Palladium-nickel alloys loaded on tungsten carbide as platinum-free anode electrocatalysts for polymer electrolyte membrane fuel cells

Electronic Supplimentary Information

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Experimental

1. Synthesis of Electrocatalysts

All the chemicals were analytical grade, purchased from Sigma-Aldrich Reagents Co., and used without further purification. Tungsten mono-carbide (WC) nanoparticles were fabricated by thermal decomposition of polymer intermediate prepared by hydrothermal process. The polymer intermediate was synthesized by first mixing Cetyl Trimethyl Ammonium Bromide (CTAB) (6.5g) and deionized (DI) water (20 ml). And, the other solution was also prepared with ammonium metatungstate (5 g), resorcinol (1.2 g) and formaldehyde (1.8 ml) in DI water (20 ml). The latter solution was added to the former solution. And then, the mixture was heated at 358 K for 1 hr. The resulting gel was moved to autoclave, and the hydrothermal process was performed at 423 K for 48 hr. The polymer gel embedded by Ammonium Meta Tungstate (AMT) and CTAB was calcined at 1173 K for 1 hr under Ar and 2 hr under H_2 gas with a flow rate of 68 µmole/sec, respectively.

Twenty wt% Pd, PdNi alloys (20 wt% Pd basis) were loaded on fabricated WC nanoparticles (~76 m^2/g, ~4.3 nm pore) and Vulcan XC-72R (~240 m^2/g, ~2 nm pore) via colloidal method, respectively. The 0.6 g of supports was added to a mixture of ethylene glycol (101 ml) and DI water (34 ml). And, a 5 wt% solution of $PdCl_2$ hydrate in water and 10 wt% HCl (20 wt% basis) were mixed in 64 ml DI water, and $NiCl_2$ hydrate precursor was input to the latter solution with the Pd precursors. These two kinds of solutions were mixed and refluxed at 413 K for 2 hr. The resulting solution was filtered and dried under ambient temperature.

20 wt% Pt/C commercial electrocatalyst was purchased from Johnson Matthey (JM). Furthermore, 20 wt% Pt/WC nanoparticles and the same Pt loading of Pt/C were prepared for the comparison of electrochemical activities with Pd, PdNi alloys loaded on WC.

2. Characterization and Electrochemical Tests

The prepared electrocatalysts were characterized by using X-ray diffractometer (MAC Science M18XHF diffractometer). The specific surface area was analyzed by the Brunauer–Emmett–Teller (BET) method (Micrometrics ASAPS2012). The morphologies and EDAX mappings were investigated by scanning transmission electron microscopy (STEM) and high-resolution transmission electron microscopy (HRTEM), which were carried out with a JEOL 2100F at 200 kV.

Synchrotron X-ray measurements for XANES analysis were performed on 5A wiggler beamline of Pohang Accelerator Laboratory (2.5 GeV; 150-180 mA), Republic of Korea. The incident beam was monochromatized using a Si(111) double crystal monochromator. The spectra for L_3-edge of W (E_o=10,207 eV) were taken in a transmission mode with separate He-filled IC Spec ionization chambers for incident and transmitted beam at room temperature. The obtained data were normalized and analyzed with ATHENA in the IFEFFIT software programs. Especially, the absorption edges were fitted by two parts of arc-tangent and lorentzian via software programs of ATHENA, and the white-line areas indicated the d-band vacancy were calculated by amplitude of fitted lorentzian plot. The oxidation states of Pd were characterized by XPS.

The three electrode system was employed to cyclic voltammetry (CV) for hydrogen oxidation and linear sweep potential (LSP) for electrochemical stability test. Glassy carbon electrode (0.0707 cm^2), Pt wire and Ag/AgCl (3 M NaCl) were used as working, counter and reference electrodes, respectively. The CV was conducted in N_2-purged 1 M H_2SO_4 aqueous solution for the study of hydrogen oxidation reaction. The electrochemical measurements were performed by using a Princeton Applied Research (PAR, 263A) potentiostat. A known amount of electrocatalytic ink comprising 20 mg of the electrocatalyst, 1000 μl of DI water and 10 μl of

5 wt% nafion solution was mounted on the glassy carbon electrode. The solvent was slowly evaporated in an oven. In addition, a 5 μl of 5 wt% Nafion was coated on the electrode as a binder, and the electrode was evaporated again. All electrocatalysts were analyzed with steady state voltammograms between -0.2 and 1.0V (vs. Ag/AgCl 3M NaCl). In case of linear sweep potential, the experiments were conducted under the same environment as CV experiments such as electrodes (Working electrode-Glassy carbon electrode, Counter electrode-Pt wire and Reference electrode-Ag/AgCl, 3 M NaCl) and electrolyte of N_2 purged 1 M H_2SO_4 including the identical procedures for preparing catalyst ink and its mounting on glassy carbon. The sweep was also measured from cathodic to anodic potential direction from -0.2 to 1.0 V (vs. Ag/AgCl, 3 M NaCl). Furthermore, for identification of substrate stability, XPS (W 4f and Ni 2p) was measured for the samples before and after CV.

