Electronic Supplementary Material (ESI) for Energy & Environmental Science. This journal is © The Royal Society of Chemistry 2018

Supporting information for

High efficient hydrogen evolution triggered by a multi-interfacial

Ni/WC hybrid electrocatalyst

Yuanyuan Ma^{1, †}, Zhongling Lang^{1, †}, Likai Yan¹, Yong-Hui Wang,¹ Huaqiao Tan^{1,*}, Kun Feng², Yujian Xia², Jun Zhong^{2,*}, Yang Liu², Zhenhui Kang^{2,*}, Yangguang Li^{1,*}

¹ Key Laboratory of Polyoxometalate Science of the Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, China.

²Jiangsu Key Laboratory for Carbon-based Functional Materials and Devices, Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123, China.

[†]Y. Ma and Z. Lang contributed equally to this work.

Table of contents

section	page
1. Experimental Section	S2
2. Characterization techniques	S2
3. Supplementary Figures	S4
4. Supplementary Tables	S27
5. Reference	S33

1. Experimental Section

Reagents. Urea, $H_3PW_{12}O_{40} \cdot nH_2O$, benzene-1,3,5 tricarboxylic acid (H_3BTC , 98%), Nickel chloride hexahydrate (NiCl₂·6H₂O), and Tris(hydroxymethyl)aminomethane hydrochloride (Tris·HCl) were purchased from Aladdin Industrial Co., Ltd. Commercial 20% Pt/C, 5% Pd/C catalysts and Nafion solution (5 wt%) were purchased from Alfa Aesar China (Tianjin) Co., Ltd. All chemicals were used as received without further purification. All solution used in experiments were prepared with Millipore water (18.2 MΩ). GO was prepared by modified Hummer's method. Na₉[A- α -PW₉O_{34}] \cdot nH_2O was prepared by literature method.¹ [Ni(en)₂(H₂O)₂]₆ {Ni₆(Tris)(en)₃(BTC)_{1.5}(*B*- α -PW₉O₃₄)}₈·12en·54H₂O (abbreviated as Ni₅₄W₇₂) was synthesized according to the literature reported by Yang *et al.*²

Synthesis of Ni/WC@C. 0.2 g Ni₅₄W₇₂/GO was directly pyrolyzed in a pipe furnace at 500 °C for 30 min under N₂ atmosphere with a heating rate of 2 °C/min, and then further heated at 650 °C for 6 h with a heating rate of 5 °C/min. The as-obtained sample is denoted as Ni/WC@C.

Synthesis of Ni/WC. 0.2 g Ni₅₄W₇₂ was directly pyrolyzed in a pipe furnace at 500 °C for 30 min under N₂ atmosphere with a heating rate of 2 °C/min, and then further heated at 650 °C for 6 h with a heating rate of 5 °C/min. The as-obtained sample is denoted as Ni/WC.

Synthesis of N-doped carbon. 0.2 g GO and 0.1 g urea were dispersed in 5 mL 1 mg/ml GO solution and heated at 90 °C under magnetic stirring until dry white powder was obtained. The powder was heated at 800 °C for 3 h under N₂ atmosphere with a heating rate of 5 °C/min. The as-obtained sample is denoted as N-doped carbon.

Synthesis of Ni@NC. The synthetic procedure is very similar to Ni/WC@NC. 0.2 g NiCl₂· $6H_2O$ and 0.1 g urea were dispersed in 5 mL 1 mg/ml GO solution and heated at 90 °C under magnetic stirring until dry green powder was obtained. Afterward, the powder was pyrolyzed under the same condition. The as-obtained sample is denoted as Ni@NC.

Synthesis of WC@NC. 0.2 g $H_3PW_{12}O_{40} \cdot nH_2O$ and 0.1 g urea were dispersed in 5 mL 1 mg/ml GO solution and heated at 90 °C under magnetic stirring until dry white powder was obtained. The powder was heated at 800 °C for 3 h under N₂ atmosphere with a heating rate of 5 °C/min. The as-obtained sample is denoted as WC@NC.

2. Characterization techniques

Characterization. Powder X-ray diffraction (PXRD) measurements were carried out on a Rigaku D/max-IIB X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were carried out on JEOL-2100F and JEM-F 200 at an accelerating voltage of 200 kV. The morphology analysis was conducted on a field-emission scanning electron microscopy (FESEM; Hitachi SU-8010) at an accelerating voltage of 3 kV.

