Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2016

Electronic supplementary information

Self-Supported Three-Dimensional Mesoporous Semimetallic WP_2 Nanowire Arrays on Carbon Cloth as a Flexible Cathode for Efficient Hydrogen Evolution

Mingyu Pi, [a] Tianli Wu, [a] Dingke Zhang, [b] Shijian Chen *[a] and Shuxia Wang*[a]

[a] School of Physics, Chongqing University, Chongqing, 401331, China

[b] College of Physics and Electronic Engineering, Chongqing Normal University, Chongqing, 401331, China.

*Corresponding author: Prof. Shijian Chen, E-mail: sjchen@cqu.edu.cn; Prof. Shuxia Wang, E-mail: wangshuxia@cqu.edu.cn. Tel: +86-2365678362

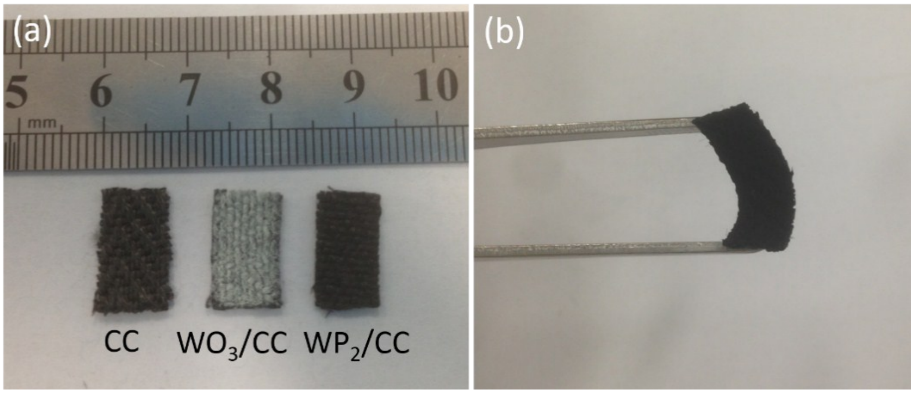

Fig. S1 (a) Photographs of bare CC, WO_3 NWs/CC and WP_2 NWs/CC. (b) Photograph of the fabricated flexible electrode.

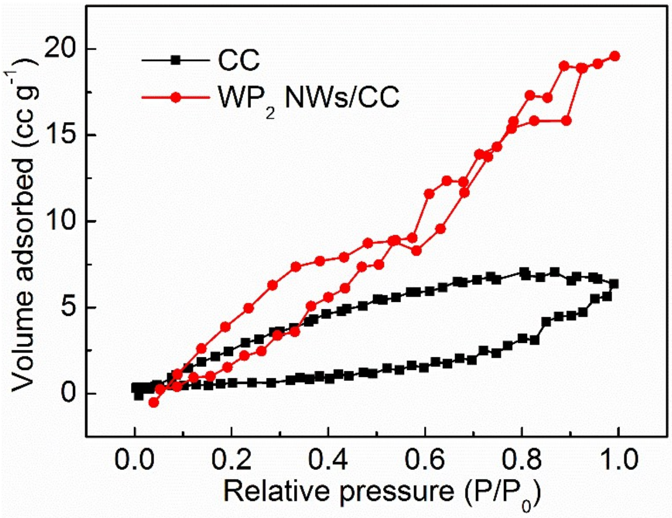

Fig. S2 Nitrogen adsorption/desorption isotherm plots of CC and WP_2 NWs/CC.

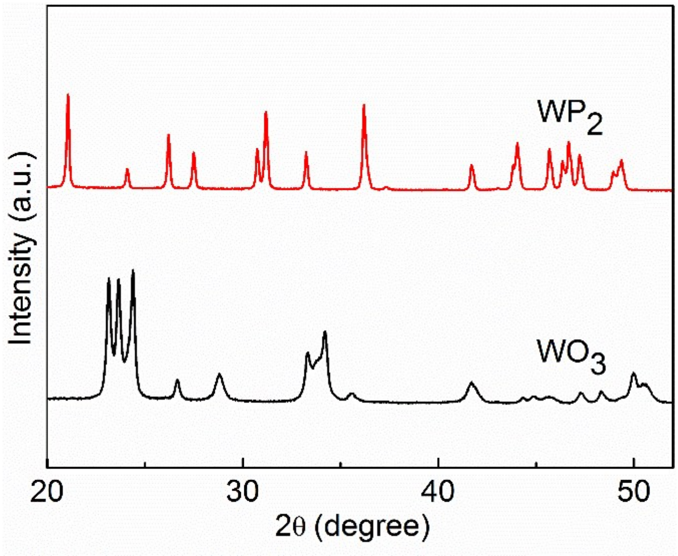

Fig. S3 XRD patterns for the WO_3 and WP_2 nanoparticles.

