

Electronic Supplementary Information**Materials and Methods**

Preparation of supported gold catalysts. Au/Fe₂O₃ catalysts were prepared by co-precipitation using the following procedure. Dilute aqueous solutions of HAuCl₄·3H₂O (Strem, 99.9%) and Fe(NO₃)₃·9H₂O (Aldrich, 99.999) which contained the calculated amounts of Au and Fe to give the desired loading on Fe₂O₃ were mixed together with stirring at 80°C. Na₂CO₃ (Aldrich, 0.25 mol l⁻¹) was added dropwise until pH 8.2 was attained. The resulting precipitate was then recovered by filtration and washed with hot deionised water (80°C, 1 l). Using this method 5 wt% Au/Fe₂O₃ was prepared and the material was either dried or calcined in air at a range of temperatures and times. Au and Au/Pd supported on Al₂O₃ were also prepared by impregnation, as we have shown that these catalysts are effective for H₂ oxidation to selectively form H₂O₂ (1, 2). Also 1 wt% Au/CeO₂ prepared by co-precipitation and 5 wt% Au/TiO₂ prepared by wet impregnation of TiO₂ (Degussa P25) with HAuCl₄·3H₂O (Strem, 99.9%) were investigated.

Catalyst testing. Catalysts (50 mg) were initially evaluated for CO oxidation in the presence of hydrogen using a fixed bed reactor (i.d. = 3 mm). CO (0.1 ml/min), H₂ (0.2 ml/min), O₂ (4 ml/min) and N₂ (20.7 ml/min), total gas hourly space velocity (GHSV) = 30000 h⁻¹ were fed to the reactor using mass flow controllers. The reactor effluent gases were analysed using on-line gas chromatography. Tests involving realistic fuel cell conditions have also been carried out. Based on published fuel cell system designs³, we have mimicked the output of an auto-thermal methanol reformer, generating a gas stream containing 1%CO 55% H₂, 24%CO₂, 5% H₂O and 15% N₂. To this stream air was added in order to oxidise the CO. Therefore our working conditions, replicating the conditions of the fuel cell environment, have been established as: 0.9%CO, 0.9%O₂, 50%H₂, 22%CO₂, 4.7%H₂O, with the balance being N₂. The mass of catalyst used was 100 mg and the total flow rate 20 ml min⁻¹, giving an hourly space velocity (GHSV) = 12000 h⁻¹.

XPS measurements. Spectra were recorded with a VG ESCALAB 220 spectrometer utilising an achromatic AlK α source and an analyser pass energy of 20 eV.

TEM measurements. Samples of all catalysts were prepared for transmission electron microscopy examination by dispersing the catalyst powder in high purity ethanol. A drop of the suspension was then allowed to evaporate on a holey-carbon film supported by a 300 mesh copper TEM grid. Imaging experiments were carried out on a JEOL 2000FX TEM operating at 200 kV with a LaB₆ source.

