

Supporting Information (SI)

Co₃W₃C Promoted Pd Catalyst Exhibiting Superior Performance to Pt/C Catalyst towards the Oxygen Reduction Reaction

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Experimental Methods

Sample preparation

The Co₃W₃C^G/C 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 ((NH₄)₆H₂W₁₂O₄₀) and sodium hexanitrocobaltate (Na₃Co(NO₂)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/Co₃W₃C^G/C catalyst was synthesized by the Intermittent Microwave Heating (IMH) method. The Na₂PdCl₆ and Co₃W₃C^G/C 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/Co₃W₃C^G/C catalyst was ca. 30 wt. %. For comparison purposes, Pd^G/C 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-III A (Rigaku Co., Japan) employing Cu K_α (λ = 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 a₁

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:

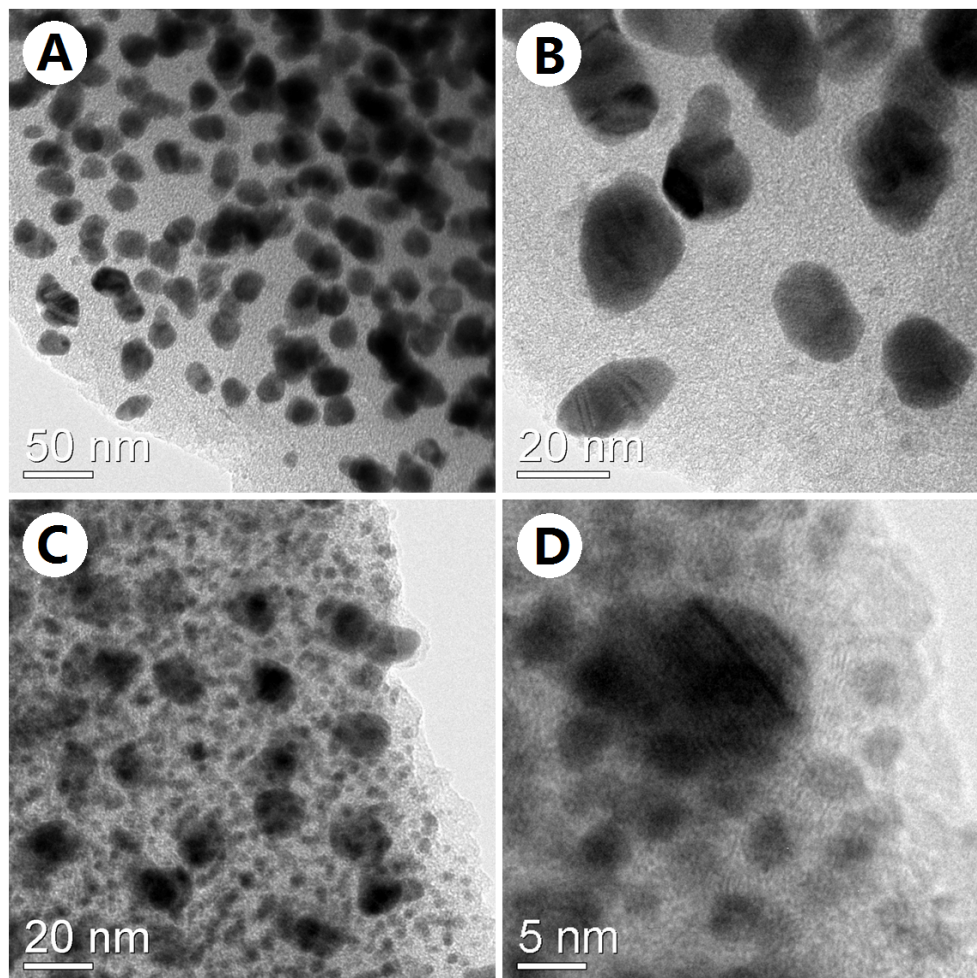


Fig. S1 Contrastive TEM images of $\text{Co}_3\text{W}_3\text{C}/\text{G/C}$ (A and B) and $\text{Pd}/\text{Co}_3\text{W}_3\text{C}/\text{G/C}$ (C and D).

In order to further demonstrate the distribution of Pd nanoparticles on the $\text{Co}_3\text{W}_3\text{C}$, we provided the contrastive TEM images of $\text{Co}_3\text{W}_3\text{C}/\text{G/C}$ (Fig. S1 A and B) and $\text{Pd}/\text{Co}_3\text{W}_3\text{C}/\text{G/C}$ (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 $\text{Co}_3\text{W}_3\text{C}$ (~20 nm).

