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Supporting Information

Novel Porous Tungsten Carbides Hybrids Nanowires on Carbon Cloth for High-performance Hydrogen Evolution

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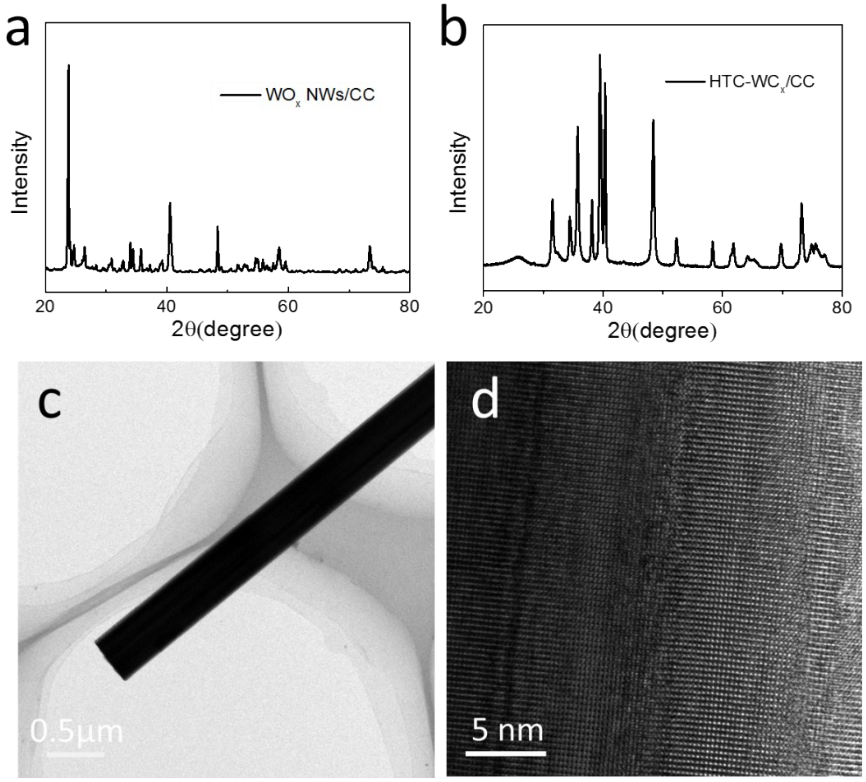

Figure S1. (a) XRD patterns for WO_x NWs/CC, $W_{18}O_{49}$(JCPDS no. 84-1516) phase was detected. (b) XRD patterns for HTC-WC_x/CC, The WC (JCPDS no. 05-0728) phase, W_2C phase (JCPDS no. 35-0776) and metallic W (JCPDS no. 01-1203) were detected.(c) TEM and (d) HRTEM images of WO_x NWs/CC.

