Synthesis of Metastable Chromium Carbide Nanomaterials and their Electrocatalytic Activity for the Hydrogen Evolution Reaction

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Supporting Information

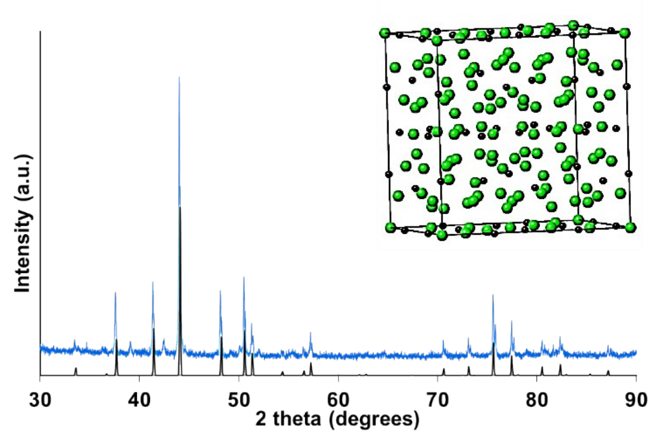


Figure S1. XRD of $Cr_{23}C_6$ with calculated $Cr_{23}C_6$ PDF# 00-035-0783

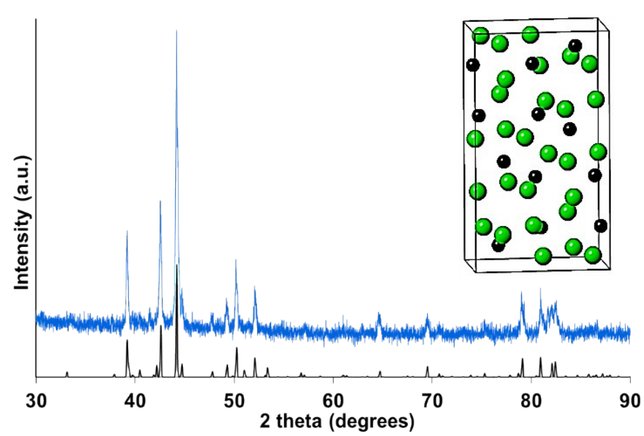


Figure S2. XRD of Cr_7C_3 with calculated Cr_7C_3 PDF# 00-036-1482

