Supporting Information

Cuboctahedral Pd nanoparticles on WC for Enhanced Methanol Electrooxidation in Alkaline Solution

Young-Woo Lee, A-Ra Ko, Sang-Beom Han, Hyun-Su Kim, Do-Young Kim,

*Si-Jin Kim, and Kyung-Won Park**

Department of Chemical and Environmental Engineering, Soongsil University

Seoul 156743, Republic of Korea

*Corresponding author. E-mail: kwpark@ssu.ac.kr

Experimental

Synthesis of WC. Tungsten oxide hydrate were synthesized by hydrothermal method. Sodium metatungstate hydrate ($3Na_2WO_4 \cdot 9WO_3 \cdot xH_2O$, Aldrich) as precursor was dissolved in 5 M hydrochloric acid (Sigma) solution by vigorous stirring at an ambient room temperature or below. The resulting precursor solutions were heated to 120 ^{o}C at a heating rate of approximately 3 ^{o}C min^{-1}. With vigorous stirring, the acidic tungstate solutions were aged at that temperature for 60 min to allow a complete precipitating reaction. The resulting precipitates were thoroughly washed with de-ionized water, filtered by using a filtration and finally dried at 70 ^{o}C overnight.

Next, Tungsten oxide obtained by hydrothermal method, was loaded into an alumina boat, which was then inserted into a vitreous silica tube inside a cylindrical furnace. A gas mixture of 20 ml min^{-1} CH_4 with 80 ml min^{-1} H_2 was passed through the quartz tube at a rate of 100 ml min^{-1} during the entire reaction. Tungsten carbide samples studied in this work were prepared at 900 ^{o}C. After carburization, all of the samples were passivated in a air gas flow for more than 5h before being removed from silica tube.

Synthesis of cuboctahedral Pd NPs on WC support catalyst. The as-prepared WC supported Pd nanoparticles were prepared by reducing Pd salt in ethylene glycol (EG) solution. A solution of 2 mM Na_2PdCl_4, 10 mM $NaNO_3$, and 20 μM $FeCl_3$ was dissolved in 50 ml of EG with 50 mg poly(vinyl pyrrolidone) (PVP, MW = 29,000). The mixed Pd salt solution and as-prepared WC (255.4 mg) treated were added to the solution and mixed with continuous stirring at room temperature. All chemicals used were of analytical grade. The solution was raised by 5 ^{o}C min^{-1} and was kept for 90 min at 250 ^{o}C until Na_2PdCl_4 was completely reduced by EG. The resulting colloid solution was cooled at room temperature, washed with water and then with ethanol several times to remove ethylene glycol and excess PVP.

Characterizations. For the structure analysis of the catalysts, X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray diffractometer with Cu K_{α} (λ = 0.15418 nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 80° was explored at a scan rate of 5° min^{-1}. For all the XRD measurement, the resolution in the scans was kept at 0.02°. The morphology and size distribution of the catalysts were characterized by field-emission transmission electron microscopy (FE-TEM) using a Tecnai G2 F30 system operating at 300 kV. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid. Energy dispersive X-ray (EDX) analysis of the catalysts was performed on a field emission transmission electron microscope (FE-TEM, Tecnai G2 F30 system).

Electrochemical properties of the catalysts were measured in a three-electrode cell at 25 ^{o}C using a potentiostat (Eco Chemie, AUTOLAB). A Pt wire and Hg/HgO (in saturated 1.0 M NaOH) were used as a counter and reference electrode, respectively. The glassy carbon electrode as a working electrode was polished with 1, 0.3, and 0.05 μm Al_2O_3 paste and then washed in deionized water. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of Millipore water. The catalyst ink was dropped onto a glassy carbon working electrode (geometrical area of 0.0706 cm^2). After drying in 50 ^{o}C oven, total metal loading of cuboctahedral Pd/WC and Pd/C was 8 and 20 μg cm^{-2}, respectively. To compare electrochemical properties and catalytic activity of the catalysts, cyclic voltammograms (CVs) were obtained between -0.8 to +0.2 V in 1.0 M KOH and 2.0 M KOH + 2 M CH_3OH, respectively.

