Supplementary Information

APXPS-compatible Fuel Cell

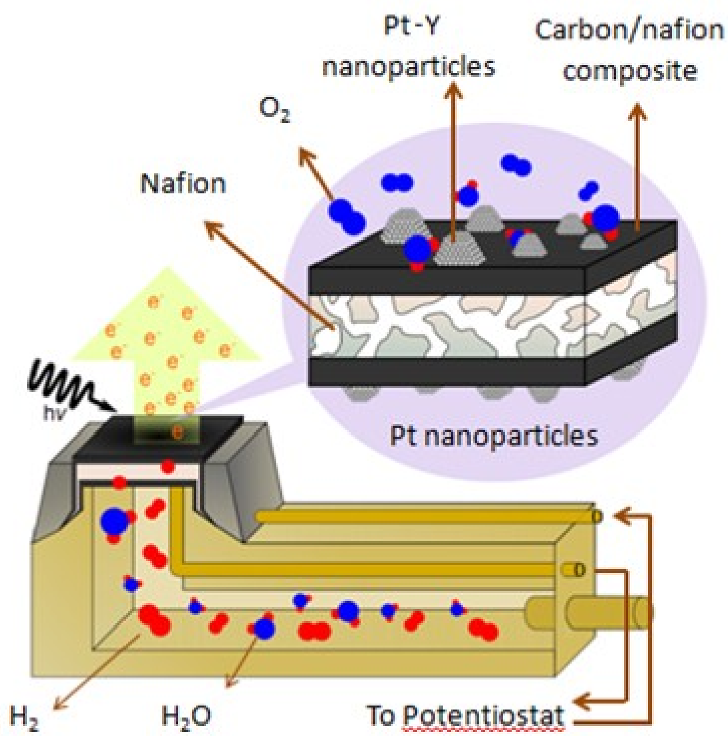

Figure S1: APXPS-compatible electrochemical cell for fuel cell investigations. The electrochemical cell has a Nafion® membrane coated on one sides with a mixture of Nafion® and carbon-supported platinum nanoparticles with catalyst loading of 4 mg/cm^2 (particle size 10-20 nm), which serves as the anode, and on the other with carbon-supported platinum yttrium nanoparticles, which serve as a cathode. The cathode side of the assembly was exposed to the APXPS gas cell, which was filled with oxygen gas. The anode chamber was filled with humidified forming gas (95% N_2/5% H_2, saturated H_2O). Red and blue circles represent hydrogen and oxygen (single red circles represent protons); the black layer represents the porous carbon-nafion support; grey circles represent the metallic platinum or Pt-Y nanoparticles. Both sides are connected through an external circuit to a PineWave potentiostat, which was used to apply potential biases.

XPS reference binding energies

	Y 3d 5/2	Y 3d 3/2	O 1s	Reference
Y	155.80	157.7		1
	155.80	157.8		2
	155.80	157.9		3
	155.87	-		4
	155.90	-		5
	155.90	158.05		6
Y_2O_3	156.40	158.50	528.70	7
	156.70	-	529.10	3
	156.70	158.70	529.50	8
	156.80	-	-	9
	157.00	158.90	530.20	10
	157.20	159.30	529.40	11
	158.40	-	-	12
	158.50	160.65	530.10	6
	158.60	-	-	5
$Y(OH)_3$	157.60	159.60	531.20	7
	158.40	160.50	531.80	11
YH_2	156.50	-		2
YH_3	157.70	-		2
YCl_3	158.70	-		3
	158.90	161.00		13
YF_3	159.10			3
	159.00	161.20		13

Table S1: XPS binding energy positions of some Y compounds. Literature positions of the Y $3d_{5/2}$, Y $3d_{3/2}$ and O 1s XPS lines for a number of Y compounds. Very good reproducibility holds for the position of metallic Y, in agreement with the values of this work (Y $3d_{5/2}$ at 155.9 eV). Contrarily, Y_2O_3 has been usually reported at moderately low binding energies (Y $3d_{5/2}$ between 156.4 and 157.2 eV) but considerably higher values have been also proposed. Y $3d_{5/2}$ lines of highly ionic compounds as YCl_3 or YF_3 exhibit very high binding energies comparable with those reported for the oxidized component of this work (Y $3d_{5/2}$ at 158.7 eV).