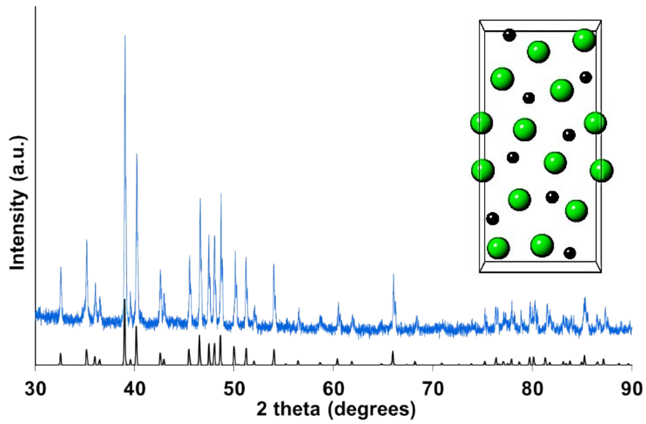


Figure S3. XRD of Cr_3C_2 with calculated Cr_3C_2 PDF# 01-074-7137

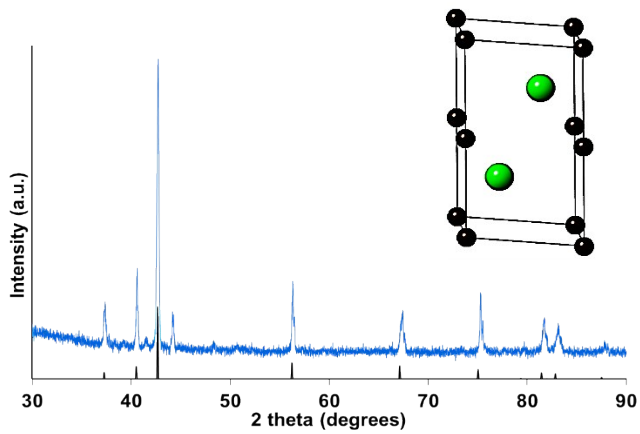


Figure S4. XRD of Cr_2C with calculated Cr_2C PDF# 00-014-0519

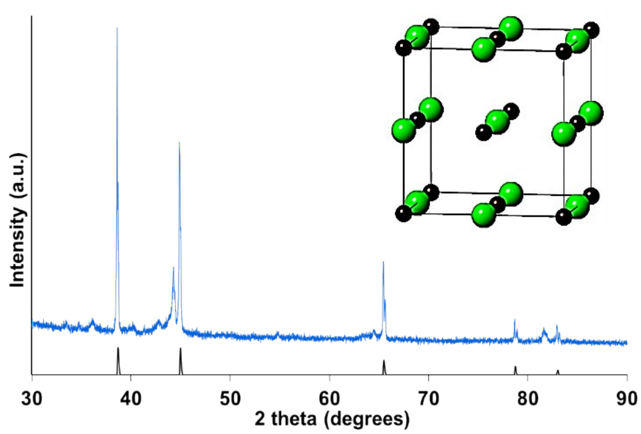


Figure S5. XRD of CrC with calculated CrC PDF# 03-065-0896

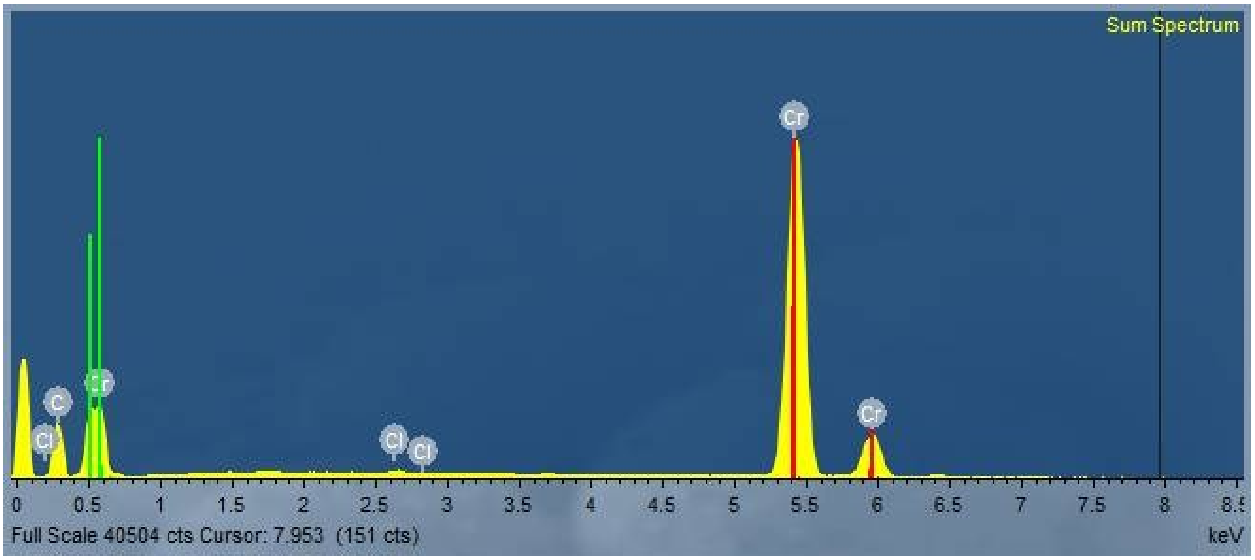


Figure S6. EDS spectrum of CrC with Cl peaks highlighted.