X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) data were collected on the BL14W beamline at the Shanghai Synchrotron Radiation Facility (SSRF), Shanghai Institute of Applied Physics (SINAP), China, operated at 3.5 GeV with injection currents of 140-210 mA. The Xray photoelectron spectroscopy (XPS) measurements were performed on a KRATOS Axis ultra DLD X-ray photoelectron spectrometer with a monochromatized Mg Ka X-ray source (hv = 1283.3 eV). The ICP-OES elemental analyses were performed on a Teledyne Leeman LabsICP-OES spectrometer. The nitrogen sorption measurement was obtained on an ASAP 2020 (Micromeritics, USA). The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area by using adsorption data. The evolved gases during HER decomposition were detected by gas chromatograph (Shimadzu, GC-2014C with a thermal conductivity detector). Raman spectrum was recorded on a Raman spectrometer (JY, Labram HR 800).

Additional electrochemical measurements.

Preparation of electrolytes: 0.5 M H_2SO_4 (pH= 0.30), 0.05 M H_2SO_4 + 0.45 M Na_2SO_4 (pH= 1.35), 5 mM H_2SO_4 + 0.49 M Na_2SO_4 (pH= 2.40), 0.5 mM H_2SO_4 +

 $0.49 \text{ M} \text{ Na}_2\text{SO}_4 \text{ (pH= 3.39)}, 0.05 \text{ mM} \text{ H}_2\text{SO}_4 + 0.49 \text{ M} \text{ Na}_2\text{SO}_4 \text{ (pH= 4.44)}, 5 \mu \text{ M}$

H₂SO₄ + 0.49 M Na₂SO₄ (pH= 5.30), 0.5 µ M H₂SO₄ + 0.49 M Na₂SO₄ (pH= 6.11),

0.5 M Na₂SO₄ (pH= 6.89), 1 M KOH (pH= 14.01), 0.1 M KOH + 0.6 M K₂SO₄ (pH= 13.19), 0.01 M KOH + 0.66 M K₂SO₄ (pH= 12.05), 1 mM KOH + 0.66 M K₂SO₄ (pH= 11.24), 0.1 mM KOH + 0.66 M K₂SO₄ (pH= 10.01), 0.01 mM KOH + 0.66 M K₂SO₄ (pH= 9.11), 1 μ M KOH + 0.66 M K₂SO₄ (pH= 8.02).

Proton Adsorption Measurements. The proton (H⁺) adsorption measurements were performed according to the method in literature.³ The concentration of 5 mM HCl solution was selected and the adsorption experiments were conducted with a dialysis method. Typically, the Ni/WC@NC catalyst solution was dialyzed using a semi-permeable membrane (MWCO 1000) in a 600 mL beaker, and the dialysate was 5 mM HCl (500 mL). If Ni/WC@NC catalyst displays good adsorption behaviour for H⁺, H⁺ would gradually cross the semi-permeable membrane and dialyze into the Ni/WC@NC catalyst solution. After stirring on a shaker for predetermined time intervals, the residual concentration of HCl solution was determined by titrating with 5 mM NaOH solution.

The amount of adsorbed H^+ (based on HCl), Q (g/g) is calculated by the following equation:

$$Q = \frac{(Co - Ce) \bullet V}{W}$$

Where C_0 and C_e are the initial and equilibrium concentration of HCl (mg/L), respectively; V is the volume of HCl solution (L) and W is the weight (mg) of Ni/WC@NC adsorbent.

3. Supplementary Figures



Figure S1. The structure of cubic polyoxometalate-organic molecular cage $Ni_{54}W_{72}$. WO₆ octahedron, red; PO₄ octahedron, purple; NiO₆/NiO₄N₂ octahedron, green.



Figure S2. The Powder XRD patterns of as-synthesized $Ni_{54}W_{72}$ and $Ni_{54}W_{72}/rGO$ composites. The peak positions of as-synthesized $Ni_{54}W_{72}$ and $Ni_{54}W_{72}/rGO$ composites are in agreement with that of simulated $Ni_{54}W_{72}$, demonstrating the good phase purity of them and the structure of $Ni_{54}W_{72}$ has been retained after the introduction of GO.



Figure S3. (a) The SEM images of $Ni_{54}W_{72}/rGO$; (b) The TEM images of $Ni_{54}W_{72}/rGO$. The results indicate that the $Ni_{54}W_{72}$ nanocrystals are well dispersed on GO.



Figure. S4 (a) XRD patterns of Ni/WC@C; (b) TEM images of Ni/WC@C; (c) HRTEM images of Ni/WC@C; (d-g) Elemental mapping of Ni/WC@C.

