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

Supporting Information

Tailoring the geometric and electronic structure of tungsten oxide with manganese or vanadium doping toward highly efficient electrochemical and photoelectrochemical water splitting

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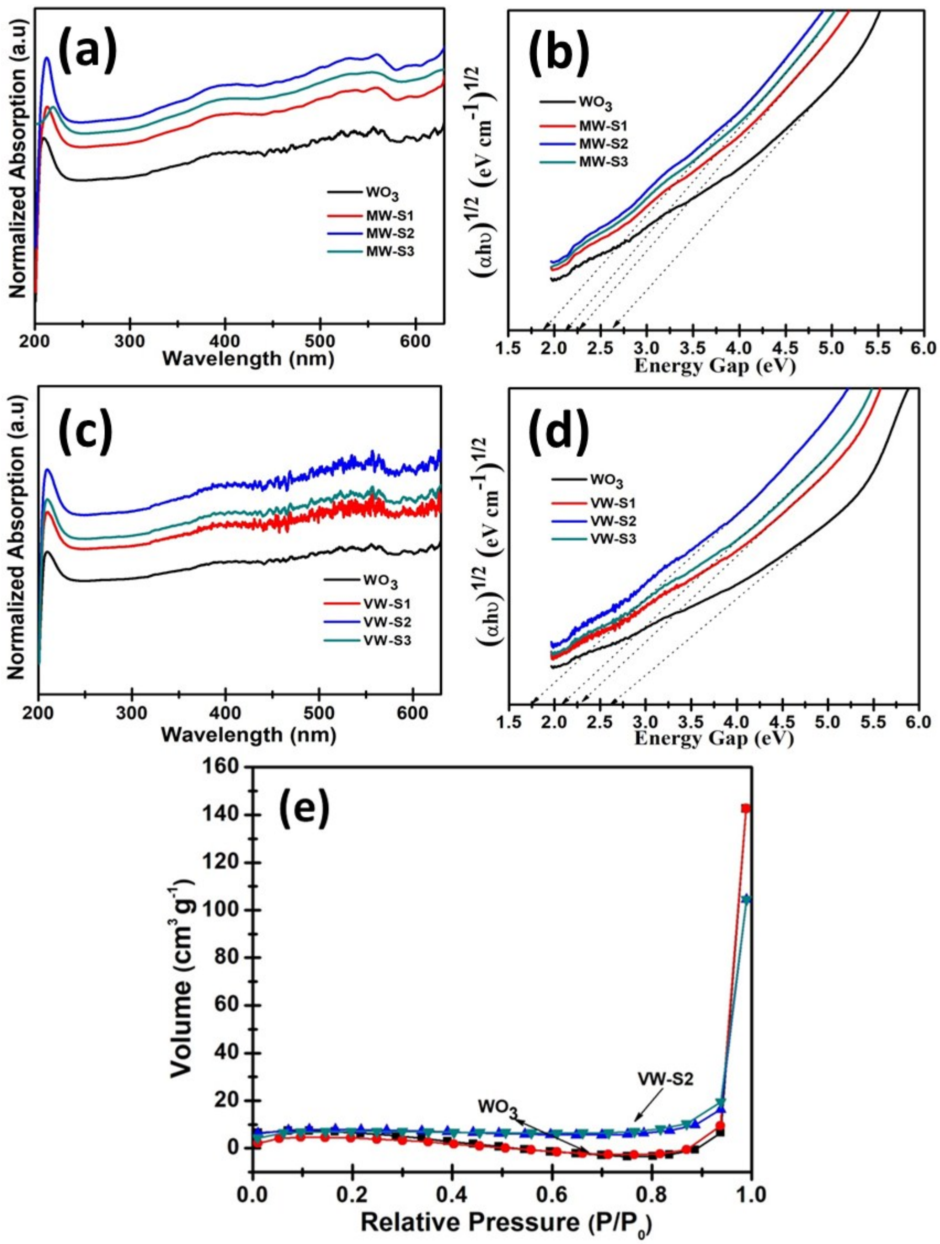


Fig. S1 UV-visible absorption spectra for prepared samples (a and c) and (b and d) are their corresponding Tauc Plots and (e) N_2 adsorption and desorption isotherms for bare WO_3 and VW-S2 sample.

