Supporting Information

Experimental Methods

Pt ALD. The precursor used for ALD was trimethyl-methylcyclopentadienyl-platinum(IV) ($MeCpPtMe_3$) (Strem Chemicals, 99%), which has been widely reported for Pt ALD.The deposition temperature was maintained at 300°C, while the bubbler holding the precursor was kept at 50°C to volatize the precursor. Gas lines were held at ~100°C to avoid precursor condensation. High purity O_2 was used as the co-reactant, and high purity N_2 was used as both the carrier and purge gases. Pressure was maintained at 1±0.1 Torr using a feed-back loop. Typical pulse times for each growth experiment were the following: 30 seconds Pt pulse, 90 second N_2 purge, 5 seconds O_2 pulse, and 90 second N_2 purge.

Electrode Preparation. Electrodes were prepared by dispersing ~15 mg of the Pt-WC powder sample in 1 ml of isopropanol (Fisher). Samples were sonicated for ~60 minutes and placed drop-wise onto a cleaned glassy carbon electrode (5mm diameter, Pine) in 5 µl increments, allowing the solvent to evaporate in between drops. In total, about 30 µl was used for each sample. The sample was submerged in 0.3 M NaOH for about one minute to remove surface tungsten oxides, and then submerged in DI Water to rinse off residual NaOH. A low flow rate of high purity N_2 stream was used to dry the sample. Finally, a 5 µl drop of 0.25 wt% Nafion/IPA was dropped on top of the sample to seal it onto the electrode.

HER Measurements. All electrochemical measurements were performed in a three-electrode cell using an interchangeable rotating disk electrode system (Pine Instruments) and a Princeton Applied Research potentiostat/galvanostat model VersaSTAT 4 at room temperature. A Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference. Samples were first electrochemically conditioned in N_2-purged 0.5 M H_2SO_4 by cycling for about 30 minutes from 0.0 V to the onset of oxidation at 50 mV/s for the WC and Pt/WC samples and 0 to 1.2 V at 50 mV/s for the Pt/C sample. For the HER measurement, a linear scan voltammogram was taken between 0.1 V to -0.4 V using a scan rate of 2 mV/s.

Determination of the Exchange Current Density, i_o. The Tafel equation (Equation S1) is the high overpotential limiting case of the Butler-Volmer equation:

$$\eta = a + b\log(i) \tag{S1}$$

The Tafel parameters are the intercept, *a*, which is actually log(i_o), and the slope, *b*. The linear scan voltammogram generated during the HER measurement (Fig S3) is replotted in the form of the overpotential, η, vs. log(i). The resulting graph is known as a Tafel plot, and Tafel parameters can be determined by fitting the linear portion of the plot. The intercept is then used to determine i_o.

Determination of Pt Surface Area. Cu stripping voltammetry was utilized to determine the active Pt surface area because it is effective in distinguishing between the Pt and WC substrate. Other methods that can determine the electrochemically active surface area, such as CO stripping voltammetry and the underpotential deposition (UPD) of hydrogen, have overlapping features representing both Pt and WC, making it difficult to differentiate which features correspond to Pt or WC. During Cu stripping voltammetry, the UPD of Cu takes place on the surface of the Pt particles. The resulting Cu monolayer is then stripped away, producing a stripping voltammogram, which is then used to calculate the Pt surface area. Cu stripping experiments were performed in an electrolyte solution containing 0.1 M H_2SO_4 and 2 mM $CuSO_4$. To deposit one atomic layer of Cu on Pt, a potential of 0.3 V vs. NHE was applied to the working electrode sample for 120 s, followed by a linear sweep voltammogram (LSV) from 0.3 V to 1.2 V vs. NHE at a scan rate of 100 mV/s. Background LSVs were measured in 0.1 M H_2SO_4 using the same scan parameters. The difference curve between the Cu stripping voltammogram and background scan was then integrated to determine the charge transferred during stripping, Q_M, and the surface area was determined using Equation S2:

$$A = \frac{Q_M}{Q_M^s} \qquad \text{(S2)}$$

where Q_M^s is 420 μC/cm^2, the commonly accepted value for 2-electron charge on polycrystalline Pt.[1, 2]

