Supporting Information

Comprehensive insights on hydrolysis-mediated hydrogen production using high entropy quintuple alloy grafted carbon black

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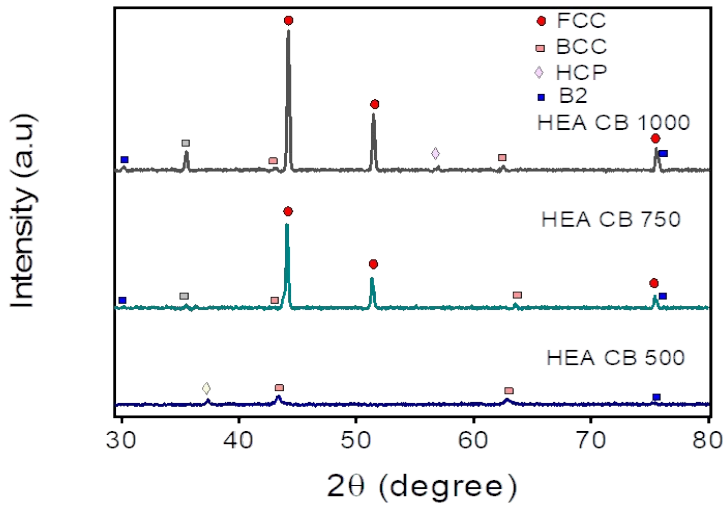


Figure S1. XRD patterns of HEA CB 1000, HEA CB 750 and HEA CB 500 indicating the development of fcc phase on raising synthesis tempearature.

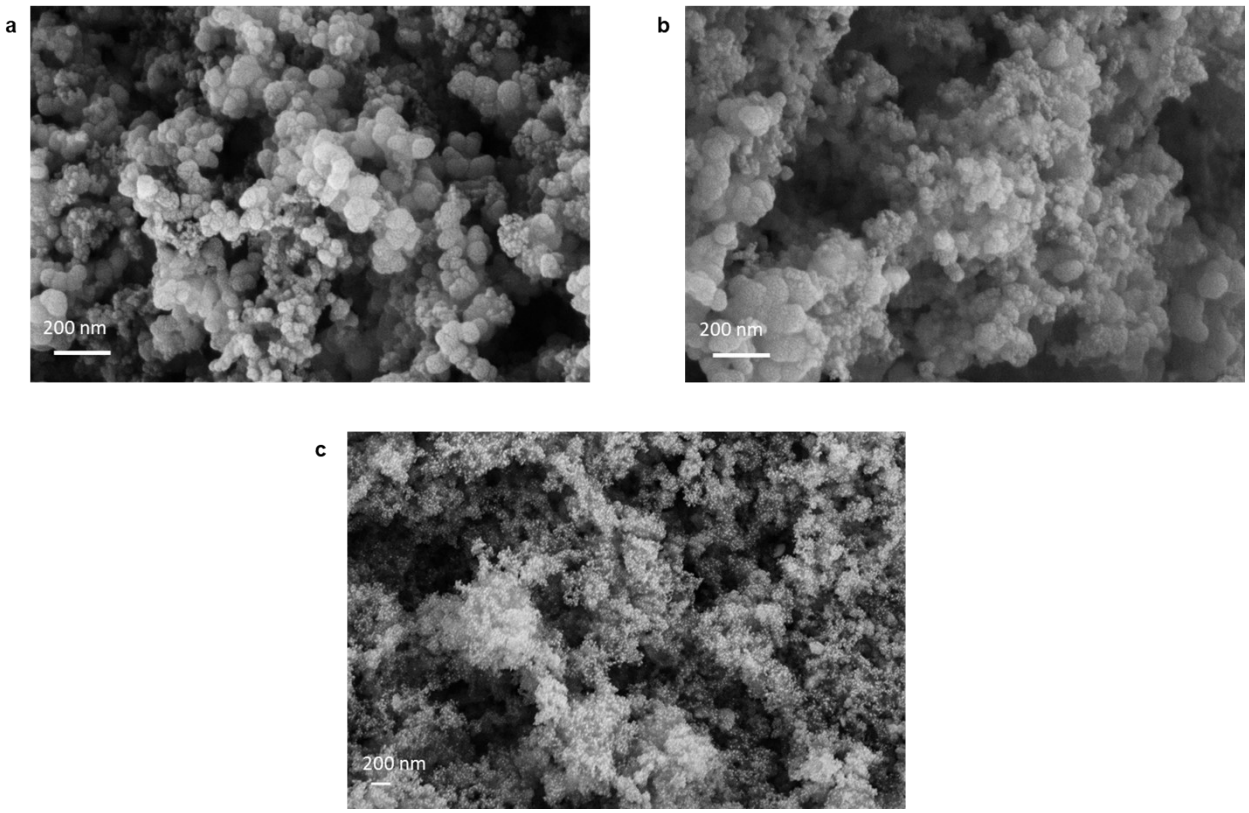


Figure S2. SEM images of (a) HEA CB 1000, (b) HEA CB 750, (c) HEA CB 500 showing that the globular conductive carbon support is decorated with HEA particles..