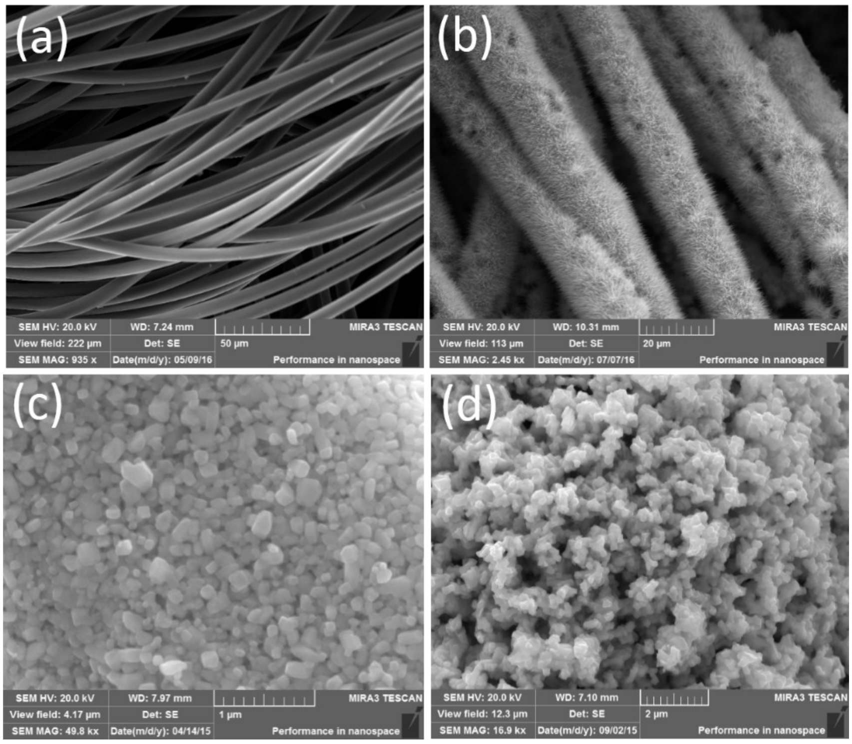

Fig. S4 Low-magnification SEM images of the bare CC substrate (a) and WO_3 NWs/CC (b). SEM images of WO_3 (c) and WP_2 nanoparticles (d).

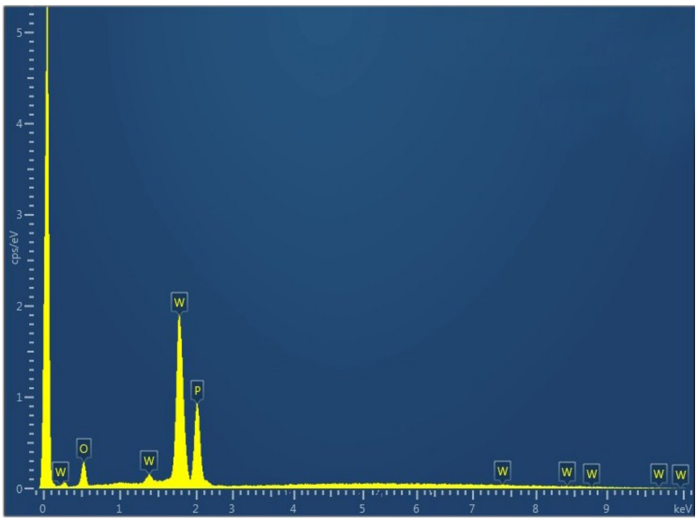

Fig. S5 EDX spectrum of the WP_2 NWs/CC.

