Electronic Supplementary Information

Mesoporous chromium nitride as high performance non-carbon support for oxygen reduction reaction

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Experimental

Mesoporous CrN: $ZnCr_2O_4$ was prepared by a solid state reaction of a stoichiometric mixture of powders of ZnO (99.99%, Aldrich) and Cr_2O_3 (99.99%, Aldrich). The powders were ground together and heated for 24 h in air at a temperature of 1300 °C. Mesoporous CrN was prepared by a solid-solid phase separation method from ammonolysis of $ZnCr_2O_4$ at 800 °C for 24 hr. The ammonolysis was done in a silica tube with air tight stainless steel end caps that had welded valves and connections to input and output gas lines. Ammonia gas were purified to remove trace amounts of oxygen or water using pellet copper, nickel, palladium and platinum with zeolites as support.

Pt/CrN: Firstly, 50 mg of mesoporous CrN (or C) was suspended in 50 ml of ethylene glycol solution, and an appropriate amount of H_2PtCl_6 solution was added. Then the mixture was heated at 140 ^oC for 3 h. Subsequently, the suspension was filtered and washed with deionized water, and then dried at 80 ^oC for 6 h to obtain the Pt/CrN catalysts (or Pt/C).

Physicochemical characterization: Finely ground powders were examined with a Rigaku Ultima VI powder X-ray diffractometer (PXRD) with CuK radiation ($K\alpha_1$, λ= 1.5406 Å and $K\alpha_2$, λ = 1.5444 Å). Crystal structures of the oxides and resultant nitrides were confirmed by PXRD profiles using GSAS. Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a LEO-1550 field emission SEM (FSEM). Pt on mesoporous CrN and Vulcan XC-72 carbon black were performed with a transmission electron microscopy (FEI T12 Spirit TEM STEM) at 120 kV. The samples for TEM were prepared by sonicating the powders in ethanol for 30 min following which 3.05 mm holy carbon copper grids were dipped into the solution and dried in air. Nitrogen adsorption/desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2020 system.

The samples were degassed at 200 °C for 24 hr on a vacuum line. A four point measurement of conductivity of compressed powders a relatively low pressure of 35 bar was used to estimate the conductivity.

Electrochemical Measurements: Electrochemical measurements were carried out with a potentiostat/galvanostat (WaveNano USB Potentiostat) and a conventional three-electrode test cell. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalysts, 1 mL ethanol, and 50 µL 5 wt.% Nafion solutions. 10 µL catalyst inks was pipetted and spread on the glassy carbon disk. A Pt foil and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