Materials Characterization. For atomic absorption spectroscopy (AAS) measurements, samples were digested in aqua regia (3:1 HCl:HNO_3) for 24 hours at room temperature. The remaining solids (assumed to be completely WC) were filtered away and the filtered solution was concentrated to 5 ml, then diluted with 10 vol% HCl to 50 ml. The AAS measurement was performed using a SOLAAR S Series Atomic Absorption Spectrometer (Thermo Elemental). Standards were made from a stock solution of 1000 ug/mlPt (SCP Science, Inc.) and diluted in 10 vol% HCl. All solutions were nebulized in an air/acetylene flame (2200°C) and are atomized using a hollow cathode lamp (Thermo Elemental) with a characteristic wavelength of 265.9 nm.

TEM samples were analyzed in a JEOL 2010f TEM equipped with a Schottky field-emission gun operated at 200 keV. The point-to-point resolution is 0.19 nm. Powder Pt-WC samples were prepared by dispersing the powder in isopropanol and sonicating for about 30 minutes. A drop was then placed on a holey carbon copper grid (200 mesh) and allowed to try for over 3 hours to allow all solvent to evaporate.

1 C. L. Green and A. Kucernak, *J. Phys. Chem. B*, 2002, **106**, 1036-1047.
2 S. Trasatti and O. A. Petrii, *Pure Appl. Chem.*, 1991, **63**, 711-734.

Powder XRD Measures for WC phase confirmation

XRD measurements were carried out with a Philips X'pert-PW3040 powder X-ray diffractometer for the bulk phase analysis of powder catalysts. A Cu Kα source with 1.54Å wavelength was used. The voltage was set to 45 kV and current to 40 mA. Spectra were collected at 2θ values between 30° to 55° using a step size of 0.02° 2θ and 2 seconds per step.

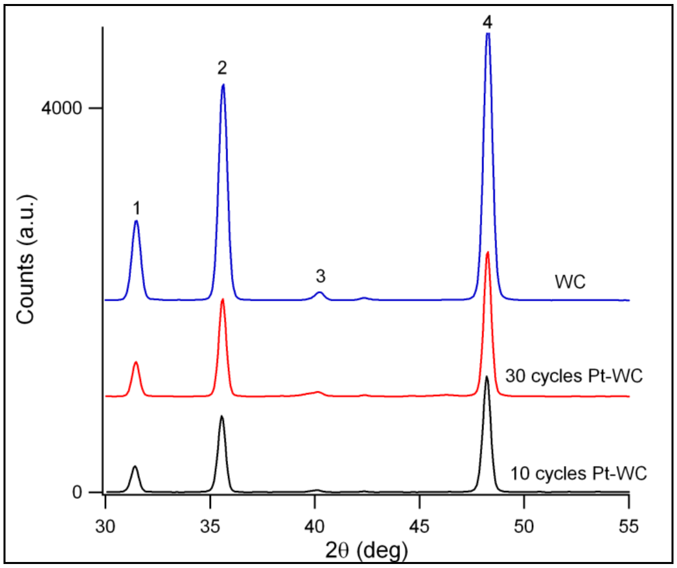

Fig. S1 Powder XRD patterns for the WC powders, 30 ALD cycles Pt on WC, and 10 ALD cycles Pt on WC. Corresponding peak identification is listed in Table S1, confirming that the WC is single phase.

Table S1 Peak identifications for powder XRD pattern in Fig. S1.

