Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Intrinsic Valley Polarization in 2D Magnetic MXenes: Surface Engineering Induced Spin-valley Coupling

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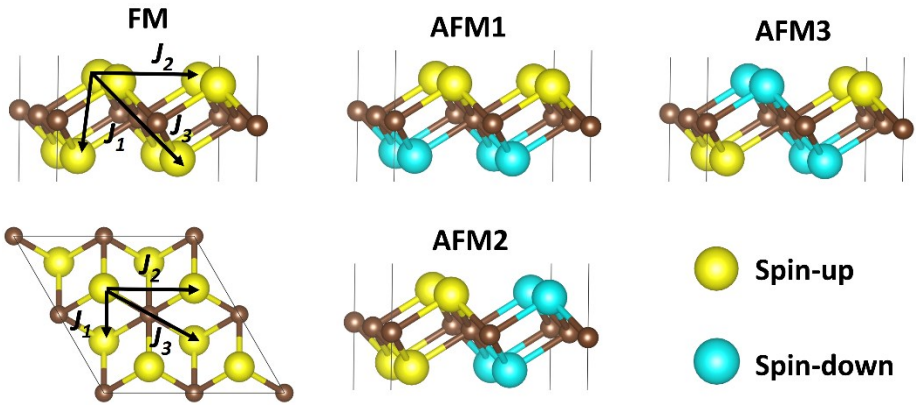

Fig. S1 Ferromagnetic (FM) and antiferromagnetic (AFM) states for Cr_2C MXenes.

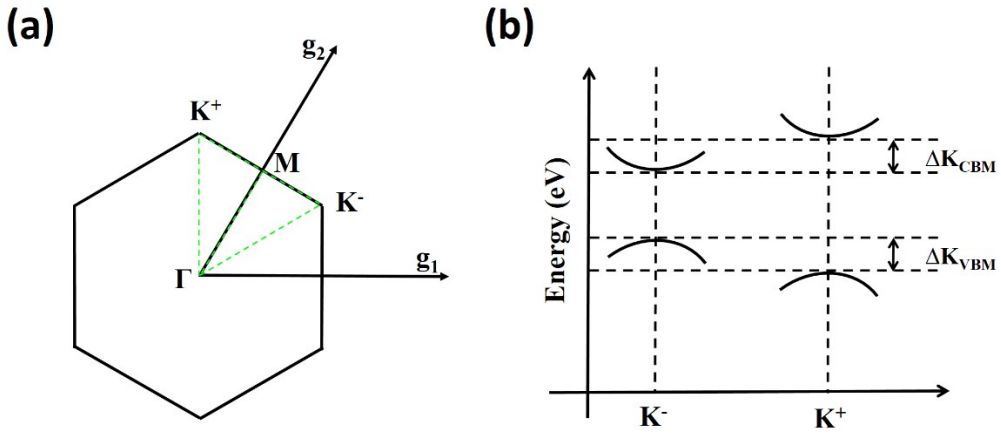

Fig. S2 (a) The high symmetry points of the first Brillouin zone for the band structure of Cr_2C MXenes. (b) Schematic drawing of the band edge structures at two valleys. Down (up) opening parabolas are used to denote valence band maximum (VBM) and conduction band minimum (CBM).

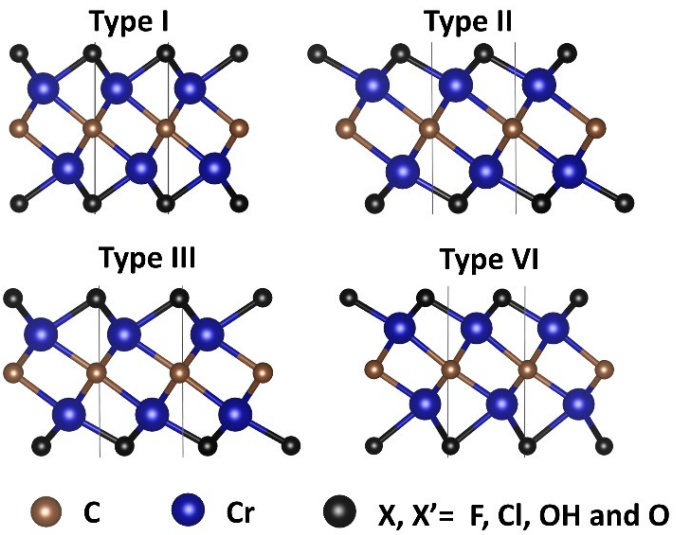

Fig. S3 Four possible types for functionalized Cr_2C MXenes.

