Supporting Information

Few layer graphene - supported palladium as highly efficient catalyst in oxygen reduction reaction

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Pd/FLG (Pd/C) preparation and characterization:

800 mg of FLG was dispersed in 300 ml of water during 10 min by tip-ultrasonication. The aqua solution of 1.33 mg of Pd nitrate was next added, followed by short ulrasonication. The suspension was kept under stirring and heated till muck was remain. The muck was next dried at 100°C for 2 h, decomposed at 250°C for 2 h and then reduced in flow hydrogen at 350°C for 2h.

The Pd/C was prepared in a similar manner, with the use of carbon black (VXC72R) - purchased from Cabot Corportaion.

The total loading of the Pd in both catalysts are around 40% (TGA).

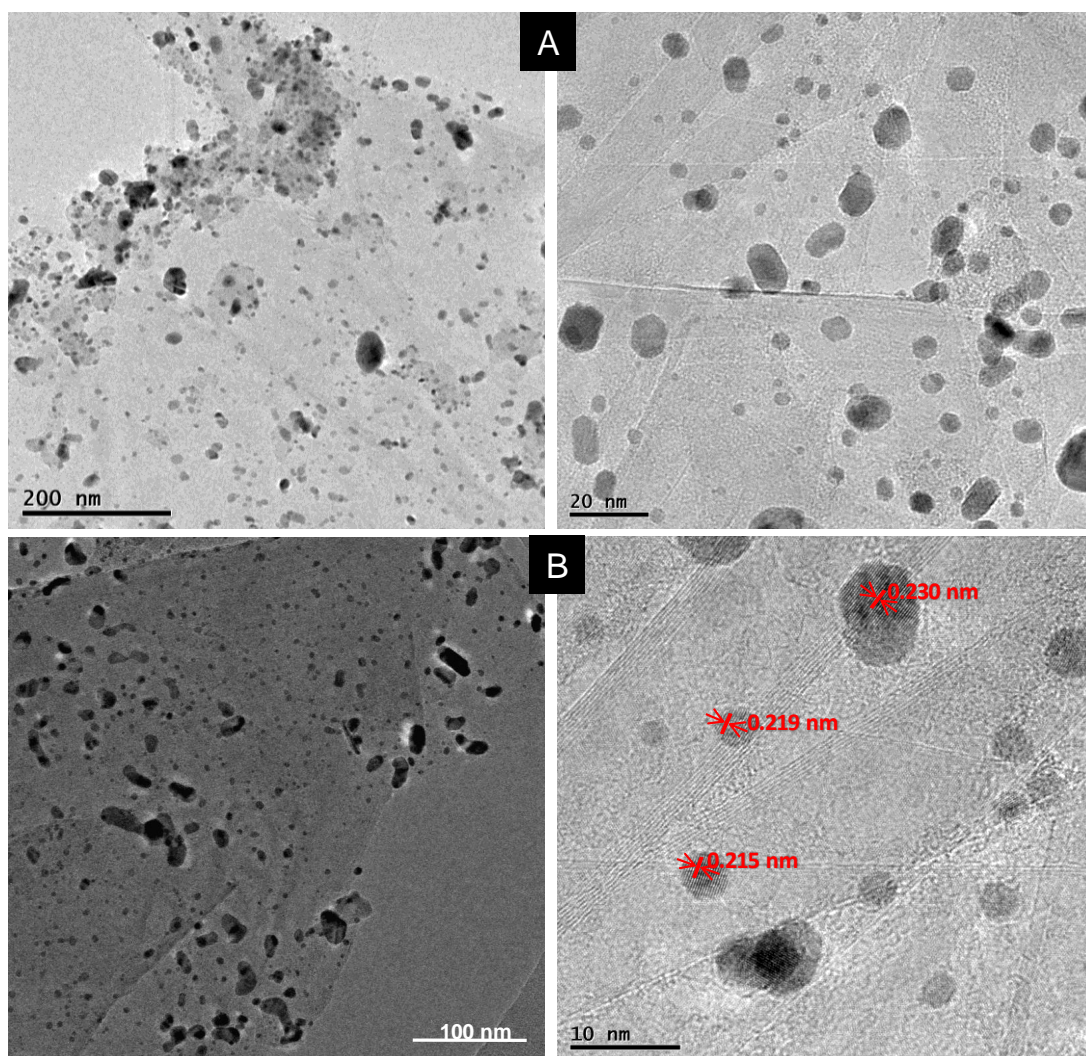The mass of commercial Pt/C (Sigma-Aldrich) was normalized with Pd catalysts.

