

## Electronic Supplementary Information

### **Hierarchical Oxygen Vacancies-Rich WO<sub>3</sub> with “Nanowire-Array-on-Nanosheet-Array” Structure for Highly Efficient Oxygen Evolution Reaction**

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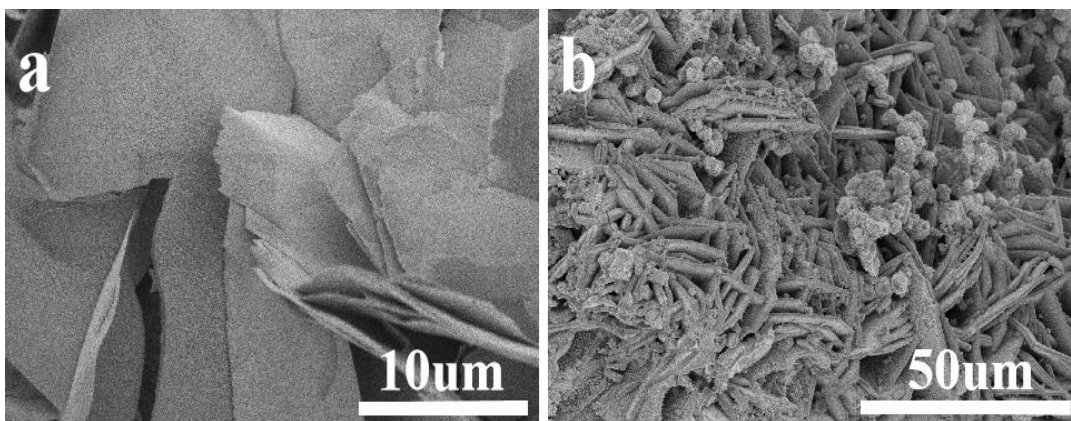


Fig. S1 The SEM image of  $\text{WO}_3$  NSs (a) and disordered  $\text{WO}_3$ (b)