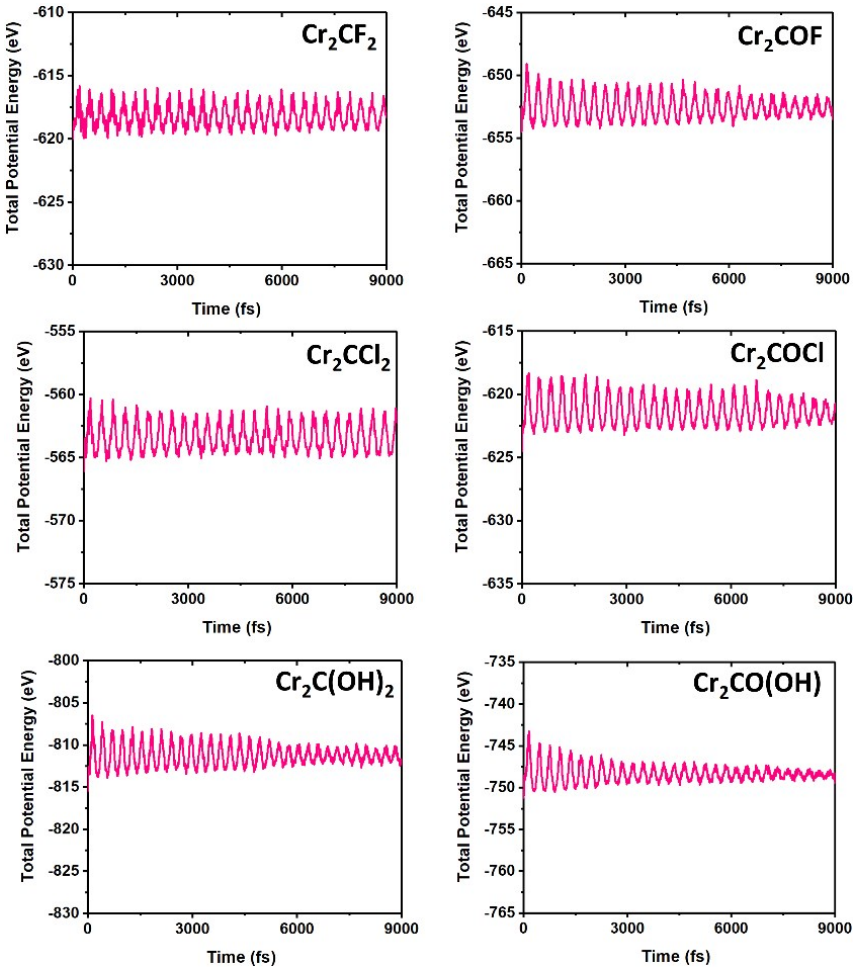

Fig. S4 Total potential energy of MXenes as a function of simulation time for Cr_2CX_2 and Cr_2COX MXenes by using ab-initio molecular dynamics (300K) in 9 ps.