Oxygenated species during closed circuit conditions

On the basis of our previous study on Pt nanoparticles, the electrical circuit was closed in order to assess the surface speciation under operating conditions. **Figure S2** shows two O1s spectra of this closed circuit system at different oxygen pressures while at identical anodic pressures. Under low oxygen conditions and low current (5 μA), the system is predominantly water. At higher pressures, the electrochemical current increases (12 μA) and the surface begins to be covered by other oxygenated species, predominantly non-hydrated hydroxide. Both of these results are in agreement with previous findings in pure platinum nanoparticles, further supporting the OCP conclusions.

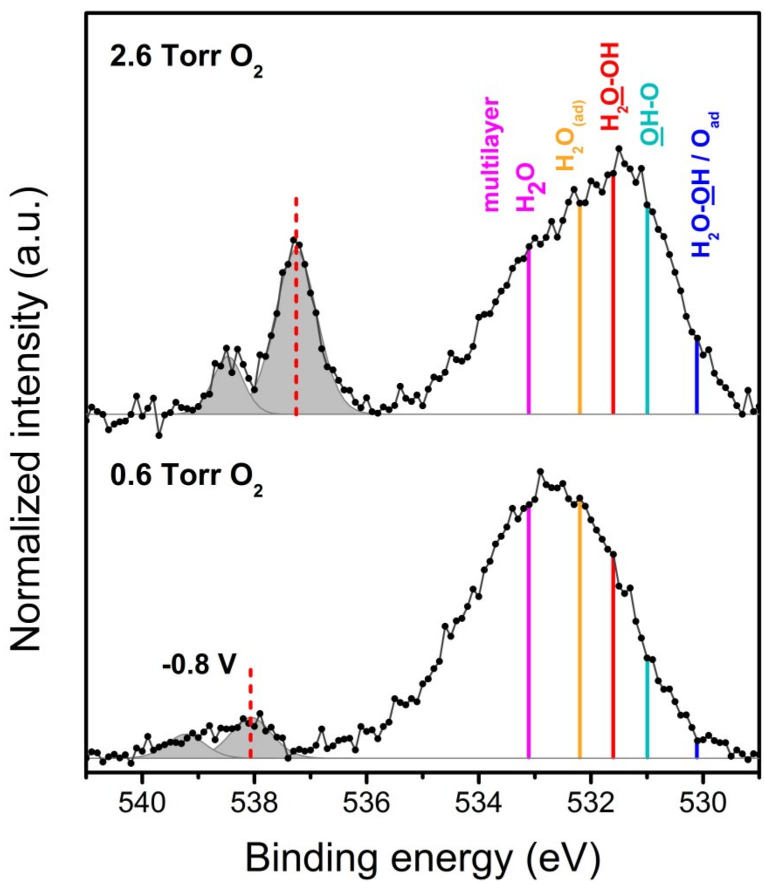

Figure S2: O1s XPS spectra of Pt-Y nanoparticles under operating fuel cell conditions. O1s XPS spectra under two different oxygen gas cathodic pressures while at constant anodic hydrogen pressure anode (600 Torr forming gas: 95% N2/5% H2). The low oxygen condition (0.6 Torr) exhibited an electrochemical current of 5 μA, while the high oxygen condition (2.6 Torr) produced a current of 12 μA. The shift in the double peak feature, corresponding to oxygen gas, can be used to determine the change in surface potential. The lines in the 529-535 eV region correspond to binding energies of multilayer H_2O (purple); H_2O(ad) (orange); $H_2\underline{O}$-OH (red); $\underline{O}$H-O (cyan); H_2O-$\underline{O}H/O_{ad}$ (blue). The incident photon energy was 700 eV.

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