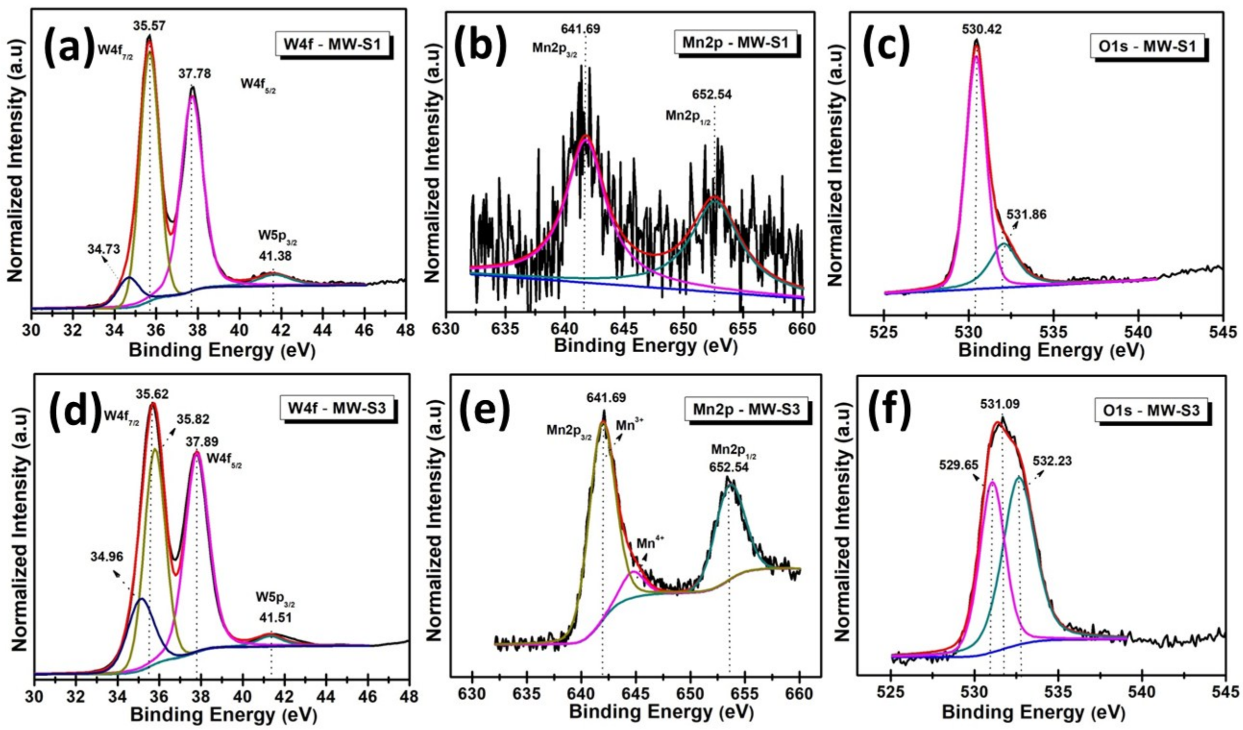


Fig. S2 (a-c) and (d-f) are W4f, Mn2p and O1s XPS core-level spectrum of MW-S1 and MW-S3 samples, respectively.

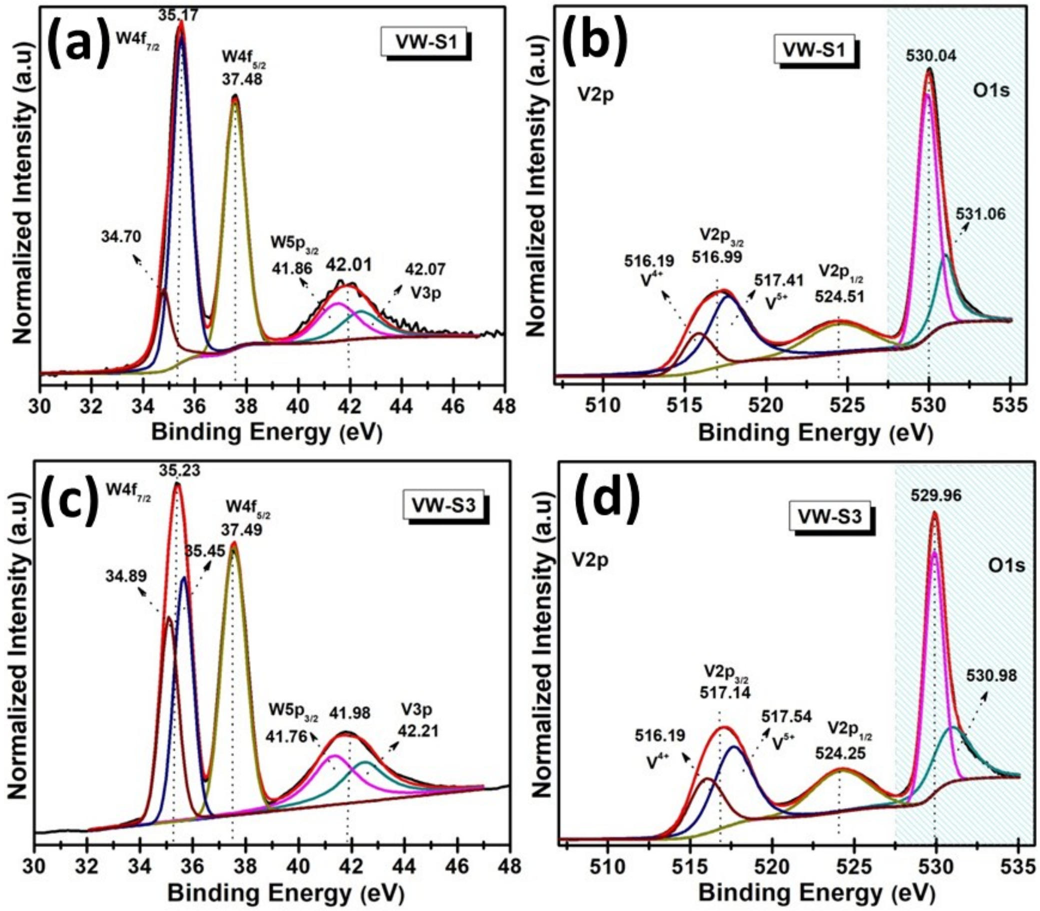


Fig. S3 (a-b) and (c-d) are W4f, V2p and O1s XPS core-level spectrum of VW-S1 and VW-S3 samples, respectively.

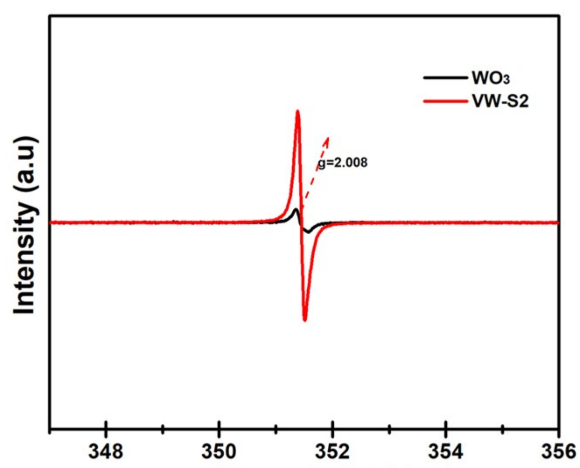


Fig. S4. Room temperature ESR spectra of pristine WO_3 and VW-S2 sample

Table S1 Experimental optical and electrical properties

Sample	Experimental Band gap (eV)	Electrical resistivity (Ω m)	Electrical conductivity (S/m)
WO_3	2.69	1.20×10^{2}	8.333×10^{-3}
MW-S1	2.51	0.92×10^{2}	1.087×10^{-2}
MW-S2	1.81	0.46×10^{2}	2.174×10^{-2}
MW-S3	2.16	0.32×10^{2}	3.125×10^{-2}
VW-S1	2.28	0.83×10^{2}	1.205×10^{-2}
VW-S2	1.75	0.11×10^{2}	0.910×10^{-1}
VW-S3	2.10	0.16×10^{2}	0.625×10^{-1}