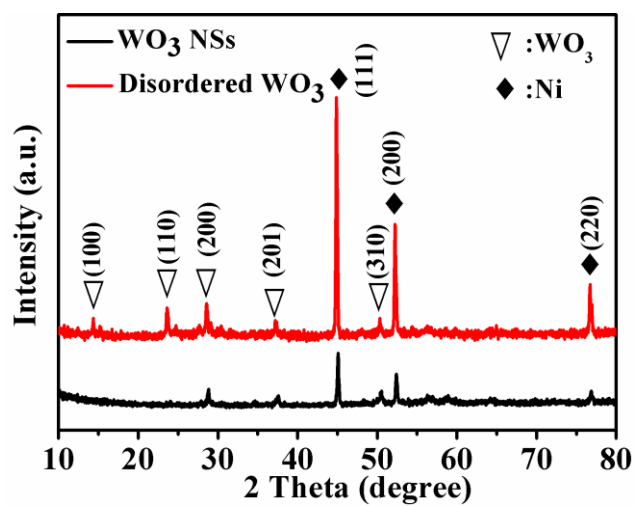


Fig. S2 The XRD patterns of  $\text{WO}_3$  NSs and disordered  $\text{WO}_3$

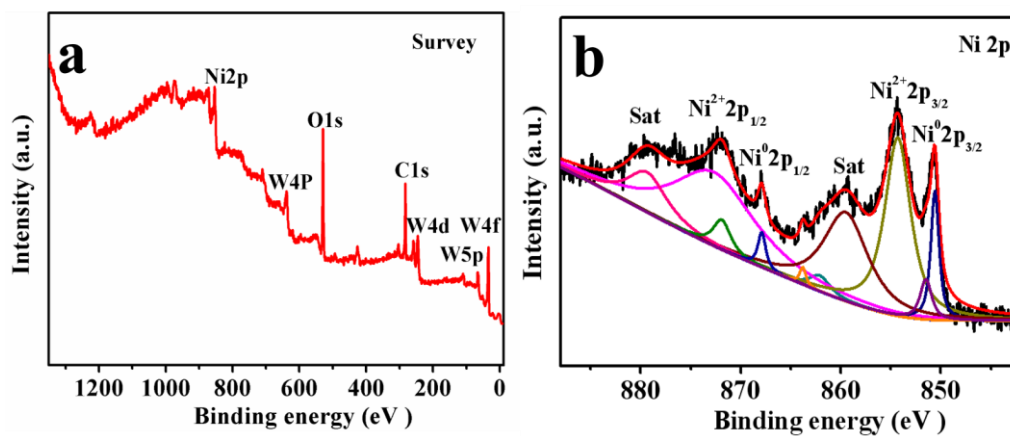


Fig. S3 The XPS survey spectra (a) and Ni 2p XPS spectra (b) of  $\text{WO}_3$  NWA-NSA catalyst

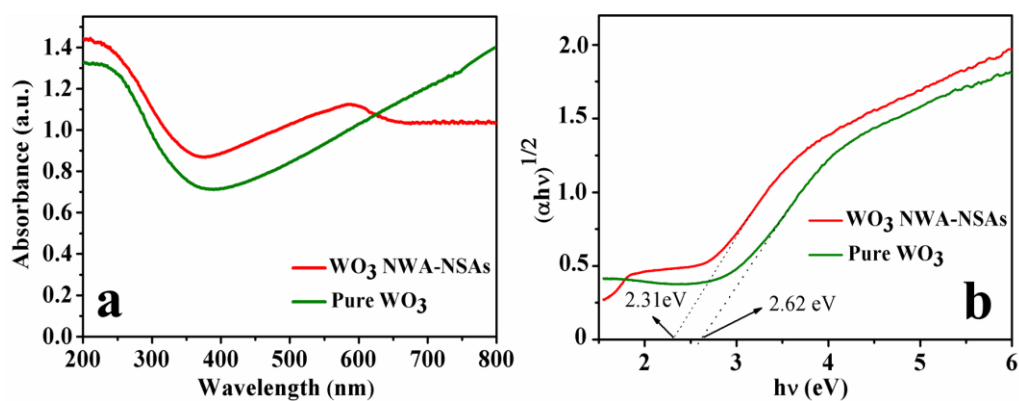


Fig. S4 (a) UV-vis spectra and (b)  $\alpha h\nu^{1/2}$  versus photon-energy plot of WO<sub>3</sub> NWA-NSA catalyst and pure WO<sub>3</sub>