The control sample without adding urea (Ni/WC@C) has been synthesized. As shown in Figure S4a, the XRD patterns shows that the characteristic peaks located at 31.58°, 35.72°, 48.41° and 64.18° are indexed to the (001), (100), (101) and (110) planes of hexagonal WC (JCPDS, No. 65-4539), respectively. The diffraction peaks at 44.35° and 51.67° are ascribed to the (111) and (200) facets of metallic Ni (JCPDS, No. 65-0380), respectively. While the position of 25° show no obvious peaks of carbon because of the lack of urea. These results confirm that the Ni/WC@C was mainly composed of metallic Ni and WC phases. The TEM images show that the Ni/WC hybrid nanoparticles with the average size of ~ 56.4 nm are distributed on carbon sheets (Figure S4b). The bigger size of Ni/WC hybrid NPs reveals the important effect of urea as partitioning agent, which can protect the Ni/WC hybrid NPs from agglomeration and coalescence during the annealing process. The high-resolution TEM images (Figure S4c) also show the lattice fringes with interplanar distances of 0.25 and 0.18 nm, which are associated with the (100) crystallographic planes of hexagonal WC and (200) crystallographic planes of metallic Ni, respectively. Elemental mapping and EDX result further confirm the element composition (Figure S4d-g). These results demonstrate the significant partitioning effect of urea.



Figure. S5 The dependence of adsorption time on the amount of absorbed H⁺ (based on the quality of HCl) on Ni/WC@NC and Ni/WC@C catalyst in 5 mM HCl aqueous solution.

Additionally, the proton adsorption experiments of Ni/WC@C and Ni/WC@NC were conducted to investigate the effect of N dopes. Figure S5 suggests that the Ni/WC@NC catalyst displays higher proton adsorption ability than that of Ni/WC@C, which can enrich protons in HER process, further promoting the electrocatalytic performance for HER.



Figure S6. (a) and (b) The SEM images of Ni/WC@NC catalyst.



Figure S7. (a-b) The TEM images of Ni/WC@NC catalyst; insert: The particle size distribution of Ni/WC@NC. (c-d) The HR-TEM of Ni/WC@NC. The diameter of Ni-WC@NC nanoparticles ranges from 4 nm to 14 nm and the average diameter is 8 nm.



Figure S8. (a-f) The EDX elemental mapping of C, N, O, Ni and W in Ni/WC@NC catalyst. The results indicated that the Ni, W, N, C and O elements are uniformly distribution in the surface of Ni/WC@NC catalyst.



Figure S9. (a) Bright-field (BF) scanning transmission electron microscopy and (b) high-angle annular dark-field STEM images of Ni/WC@NC catalyst; (c-e) The EDX elemental mapping of Ni and W in Ni/WC@NC. (f) The EDX spectra of Ni/WC@NC catalyst. These results jointly verify that the multiple interfaces between Ni and WC are extensively present in Ni/WC@NC catalyst.



Figure S10. Raman spectra of Ni/WC@NC catalyst. In the Raman spectra, the intensity ratio between D (1356 cm⁻¹) and G band (1580 cm⁻¹) of Ni/WC@NC catalyst is 1.66, which implies the presence of microstructural disordering and many defects within carbon materials, presumably originating in the large amount of N dopants in the carbon layers.⁴



Figure S11. N₂ sorption isotherms of Ni/WC@NC catalyst, which presents a typical IV hysteresis loop and the BET surface area is $113 \text{ m}^2 \cdot \text{g}^{-1}$.



Figure S12. Calculation of exchange current density of Ni/WC@NC in 0.5 M H₂SO₄. The exchange current density (j_o) was calculated using extrapolation methods.⁵ When the overpotential value is 0, the log(j) value for Ni/WC@NC is -0.081, respectively. Based on Tafel equations, j_o for Ni/WC@NC was calculated to be 0.83 mA/cm².



Figure S13. Faradaic Efficiency (FEs) of Ni/WC@NC toward HER in 0.5 M H₂SO₄ at overpotential of 170 mV during 60 min.



Figure S14. (a) The XRD patterns of Ni/WC@NC catalyst before and after catalytic reaction. (b) The TEM image of Ni/WC@NC catalyst after catalytic reaction. These results show that the composition and morphology of catalyst almost keeps unchanged.



Figure S15. XPS spectrum of Ni/WC@NC after HER test. (a) C 1s, (b) N 1s, (c) W 4f, (d) Ni 2p.