Fig.S1. TEM micrographs of Pd/FLG catalyst before (A) and after ORR test in alkaline media
(B). No significant modification of the catalyst after ORR test has been observed.
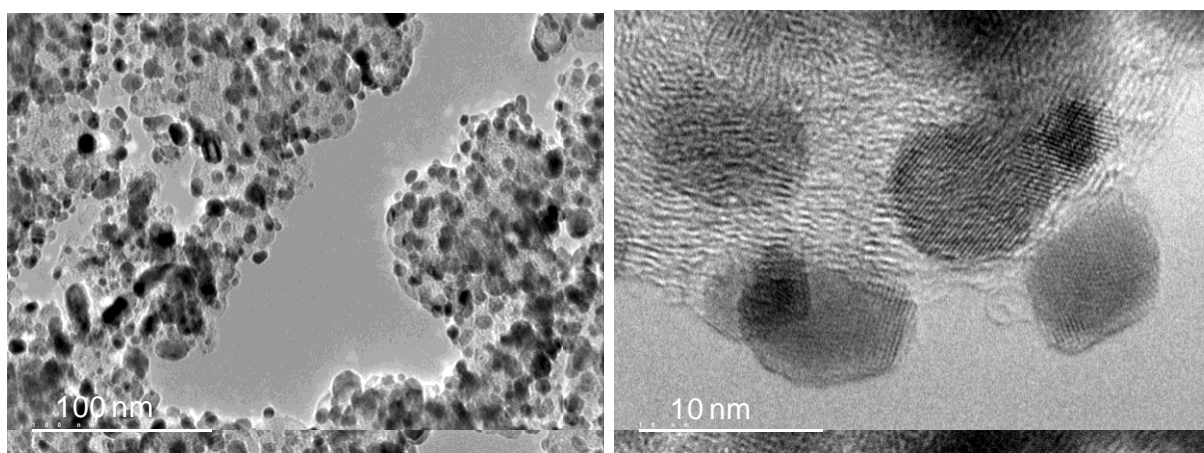
Fig.S2. TEM micrographs of Pd/C.

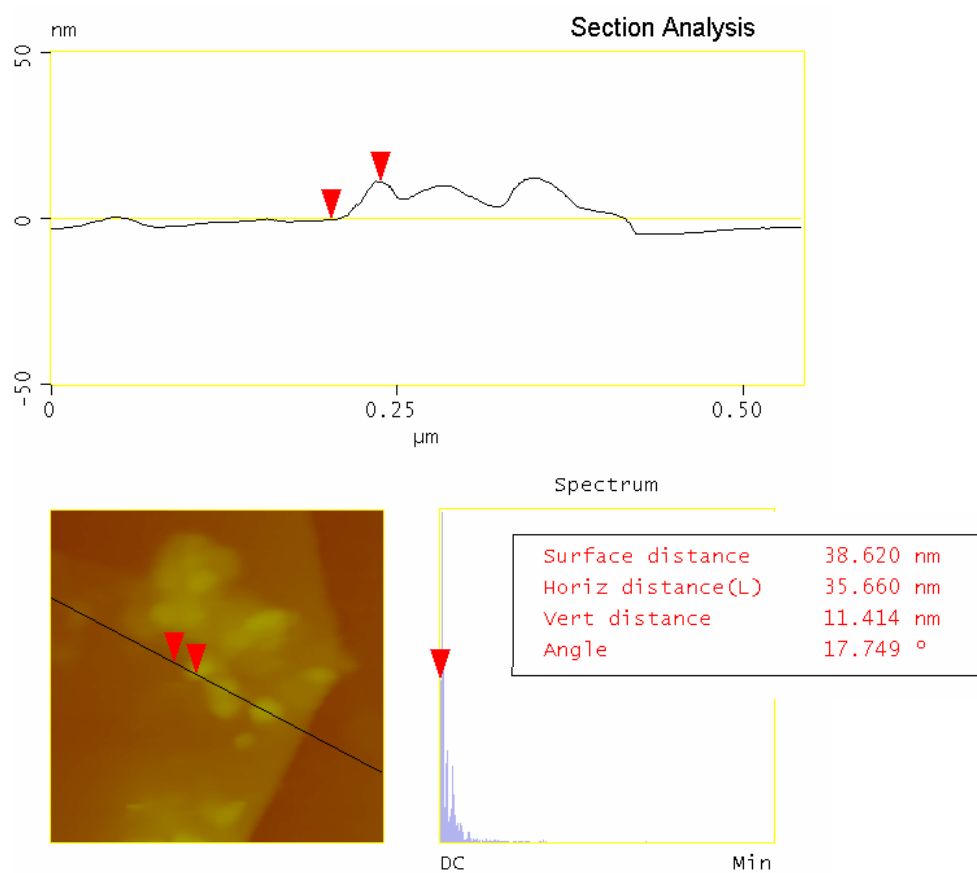|	
Surface distance	38.620 nm
Horiz distance(L)	35.660 nm
Vert distance	11.414 nm
Angle	17.749 °