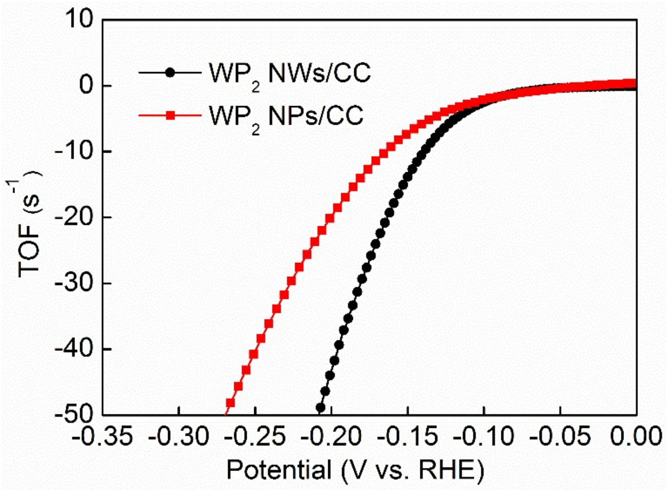

Fig. S6 Turnover frequencies (TOF) for the WP_2 NWs/CC and WP_2 NPs/CC.

The number of active sites (n) was examined via cyclic voltammograms in phosphate buffer (pH = 7) at a scan rate of 50 mV s^{-1} between -0.2V and +0.6V vs. RHE and n (mol) could be determined with the following equation:

$$n = Q / 2F$$

Where Q (C) is the voltammetric charge, F is Faraday constant (96480 C mol^{-1}). For WP_2 NWs/CC, Q is 2.68×10^{-3} C, n is 1.39×10^{-8} mol. For WP_2 NPs/CC, Q is 4.98×10^{-4} C, n is 2.58×10^{-9} mol. TOF (s^{-1}) could be calculated with the following equation:

$$TOF = I / 2nF$$

Where I (A) was the current of the polarization curve obtained by LSV measurements.

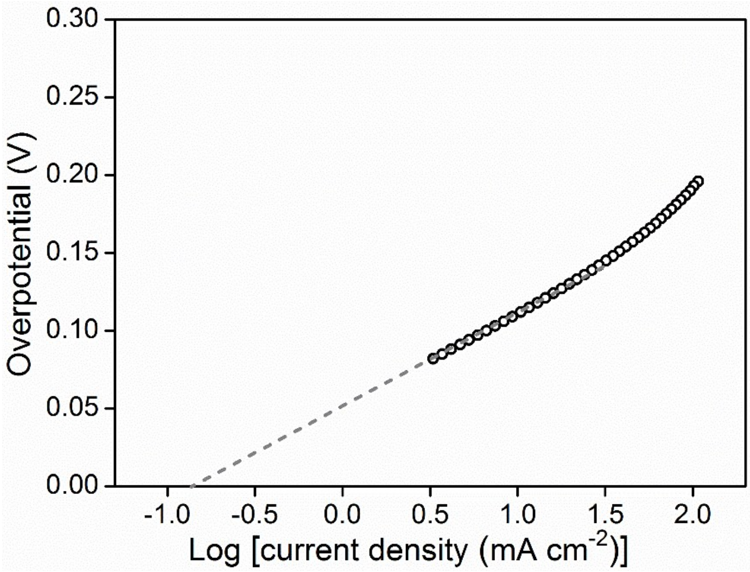

Fig. S7 Calculated exchange current density for the WP_2 NWs/CC in 0.5 M H_2SO_4 by applying extrapolation method to the Tafel plot.

Table S1. Comparison of HER performance of in acidic media of WP_2 NWs/CC with other non-noble metal electrocatalsts (NWs: nanowires, NRs: nanorods, NSs: nanosheets, NPs: nanoparticles and SPs: submicron particles)