Figure S16. The HER polarization plots of Ni/WC@NC, Ni/WC, N-doped C and Bare GCE in 0.5 M H_2SO_4 at scan rate of 5 mV s⁻¹.



Figure S17. (a) The TEM image of Ni/WC catalyst. (b) The high-magnified TEM image of Ni/WC catalyst. The images show that without the dispersion of GO Ni/WC NPs tend to agglomerate during the heat treatment to form large aggregates, which decreases the exposed active interfaces of Ni/WC.



Figure S18. The Powder XRD patterns of Ni/WC catalyst. the characteristic peaks located at 31.58°, 35.72°, 48.41° and 64.18° are indexed to the (001), (100), (101) and (110) planes of hexagonal WC (JCPDS, No. 65-4539), respectively. The diffraction peaks at 44.35° and 51.67° are ascribed to the (111) and (200) facets of metallic Ni (JCPDS, No. 65-0380) separately.



Figure S19. (a) The Powder XRD patterns of Ni@NC; (b) N₂ sorption isotherms of Ni@NC catalyst, which presents a typical IV hysteresis loop and the BET surface area is 93 m²·g⁻¹.



Figure S20. (a) Full scan XPS spectrum of Ni@NC. (b-d) XPS spectrum of Ni@NC. (b) C 1s, (c) N 1s, (d) Ni 2p. The full scan XPS spectrum shows that Ni@NC catalyst consists of C, N, O and Ni elements. The C 1s XPS spectrum shows four pronounced peaks centered at 284.4, 285.2 and 286.2 eV, which are corresponding to C=C, C-N and C-O species, respectively. The N 1s spectrum reveals three typical N status including pyridinic N (398.6 eV), pyrrolic N (399.9 e V) and graphitic N (401.6 eV) species. The high-resolution Ni 2p XPS spectrum exhibits two peaks at 851.7 and 869.1 eV, which are ascribed to Ni 2p 3/2 and 2p 1/2, respectively.



Figure S21. (a) The Powder XRD patterns of WC@NC; (b) N_2 sorption isotherms of WC@NC catalyst, which presents a typical IV hysteresis loop and the BET surface area is 96 m²·g⁻¹.



Figure S22. (a) Full scan XPS spectrum of WC@NC. (b-d) XPS spectrum of WC@NC. (b) C 1s, (c) N 1s, (d) W 4f. The full scan XPS spectrum shows that WC@NC catalyst consists of C, N, O and W elements. In the C 1s XPS spectrum, the peaks at 283.3 eV could be ascribed to the C-W species, three other pronounced peaks centered at 284.5, 285.2 and 286.1 eV are corresponding to C=C, C-N and C-O species, respectively. The N 1s spectrum reveals three typical N status including pyridinic N (398.4 eV), pyrrolic N (400.4 e V) and graphitic N (401.6 eV) species. W 4f XPS spectrum is featured with two peaks at 31.59 and 33.74 eV, which are assigned to 4f 7/2 and 4f 5/2 of WC. The peaks at higher binding energy are arose from ineluctable surface oxidation.⁵



Figure S23. The HER polarization plots of Ni/WC@NC and the physical mixture of Ni@NC and WC@NC in 0.5 M H_2SO_4 at scan rate of 5 mV s⁻¹.



Figure S24. Cyclic voltammograms (CVs) of (a) Ni@NC and (b) WC@NC sweeping over the potential area from 0.06 to 0.16 V without redox current peaks in 0.5 M H_2SO_4 .



Figure S25. Nyquist plots of electrochemical impedance spectra (EIS) of Ni/WC@NC recorded in 0.5 M H₂SO₄ aqueous solution. As shown in Fig.S22, the charge transfer resistances (R_{ct}) of Ni/WC@NC sharply decrease with the increasing overpotential. The small R_{ct} values of Ni/WC@NC (5.53 Ω in 0.5 M H₂SO₄) suggest that the catalyst exhibits fast electron transfer ability and higher catalytic activities for HER.



Figure S26. Nyquist plots of electrochemical impedance spectra (EIS) of (a) Ni@NC and (b) WC@NC recorded in 0.5 M H_2SO_4 aqueous solution.



Figure S27 The HER polarization plots of Ni/WC@NC samples etching for different times in 0.5 M H₂SO₄.



Figure S28. (a) XRD of Ni/WC@NC samples etching for different times; (b-d) the EDX results of Ni/WC@NC samples etching for different times. From the results observed, the amount of Ni gradually decreases with the increase of etching time. After almost 6 hour, the characteristic peaks of Ni can not be observed.



