Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Ultrasmall tungsten phosphide nanoparticles embedded in nitrogen-doped carbon as a highly active and stable hydrogen-evolution electrocatalyst

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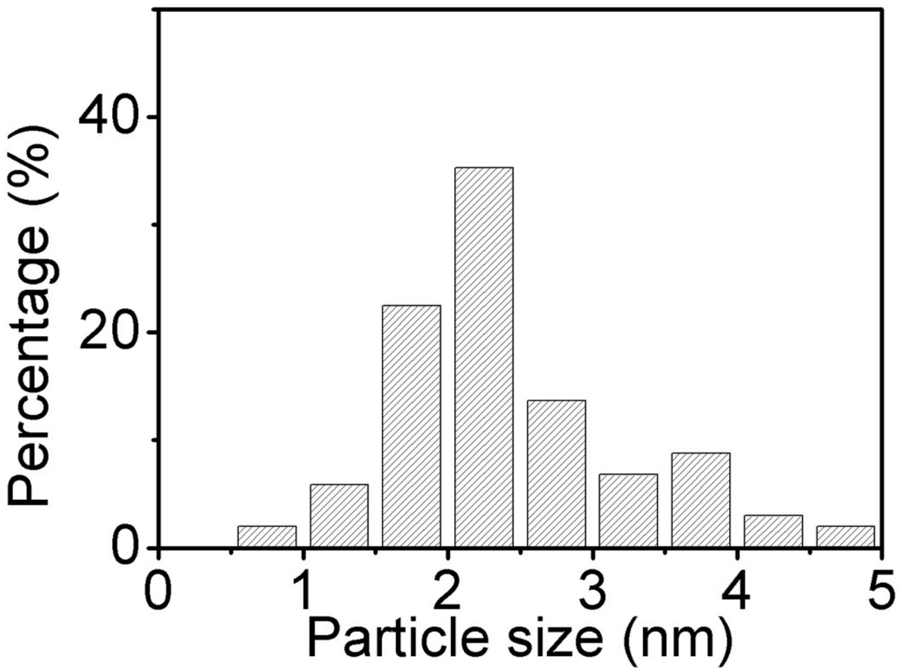

Fig. S1 Size distribution of WP NPs in WP NPs@NC.

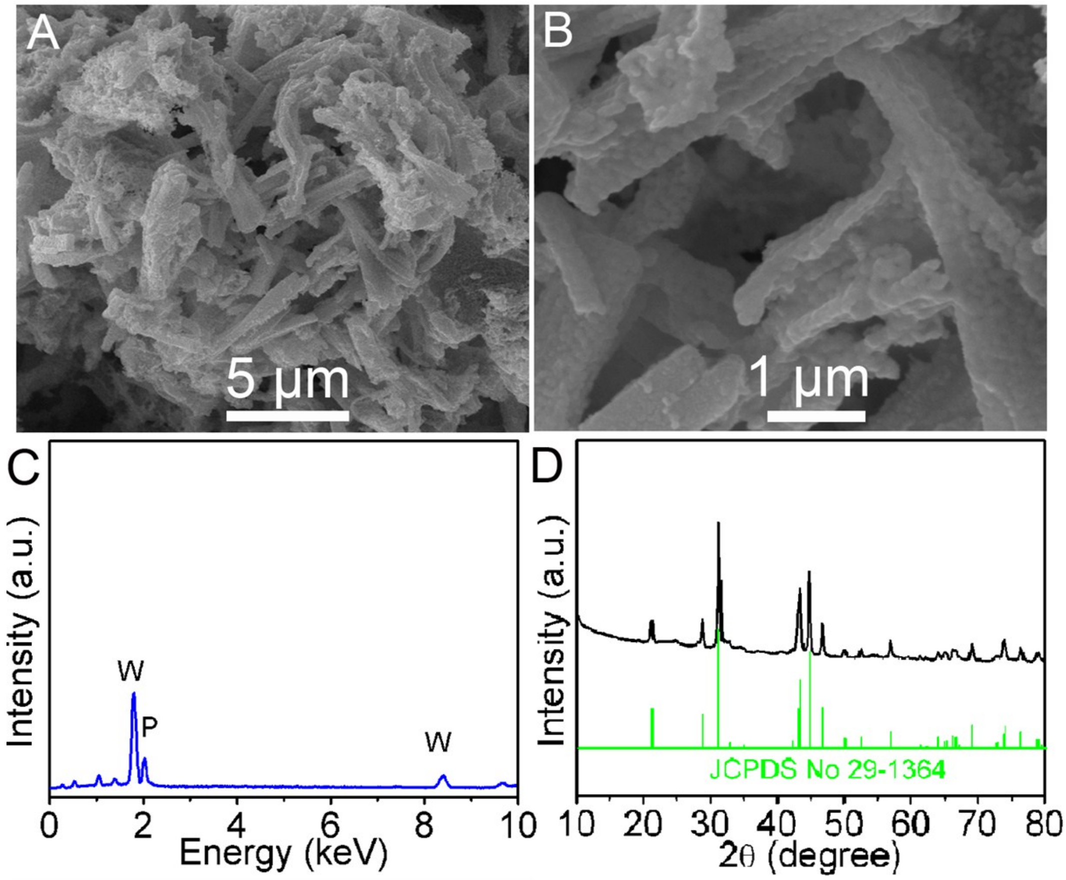

Fig. S2. (A) Low- and (B) high-magnification SEM images of bulk WP. (C) EDX spectrum and (D) XRD pattern of bulk WP.