Catalyst	Current Density (mA cm^{-2})	Corresponding overpotential (mV)	Reference
WP_2 NWs/CC	10	109	*This work*
W_2C	10	~140	*J. Mater. Chem. A, 2016, 4, 8204-8210*
WC	10	264	*Int. J. Hydrogen Energy, doi:10.1016/j.ijhydene.2016.06.063*
WN NRs/CC	10	198	*Electrochim. Acta., 2015, 154, 345-351*
WS_2	10	310	*Chem. Commun., 2015, 51, 8334-8337*
$WO_{2.9}$	10	70	*Nat. Commun., 2015, 6, 8064*
WO_2-carbon NWs	10	58	*J. Am. Chem. Soc., 2015, 137, 6983-6986*
α-WP_2 NRs	10	~200	*Energy Environ. Sci., 2016, 9, 1468-1475*
α-WP_2 SPs	10	161	*ACS Catal., 2015, 5, 145-149*
β-WP_2 NRs	10	148	*J. Power Sources, 2015, 278, 540-545*
WP NRs/CC	10	130	*ACS Appl. Mater. Interfaces, 2014, 6, 21874-21879*
Amorphous WP NPs	10	120	*Chem. Mater., 2014, 26, 4826-4831*
MoP_2 NPs/Mo	10	143	*Nanoscale, 2016, 8, 8500-8504*
MoP NSs/CF	10	200	*Appl. Catal. B: Environ., 2015, 164, 144-150*
MoP/NC	10	~130	*Electrochim. Acta., 2016, 199, 99-107*
MoP-CA2	10	125	*Adv. Mater., 2014, 26, 5702-5707*
FeP_2/C	10	＞500	*J. Mater. Chem. A, 2015, 3, 499-503*
FeP_2 NWs	10	61	*Chem. Commun., 2016, 52, 2819-2822*
FeP NSs	10	＞200	*Chem. Commun., 2013, 49, 6656-6658*
Cu_3P NW/CF	10	143	*Angew. Chem. Int. Ed., 2014, 53, 9577-9581*
CoP NPs	10	~150	*Electrochim. Acta., 2016, 199, 99-107*
CoP NWs/CC	10	67	*J. Am. Chem. Soc., 2014, 136,7587-7590*
CoP/CNT	10	122	*Angew. Chem. Int. Ed., 2014, 53, 3710-6714*
NiP_2 NSs/CC	10	75	*Nanoscale, 2014, 6, 13440-13445*
Ni_2P hollow NPs	10	116	*J. Am. Chem. Soc., 2013, 135, 9267-9270*
$Ni_{12}P_5$/NC	10	~230	*Electrochim. Acta., 2016, 199, 99-107*

Table S2. Comparison of exchange current density of WP_2 NWs/CC with other non-noble metal electrocatalsts (NWs: nanowires, NRs: nanorods, NSs: nanosheets, NPs: nanoparticles and SPs: submicron particles)

Catalyst	Exchange current density (mA cm^{-2})	Reference
WP_2 NWs/CC	0.13	*This work*
MoS_2/FTO	6.9×10^{-4}	*Nat. Mater., 2012, 11, 963-969*
defect-rich MoS_2	8.9×10^{-3}	*Adv. Mater., 2013, 25, 5807-5813*
MoO_3-MoS_2/FTO	8.2×10^{-5}	*Nano Lett., 2011, 11, 4168-4175*
bulk Mo_2C	1.3×10^{-3}	*Angew. Chem. Int. Ed., 2012, 51, 12703-12706*
bulk MoB	1.4×10^{-3}	*Angew. Chem. Int. Ed., 2012, 51, 12703-12706*
Co-NRCNTs	0.01	*Angew. Chem. Int. Ed., 2014, 126, 4372-4376*
WS_2 NSs	0.02	*Nat. Mater., 2013, 12, 850-855*
$CoSe_2$ NP/CP	$(4.9\pm1.4)\times10^{-3}$	*J. Am. Chem. Soc., 2014, 136, 4897-4900*
Ni_2P hollow NPs	0.033	*J. Am. Chem. Soc., 2013, 135, 9267-9270*
NiP_2 NS/CC	0.26	*Nanoscale, 2014, 6, 13440-13445*
Cu_3P NW/CF	0.18	*Angew. Chem. Int. Ed., 2014, 53, 9577-9581*
FeP_2/C	1.75×10^{-3}	*J. Mater. Chem. A, 2015, 3, 499-503*
FeP_2 NWs	0.55	*Chem. Commun., 2016, 52, 2819-2822*
CoP NWs/CC	0.288	*J. Am. Chem. Soc., 2014, 136,7587-7590*
CoP/CNT	0.13	*Angew. Chem. Int. Ed., 2014, 53, 3710-6714*
WP NRs/CC	0.29	*ACS Appl. Mater. Interfaces, 2014, 6, 21874-21879*
α-WP_2 SPs	0.017	*ACS Catal., 2015, 5, 145-149*
β-WP_2 NRs	0.013	*J. Power Sources, 2015, 278, 540-545*
bulk MoP	0.034	*Energy Environ. Sci., 2014, 7, 2624-2629*
MoP-CA2	0.086	*Adv. Mater., 2014, 26, 5702-5707*
MoP_2 NS/CC	0.83	*J. Mater. Chem. A, 2016, 4, 7169–7173*
MoP_2 NPs/Mo	0.06	*Nanoscale, 2016, 8, 8500-8504*