Figure S29 (a-b) TEM and HRTEM images of Ni/WC@NC etching for 1 hour; (c-d) TEM and HRTEM images of Ni/WC@NC etching for 2 hour; (e-f) TEM and HRTEM images of Ni/WC@NC etching for 6 hour.



Figure S30. The HER polarization plots of Ni/WC@NC samples annealing at different temperature in $0.5 \text{ M H}_2\text{SO}_4$.



Figure S31. XRD patterns of Ni/WC@NC annealing at different temperature. From the result, the crystallinity of Ni/WC@NC increases with the increase of annealing temperature.



Figure S32. (a) The TEM of Ni/WC@NC catalyst annealing at 750 °C; (b) The HR-TEM of Ni/WC@NC catalyst annealing at 750 °C; (c) The TEM of Ni/WC@NC catalyst annealing at 850 °C; (b) The HR-TEM of Ni/WC@NC catalyst annealing at 850 °C. As shown in Fig. S29, when annealing at 750 °C, the average size of Ni/WC NPs increase from 8 nm to 12 nm, the nanoparticles exhibit slightly aggregation. When the annealing temperature enhances to 850 °C, the average size of Ni/WC@NC catalyst increase to 26 nm. The nanoparticles are seriously aggregated.



Figure S33. (a-d) The element mapping of Ni/WC@NC catalyst annealing at 750 °C; (e-f) The element mapping of Ni/WC@NC catalyst annealing at 850 °C.



Figure S34. Three-dimensional charge density difference (CDD) for Ni_{1L}/WC(001) composites from side view. The purple region represents charge accumulation, and the yellow regions indicate charge depletion. The isovalue is set to 0.005 e/Bohr³ in Vesta code.



Figure S35. (a) XANES spectra at W *K*-edge collected on W foil, WC and two-center Ni/WC@NC catalyst; (b) The corresponding Fourier transform of the EXAFS data at W *K*-edge. The results shows that the W in Ni/WC@NC exists in the form of WC. The corresponding extended X-ray absorption fine structure (EXAFS) spectra present two peaks in the range of 1-3 Å. The first one ranging from 1.2 to 2.4 Å correspond to W-C pair, and the second one in the range of 2.4 to 3 Å is due to the scattering pair of W-W.



Figure S36. (a) XANES spectra at W *K*-edge collected on two-center Ni/WC@NC catalyst in the states of initial, quick stop for HER and stop for 10 min in 0.5 M H_2SO_4 . (b) The corresponding Fourier transform of the EXAFS data at W *K*-edge.



Figure S37. The hydrogen diffusion pathway on the Ni/WC interface.



Figure S38. linear sweep voltammetry (LSV) curves of Ni@NC (a) and WC@NC (b) at different rotation rates (225 - 2500 rpm) in 0.5 M H₂SO₄.



Figure S39. Linear sweep voltammetry (LSV) curves of Ni/WC@NC catalyst at different rotation rates (225 - 2500 rpm) in 0.5 M H₂SO₄.



Figure S40. The HER polarization plots of Ni/WC@C and commercial 20% Pt/C catalyst in pH 2.40 (a), 3.39 (b), 4.44 (c), 5.30 (d), 6.11 (e) and 6.89 (f) electrolytes at scan rate of 5 mV s⁻¹. Inset: The corresponding Tafel plots for Ni/WC@C and Pt/C catalysts.



Figure S41. The HER polarization plots of Ni/WC@C and commercial 20% Pt/C catalyst in pH 8.02 (a), 9.11 (b), 10.01 (c), 11.24 (d), 12.05 (e) and 13.19 (f) electrolytes at scan rate of 5 mV s⁻¹. Inset: The corresponding Tafel plots for Ni/WC@C and Pt/C catalysts.

4. Supplementary Tables

Table S1. The C, N, O, Ni, W, and P components of Ni/WC@NC recorded from the EDX quantitative analyses.

Element	Percentage by weight /%	Percentage by atoms /%
СК	26.66	56.89
N K	11.16	20.42
O K	6.42	10.29
P K	1.58	1.31
Ni K	11.92	5.21
W L	42.26	5.89

Table S2. The C, N, O, Ni, W, and P components of Ni/WC@NC obtained from the XPS analyses.