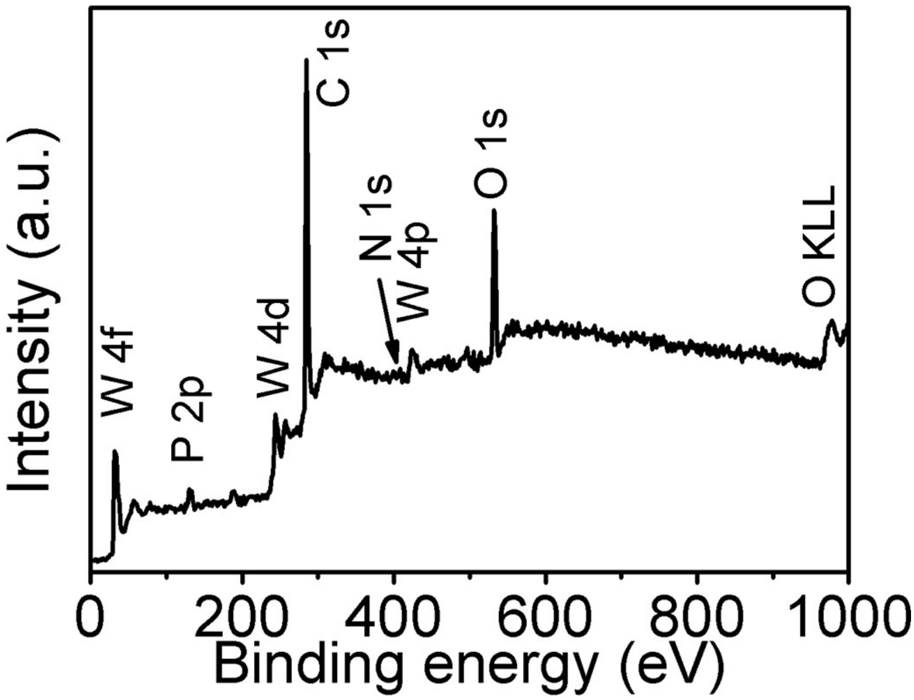

Fig. S3. The survey XPS spectra of the WP NPs@NC.

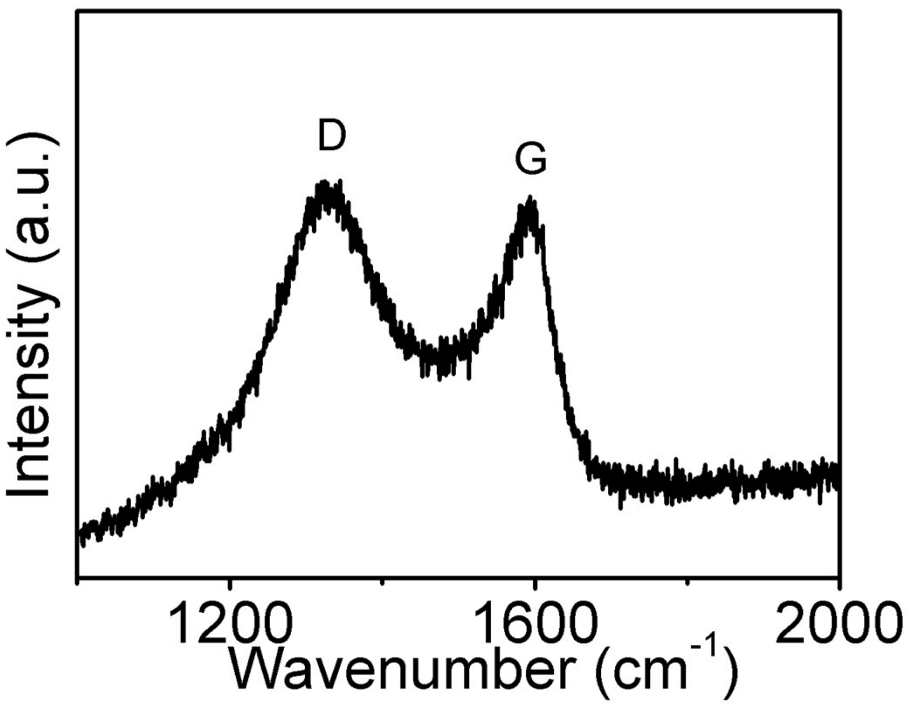

Fig. S4. Raman spectrum of the as-prepared WP NPs@NC.