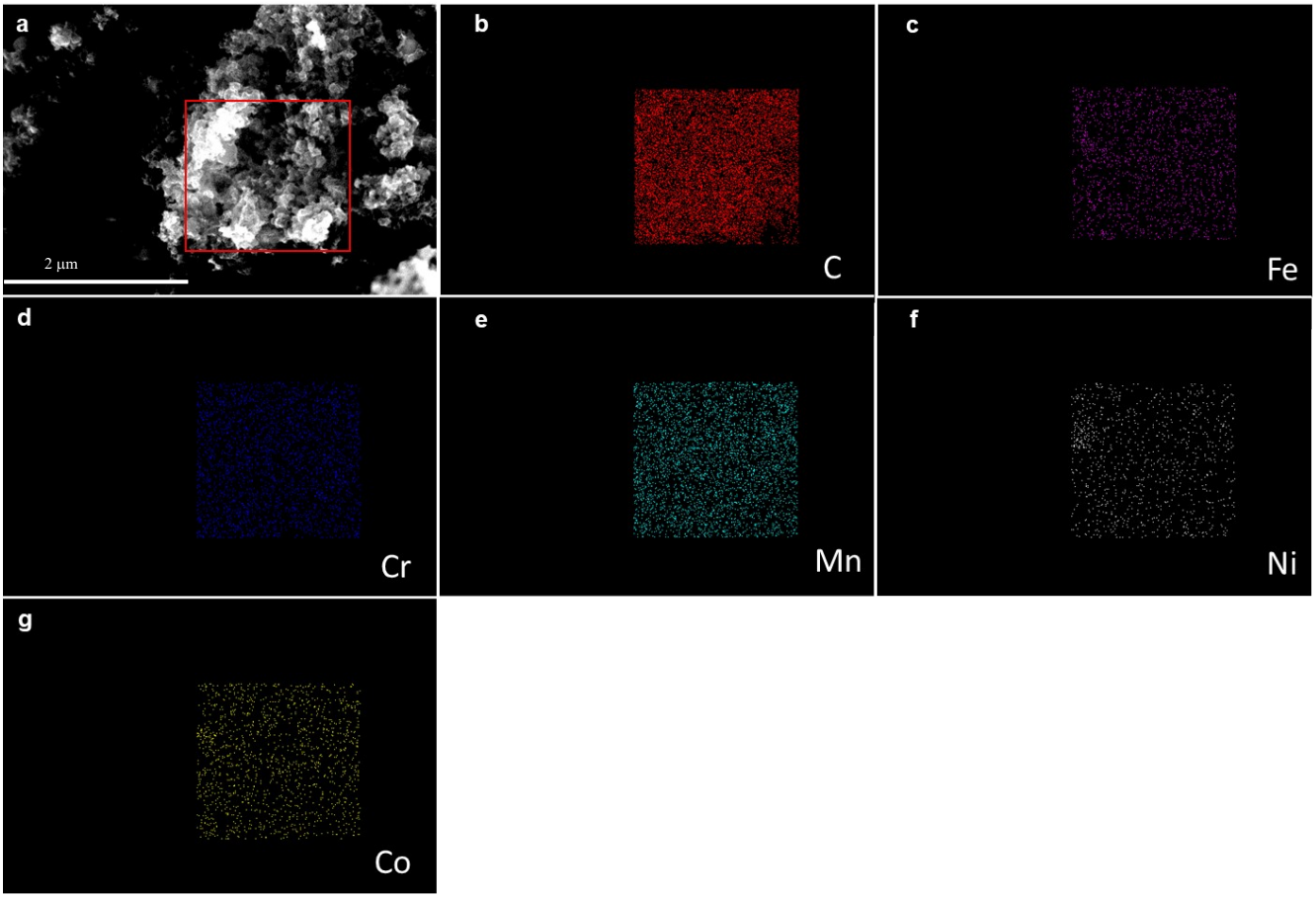
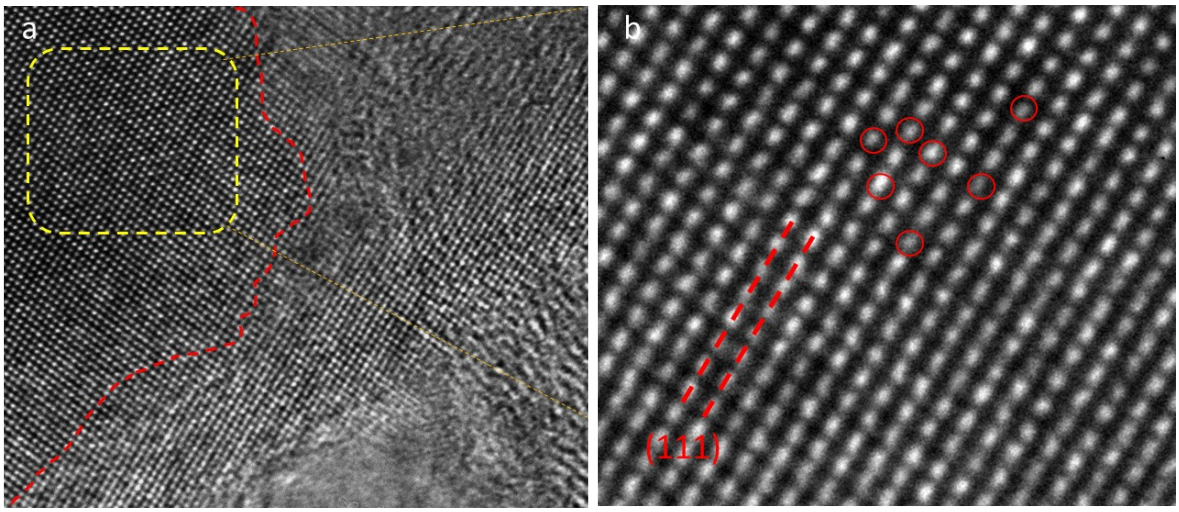


Figure S3. (a) SEM images of a representative region of HEA CB 1000 and EDS elemental map of (b) carbon, (c) iron, (d) chromium, (e) manganese, (f) nickel, and (g) cobalt.



FigureS4. (a) Aberration corrected HR TEM of HEACB 1000, and (b) enlarged image of the fringes showing the contrast in the different atoms.

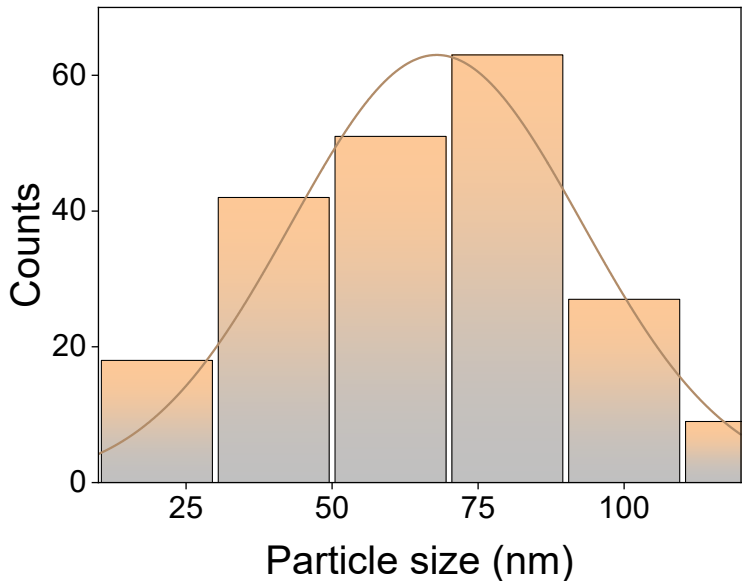


Figure S5. Particle size distribution plot of HEACB 1000 catalyst.