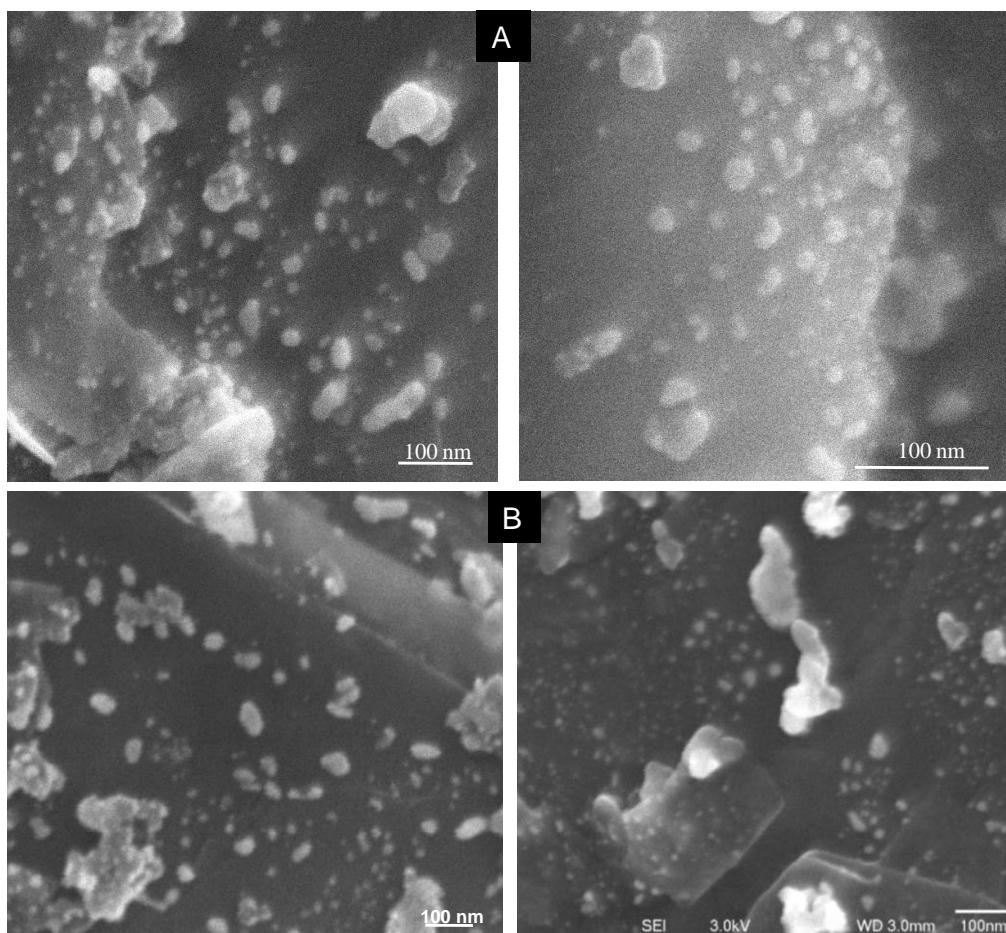Fig.S3. AFM analysis profile of Pd/FLG catalyst

