Electronic Supplementary Information

Hybrid chitosan derivative-carbon support for oxygen reduction reactions

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Experimental details

All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. Chitosan (Sigma Aldrich medium molecular weight) was used as the polymeric component. Methyl acrylate (MA) and diethylenetriamine were purchased from Merck chemical company. Hexachloroplatonic acid was purchased from Johnson Matthey.

(1) Synthesis of chitosan derivative (CSD) (scheme 1)

First step (Michael reaction): In a three-neck round bottom flask equipped with condenser, 2 g (12.4 mmol) chitosan (CS) in 50 ml of methanol was stirred at 50 ºC for 2 h. To this suspension, a solution of methyl acrylate (49.8 mmol) in 25 ml of methanol was added and then the mixture was stirred at the same temperature for 72 h under nitrogen atmosphere. The resultant mixture was cooled and the solid filtered, washed with methanol and dried under vacuum for 12 h to give N-carboxyethyl chitosan methyl ester (compound 1).

Second step (amidation reaction): New chitosan derivative (CSD) was prepared following the same procedure as for first step except that a solution of diethylenetriamine (37.3 mmol) in 25 ml of methanol was added to the compound 1 in 50 ml of methanol.

(2) Synthesis of hybrids chitosan derivative-carbon black (CSD.C)

The hybrids chitosan derivative-carbon black (CSD.C) were synthesized by two different methods:

Method 1 (M1): the carbon black Vulcan XC 72R (200 mg) was dispersed in 150 ml of 50% isopropanol solution under stirring for 1 hour, then the appropriate amount of chitosan derivative with concentration of 0.5mg/ml in 2 wt.% % acetic acid solution was added to the carbon black mixture drop by drop and stirred vigorously for 2h. Finally the solvent was evaporated by rotary and the sample was dried under reduced pressure at 80 ^{o}C for 4h.

Method 2 (M2): Chitosan (1 g) was dissolved in 200 mL of 2 wt.% acetic acid aqueous solution under stirring at 80 ^{o}C. Simultaneously, 200 mg carbon black was added to this solution and dispersed with ultrasonic treatment for 30 min. the mixture stirred at room temperature for 24 h and then the hybrid sample was separated by centrifuge at 14000 rpm. Finally, the sample was dried in the oven at 100 ^{o}C for 12 h.

(3) Synthesis of Pt/hybrids chitosan derivative-carbon black

The hybrid sample (125 mg) was added in 250 ml Mili Q water and sonicated in ultrasonic bath for 30 min to dispersed hybrid sample. A solution of 256 ml hexachloroplatonic acid (1 mM) and 125 ml isopropanol was added drop by drop to the mixture of hybrid sample and the mixture stirred for another 1 h. Finally platinum ions were reduced to nano particles by using $NaBH_4$ solution and the sample was separated by centrifuge, washed with hot water several times and dried in the oven at 100 ^oC for 12 h.

(4) Charaterization of catalysts

The Fourier transform infrared spectroscopy (FT-IR) analysis was performed using a Fourier transform infrared spectrometer (Jasco FT/IR-680 plus spectrophotometer) (Fig. S1). The nuclear magnetic resonance (NMR) was performed using a NMR Spectrometer AVANCE II (BRUKER), 9.4 Tesla magnet (Fig. S2). Particle size and morphology were evaluated from the transmission electron microscopy (TEM) images obtained in a JEM 2100F microscope operated with an accelerating voltage of 200 kV. XP spectra were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer (constant pass energy of 50 eV) and a non-monochromatic ($h\nu$ = 1254.6 eV) X-ray source, powered at 120 W. Textural properties have been evaluated from the N_2 adsorption-desorption isotherms of the samples, recorded at -196 ºC with a Micromeritics ASAP 2000 apparatus. Elemental Analysis has been evaluated in a LECO CHNS-932. X-ray diffraction profiles of the powder catalysts were obtained on a PANalytical X'Pert Pro X-ray diffractometer with a Cu Kα source (Fig. S3).

(5) Electrochemical measurements

All electrochemical experiments were carried out at room temperature in a three-electrode cell connected to an electrochemical analyzer (Autolab PGstat302N). A high surface area carbon rod was used as counter electrode and a reversible hydrogen electrode (RHE) in the supporting electrolyte was employed as reference electrode.