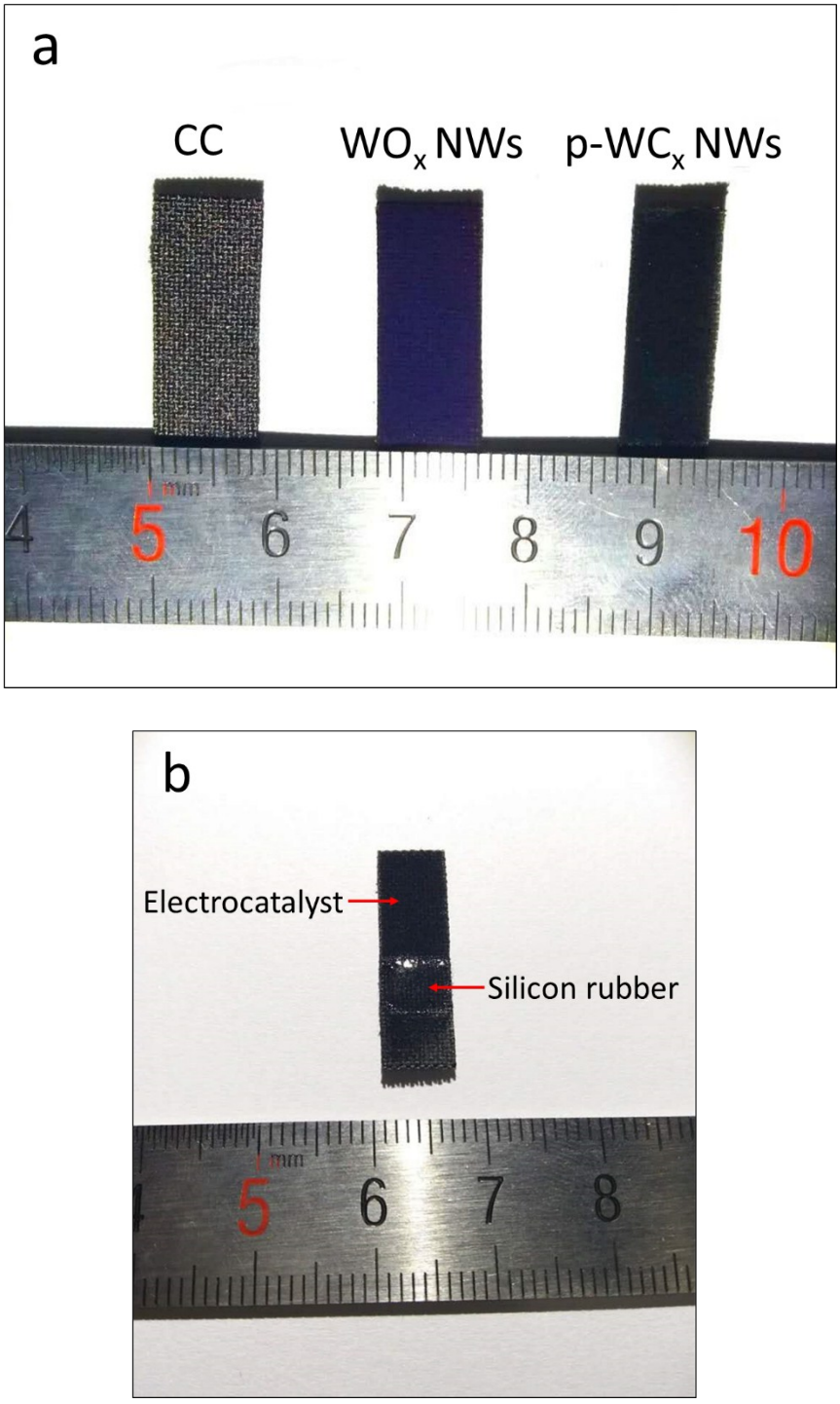

Figure S2. (a) Optical photograph of bare CC (left), WO_x/CC (middle), and p-WC_x NWs/CC (right). (b) Optical photograph of fabricated WC_xHPNWs/CC electrode, electrochemically inert silicon rubber was used to define an active geometric area.