Table S2 Chemical composition analysis by EDS and XPS analysis

Sample	EDS analysis								XPS analysis			
	Weight. %				Atomic. %				Atomic. %			
	W	Mn	V	O	W	Mn	V	O	W	Mn	V	O
WO_3	74.66	-	-	25.44	20.34	-	-	79.66	19.74	-	-	80.26
MW-S1	73.58	1.04	-	25.29	20.01	0.95	-	79.04	19.72	0.95	-	79.33
MW-S2	71.45	3.04	-	25.51	19.07	2.71	-	78.22	19.17	2.80	-	78.03
MW-S3	71.46	4.77	-	23.77	19.82	4.43	-	75.75	19.76	4.91	-	75.68
VW-S1	76.38	-	1.09	22.53	22.52	-	1.16	76.32	22.26	-	1.10	76.65
VW-S2	77.59	-	3.02	19.39	24.93	-	3.50	71.57	24.89	-	3.23	71.88
VW-S3	77.21	-	4.98	17.80	25.76	-	6.00	68.24	25.85	-	5.12	68.41

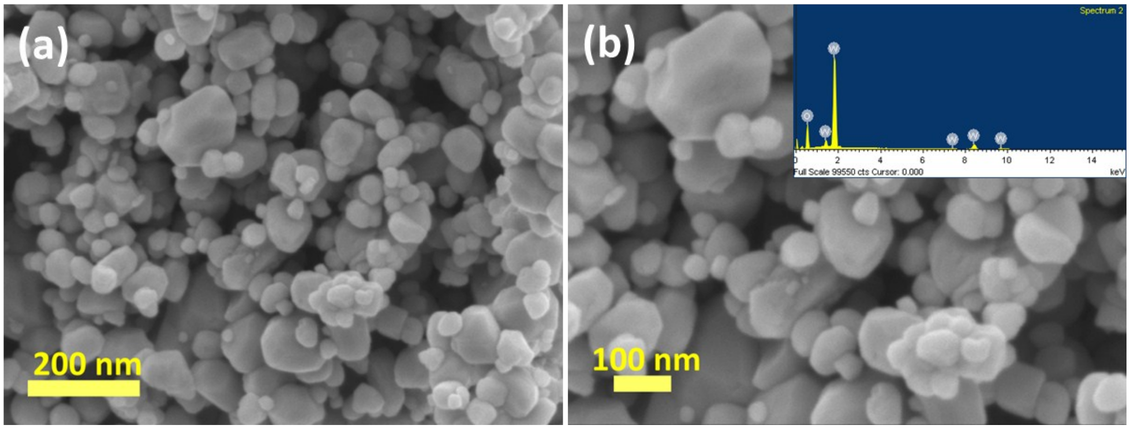


Fig. S5 FE-SEM images of undoped WO_3 sample and insert shows the EDS spectra of WO_3

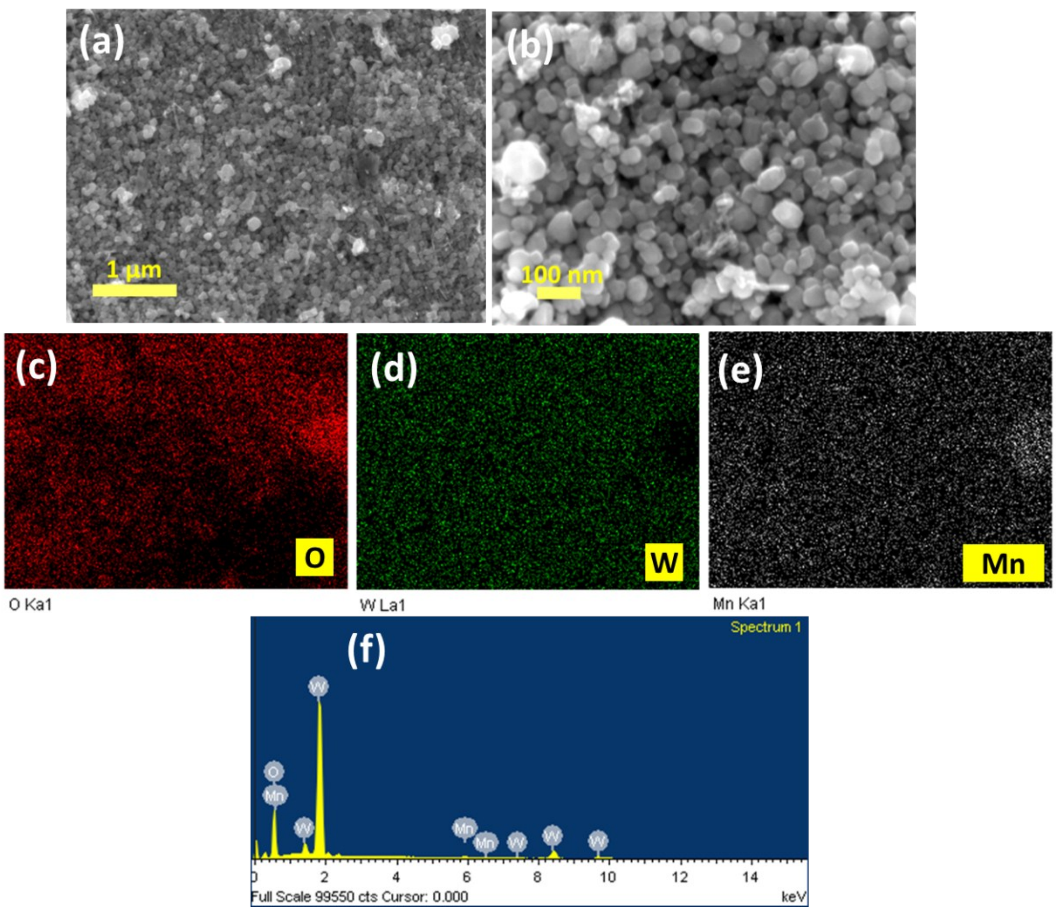


Fig. S6 (a-b) FE-SEM images, (c-e) electron density mapping and (f) EDS spectrum of MW-S1 sample