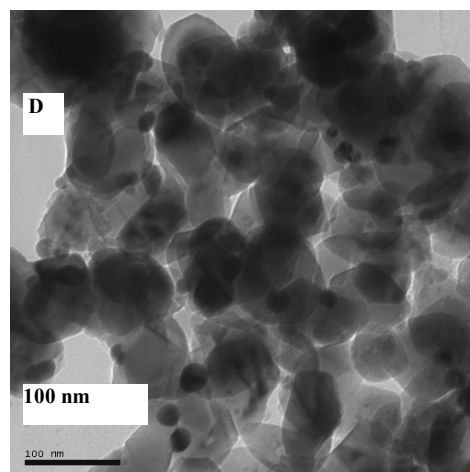
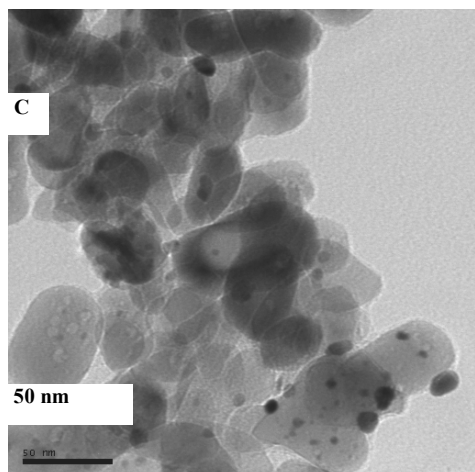
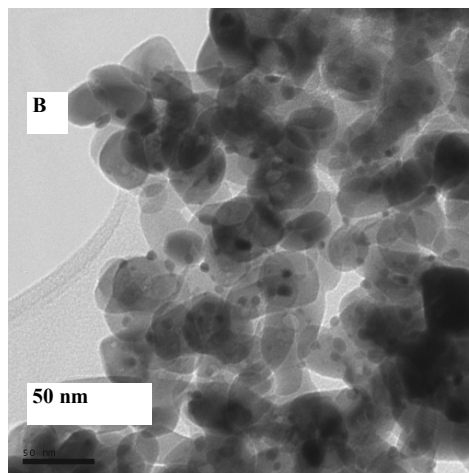
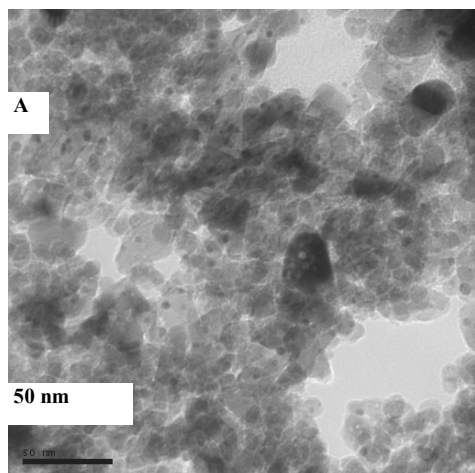
References

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2. B. T. Qiao, Y. Q. Deng, *Chem. Commun.* 2192 (2003).
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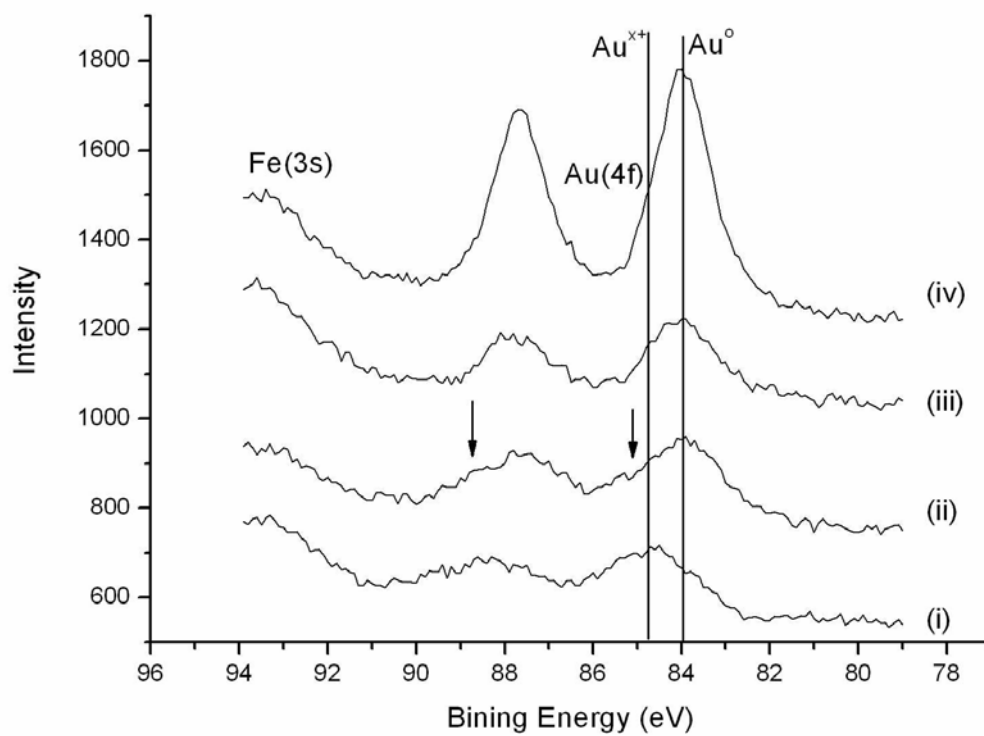
Supplementary Figures

Supplementary Figure 1. TEM of Au/Fe₂O₃ samples. Key: **A** calcined at 400°C, 3 h, **B** calcined at 400 and 550°C, **C** calcined at 550°C, 3 h, **D** calcined at 600°C, 3 h.