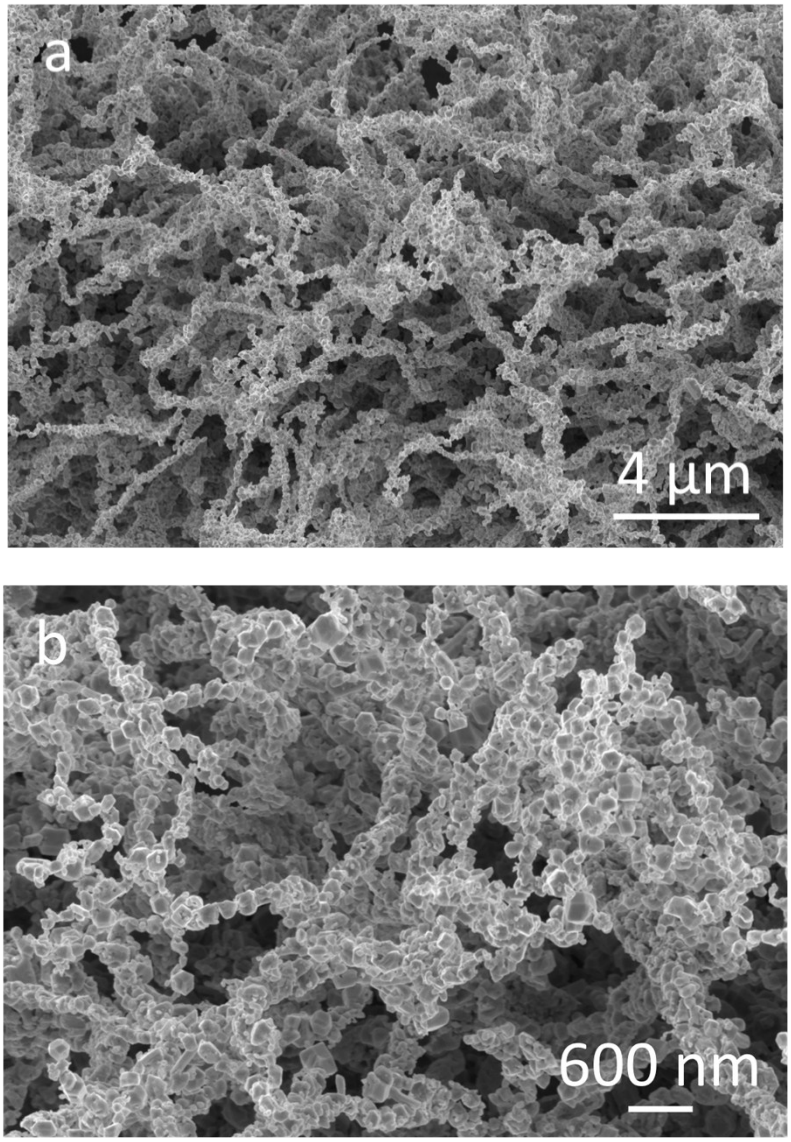

Figure S3. Different magnificationSEM images of the HTC-WC_x/CC, and it's composed of stacked particles.

