

## **Electronic supplementary information (ESI)**

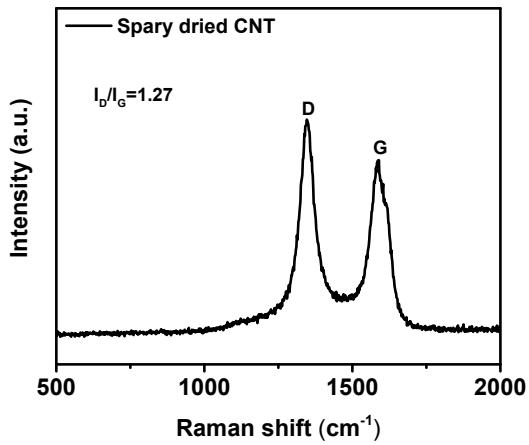
### **W<sub>2</sub>C nanodots decorated CNT networks as highly efficient and stable electrocatalyst for hydrogen evolution in acidic and alkaline media†**

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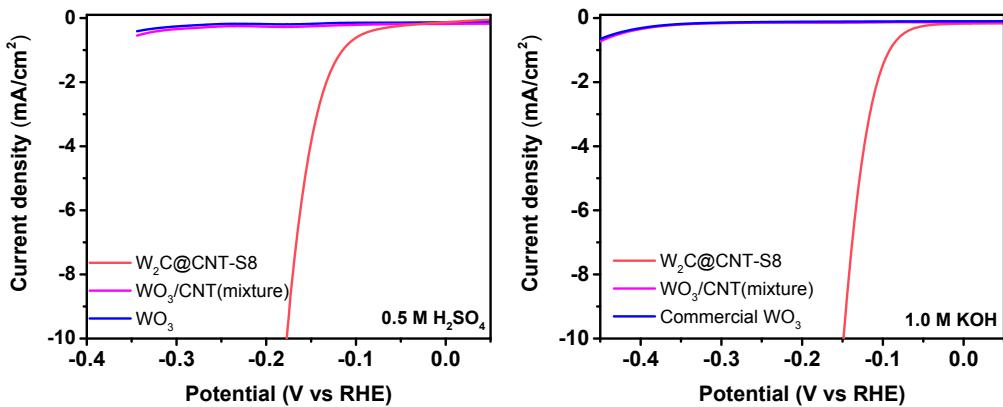
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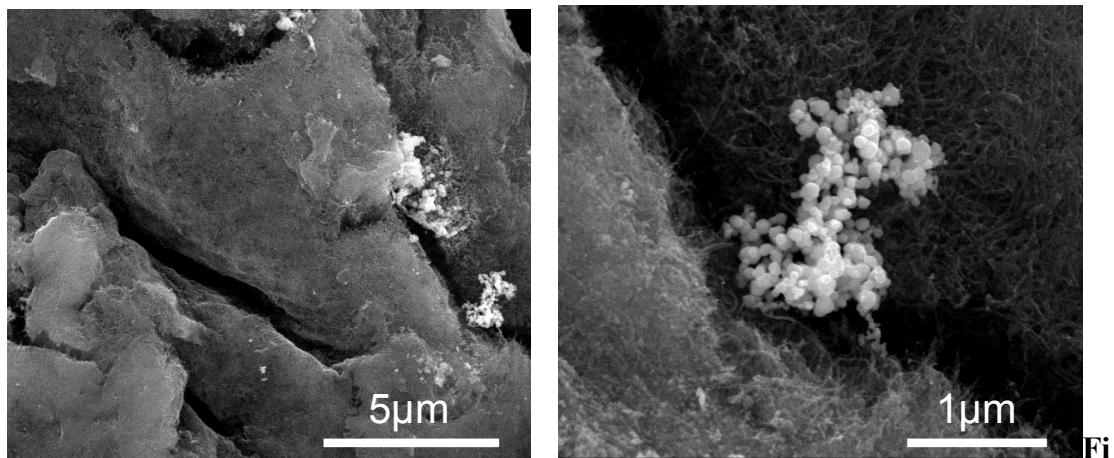


