**Supplementary Information for** 

# Deconvolution of Phase-Size-Strain Effects in Metal Carbide Nanocrystals for Enhanced Hydrogen Evolution

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## **Experimental details**

## 1. Chemicals and Reagents

All the chemicals are obtained from certified reagent sources used without any further purification. Sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, AR, 99%), sodium tungstate dihydrate (Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, AR, 99%), cupric chloride dihydrate (CuCl<sub>2</sub>·2H<sub>2</sub>O, AR, 99.9%) and concentrated hydrochloric acid (HCl), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and potassium hydroxide (KOH) were purchased from SDFCL. 4,4'- bipyridyl (C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>), AR) and glacial acetic acid (CH<sub>3</sub>COOH, 16N, 99.99%), phosphomolybdic acid (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>), phosphotungstic acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) and melamine (C<sub>3</sub>H<sub>6</sub>N<sub>6</sub>) were bought from Sigma-Aldrich. Disodium hydrogen phosphate dihydrate (Na<sub>2</sub>HPO<sub>4</sub>·2H<sub>2</sub>O, AR) was purchased from Merck. Deionized water (TKA, 18.2 MΩ.cm) was used throughout the syntheses and all electrochemical measurements.

## 2. Synthesis:

*I\_Mo*: [H(C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>)Cu<sub>2</sub>][PMo<sub>12</sub>O<sub>40</sub>] & *2\_W*: [H(C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>)Cu<sub>2</sub>][PW<sub>12</sub>O<sub>40</sub>]. The POMOF crystals were synthesized using hydrothermal method according to literature procedure reported earlier by our group.<sup>1</sup> In a typical synthesis 0.5 g (2.07 mmol) Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O or 0.682 g (2.07 mmol) of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, 0.42 g (1.391 mmol) Na<sub>2</sub>HPO<sub>4</sub>, 0.238 g (1.396 mmol) CuCl<sub>2</sub>·2H<sub>2</sub>O and 0.268 g (1.387 mmol) of 4,4 $\square$ -bp was added sequentially in a 50 mL Teflon line autoclave, containing 35 mL distilled water and the final

pH of the reaction was adjusted to ~2 by adding glacial acetic acid and conc. HCl. Finally, the reaction mixture was kept at 180 °C for a period of 5 days, which on cooling yielded nice rectangular crystals of  $[H(C_{10}H_{10}N_2)Cu_2][PMo_{12}O_{40}]$  and  $[H(C_{10}H_{10}N_2)Cu_2][PW_{12}O_{40}]$ .

In the next step  $I_Mo$  and  $I_W$  were separately mixed with melamine (1:1 or 1:2 molar ratio of POM:Melamine) by thorough mechanical grinding and 100 mg of that homogeneous mixture was vacuum sealed in quartz ampules (13 mm dia) under ~ 10<sup>-5</sup> bar pressure and annealed at 900 °C in a tube furnace for 5 h with a heating rate of 3 °C/min. For controlled studies the carbonization was conducted at 3 different temperatures 800 °C, 900 °C and 1000 °C under varying ramp rates of 2 °C/min and 5 °C/min and quenching in the cooling step. As controls, only commercially obtained precursors (H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub>, H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) were also carbonized with melamine in the same molar ratio following similar temperature profiles. To check the effect of melamine during the annealing process, melamine in the first step is expected to convert to carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) around 500 °C and subsequently to N-doped graphitic carbon (NGC) at elevated temperatures. Melamine along with organic ligands of the POMOF structures also leads to carbonization and reduction of the transition metal oxide clusters after their thermal degradation.

The black powder samples after carbonization were etched with 0.5 M  $H_2SO_4$  at 80 °C for 12 h. The compounds after acid etching were thoroughly washed, alternatively with deionized water and ethanol. After each wash, the solution was centrifuged at 8000 rpm to remove the supernatant containing unstable and inactive species. The samples after washing, were dried under vacuum and used for further characterization and electrochemical studies.