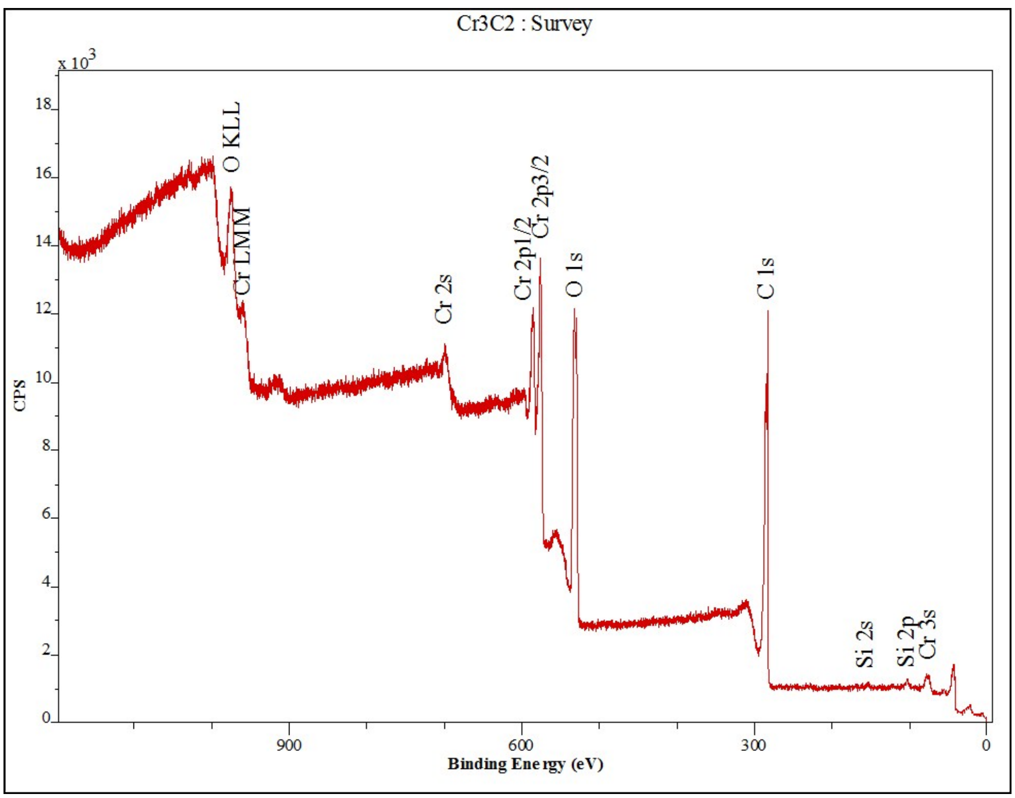


Figure S7. XPS survey spectrum of Cr_3C_2

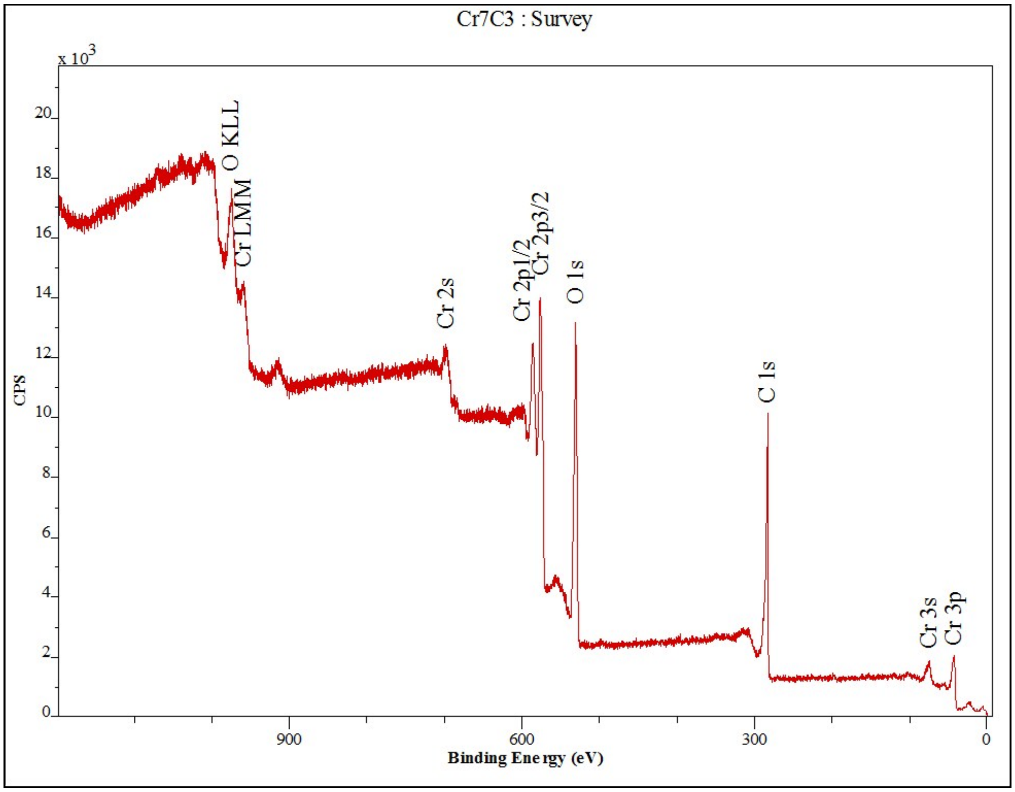