**Fig. S1** Raman spectra of spray-dried CNT.

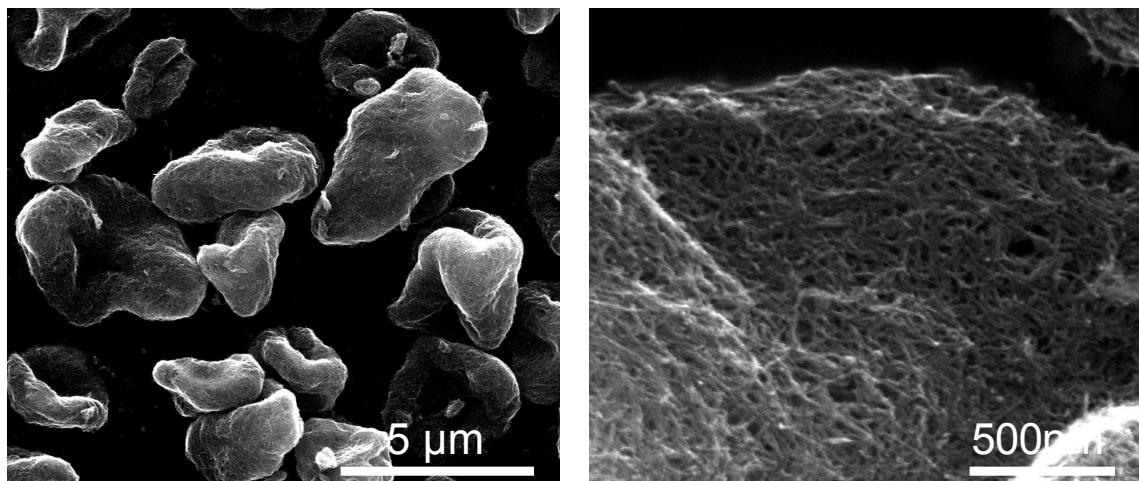


**Fig. S2** Polarization curves of the  $\text{W}_2\text{C}@\text{CNT-S8}$ , commercial  $\text{WO}_3/\text{CNT}$  mixture and commercial  $\text{WO}_3$  in 0.5 M  $\text{H}_2\text{SO}_4$  and 1.0 M KOH.

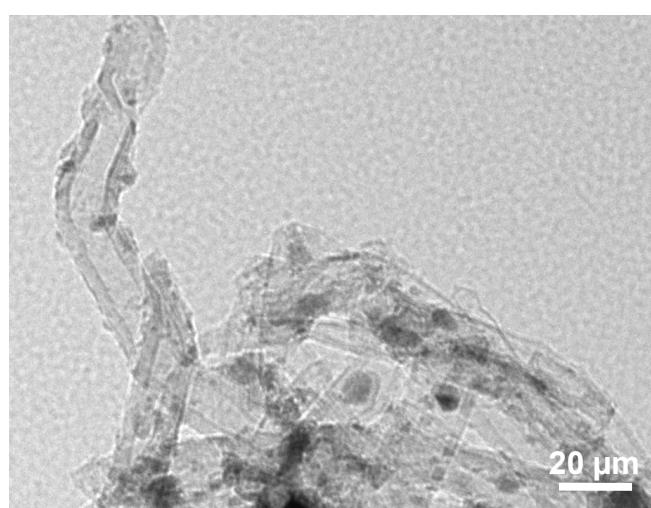
In order to further check the HER activity of  $\text{WO}_3$ , the HER performance in both acidic and alkaline media of commercial  $\text{WO}_3$  and commercial  $\text{WO}_3/\text{CNT}$  mixture has been performed, as shown in the Fig. S2. From Fig. S2, compared to  $\text{W}_2\text{C}@\text{CNT-S8}$ , the  $\text{WO}_3/\text{CNT}$  mixture and commercial  $\text{WO}_3$  show much worse HER catalytic activities.