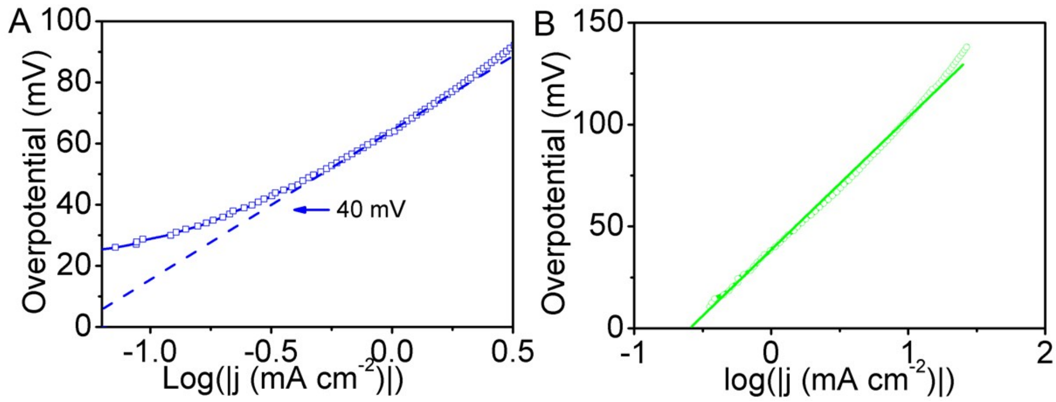

Fig. S5. (A) Tafel plot in the region of low current densities of WP NPs@NC in 0.5 M H_2SO_4. (B) Calculation of exchange current density of WP NPs@NC by applying extrapolation method to the Tafel plot.

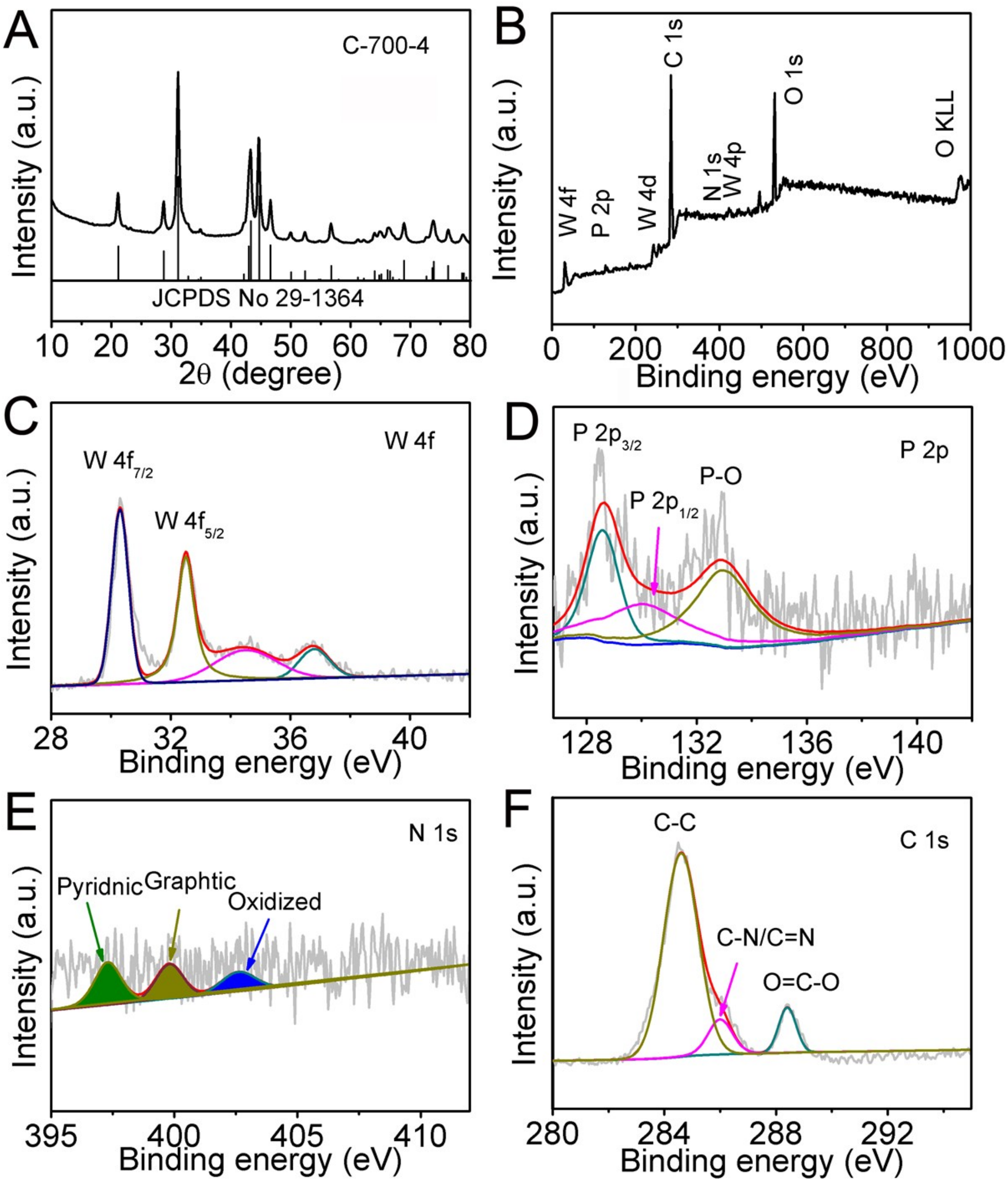

Fig. S6. (A) XRD pattern of C-700-4. (B) The survey XPS spectra of the C-700-4. (C-F) The high-resolution XPS spectra of the C-700-4.