For single cell test, the catalyst slurries were prepared with Pd/WC, Pd_3Ni_1/WC, Pd_3Ni_1/WC, Pt/C (lab-made) and commercial Pt/C (Johnson-Matthey, JM) for anode electrode, respectively. The slurries prepared with the electrocatalyst, isopropyl alcohol (IPA) and Nafion solution were sprayed on carbon paper with the electrode area of 6.25 cm^2. The loading amounts of anode electrocatalysts on carbon paper were 0.3 mg_{Pd}/cm^2 for Pd-based materials and 0.3 mg_{Pt}/cm^2 for Pt-based catalysts, respectively. The cathode side was also prepared with commercial 20 wt% Pt/C (JM) electrocatalyst throughout the same procedure as anode side on the basis of 0.3 mg_{Pt}/cm^2. The membrane-electrode assembly (MEA) was fabricated via hot-pressing method with the anode, cathode and Nafion 212 membrane under 1500 psi at 398 K for 3 min. The single cell performances were evaluated with H_2 and air flow rate of 150 ml/min and 1 L/min, respectively. The actual cell, anode humidified and cathode humidified temperatures were 333 K, 333 K and 328 K, respectively. The initial stability of the electrocatalyst was estimated by comparing the maximum power densities from the current density-voltage (I-V) polarization curve before and after continuous operation over 50 h after activation process. For the long-term stability, the electrocatalyst was tested in the V-t galvanostatic operation mode at open circuit voltage (OCV) and 0.1 A/cm^2 in single cell. In case of the fixed current density of 0.1 A/cm^2, the intrinsic electrocatalytic property could be clearly observed without the interruption of ohmic loss and mass transfer phenomenon. In addition, the V-t curves of Pd_3Ni_2/WC, commercial Pt/C (JM), Pt/C (Lab-made) and Pd/C were also compared for a similar operating period. The single cell test was evaluated with SMART (Won-A Tech. co. Korea).

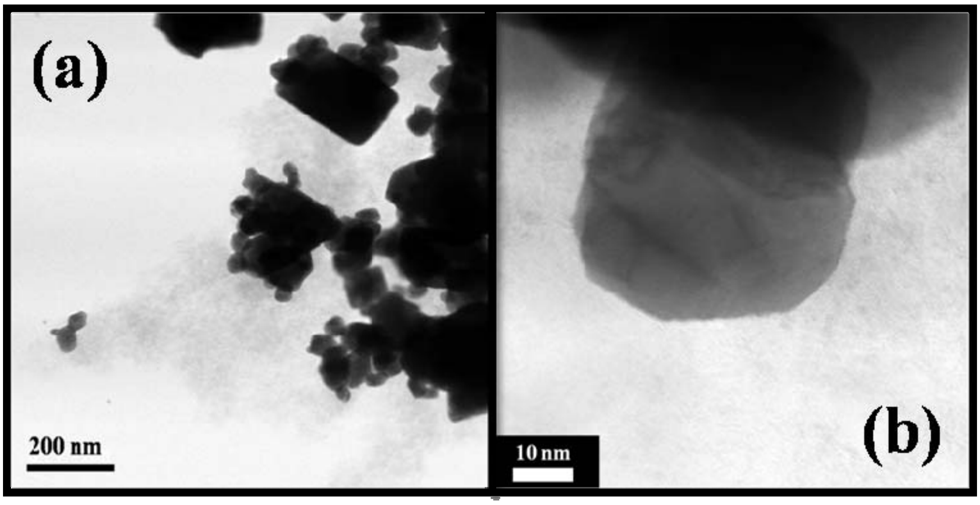

Fig.S1. HRTEM images of pure WC in (a) low magnitude and (b) high magnitude.

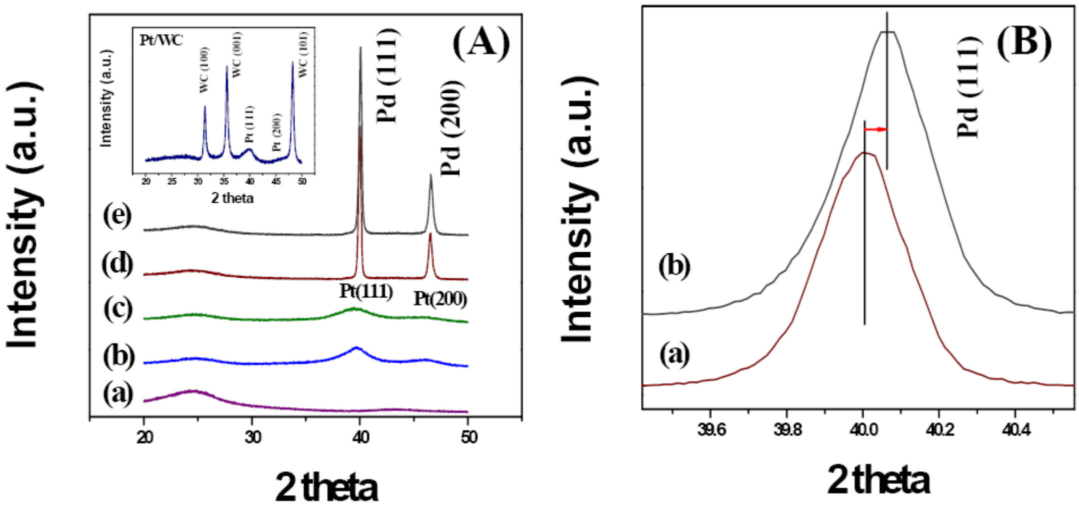

Fig.S2 (A) XRD patterns of (a) Vulcan XC-72R carbon, (b) Pt/C (JM), (c) Pt/C (Lab-made), (d) Pd/C (Lab-made) and (e) Pd_3Ni/C including the inset for Pt/WC. (B) Peak shift of Pd (111) plane of (a) Pd/C (Lab-made) and (b) Pd_3Ni/C.