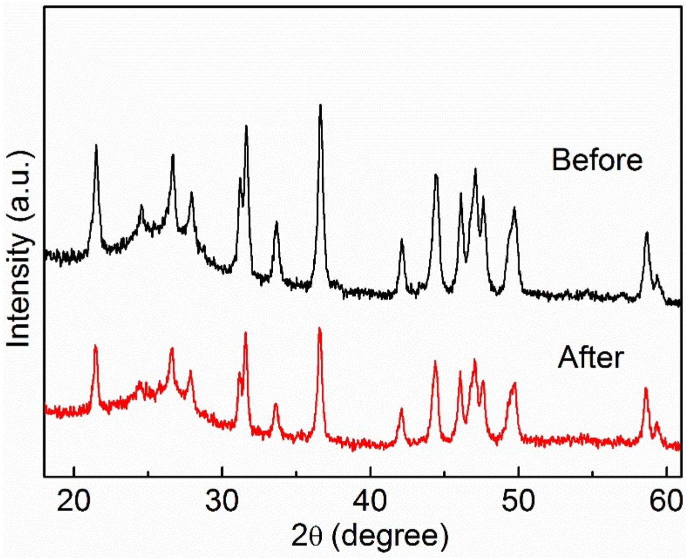

Fig. S8 XRD patterns before and after reaction for the WP_2 NWs/CC.

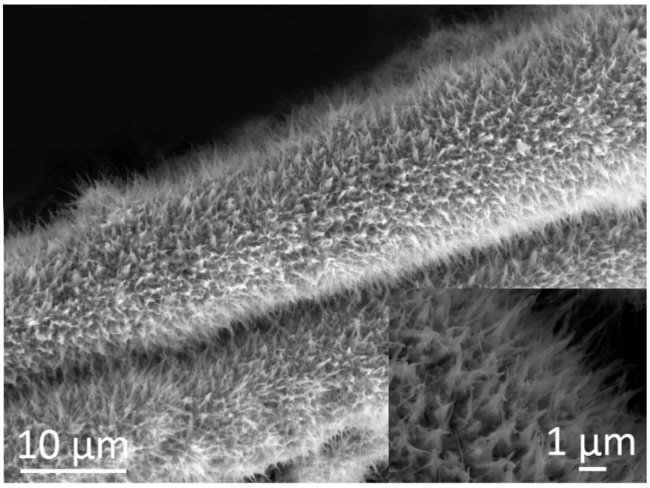

Fig. S9 SEM images of the WP_2 NWs/CC after 1000 CV sweeps.

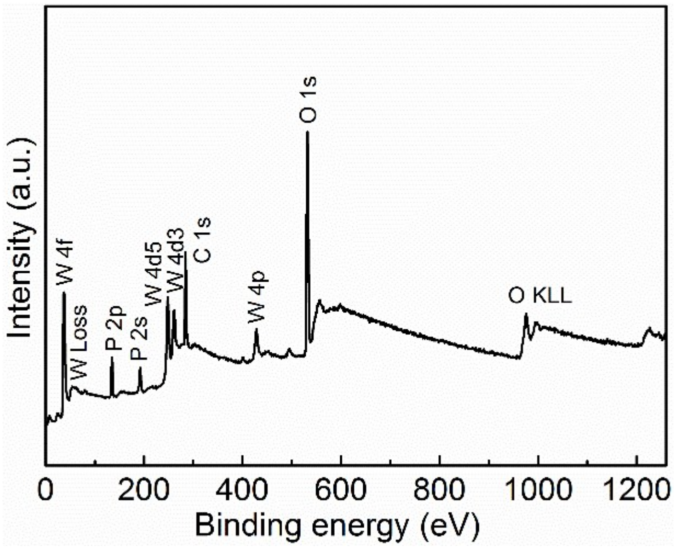

Fig. S10 XPS survey spectra for the WP_2 NWs/CC.