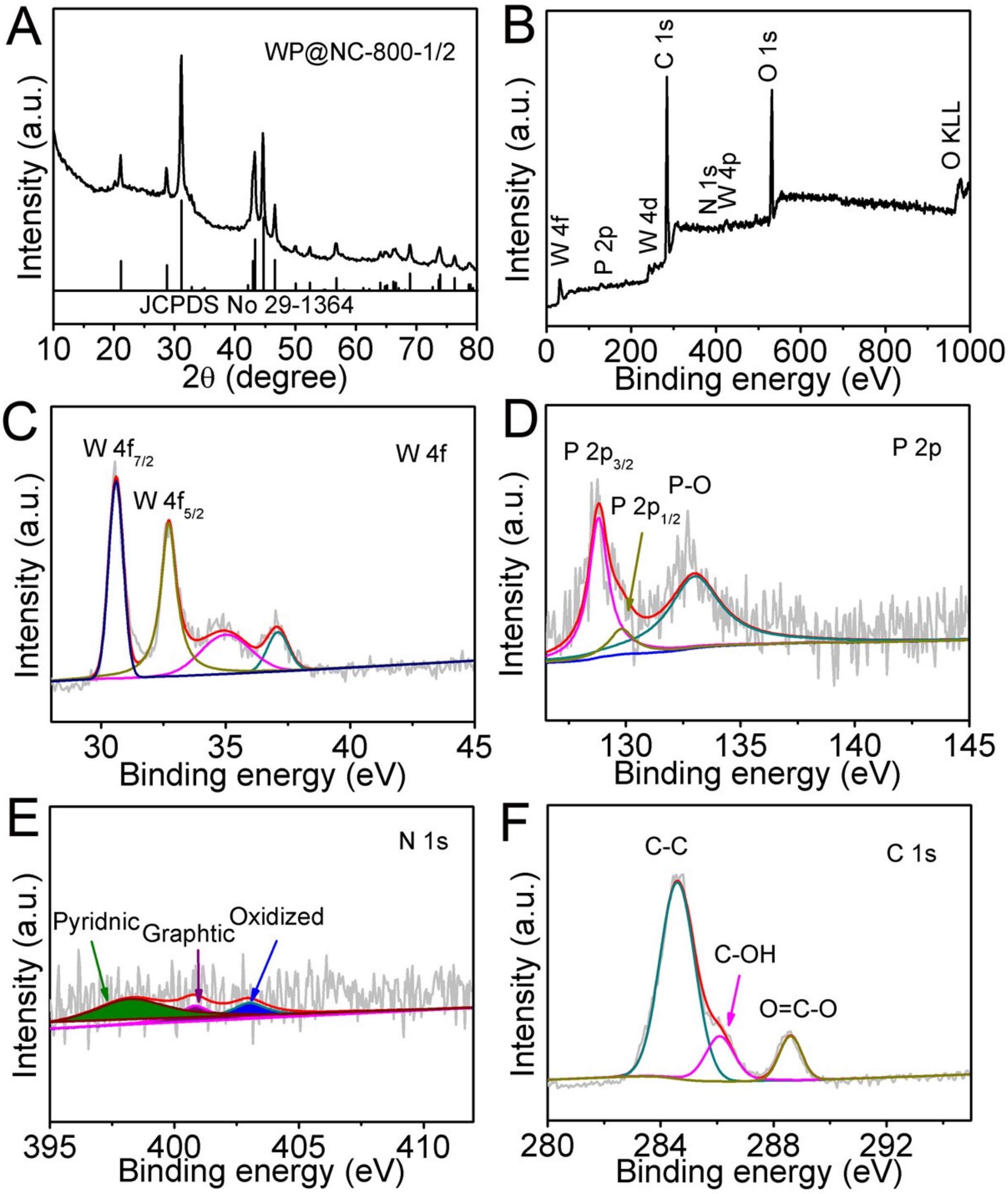

Fig. S7. (A) XRD pattern of C-800-2. (B) The survey XPS spectra of the C-800-2. (C-F) The high-resolution XPS spectra of the C-800-2.