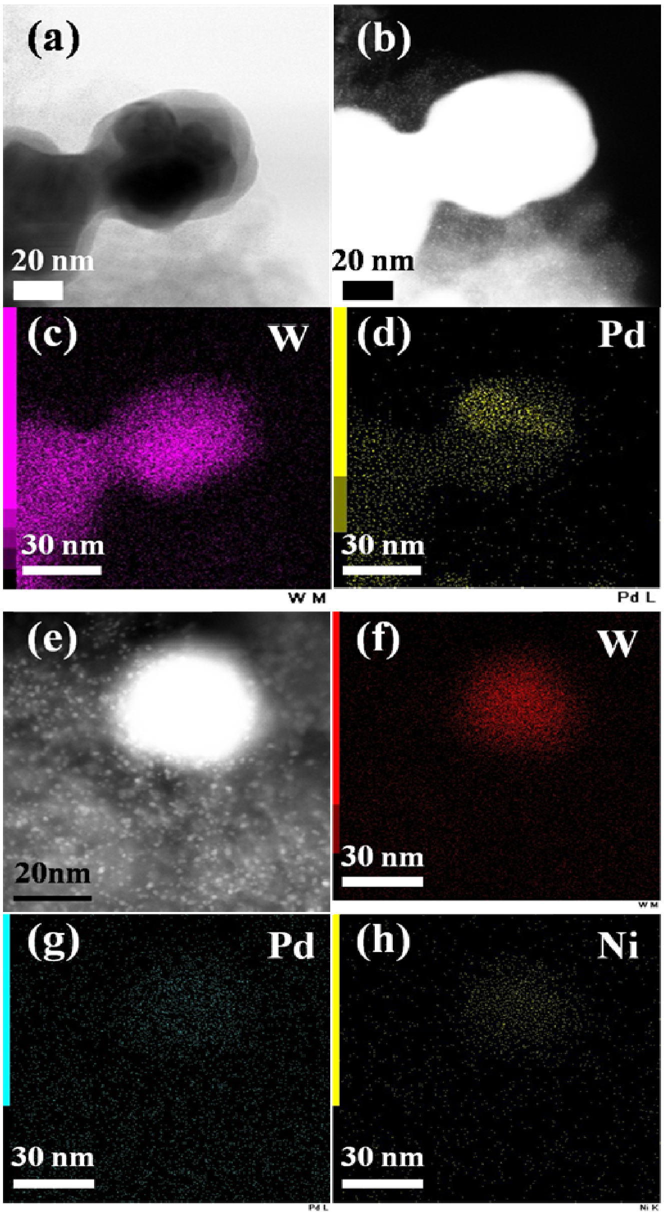

Fig.S3 HRTEM bright/dark field images and EDAX element mapping for Pd, Ni and W of (a-d) Pd/WC, (e-h) Pd_3Ni/WC.

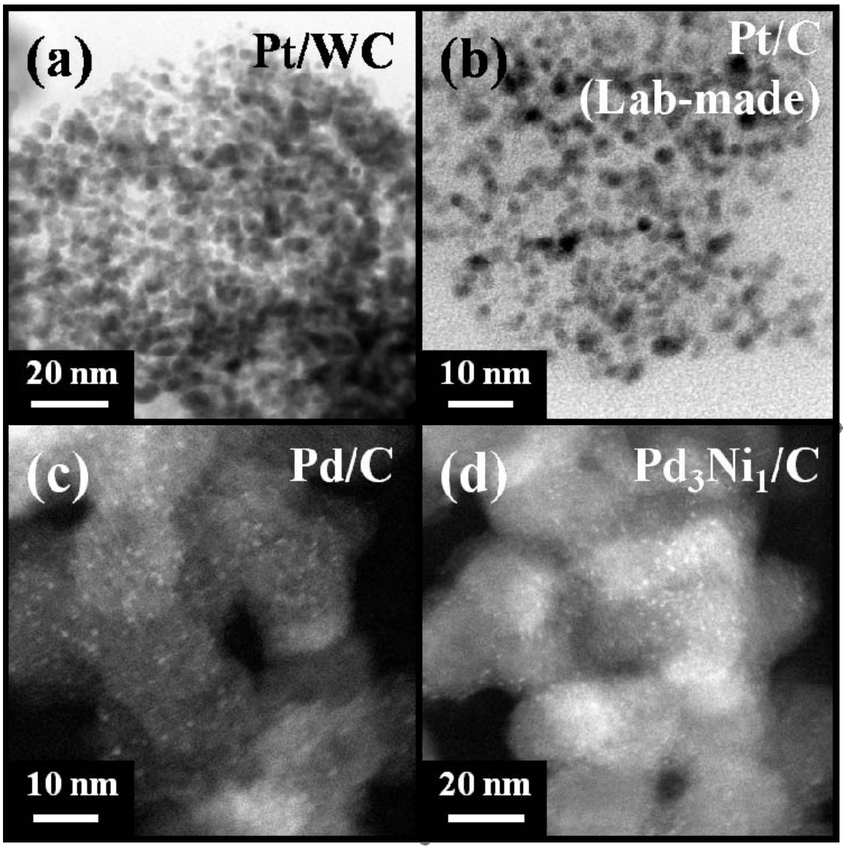

Fig.S4 (a) HRTEM image of Pt/WC, (b) HRTEM image of Pt/C (Lab-made). Dark field image of HRTEM for (c) Pd/C (Lab-made) and (d) Pd_3Ni/C.