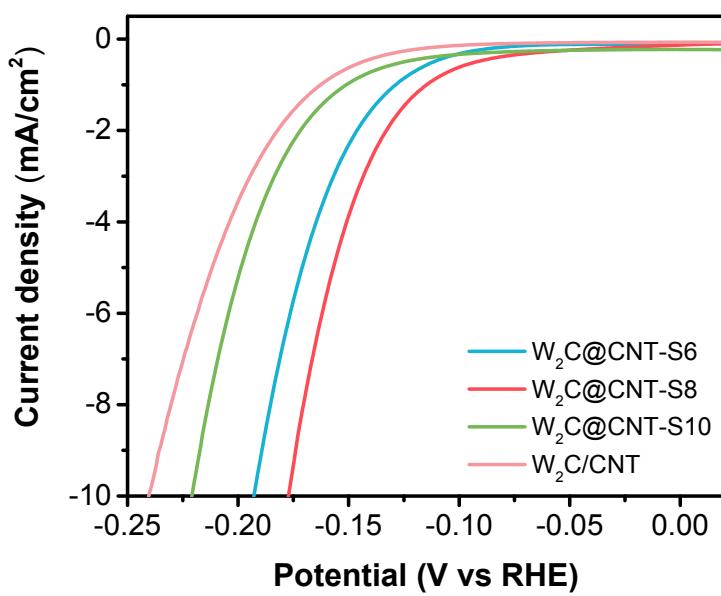
**g. S3** SEM images of the W<sub>2</sub>C/CNT.



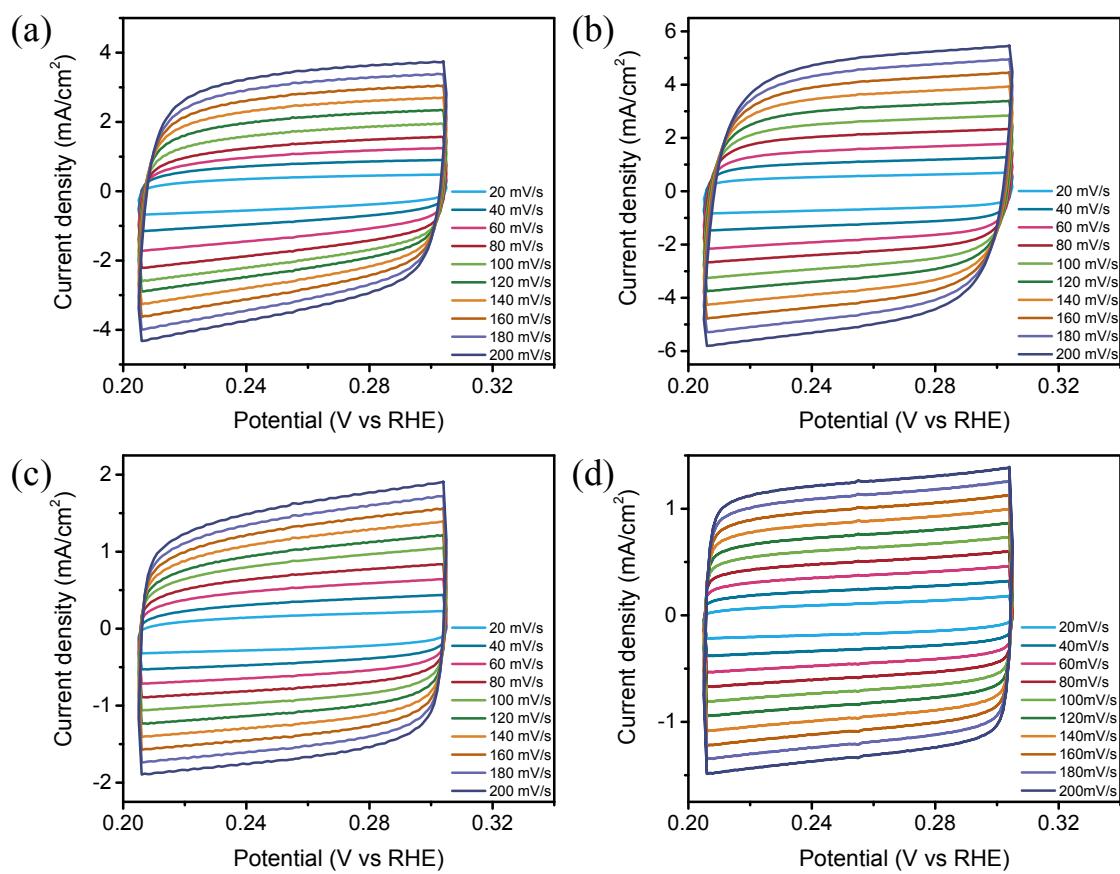
**Fig. S4** SEM images of the pure CNT networks.