Catalyst	Hybrid precursor	ТМ	POM:Mel Ratio	Annealing Temp (°C)	Heating Rate (°C/min)
2-W(1:1)-2	2	Tungsten	1:1	900	2
1-Mo(1:1)-2	1	Molybdenum	1:1	900	2
2-W(1:2)-5	2	Tungsten	1:2	900	5
1-Mo(1:2)-2	1	Molybdenum	1:2	900	2
2-W(1:1)-5-Q	2	Tungsten	1:1	900	5
2-W(1:1)-5	2	Tungsten	1:1	900	5
2-W-1000-5	2	Tungsten	1:1	1000	5
PW12-Ctr	POM	Tungsten	1:1	900	5

Sample Code Table:

#### 3. Characterization

3.1 Powder X-ray Diffraction (PXRD). Powder X-ray diffraction patterns of the samples were measured at room temperature on a Rigaku Miniflex X-ray diffractometer having a Cu–K $\alpha$  X-ray source ( $\lambda = 1.5406$  Å), equipped with a position sensitive detector in the angular range of  $10^{\circ} \le 2\theta \le 90^{\circ}$ . The measurements were conducted between  $10^{\circ}$  to  $90^{\circ}$  at a step size of  $0.02^{\circ}$  and a scan rate of 0.5 s/step, calibrated against corundum standards. To check phase purity, the experimental PXRD patterns were matched with the simulated patterns of relevant phases reported in literature.

Scherrer Equation: To analyse the average crystallite size from PXRD, the peak at  $2\theta$  =

48.32° was fit with the Scherrer equation,  $B_C = \frac{k\lambda}{LCos\theta}$ , where  $\lambda$  = Wavelength (1.54 nm for Cu-K $\alpha$ ), L = Average crystallite size ( $\perp$  to surface of specimen), k = 0.94 [k  $\in$  (0.89, 1.39)],  $B_C$  is the peak width (full width at half maxima) in radian.

Williamson-Hall plot: To deconvolute the size and strain effect in PXRD peak broadening, the Williamson-Hall plot was constructed using the formula, where the notations have their usual meanings as mentioned above.<sup>2</sup> A plot of  $B_r Cos(\theta)$  vs

 $\frac{k\lambda}{L}$ , where L is the crystallite size, while the slope  $\eta Sin(\theta)$  gives the strain. Larger the slope, larger is the strain while larger is the intercept, smaller is the crystallite size. The peak parameters used in the W-H plot were extracted from the XRD patterns of the samples by fitting it in the *Fityk* software package with pseudo-Voigt analytical function.

**3.2** Elemental Analysis. Quantitative compositional analyses on all the samples was performed using an FEI NOVA NANOSEM 600 instrument equipped with an EDAX instrument. Individual data were obtained at an accelerating voltage of 20 kV and a 100 s accumulation time. The EDAX analysis was carried out by the P/B-ZAF standard less method (where P/B = peak to background model, F = fluorescence factor, A = absorption correction factor, Z = atomic no. correction factor) on selected areas and points.

**3.3 Transmission Electron Microscopy (TEM).** TEM images, high resolution TEM analysis, selected area electron diffraction (SAED) patterns and elemental colour mapping were performed using TECNAI and JEOL 200 kV TEMs. The samples for microscopic measurements were prepared by ultrasonication of minute quantity of the nanocrystalline

powders in ethanol and drop casting a very small volume of that onto a carbon-coated copper grid. For elemental colour mapping/EDS analyses, Ni grid was used instead of Cu, as our samples may have contained Cu.

**3.4 X-ray Photoelectron Spectroscopy (XPS).** An Omicron Nanotechnology spectrometer was used for the XPS measurement which was equipped with a Mg–K $\alpha$  (1253.6 eV) X-ray source with a relative composition detection power better than 0.1%. Surveyscans and XPS spectra at individual elemental windows are measured and qualitative analyses were done after fitting the spectra using the Fityk software.

**3.5** Raman Spectroscopy: Raman spectra on the powdered nanocrystalline samples were measured in the backscattering geometry using a custom built Raman spectrometer equipped with a 532 nm laser excitation. A laser power of  $\sim$ 2 mW was used to obtain the unpolarized Raman spectra at room temperature.

3.6 X-ray Absorption Spectroscopy.: X-ray absorption near edge spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) experiments at 300 K were performed at the 11.1R, of the ELETTRA Synchrotron Radiation facility, Trieste, Italy and at BM26A beamline at ESRF, Grenoble, France. Monochromatic X-rays were produced using a Si (111) double crystal monochromator, calibrated by defining the inflection point (first derivative maxima) of Cu foil as 8980.5 eV. The transmitted signals were recorded using a CCD detector. The measurements were done at room temperature in the transmission mode using three ionization chambers mounted in series for simultaneous measurements on the sample and a reference. About 5-15 mg of the powdered samples were finely mixed and ground with inert cellulose matrix and uniform pellets of 10 mm were prepared by pressing. To ensure the reproducibility of the spectral features and to have high signal to noise ratio, at each temperature more than one X-ray absorption scans were collected. EXAFS measurements were done in transmission mode at the K-edges of: Mo (K edge: 19.9995 keV), W (LIII edge: 10.2068 keV) at ambient pressure. The data analyses (background subtraction, normalization, and alignment of the EXAFS data) and EXAFS fitting were done using the Athena and Demeter software packages.<sup>3, 4</sup> EXAFS data of the catalyst materials were Fourier transformed, plotted in *R* space and analyzed.