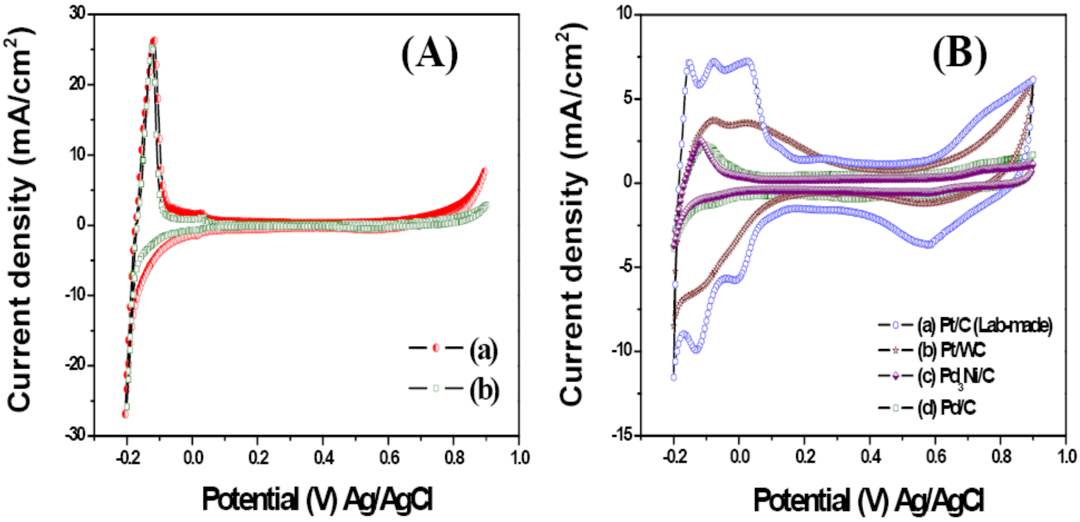

Fig.S5 (A) CV of (a) Pd_3Ni_2/WC and (b) Pd_3Ni/WC. (B) Cyclic voltammograms of (a) Pt/C (Lab-made), (b) Pt/WC and (c) Pd_3Ni/C and (d) Pd/C.

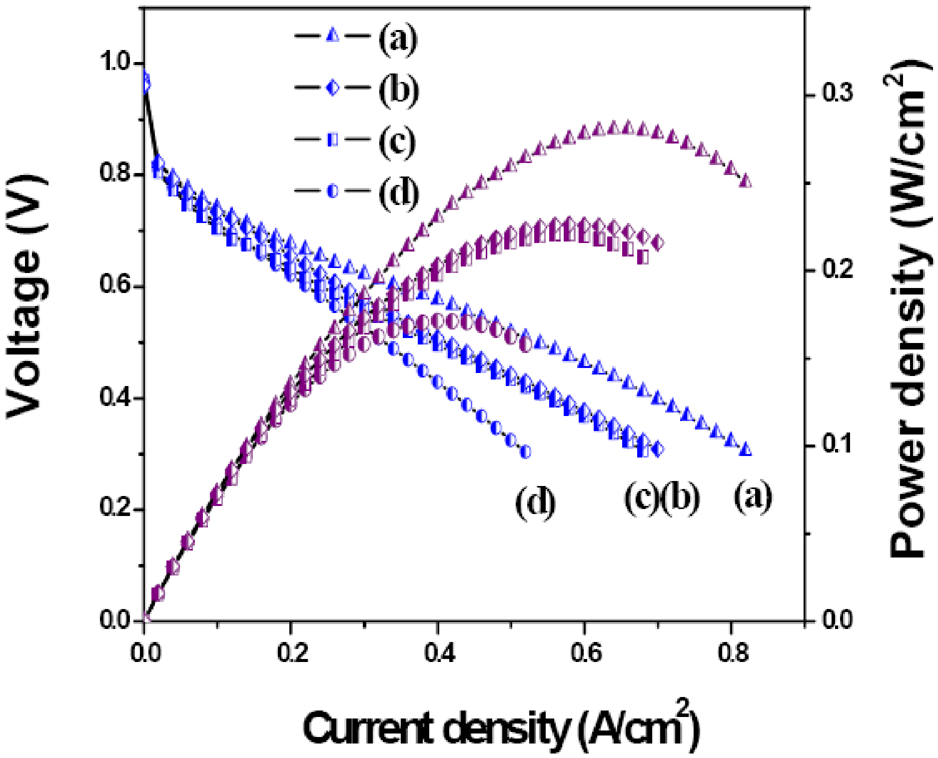

Fig.S6 Single cell performances after continuous operation for 50 h of (a) Pt/C(JM), (b) Pd_3Ni_2/WC, (c) Pd_3Ni/WC and (d) Pd/WC.