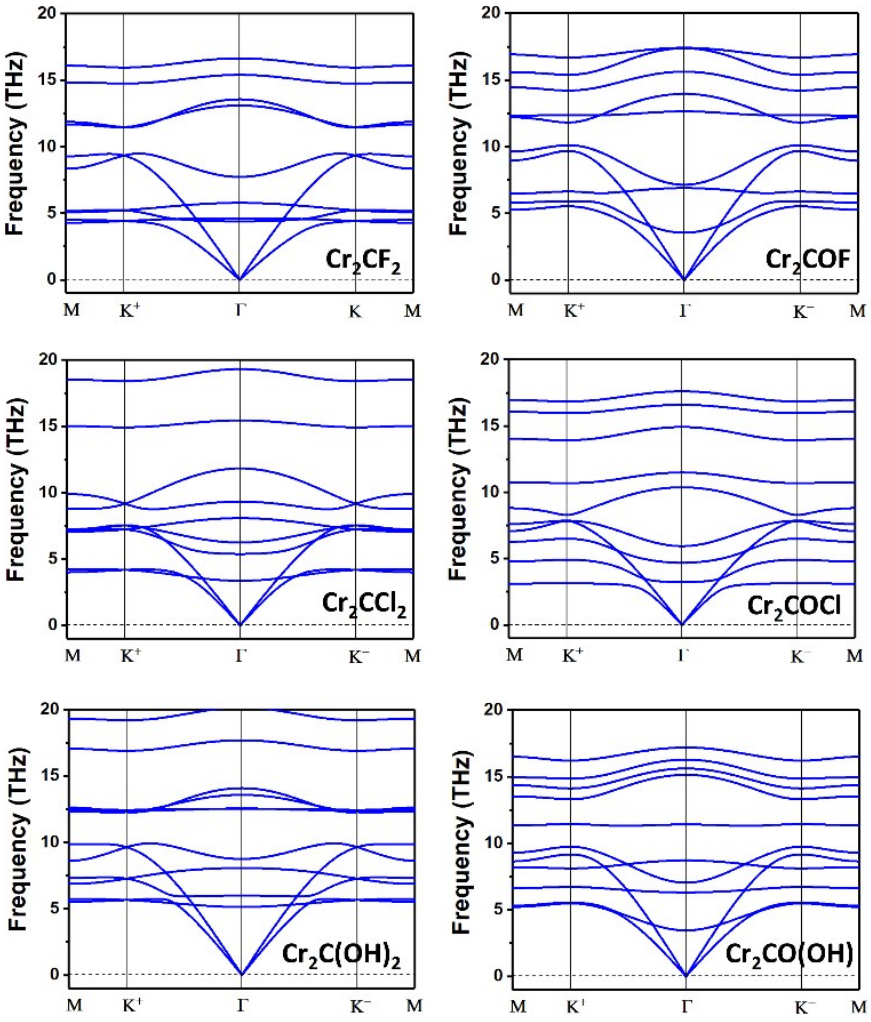

Fig. S5 Phonon spectra for Cr_2CX_2 and Cr_2COX MXenes

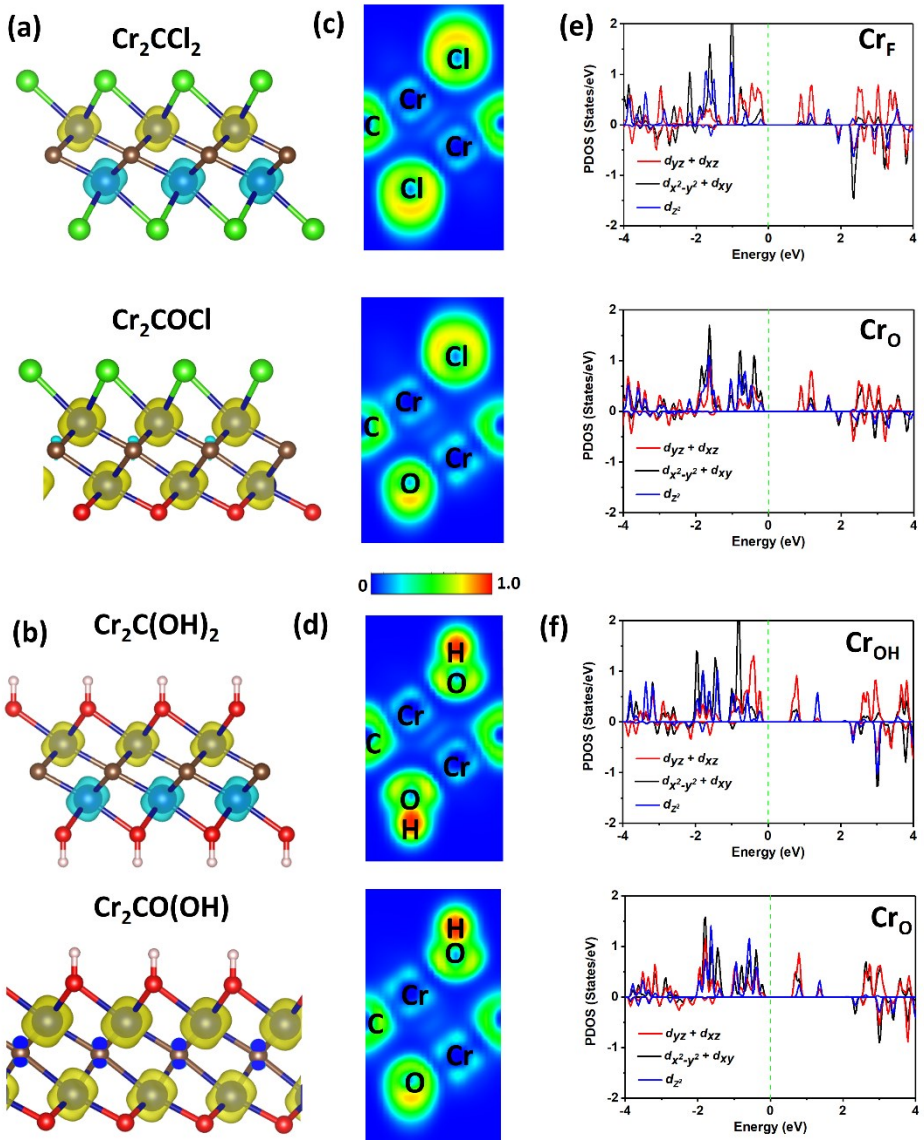

Fig. S6 Spin polarized charge densities on (a) Cr_2CCl_2 and Cr_2COCl and (b) $Cr_2C(OH)_2$ and $Cr_2CO(OH)$ MXenes, where spin-up and spin-down densities are shown in yellow and blue, respectively. The isosurface is 0.045 e·Bohr^{-3}. Electron localization functions (ELF) on (c) Cr_2CCl_2 and Cr_2COCl and (d) $Cr_2C(OH)_2$ and $Cr_2CO(OH)$ MXenes. The color scale (from 0 to 1) shows the probability. The partial electronic density of states (PDOS) of (e) Cr_2COCl and (f) $Cr_2CO(OH)$ MXenes.

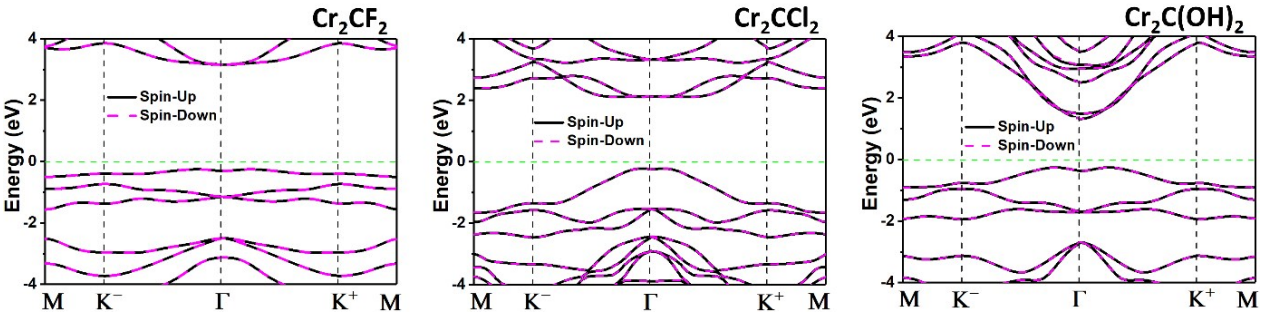

Fig. S7 Band structures of Cr_2CX_2 at HSE06 level. Spin-up and spin-down bands are respectively denoted by black and pink lines.

