

## Self-Supported Tungsten/Tungsten Dioxide Nanowires Array as an Efficient Electrocatalyst in Hydrogen Evolution Reaction

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### Electronic Supplementary Information

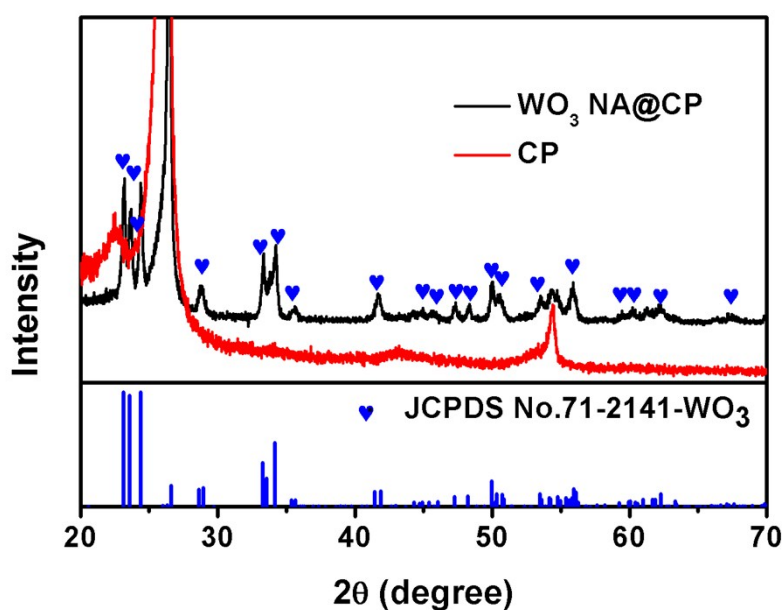
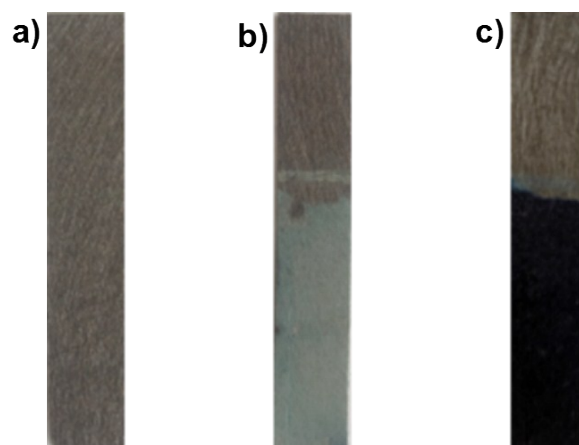
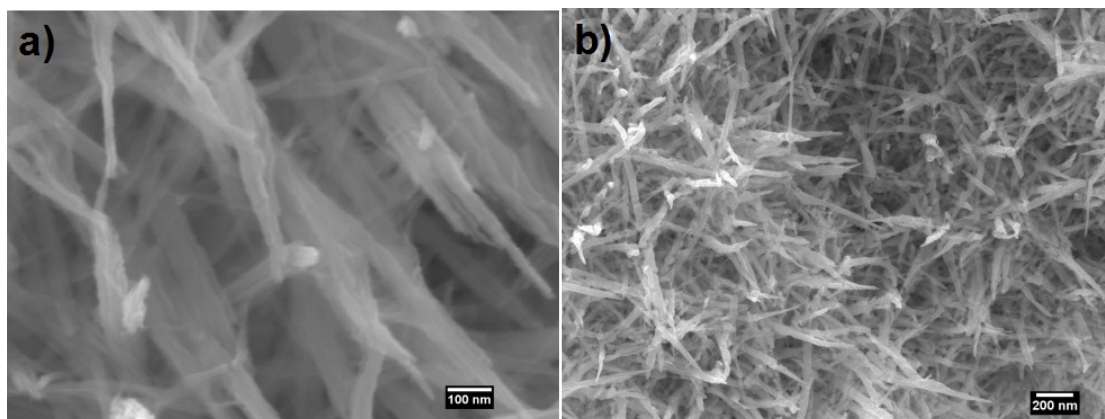


Fig. S1 XRD pattern of WO<sub>3</sub> NA@CP.