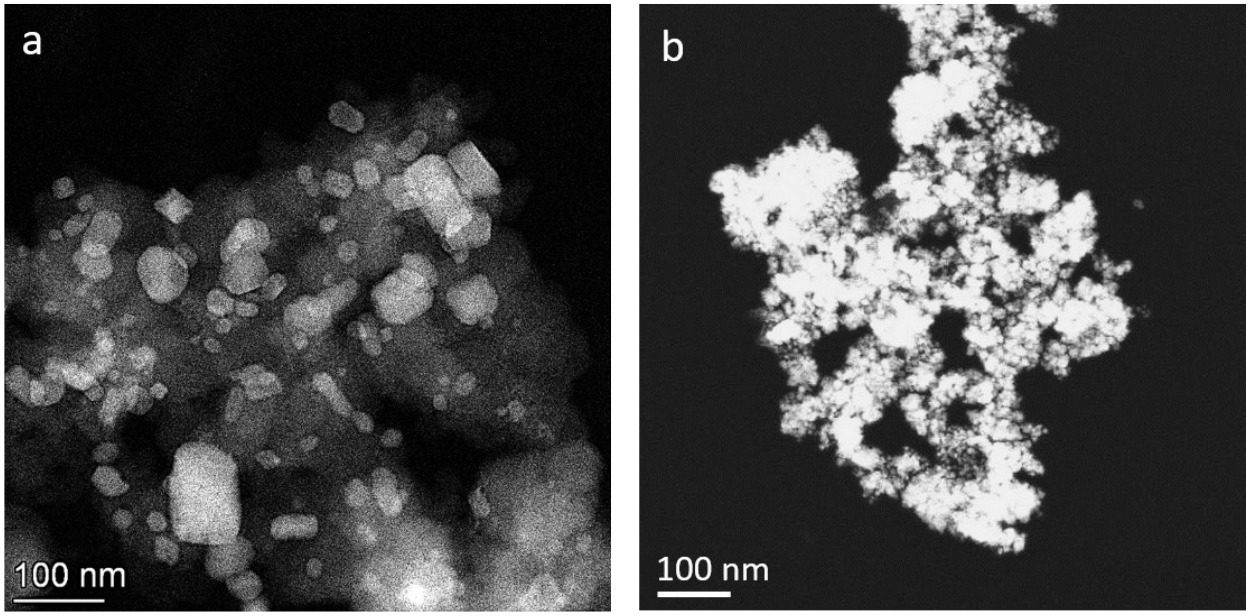


Figure S6. (a) Dark field TEM image of HEACB 1000 and (b) bare HEA

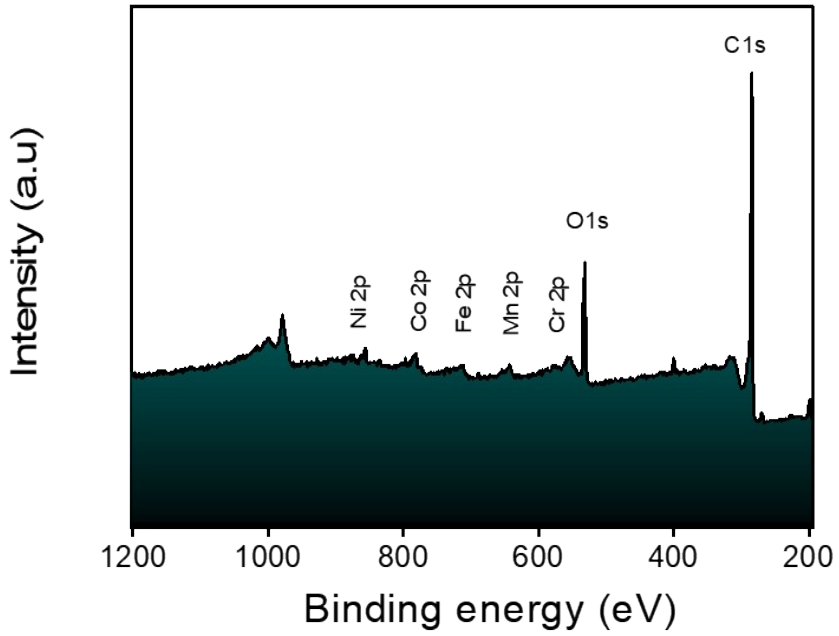


Figure S7. XPS wide spectra of HEA CB 1000 indicating the peaks corresponding to Co, Cr, Mn, Ni, Fe along with C.