Figure S8. XPS survey spectrum of $Cr7C_3$

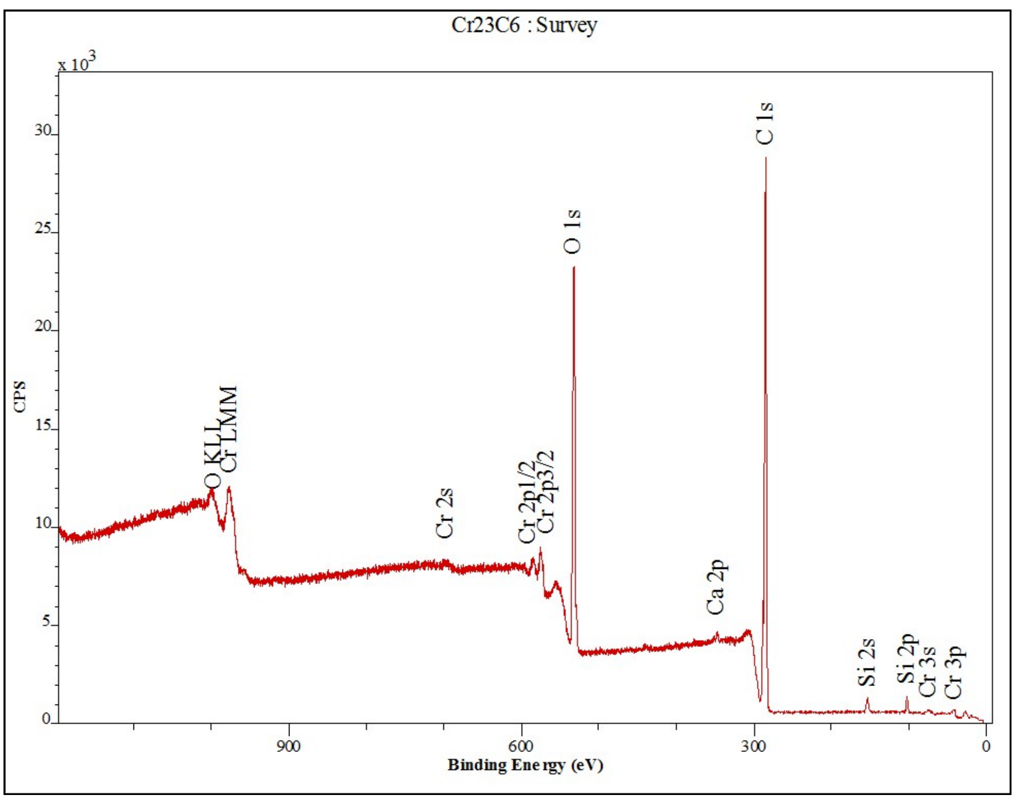


Figure S9. XPS survey