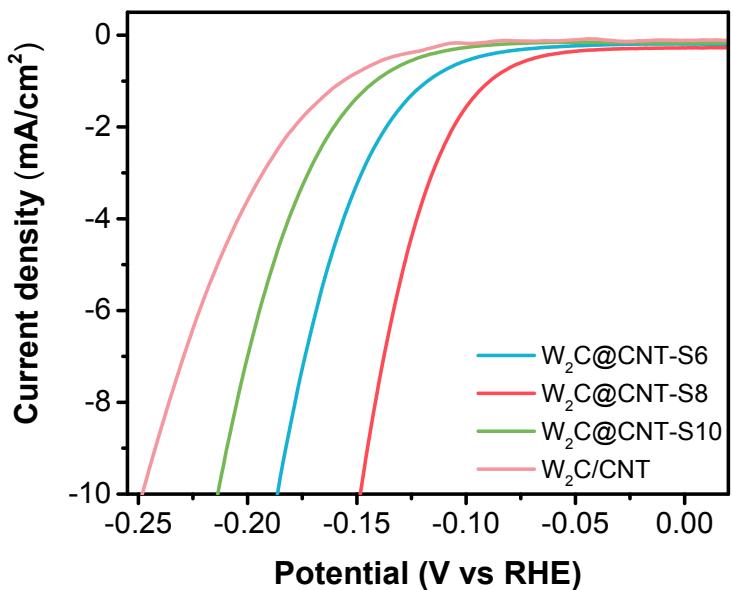
**Fig. S5** TEM image of W<sub>2</sub>C@CNT-S8.



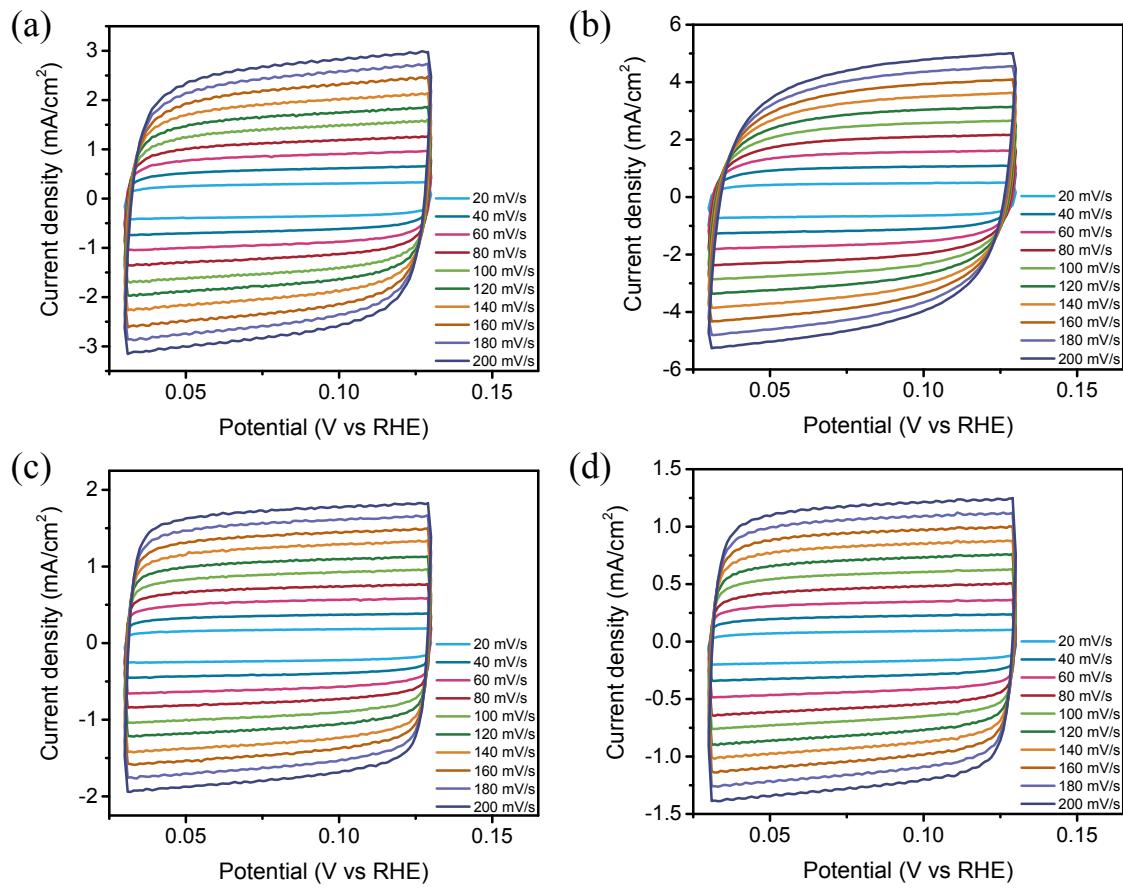
**Fig. S6** Polarization curves for  $\text{W}_2\text{C}/\text{CNT}$ ,  $\text{W}_2\text{C}@\text{CNT-S6}$ ,  $\text{W}_2\text{C}@\text{CNT-S8}$  and  $\text{W}_2\text{C}@\text{CNT-S10}$  in  $0.5 \text{ M H}_2\text{SO}_4$  with a scan rate of  $5 \text{ mV s}^{-1}$ .