**Fig. S2** Optical photograph of (a) pristine CP, (b)  $\text{WO}_3$  NA@CP, (C)  $\text{WO}_2/\text{W}$  CSNA@CP



**Fig. S3** The SEM image of precursor (a) and  $\text{WO}_3$  NA@CP.

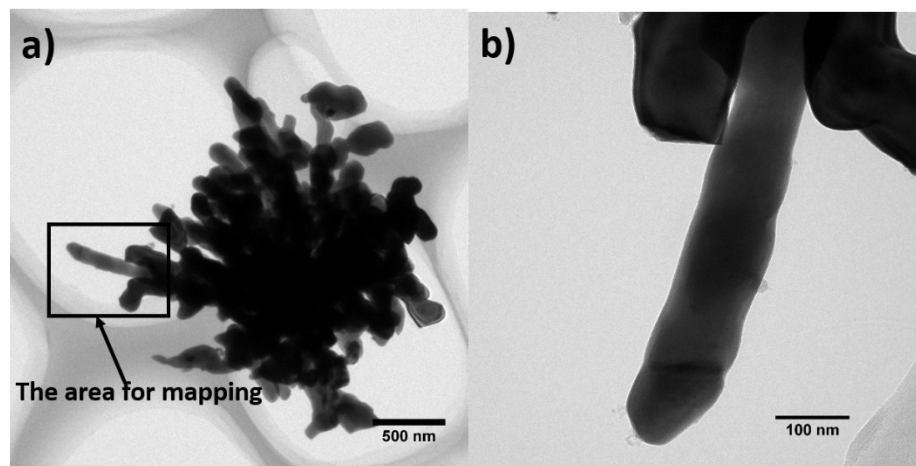


Fig. S4 a) and b) are the TEM images of the W/WO<sub>2</sub> nanorod.

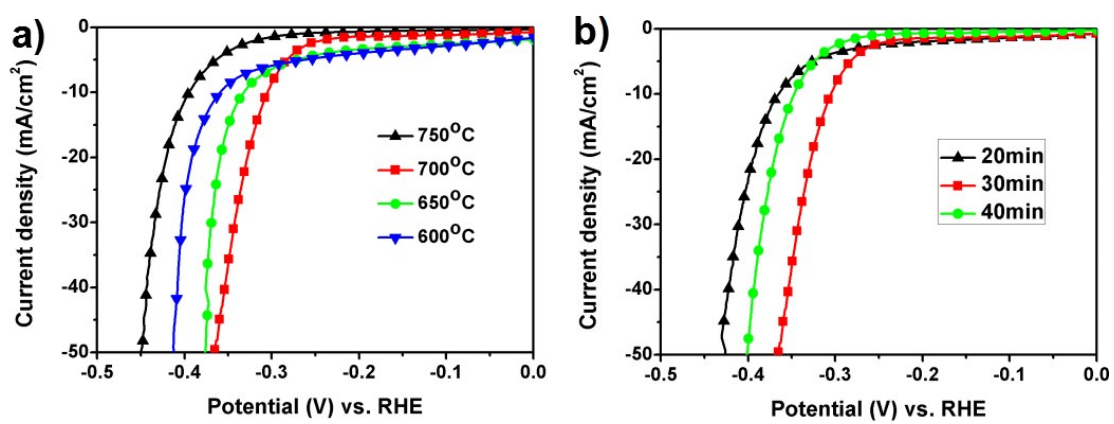


Fig. S5 (a) and (b) show different conditions of annealing, different temperatures and different annealing times are shown for comparison in acidic solution.