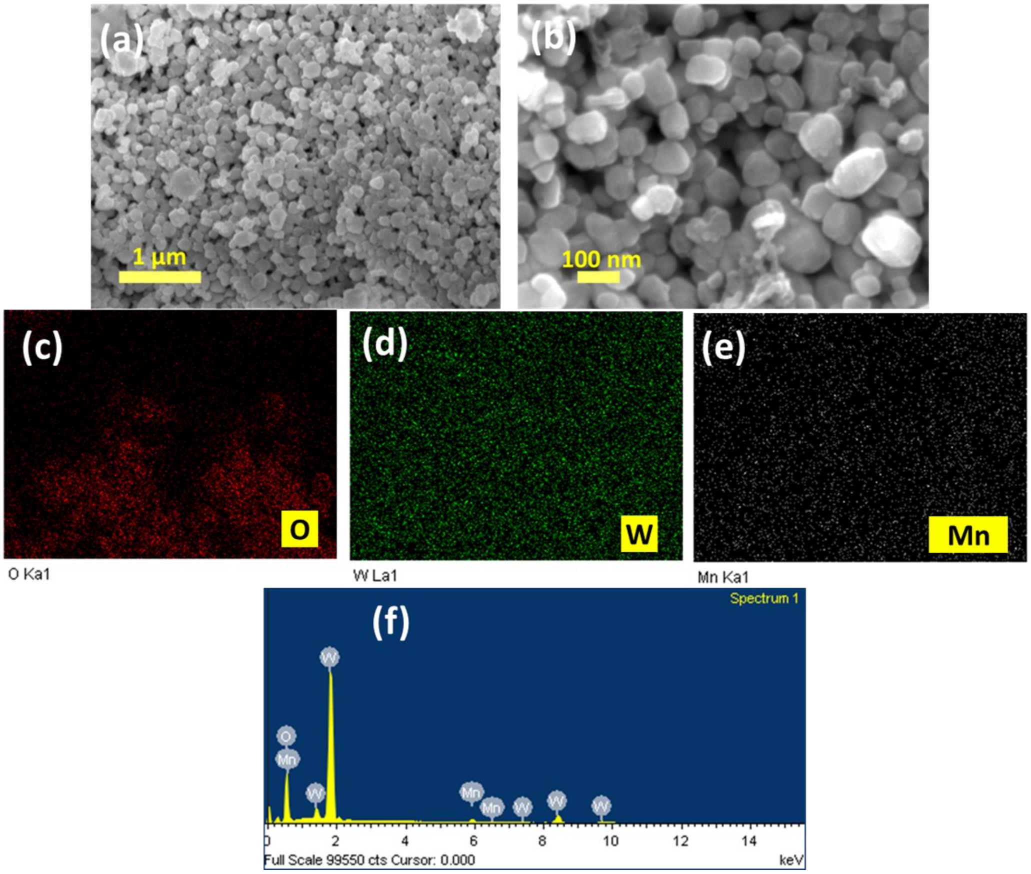


Fig. S7 (a-b) FE-SEM images, (c-e) electron density mapping and (f) EDS spectrum of MW-S2 sample

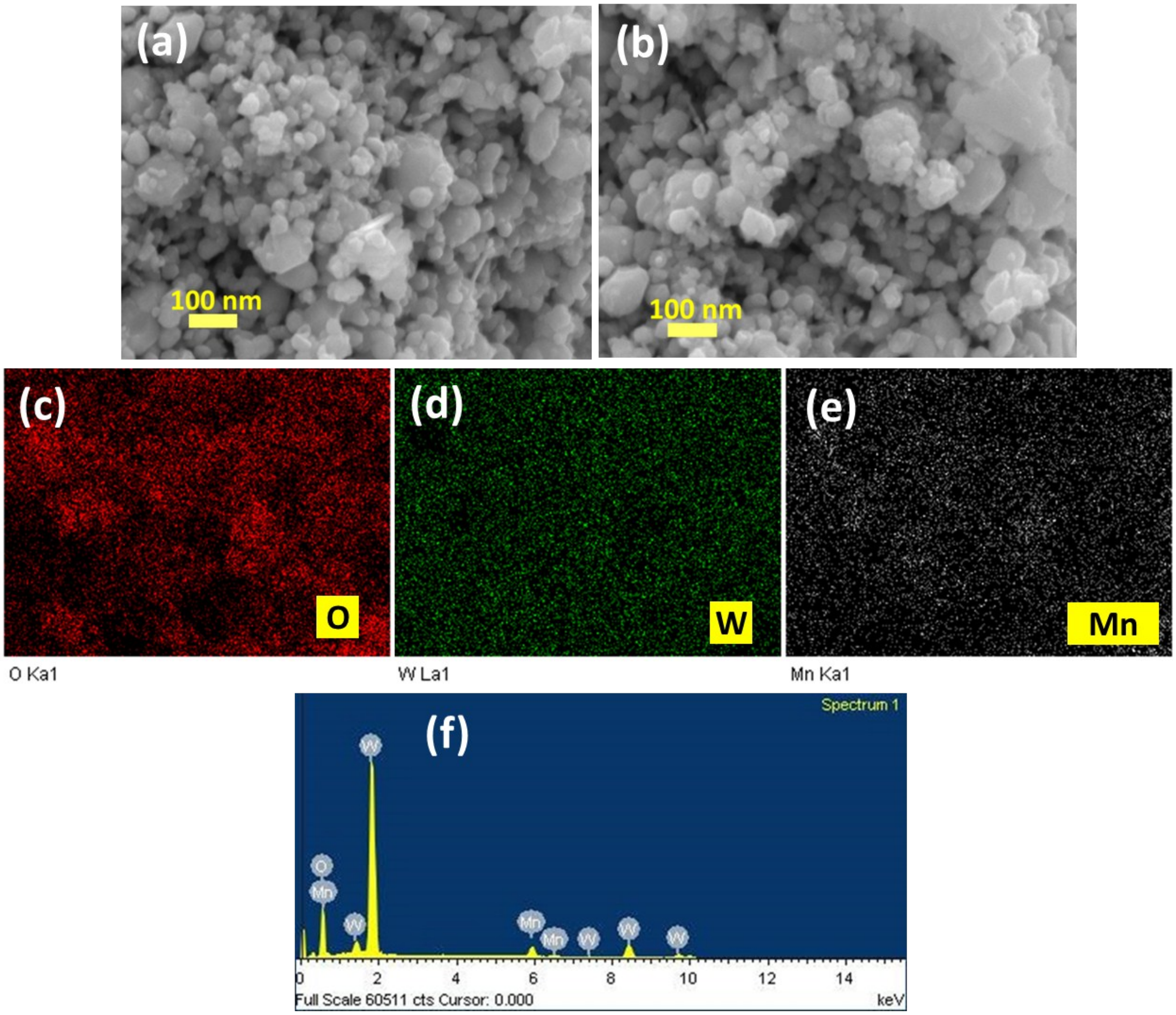


Fig. S8 (a-b) FE-SEM images, (c-e) electron density mapping and (f) EDS spectrum of MW-S3 sample