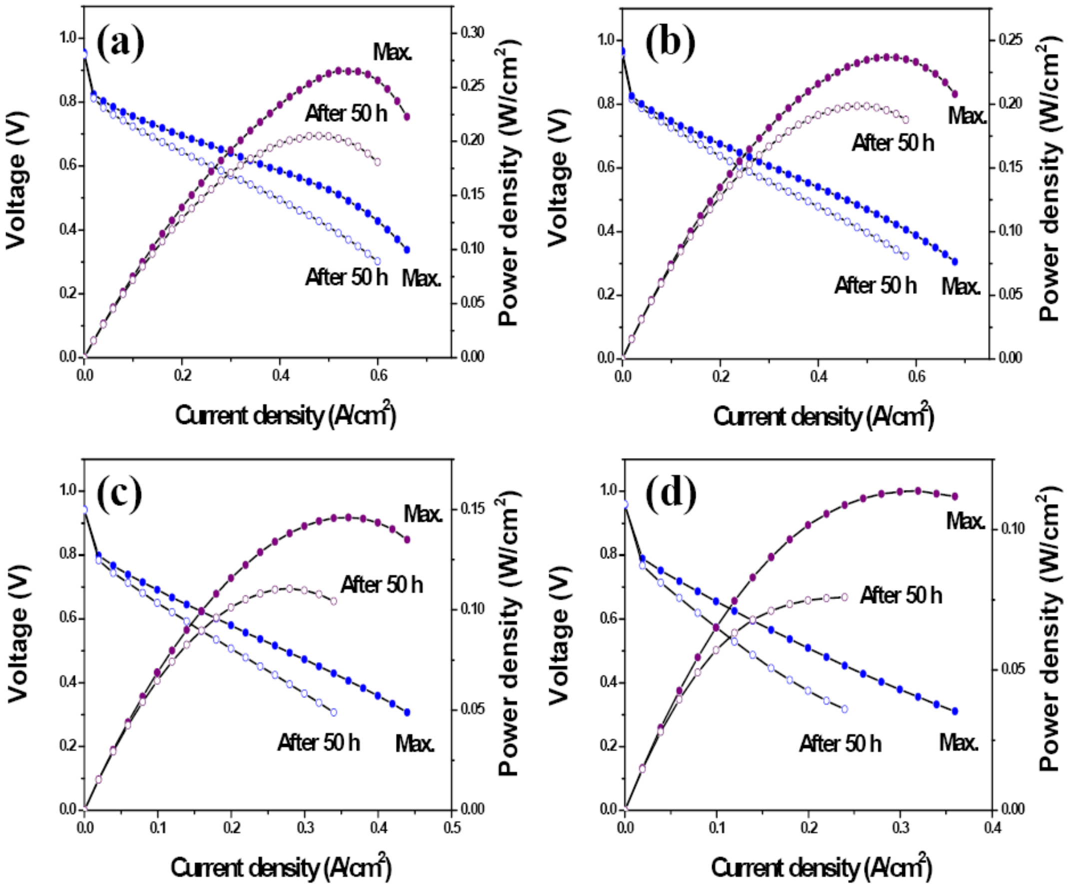

Fig.S7 Single cell maximum performances and initial long-term stabilities after 50 h of (a) Pt/C (Lab-made), (b) Pt/WC, (c) Pd_3Ni/C and (d) Pd/C (Lab-made).