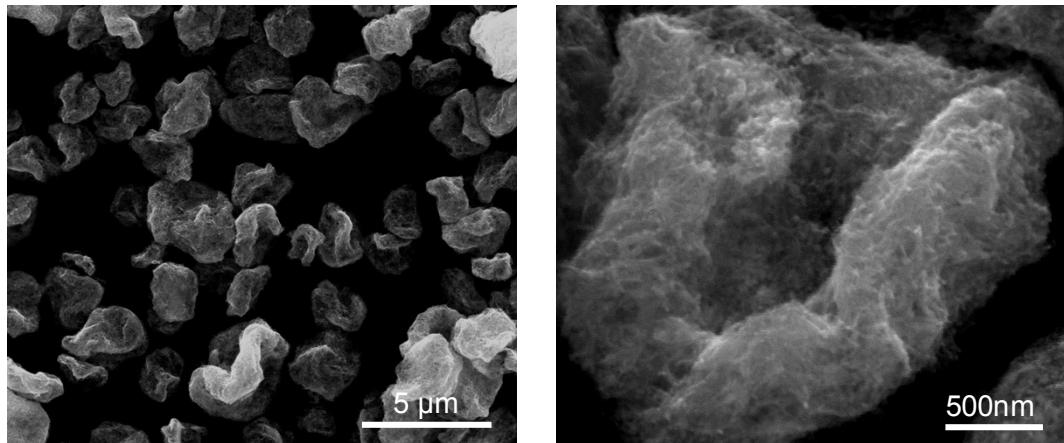
**Fig. S7** The cyclic voltammograms (CV) of W<sub>2</sub>C@CNT-S6 (a), W<sub>2</sub>C@CNT-S8 (b), W<sub>2</sub>C@CNT-S10 (c) and W<sub>2</sub>C/CNT (d) are measured at various scan rates range from 0.205-0.305 V (vs. RHE) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.