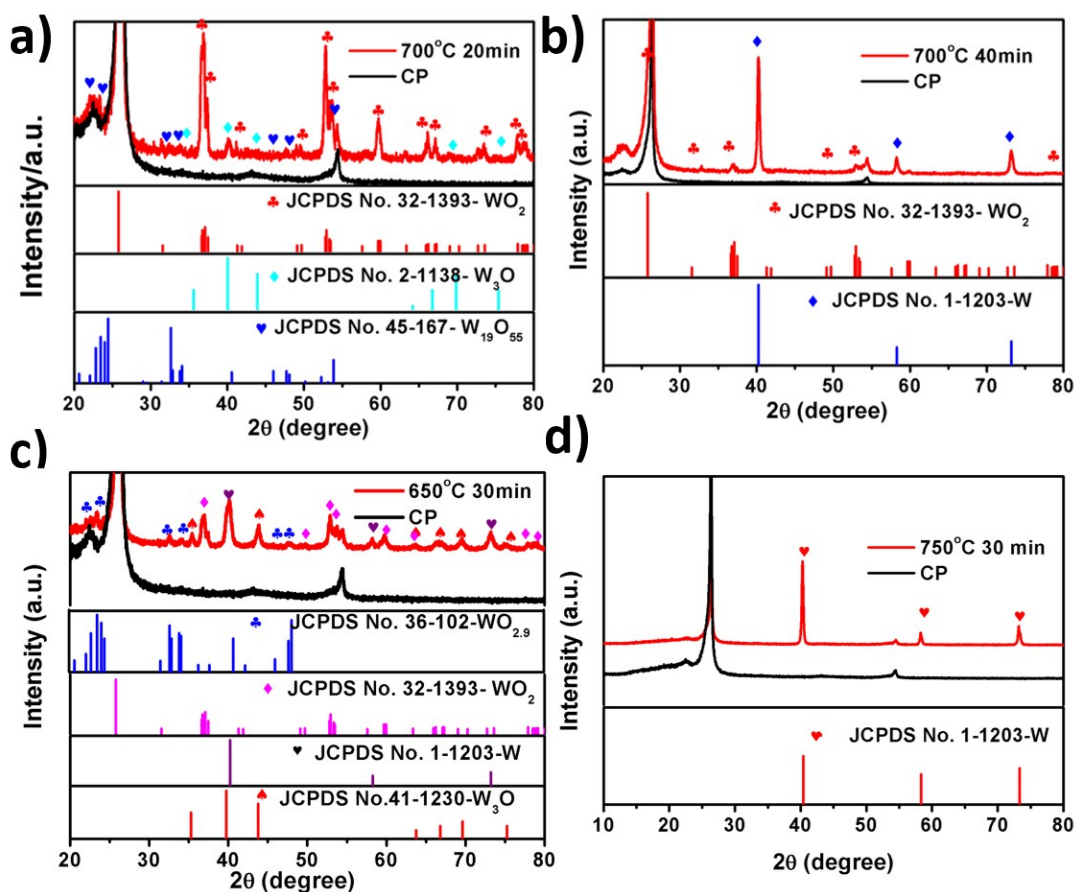


Fig. S6 The XRD patterns of different conditions of annealing.

Table S1 Summary of HER performance of representative tungsten oxides catalysts.

Catalyst	Substrate	Current density (mA/cm <sup>2</sup> )	Overpotential (mV)	Tafel slope (mV/dec)	Electrolyte
WO <sub>3</sub> /CNT <sup>1</sup>	GCE	3.8	426	104	0.1M H <sub>2</sub> SO <sub>4</sub>
WO <sub>3</sub> .H <sub>2</sub> O and WO <sub>3</sub> Nanoplates <sup>2</sup>	GCE	7.5	318	97	1M H <sub>2</sub> SO <sub>4</sub>
Ta-doped WO <sub>3</sub> <sup>3</sup>	GCE	10.72	528	65	1M H <sub>2</sub> SO <sub>4</sub>
WO <sub>3</sub> nanoparticles <sup>4</sup>	GCE	20	406		1M H <sub>2</sub> SO <sub>4</sub>
WO <sub>3</sub> Nanorods <sup>5</sup>	GCE	20	396	188	1M H <sub>2</sub> SO <sub>4</sub>
WO <sub>3</sub> /C nanoparticles <sup>6</sup>	GCE	0.7	3	29	0.5M H <sub>2</sub> SO <sub>4</sub>