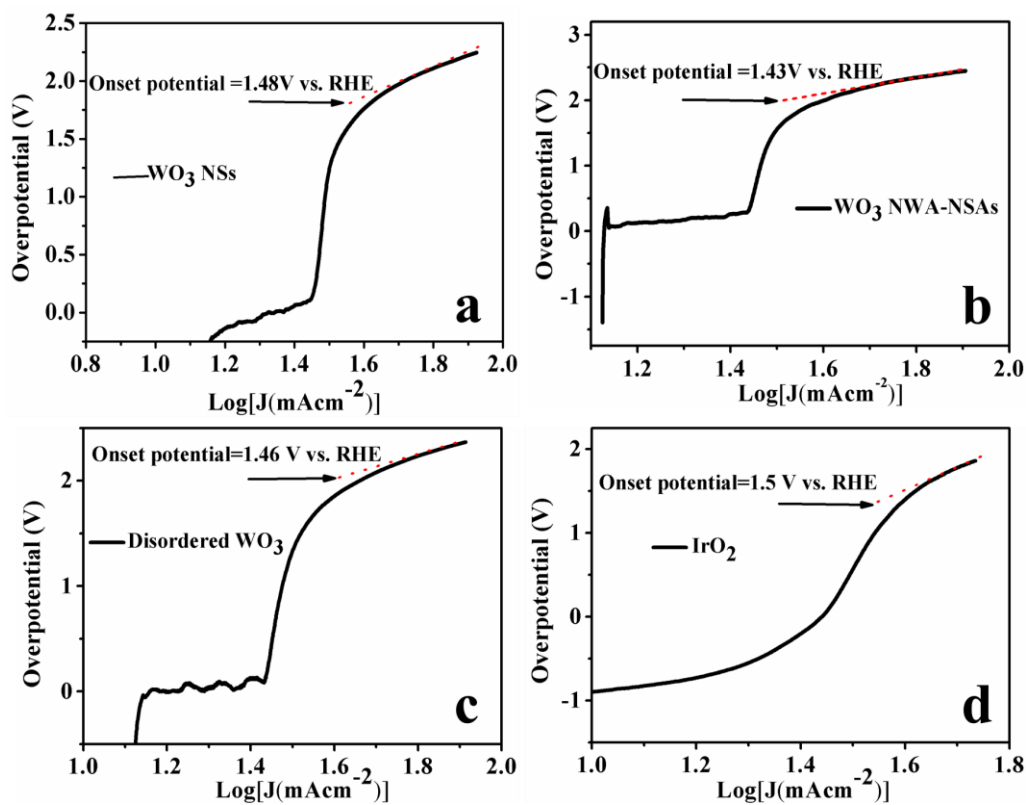


Fig. S5 The plots of overpotential vs.  $\log[J/(mA\ cm^{-2})]$  for WO<sub>3</sub> NSs, WO<sub>3</sub> NWA-NSAs, disordered WO<sub>3</sub> and IrO<sub>2</sub>, respectively

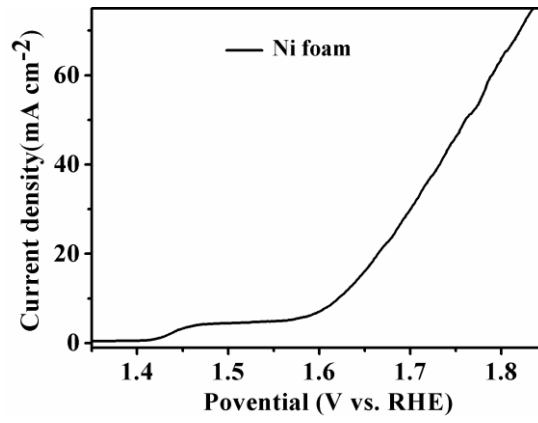


Fig. S6 LSV polarization curve of Ni foam treated under same condition for 6 h without the addition of ATT.

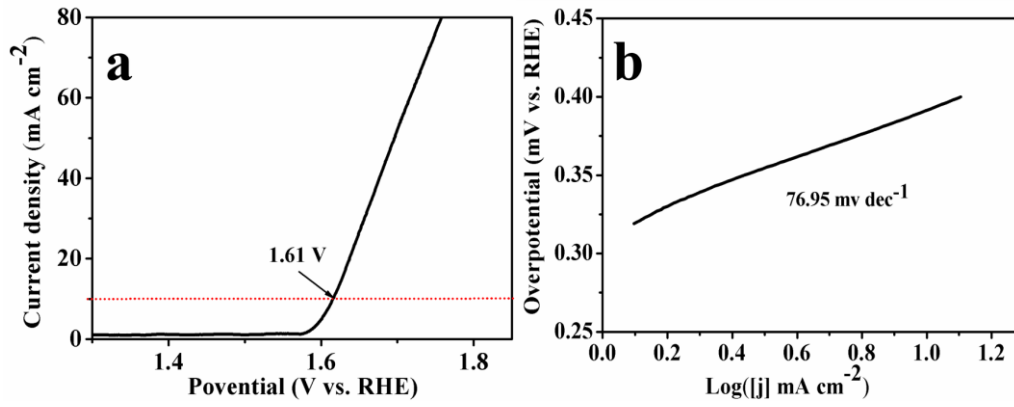


Fig. S7 The LSV polarization curve (a) and Tafel plot (b) of WO<sub>3</sub> with less oxygen vacancies.