**4. Electrochemical Studies.** All the electrochemical measurements were performed in a three-electrode setup using a CHI 760E electrochemical workstation. Commercial glassy carbon (GC) electrode (3 mm diameter) as used as the working electrode (WE), platinum wire and carbon rod as the counter electrodes (CE), and saturated calomel electrode (SCE) (acidic) or Hg/HgO (MMO) (alkali) as the reference electrode (RE). Five μL of the catalyst

ink (2 mg catalyst in 200  $\mu$ L of IPA: H<sub>2</sub>O, 1:2 v/v) was drop casted on GC WE (0.7 mg/cm<sup>2</sup>), with a subsequent coating of 5 µL of 0.1 % nation binder on the top. The WEs were dried overnight in air before use. For cleaning, the GCE was polished with 0.05 µm alumina slurry and cleaned repeatedly with distilled water/IPA. 20 wt% Pt/C and Pd/C (commercial, Sigma Aldrich) were used for comparative activity study with the reported electrocatalysts. All polarization curves obtained from linear sweep voltammetry (LSV) studies were recorded at a scan rate of 5 mV s<sup>-1</sup> at room temperature. LSV studies were preceded by 40 cyclic voltammetry (CV@50 mV/sec) cycles in the non-HER region (0.0 V to 0.6 V) to clean surface impurities and obtain stable CV currents in consecutive cycles. The Tafel slope is an indicator of the rate determining step (r.d.s.) and mechanism of HER, which was be obtained by fitting the linear Tafel equation ( $\eta = b \log j + a$ , where  $\eta = overpotential$ , j = currentdensity and b =Tafel slope) near the onset region of the polarization curves. Electrochemical impedance spectroscopic (EIS) studies were performed at different applied DC potentials (depending on onset of a particular reaction) in the frequency range from 10 mHz to 100 kHz. All electrochemical experiments were performed using deaerated electrolytes, after min. 30 mins of N<sub>2</sub> purging.

All the REs were calibrated w.r.t. the reversible hydrogen electrode (RHE), using Pt as both WE & CE in the respective electrolytes. The calibration values obtained as: acidic medium (0.5M H<sub>2</sub>SO<sub>4</sub>),  $E_{RHE} = E_{SCE} + 0.26905$  V; alkaline medium (0.5M KOH),  $E_{RHE} = E_{MMO} + 0.9414$  V.

**4.1 Estimation of effective electrode surface area.** Electrochemical double layer capacitance ( $C_{dl}$ ) at non-Faradaic regions was used to qualitatively estimate the electrochemically active surface area (ECSA) of the catalysts. For  $C_{dl}$  studies, cyclic voltammetry (6 cycles) at different scan rates (10, 20, 30, 50, 80, 100 mV s<sup>-1</sup>, **Figure S8**). A 1

plot of  $\overline{2}\Delta J (J_{\text{anodic}} - J_{\text{cathodic}} @ E_{1/2} \text{ of the potential window) vs. the scan rate showed a linear trend ($ **Figure 9a**), the slope of which gave the corresponding C<sub>dl</sub> values (Slope = 2 x C<sub>dl</sub>), which is proportional to the ECSA of the catalysts.

**4.2** Calculation of TOF. The turn over frequency (TOF) of the catalysts is expected to be a function of the number of active sites which can be calculated from the integrated area under the cyclic voltammogram.<sup>5</sup>

Number of active sites (in mol) = Area under the curve / (2 \* F)

TOF  $(in s^{-1}) = I / 2nF$ 

Where, I = Current (in A) from LSV, F = Faraday constant (in C mol<sup>-1</sup>), n = Number of active sites (in mol).

The factor of 1/2 comes from the number of electrons involved (2) in HER.

The area under the CV curve for the catalysts are calculated by integration of the CV plots.