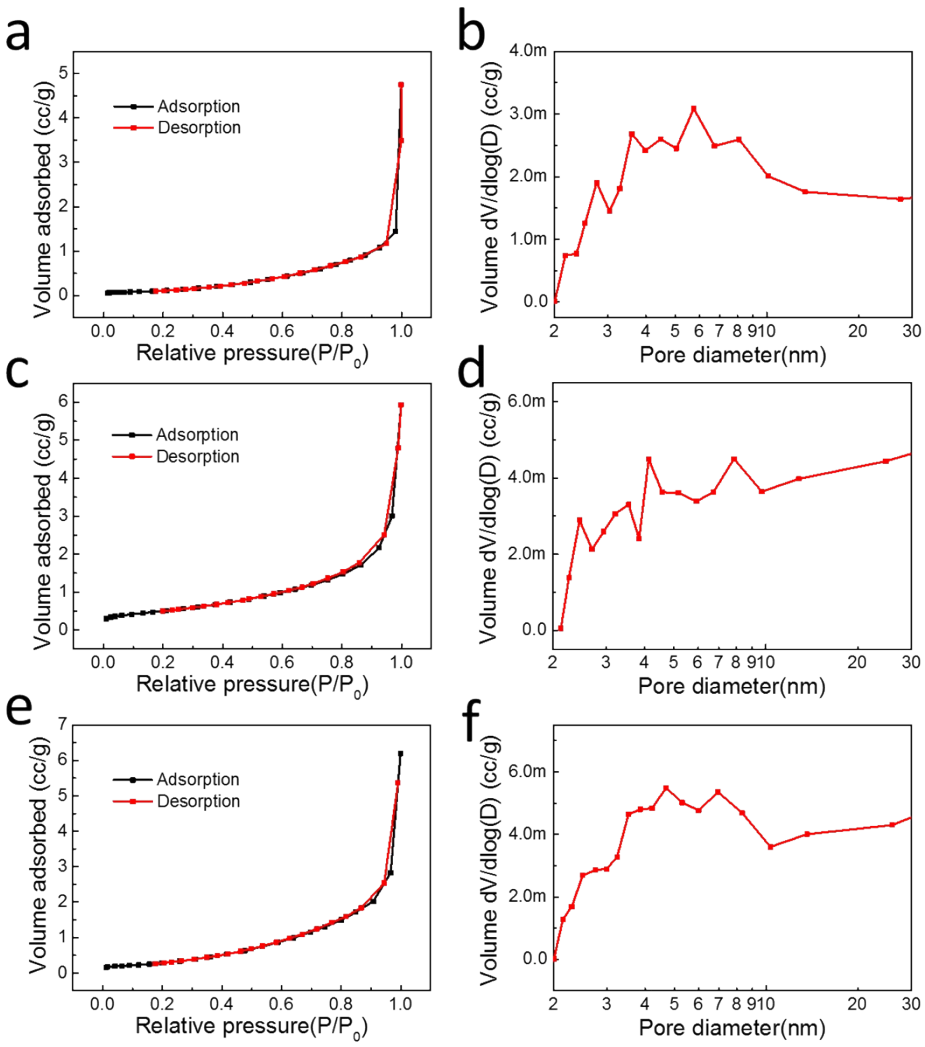

Figure S4.(a, c,e) Nitrogen adsorption/desorption isotherm plots and (b, d, f) the BJHpore-size distribution curves of CC, WO_xNWs/CC and HTC-WC_x/CC, respectively.

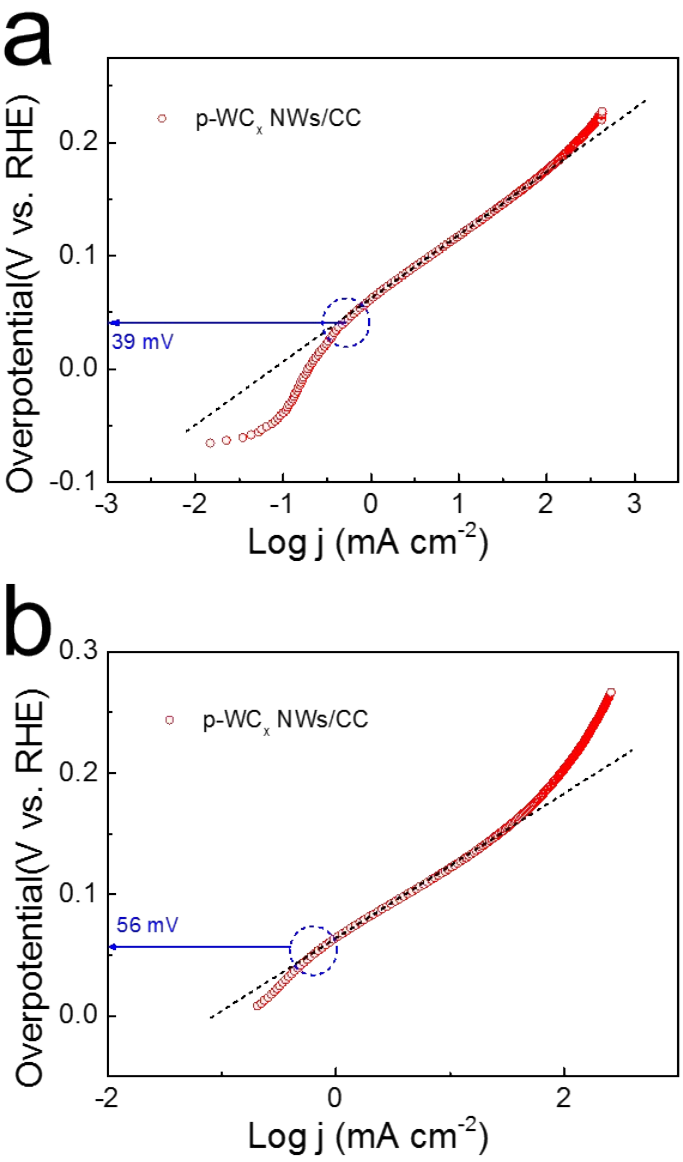

Figure S5. Tafel plot of WC_x NWs/CC in (a) 0.5 M H_2SO_4 and (b) 1 M KOH. The onset overpotential is determined by the potential when the plot starts to deviate from the linear region as indicated by the blue circle.