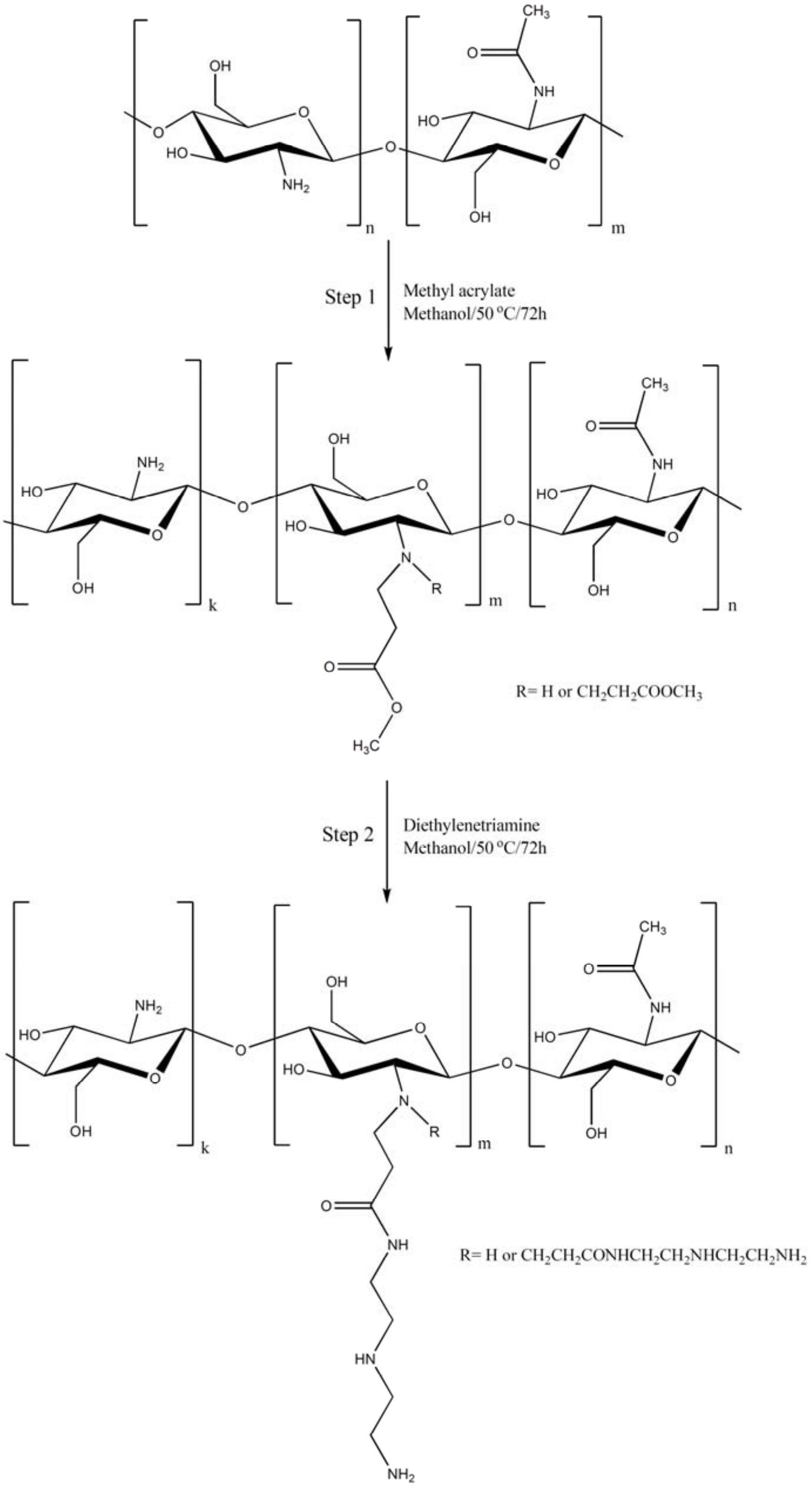
All potentials in the text are referenced to this electrode. The working electrode was prepared by ultrasonically dispersing 2 mg of the electrocatalysts in 0.5 mL of pure water (Millipore) and 15 µl of Nafion. Before electrochemical experiments, an activation step was carried out cycling between 0.05 and 1 V at a scan rate of 0.1 $V \cdot s^{-1}$ until the acquisition of a stable voltammogram was obtained. After the activation step, a blank cyclic voltammogram (CV) was recorded at a scan rate of 0.02 $V \cdot s^{-1}$ (Fig S4).

