Supporting Information

Electrochemically Chopped WS_2 Quantum Dots as an Efficient and Stable Electrocatalyst for Water Reduction

S. Anantharaj[†,‡,ƨ], Manila O. Valappil[†,‡,ƨ], K. Karthick[†,‡], Vijayamohanan K. Pillai[†,‡], Subbiah Alwarappan[†,‡,] and Subrata Kundu[†‡*]*

[†]Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Electrochemical Research Institute (CSIR-CECRI) Campus, New Delhi, India

[‡]CSIR-Central Electrochemical Research Institute (CECRI), Karaikudi-630003, Tamil Nadu, India

[ƨ]These authors have contributed equally.

E-mail: kundu.subrata@gmail.com;salwarap@gmail.com.

Reagents and Instruments

Sulphuric acid was purchased from RANKEM India. Commercial Pt/C 20 wt.% catalyst and 5 % Nafion suspension in alcohol water mixture were obtained from Sigma Aldrich. High purity WS_2 (99.9%) was procured from Alfa Aesar. $LiClO_4$ and the solvent propylene carbonate were procured from Merck and Thermofischer Scientific. Hg/$HgSO_4$ reference electrodewas purchased from CH InstrumentsPvt. Ltd. Deionized water (18.2 $M\Omega cm^{-2}$) was used for the entire electrochemical study wherever required. TEM analysis was done with TECNAI made which operates with 200 kV bias. TheEnergy Dispersive X-ray Spectroscopy (EDS) analysis was done with the HR-TEM instrument (TECNAI) with a separate EDS detector connected to that instrument. The XRD analysis was done with a scanning rate of 5° min^{-1} using a Bruker X-ray powder diffractometer (XRD) with Cu K_α radiation (λ = 0.154 nm). X-ray photoelectron spectroscopic (XPS) analysis was performed using a Theta Probe AR-XPSsystem (Thermo Fisher Scientific, UK). UV-Vis and PL spectra were acquired with UNICO double beam spectrophotometer. Electrochemical analyzer AUTOLAB version AUT86853 was used for the entire electrochemical characterization.

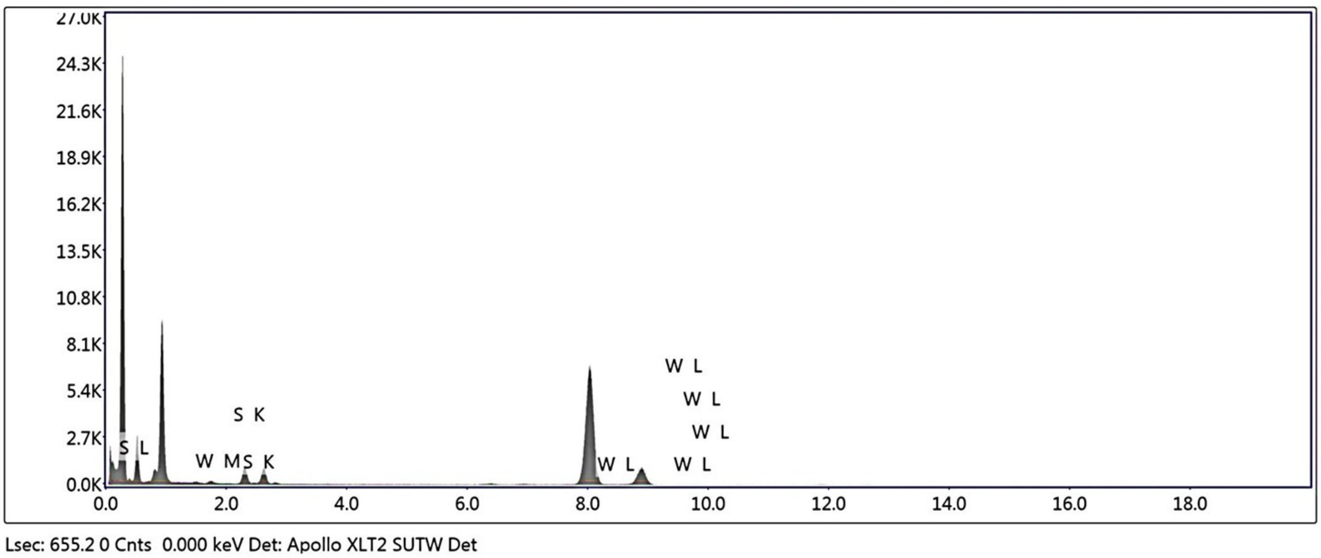

Fig. S1: EDS spectrum of WS_2 QDs showing the presence of W and S for various shells.