Fig.S4. SEM micrographs of Pd/FLG before (A) and after (B) ORR test in alkaline media. No significant modification of the catalyst after ORR test has been observed.
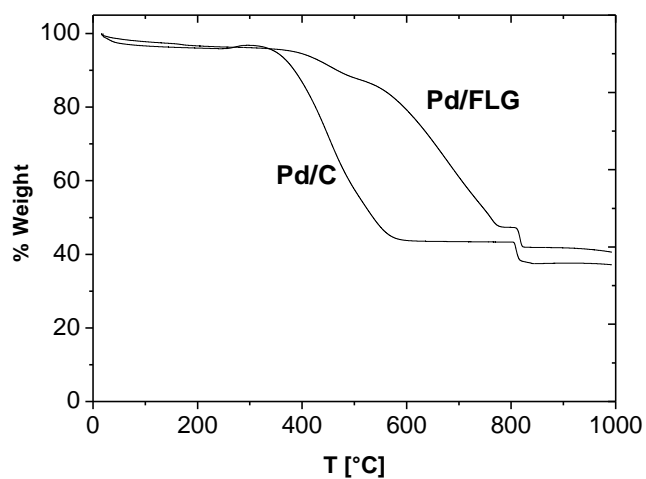

Fig. S5. TGA profiles of Pd/FLG and Pd/C catalysts.

Characterization tools:

High magnification transmission electron microscopy (TEM) was carried out on a JEOL 2100F working under an accelerated voltage of 200 kV with a point-to-point resolution of 0.23 nm. The low magnification transmission electron microscopy was carried out on a Topcon 002B-UHR microscope working with an accelerated voltage of 200 kV and a point-to-point resolution of 0.17 nm. The sample was crushed in a powder form and dispersed by ultrasounds in an ethanol medium for few minutes and a drop of this suspension was deposited onto a holey carbon coated copper TEM grid for examination.

X-ray diffraction (XRD) measurements were carried out in a Bruker D-8 Advance diffractometer equipped with a Vantec detector. The powdered sample was packed onto a glass slide. ASTM powder diffraction files were used to identify the phase present in the sample.

Atomic force microscopy (AFM) measurements were carried out with Dimension 3100 model from Veeco. The images were recorded using the tapping operating mode. We used standard cantilever with integrated Si tip; the resonant frequencies were in the range of 200−400 kHz (PPP-NCHR POINTPROBE-PLUS from Nanosensors).

Scanning electron microscopy (SEM) analysis was performed on SEM was carried out on a Jeol JSM-6700F working at 3 kV accelerated voltage, equipped with a CCD camera. The sample was previously deposited on SiO_2 wafer.

XPS analyses were performed with a MULTILAB 2000 (THERMO) spectrometer equipped with Al K α anode (hν= 1486.6 eV).

TGA analyses were carried out on TA instrument SDT Q600.

<u>Electrochemical measurements, ORR property:</u>

<u>A) Alkaline media</u>

Electrochemical studies were performed at 25°C in a three-electrode cell in 0.1 M KOH supporting electrolyte, using Autolab PGSTAT30 (Eco Chemie, The Netherlands) potentiostat equipped with an analogue linear sweep generator at the sweep rate of 10 mV s^{-1}. Mercury oxide (Hg/HgO) electrode and Pt-wire electrodes were used as reference and counter electrodes, respectively. All potentials are referred to the reversible hydrogen electrode (RHE). The electrochemical impedance spectroscopic (EiS) is used to determine the resistance of electrolyte solution.

10.0 mg of the catalyst sample, 5 mL isopropanol, and 50μL Nafion solution (5 wt.%) were ultrasonically mixed to form a homogenous catalyst ink. For the RRDE test, the working electrode (PINE, AFE6R2GCPT) was prepared by loading x (Pd or Pt) μL of catalyst ink onto a pretreated glassy carbon (GC) electrode (5.5 mm diameter and 0.2376 cm^2 geometrical area) and then dried at room temperature. The reference Pt/C data were recorded with a 20 wt% Pt/C (Sigma) catalyst with loading of 25 $\mu g_{Pt} \text{ cm}^{-2}$.

All aqueous solutions were prepared using ultrapure water (18MΩcm, < 3 ppb TOC) and supra-pure KOH (Sigma-Aldrich). In O_2-reduction experiments O_2 was constantly bubbled through the solution in order to maintain the saturation level and the ring potential was set at 1.2 V RHE in accordance with previous studies. Collection efficiency (N) was calculated from the experimental data obtained in 10 mM K_3FeCN_6 in 0.1M NaOH at standard measurement conditions (potential sweep rate 10 mV s^{-1}, 25°C). The collection efficiency for the catalysts electrode was found to be 37%. The collection efficiency (N) was calculated using $Fe(CN)_6^{3-} / Fe(CN)_6^{4-}$ reference system, with Pt/C.