1. BET

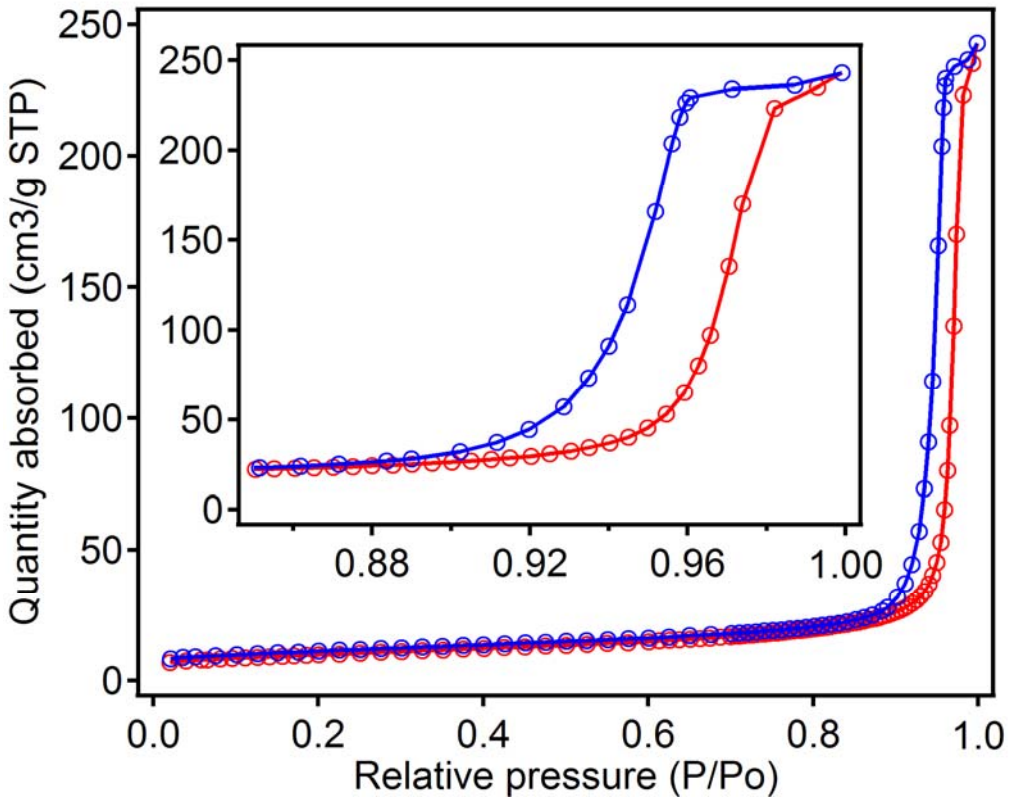

Fig. S1 Isotherm plot of N_2 absorption at 77 K for mesoporous CrN

2. Rietevld refinement of PXRD

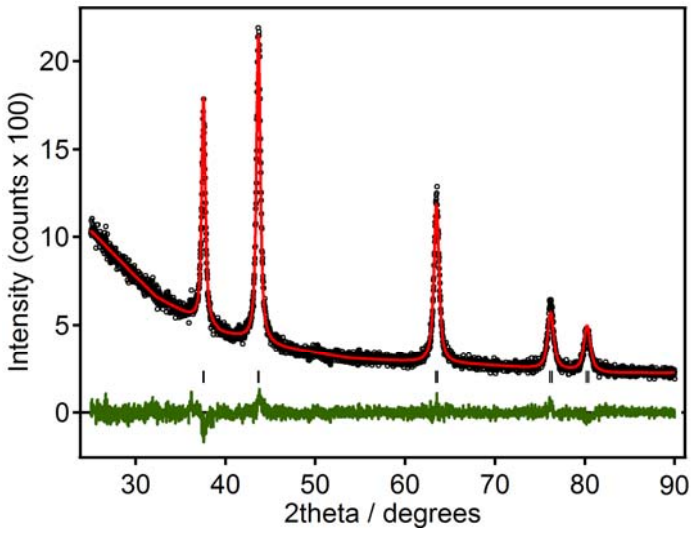

Fig. S2 Rietveld refinement of mesoporous CrN

3. The histograms of Pt particle diameters of Pt/CrN (a) and Pt/C (b).

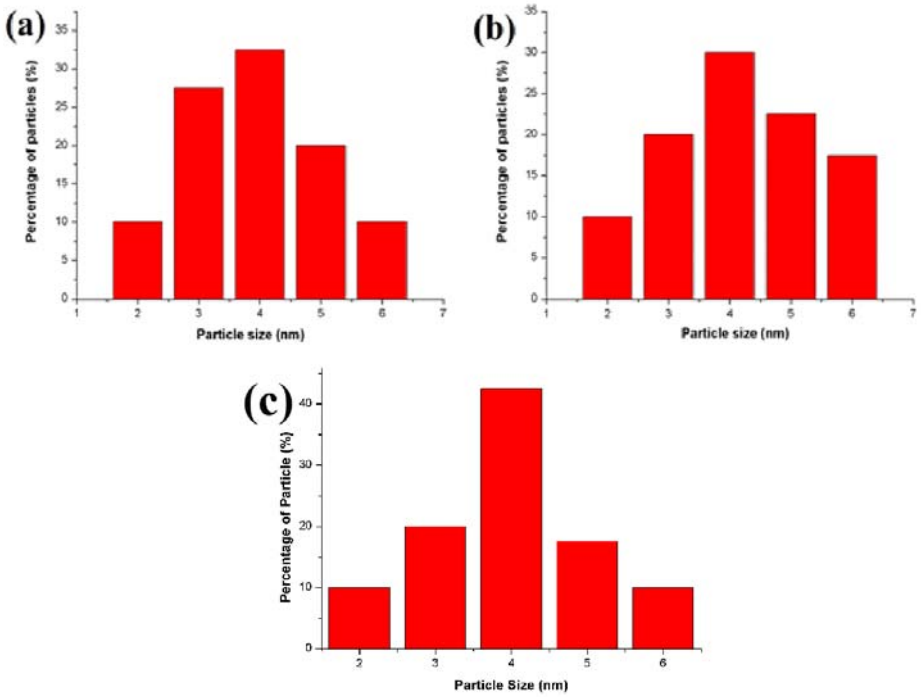

Fig.S3 The histograms of Pt particle diameters of Pt/CrN (a),Pt/C (E-TEK) and Pt/C (c).