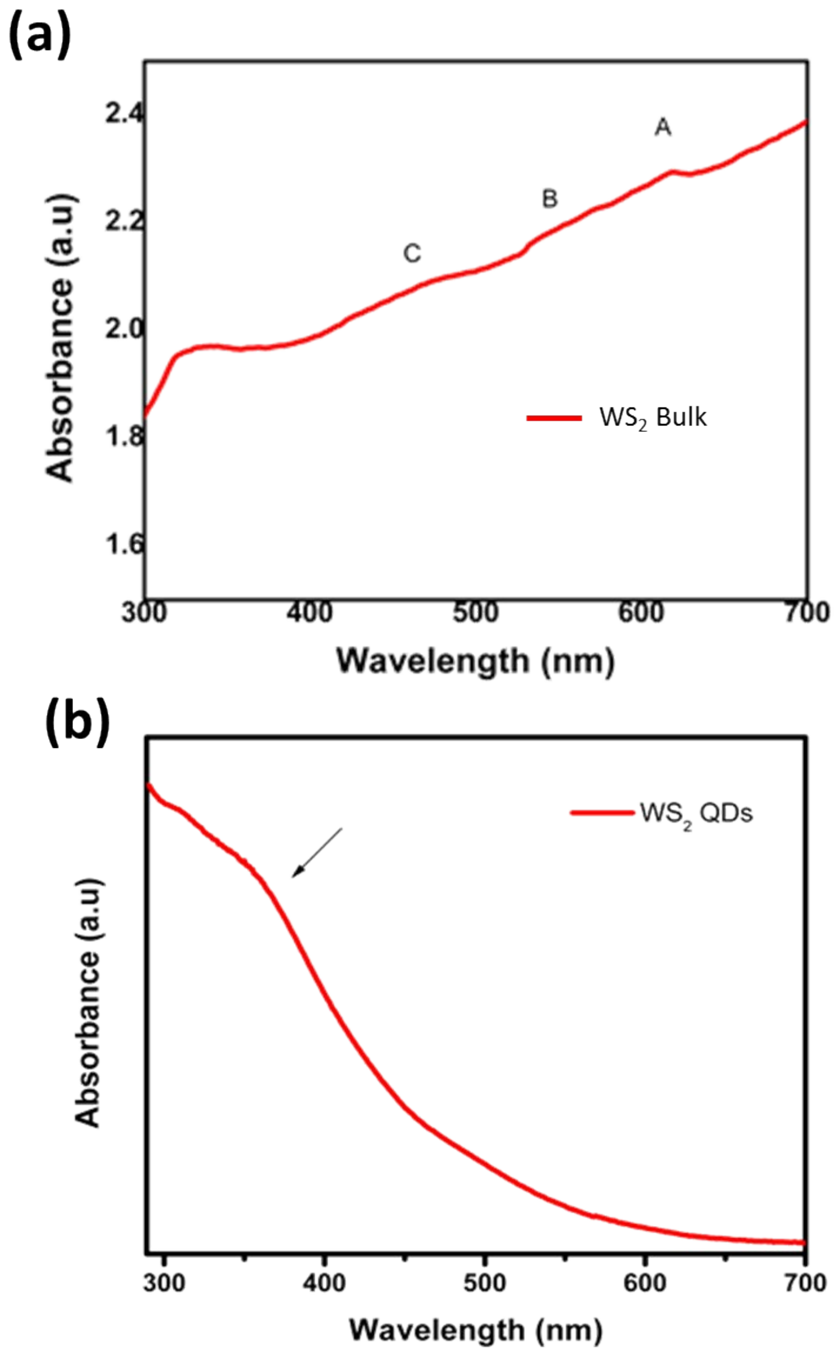

Fig. S2: (a-b)UV-Vis spectrum of Bulk WS_2 and WS_2 QDs showing differences in their absorption features.