spectrum of $Cr_{23}C_6$

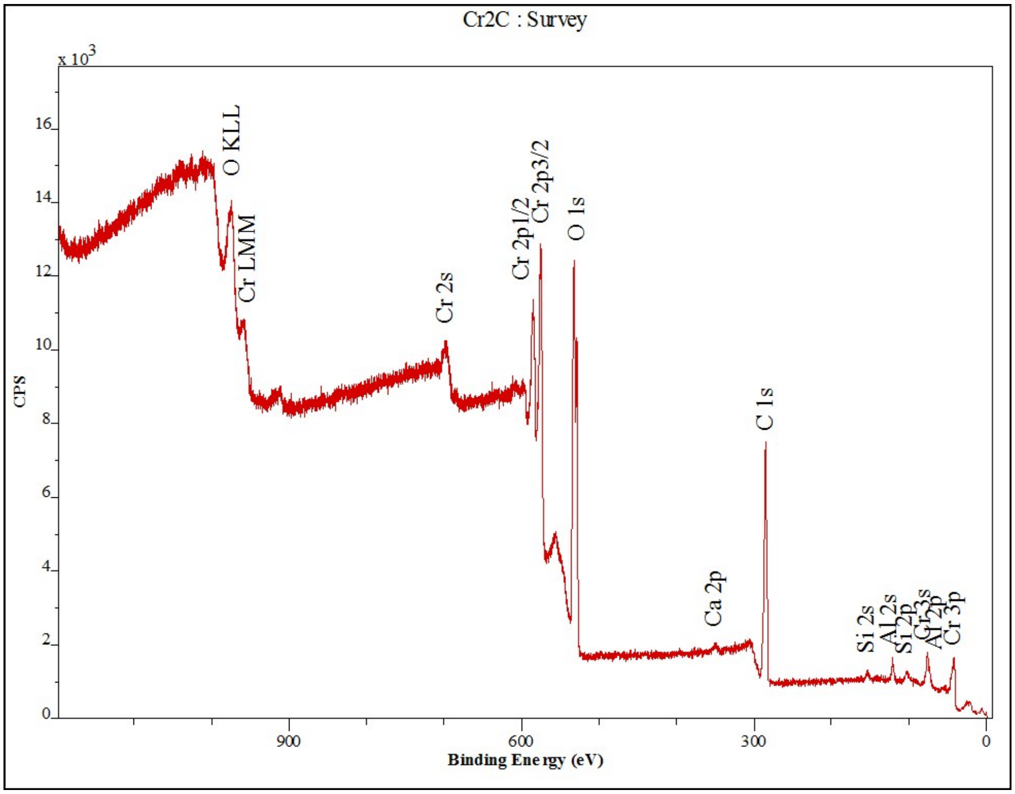


Figure S10. XPS survey spectrum of Cr_2C

