirring (1200 rpm) was commenced on reaching the desired temperature (2 °C), and experiments were carried out for 30 min. H₂O₂ yield was determined by titration of aliquots of the final filtered solution with acidified Ce(SO₄)₂. Ce(SO₄)₂ solutions were standardized against (NH₄)₂Fe(SO₄)₂·6H₂O using ferroin as indicator. Based on multiple analyses and experiments the experimental error associated with these measurements was of the order of ca. 1–2%.

Hydrogenation experiments were carried out as outlined above, but in the absence of 25% O₂/CO₂ in the gas stream and in the presence of 4 wt% H₂O₂ in the solvent (5.6 g methanol, 2.22 g H₂O, 0.68 g 50% H₂O₂) and the catalyst (10mg).

Decomposition experiments were carried out as outlined above, in air and atmospheric pressure and in the presence of 4 wt% H₂O₂ in the solvent (5.6 g methanol, 2.22 g H₂O, 0.68 g 50% H₂O₂) and the catalyst (10 mg).

1.4. Characterization

- a) The metal content was checked by ICP analysis of the filtrate on a Jobin Yvon JY24.
- b) Morphology and microstructures of the catalysts were characterized by transmission electron microscopy (TEM). The powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted onto copper grids covered with holey carbon film. A Philips CM200 FEG electron microscope, operating at 200 kV and equipped with EDX DX4 analyzer system and a FEI Titan 80-300 electron microscope, operating at 300 kV and equipped with EDX SUTW detector were used for TEM observation.
- c) X-ray photoelectron spectroscopy (XPS) data were collected using a PHI 3056 XPS with an Al anode source operated at 15kV and an applied power of 350W. The energy scale calibration of the instrument is checked using a sputter cleaned piece of Ag. Samples were manually pressed between two pieces of indium foil; the piece of In foil with the sample on it was then mounted to the sample holder with a piece of carbon tape (Nisshin E.M. Co. LTD). Indium was used as a support since the most intense C1s binding energy, from the support material, overlapped with the C signal from the tape. The lowest C1s BE was always measured around 248.8 eV, but the peaks were shifted to 284.8 eV for comparison to literature values. There were no treatments (i.e. cleaning, heating, processing) to the samples before the XPS measurements. High resolution scans were acquired with a 23.5 eV pass energy and 0.05 eV steps a minimum of 50 times; survey scans were measured with a 93.9 eV pass energy and 0.5 eV energy steps a minimum of 25 times. Surface concentrations are calculated by integrating the peaks area and using standard atomic sensitivity factors supplied by the equipment manufacturer. The spectra were deconvoluted using Gaussian-Lorentzian functions and a Shirley-type background.
- d) Surface area, pore size and pore volume were determined by low temperature N₂ adsorption using a SA3100 Coulter apparatus. Before measurement, samples were outgassed at 80°C for 3 h.