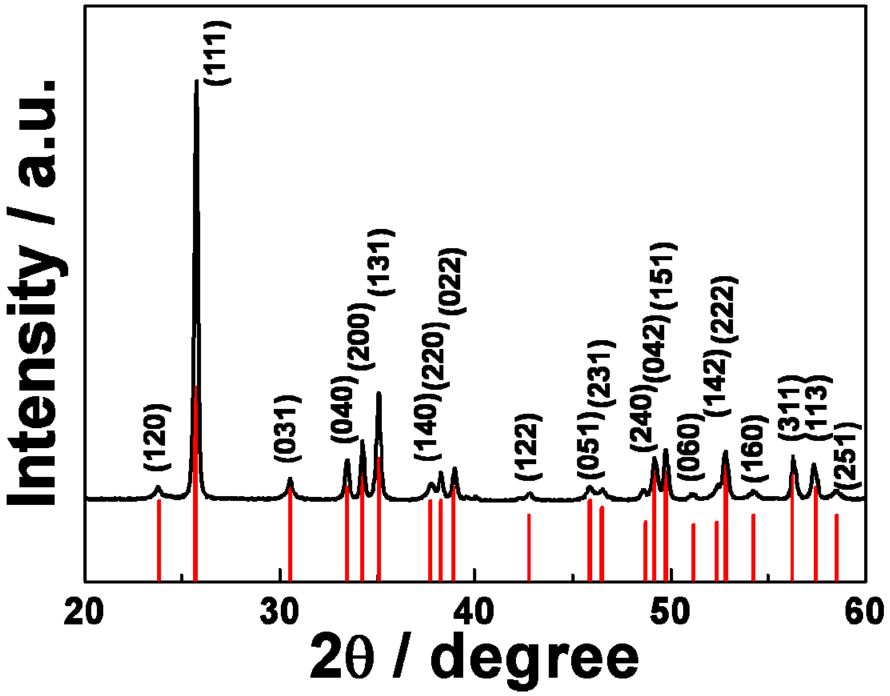


Figure S1. X-ray diffraction pattern of as-prepared $WO_3 \cdot H_2O$ measured in the scan range 20-60° as compared with that of the reference (JCPDS No. 43-0679).