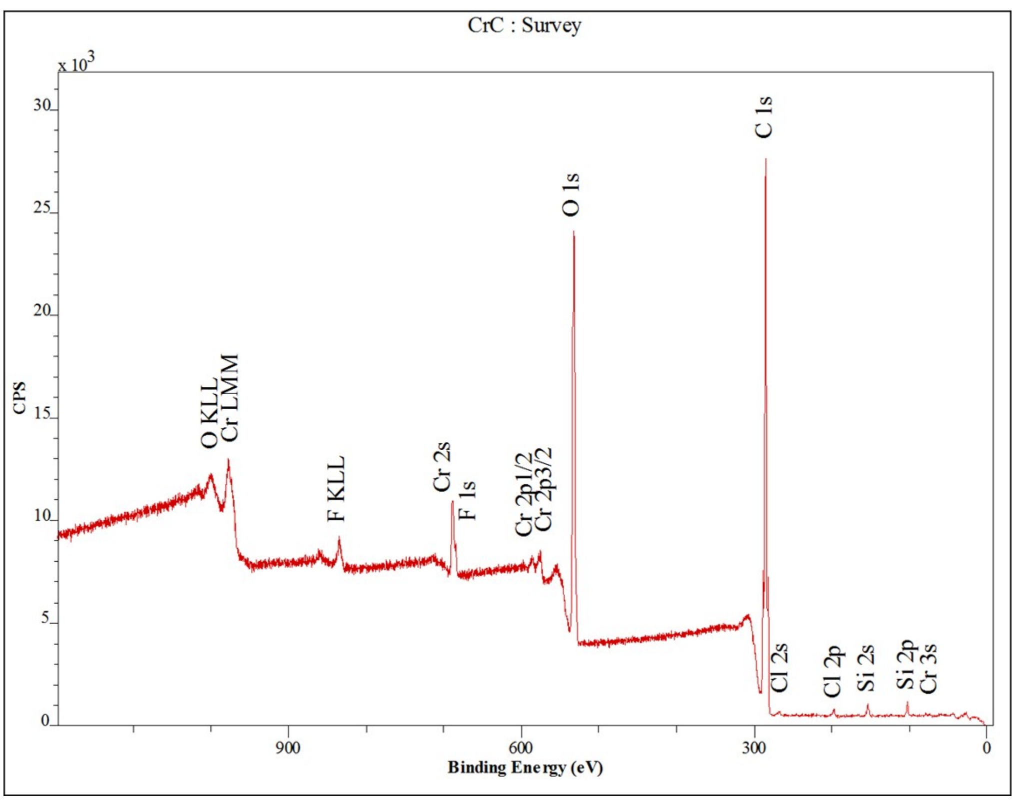
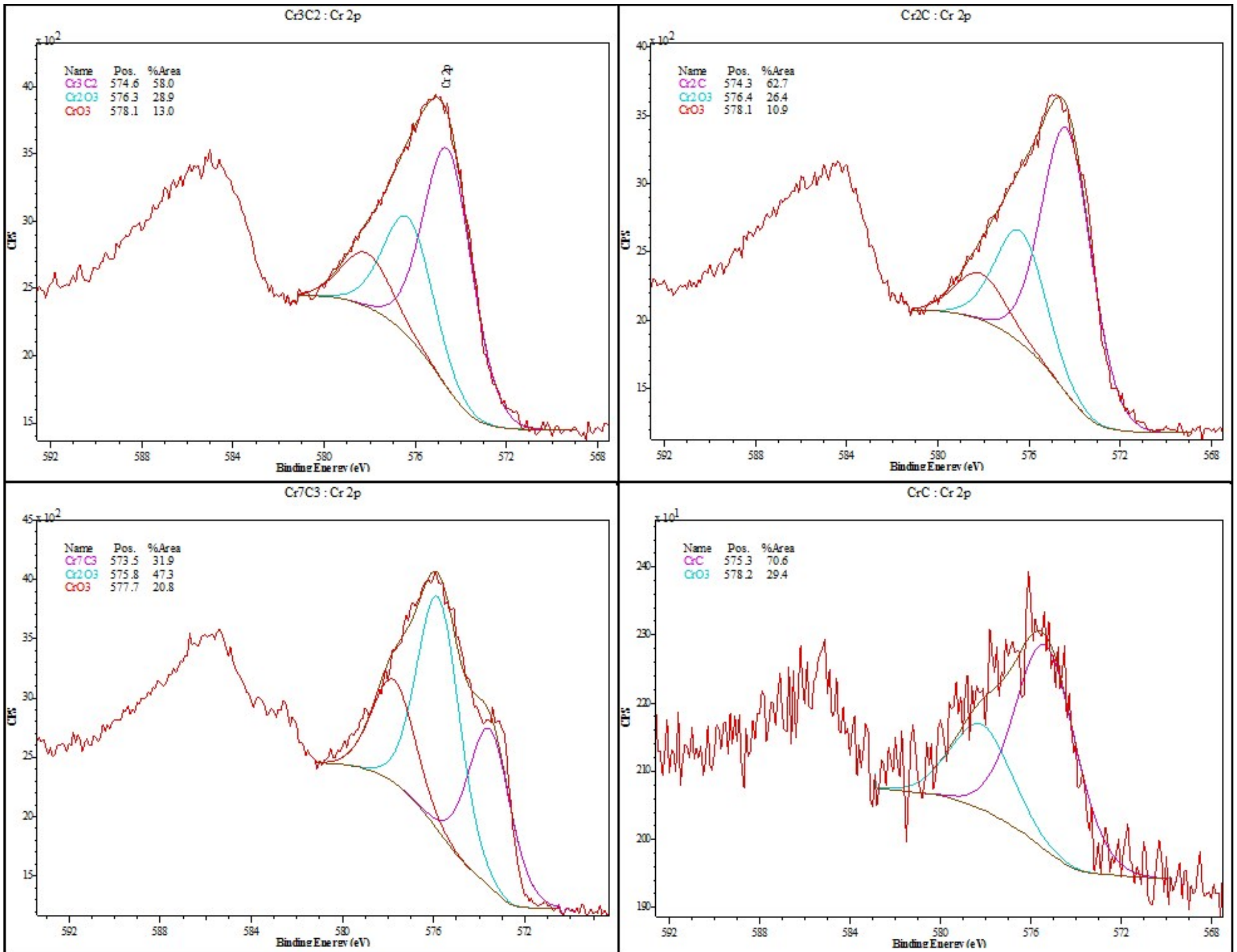
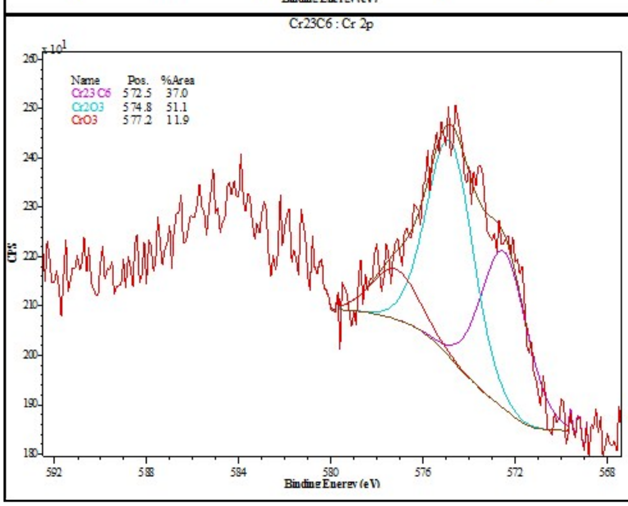