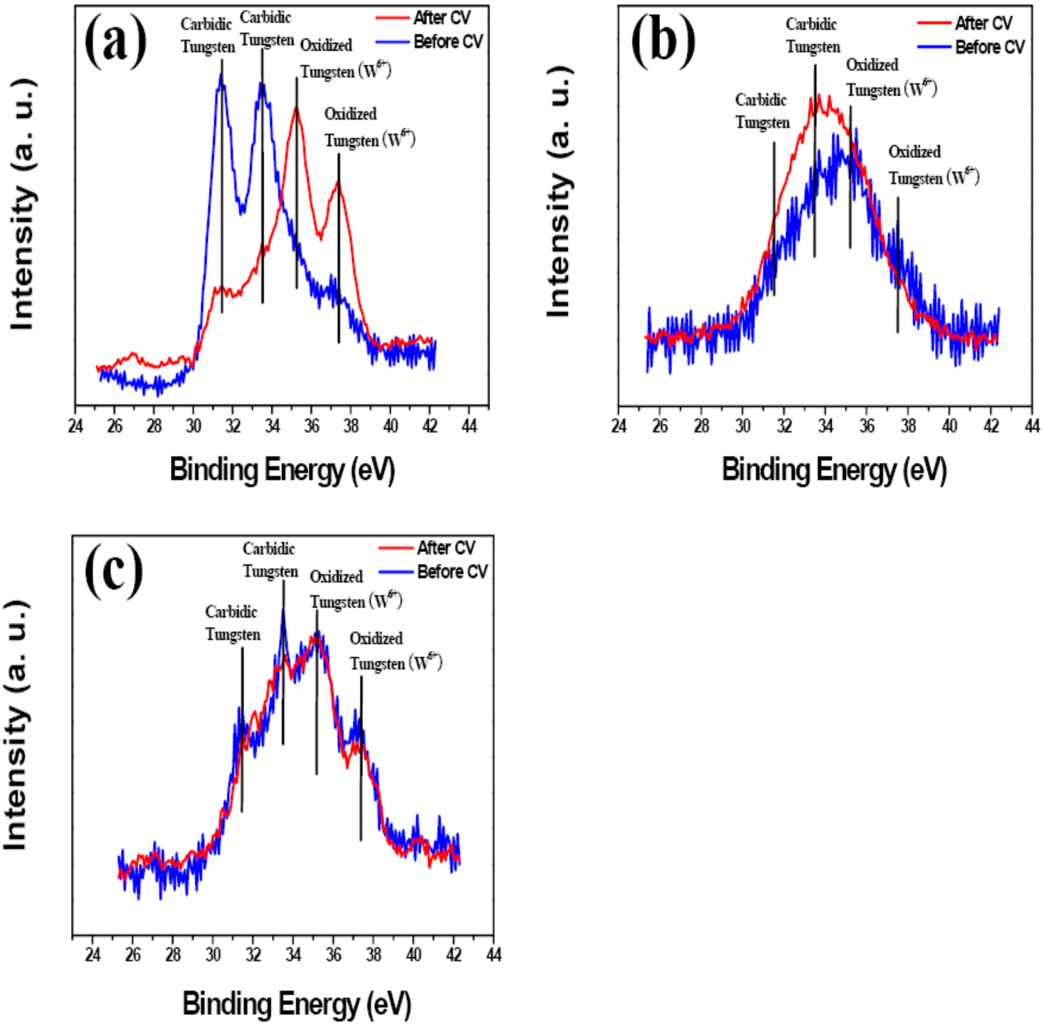

Fig. S8. XPS results of W 4f before and after cyclic voltammetry in the range of -0.2 to 1.0 V (vs. Ag/AgCl 3M NaCl) for (A) pure WC, (B) Pd/WC and (C) Pd_3Ni/WC.

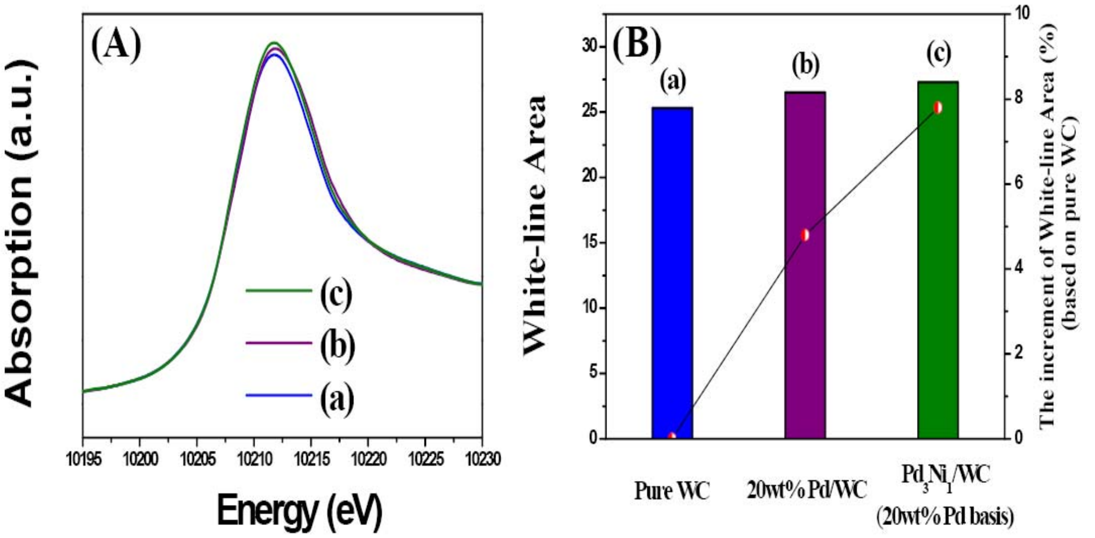

Fig. S9 (A) XANES regions of (a) pure WC, (b) Pd/WC and (c) Pd_3Ni/WC. (B) The comparison of white-line area and the percentage increment of white-line area based on pure WC. (a) Pure WC, (b) Pd/WC and (c) Pd_3Ni/WC. The increment of white-line area (based on pure WC) of Pd_3Ni_2/WC was 7.9% not shown in XANES spectrum due to overlapping.