Element	Peak BE	FWHM	Area	At. %
C 1s	284.56	0.98	10799.25	70.97
N 1s	398.6	1.8	2642.58	9.76
O 1s	531.97	3.83	5835.01	13.09
Р 2р	132.8	0	161.04	0.39
Ni 2p3/2	852.14	0.87	4106.56	2.06
W 4f7/2	32.22	0.83	3165.43	3.74

Table S3. The ICP result of Ni/WC@NC catalyst.

Element	Content /(mg/kg)
Ni	9.72×10^4
W	4.32×10 ⁵

Catalyst	Current	Overpotential	Tafel slope	J_o (mA cm ⁻	Ref.
	density	(mV)	(mV dec ⁻¹)	²)	
	$(mA cm^{-2})$				
Ni/WC@NC	10	53	43.5	0.83	This work
WC-CNTs	10	145	72	N.A.	Ref. 6
W ₂ C/MWNT	10	125	45	N.A.	Ref. 7
Ni/Mo ₂ C-PC	10	179	101	0.2	Ref. 8
P-W ₂ C@NC	10	89	53	0.316	Ref. 9
N-WC array	10	89	75	N.A.	Ref. 10
$(Mo_2C)_{0.34}$ -	10	100	53	0.419	Ref. 11
(WC) _{0.32} /NG					
P-WC _x NWs	10	118	55	0.0165	Ref. 12
C-CWC	10	73	75	N.A.	Ref. 13
W ₂ C@GL	10	135	68	0.24	Ref. 14
0.5W-Mo _x C	20	148	56	N.A.	Ref. 15
np-Mo ₂ C	10	229	100	N.A.	Ref. 16
Mo ₂ C/C-N	10	98	60	0.311	Ref. 17
W _x C@WS ₂	10	146	61	0.042	Ref. 18
Mo ₂ C-GNR	10	152	65	N.A.	Ref. 19
MoP/Mo ₂ C@	10	89	45	0.215	Ref. 20
С					
Co-Mo ₂ C	10	140	39	0.005	Ref. 21
Mo _x C-	10	75	45	0.35	Ref. 22
Ni@NCV					
Fe ₃ C/Mo ₂ C@	10	98	45.2	0.104	Ref. 23
NPGC					
Mo _x C@C-1	10	79	56	0.27	Ref. 24
N@MoPC _x -	10	108	69.4	0.342	Ref. 25
800					
MoP/rGO	10	119	58	0.178	Ref. 26
WO _{2.9}	10	70	50	0.4	Ref. 27
Se-MoS ₂	10	104	59	0.2	Ref. 28
MoN-NC	10	62	54	0.778	Ref. 29
Mo ₂ B ₄	3.5	270	80	N.A.	Ref. 30

 Table S4. Comparison of HER performance in acidic media for Ni/WC@NC with other HER electrocatalysts.

Element	Peak BE	FWHM	Area	At. %
C 1s	284.44	1.56	24985.54	72.88
N 1s	398.6	1.97	5566.52	9.13
O 1s	532.36	2.66	14541.85	14.91
Р 2р	133.1	0	322.08	0.78
Ni 2p3/2	852.32	0.74	3435.06	0.76
W 4f7/2	32.11	0.9	2949.41	1.55

Table S5. The C, N, O, Ni, W, and P components of Ni/WC@NC after HER test obtained from the XPS analyses.

Table S6. The C, N, O and Ni components of Ni@NC recorded from the EDX quantitative analyses.

Element	Percentage by weight /%	Percentage by atoms /%
СК	39.48	55.12
N K	5.46	6.53
O K	13.87	14.57
Ni K	41.19	23.78

Table S7. The C, N, O and Ni components of Ni@NC obtained from the XPS analyses.

Element	Peak BE	FWHM	Area	At. %
C 1s	284.57	1.74	13608.6	72.73
N 1s	398.8	2.38	3195.03	9.59
O 1s	531.43	2.07	7012	13.17
Ni 2p3/2	855.48	1.73	11067.6	4.51

Table S8. The ICP result of Ni@NC catalyst.

Element	Content /(mg/kg)
Ni	4.53×10 ⁵

Element	Percentage by weight /%	Percentage by atoms /%
СК	12.85	51.81
N K	3.02	10.45
O K	4.73	14.32
РК	1.93	3.02
W L	77.48	20.41

Table S9. The C, N, O, W, and P components of WC@NC recorded from the EDX quantitative analyses.

Table S10 The C, N, O, W, and P components of WC@NC obtained from the XPS analyses.