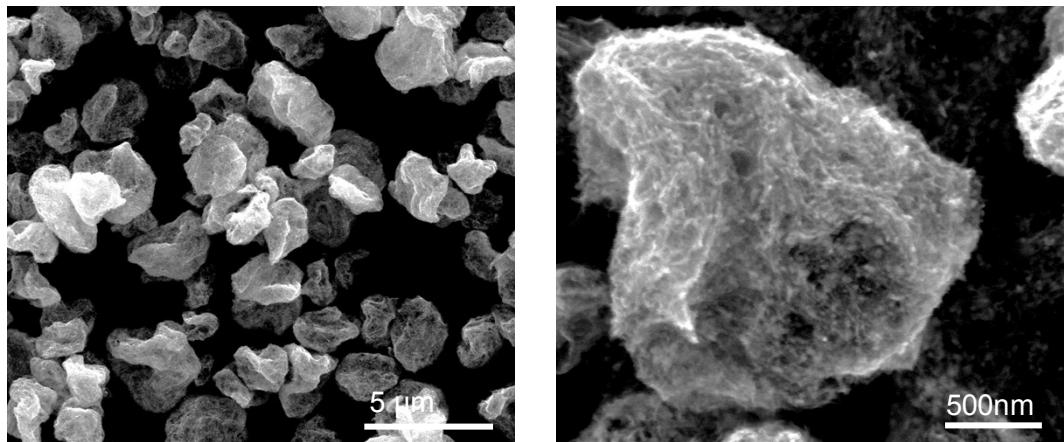
**Fig. S8** Polarization curves for  $\text{W}_2\text{C}/\text{CNT}$ -S6,  $\text{W}_2\text{C}/\text{CNT}$ -S8,  $\text{W}_2\text{C}/\text{CNT}$ -S10 and  $\text{W}_2\text{C}/\text{CNT}$  in 1 M KOH with a scan rate of 5 mV s<sup>-1</sup>.



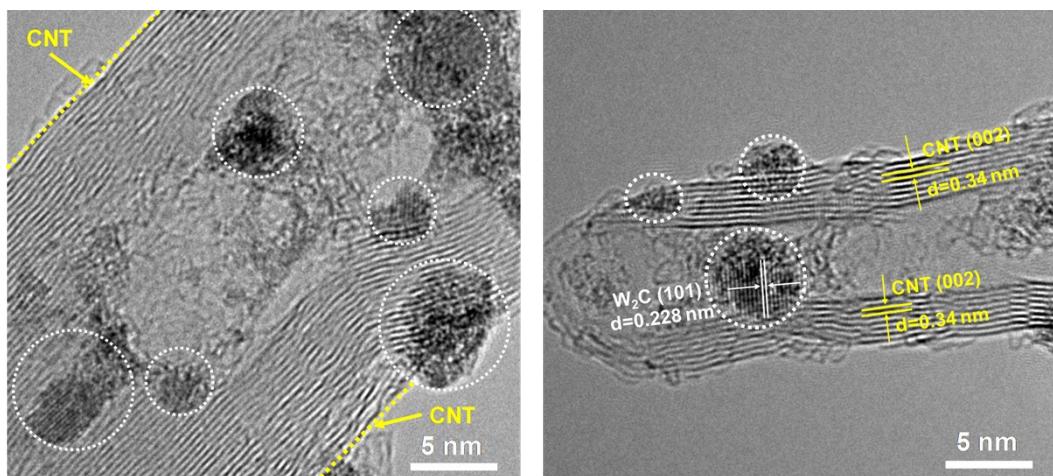
**Fig. S9** The cyclic voltammograms (CV) of W<sub>2</sub>C@CNT-S6 (a), W<sub>2</sub>C@CNT-S8 (b), W<sub>2</sub>C@CNT-S10 (c) and W<sub>2</sub>C/CNT (d) are measured at various scan rates range from 0.205-0.305 V (vs. RHE) in 1 M KOH solution.



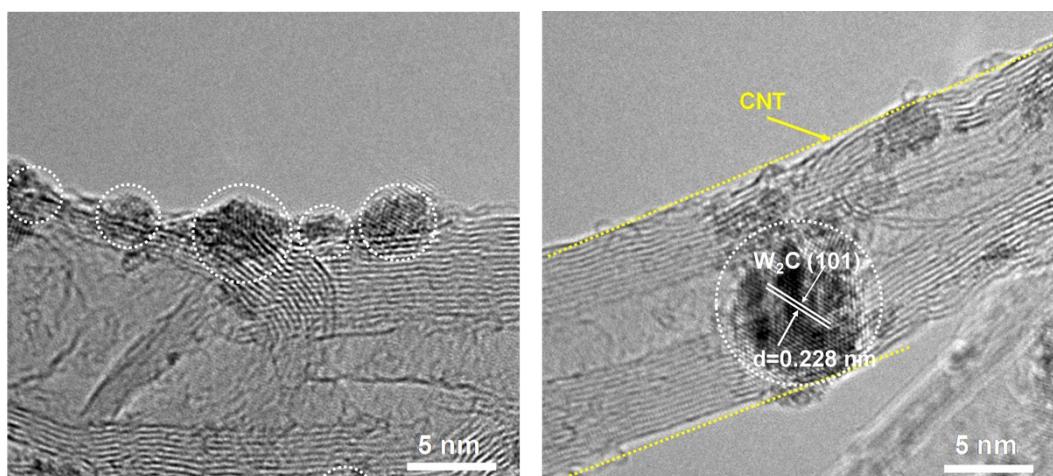
**Fig. S10** (a, b) SEM images of the W<sub>2</sub>C@CNTS8 after the HER stability test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Fig. S11 (a, b)** SEM images of the W<sub>2</sub>C@CNTS8 after the HER stability test in 1.0 M KOH.



