Co$_3$W$_3$C Promoted Pd Catalyst Exhibiting Superior Performance to Pt/C Catalyst towards the Oxygen Reduction Reaction

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Experimental Methods

Sample preparation

The Co$_3$W$_3$C/GC support was synthesized by a ion-exchange-assisted procedure: 50 g of macroporous acrylic-type anion-exchange resin (D314) was firstly exchanged with 1,000 mL of 0.1 M ammonium metatungstate hydrate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$) and sodium hexanitrocobaltate (Na$_3$Co(NO$_2$)$_6$) solution. The resulting resin complex (Co and W contained anions) was then sintered at 1,400 °C for 2 h under a pure Ar flow. The support material was crushed into fine powders by mechanical milling. The Pd/Co$_3$W$_3$C/GC catalyst was synthesized by the Intermittent Microwave Heating (IMH) method. The Na$_2$PdCl$_6$ and Co$_3$W$_3$C/GC were mixed with ethylene glycol in an ultrasonic bath for 30 min. The mixture was subjected to microwave heating (5 s on and 5 s off for 20 cycles) using a homemade microwave oven (2,000 W, 2.45 GHz). The content of Pd in Pd/Co$_3$W$_3$C/GC catalyst was ca. 30 wt. %. For comparison purposes, Pd/GC and Pd/C (Vulcan XC-72, Cabot, USA) catalysts with equivalent content of Pd were also synthesized.

Sample Characterizations

The X-Ray Diffraction (XRD) measurements were carried out on a D/Max-IIIA (Rigaku Co., Japan) employing Cu K$_\alpha$ ($\lambda = 0.15406$ nm) as the radiation source at 40 kV and 40 mA with a scanning rate of 8° min$^{-1}$. The morphologies of the samples were observed by Scanning Electron Microscopy (SEM) (LEO-1530VP, Germany). The Transmission Electron Microscopy (TEM) investigations were performed on a JEOL JEM-2010 operating at 200 kV. The catalytic activities of the electrocatalysts for the ORR were evaluated by using a Rotating Ring Disc Electrode (RRDE) with a...
biopotentiostat (AFCBP1E, Pine Instrument Co., USA) in a thermostat-controlled standard electrochemical cell at 25 °C with GC as working electrode, Pt flag as counter electrode and homemade RHE as reference electrode.

Additional Results:

![Contrastive TEM images of Co3W3C/GC (A and B) and Pd/Co3W3C/GC (C and D).](image)

In order to further demonstrate the distribution of Pd nanoparticles on the Co3W3C, we provided the contrastive TEM images of Co3W3C/GC (Fig. S1 A and B) and Pd/Co3W3C/GC (Fig. S1 C and D). From the contrastive TEM images, it can be clearly seen that Pd nanoparticles (~3 nm) have been successfully deposited on the Co3W3C (~20 nm).
“Synergistic effect” is a kind of general enhancement originated from two or more different components. In principle, the closer distance between the two components often contributes to more powerful synergistic effect. In order to evaluate the potential synergistic effect, we indicate that how much Pd actually is deposited on the Co$_3$W$_3$C by the TEM observation in selected constitutional unit as shown in Fig. S2. It can be seen that 32 Pd distribute in this constitutional unit, where 5 Pd are on the Co$_3$W$_3$C and 6 Pd are around the Co$_3$W$_3$C. Therefore, 34.37% Pd are contacting to the Co$_3$W$_3$C particles in this selected unit. As a whole, about 30% Pd could be estimated to deposit on/around the Co$_3$W$_3$C particles in the present sample.
Fig. S3 shows the Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS) for the Pd/GC, Pd/Co3W3C/GC and Pd/Co3W3C/C. The larger semicircles (larger charge transfer resistance) was observed for Pd/Co3W3C/C (3.95 Ω), whereas only small semicircle was shown for Pd/Co3W3C/GC (0.75 Ω) and Pd/GC (0.85 Ω). Therefore, it is reasonable that the Pd/Co3W3C/GC catalyst system shows much lower impedance than that of the Pd/Co3W3C/C catalyst system, due to the better electronic conductivity of the GC (graphitic carbon).

Fig. S4. Cyclic Voltammograms (CV) of the (a) commercial Pt/C and (b) Pd/Co3W3C/GC at 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ solution before and after the 1,000th CV cycles (+0.6–+1.2 V, 200 mV s⁻¹, O₂-saturated 0.1 M HClO₄ solution).