RDE measurements were performed in the oxygen-saturated 0.5 M sulphuric acid solution at rotation rates varying from 400 to 2500 rpm and with the scan rate of 2 mV/s. Rotating ring-disc electrode (RRDE) voltammogram was recorded using a GC ring-disk electrode with a 5-mm diameter glass carbon core and 9-mm outer diameter. RRDE experiments were carried out on a MSR electrode rotator (pine Instrument Co.). In this case, the extent of hydrogen peroxide formation during the ORR (i.e. the so-called two-electron pathway) can be determined in parallel to the overall ORR activity. In RRDE experiments, the ring potential was set to 1.2 V for detecting hydrogen peroxide formation. The four-electron selectivity of catalysts was evaluated based on the H_2O_2 yield, calculated from the following equation:

$$H_2O_2\,(\%) = 200 \times \frac{I_R/N}{(I_R/N) + I_D}$$

Here, I_D and I_R are the disk and ring currents, respectively, and N is the ring collection efficiency (26%).

Scheme 1. Synthesis process of the CSD. Step 1) Michael reaction. Step 2) amidation reaction.



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CSD

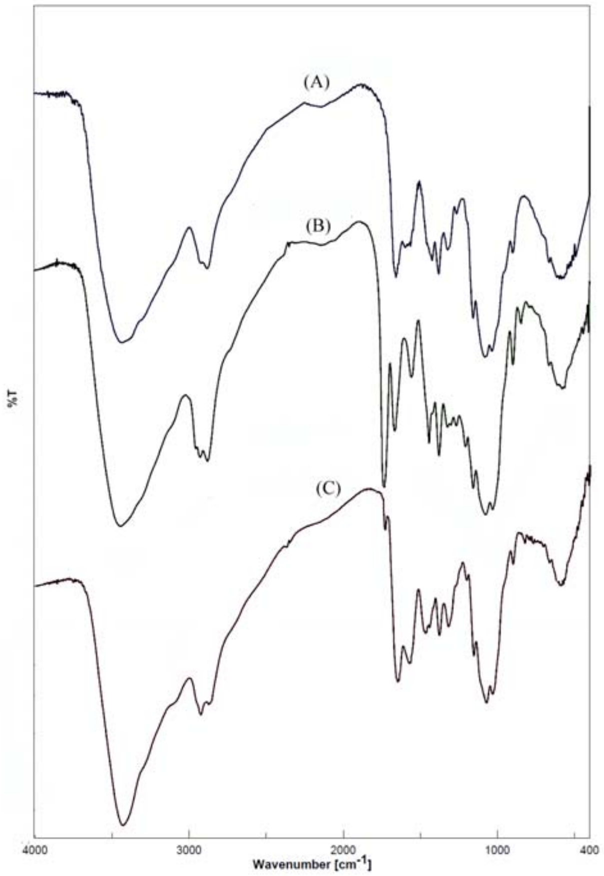
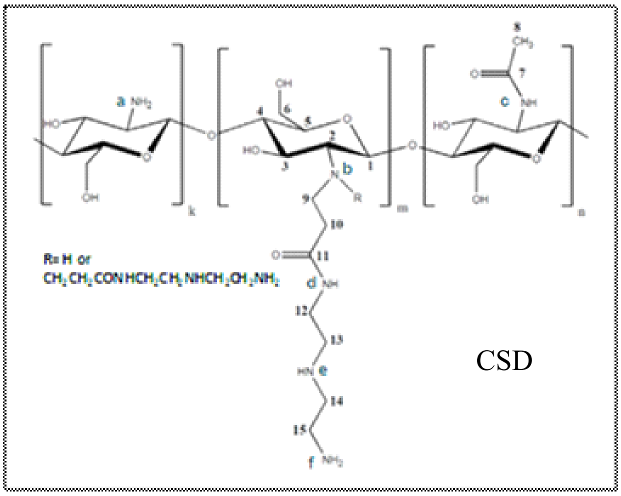