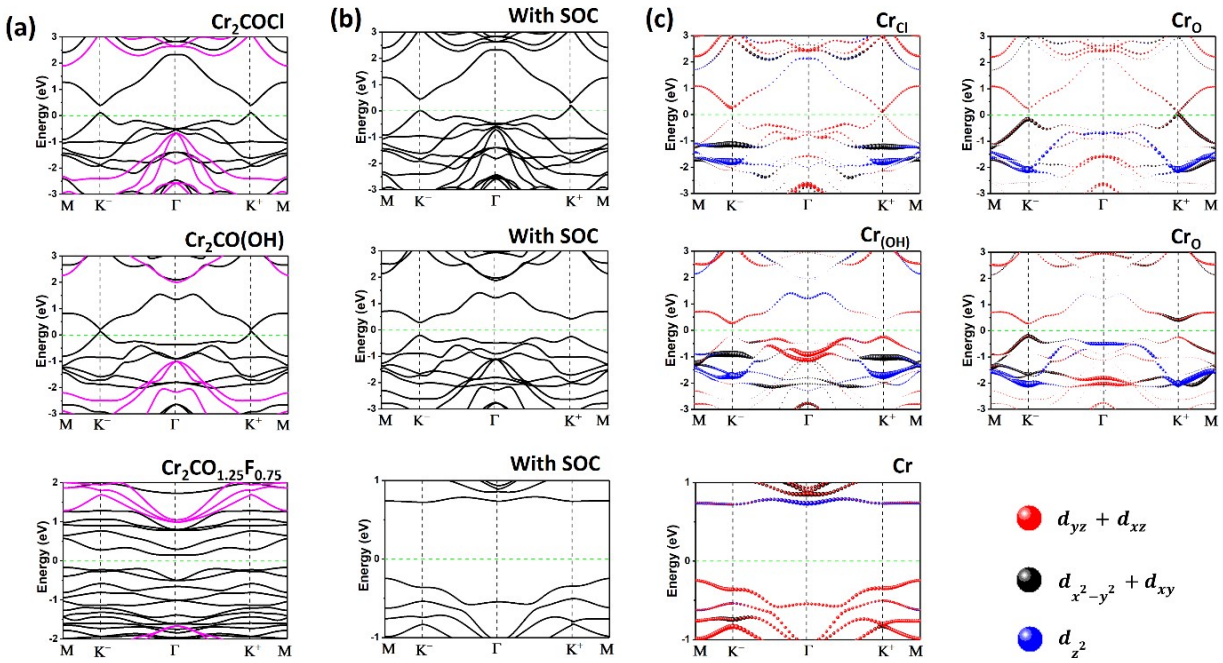

Fig. S8 (a) Band structures at HSE06 level. Spin-up and spin-down bands are respectively denoted by black and pink lines. (b) Band structures with spin-orbit coupling (SOC). (c) Orbital projected band structures with SOC. Red, black and blue circles represent $d_{yz} + d_{xz}$, $d_{x^2-y^2} + d_{xy}$ and d_{z^2} orbital composition. The sizes of the dots denote the weight of contribution. Note that each *d* orbital of Cr atoms in mixed MXenes was not further analyzed.

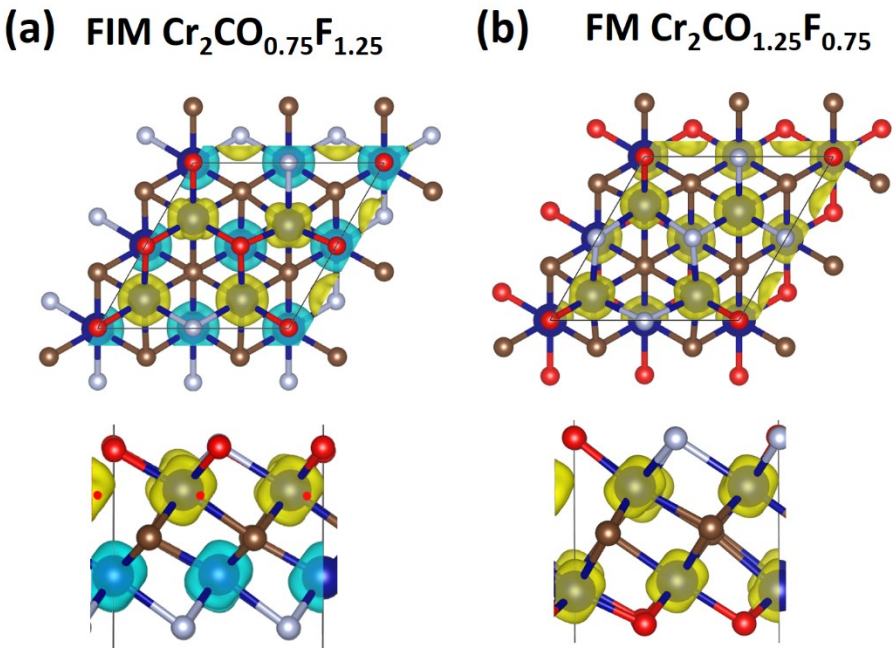

Fig. S9 Spin polarized charge densities on (a) ferrimagnetic (FIM) $Cr_2CO_{0.75}F_{1.25}$ (b) ferromagnetic (FM) $Cr_2CO_{1.25}F_{0.75}$ MXenes, where spin-up and spin-down densities are shown in yellow and blue, respectively. The isosurface is 0.045 e·Bohr^{-3}.