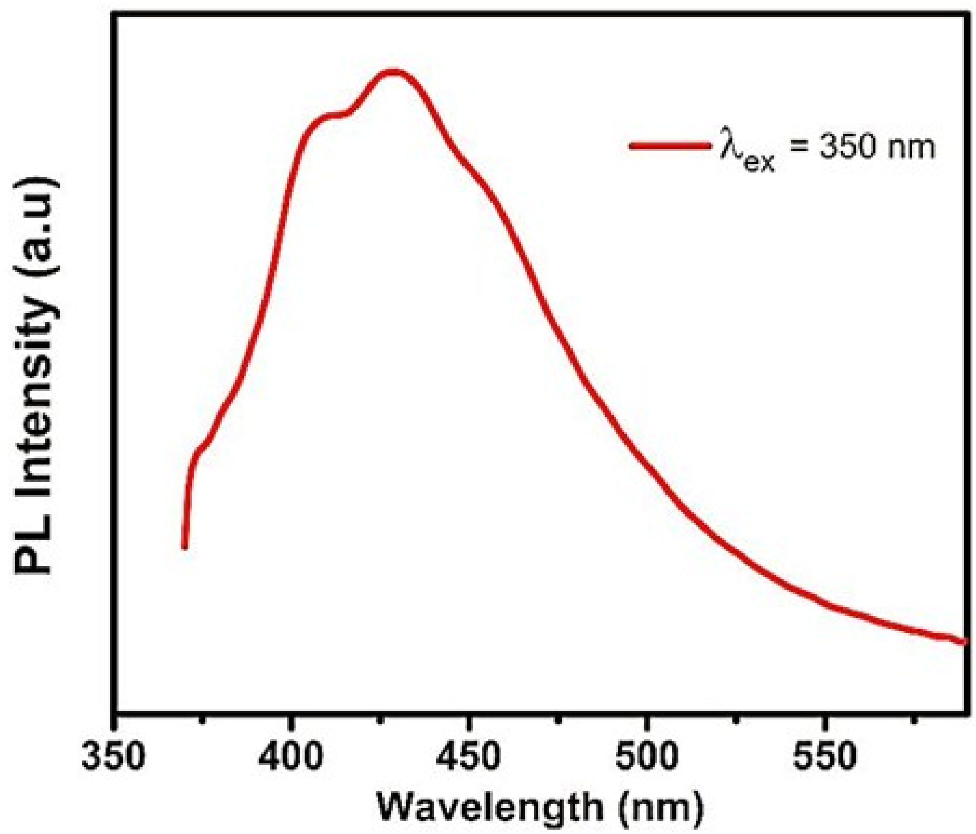

Fig. S3: PL spectrum of WS_2 QDs obtained with an exciting wavelength of 350 nm.

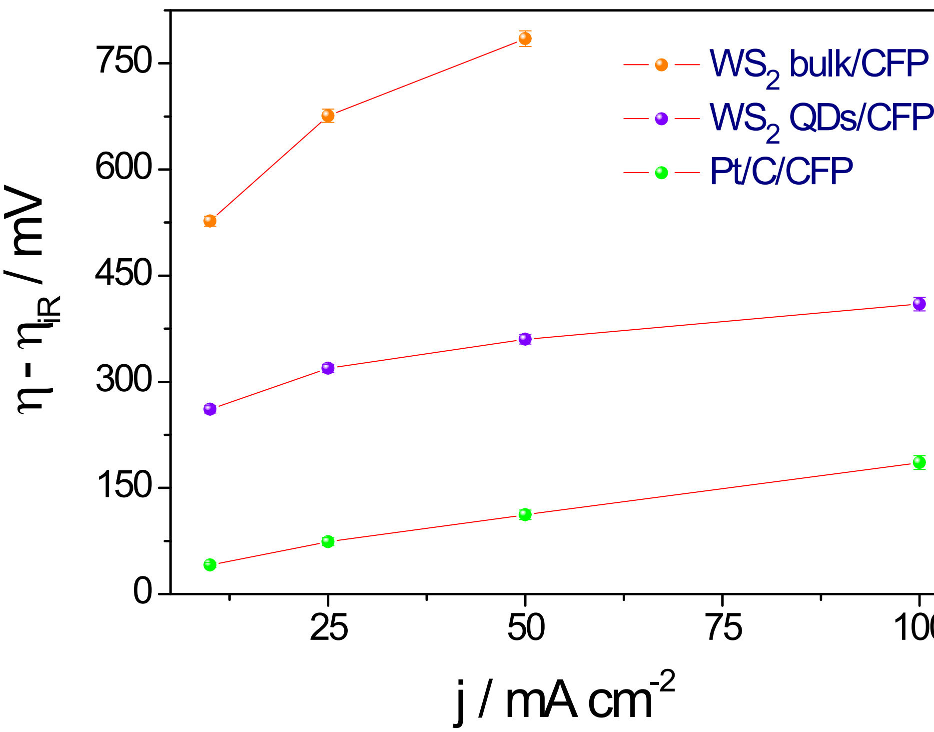

Fig. S4: Plot of *j vs. overpotential* measured at repeated experiments showing the high reproducibility with minimum magnitude of deviation.