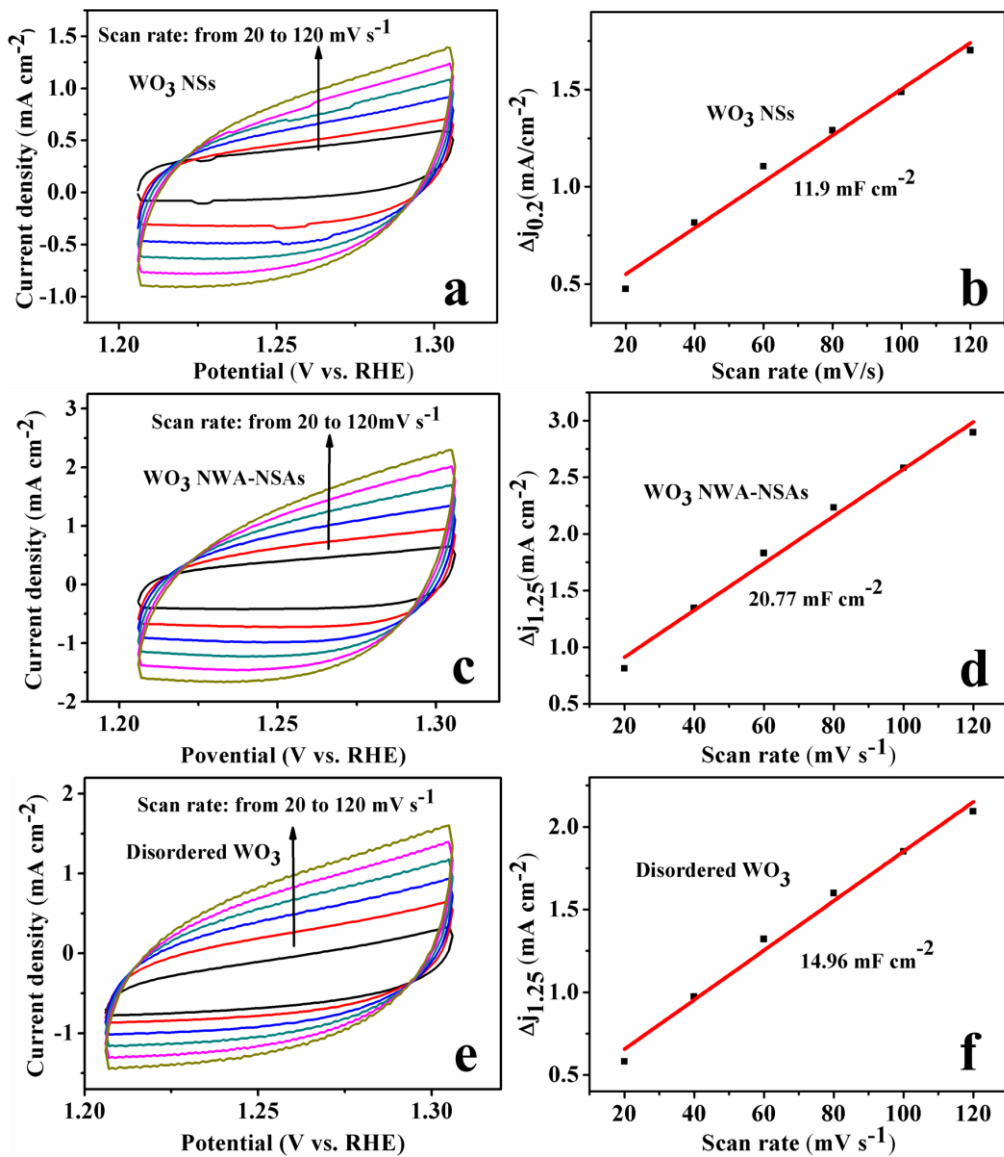


Fig. S8 The CV (a, c, e) and ECSA (b, d, f) of WO<sub>3</sub> NSs, WO<sub>3</sub> NWA-NSAs and disordered WO<sub>3</sub>

Table S1. The comparison of WO<sub>3</sub> NSA-NWAs and the reported Ni foam supported OER catalysts

