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1D transition-metal dichalcogenides/carbon core-shell composites for Hydrogen Evolution Reaction

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Table of Contents

Tables

Table S1	XPS Peak Table of different elements	2
Table S2	XPS % calculation of tungsten	2
Table S3	Comparison of electrochemical performances	3
	of similar electrocatalysts	
Table S4	Values of EIS spectra in 0.5 M H_2SO_4	4
Figures		
Figure S1	Low magnification STEM image	5
Figure S2	EDS of the carbon-coated WS ₂ tube	5
Figure S3	Percentage analysis of XRD spectrum	6
Figure S4	Absolute absorption spectra	6
Figure S5	Raman spectroscopy of the WS_2/C composites	7
Figure S6	Full XPS spectrum of the WS ₂ /C composites	7
Figure S7	XPS of S2p and N1s for of the WS ₂ /C composites	8
Figure S8	XPS of pristine WS2 Peak splitting of W4f and C1s	8
Figure S9	MS results of chronoamperometry	9
Figure S9	LSVs of the Toray carbon paper	9
Figure S10	CVs of the WS ₂ /C composites in 0.5 M H_2SO_4	10
Figure S11	O-WS ₂ /C at acidic and neutral solutions.	10
Figure S12	A-WS ₂ /C at acidic and neutral solutions.	11
Figure S13	Tafel slope in different pH solutions	11
Figure S14	CV before and after the 12 h of chronoamperometry	12

Tables

Samples	WS ₂	A-WS ₂ /C	O-WS ₂ /C	R-WS ₂ /C
 Carbon	33.18	40.21	41.74	31.85
C-C	22.48	33.64	26.15	15.85
C-0	9.35	4.84	12.52	13.55
C=O	2.19	1.88	3.86	2.01
Oxygen (O1s)	14.64	5.49	9.01	21.65
Sulphur (s2p)	11.41	7.04	2.87	6.84
Tungsten (W4f)	4.82	3.32	1.79	4.77
Nitrogen (N1s)	2.46	3.58	2.07	3.5

Table S1: XPS Peak table for all the carbon-coated samples along with pristine WS₂.

Table S2: Atomic % of WS₂ $(4f_{7/2}+4f_{5/2})$ and WO₃ $(4f_{7/2}+4f_{5/2})$ content in the catalysts compared with total atomic % of W, obtained in XPS.

Samples	Atomic % of WS_2 or	Atomic % of WO ₃	Total atomic % of
	WO ₂	$(4f_{7/2}+4f_{5/2})/W$	W
	$(4f_{7/2}+4f_{5/2})/W$		
WS ₂	95	0	7.67
A-WS ₂ /C	89	0	3.17
O-WS ₂ /C	53.73	44.17	3.35
R-WS ₂ /C	35.61	61.75	8.76

Catalysts	Current density, mA cm ⁻²	Overpotential (mV vs. RHE)	Journal, Year of Publication	Ref.
2D graphene/WS ₂ nanosheet	10	180	ACS Appl. Energy Mater., 2021	42
WS ₂ /C	10	179	Journal of Fuel Chemistry and Technology, 2021	43
WS ₂ /OCF	10	278	Applied Surface Science, 2017	44
WS ₂ /rGO	10	170	Nanoscale, 2015	45
hierarchical triple-shelled (WS2- C-WS2) hollow nanospheres	10	175	Journal of Material Chemistry A, 2018	46
Carbon foam-N-doped Graphene- @ MoS2	10	170	Journal of Material Chemistry A, 2013	47
N-enriched C foam@WS ₂	10	153	Applied Surface Science, 2019	48
N,S doped graphene	10	390	Angewandte Chemie, 2014	49
N, P co-doped carbon- encapsulated CoP/MoP hybrid	10	183	Journal of Colloid and Interface Science, 2023	50
WS ₂ Nanoribbons	10	225	Advanced Energy Materials, 2014	17
$MoS_2 - WS_2$	10	129	ACS Sustainable Chem. Eng., 2018	51
R-WS ₂ /C	10	172		This work

Table S3: Comparison of electrocher	mical performan	ces of similar e	lectrocatalysts

	R _s (Ohm)	R ₁ (Ohm)	CPE ₁ (µF)
WS ₂	3.48	56.7	6.25
Carbon	2.71	9.01	8.08
A-WS ₂ /C	4.13	13.77	242
O-WS ₂ /C	2.78	11.21	7605
R-WS ₂ /C	4.8	8.87	1642

Table S4: Values of resistances and capacitances from EIS spectra in $0.5 \text{ M H}_2\text{SO}_4$

The equivalent circuit contains a resistor (Rs) connected with two parallel units in series: a constant phase element and a resistor (CPE_1-R_{ct}). The R_s represents the solution resistance, and the CPE_1 - R_{ct} pair is equivalent to resistor and capacitor in parallel combination related to the charge transfer.

Figures



Figure S1: Low magnification STEM image of WS₂ NTs/carbon composite showing the NTs are well dispersed throughout the grid.



Figure S2: *left*. Low voltage SEM image of the carbon-coated WS_2 tube on silicon wafer. *Right*. EDS analysis of different points on the nanotube shown, revealing 100% carbon adjacent to the wall of the tube (point #5) as compared to elements content in the middle of the tube (point #6). The high content carbon proves that the carbon efficiently wraps all over the nanotube.



Figure S3. XRD analysis of three different samples with pristine WS_2 shows the presence of WO2 oxide phase in pristine and first annealed (A-WS₂/C) sample whereas the other two samples (O-WS₂/C AND R-WS₂/C) contain WO₃ phase. Importantly, for every sample WS₂ (002) peak at 2 Θ =14.5 remains a higher percentage proving the unharmed crystallinity.



Figure S4: Absolute absorption spectra of prepared A-WS₂/C showing no shift at the exciton of the nanotube. An additional peak near 340 nm appears due to the attachment of carbon with the nanotube.



Figure S5: Raman spectroscopy of the WS_2/C composites.



Figure S6: Full XPS spectrum of the WS₂, A-WS₂/C, O-WS₂/C, R-WS₂/C.



Figure S7: XPS of S2p and N1s for all samples.



Figure S8: XPS spectrum of pristine WS2 after peak splitting of W4f and C1s scan.



Figure S9. Mass spectroscopy (MS) was collected from A-WS2/C after 10 minutes of CA at its overpotential, confirming hydrogen production.



Figure S10: LSVs of the Toray carbon paper showing a negligible effect on the catalytic performance.



Figure S11: CV for all the samples in $0.5 \text{ M H}_2\text{SO}_4$.



Figure S12: Onset potential at a current density of -10 mAcm⁻² of O-WS₂/C at acidic and neutral solutions.



Figure S13: Onset potential at a current density of -10 mAcm⁻² of A-WS₂/C at acidic and neutral solutions



Electrolyte Solutions

Figure S14: Tafel slope in different pH solutions.



Figure S15: CV before and after the 12 h of chronoamperometry test with an applied voltage of -0.150V vs. RHE for the prepared WS₂/C catalyst indicates that the catalyst is stable even after a long duration of hydrogen production.