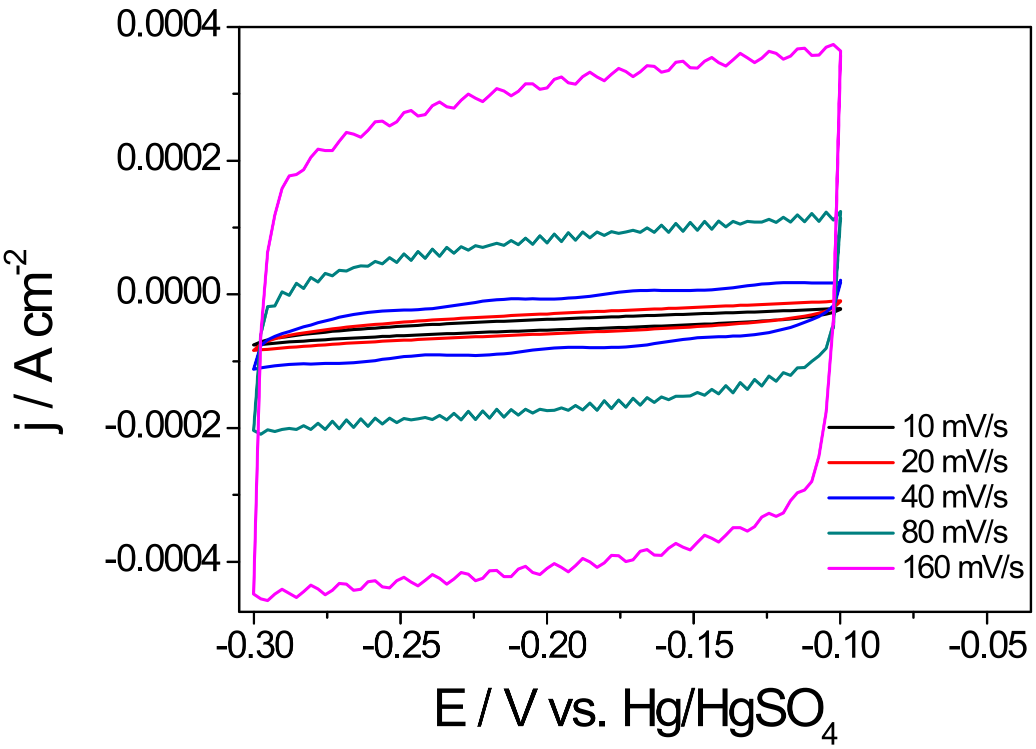

Fig. S5: CVs recorded for WS_2 QDs/CFP electrode in a non-faradaic region with increasing scan rate for the determination of ECSA from its double layer capacitance.