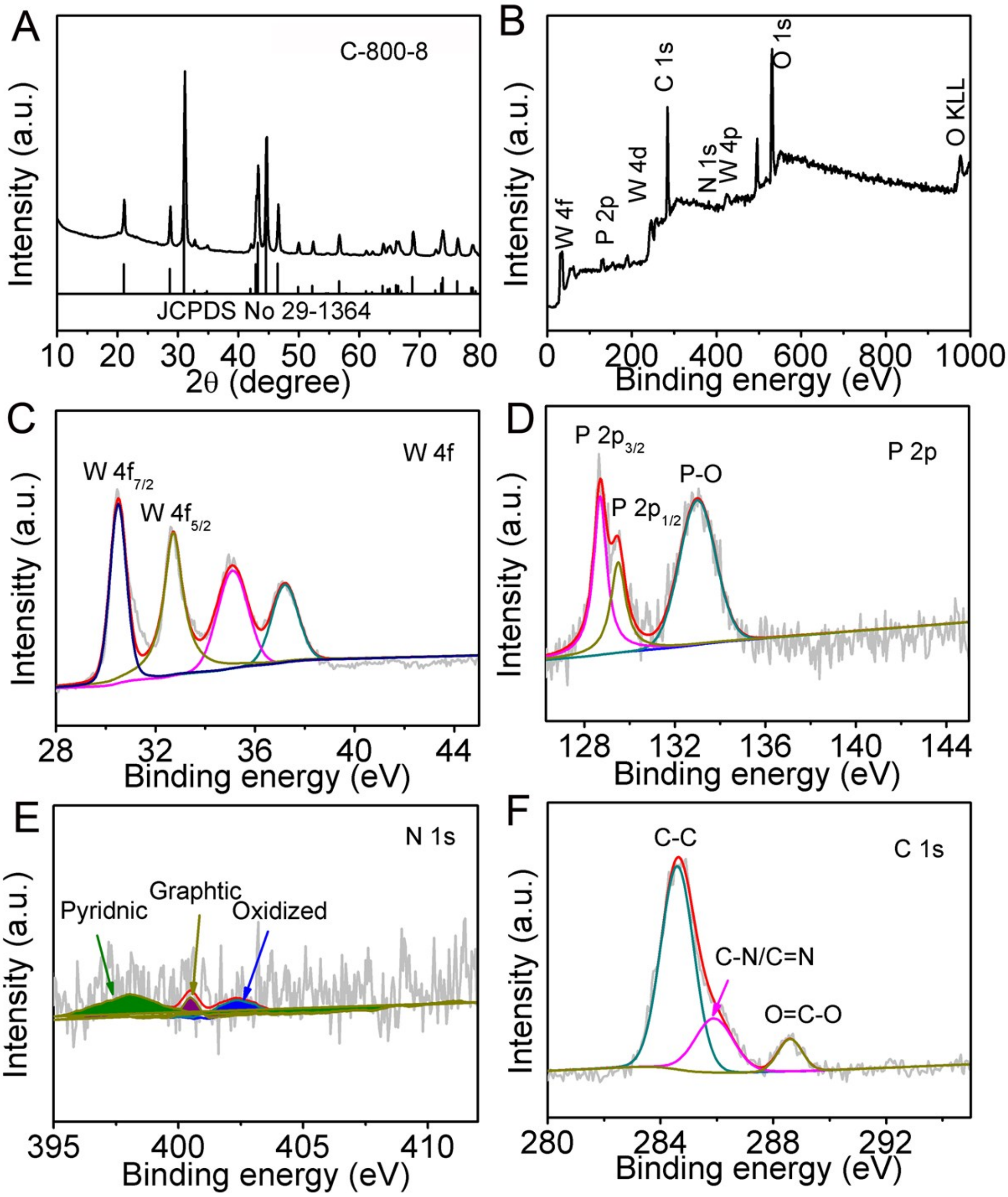

Fig. S8. (A) XRD pattern of C-800-8. (B) The survey XPS spectra of the C-800-8. (C-F) The high-resolution XPS spectra of the C-800-8.