The H_2O_2 yield was calculated from the following equation:

$$H_2O_2(\%) = 200(J_R/N)/(J_R/N-J_D)$$

Here, J_D and J_R are the disk and ring currents density, respectively, and N is the ring collection efficiency.

The electron transfer number can be calculated in two ways. The first is to use the ring current and the disk current n = $-4J_D/(J_R/N-J_D)$. The second way to calculate n is by using the first-order Koutecky-Levich equation:

$$1/J_D = 1/j_k + 1/j_d$$

where j_k is the kinetic current density and j_d is the diffusion-limited current density through the expression $j_d = B\omega^{1/2} = 0.62nF\gamma^{-1/6}D_{O2}^{2/3}C_{O2}\omega^{1/2}$. Here n is the average electron transfer number; F is the Faraday constant; γ is the kinematic viscosity of the electrolyte; D_{O2} is the oxygen diffusion coefficient ($1.15 \times 10^{-5} \text{ cm}^2/\text{s}$); C_{O2} is the bulk oxygen concentration in the electrolyte ($1.4 \times 10^{-6} \text{ mol/cm}^3$); and ω is the angular velocity of the electrode. The kinetic current density (j_k) and the Koutecky-Levich slope ($1/B$) can be obtained from a plot of $1/j$ versus $1/\omega^{1/2}$.

The Fig. S6 represents the cyclic voltammograms curves (under N_2) of Pd/FLG, Pd/C and Pt/C catalysts:
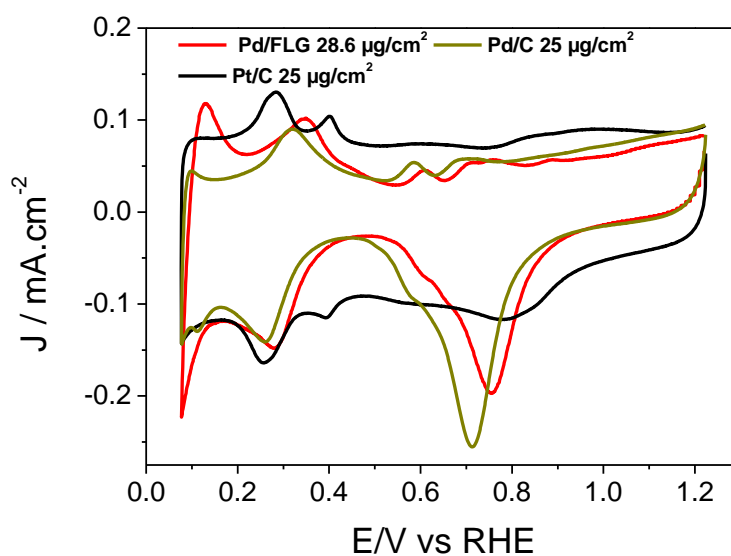

Fig.S6

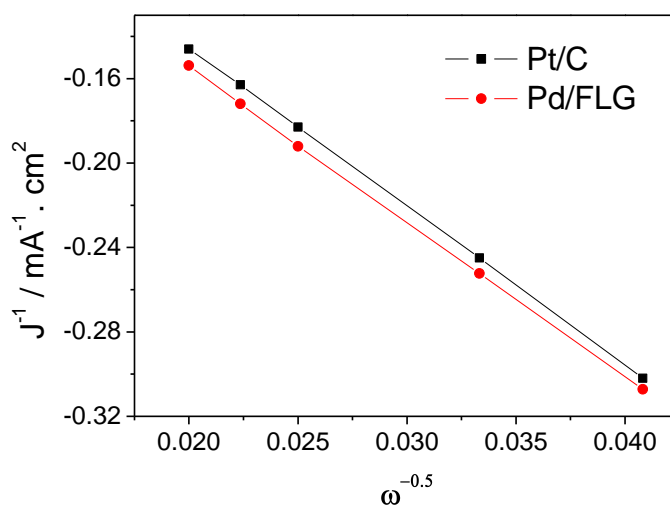The Pd/FLG exhibits a four-electron ORR process similarly to Pt/C (Fig.S7):