Materials	Mass loading on Ni foam (mg cm <sup>-2</sup> )	Working electrode area (cm <sup>2</sup> )	Electrolyte	Onset potential (V vs. RHE)	Overpotential (V at 10 mA cm <sup>-2</sup> )	Tafel slope (mV dec <sup>-1</sup> )	References
WO <sub>3</sub> NSA-NWAs	26	0.25	1 M KOH	0.20	0.23	33	This work
Ni <sub>3</sub> Se <sub>2</sub>	8.87	1	1 M KOH	~0.22	~0.24	144	S1
NiO	5	4.84	1 M KOH	0.32	0.41	109	S2
NiSe <sub>2</sub> /Graphene	2.5	3	0.1 M KOH	\	~0.30	89	S3
MoS <sub>2</sub>	25	1	1M KOH	~0.25	\	105	S4
Carbon dots/Ni <sub>3</sub> S <sub>2</sub>	4.2	4	1M KOH	\	0.27	67	S5
Ni <sub>3</sub> S <sub>2</sub> /Ni foam	2.5	8	1M KOH	0.30	\	95.4	S6
Co <sub>3</sub> O <sub>4</sub> -C	1.8	12	0.1M KOH	\	0.32	73	S7
Ni-Fe-O	5.4	1	1 M KOH	0.24	0.27	\	S8

Table S2. The comparison of  $\text{WO}_3$  NSA-NWAs and the reported OER catalyst powders dipped on glassy carbon electrodes

Materials	Electrolyte	Onset potential(mV vs. RHE)	Overpotential (mV at10 $\text{mA cm}^{-2}$ )	Tafel slope ( $\text{mV}\cdot\text{dec}^{-1}$ )	References
$\text{WO}_3$ NSA-NWAs	1M KOH	200	230	30	This work
NiFe	1M KOH	200	320	113	S9
N-Co-Fe-LDH	1M KOH	240	280	57.37	S10
$\text{SrCo}_{0.4}\text{Fe}_{0.2}\text{W}_{0.4}\text{O}_{3-\delta}$	1M KOH	296	399	50	S11
Co-Fe-P	0.1M KOH	230	325	98.1	S12
NiCo@NiCoO <sub>2</sub>	1M KOH	270	315	83.97	S13
$\text{IrO}_2/\text{MoO}_3$	0.1M NaOH	230	360	55	S14
Ni-MnO/rGO	0.1M KOH	270	370	82	S15
Fe-Ni <sub>3</sub> C	1.0 KOH	250	275	62	S16
CoOx/Graphene	0.1M KOH	240	295	57	S17

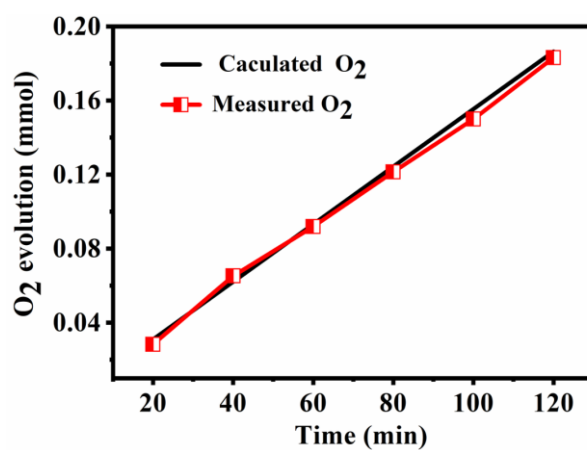


Fig. S9 the oxygen production of WO<sub>3</sub> NWA-NSA at the current density of 10 mA cm<sup>-2</sup> for 120 min

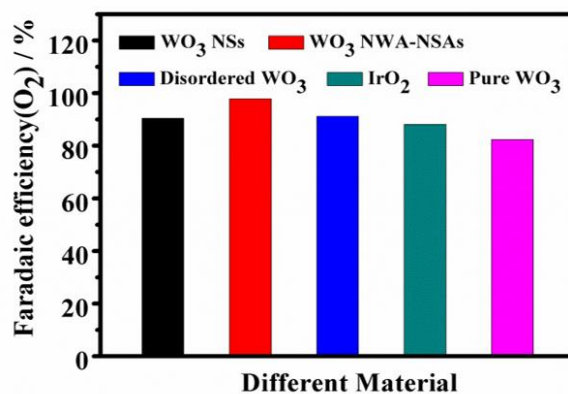


Fig. S10 FEs of WO<sub>3</sub> NSs, WO<sub>3</sub> NWA-NSAs, disordered WO<sub>3</sub>, IrO<sub>2</sub> and pure WO<sub>3</sub> at potential of 1.55 V