4. Stability test of CrN in H_2SO_4 at 80 °C for 2 weeks.

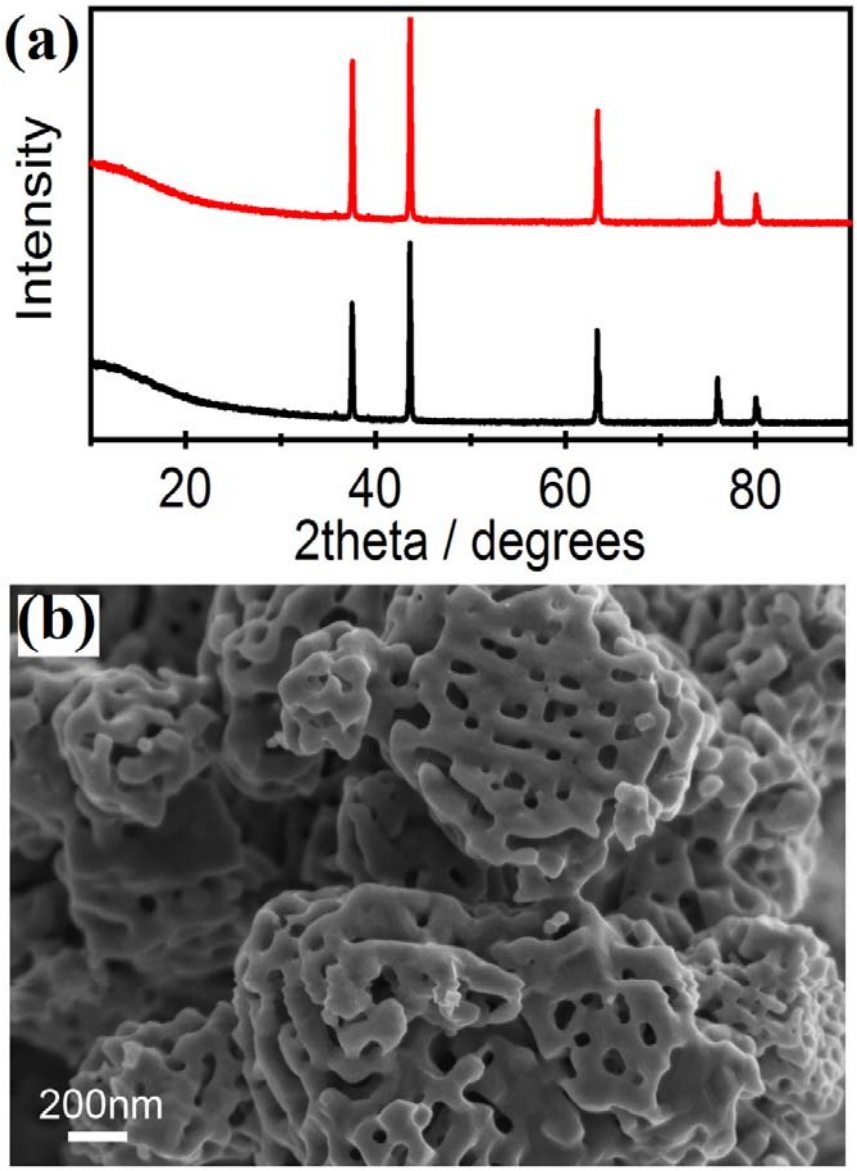

Fig. S4 XRD pattern of orginal CrN (black) and acid treated CrN (red); SEM image of acid treated CrN.