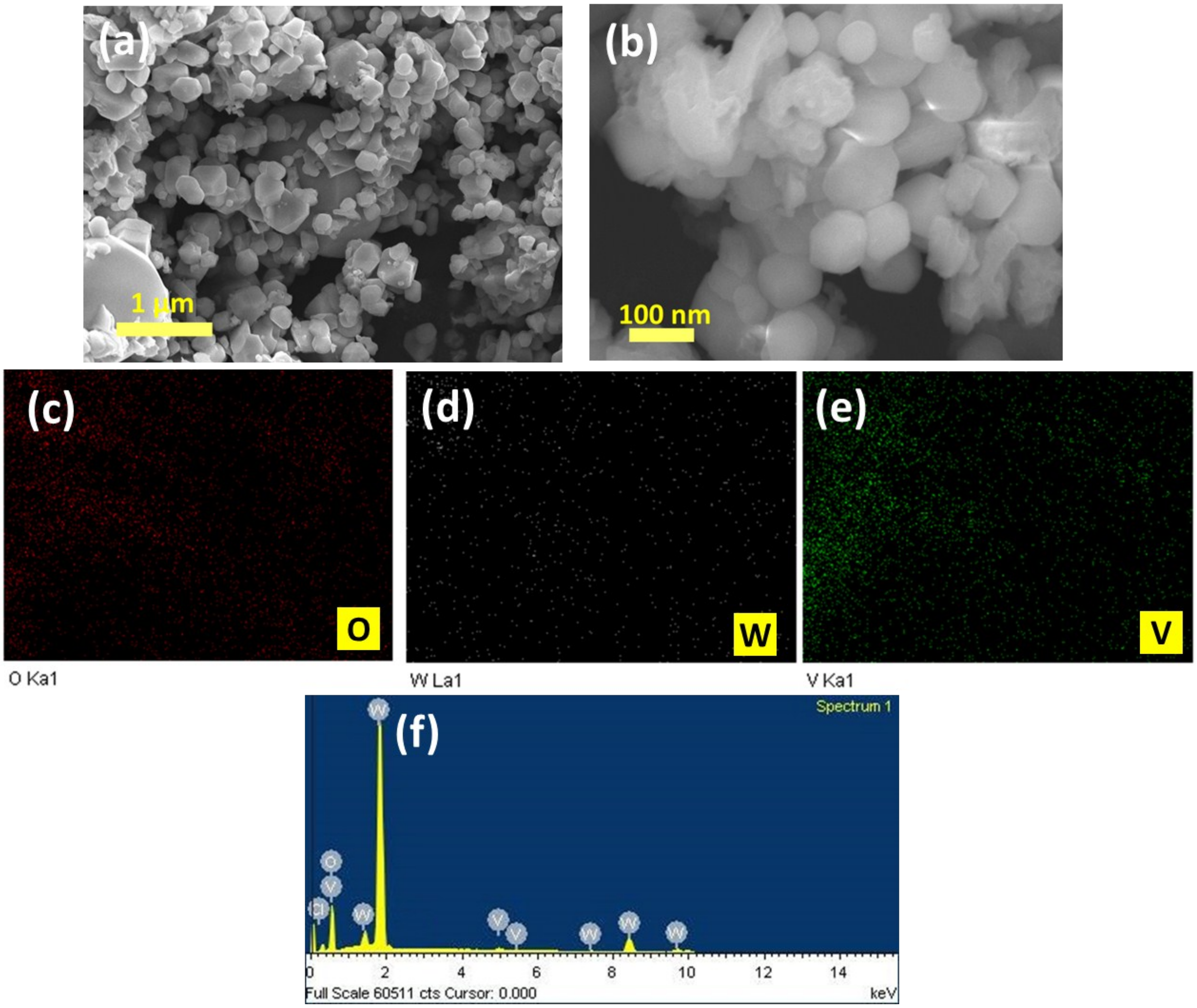


Fig. S9 (a-b) FE-SEM images, (c-e) electron density mapping and (f) EDS spectrum of VW-S1 sample