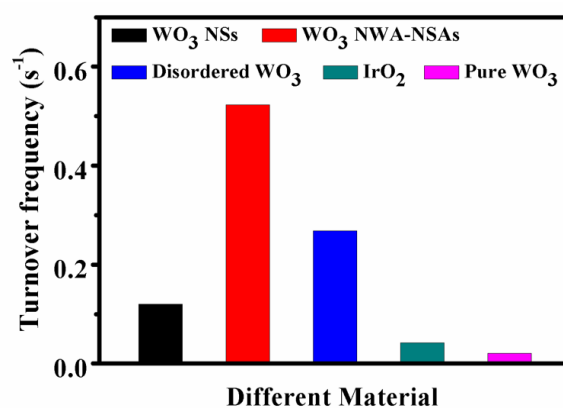


Fig. S11 TOFs of WO<sub>3</sub> NSs, WO<sub>3</sub> NWA-NSAs, disordered WO<sub>3</sub>, IrO<sub>2</sub> and pure WO<sub>3</sub> under 1.55 V



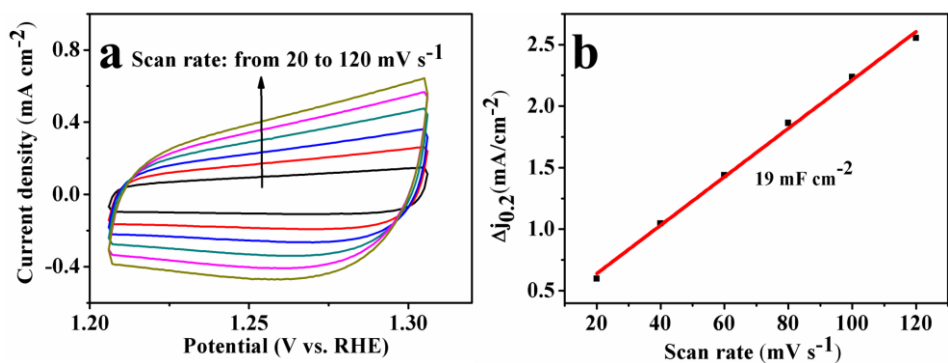


Fig. S12 ECSA of WO<sub>3</sub>NWA-NSA catalyst after cycling test

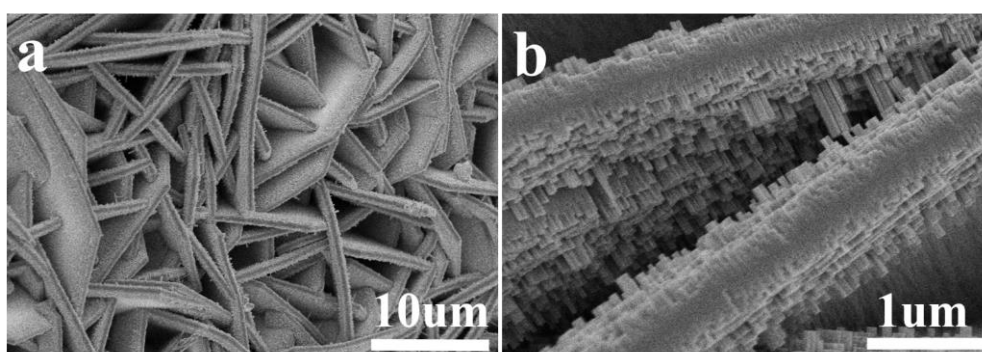


Fig. S13 SEM images of WO<sub>3</sub>NWA-NSA catalyst after cycling test

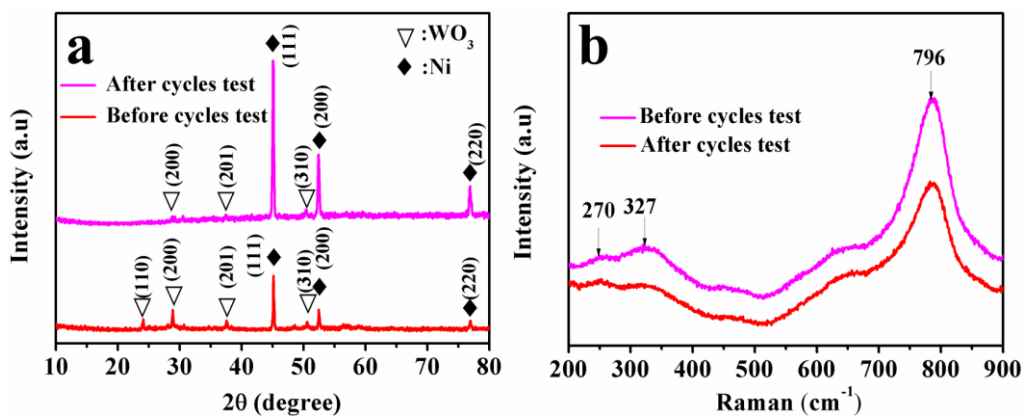