**Fig. S12 (a, b)** TEM images of the W<sub>2</sub>C@CNTS8 after the HER stability test in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Fig. S13 (a, b)** TEM images of the W<sub>2</sub>C@CNTS8 after the HER stability test in 1.0 M KOH.

**Table S1.** Comparison of HER performance for W<sub>2</sub>C@CNT-S, W<sub>2</sub>C/CNT and other non-noble metal-based electrocatalysts.

Catalyst	Electrolyte	$\eta_{\text{onset}}$ (mV)	$\eta_{10}$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Reference
W <sub>2</sub> C@CNT-S6	0.5 M H <sub>2</sub> SO <sub>4</sub>	70	192	59.8	This work
	1 M KOH	60	186	60.7	
W <sub>2</sub> C@CNT-S8	0.5 M H <sub>2</sub> SO <sub>4</sub>	60	176	57.4	This work
	1 M KOH	40	148	56.2	
W <sub>2</sub> C@CNT-S10	0.5 M H <sub>2</sub> SO <sub>4</sub>	90	220	68.6	This work
	1 M KOH	80	213	63.8	
W <sub>2</sub> C/CNT	0.5 M H <sub>2</sub> SO <sub>4</sub>	110	240	72.3	1
	1 M KOH	100	248	88.6	
W <sub>2</sub> C/WC NPs	0.5 M H <sub>2</sub> SO <sub>4</sub>	N/A	310	108	1
W NPs	0.5 M H <sub>2</sub> SO <sub>4</sub>	N/A	295	156	2
W <sub>2</sub> C@WC <sub>1-x</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	N/A	240	86	3
W <sub>2</sub> C-WN/GnP	0.5 M H <sub>2</sub> SO <sub>4</sub>	N/A	120	64.7	4
WC-CNT	0.5 M H <sub>2</sub> SO <sub>4</sub>	15	145	72	5
	1 M KOH	16	137	106	
W@WC	0.5 M H <sub>2</sub> SO <sub>4</sub>	N/A	264	85	6
WC nanowall	0.5 M H <sub>2</sub> SO <sub>4</sub>	52	160	67	7
C-WP/W	0.5 M H <sub>2</sub> SO <sub>4</sub>	N/A	109	79.8	8
W <sub>x</sub> C@WS <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	70.3	146	61	9
WS <sub>2</sub> /WO <sub>2</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	90	160	63	10
WSe <sub>2</sub> /CNT	0.5 M H <sub>2</sub> SO <sub>4</sub>	~120	230	59.7	11
P-WN/rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	46	85	54	12
CoWS <sub>x</sub>	0.5 M H <sub>2</sub> SO <sub>4</sub>	95	N/A	78	13
WC	0.5 M H <sub>2</sub> SO <sub>4</sub>	~120	~270	69	14
WS <sub>2</sub> /rGO	0.5 M H <sub>2</sub> SO <sub>4</sub>	150	300	58	15
CoW/CN	1 M KOH	31	98	125	16
WS <sub>2</sub> /WC <sub>2</sub> @NSPC	1 M KOH	80	205	72	17
p-WC <sub>x</sub> NWs	1 M KOH	56	122	56	18
MoSe <sub>2</sub> -CoSe <sub>2</sub>	1 M KOH	127	237	79	19
NiS <sub>2</sub> /MoS <sub>2</sub>	1 M KOH	69	204	65	19

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