Fig.S7

To confirm the conclusion obtained from the K–L plots, we implemented rotating-ring-disk electrode (RRDE) measurements, by which the yield of H_2O_2 and the electron transfer number (n) could be accurately calculated from the disk and ring currents (Fig.S8):
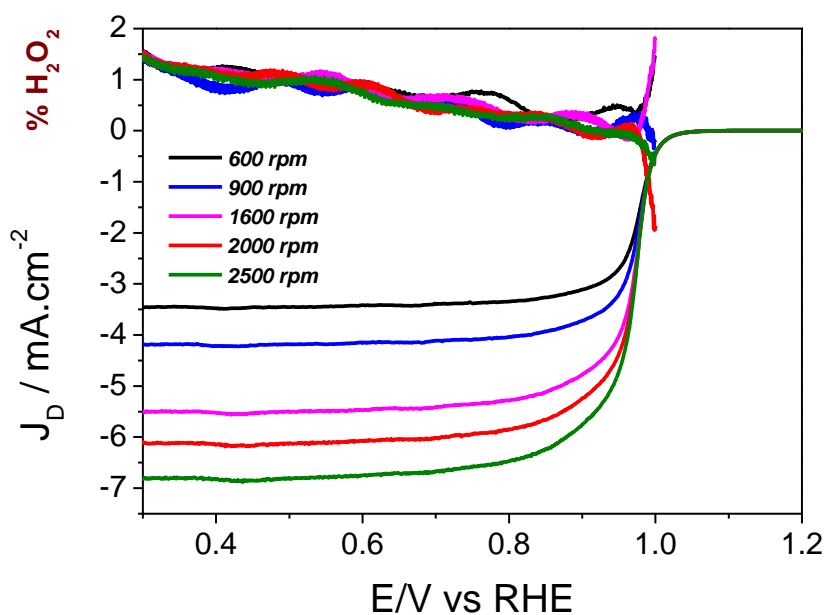
Fig.S8

The onset potentials (Eon), the half-wave potentials, the intensity at 0.9V and the number of transferred electrons per O_2 molecule (n) measured for each catalyst are listed in a table below. Taking the average of n calculated by the two methods above, gives n = 4 for both catalysts. The half potential of Pd/FLG is improved (~50mV). The E1/2 and the current intensity at 0.9V show superior to Pt/C and Pd/C activity of Pd/FLG catalyst.

	E_{on} / mV (± 5)	$E_{1/2}$ / mV	j at 0.9V (mA.cm^{-2})	n / e
Pt/C	1050	905 $\pm$ 5	-2.35	4
Pd/FLG	1100	955 $\pm$ 5	-5.46	4
Pd/C	1050	905 $\pm$ 5	-2.74	4

The stability of Pd/FLG catalyst was also investigated under potential cycling between 0.2 V and 1.2 V at 100 mV.s^{-1} and 900 rpm in 0.1 M KOH at 25°C. As shown in Fig.S8, the cyclic voltammogram measured after each 150 scan does not change during 2500 continuous potential cycles.
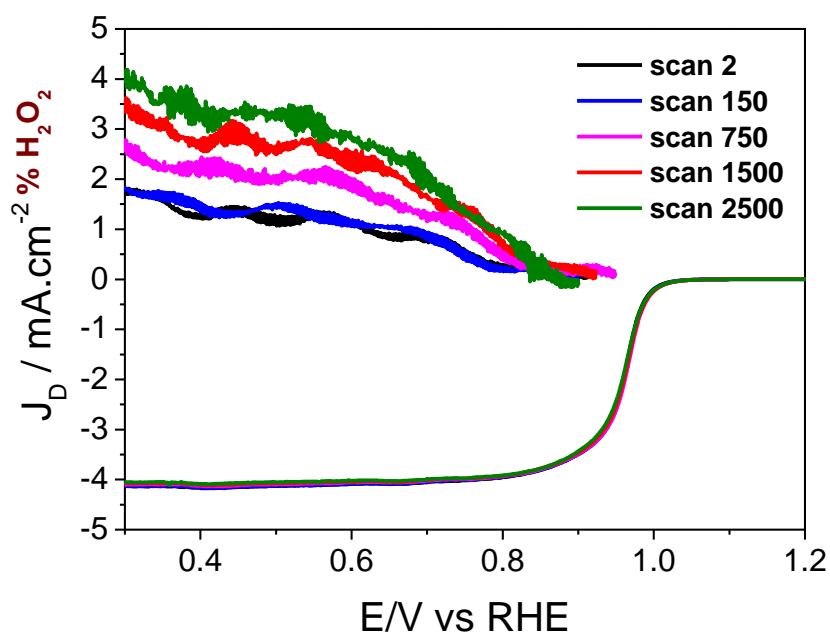
Fig.S9

Methanol Tolerance:

Fig. 10 A presents the polarization curves of the ORR test on Pd/FLG and Pt/C catalysts with and without methanol (0.1M). While the Pd/FLG shows higher oxidation of methanol than Pt/C, only Pt/C exhibits negative shift of 20 mV.