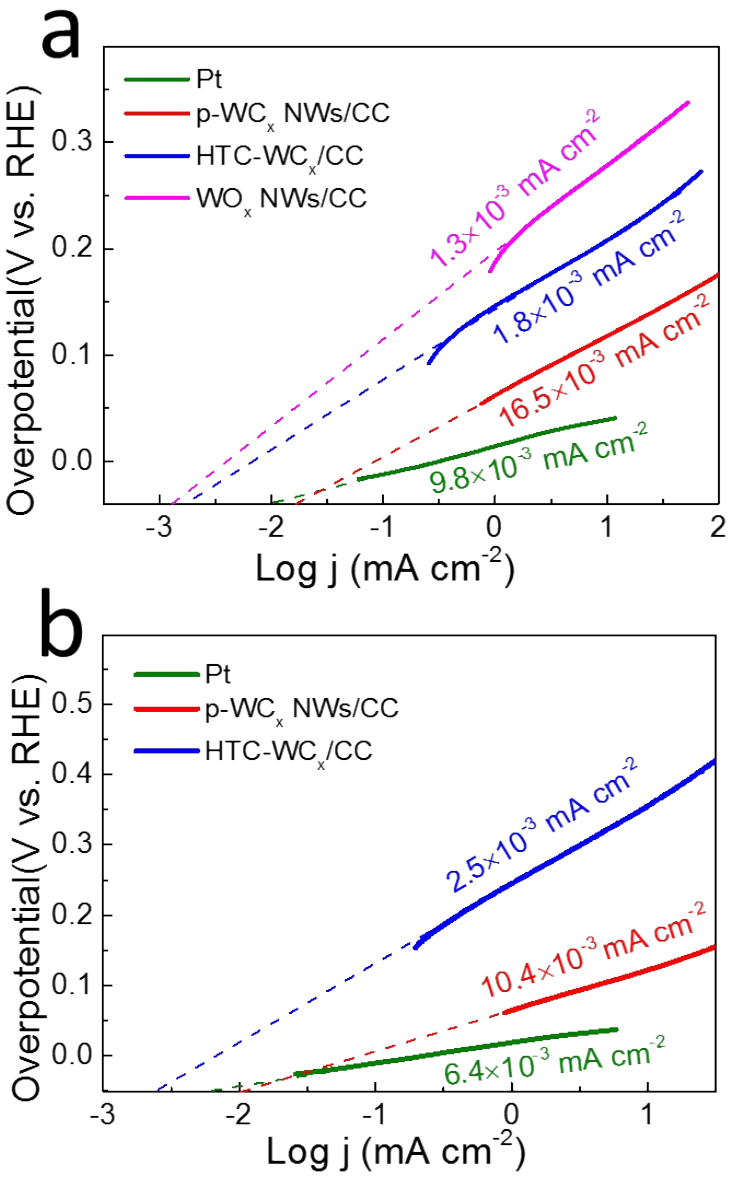

Figure S6. Exchange current densities for different samples in (a) 0.5 M H_2SO_4 and (b) 1 M KOH, which were calculated from Tafel plots by extrapolation method.

