The beneficial effect of the addition of tungsten carbides to Pt catalysts on the oxygen electroreduction

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Preparation of tungsten carbides nanocrystals and tungsten carbides nanocrystals modified Pt electrocatalysts and the electrodes:

**Tungsten carbides nanocrystals**: 1 g tungsten powder was added to the 25 ml aqueous solution containing 10 ml 30v/v% H₂O₂, 5 ml isopropanol and 10 ml water. The solution was put steadily for 24 hours before 1 g Vulcan XC-72 carbon powder (Cabot Corp., USA) was added. The mixture was treated in an ultrasonic bath to form uniformly dispersed ink. The ink was then dried in a microwave oven with a heating procedure of 5s heating and 5s pause for six times. The dried powder was used as the precursor of tungsten carbides. The precursor powder in quartz tube was further treated by intermittent microwave heating procedure after 10 minutes argon bubbling.

**Tungsten carbides nanocrystals modified Pt catalysts**: Typically, 4mg as-prepared W₂C/C powder and 3.5mg 40% Pt/C catalyst were added into 1ml isopropanol. The well mixed material was IMH treated for 30 min to result in the further uniformly dispersed Pt-W₂C/C catalysts.

**Electrodes**: The graphite stick with the diameter of 6mm was used as electrode substrate and the top surface of the stick was pre-cleaned. 4mg catalysts were added into 1ml isopropanol, the mixture was treated with ultrasonic for 30 min for uniform dispersion. Then a quantity of mixture was dropped onto the top surface of the graphite stick. Finally, a drop of 0.5wt% Nafion solution was covered on the top to prevent the damage of the catalyst layer.

Characterization of tungsten carbides nanocrystals and tungsten carbides nanocrystals modified Pt catalysts:

The morphology and the particle size and distribution of the samples were studied by high resolution transmission electron microscopy: JOEP JEM-2010 HRTEM (JEOL Ltd) operating at 200 kV. XRD measurements were carried out with diffratometer D/Max-IIIA (Rigaku Co., Japan) using CuKα1(λ=1.54056Å) as radiation source. Electrochemical measurements were carried out on VoltaLab 80 Universal Electrochemical Laboratory (Radiometer Analytical Company, France). A standard three-electrode cell with separate anode and cathode compartments was used. A platinum foil and Hg/HgO electrodes were used as counter electrode and reference electrode, respectively.
All potentials shown in the figures are against Hg/HgO electrode. All the electrochemical measurements were carried out in 1 mol dm⁻³ KOH solution at 25°C.

Fig.S1 XRD patterns of W₂C/C, Pt/C and Pt-W₂C/C catalysts.
Fig.S2 TEM image of W_2C/C powder.
Fig. S3 Linear sweep curves of oxygen reduction on W₂C/C and W₂C modified Pt/C at different amount of Pt in O₂ saturated 1mol dm⁻³ KOH solution at 25°C, sweep rate: 2mV s⁻¹.