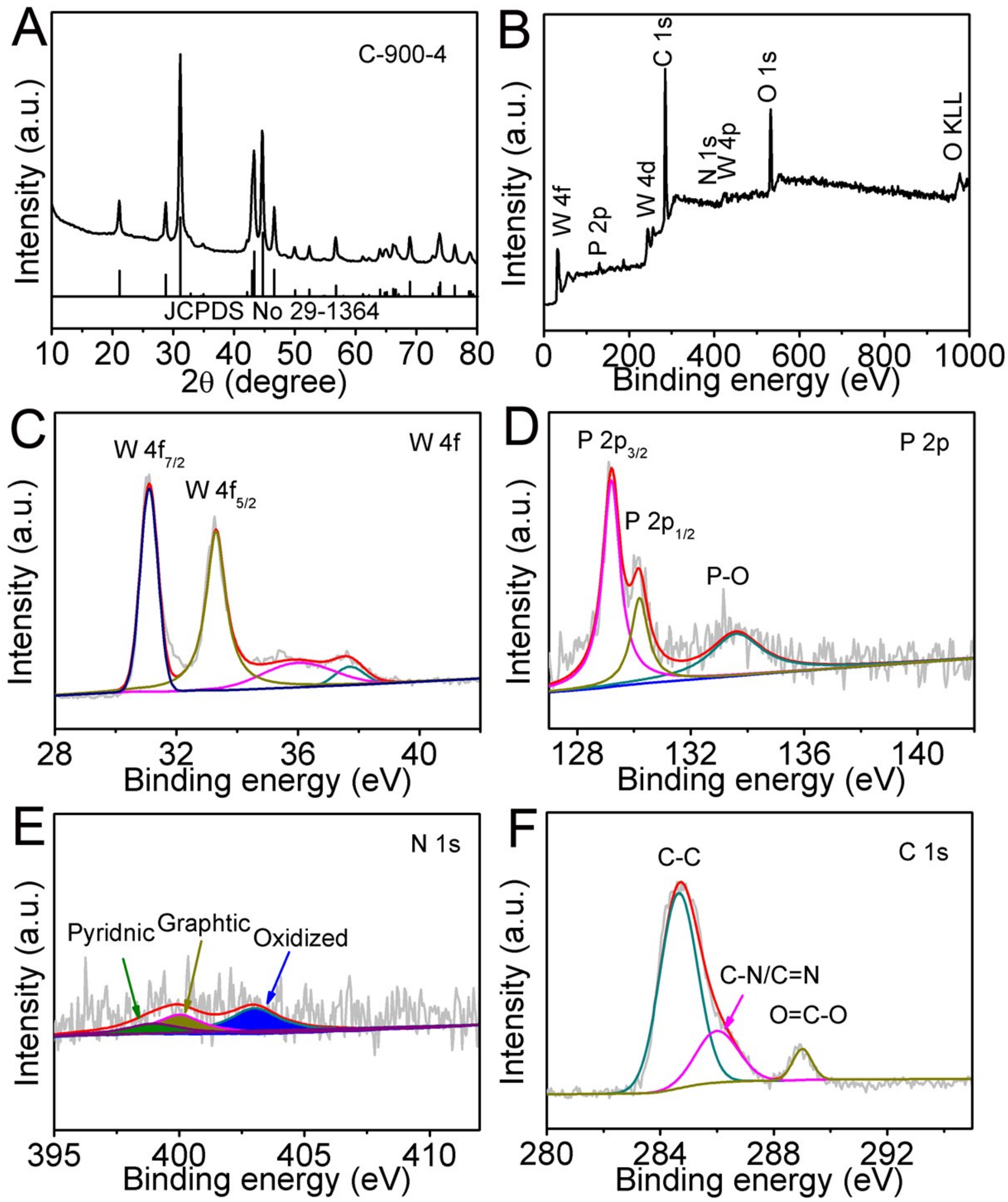

Fig. S9. (A) XRD pattern of C-900-4. (B) The survey XPS spectra of the C-900-4. (C-F) The high-resolution XPS spectra of the C-900-4.

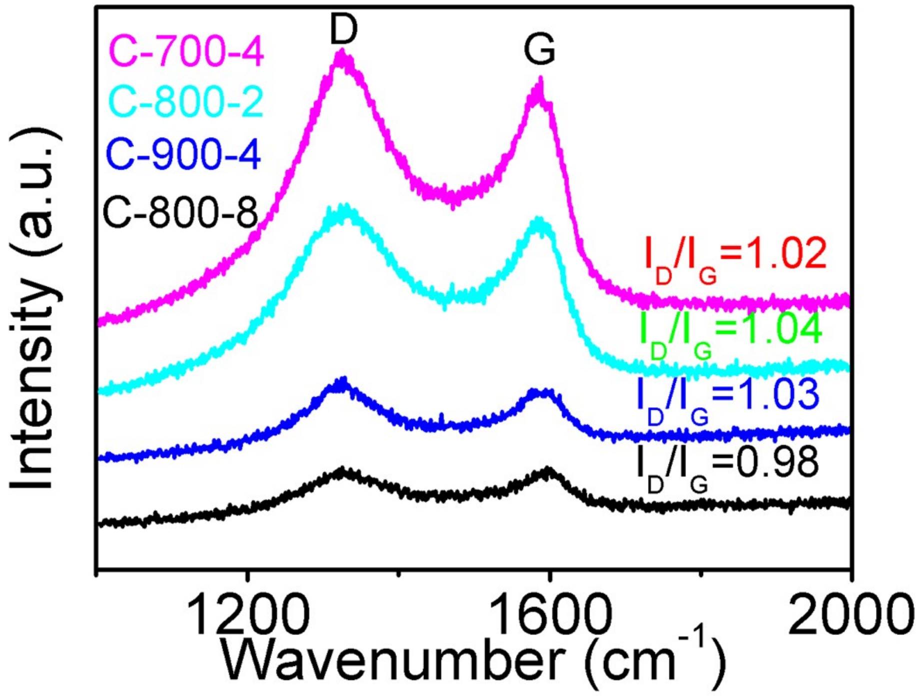

Fig. S10. Raman spectra for the C-700-4, C-800-2, C-900-4 and C-800-8.