5. Electrochemical Test

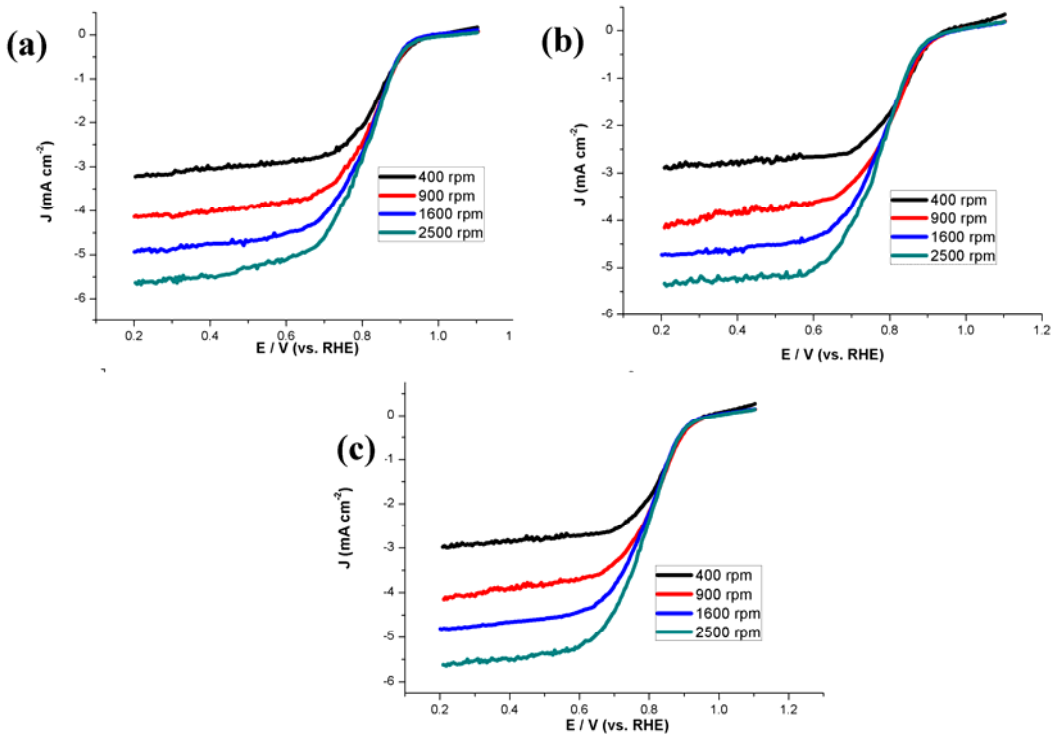

Fig. S5. Voltammograms for (a) Pt/CrN, (b) Pt/C (E-TEK) and (c) Pt/C catalysts obtained at different rotation rates in O_2-saturated 0.1M H_2SO_4.

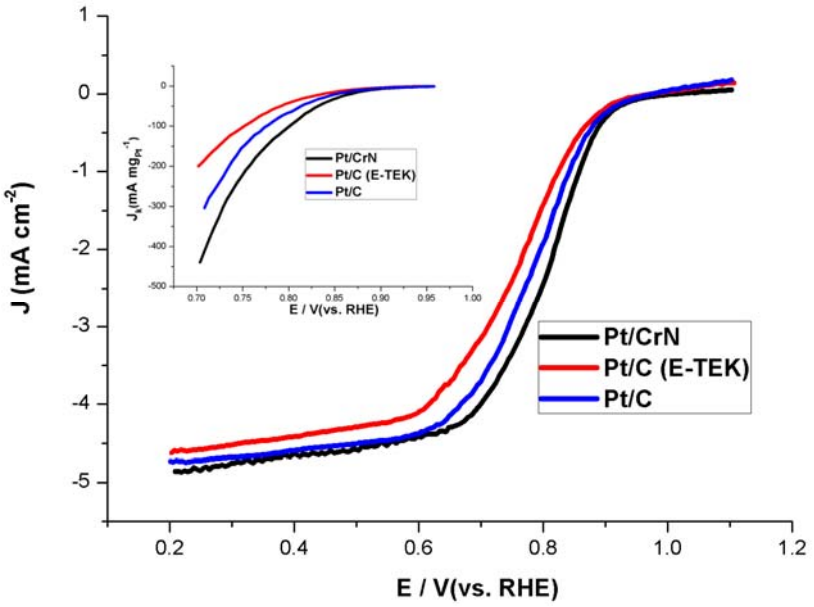

Fig. S6 ORR polarization curves in O_2-saturated 0.1 M H_2SO_4 after stability tests of 10000 cycles. The inset is kinetic current density of for Pt/CrN, Pt/C (E-TEK) and Pt/C for ORR.