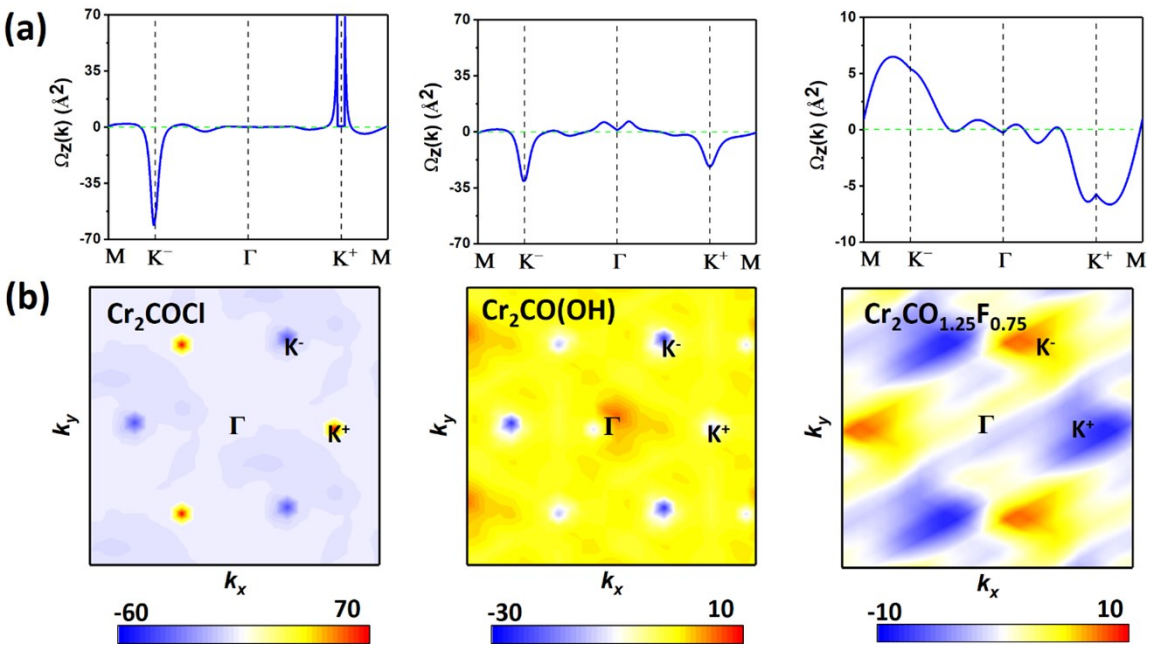

Fig. S10 Berry curvatures of Cr_2COCl, $Cr_2CO(OH)$ and $Cr_2CO_{1.25}F_{0.75}$ along high-symmetry points (a) and in the full Brillouin zone (b). Unit of Berry curvatures is $Å^2$.