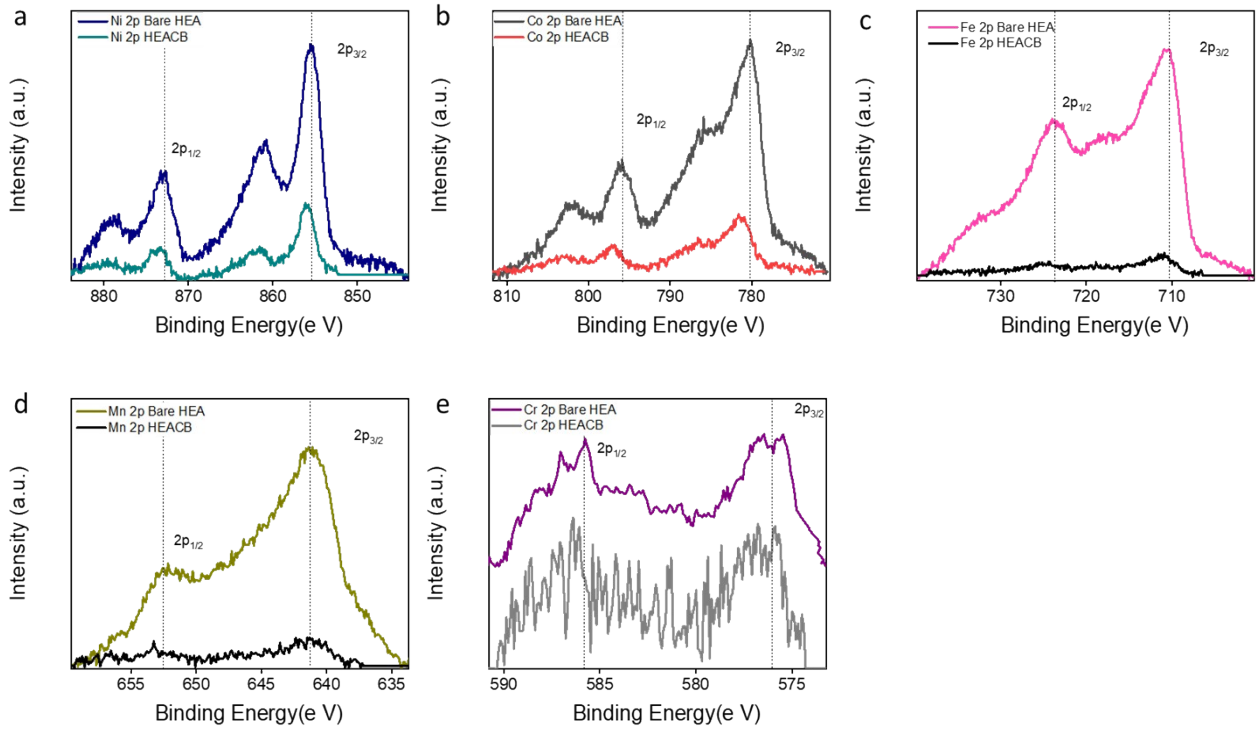


Figure S8. (a-e) Comparitivve XPS analysis of Ni, Co, Fe, Mn, Cr respectively of HEACB and bare HEA catalyst.

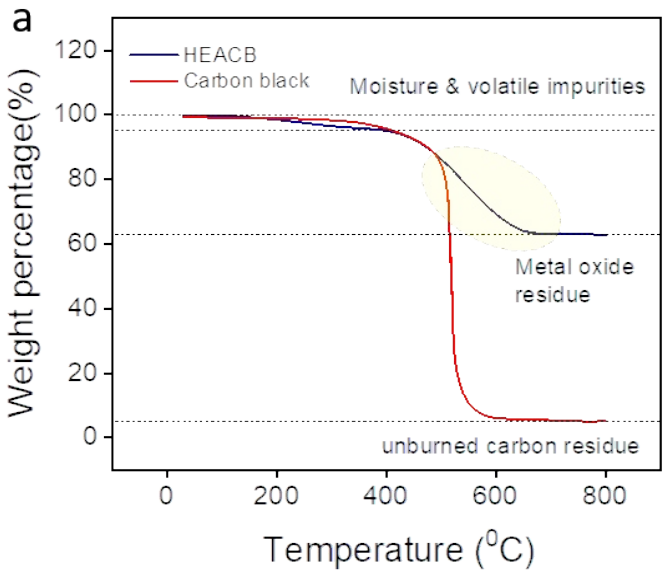


Figure S9. (a) TGA profile of HEACB 1000 and bare CB in oxygen atmosphere,

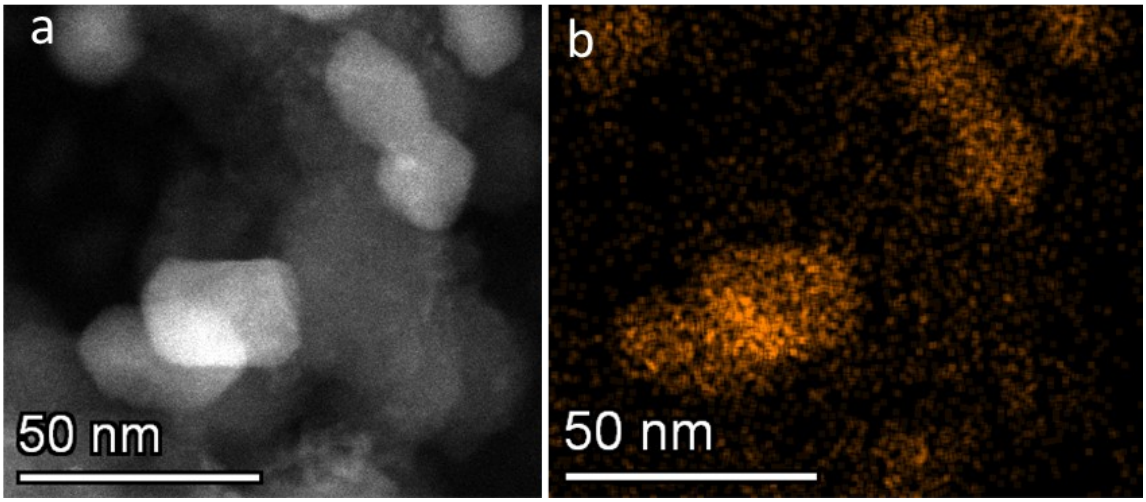


Figure S10. (a) TEM image of a representative HEACB 1000 particle and (b) corresponding oxygen elemental mapping

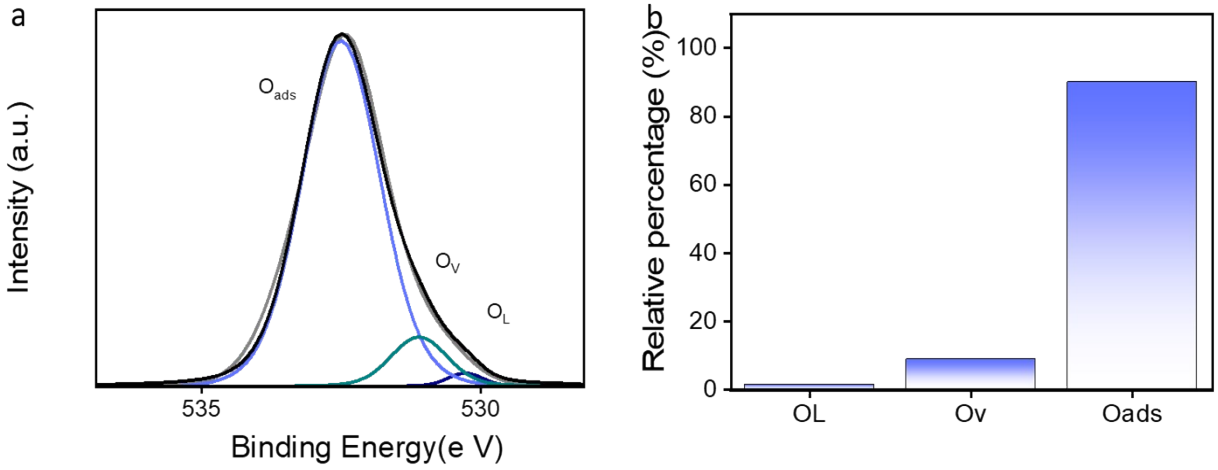


Figure S11. (a) Resolved HR XPS of O1s of HEACB 1000 and (b) percentages of oxygen types represented as bar diagram