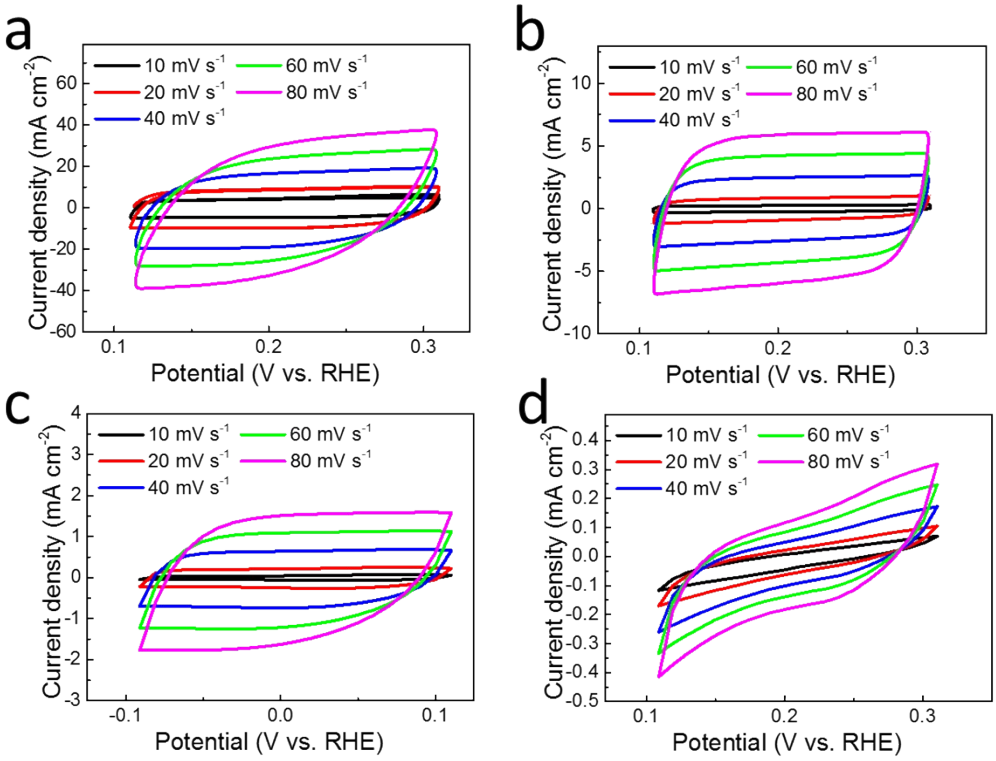

Figure S7. Electrochemically active surface area measurements. CV curves measured from 10 to 80 mV s^{-1} of the p-WC_x NWs/CC in (a) 0.5 M H_2SO_4 and (b) 1 M KOH. CV curves measured from 10 to 80 mV s^{-1} of the HTC-WC_x/CC in (c) 0.5 M H_2SO_4 and (d) 1 M KOH. The capacitive currents (Δj) at 0.21V vs RHE were plotted as a function of scan rate (Figure 4c,d), and the plot was linear-fitted to calculate double layer capacitance (C_{dl}) by the equation of C_{dl} = slope/2.

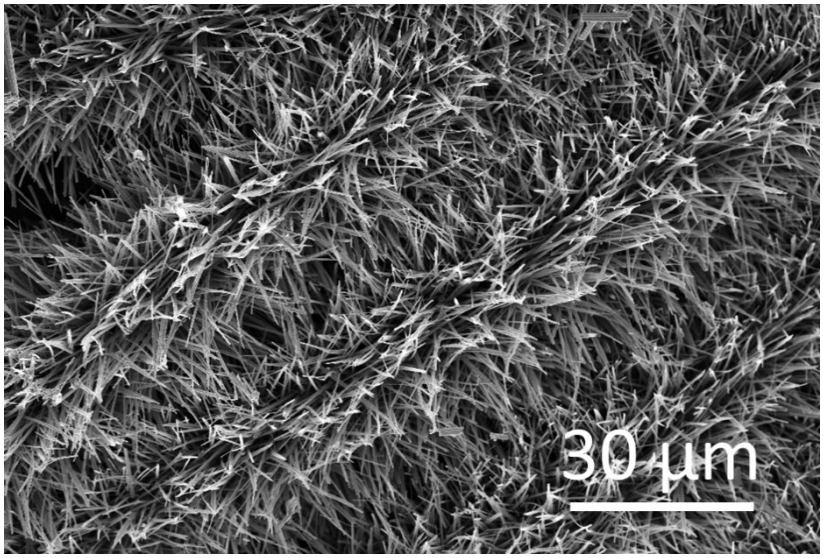

Figure S8. SEM images of the p-WC_x NWs/CC after chronoamperometry measurement (at a static current density of -20mA cm^{-2} for more than 40 hours) in 0.5 M H_2SO_4.