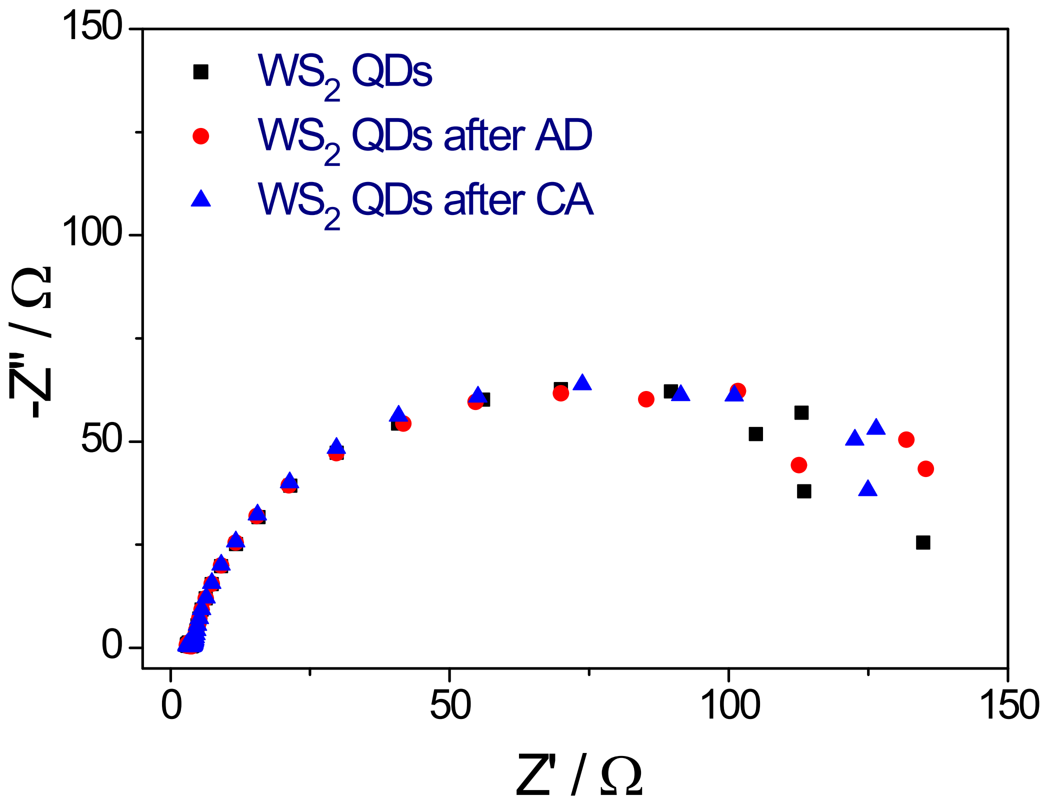

Fig. S6: Nyquist plots of WS_2 QDs/CFP interface obtained before and after stability studies.

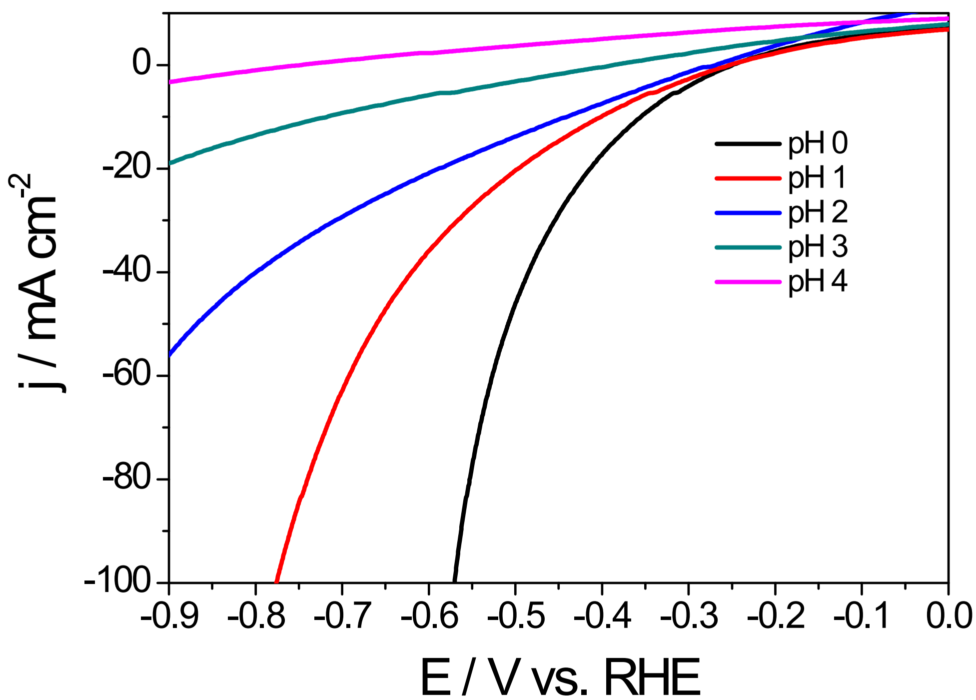

Fig. S7: pH dependent LSVs of WS_2 QDs/CFP interface acquired at 5 mV s^{-1} without iR drop compensation.