Fig. 10 B shows the j(t) chronoamperometric responses obtained at 0.825 V in 0.1 M KOH under magnetic stirring (600 rpm) and N_2-protection over 0 to 120 s, followed by an introduction of O_2. The arrow indicates the sequential addition of methanol into the air-saturated electrochemical cell.[S1]
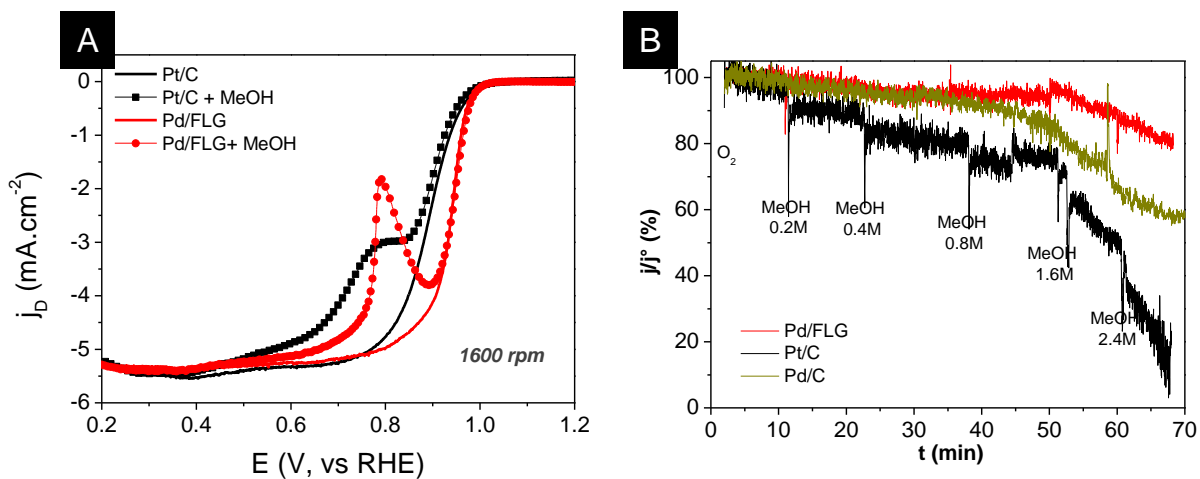
Fig. S10 A and B

B) Acid media

Electrochemical tests in acid media were performed in 0.5 M H_2SO_4 under the same condition and with the same set-up than the test in the alkaline media. Fig. S 11. demonstrates the obtained polarization curves for Pd/FLG and Pt/C catalysts.
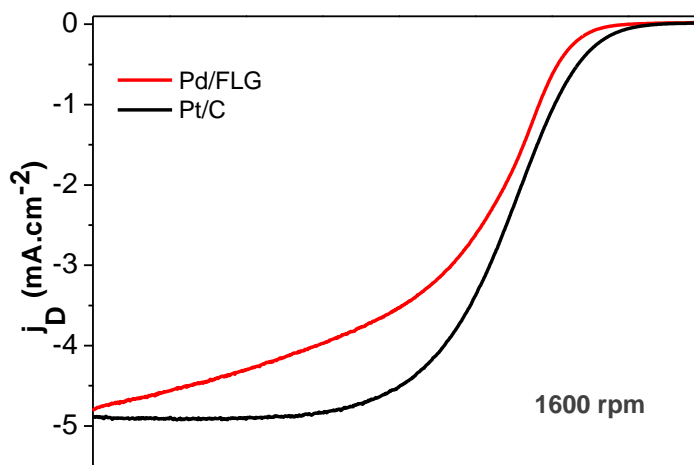

Fig.S 11

S1. K. Gong, F. Du, Z. Xia, M. Dustock, L. Dai, *Science* 2009, **323**, 760.