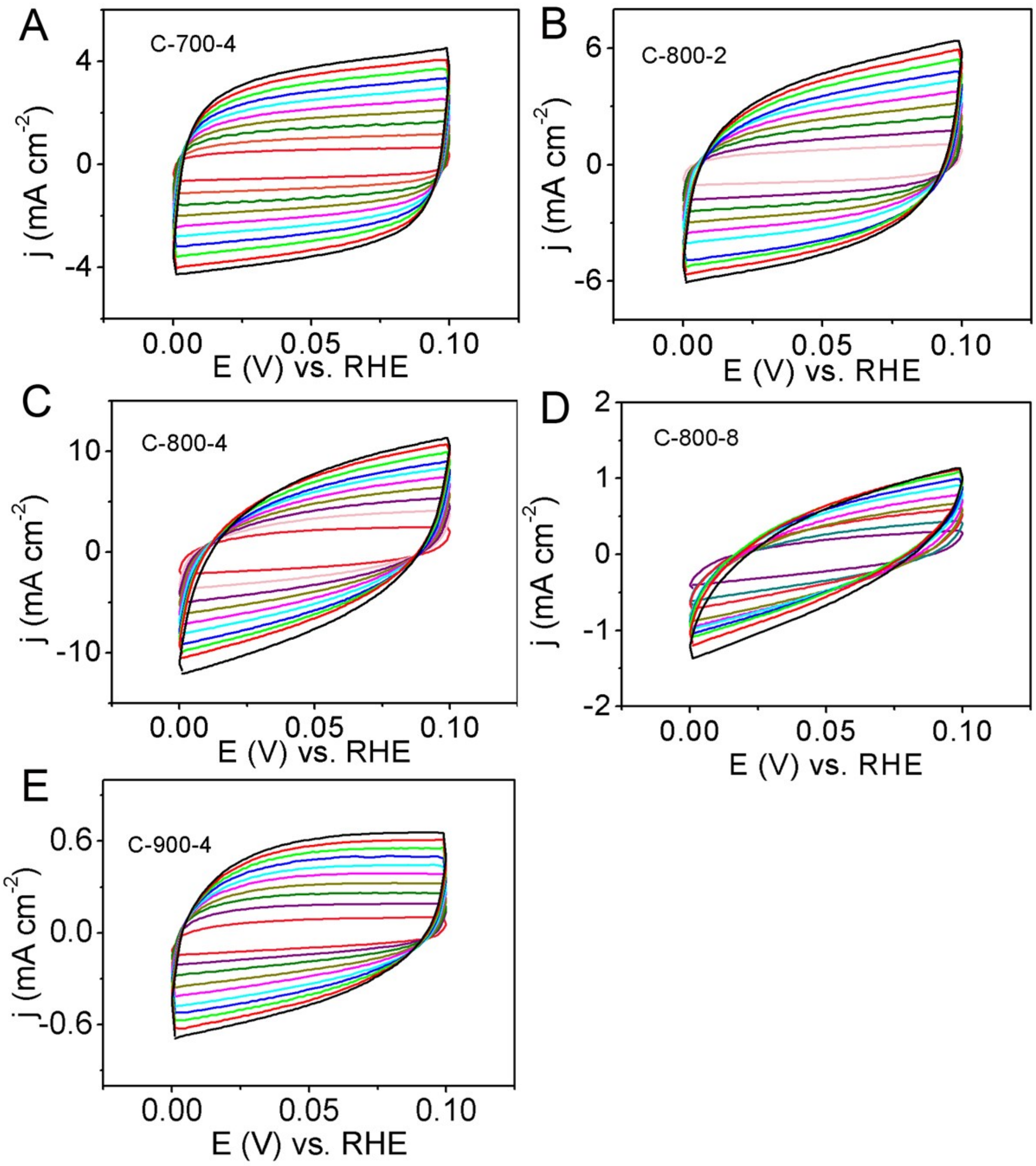

Fig. S11. CVs for (A) C-700-4, (B) C-800-2, (C) C-800-4, (D) C-800-8 and (E) C-900-4.

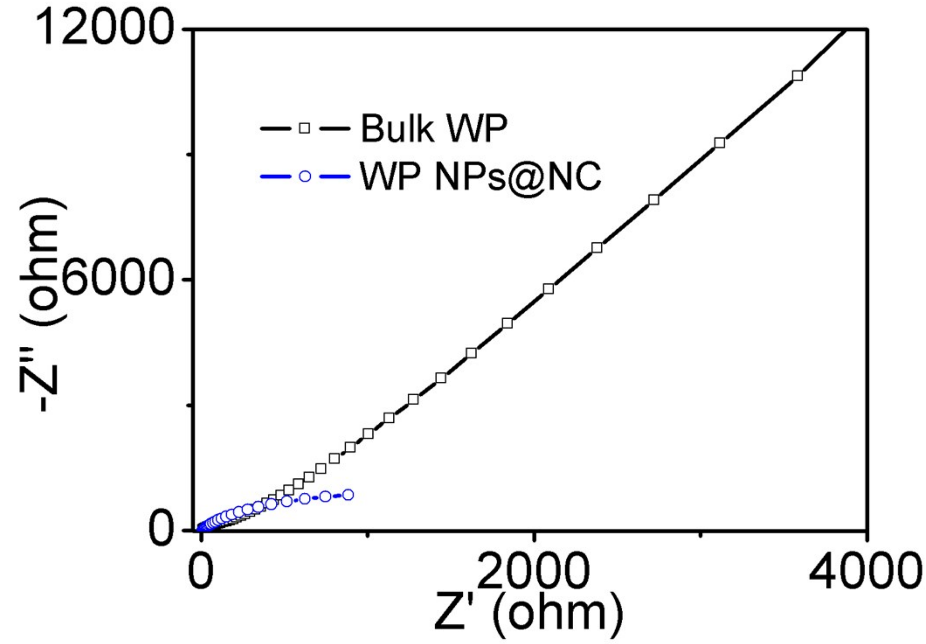

Fig. S12. EIS data for WP NPs@NC and bulk WP

Table S1. Comparison of HER performance in acidic media for WP NPs@NC with tungsten phosphide-based HER electrocatalyst.

