Supplementary Information

Table SI 1 Details of the amount of materials used for the synthesis of the different electrocatalysts

Material	$HAuCl_4.3H_2O$ /mg	PVA /mg	Volume /dm^3	Carbon /mg
Au/C noPVA	75	-	1.5	150
Au/C-50	100	25.0	1	200
Au/C -35	70	17.5	1	140
Au/C-25	75	18.8	1.5	150
Au/C -15	45	11.3	1.5	90

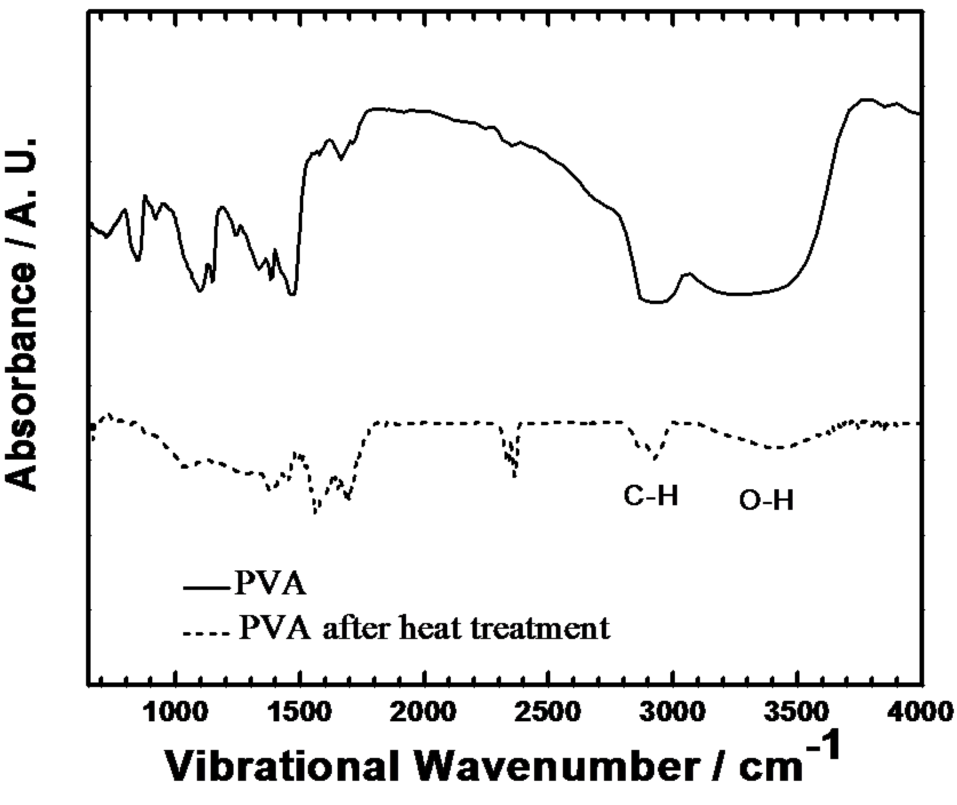

Figure SI-1 FTIR spectra of PVA (solid line) and of the residue after PVA thermal decomposition (dashed line).