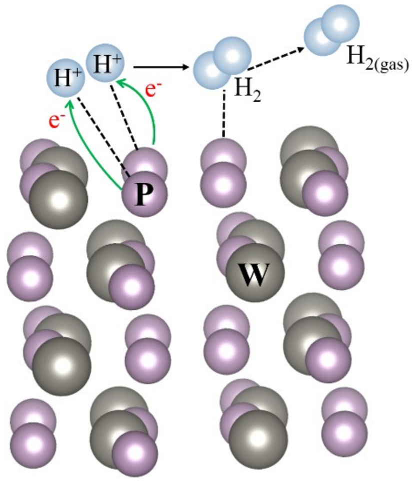

Fig. S11 Schematic reaction pathway of hydrogen evolution on phosphorus atom of WP_2 in acid environment.

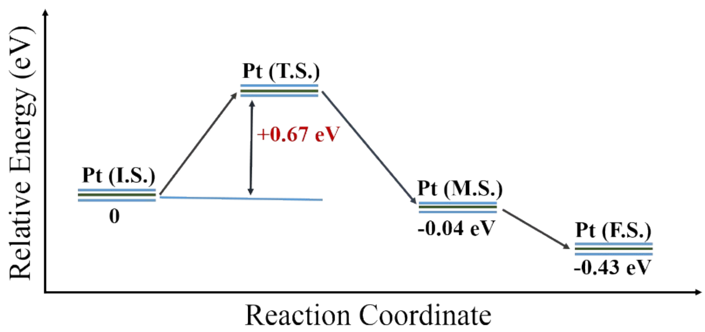

Fig. S12 Kinetic energy barrier profiles of hydrogen evolution reaction on Pt catalysts.

Table S3. Comparison of energy barrier for transition state of hydrogen atom adsorption and bond length for the WP_2 catalyst with the other catalysts.

Catalyst	Energy barrier for transition state of hydrogen atom adsorption (eV)	Bond length (Å)	Reference
WP_2	0.75	1.43	*This work*
Pt	0.67	-	
Pt	0.67	-	*J. Power Sources, 2016, 328, 551-557*
MoP_2	0.93	1.44	
MoP	1.05	1.42	
Pt	0.69	-	*J. Am. Chem. Soc., 2015, 137, 1587-1592.*
FeS_2/CNT	1.62	1.361	
Co-FeS_2/CNT	1.23	1.365	
MoS_2/$CoSe_2$	1.13	-	*Nat. Commun., DOI: 10.1038/ncomms6982*

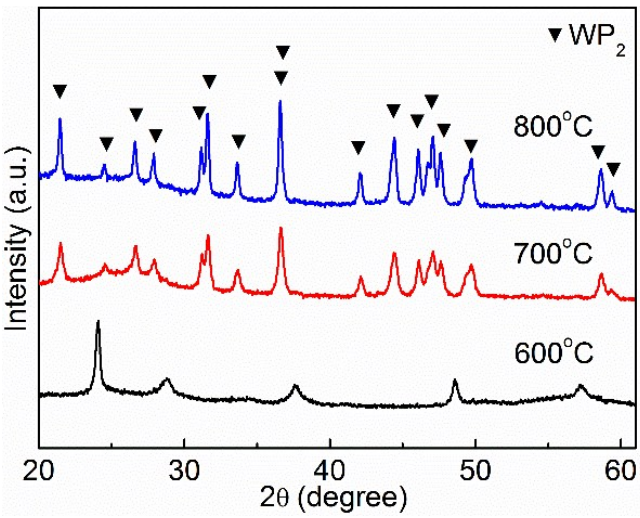

Fig. S13 XRD patterns for the WP_2 NWs/CC obtained at 600, 700 and 800 °, respectively.