# 5. Theoretical Calculations

All the calculations were carried out using Dmol3 program.<sup>6</sup> GGA-PBE functional was used to describe the electronic exchange and correlation effects. DND is chosen as the basis set with orbital cut-off of 3.5 Å. The convergence threshold values for energies, gradient and displacement are specified as  $2x10^{-5}$  Ha,  $5x10^{-3}$  Å, respectively, while the SCF convergence threshold is  $1x10^{-5}$  Ha. Electron thermal smearing value of 0.005 Ha is employed for all the calculations to enhance SCF convergence efficiency. A vacuum slab of 10 Å was used to prevent any interaction with the neighboring slab along *c* direction.

We applied the *d*-band model proposed by Hammer and Nørskov.<sup>7</sup> According to this model, the higher the *d*-band center, the greater the binding and, hence, the catalytic activity. The *d*-band center ( $\varepsilon_d$ ) is given by the following relation in this model:

$$\varepsilon_{\text{avg}} = \frac{\int_{-\infty}^{E_f} E\rho(E) dE}{\int_{-\infty}^{E_f} \rho(E) dE}$$

where  $\rho$  is the projected density of *d*-states of surface atoms, *E* is the energy, and *E<sub>F</sub>* is the Fermi-level.

## Tables

Element	H/POM:Mel	Temp (°C)	Rate	Major phase	Minor Phase
	ratio		(°C/min)		
Мо	1:1	900	2	Mo <sub>2</sub> C_Pbcn	MoC_ <i>Fm</i> <sup>3</sup> m
			5	Mo <sub>2</sub> C_Pbcn	MoC_ <i>Fm</i> <sup>3</sup> m
		800	5	-	-
	PMo <sub>12</sub> -Ctr	900	2	MoC_Fm <sup>3</sup> m	Mo <sub>2</sub> C_Pbcn
	1:0	900	5	$M_0O_2_P2_1/c$	-
	1:2	900	2	MoC_ <i>Fm</i> <sup>3</sup> m	Mo <sub>2</sub> C_Pbcn
			5	MoC_ <i>Fm</i> <sup>3</sup> <i>m</i>	Mo <sub>2</sub> C_Pbcn

Table S1. Results of synthetic outcomes forming different phase of molybdenum carbide.

Element	H/POM:Mel	Temp (°C)	Rate	Major phase	Minor Phase
	ratio		(°C/min)		
W	1:1	900	2	WC_ $P^{\overline{6}}m2$	-
			5	WC_ $P^{\overline{6}}m^2$	-
		800	5	-	-
		1000	5	WC_ <i>P</i> <sup>6</sup> <i>m</i> 2	-
	PW <sub>12</sub> -Ctr	900	5	WC $P^{\overline{6}}m2$	-
	1:0	900	5	$WO_3 P^{\overline{1}}$	-
		1000	5	$W_{Im}^{3}m$	$WO_2 P2_1/c$
	1:2	900	2	WC_Fm <sup>3</sup> m	-
			5	WC_Fm <sup>3</sup> m	-

Table S2. Results of synthetic outcomes forming different phase of tungsten carbide.

**Table S3.** Results of electrochemical HER studies on different electrocatalysts reported in this work.

Catalyst	Onset	η10	η25	η50	η120	Tafel Slope	R <sub>CT</sub>	C <sub>dl</sub>	TOF
			mV			mV/dec	ohm	mF/cm <sup>2</sup>	sec <sup>-1</sup>
Pt	5	17	30.5	53	138	30.2			
Pd	10	28	58	105	240	52.7			
2-W(1:1)-2	77	184	247.7	320		119.4			
1-Mo(1:1)-2	150	246	302.5	358.5		100.1	580		
2-W(1:2)-5	185	277	350		-	90.1			
1-Mo(1:2)-2	100	285		-		178.1	890		
2-W(1:1)-5-Q	82	162	205	251	350	77.5	180	47.95	45
2-W(1:1)-5	68	159	210	266	380	94.6	310	63.77	30
2-W-1000-5	88	258	374			128.3		10.85	
PW12-Ctr	96	257	344			132.4		15.65	

TableS 4. Results of size-strain modulation	of different 2	_W(1:1) samples a	as obtained from
Scherrer and W-H analyses.			

Sample	Size (Scherrer) nm	Size (W-H) nm	Strain x 10 <sup>-3</sup>
2-(1:1)-1000-5	25.27	26.1	2.3
PW12-Ctr-5	18.19	24.1	19.3
2-(1:1)-2	11.09	10.97	21.5
2-(1:1)-5	6.15	5.7	19
2-(1:1)-5-Q	5.68	5.9	56

 Table S5. XAFS R-Space fitting for primary sphere of W-C paths.