Element	Peak BE	FWHM	Area	At. %
C 1s	284.57	1.18	12401.4	66.05
N 1s	401.25	1.94	2406.72	7.2
O 1s	530.64	1.98	8164.68	15.28
Р 2р	133.16	0.13	368.99	1.63
W 4f7/2	31.56	0.88	10285.21	9.84

Table S11. The ICP result of WC@NC catalyst.

Element	Content /(mg/kg)
W	7.61×10 ⁵

Table S12. The value of charge transfer resistance (Rct) and a series resistance (Rs) for Ni/WC@NC from 40 to 200 mV in $0.5 \text{ M H}_2\text{SO}_4$.

Potential (mV vs. RHE)	Ni/WC@NC	
	$\operatorname{Ret}(\Omega)$	$\operatorname{Rs}\left(\Omega ight)$
40	415	8.21
80	83.4	8.16
120	22.5	8.29
160	9.8	8.32
200	5.53	8.41

Potential (mV vs. RHE)	Ni@NC		WC@NC	
	Rct (Ω)	$\operatorname{Rs}(\Omega)$	Rct (Ω)	Rs (Ω)
40	680	5.59	6300	5.96
80	559	5.36	2127	6.12
120	185	5.43	479	6.23
160	41.4	5.45	135	6.31
200	20.6	5.54	56.7	6.27

Table S13. The value of charge transfer resistance (Rct) and a series resistance (Rs) for Ni@NC and WC@NC with overpotential from 30 to 230 mV in 0.5 M H_2SO_4 .

Table S14. The C, N, O, Ni, W, and P components of Ni/WC@NC etched for 1 h recorded from the EDX quantitative analyses.

Element	Percentage by weight /%	Percentage by atoms /%
СК	18.95	51.45
N K	3.72	8.67
O K	12.03	24.52
P K	1.14	1.2
Ni K	7.36	4.09
W L	56.8	10.08

Table S15. The C, N, O, Ni, W, and P components of Ni/WC@NC etched for 2 h recorded from the EDX quantitative analyses.

Element	Percentage by weight /%	Percentage by atoms /%
C K	24.33	61.23
N K	5.64	12.17
O K	7.12	13.45
РК	1.32	1.29
Ni K	4.94	2.54
W L	56.66	9.32

Element	Percentage by weight /%	Percentage by atoms /%
СК	19.4	50.9
NK	5.75	12.94
O K	12.77	25.14
РК	0.02	0.05
Ni K	1.0	0.5
W L	61.05	10.46

Table S16. The C, N, O, Ni, W, and P components of Ni/WC@NC etched for 6 h recorded from the EDX quantitative analyses.

5. References

1. A. P. Ginsberg, *Inorganic Syntheses*. (John Wiley& Sons, 1990).

2. S. T. Zheng, J. Zhang, X. X. Li, W. H. Fang, G. Y. Yang, J. Am. Chem. Soc., 2010, 132, 15102.

3. H. Li, W. Q. Kong, J. Liu, N. Y. Liu, H. Huang, Y. Liu, Z. H. Kang, *Carbon*, 2015, **91**, 66.

4. Y. P. Liu, G. T. Yu, G. D. Li, Y. H. Sun, T. Asefa, W. Chen, X. X. Zou, *Angew. Chem. Int. Ed.*, 2015, **54**, 10752.

5. J. Zhang, T. Wang, P. Liu, Z. Q. Liao, S. H. Liu, X. D. Zhuang, M. W. Chen, E. Zschen, X. L. Feng, *Nat. Commun.*, 2017, **8**, 15437.

6. X. J. Fan, H. Q. Zhou, X. Guo, ACS nano, 2015, 9, 5125.

7. Gong, Q. F.; Wang, Y.; Hu, Q.; Zhou, J. G.; Feng, R. F.; Duchesne, P. N.; Zhang, P.; Chen, F. J.; Han, N.; Li, Y. F.; Jin, C. H.; Li, Y. G.; Lee, S. T. *Nat. Commun.*, 2016, 7, 13216.

8. Z. Y. Yu, Y. Duan, M. R. Gao, C. C. Lang, Y. R. Zheng, S. H. Yu, *Chem. Sci.*, 2017, **8**, 968.

9. G. Yan, C. X. Wu, H. Q. Tan, X. J. Feng, L. K. Yan, H. Y. Zang, Y. G. Li, J. Mater. Chem. A, 2017, 5, 765.

10. N. N. Han, K. R. Yang, Z. Y. Lu, Y. J. Li, W. W. Xu, T. F. Gao, Z. Cai, Y. Zhang, V. S. Batista, W. Liu, X. M. Sun, *Nat. Commun.*, 2018, **9**, 13216.