Figure S1 Pd and AuPd particle size and distribution

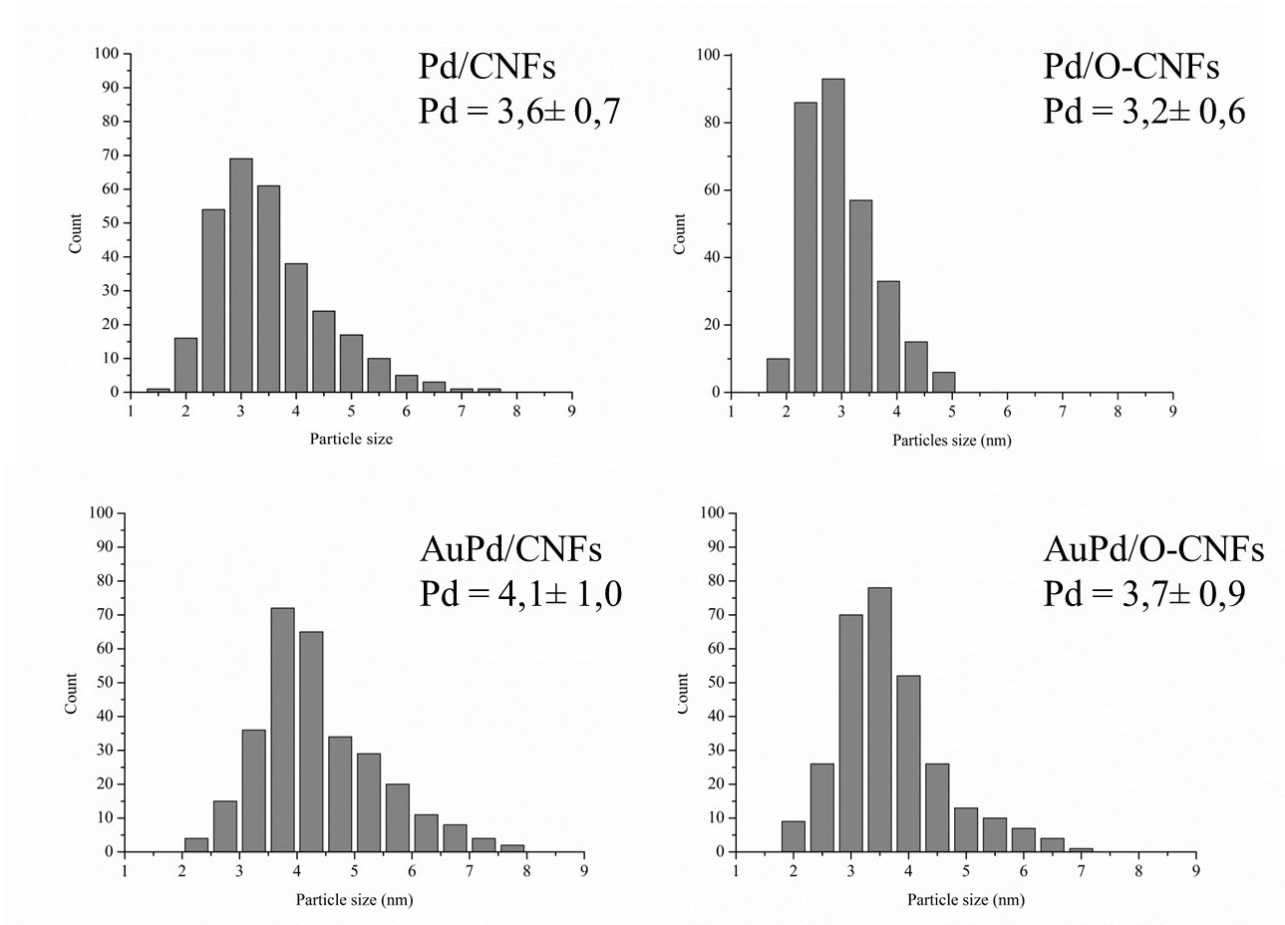


Figure S2 Representative HRTEM image of AuPd nanoparticles

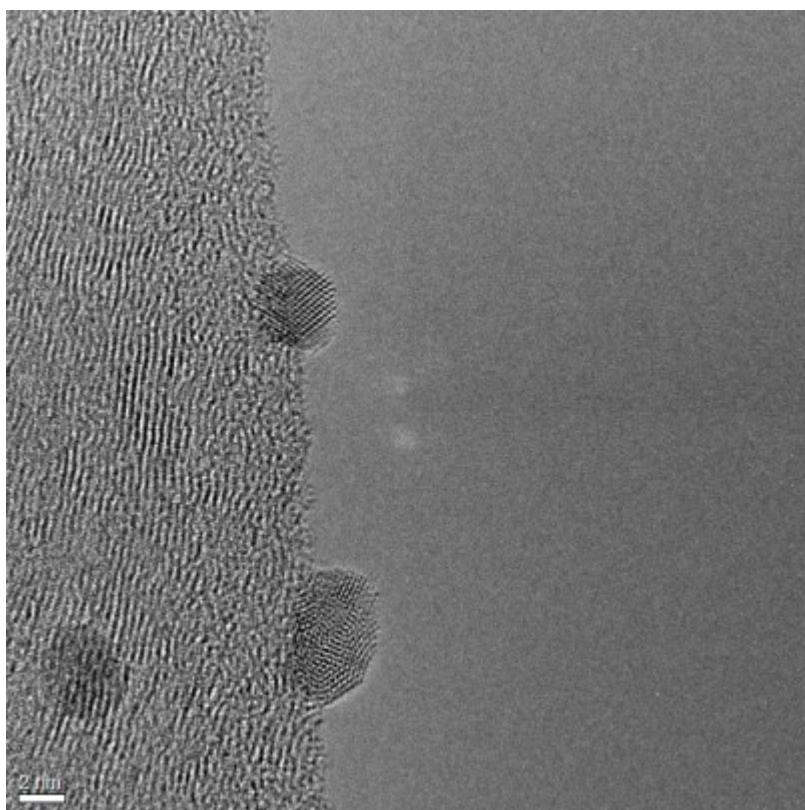


Table S1 Textural properties of CNFs based catalysts

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)
CNFs	40	5.12
O-CNFs	38	5.21
AuPd/CNFs	39	5.10
AuPd/CNFs	36	5.16

Table S2 Additional XPS results of CNF based catalysts

Sample	C1s						O1s		
	C-C, C-H	C-O	C=O	O-C=O	-CO ₃	C6	C=O	C-O	C-O-C
CNF	284.79	28610	287.19	288.75	290.30	291.68	530.82	532.96	534.99
%	52.4	18.1	16.7	6.1	4.8	1.9	7.8	62.2	24.1
O-CNF	284.78	286.01	287.10	288.77	290.40	292.13	530.82	532.98	535.05
%	48.7	17.9	17.5	9.1	4.9	1.9	33.8	46.5	20.9

Sample	O1s		
	C=O	C-O	C-O-C
Pd/O-CNF	530.80	532.06	533.80
%	35.8	43.6	21.3
AuPd/O-CNF	531.09	532.49	534.47
%	36.5	47.1	16.2

Table S3 Comparison of AuPd supported on different carbon materials for H₂O₂ synthesis