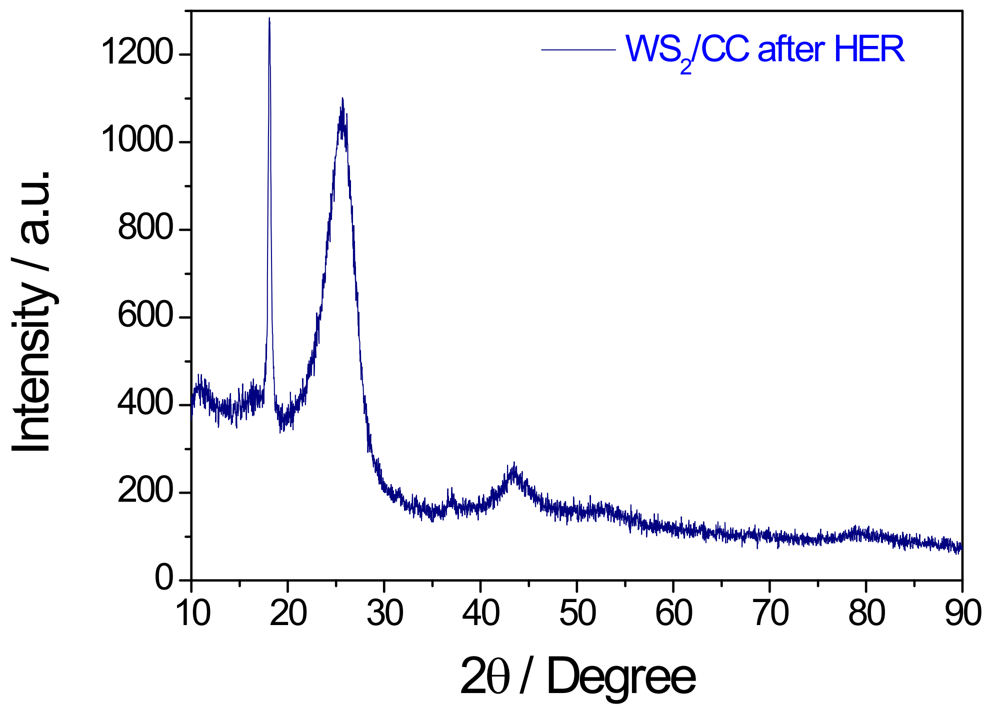

Fig. S8: XRD pattern of WS2 QDs/CFP electrode after prolonged chronoamperometry.

Table S1: Results of the electrocatalytic HER study in comparison with other reports

Catalyst	*Loading ($mg\ cm^{-2}$)*	*Overpotential at 10 $mA\ cm^{-2}$ (mV)*	*Tafel slope mV/dec*	*Reference*
Bulk WS_2 Sheets	**0.205**	**522**	**159**	***This work***
WS_2 QDs	**0.0132**	**255**	**90**	***This work***
WS_2-CNT	(a)	684	182	*J. Mater. Chem. A,* 2015, 3, 14609–14616
NiWSx	(a)	340 (5 $mA\ cm^{-2}$)	96	*Energy Environ. Sci.,* 2013, 6, 2452–2459
CoWSx	(a)	238 (5 $mA\ cm^{-2}$)	78	
WS_2-ND	0.0163	~120	51	*ACS Nano*, 2016, 10, 2159−2166
WS_2-NF	0.35	~410	48	*Angew. Chem. Int. Ed.* 2014, 53, 7860 –7863
WS_2-NF	1	~355	200	*Nano Research 2013, 6,921–928*
WS_2@NCNF	(a)	240	110	*ACS Appl. Mater. Interfaces.*, 2015, 7, 28116−28121
WS_2-NR	(a)	225	68	*Adv. Energy Mater.* 2014, *4*, 1301875
WS_2-NS	(a)	~215	60	*Nature Materials*. 2013, *12*, 850-853
WS_2-NS	0.285	150	138	*Applied Catalysis B: Environmental.,*125 (2012) 59– 66
WS_2-NS on Au foil	(a)	~325	100-104	*Nano Research.,* 8, (2015) 2881-2890
amorphous NiWS	(a)	265	55	*Applied Surface Science.,* 341 (2015) 149–156
amorphous CoWS	(a)	330	74	
$WS_{2(1-x)}Se_{2x}$	0.21	~ 255	105	*Acs Nano.,* 8 (2014), 8468-8476
$WS_{2(1-x)}Se_{2x}$ NR	~0.30± 0.02	170	68	*Adv. Funct. Mater.* 2015, *25*, 6077–6083
$WS_{2(1-x)}Se_{2x}$ on $NiSe_2$ foam	5.4	88	46.7	*Nano Lett.* 2016, 16, 7604−7609
WS_2-G	~ 6	119	43	*J. Mater. Chem. A,* 2016, 4, 9472–9476
WS_2/rGO hybrid NS	0.4	~ 260	58	*Angew. Chem. Int. Ed.* 2013, 52, 13751 –13754
WS_2-G	(a)	229	73	*Nanoscale,* 2015, 7, 14760–14765
(WS_3−x)	(a)	494	43.7	*ACS Appl. Mater. Interfaces* 2016, 8, 3948−3957
WSe_2	(a)	300	77.4	*Nano Lett.* 2013, 13, 3426−3433

Note: (a) - There is no information on the loading of the catalyst compared here. '~' denotes that the corresponding values were calculated from the available related data in the cited reports.