Fig. S14 XRD and Raman spectra of WO<sub>3</sub> NWA-NSA catalyst after cycling test

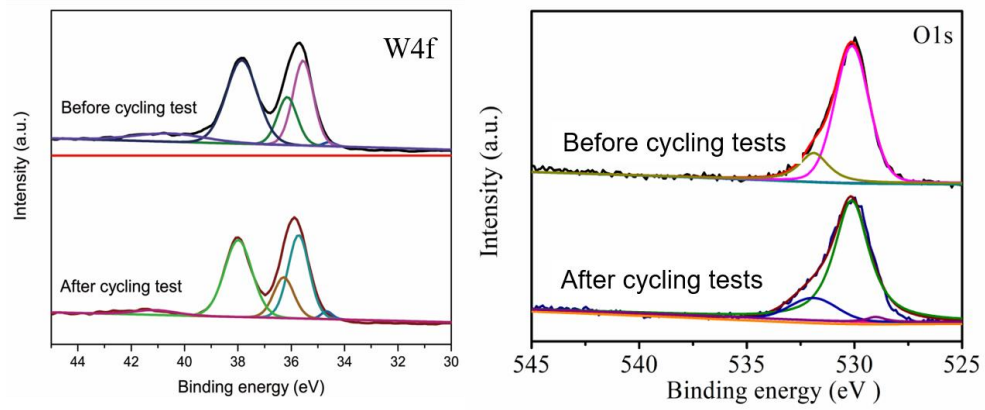


Fig. S15 XPS spectra of WO<sub>3</sub>NWA-NSA catalyst after cycling test

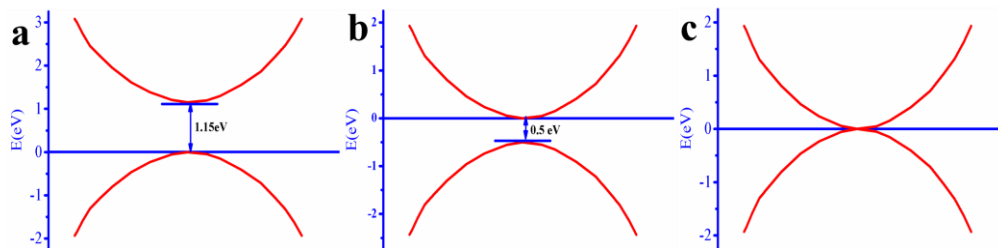


Fig. S16 the electronic band structure scheme of WO<sub>3</sub> (a), WO<sub>x</sub>-B (b) and WO<sub>x</sub>-S (c) on the around  $\Gamma$  point.

## References

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