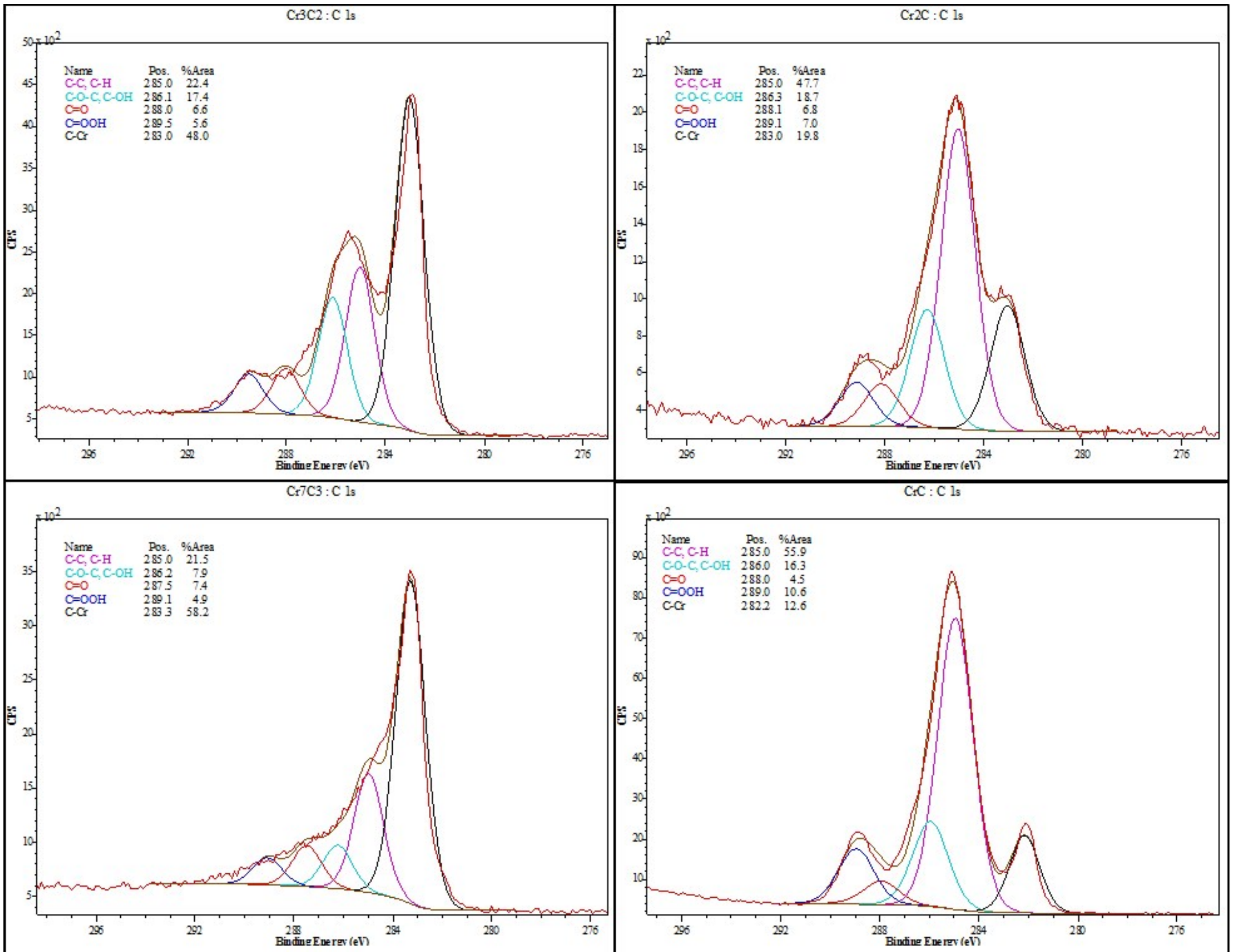
Figure S11. XPS survey spectrum of CrC

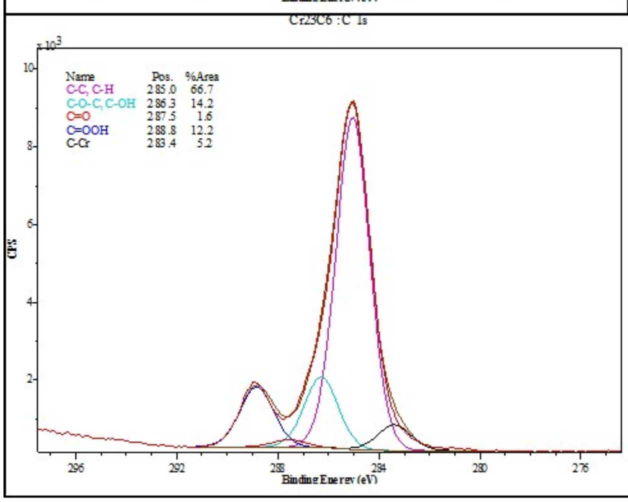




Phase	Cr $2p^{3/2}$ position (eV)	Cr-C amount (%)
CrC	575.3	70.6
Cr_3C_2	574.6	58
Cr_2C	574.3	62.7
$Cr_{23}C_6$	572.5	37
Cr_7C_3	573.5	31.9

Figure S12. High resolution XPS Cr 2p spectra and table of results





Phase	C 1s position (eV)	Cr-C amount (%)
CrC	282.2	12.6
Cr_3C_2	283	48
Cr_2C	283	19.8
$Cr_{23}C_6$	283.4	5.2
Cr_7C_3	283.3	58.2

Figure S13. High resolution XPS C 1s spectra and table of results

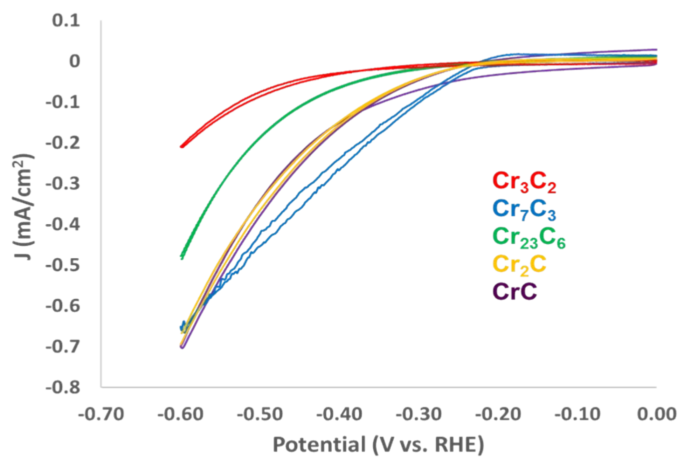


Figure S14. Cyclic Voltammetry (CV) curves for all five phases of chromium carbide in 0.5 M H_2SO_4. The catalyst loading for all is 0.28 mg/cm^2. (Color of phase label correlates with color of each CV curve.)

Table S1. Comparison of all five crystal structures through coordination environments of C and Cr (Cr# indicating crystallographic site), (Cr-C and Cr-Cr) bonding types, Cr XPS values, DOS[1], and current density for HER.