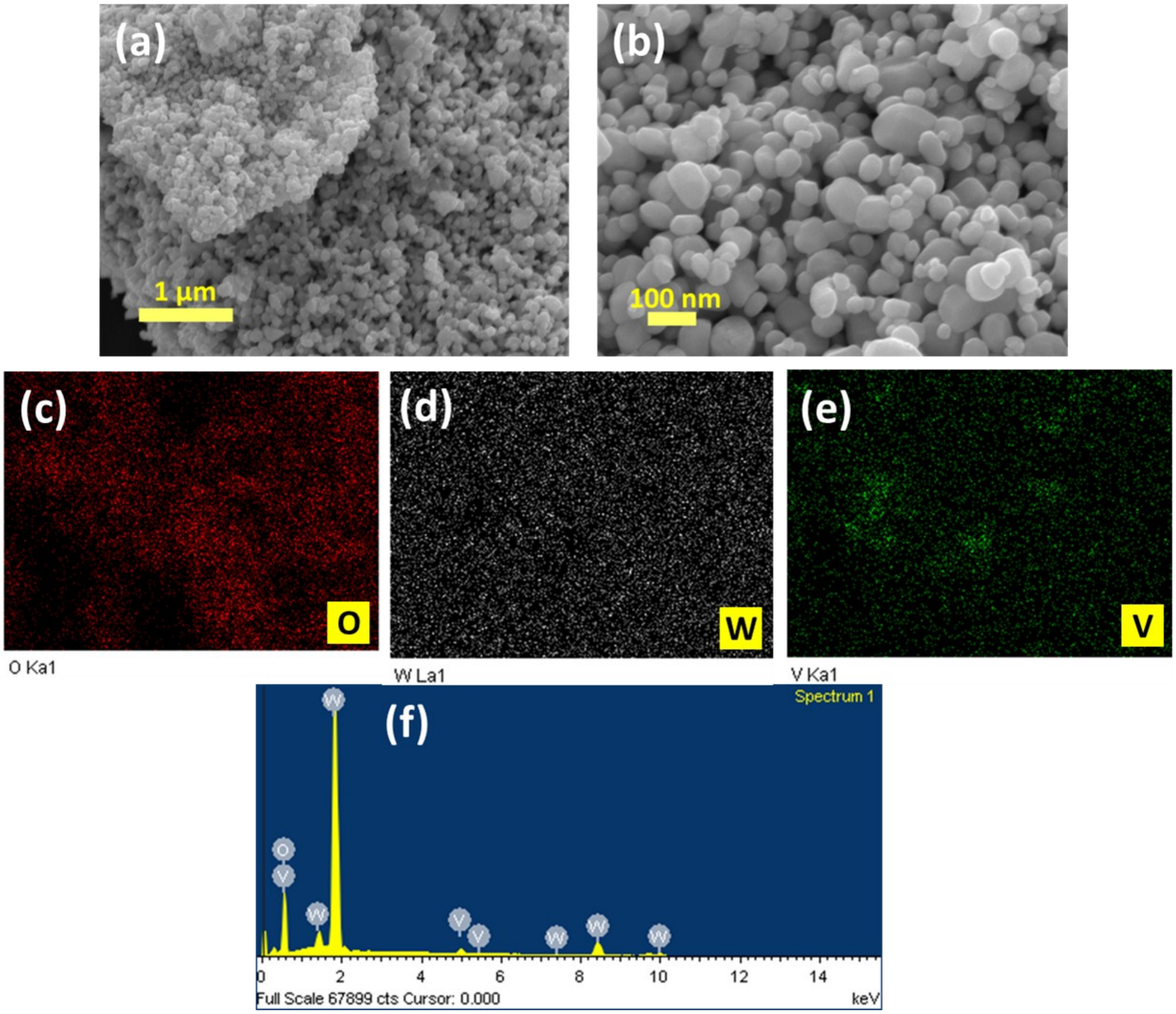


Fig. S10 (a-b) FE-SEM images, (c-e) electron density mapping and (f) EDS spectrum of VW-S2 sample

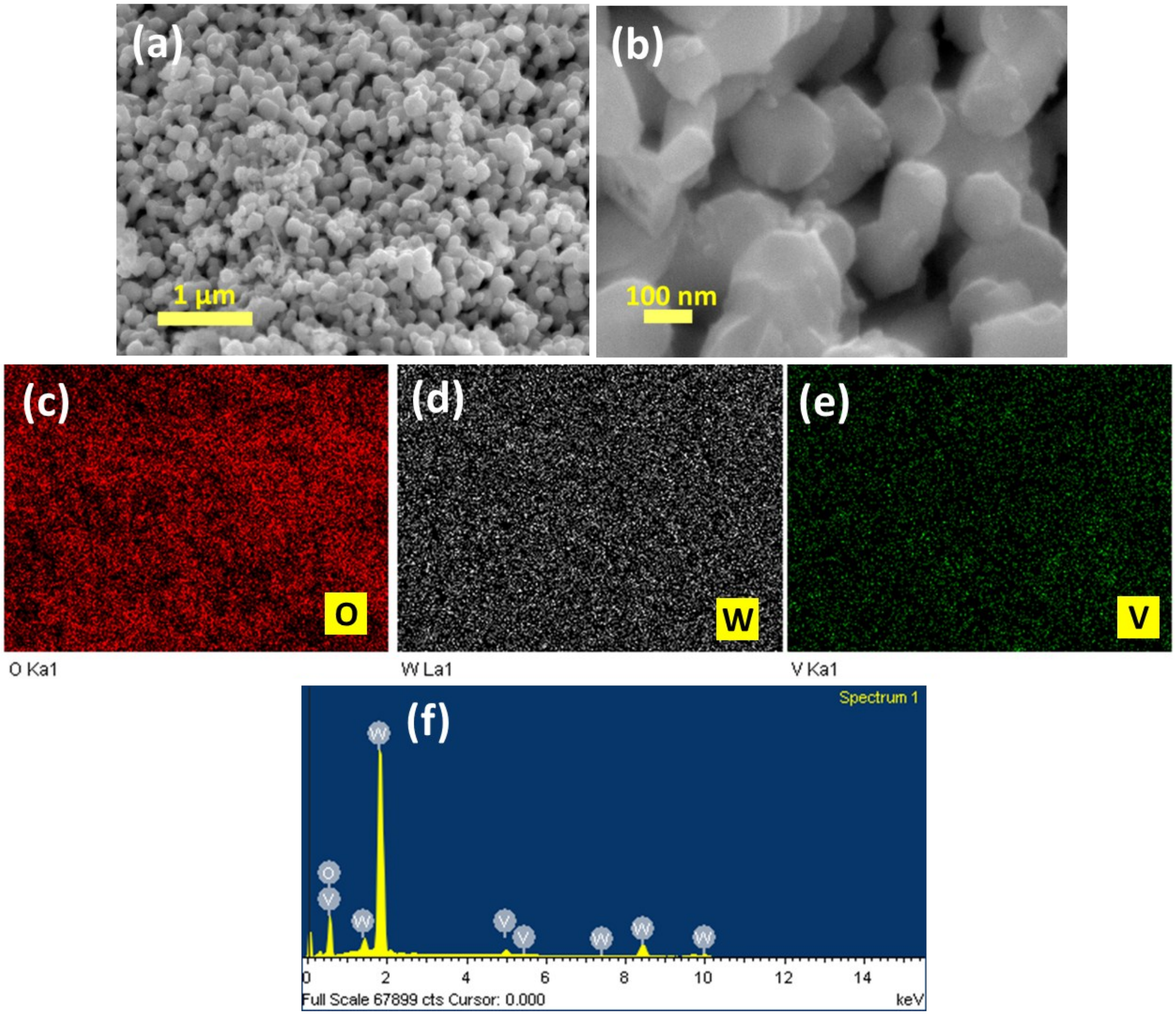


Fig. S11 (a-b) FE-SEM images, (c-e) electron density mapping and (f) EDS spectrum of VW-S3 sample