11. L. L. Huo, B. C. Liu, Z. Q. Gao, J. Zhang, J. Mater. Chem. A, 2017, 5, 18494.

12. B. W. Ren, D. Q. Li, Q. Y. Jin, H. Cui, C. X. Wang, J. Mater. Chem. A, 2017, 5, 13196.

13. Y. P. Liu, G. D. Li, L. Yuan, L. Ge, H. Ding, D. J. Wang, X. X. Zou, *Nanoscale*, 2015, 7, 3130.

14. Y. Zhou, R. G. Ma, P. X. Li, Y. F. Chen, Q. Liu, G. Z. Cao, J. C. Wang, *J. Mater. Chem. A*, 2016, **4**, 8204.

15. K. Zhang, G. Zhang, J. H. Qu, H. J. Liu, ACS Appl. Mater. Interfaces, 2018, 10, 2451.

16. J. S. Kang, J. Kim, M. J. Lee, Y. J. Son, D. Y. Chung, S. Park, J. Jeong, J. M. Yoo, H. Choe, H. S. Park, Y. E. Sung, *Adv. Sci.*, 2018, **5**, 1700601.

17. G. L. Zhi, B. C. Liu, S. S. Wang, L. L. Huo, Z. Q. Gao, J. Zhang, *Electrochimica Acta.*, 2017, **258**, 970.

F. M. Wang, P. He, Y. C. Li, T. A. Shifa, Y. Deng, K. L. Liu, Q. S. Wang, F. Wang, Y. Wen, Z. X. Wang, X. Y. Zhan, L. F. Sun, J. He, *Adv. Funct. Mater.*, 2017, 27, 1605802.

19. X. J. Fan, Y. Y. Liu, Z. W. Peng, Z. H. Zhang, H. Q. Zhou, X. M. Zhang, B. I. Yakobson, W. A. Goddard III, X. Guo, R. H. Hauge, J. M. Tour, *ACS nano*, 2017, **11**, 384.

20 L. N. Zhang, S. H. Li, H. Q. Tan, S. U. Khan, Y. Y. Ma, H. Y. Zang, Y. H. Wang, Y. G. Li, *ACS Appl. Mater. Interfaces*, 2017, **9**, 16270.

21. H. L. Lin, N. Liu, Z. P. Shi, Y. L. Guo, Y. Tang, Q. S. Gao, Adv. Funct. Mater.,

2016, 26, 5590.

22. S. P. Wang, J. Wang, M. L. Zhu, X. B. Bao, B. Y. Xiao, D. F. Su, H. R. Li, Y. Wang, J. Am. Chem. Soc., 2015, 137, 15753.

23. J. S. Li, Y. J. Tang, C. H. Liu, S. L. Li, R. H. Li, L. Z. Dong, Z. H. Dai, J. C. Bao, Y. Q. Lan, *J. Mater. Chem. A*, 2016, **4**, 1202.

24. X. J. Yang, X. J. Feng, H. Q. Tan, H. Y. Zang, X. L. Wang, Y. H. Wang, E. B. Wang, Y. G. Li, *J. Mater. Chem. A*, 2016, **4**, 3947.

25. Y. C. Huang, J. X. Ge, J. Hu, J. W. Zhang, J. Hao, Y. G. Wei, *Adv. Energy Mater.*, 2017, 1701601.

26. H. J. Yan, Y. Q. Jiao, A. P. Wu, C. G. Tian, X. M. Zhang, L. Wang, Z. Y. Ren, H. G. Fu, *Chem. Commun.*, 2016, **52**, 9530.

27. Y. H. Li, P. F. Liu, L. F. Pan, H. F. Wang, Z. Z. Yang, L. R. Zheng, P. , H. J. Zhao, L. Gu, H. G. Yang, *Nat. Commun.*, 2015, **6**, 8064.

28. J. Hu, B. L. Huang, C. X. Zhang, Z. L. Wang, Y. M. An, D. Zhou, H. Lin, M. K. H. Leung, S. H. Yang, *Energy Environ. Sci.*, 2017, **10**, 593.

29. Y. P. Zhu, G. Chen, X. M. Xu, G. M. Yang, M. L. Liu, Z. P. Shao, ACS Catal., 2017, 7, 3540.

30. H. Park, Y. M. Zhang, J. P. Scheifers, P. R. Jothi, A. Encinas, B. P. T. Fokwa, J. Am. Chem. Soc., 2017, **139**, 12915.