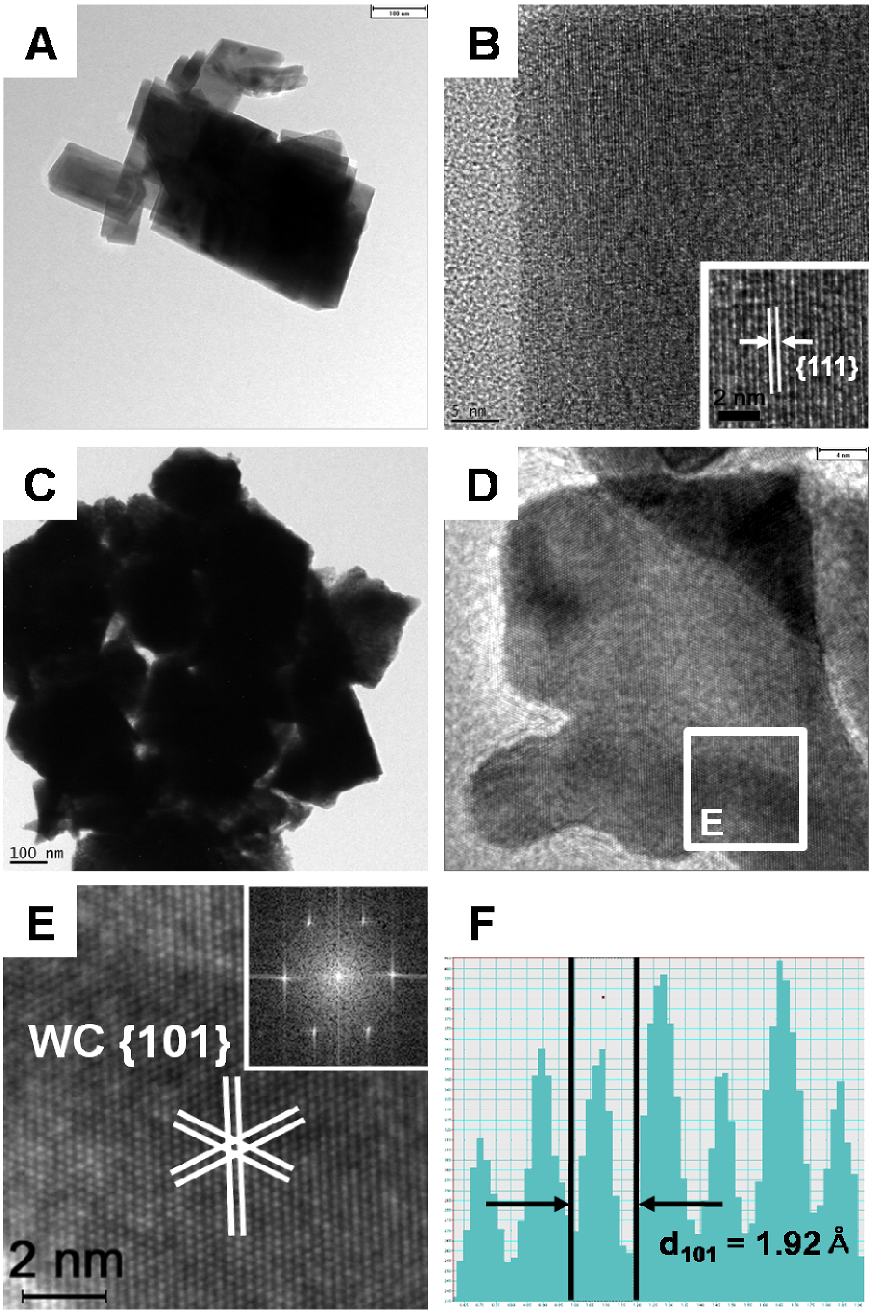
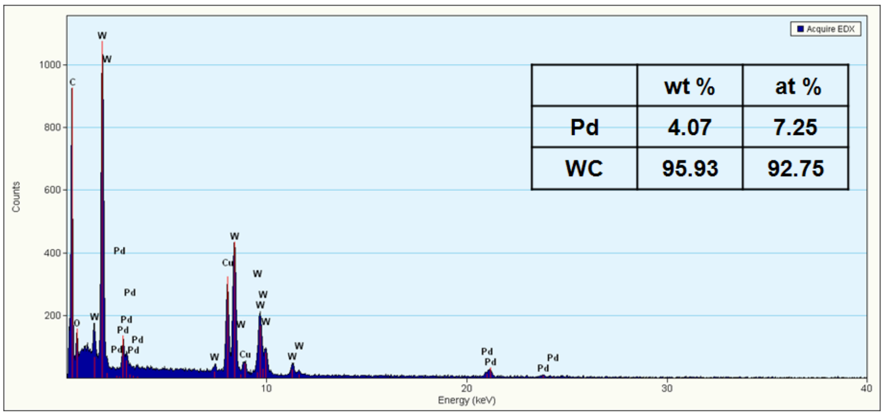


Figure S2. (A) Field-emission transmission electron microscopy (FE-TEM) and (B) high-resolution transmission electron microscopy (HR-TEM) images of as-prepared $WO_3 \cdot H_2O$ particles. (C) FE-TEM and (D) HR-TEM images of as-synthesized WC particles. (E) HR-TEM image of WC containing {101} facets. The inset indicates a FFT pattern of WC. (F) The profile of the lattice fringe of WC with {101} facets.



	wt %	at %
Pd	4.07	7.25
WC	95.93	92.75

Figure S3. Composition and weight ratio of Pd NPs and WC obtained by means of EDX analysis.