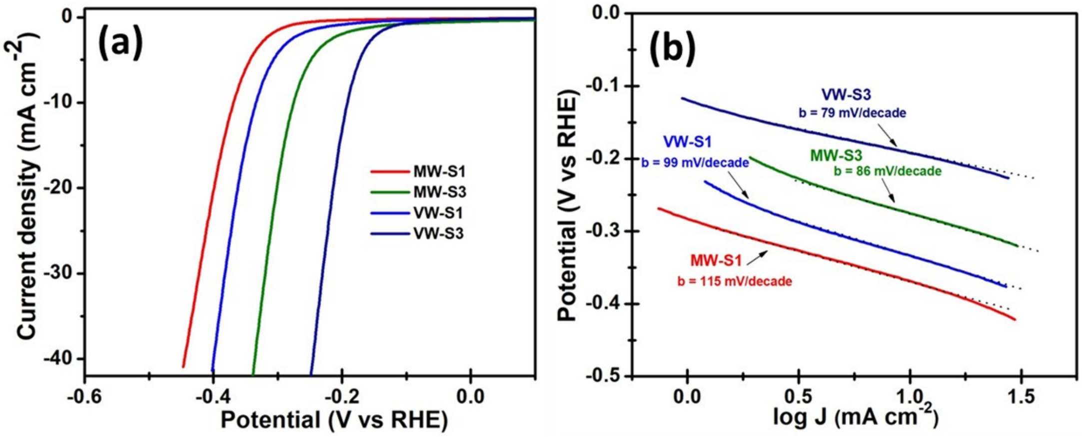
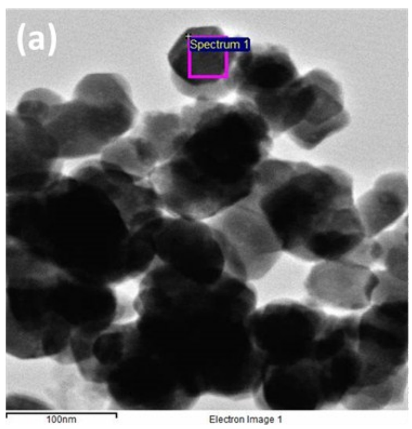
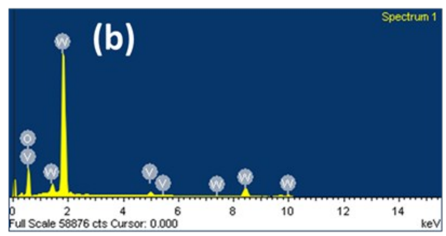


Fig. S12 (a) Electrocatalytic HER activity (a) Polarization curves for the MW-S1, MW-S3, VW-S1 and VW-S3 samples, and (b) their corresponding Tafel Plots. All electrocatalytic studies were performed in 0.5M H_2SO_4 at room temperature with a sweep rate of 5 mV sec^{-1}.





(c)

Element	Weight%	Atomic%
O K	19.39	71.69
V K	2.82	3.28
W M	77.79	25.03
Totals	100.00	

Fig. S13 (a) TEM and (b-c) EDS analysis for VW-S2 sample after durability test

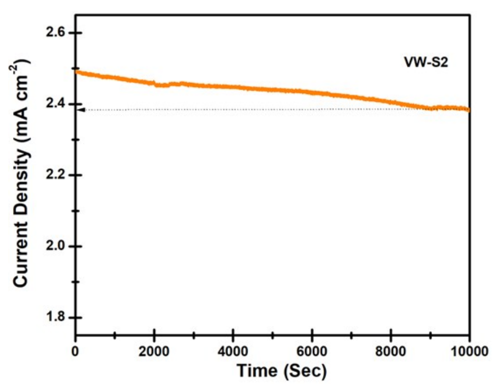


Fig. S14 Long term PEC water splitting durability test for VW-S2 photoelectrode at fixed potential of 1.23 V *vs.* RHE in 0.1 M Na_2SO_4.

Table S3 Summarized electrocatalytic HER performance of some previously reported high performance catalysts

Electrocatalyst (mg cm^{-2})	Electrolyte	Current density (J, mA cm^{-2})	Corresponding overpotential (ŋ, mV)	Tafel plot (mV per decade)	Exchange current density (J_0, mA cm^{-2})	Reference
WO_3 (0.285) MW-S2 (0.285) VW-S2 (0.285) 20 wt.% PtC(0.285)	0.5 M H_2SO_4	10 10 10 10	-411 -97 -38 -17	121 68 41 32	$1.25x10^{-5}$ $2.01x10^{-3}$ 0.098 0.210	**This work**
$WO_{2.9}$ (0.285)	0.5 M H_2SO_4	10	**-70**	50	0.4	[1]
WO_3-r NSs (0.285)	0.5 M H_2SO_4	10	-38	38	-	[2]
$WO_3{\cdot}H_2O$ (28.57)	0.5 M H_2SO_4	10	-66	34.8	14.2 $x10^{-3}$	[3]
3D urchin-like Mo-$W_{18}O_{49}$ nanostructure (0.16)	0.5 M H_2SO_4	10	-45	54	-	[4]
WO_2-C mesoporous nanowires (0.35)	0.5 M H_2SO_4	10	-58	46	0.64	[5]
P-modified WN/rGO (0.337)	0.5 M H_2SO_4	10	-85	54	-	[6]
WS_2 nanosheets (0.1×10^{-3}-0.2×10^{-3})	0.5 M H_2SO_4	10	-240	60	-	[7]
WC-CNTs [a]	0.5 M H_2SO_4	10	26.5	30	-	[8]
$NiWS_x$ [a] $CoWS_x$ [a] $CoMoS_x$ [a]	PBS	10	373 271 241	96 (η=120−150) 78 (η=120−150) 85 (η=120−150)	$10^{-2.66}$ $10^{-2.25}$ $10^{-2.89}$	[9]
Hex-WO_3 [a]	1 M H_2SO_4	-	-	−0.116	6.61	[10]

V-doped Ni_3S_2/NF[b]	1 M KOH	10	68 mV	112	-	[11]
WC (20) N doped WC (16 mg)	0.5 M H_2SO_4	10	−114 -89	110 75	-	[12]
W + Ru/C + BP_{2000} (0.1466)	0.5 M H_2SO_4	10	-85	46	-	[13]
Co:WS_2/Co:$W_{18}O_{49}$ [b]	0.5 M H_2SO_4	10	-210	49	-	[14]
MoS_2/WS_2 (0.707)	0.5 M H_2SO_4	10	-113	37	-	[15]
V-CoP/CC [b]	0.5 M H_2SO_4	10	47	67.6	0.897	[16]
V and N co-doped MoS_2 on rGO (0.2)	0.5 M H_2SO_4	10	68	41	-	[17]
carbon coated V_8C_7[b]	0.5 M H_2SO_4	10	38	34.5	-	[18]
Co_4N [b]	1.0 M KOH	10	37	44		[19]
$CoW(OH)_x$ [b]	1.0 M PBS	10	73.6	149.59	-	[20]

[a] mass loading is not available and [b] catalysts were loaded on conductive support

Table S4 Summarized photoelectrochemical water splitting performance of some previously reported high performance photoelectrodes