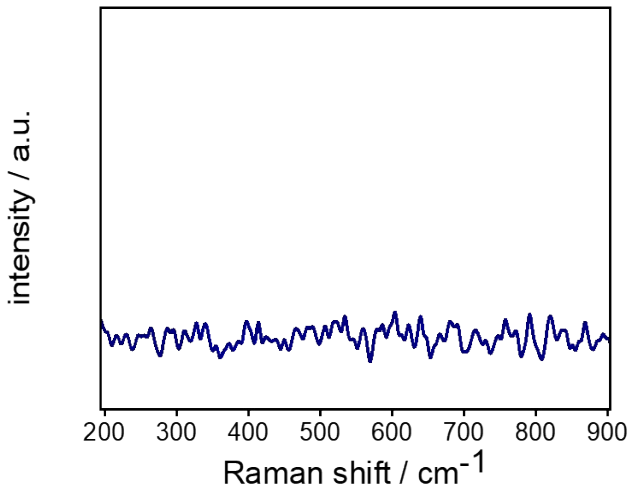


Figure S12. Raman spectra in the lower wavenumber region for HEACB 1000.

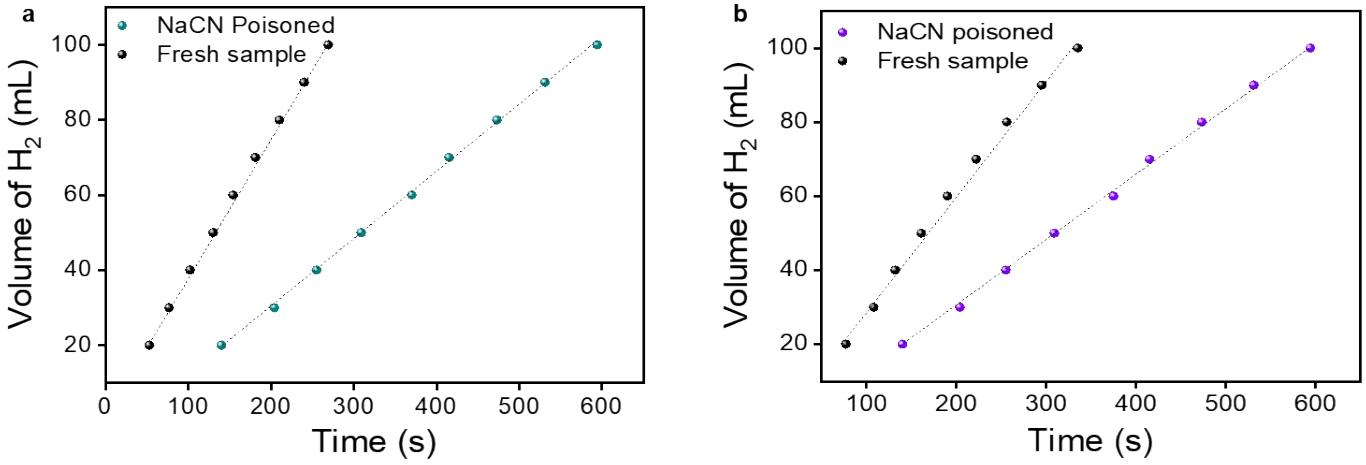


Figure S13. Effect of cyanide poisoning on the rate of hydrogen evolution of -(a) HEA CB 750, and (b) HEA CB 500.

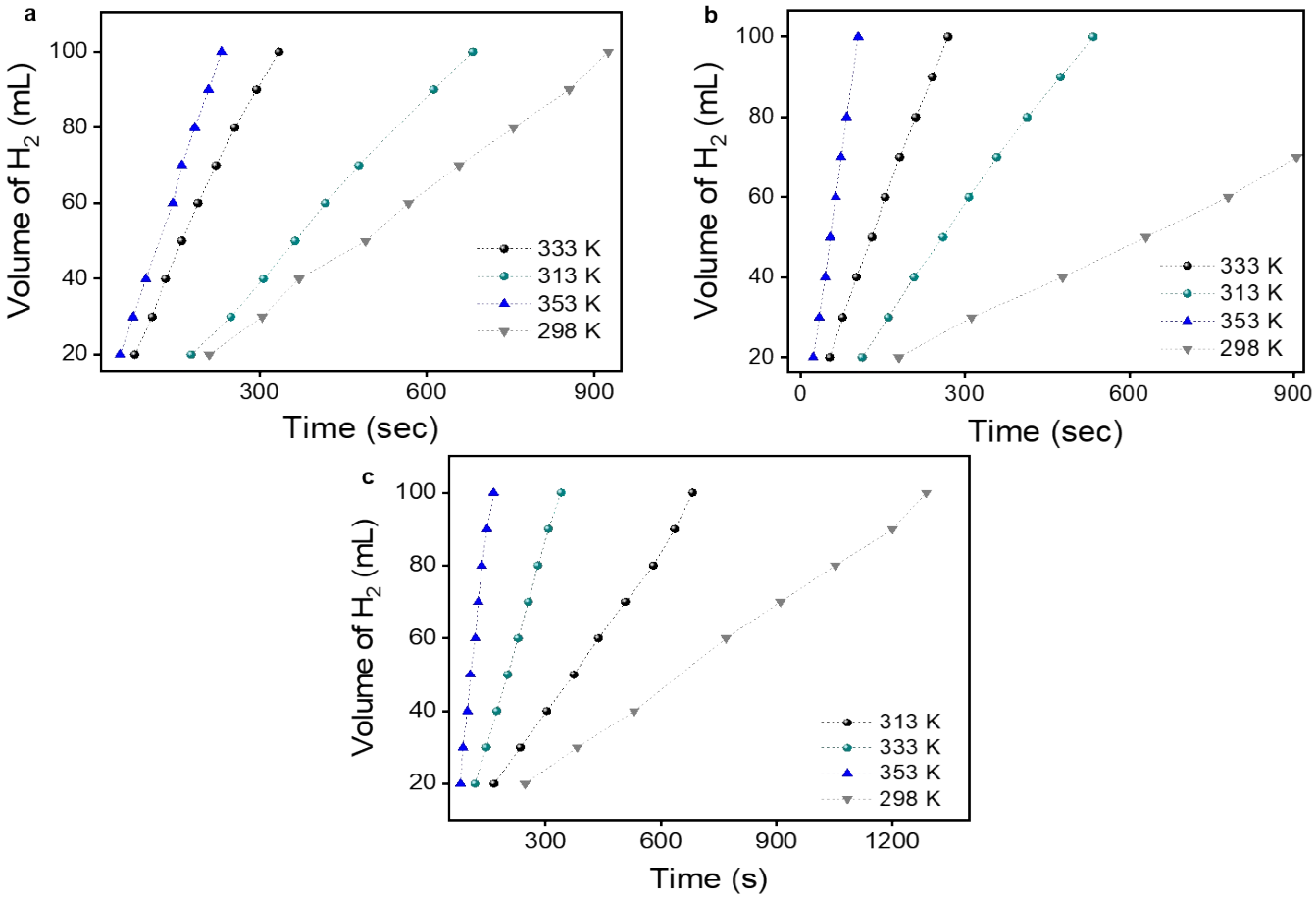


Figure S14. Rate of hydrogen evolution study (a) HEA CB 750, (b) HEA CB 500, and (c) bare HEA.