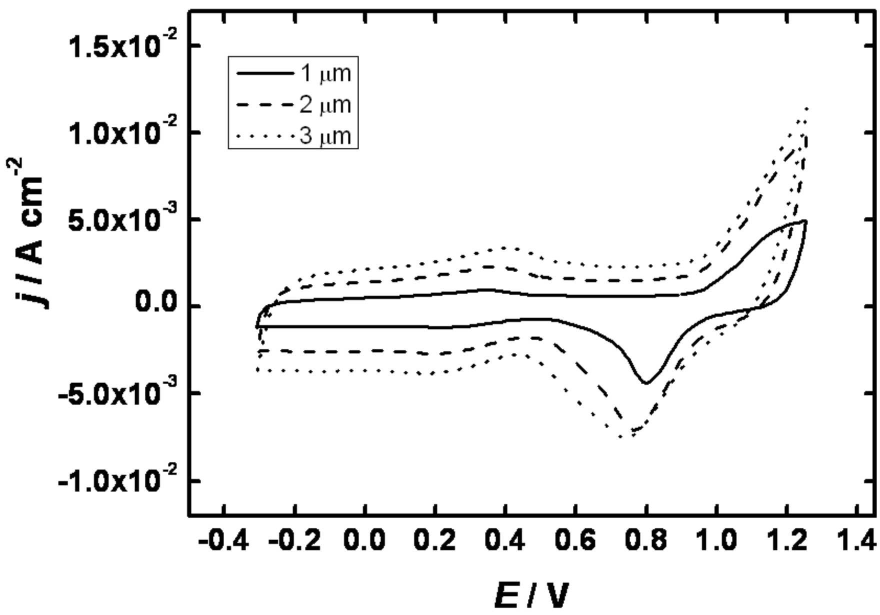

Figure SI-2 Cyclic voltammograms for electrodes prepared with different amounts of Au/C-35 material in 0.1M $HClO_4$. Sweep rate = 200mV/s.

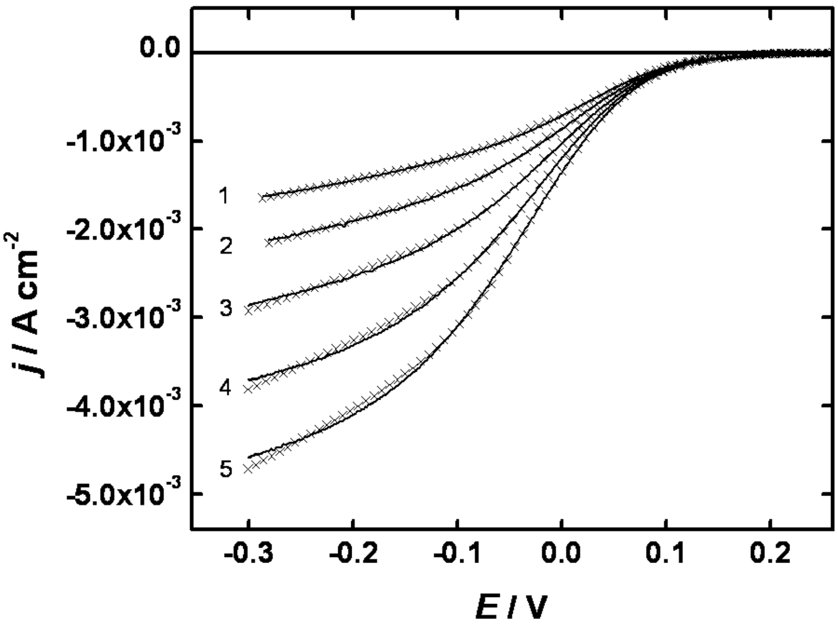

Figure SI-3. Polarization curves for the ORR for the Au/C-25 material at different rotation rates: 200 (1), 400 (2), 800 (3), 1500 (4) and 2500 RPM (5). The crosses are the results of the corresponding NLR fits.