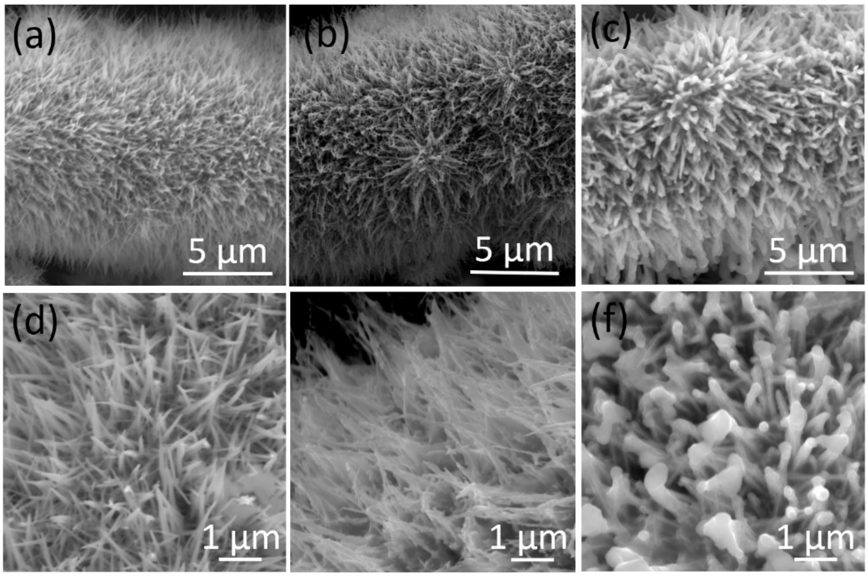

Fig. S14 SEM images for the WP_2 NWs/CC obtained at (a, d) 600, (b, e) 700 and (c, f) 800 ^{o}C, respectively.

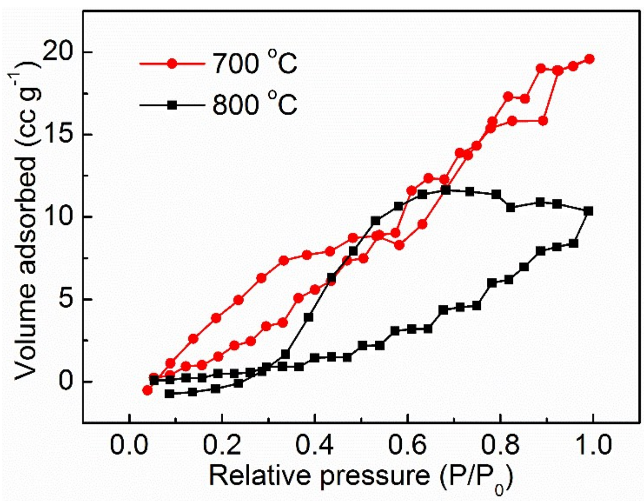

Fig. S15 Nitrogen adsorption /desorption plots for the WP_2 NWs/CC obtained at 700 and 800 ^{o}C, respectively.

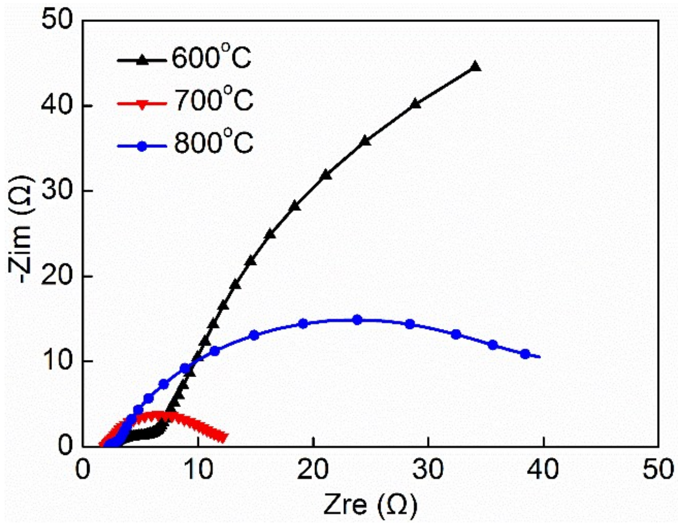

Fig. S16 Niquist plots for the WP_2 NWs/CC obtained at 600, 700 and 800 ^oC, respectively.