Photoelectrode	Electrolyte	Light condition	Current density (J_0)mA cm^{-2}	Current density (J_0) at over potential (V)	Reference
WO_3 MW-S2 VW-S2	0.1 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.61 1.38 2.49	@1.23 V vs. RHE	**This work**
WO_3 RuO_2(0.001 wt%)/WO_3 PtO_x(0.5 wt%)/WO_3 RuO_2(0.001 wt%)/PtO_x(0.5 wt%)/WO_3	0.1 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.16 0.43 0.10 0.20	@1.0 V *vs.* Ag/AgCl.	[21]
WO_3/W	1 mM $B_{10}Br_{10}^{\cdot-/2-}$ and 0.50 M $TBASO_3CH_3$ in Acetonitrile	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.0	@1.23 V vs. NHE	[22]
WO_3	0.5 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.55	@1.23 V vs. RHE	[23]
$CuWO_4$ $CuW_{0.35}Mo_{0.65}O$	0.1 M PBS	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.125 0.210	@1.23 V vs. RHE	[24]
HO–WO_3	0.1 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.175	@1.2 V vs. RHE	[25]
BVO –WO with 75 nm thicknesses	0.5 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.55	@1.0 V *vs.* Ag/AgCl.	[26]
WO_3 2 mol% Fe-doped WO_3	0.5 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.69 0.88	@1.23 V vs. RHE	[27]
Plasma method Nano sized WO_3	3 M H_2SO_4	Visible light under AM 1.5G (100 mW	1.00	@1.75 V vs. RHE	[28]

		cm^{-2}) irradiation			
WO_3/WO_{3-x}	0.1 M K_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	2.10	@1.23 V vs. RHE	[29]
WO_3	1.0 M $HClO_4$ with 0.20 M 4-cyanopyridine *N*-oxide	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.4	@1.23 V vs. RHE	[30]
WO_3 CoO_x/WO_3	0.1 M KPi	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.80 1.55	@1.23 V vs. RHE	[31]
WO_3 WO_3 MCs/Sb_2S_3 heterojunction structures	1 M H_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	0.40 1.65	@0.8 V vs. RHE	[32]
WO_3 4% Gd-WO_3	0.2 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.10 2.51	@1.23 V vs. RHE	[33]
Dual etched and reduced WO_3	1 M H_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.18	@1.0 V *vs.* Ag/AgCl.	[34]
Annealed Nano wire WO_3	0.1 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.45	@1.23 V vs. RHE	[35]
WO_3-Fe_2O_3	1 M NaOH	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.41	@1.23 V vs. RHE	[36]
(W, Mo)-$BiVO_4$	0.5 M K_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.55	@1.23 V vs. RHE	[37]
Ag doped WO_3	1 M H_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	2.10	@0.35 V vs. Hg/HgCl	[38]
Au doped WO_3	0.1 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	2.3	@1.0 V *vs.* SCE	[39]
H-WO_3 (350°C)	1.0 M Na_2SO_4	Visible light under AM 1.5G (100 mW cm^{-2}) irradiation	1.05	@1.2 V *vs.* Ag/AgCl.	[40]

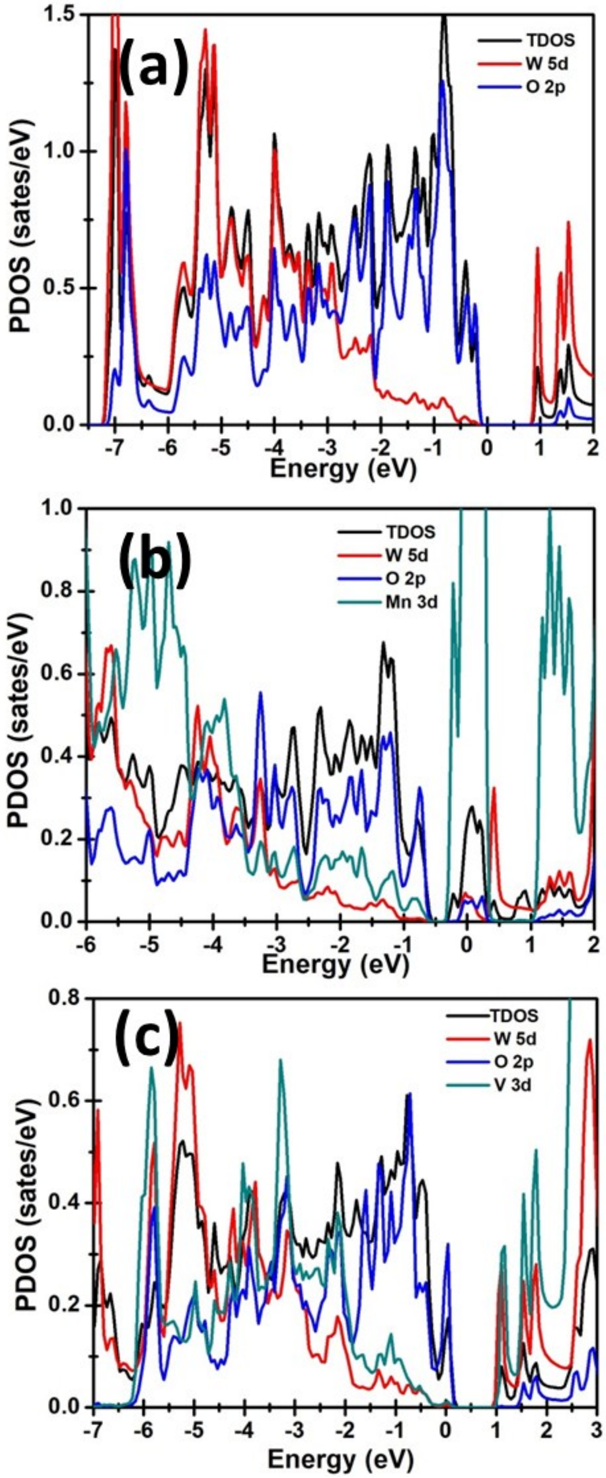


Fig. S15 DFT- PDOS analysis for (a) the undoped WO_3, (b) Mn doped WO_3 and (c) V doped WO_3

Table S5 Total energies and band gaps for pristine WO_3 and Mn or V-doped WO_3

	Pristine WO_3	**Mn doped WO_3**	**V doped WO_3**
E_{tot} (eV)	-317.21	-307.81	-311.42
Band Gap (eV)	1.31	1.05	0.95

Table S6 Relative stability of Mn or V doping in surface and subsurface layer of $WO_3(001)$ surface.

	Mn (eV)	**V (eV)**
Surface layer	-1.79	-0.95
Subsurface layer	0	0

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