Peak No.	**2θ (°)**	**Measured *d*-spacing (Å)**	**Expected *d*-spacing (Å)**	**Identified phase**
1	31.500	2.838	2.839	WC(0001)
2	35.650	2.516	2.517	WC($10\bar{1}0$)
3	40.260	2.238	2.237	W(110)
4	48.190	1.887	1.883	WC($10\bar{1}1$)

Cyclic Voltammetry (electrochemical characterization)

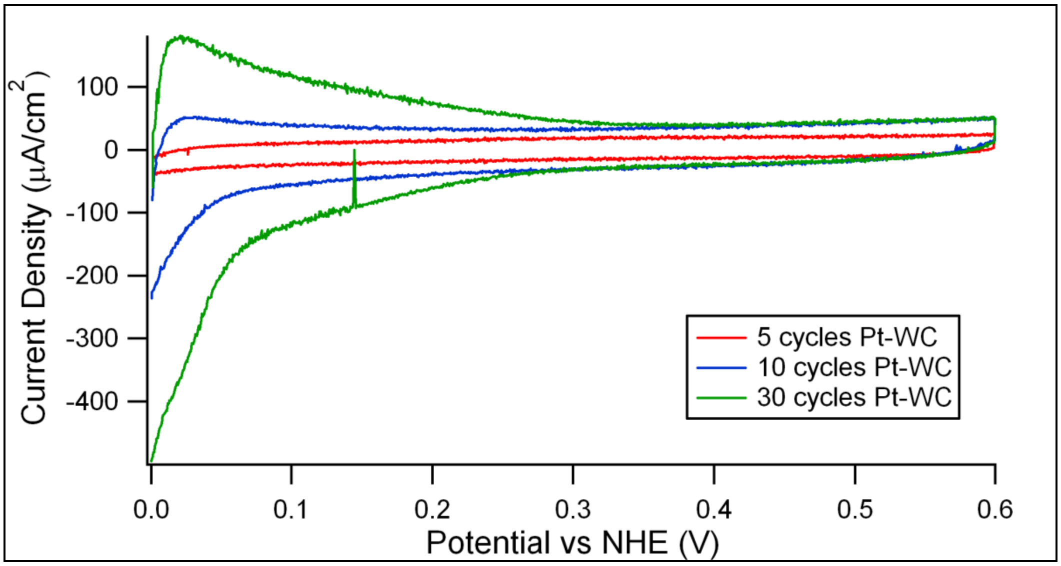

Fig. S2 Cyclic voltammograms of the 5, 10, and 30 ALD cycles Pt-WC samples in N_2-saturated 0.5 M H2SO4. Scan rate 50 mV/sec.

HER Linear scan voltammograms (I-V curves)

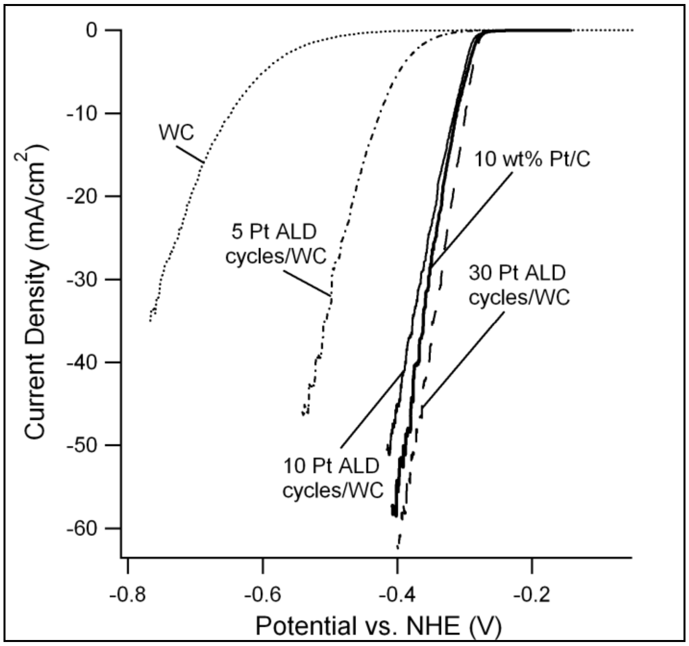

Fig. S3 HER linear scan voltammograms for each of the catalysts analyzed: WC powder, 5 Pt ALD cycles on WC, 10 Pt ALD cycles on WC, 30 Pt ALD cycles on WC, and 10 wt% Pt supported on carbon black. This data was then used to generate Tafel plots and determine the exchange current density. Current is normalized with respect to the geometric electrode surface area. Scan rate 2 mV/s.