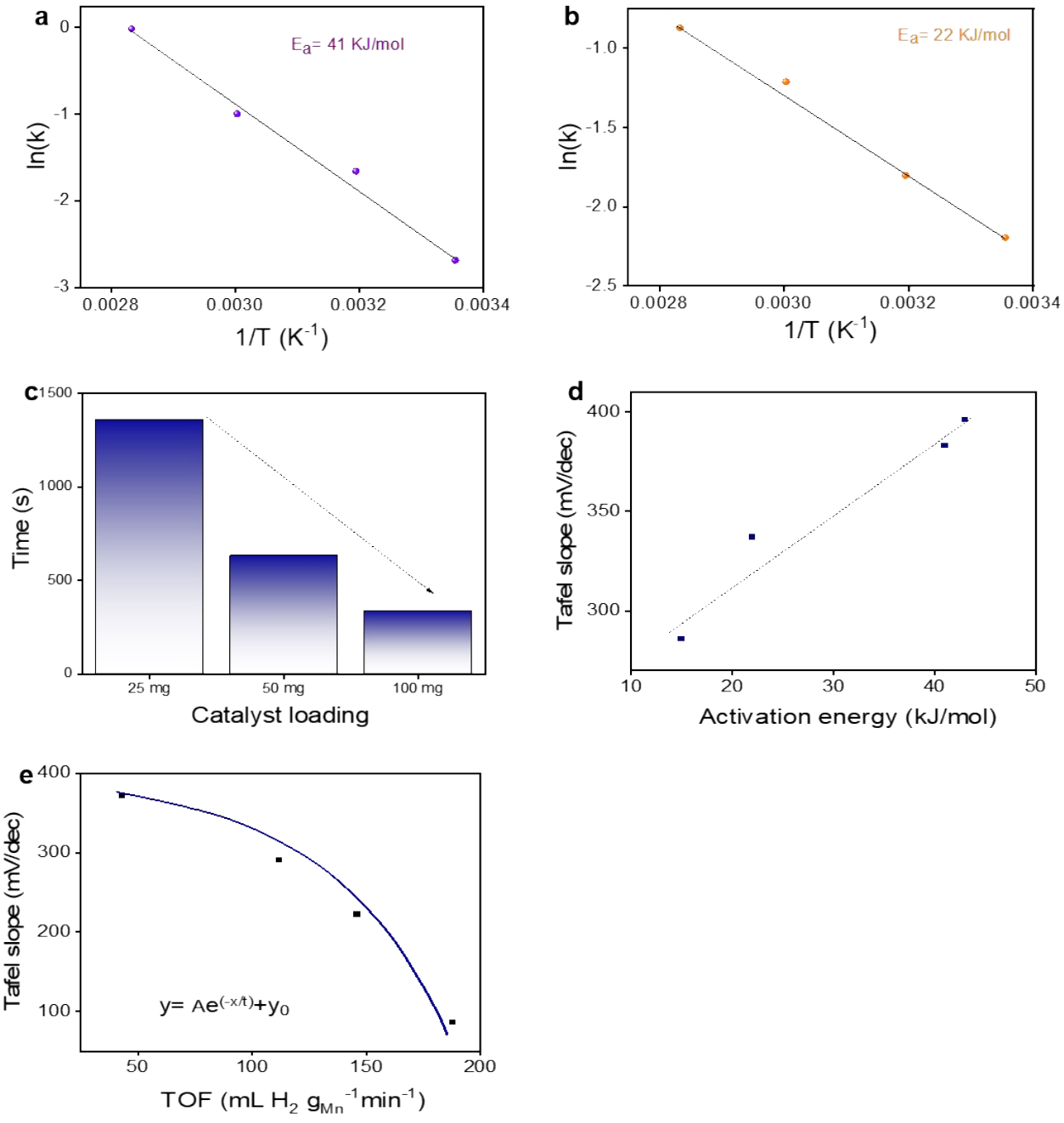


Figure S15. (a) Arrhenius plot and the corresponding activation energy of (a) HEA CB 500, (b) HEA CB 750, (c) time required for HEACB 1000 catalyst to produce 100 mL of hydrogen with respect to the loading of catalyst, (d) correlation between the Tafel slope and activation energy, and (e) correlation between the Tafel slope and TOF of HEACB samples.