Structure	Cr-Coordination	Cr-C bonding	Cr-Cr bonding	Bonding type	XPS Cr $2p^{3/2}$	Cr:C	DOS at Fermi level	Current Density (mA/cm^2)
$Cr_{23}C_6$	Cubooctahedron, cubes with interconnected tetrahedra	Cr1 (0) Cr2 (0) Cr3 (3) Cr4 (2)	Cr1 (12) Cr2 (4) Cr3 (4) Cr4 (6)	Metallic Polar-Covalent	572.5	3.83	~20	-0.917
Cr_7C_3	Octahedra	Cr1 (3) Cr2 (4) Cr3 (3) Cr4 (3) Cr5 (4)	Cr1 (3) Cr2 (5) Cr3 (1) Cr4 (2) Cr5 (5)	Metallic Polar-Covalent	573.5	2.33	~30	-1.23
Cr_2C	Distorted octahedra	Cr (6)	Cr (0)	Polar-Covalent	574.3	2	N/A	-1.05
Cr_3C_2	Octahedra	Cr1 (4) Cr2 (5) Cr3 (5)	Cr1 (2) Cr2 (2) Cr3 (6)	Polar-covalent Metal	574.6	1.5	~10	-0.321
CrC	Octahedra	Cr (6)	Cr (0)	Polar-Covalent	575.3	1	N/A	-0.853

References

1. Jiang, C., First-principles study of structural, elastic, and electronic properties of chromium carbides. *Applied Physics Letters* **2008,** *92* (4), 041909