Supplementary Figure 2 Au(4f) X-ray photoelectron spectra for a series of Au/Fe₂O₃ catalysts: (i) dried at 120 °C, (ii) calcined at 400 °C, (iii) calcined at 400 °C and 550 °C and (iv) calcined at 600 °C. Arrows indicate the presence of cationic gold in (ii) which is absent in (iii).



Supplementary Figure 1



Supplementary Figure 2

Supplementary Table 1 Catalysts for the selective oxidation of CO in the presence of H₂

Catalyst	Reaction mixture composition (%)						Conv (%)	Sel (%)	T (°C)	GHSV (h ⁻¹)	Ref. †
	CO	O ₂	H ₂	H ₂ O	CO ₂	Bal					
Target	0.8-1.0	0.4-1.0	50	2-10	20-24	Inert N₂ He	>99.5	>50	80-110[§]	-	
Au/Fe ₂ O ₃ (400+550°C)	0.9	0.9	50	4.7	22	He	99.8	51	80	12000	This work
Au/Fe ₂ O ₃ (120°C)	0.9	0.9	50	4.7	22	He	92	47	80	12000	This work
Au/CeO ₂ (120°C)	0.9	0.9	50	4.7	22	He	68	35	80	12000	This work
CuO-CeO ₂ (urea DP)	1	1	50	10	20	He	~0	-	80	10000	18
CuO-CeO ₂ (urea DP)	1	1	50	10	20	He	99	65	165	10000	18
CuO-CeO ₂ (CP)	1	1.25	50	10	15	He	99	63	170	10000	21
Supported Pt/Al ₂ O ₃ -	0.1	0.05	20	0	0	N ₂	75	80	90	120000	22
Au/CeO ₂	1	1.5	48	0	24	He	20	20	80	110000	23
Au/Fe ₂ O ₃ (400°C)	0.1	0.1	66	10	22	-	*	29	80	**	20
Au/Fe ₂ O ₃ (120°C)	1	4	50	0	0	He	100	100	50	20000	11
Au/CeO ₂ (120°C)	0.8	0.4	58.4	0	0	-	60	99.7	60	165000	13
Au/Fe ₂ O ₃ (400°C)	1	1.25	50	10	15	-	65	60	80	25000	19
Au/Fe ₂ O ₃ (400°C)	1	1.25	50	10	15	-	99.5	54.5	100	25000	19
Au-Co/CeO ₂ /TiO ₂ /SnO ₂ (400°C)	0.5	0.8	2	0	0	N ₂	76	85	80	**	12
	0.5	0.8	2	0	0	N ₂	91	91	100	**	12
Au/CeO ₂ (500°C)	1	1	40	10	2	He	76	62	90	30000	24
Au/CeO ₂ (500°C)	1	1	40	10	2	He	18	56	90	30000	24

* activity quoted as 0.003 mol CO/(g Au.s) ** not indicated § most PEFCs currently run at 80 °C

Figures in **bold italics** show where target conditions or target conversion/selectivity are not achieved.

† Additional references:

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23. G. Panzera *et al.*, *J. Power Sources* 2004, **135**, 177.
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Supplementary Table 2 Competitive oxidation of CO in the presence of H₂^a

Catalyst (calcination conditions)	CO conversion (%)				H ₂ conv. (%)		
	<i>No H₂</i> ^b	27	50	73	27	50	73
	27°C	°C	°C	°C	°C	°C	°C
5 wt% Au/Al ₂ O ₃ (400°C, 3 h)	-	0	0	0	0	0	0
2.5 wt% Au/2.5 wt% Pd/Al ₂ O ₃ (400°C, 3 h)	-	0	0	0	0	0	19
5 wt% Pd/Al ₂ O ₃ (400°C, 3 h)	-	0	0	0	0	3	30
5 wt% Au/TiO ₂ (400°C, 3 h)	-	0	0	0	0	0	0
1 wt% Au/CeO ₂ (400°C, 3 h)	-	30	59	80	0	0	20

^a 0.4 vol % CO, 0.8 vol % H₂, 16 vol % O₂, 50 mg catalyst, GHSV = 30 000 h⁻¹^b 0.5% CO in air, 50 mg catalyst; GHSV = 24 000 h⁻¹