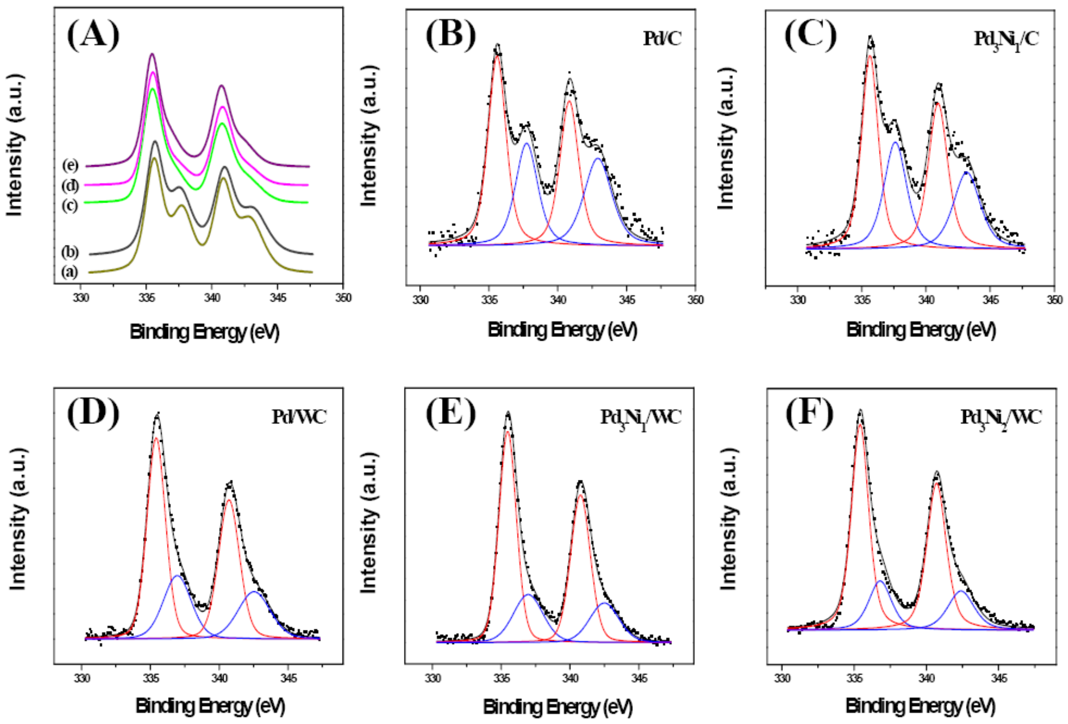

Fig.S10 (A) The XPS results for Pd 3d of (a) Pd/C, (b) Pd$_3$Ni/C, (c) Pd/WC, (d) Pd$_3$Ni/WC and (e) Pd$_3$Ni$_2$/WC. XPS spectra of (B) Pd/C, (C) Pd$_3$Ni/C, (D) Pd/WC, (E) Pd$_3$Ni/WC and (F) Pd$_3$Ni$_2$/WC. The fitting was conducted by Gaussian-Lorentzian curves for each spectra spectrum.

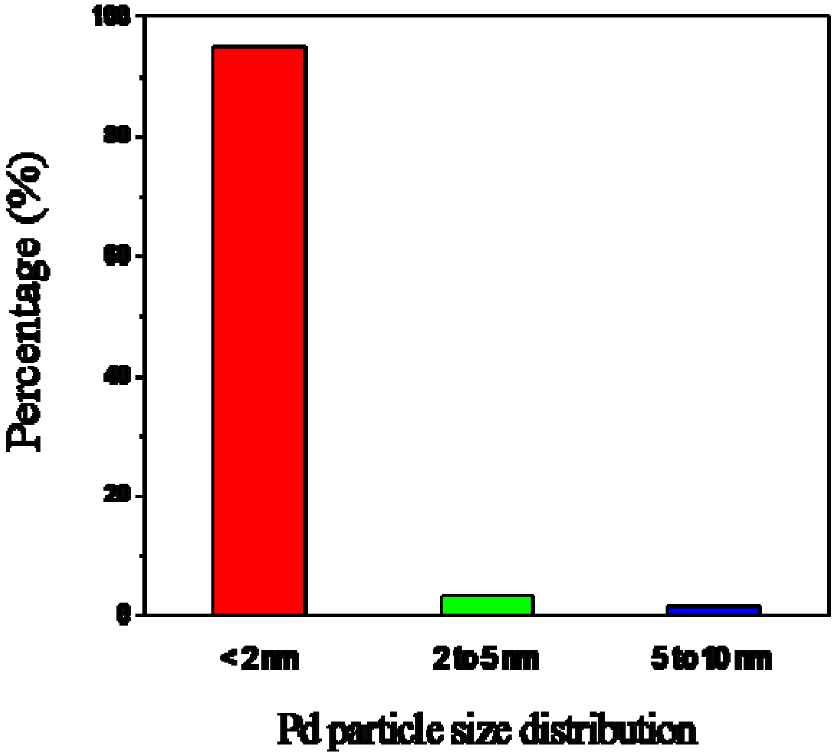

Fig. S11. Pd particle size distribution in Pd/WC obtained from TEM images.

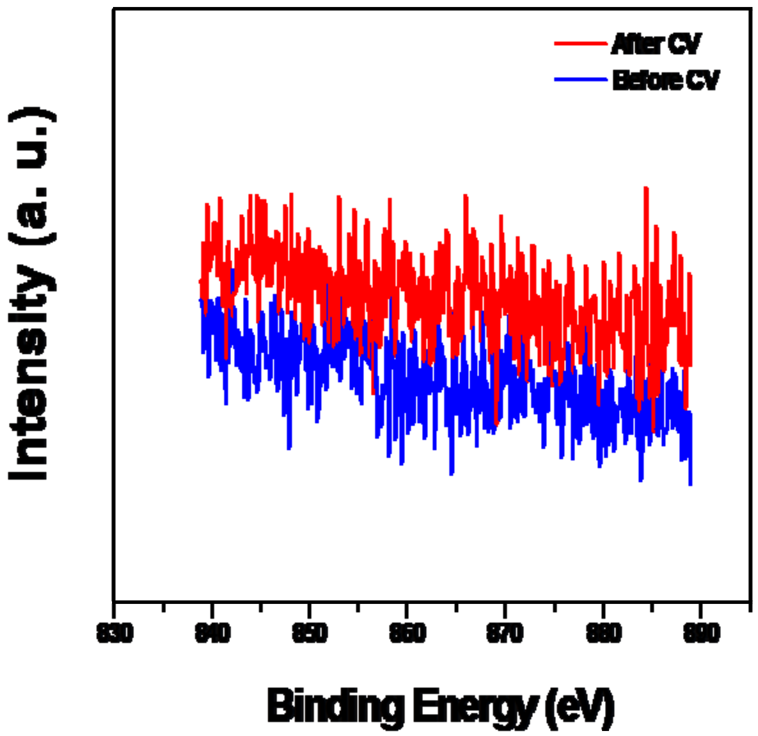

Fig. S12. XPS results of Ni 2p before and after cyclic voltammetry in the range of -0.2 to 1.0 V (vs. Ag/AgCl 3M NaCl) for Pd_3Ni/WC.