Sample		Ν	<b>S</b> <sub>0</sub> <sup>2</sup>	$\Sigma^2$	e0	del r	R <sub>eff</sub>	R
2-(1:1)-900-5	С	6	0.747	0.0071	7.756	-0.00339	2.189	2.186
	W	6	0.801	0.0029	7.756	-0.00489	2.897	2.892
PW <sub>12</sub> -Ctr-5	С	6	1.6	0.0166	7.020	-0.00448	2.1899	2.1854
	W	6	0.92	0.0034	7.020	0.00476	2.8970	2.9017

 Table S6. TOF analyses of different electrocatalysts.

Sample	Particle Size (nm)	TOF@350 mV (s <sup>-1</sup> )	TOF@250 mV (s <sup>-1</sup> )
2-W(1:1)-1000-5	25.7	43.65319	18.30618
PW12-Ctr-900-5	21	39.49329	13.71088
2-W(1:1)-900-2	11	78.17722	32.63291
2-W(1:1)-900-5-Q	6.05	44.91717	18.38855
2-W(1:1)-900-5	5.65	30.19146	12.20324
1-Mo(1:1)-900-2		72.40773	19.33216

Catalysts	WE	СЕ	RE	Electrolyte	Onset	Tafel	R <sub>CT</sub>	η10	η50	Ref
					mV	mV/dec	ohm	mV	mV	
2-W(1:1)-2	GC	Pt/C-rod	SCE	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	77	119.4		184		
2-W(1:1)-5	GC	Pt/C-rod	SCE	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	68	94.6	310@0.18V	159	266	This
2-W(1:1)-5-Q	GC	Pt/C-rod	SCE	$0.5 \mathrm{M} \mathrm{H}_2 \mathrm{SO}_4$	82	77.5	180@0.18V	162	251	Work
Mo <sub>2</sub> C-NCNT	Carbon sheet	Carbon rod	Ag/AgCl	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	72	71	53 @0.1V	147	320	8
α-Mo <sub>2</sub> C-NP	GC-RDE	Carbon rod	MMO	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	-	56	-	198		9
Mo <sub>0.06</sub> W <sub>1.94</sub> C/CB	GC	Pt	Ag/AgCl	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	-	-	-	220		10
Mo <sub>2</sub> C-carbon	GC-RDE	Carbon rod	Ag/AgCl	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	100	110	-	N/A		11
nanocomposite										
β- Mo <sub>2</sub> C	GC			0.1 M HClO <sub>4</sub>	N/A	120		N/A		12
np-Mo <sub>2</sub> C	GC-RDE	Pt mesh	SCE	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	N/A	100.7		229		13
$Mo_2B_4$	Carbon sheet	Graphite	SCE	$0.5 \text{ M} \text{H}_2 \text{SO}_4$		80	46 @0.2V	270		14
		rod						(ŋ <sub>3.5</sub> )		
W <sub>2</sub> C/MWNT	GC	Carbon rod	SCE	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	50	45	20 @0.18 V	123		15
WC/MWNT	GC	Graphite	SCE	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	~150	78	300 @0.18 V	250		15
		rod								
WC	CFP	Carbon rod	Ag/AgCl	$0.5 \text{ M H}_2 \text{SO}_4$	-	166	-	193	322	16
WC nano array	CFP	Carbon rod	Ag/AgCl	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	-	110	-	160	245	16

 Table S7. Comparative catalytic activity table for some of the related electrocatalysts reported in literature

# Figures



Scheme S1. Schematic illustration of synthetic outcomes of the electrocatalysts in MoC and WC systems.



Figure S1. Raman spectra showing the D and G bands of the electrocatalysts.



Figure S2. (a) & (b) shows the I<sub>D</sub> and I<sub>G</sub> bands in the Raman spectra of  $2_W(1:1)$ -900-5 &  $1_Mo(1:1)$ -900-2 and (c) & (d) respectively shows the survey scan and Mo-3d XPS spectra of  $1_Mo(1:1)$ -900.



Figure S3. XPS spectra of the (a) C1s, (b) N1s of 1\_Mo(1:1)-900, and XPS spectra of the (d) C1s, (e) W4f, (f) N1s of 2\_W(1:1)-900.



Figure S4. PXRD patterns of controlled synthesis. (a) Comparison of PXRD patterns of controlled MoC synthesis using different precursors and precursor ratios, (b) PXRD patterns  $1_Mo(1:1)$  &  $2_W(1:1)$  synthesized at 800 °C, (c) PXRD patters of  $2_W$  synthesized at different temperatures without melamine precursor, and (d) PXRD of  $1_M$  synthesized in absence of melamine precursor.