Catalyst ^a	Productivity [Mol H ₂ O ₂ kg _{cat} ⁻¹ h ⁻¹]	Productivity [Mol H ₂ O ₂ mol _{metal} ⁻¹ h ⁻¹]	Ref
1% Au ₆ Pd ₄ /CNFs	12 ^a	200 ^a	This work
1% Au ₆ Pd ₄ /CNFs <i>treated with HNO₃</i>	18 ^a	284 ^a	This work
5% Au ₁ Pd ₁ /AC (Aldrich G60)	110 ^a	359 ^a	11
5% Au ₁ Pd ₁ /AC (Aldrich G60) <i>treated with HNO₃</i>	160 ^a	503 ^a	11
5% Au ₁ Pd ₁ /CMK-3	400 ^b	1214 ^b	19
5% Au ₁ Pd ₁ /CMK-3 <i>treated with HNO₃</i>	853 ^b	2589 ^b	19
5% Au ₁ Pd ₁ /AC (Norit)	293 ^b	890 ^b	19
5% Au ₁ Pd ₁ /AC (Norit) <i>treated with HNO₃</i>	507 ^b	1537 ^b	19

Reaction conditions:

- a) 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, 30 min.
- b) H₂/O₂/Ar (5/10/85%) (2 MPa) (75 ml MeOH, 0.04 M HCl), 0.075g catalyst, 5°C, 60 min.

References

11. J. K. Edwards, B. Solsona, E. N. Ntainjua, A. F. Carley, A. A. Herzing, C. J. Kiley, G. J. Hutchings, *Science*, 2009, 323, 1037.
19. T. Garcia, R. Murillo, S. Agouram, A. Dejoz, M. J. Lazaro, L. Torrente-Murciano, B. Solsona, *Chem. Commun.*, 2012, **48**, 5316.