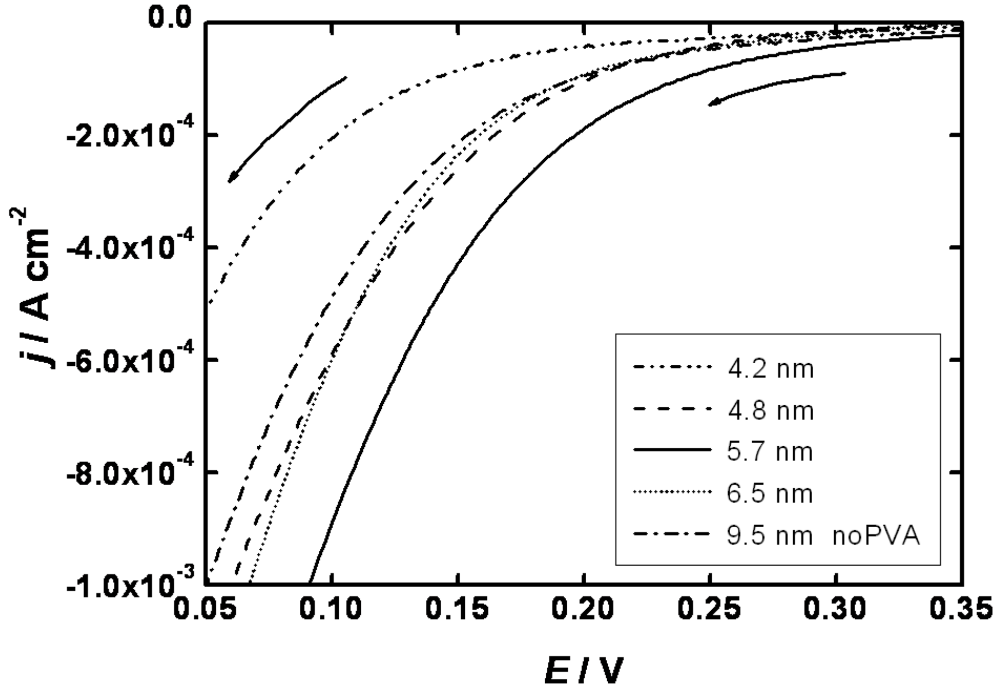

Figure SI-4 Comparison of the polarization curves in the region of the onset of the ORR for carbon–supported nanoparticles of different sizes.

Table SI 2 Parameters employed in NLR for approximation of the dependence of *n* on *E*.

Material	a	b	*E* at *n*=2 / V
Au/C noPVA	-2.1	2.5	0.23
Au/C-50	-3.4	2.3	0.09
Au/C -35	-3.3	2.1	0.03
Au/C-25	-4.3	1.9	-0.02
Au/C -15	-3.3	1.9	-0.03

Specific surface area calculation

The surface area of gold was calculated assuming a cubo-octahedral geometry (truncated octahedron) for which the volume is:

$$V = 32r^3 \quad \text{(SI-1)}$$

where r is a radius (half of the longest diagonal of the truncated octahedron).

The surface area is:

$$A = \left(12 + 24\sqrt{3}\right)r^2 \quad \text{(SI-2)}$$

The specific surface area of a gold particle with cubo-octahedral geometry with a radius r_i is then given by:

$$A_{r_i} = \frac{3.35}{r_i \rho} \quad \text{(SI-3)}$$

where ρ is crystallographic density of gold (19.3 g cm^{-3}).

For the sample of particles with sizes given by a probability density function $f(r)$, the total specific area is:

$$A_{\text{tot}} = \int_0^{r_{\text{max}}} \frac{3.35}{r\rho} f(r)\, dr \quad \text{(SI-4)}$$

The probability density functions were obtained by fitting the histograms shown in Figure 3 to a normal distribution and by normalizing it. The probability density function for size distribution shown in Figure 2 was approximated by the raw data from the histogram (numerical integration where the bin size was the integration step). The total gold surface area per g of Au/C material, A_S, was then calculated from the Au/C weight ratio (Table 1).

Derivation of equation (10)

From equations (8) and (9), the current is given by:

$$I_{\mathrm{D}} = \frac{4\mathrm{F}Ak_2\, c^{\mathrm{b}}_{\mathrm{O_2}} k_{\mathrm{M}}(\mathrm{O_2})}{k_2 + k_{\mathrm{M}}(\mathrm{O_2})} + \frac{I_{\mathrm{R}}}{N} \tag{SI-5}$$

Hence

$$k_2 I_{\mathrm{D}} + k_{\mathrm{M}}(\mathrm{O_2}) I_{\mathrm{D}} = \left(-4\mathrm{F}Ac^{\mathrm{b}}_{\mathrm{O_2}} k_{\mathrm{M}}(\mathrm{O_2}) + \frac{I_{\mathrm{R}}}{N}\right) k_2 + \frac{I_{\mathrm{R}}}{N} k_{\mathrm{M}}(\mathrm{O_2}) \tag{SI-6}$$

From (SI-6), the rate constant k_2 is:

$$k_2 = \frac{\left({}^{I_{\mathrm{R}}}/_{N}\right) k_{\mathrm{M}}(\mathrm{O_2}) - k_{\mathrm{M}}(\mathrm{O_2}) I_{\mathrm{D}}}{I_{\mathrm{D}} + 4\mathrm{F}Ac^{\mathrm{b}}_{\mathrm{O_2}} k_{\mathrm{M}}(\mathrm{O_2}) - \left({}^{I_{\mathrm{R}}}/_{N}\right)} \tag{SI-7}$$

Dividing by the disc area, Equation (10) follows.