**Figure S5.** (a) TGA plots of hybrids 1(Mo) & 2(W),<sup>1</sup> (b) ) Magnified PXRD peak of (101) plane of different 2\_W(1:1) samples, (c) Profile fitting of different samples of 2\_W(1:1), (d) Plot of parameters obtained from W-H analyses for different 2\_W(1:1) sample.



Figure S6. TEM analyses of  $1_Mo(1:1)$ -900 and  $2_W(1:1)$ -900 samples. (a) SAED pattern, (b) HR-TEM showing the d-spacing of (111) plane of MoC phase, (c) & (d) elemental colour mapping of Mo in  $1_Mo(1:1)$ -900, (e) SAED pattern of  $2_W(1:1)$ -900, (f) microscopic image showing the layers of graphitic carbon, (g) & (h) HR-TEM images on particles of  $2_W(1:1)$ -900 showing the d-spacing corresponding to the (100) & (111) planes of WC hexagonal phase, (i-l) elemental colour mapping images of  $2_W(1:1)$ -900. One of the red boxes (1/2) in the elemental mapping figures signifies the actual scan area for colour mapping, while the other (2/1) corresponds to the reference position of red box 1.



Figure S7. TEM analyses of particle size distribution and nature of the electrocatalysts, (a)  $2_W(1:1)$ -900-5, (b)  $2_W(1:1)$ -900-5-Q, (c)  $2_W(1:1)$ -900-2, (d)  $PW_{12}$ -Ctr-900-5 (e)  $2_W(1:1)$ -1000-5.



Figure S8. CV at different scan rates in the non-Faradaic region for determination of  $C_{dl}$  for (a) 2\_W(1:1)-900-5, (b) 2\_W(1:1)-900-5-Q, (c)  $PW_{12}$ -Ctr(1:1)-900-5 and (d) 2\_W(1:1)-1000-5.



Figure S9. (a) CV at different scan rates in the non-Faradaic region and (b)  $\Delta j$  vs Scan rate plots for 2\_*W*(1:1)-900-5-*Q* for determination of C<sub>dl</sub> after electrochemical ADT.



Figure S10. Fitted R-space XAFS spectra of (a) PW12-Ctr-900-5 and (b) 2(1:1)-900-5.



Figure S11. (a) Comparison of the HER polarization curves of the best WC & MoC catalysts, (b) Comparative HER LSVs for two of the best WC catalysts ( $2_W(1:1)$ -900-5-Q &  $2_W(1:1)$ -900-5), (c) Comparison of HER polarization curves of  $2_W(1:1)$ -900-5-Q in acidic and alkaline media, (d) Comparative HER LSVs for two of the best WC catalysts in 0.5 M KOH, (e) j/C<sub>dl</sub> plots for different WC catalysts and (f) LSVs demonstrating the electrochemical HER stability of 1 Mo(1:1)-900 after 2000 ADT cycles.



Figure S12. (a) Comparison of the PXRD patterns of different carbon samples (controls)



**Figure S13.** (a) Comparison of the HER polarization curves of different carbon samples (controls), (b)  $C_{dl}$  plots for different carbon samples (controls)



**Figure S14.** Quantitative analysis of parameter-activity relationships: (a) d-band centre of different phases vs. current density @ -0.35 V (vs. RHE) of the catalysts obtained from the polarization curves for HER in acidic media, (b) crystallite size (average of those obtained from Scherrer and W-H analyses) of different catalysts vs. current density @ -0.35 V (vs. RHE) of the catalysts obtained from the polarization curves for HER in acidic media, (c) C<sub>dl</sub> of different catalysts vs. current density @ -0.35 V (vs. RHE) of the catalysts obtained from the polarization curves for HER in acidic media, (d) strain of different catalysts obtained from the polarization curves for HER in acidic media, (d) strain of different catalysts obtained from the polarization curves for HER in acidic media, (d) strain of the catalysts obtained from the polarization curves for HER in acidic media.



**Figure S15.** Quantitative analysis of size-strain-activity relationships: (a) Linear fit of crystallite sizes of selected catalysts vs. current density @ -0.35 V (vs. RHE) of the catalysts obtained from the polarization curves for HER in acidic media, (b) Linear fit of  $C_{dl}$  of selected catalysts vs. current density @ -0.35 V (vs. RHE) of the catalysts obtained from the polarization curves for HER in acidic media.

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