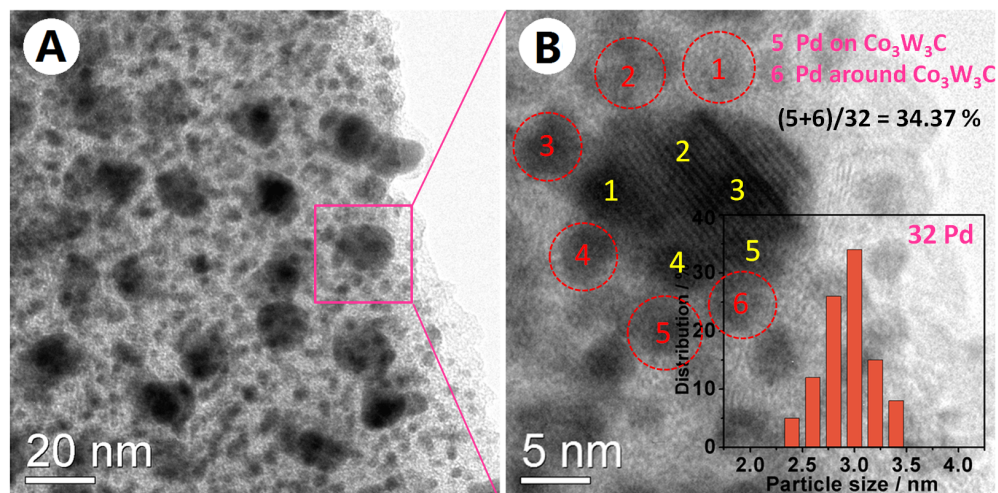


Fig. S2 Evaluation of Pd contacting to Co₃W₃C by TEM observation.

“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 Co₃W₃C 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 Co₃W₃C and 6 Pd are around the Co₃W₃C. Therefore, 34.37% Pd are contacting to the Co₃W₃C particles in this selected unit. As a whole, about 30% Pd could be estimated to deposit on/around the Co₃W₃C particles in the present sample.

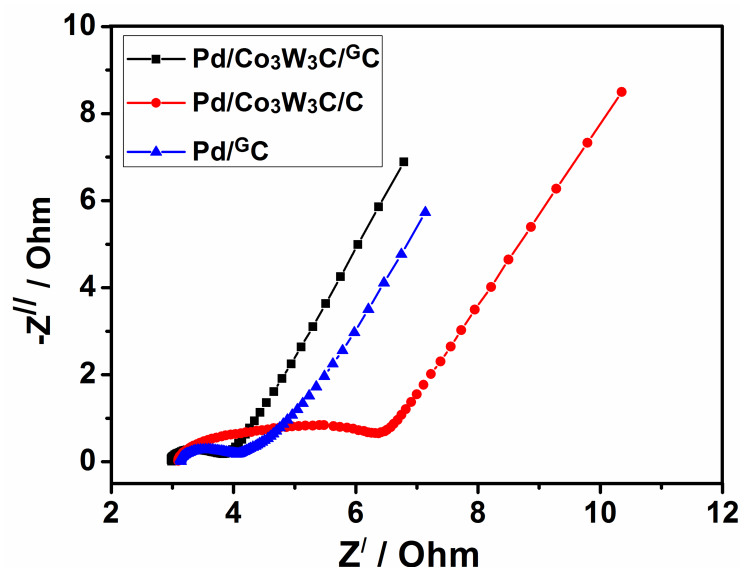


Fig. S3 Nyquist plots obtained from the electrochemical impedance spectroscopy (EIS)

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).

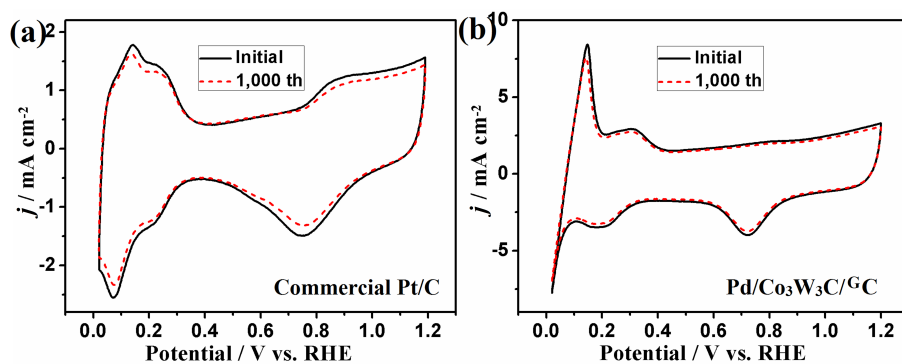


Fig. S4. Cyclic Voltammograms (CV) of the (a) commercial Pt/C and (b) Pd/Co₃W₃C/GC at 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ solution before and after the 1,000th CV cycles (+0.6-+1.2 V, 200 mV s⁻¹, O₂-saturated 0.1 M HClO₄ solution).