Catalyst	**Electrolyte**	**Onset overpotential (mV)**	**Current density (*j*, mA cm^{-2})**	**η at the corresponding *j* (mV)**	**Exchange current density (mA cm^{-2})**	**Ref.**
WP NPs@NC	0.5 M H_2SO_4	40	10	102	0.25	This work
amorphous WP nanoparticles	0.5 M H_2SO_4	-	10	120	-	1
WP_2 submicroparticles	0.5 M H_2SO_4	54	10	161	0.017	2
WP_2 nanorods	0.5 M H_2SO_4	56	10	148	0.013	3
WP NAs/CC	0.5 M H_2SO_4	50	10	130	0.29	4

Table S2. Comparison of HER performance in acidic media for WP NPs@NC with other non-noble-metals HER electrocatalyst.

Catalyst	**Electrolyte**	**Onset overpotential (mV)**	**Current density (*j*, mA cm^{-2})**	**η at the corresponding *j* (mV)**	**Exchange current density (mA cm^{-2})**	**Ref.**
WP NPs@NC	0.5 M H_2SO_4	40	10	102	0.25	This work
Ni_2P hollow nanoparticles	0.5 M H_2SO_4	-	10	116	0.033	5
Ni_2P nanoparticles	1.0 M H_2SO_4	46	20	140	-	6
FeP nanosheets	0.5 M H_2SO_4	100	10	~240	-	7
CoP/CNT	0.5 M H_2SO_4	54	10	122	0.288	8
interconnected network of MoP nanoparticles	0.5 M H_2SO_4	40	10	125	0.086	9
bulk MoP	0.5 M H_2SO_4	50	30	180	0.034	10
exfoliated WS_2 nanosheets	0.5 M H_2SO_4	80-100	10	~220	0.02	11
WS_2/graphene	0.5 M H_2SO_4	150-200	10	~270	-	12
WS_2 nanoribbons	0.5 M H_2SO_4	-	10	~225	-	13
WS_2 nanoflakes	0.5 M H_2SO_4	100	10	~130	-	14
WS_2 nanosheets	0.5 M H_2SO_4	75	10	~140	-	15
W_2N nanorods	0.5 M H_2SO_4	-	10	500	-	16
WO_2	0.5 M H_2SO_4	-	10	58	0.64	17
$WO_{2.9}$	0.5 M H_2SO_4	-	10	70	0.4	18
nanoporous Mo_2C nanowires	0.5 M H_2SO_4	70	60	200	-	19
$NiMoN_x$/C	0.1 M $HClO_4$	78	5	220	0.24	20
$Co_{0.6}Mo_{1.4}N_2$	0.1 M $HClO_4$	-	10	200	0.23	21
Co-NRCNTs	0.5 M H_2SO_4	50	10	260	0.01	22
$CoSe_2$ nanobelts	0.5 M H_2SO_4	50	10	~125	8.4×10^{-3}	23

Table S3. Comparison of HER performance in neutral media for WP NPs@NC with other non-precious metal HER electrocatalyst.

Catalyst	Electrolyte/pH	Current density (*j*, mA cm^{-2})	Overpotential at the corresponding *j* (mV)	Ref.
WP NPs@NC	1.0 M PBS	2 10	118 196	This work
WP_2 submicroparticles	1.0 M PBS	2	143	2
WP_2 nanorods	1.0 M PBS	2	172	3
WP NAs/CC	1.0 M PBS	2	95	4
Co-NRCNTs	0.1 M PBS	2	380	22
FeP/Ti	1.0 M PBS	10	102	24
bulk Mo_2C	pH=7	1	200	25
bulk Mo_2B	pH=7	1	250	25
H_2-CoCat/FTO	0.5 M KPi	2	385	26
Co-S/FTO	1.0 M PBS	2	83	27
$CuMoS_4$ crystals	pH=7	2	210	28

Table S4. Comparison of HER performance in basic media for WP NPs@NC with other non-precious metal HER electrocatalyst.

Catalyst	Electrolyte	Current density (j, mA cm^{-2})	Overpotential at the corresponding j (mV)	Ref.
WP NPs@NC	1.0 M KOH	2 10	92 150	This work
WP_2 submicroparticles	1.0 M KOH	10	153	2
WP_2 nanorods	1.0 M KOH	2	149	3
WP NAs/CC	1.0 M KOH	10	150	4
Ni_2P nanoparticles	1.0 M KOH	20	250	6
Co-NRCNTs	1.0 M KOH	10	370	22
bulk Mo_2B	1.0 M KOH	1	250	25
Ni	1.0 M KOH	10	400	25
Co-S/FTO	1.0 M KOH	1	480	27
Ni wire	1.0 M NaOH	10	350	29
Ni-Mo alloy/Ti foil	1.0 M NaOH	10	80	29

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