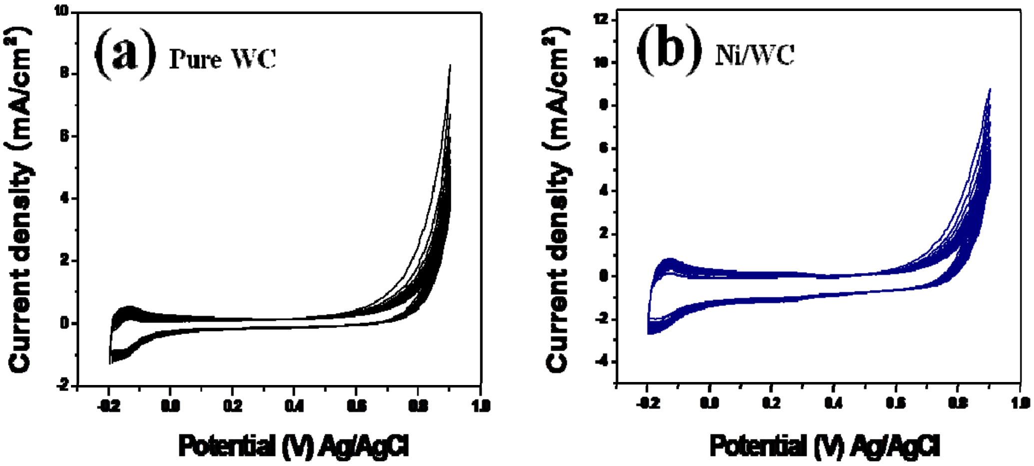

Fig. S13. Cyclic Voltammograms of (a) Pure WC and (b) Ni/WC.

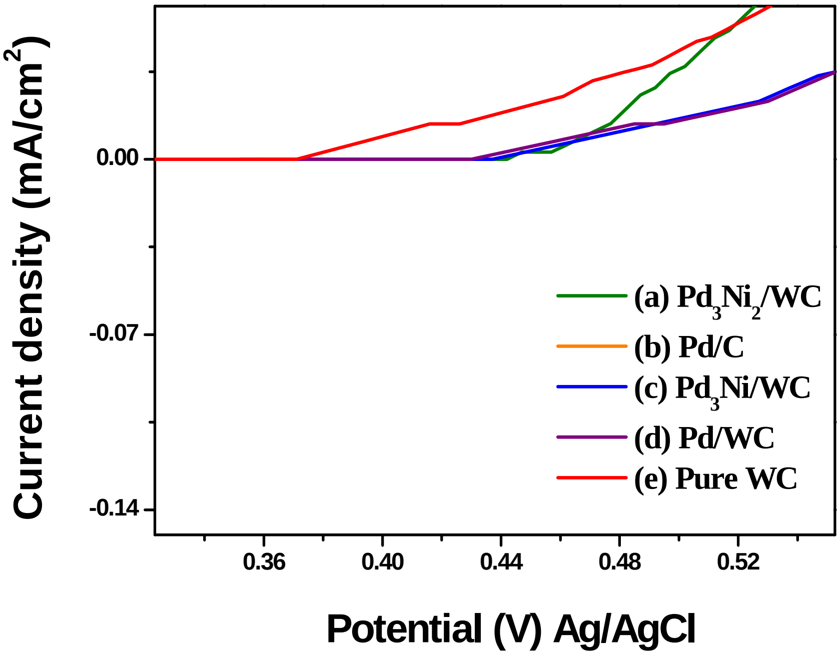

Fig. S14. Linear sweep voltammetry of various samples at the high potential region.

Table S1 Particle sizes of various metals on supports calculated via HRTEM results.

Electrocatalysts	**Mean metal particle sizes (nm)**
Pt/C (Commercial JM)	**2.8**
Pt/C (Lab-made)	**2.6**
Pd_3Ni_2/WC	**1.9**
Pd_3Ni/WC	**1.8**
Pd/WC	**1.6**
Pt/WC	**3.8**
Pd_3Ni/C	**1.5**
Pd/C	**1.4**

Table S2 XANES fitting values for identification of White-line area.

	Function	**Amplitude[a] (White-line area)**	**Width[b]**
Pure WC	**Arc-tangent**	**0.911**	**1.012**
	Lorentzian (White-line area)	**25.309**	**8.376**
Pd/WC	**Arc-tangent**	**0.889**	**0.986**
	Lorentzian (White-line area)	**26.513**	**8.446**
Pd_3Ni/WC	**Arc-tangent**	**0.864**	**0.849**
	Lorentzian (White-line area)	**27.291**	**8.498**

[a] The fitting error range of amplitude in Arc-tangent and Lorentzian was ± 0.97 %.

[b] The fitting error range of Width in Arc-tangent and Lorentzian was ± 1.30 %.

Table S3 The proportion of Pd^o and Pd^{2+} estimated by curve fitting of in XPS spectra.

Electrocatalysts	**Pd^0 (%)**	**Pd^{2+} (%)**
Pd/C	**57**	**43**
Pd_3Ni/C	**59**	**41**
Pd/WC	**67**	**33**
Pd_3Ni/WC	**72**	**28**
Pd_3Ni_2/WC	**75**	**25**