Fig. S1 The FTIR spectrum of Chitosan (A) Chitosan derivative after Michael addition (B) Chitosan derivative after amidation reaction (C)

The FTIR spectrum of the chitosan (A) shows strong peak at 3440 cm^{-1}, which could be attributed to the stretching of O-H and N-H bonds, and other peak at 2879 cm^{-1} attributed to the C-H stretching. The bands centered at 1650cm^{-1} and 1580 cm^{-1}, corresponding to the amide I and amide II vibrations, respectively. The bands in the range 1000–1150 cm^{-1} are characteristic of chitosan's saccharide structure, including the glycosidic bonds, of the C-O and C-O-C stretching [1-4]. After Michael addition reaction with methyl acrylate the FTIR spectrum (B) shows an additional peak around 1730 cm^{-1}, which is attributed to the carbonyl group in the ester moiety. After amidation reaction the peak originated from ester group disappeared, indicative of the conversion of ester group to a new amide group in the chitosan derivative structure (C).



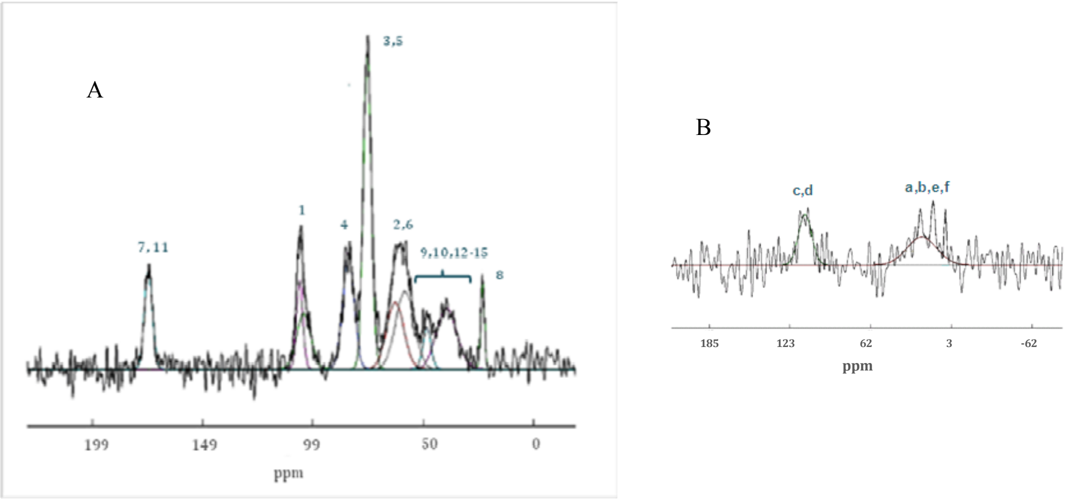


Fig. S2 ^{13}C CP-MAS NMR (A) and ^{15}N CP-MAS NMR (B) spectra of the CSD.

According to the literature, the peaks at 105, 83, 60 and 55 ppm in the ^{13}C CP-MAS NMR analysis are attributed to C1, C4, C6 and C2, as well as the peak at 75 ppm attributed to C3 and C5 in the chitosan structure, respectively. The peaks at about 23 and 173 ppm are attributed to the carbon atoms of the methyl moieties (C8) and carbonyl groups in the acetamido groups C7 and C11 [3,5]. The peaks in the range 30-50 ppm were assigned to the methylene carbons of the substituted groups anchored to the chitosan polymer chain (C9,C10,C12-C15). The ^{15}N CP-MAS NMR spectrum of chitosan displays two unique peaks at 115 ppm for the amide groups (c,d) and 20 ppm for the amine groups (a,b,e,f) [6].