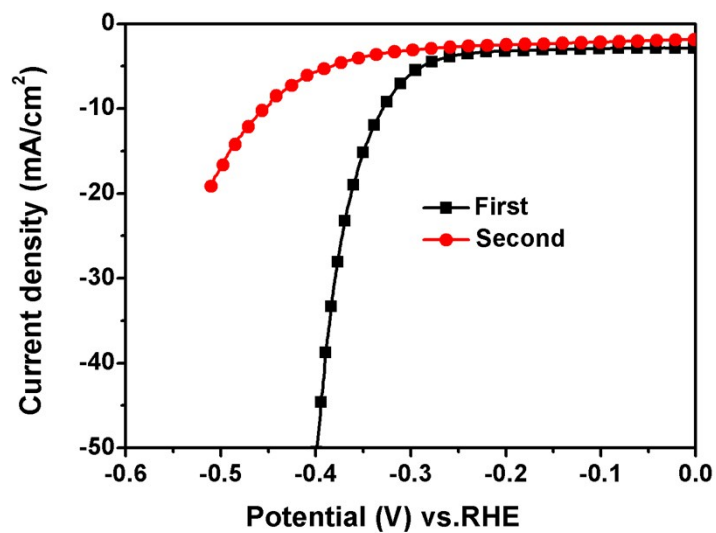


Fig. S7 Polarization curves of the  $\text{WO}_2/\text{W NA@CP}$  in basic solution.

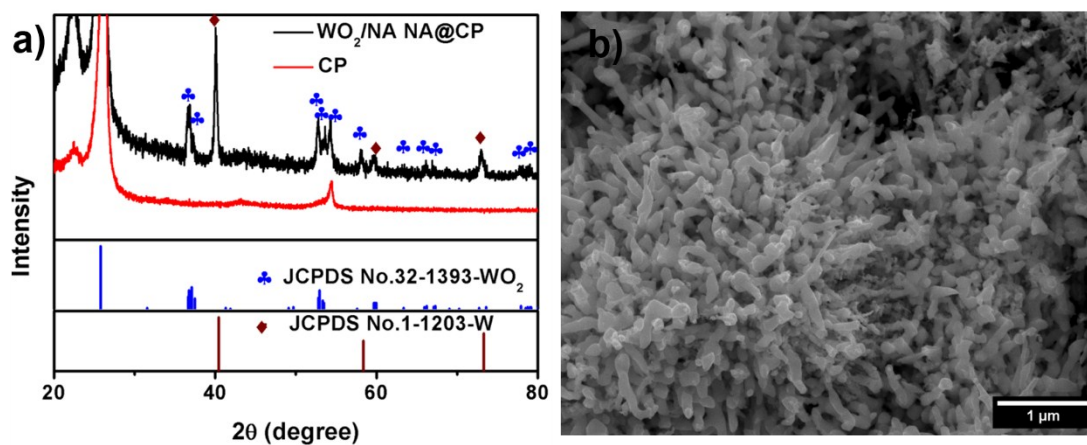
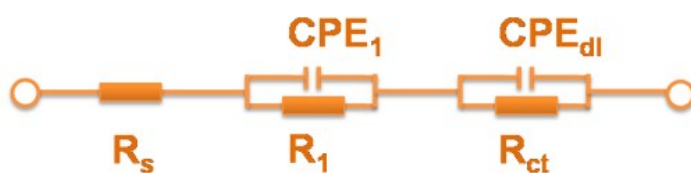


Fig. S8 (a) XRD pattern of  $\text{WO}_2/\text{W NA@CP}$  after it. (b) SEM image of  $\text{WO}_2/\text{W NA@CP}$  after it



**Fig. S9** Equivalent circuit used to fit the EIS data.  $R_s$  is the overall series resistance,  $CPE_1$  and  $R_1$  are the constant phase element and resistance describing electron transport at substrate/catalyst interface, respectively,  $CPE_{dl}$  is the constant phase element of the catalyst/electrolyte interface, and  $R_{ct}$  is the charge transfer resistance at catalyst/electrolyte interface.

**Table S2.** The fitting results of EIS spectra

Sample	$R_s(\Omega \text{ cm}^2)$	$Q_{ct}$ ( $F \text{ cm}^{-2} \text{ S}^{-n}$ $^1/\text{cm}^2$ )	$N_{ct}$	$R_{ct}(\Omega$ $.\text{cm}^2)$	$Q_1$ ( $F \text{ cm}^{-2} \text{ S}^{-n}$ $^1/\text{cm}^2$ )	$N_1$	$R_1(\Omega$ $\text{cm}^2)$
$\text{WO}_3 \text{ NA@CP}$	1.45	0.0637	0.651	149.4	$7.539 \times 10^{-6}$	0.804	0.80
$\text{WO}_2/\text{W}$ $\text{CSNA@CP}$	0.92	0.0647	0.823	14.69	$4.09 \times 10^{-5}$	0.947	1.91

## Reference

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