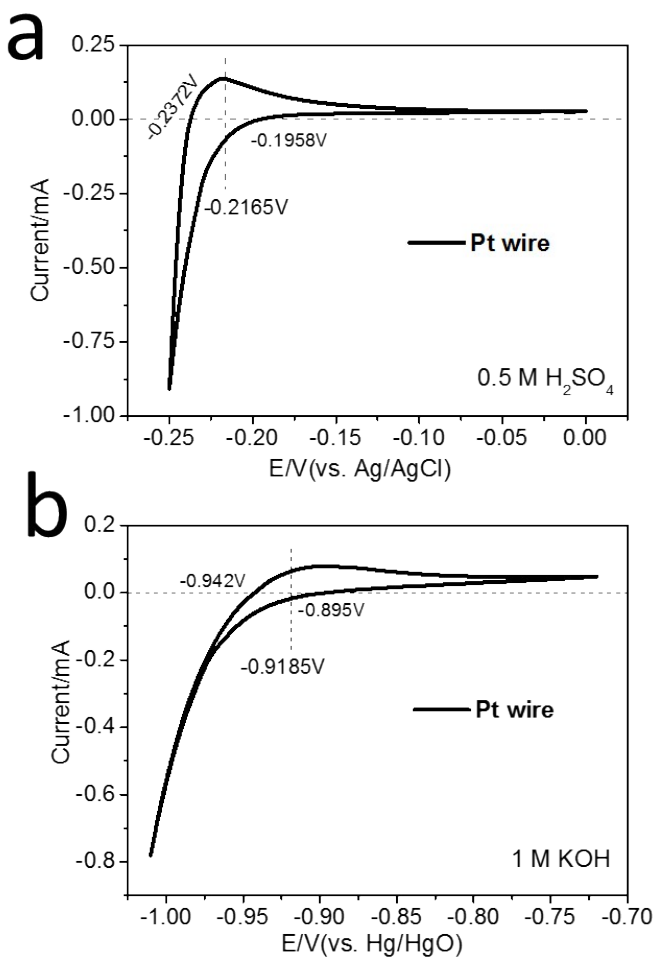

Figure S9. RHE calibration in (a) 0.5 M H_2SO_4 and (b) 1 M KOH. The calibration performed in the high purity hydrogen saturated electrolyte with a Pt wire as the working electrode. CV cycles were conducted at a scan rate of 5 mV s^{-1}, and the average of thetwo zero-current potentials was takento be the thermodynamic potential for the hydrogenelectrode reactions. The pH value is 0.18 for an 0.5 M H_2SO_4 solution and the E(RHE) = E(Ag/AgCl) + 0.20588 + 0.059 pH = E(Ag/AgCl) + 0.2165. The pH value is 13.92 for a 1 M KOH solution and the E(RHE) = E(Hg/HgO) +0.09722 + 0.059 pH = E(Hg/HgO) + 0.9185.

Calculation of the mass loading on carbon cloth

To calculate the mass loading of the WO_x NWs/CC, the samples were dissolved in KOH solution and the concentration of W ion in the solution was measured by Inductively coupled plasma atomicemission spectroscopy (ICP-AES) measurements. In addition, we presume that the mass of the W element in the reaction process is constant, and WC_x has a relative molecular mass molar ratio of 189.85 (we estimate the molar ratio of W, WC and W_2C was 1:1:1). Therefore, the mass loading of the p-WC_x NWs can be calculated as 1.08 $mgcm^{-2}$.

Calculation of the BET specific surface area

The BET specific surface area of bare CC, WO_x NWs/CC, HTC-WC_x/CC and p-WC_x NWs/CC are 0.3295, 1.8402, 0.9613 and 7.4709m^2 g^{-1}, respectively. It suggests p-WC_x NWs/CC has relatively high specific surface area than other samples, and holds a porous structure. In order to obtainBET surface area of separate p-WC_x NWs sample (withoutsubstrate), we assume that the BET surface area of p-WC_x NWs/CC is the arithmetic sum of separate p-WC_x NWs and bare CC. Afterwards, bare CC was weighed 13.9 $mgcm^{-2}$ using a Mettler-Toledo XP2U microbalance, and the mass loading of p-WC_x NWs/CC was 1.08 $mgcm^{-2}$ determined by ICP. Therefore, we calculated the mass ratio of the two substances on the unit geometric area, and according to the BET surface area ofp-WC_x NWs/CC and bare CC, we finally obtain the separate p-WC_x NWs with a BET surface area of ~99.38 m^2 g^{-1}. In addition, the BET surface area of other samples were calculated in the same way. The results are 18.12 and 9.09 m^2 g^{-1} for WO_x NWs and HTC-WC_x, respectively.