6. TEM images of the catalysts after the stability test

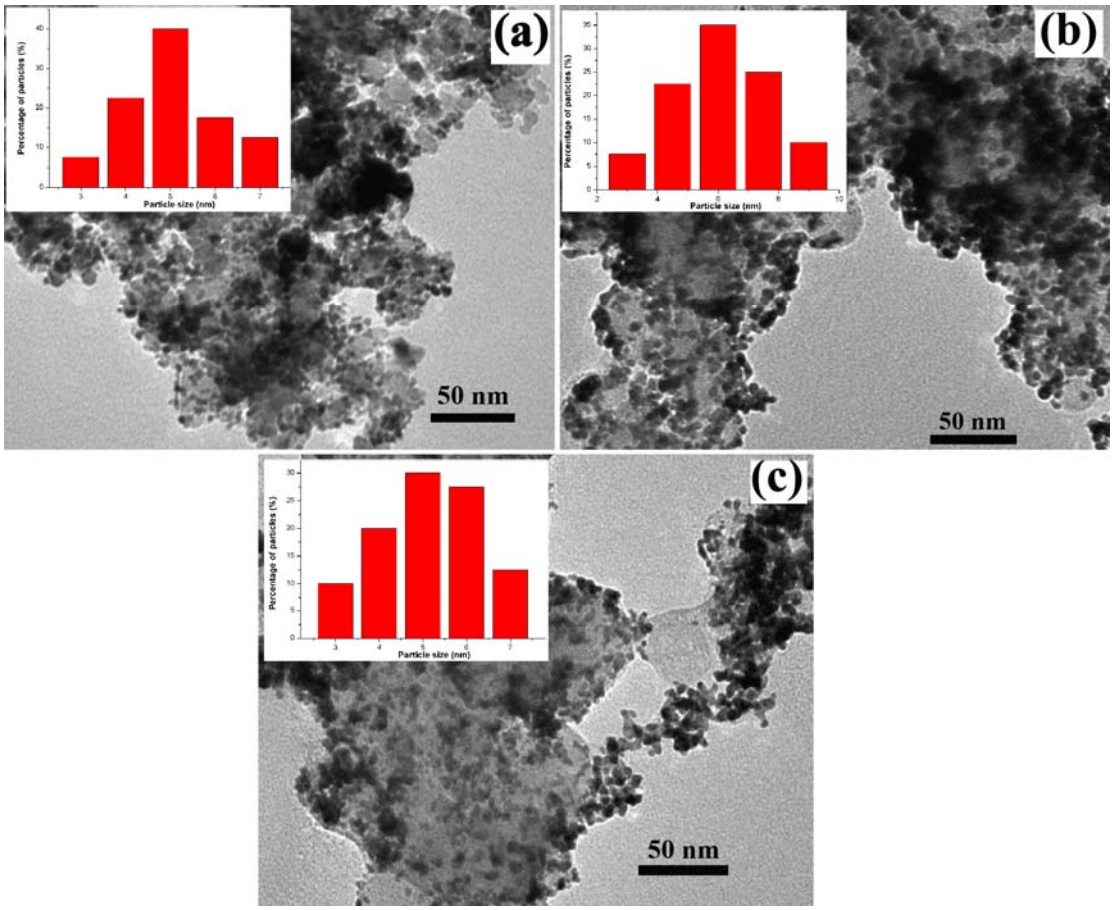

Fig. S7. TEM images for (a) Pt/CrN, (b) Pt/C (E-TEK) and (c) Pt/C catalysts after stability test.

The average sizes of the Pt particles in the Pt/CrN, Pt/C and Pt/C (E-TEK) catalysts as estimated from their histograms is approximately 5.0 ± 1.2 nm, 5.2 ± 1 nm and 6.1 ± 1.5 nm, respectively.