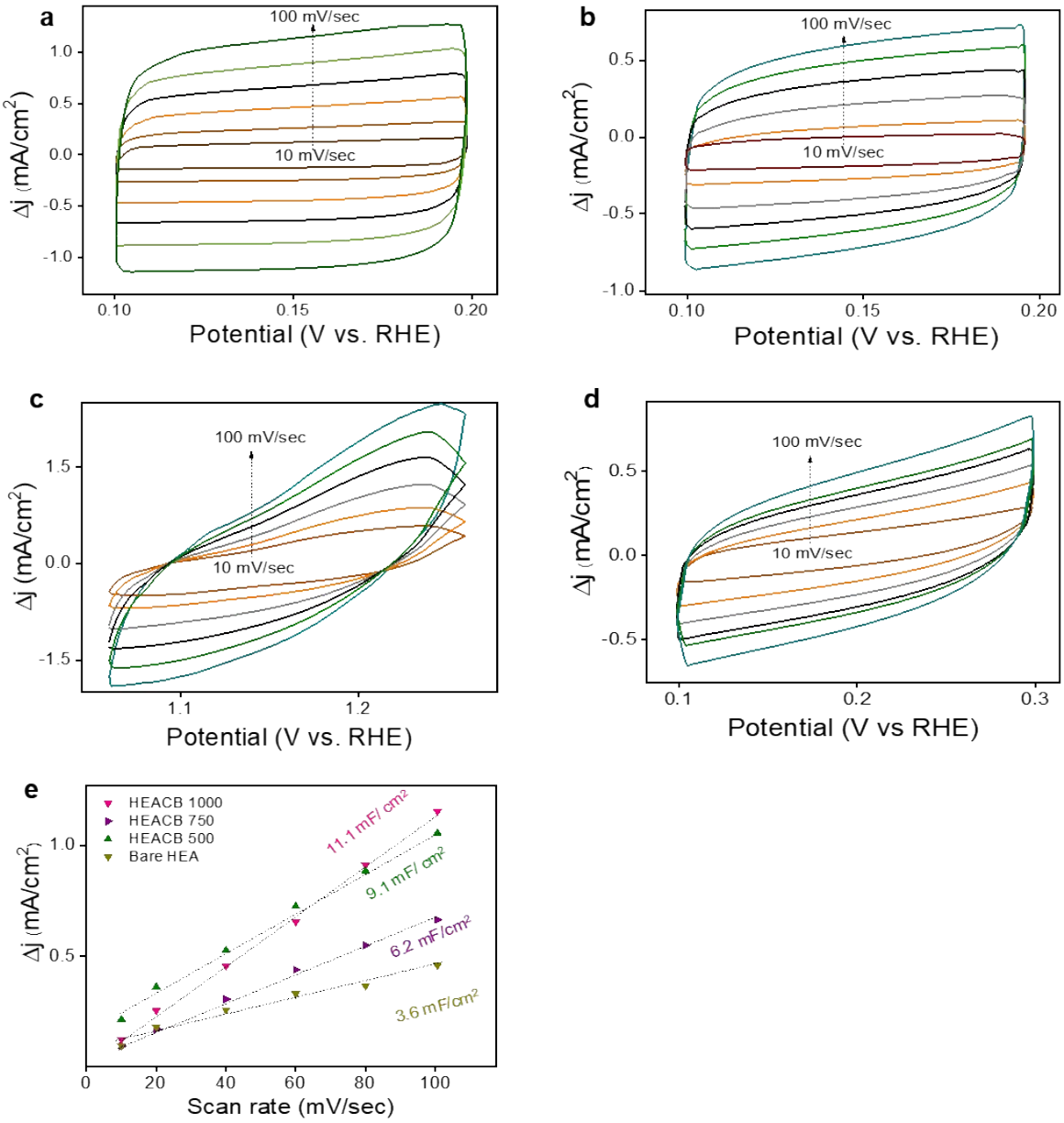


Figure S16. CV profile of (a) HEACB 1000, (b) HEACB 750, (c) HEACB 500, (d) bare HEA in the non-fardaic region, and (e) combined double layer capacitance plot.

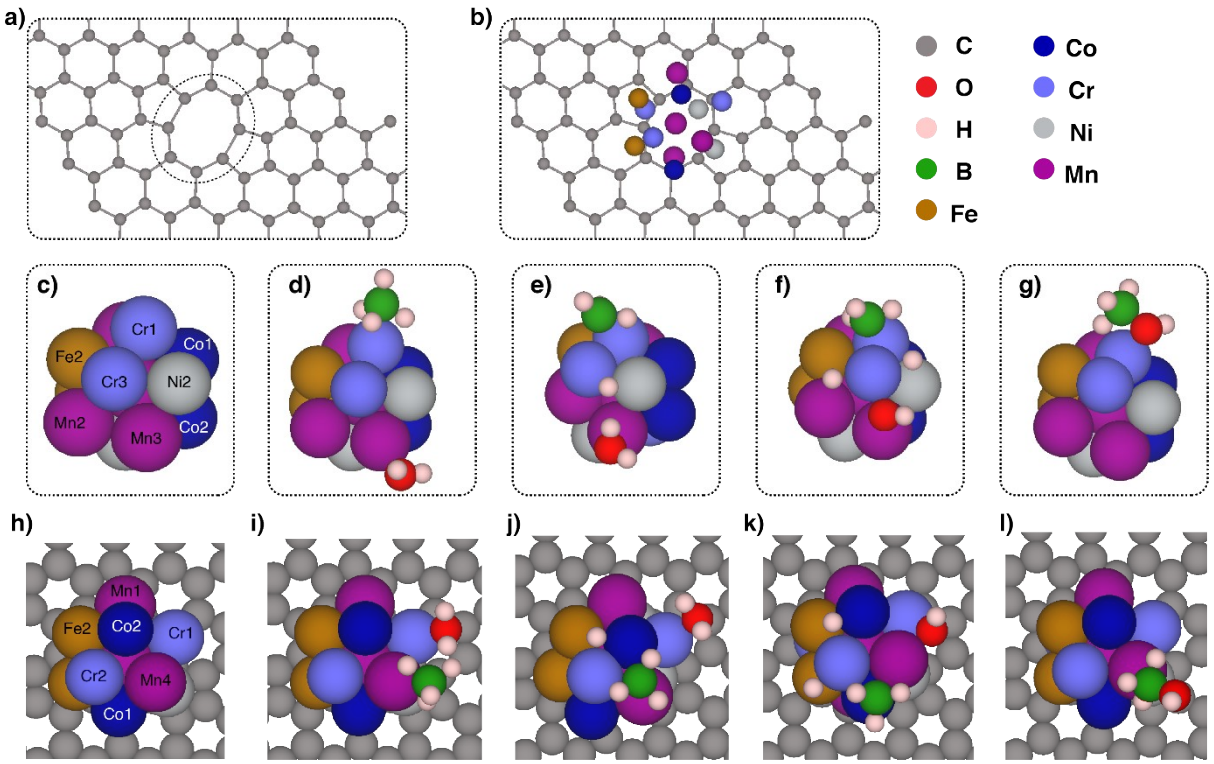


Figure S17. Top view of optimized structure (a) amorphous carbon (defected region is shown in circle), (b) composite HEA, (c) bare HEA nanoparticle (exposed metals are labelled), adsorbed intermediates on bare HEA (d) $*BH_4 + *OH_2$, (e) $*BH_3 + *H + *OH_2$, (f) $*BH_3 + *H + *OH + *H$, (g) $*BH_3OH$, (h) composite HEA (exposed metals are labelled), adsorbed intermediates on composite HEA (i) $*BH_4 + *OH_2$, (j) $*BH_3 + *H + *OH_2$, (k) $*BH_3 + *H + *OH + *H$, (l) $*BH_3OH$.