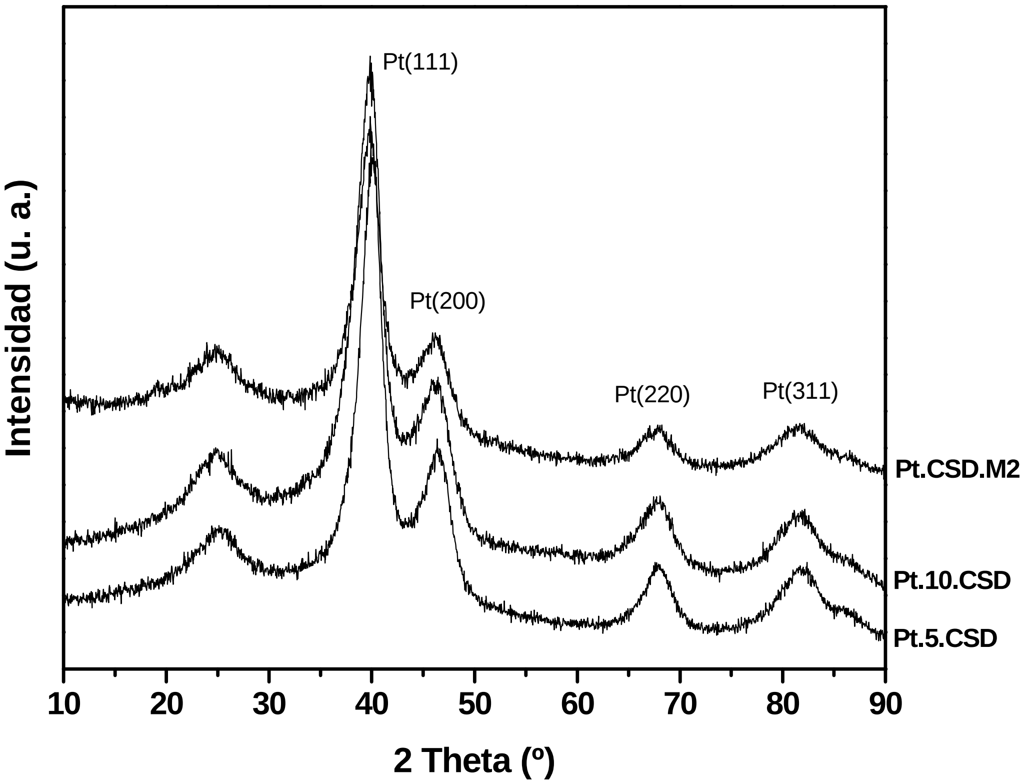


Fig. S3 X-Ray diffraction of electrocatalysts

All catalyst patterns display diffraction lines of Pt fcc (JPCDS 004-0802) and the characteristic diffraction pattern of graphitic carbon (24.9, 43.3 and 79.6º)

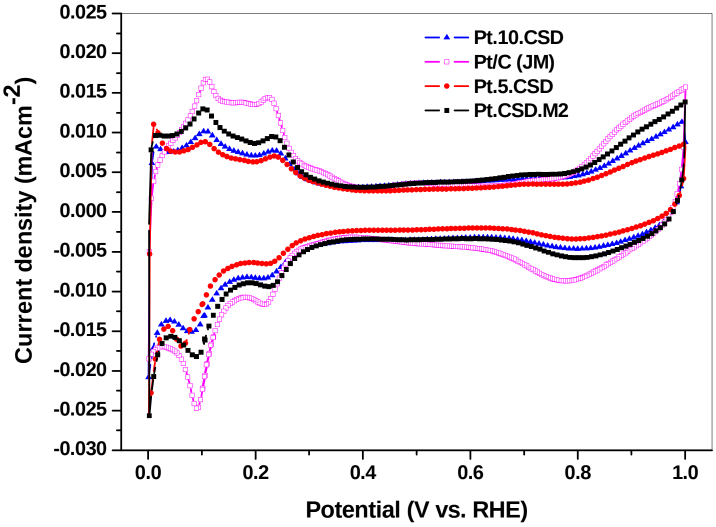


Fig. S4 CV curves for the electrocatalysts in 0.5M H_2SO_4 at 25 ºC, v = 0.02V s^{-1}. Current scale is normalized respect the ECSA

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