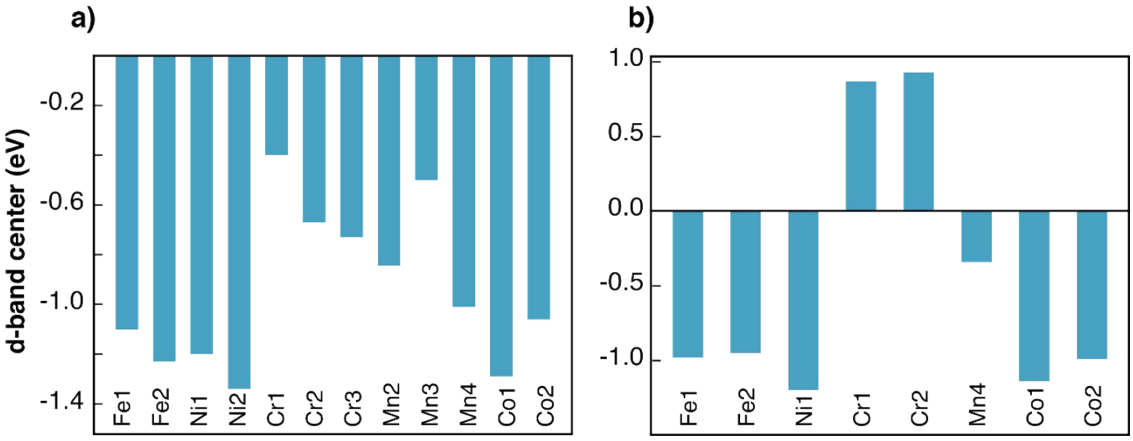


Figure S18. d-band centre value of exposed metals on the (a) bare HEA and (b) composite HEA.

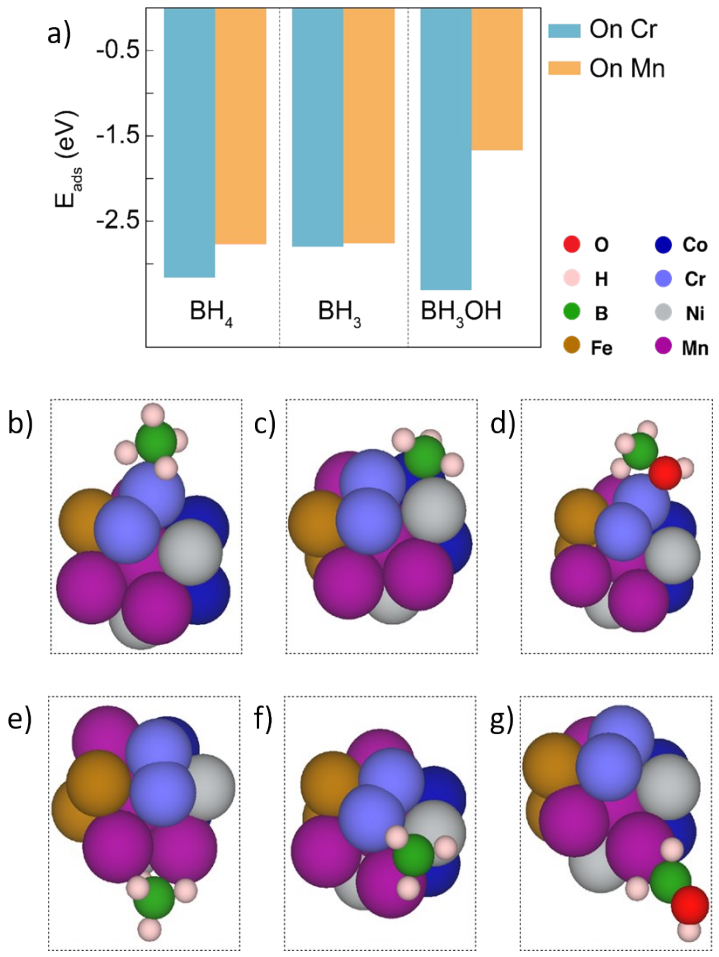


Figure S19. a) The adsorption energy of different boron containing intermediates (BH_4, BH_3, and BH_3OH) on Cr and Mn active sites. Optimized structure of BH_4, BH_3, and BH_3OH on Cr (b-d) and Mn (e-g) active sites respectively.

Table S1. Calculation of crystallite size from XRD analysis

Sample	Unit cell dimension (nm)	FWHM (degrees)	Strain $X10^{-3}$	Crystallite size (nm)
HEA CB 1000	0.355	0.219	2.35	40.8
HEACB 750	0.355	0.239	2.58	37.42
HEACB 500	0.295	0.398	4.31	22.5

Table S2. Atomic percentages of the five elements present in the HEA alloy extracted from the SEM EDS elemental spectrum.

Element	Atomic percentage
Cr	23.3
Mn	33
Fe	16.5
Co	13.6
Ni	13.6

Table S3. Atomic percentages of the five elements present in the HEA alloy through ICPMS.

Metal	PPM	Relative percentage
Ni	48	15.5
Mn	103	33.3
Fe	36	11.6
Co	39	12.6
Cr	83	26.8

Table S4. Atomic percentages of the five elements present in the HEA alloy extracted from the XPS elemental spectrum.

Metal	Area	RSF	Relative percentage
Ni	18111	22.18	18.3
Mn	18210`	13.90	28.4
Fe	10504	16.42	14
Co	14058	19.16	16.1
Cr	12430	11.67	23.2

Configurational entropy values for HEACB 1000

$\Delta S_{configuration}$ EDS= 1.54 R

$\Delta S_{configuration}$ XPS = 1.57 R

$\Delta S_{configuration}$ ICP-MS =1.52 R

ECSA calculation

ECSA= (Cdl/ Cs)*S

Cs is standard capacitance for atomically flat surface per unit area 0.04 mF/cm2.

S is the geometrical surface area

Table S5. Calculation of ECSA from the CV in the non-faradaic region.

Samples	C_{dl} value	ECSA
HEACB 1000	11.1	19
HEACB 750	6.2	10.8
HEACB 500	9.1	15.9
Bare HEA	3.6	6.3

Table S6. Impedance spectroscopy analysis

Samples	R1 –solution resistance	R2-charge transfer resistance	R3-surface porosity
HEACB 1000	4.1	19.2	775.2
HEACB 750	4.4	23.8	882.9
HEACB 500	4.2	31.2	1084
Bare HEA	3.9	44.9	2145

Table S7. Energy of reference molecules BH_3, H_2O and H_2 in gas phase.

System	**Energy (eV)**
BH_3	-15.814
H_2O	-14.224
H_2	-6.69