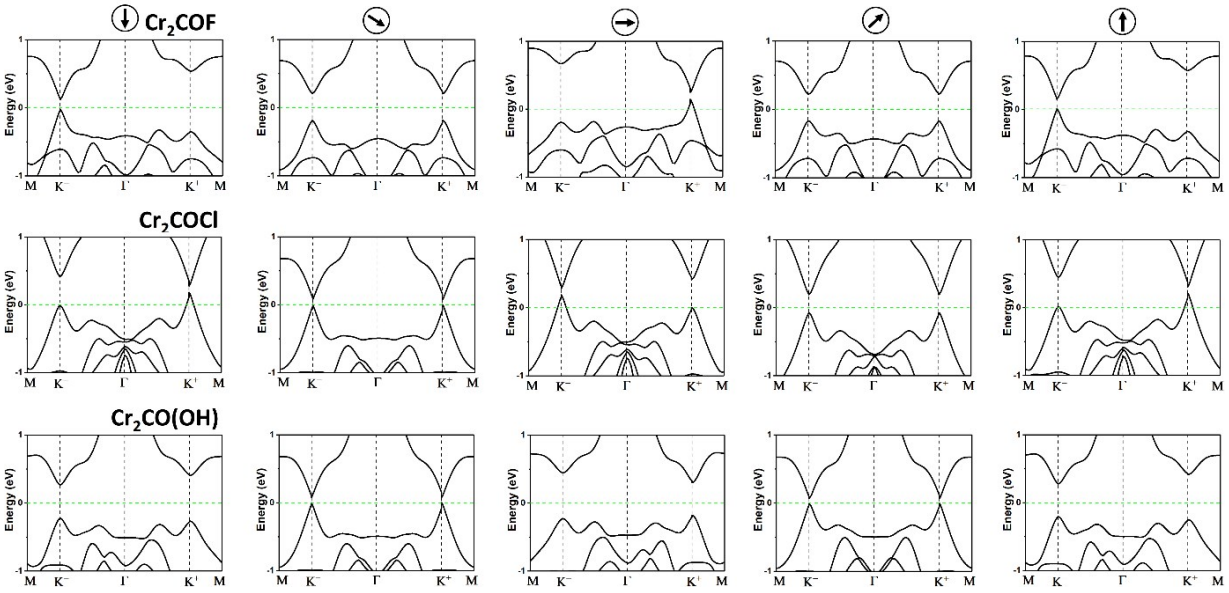

Fig. S11 Band structures of Cr_2COX with spin-orbit coupling (SOC) at HSE06 level. The black arrows in circles show the magnetization direction (θ) in the xz plane from -90 to 90.

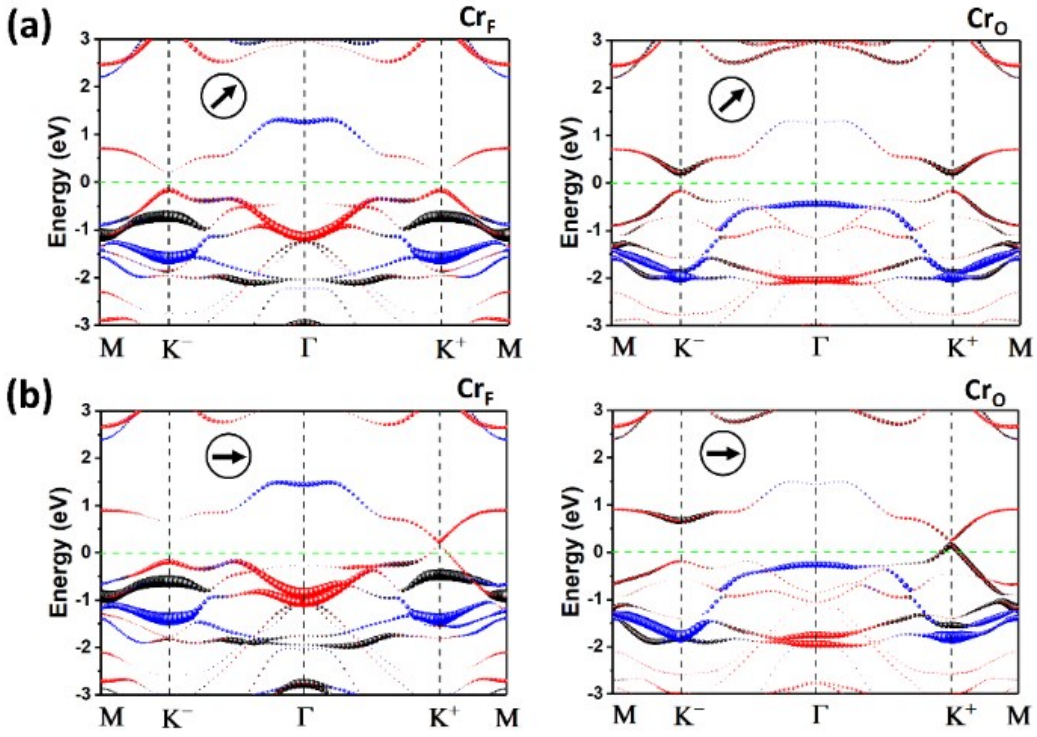

Fig. S12 Orbital projected band structures of Cr_2COF MXene with SOC when (a) θ = 45 and (b) θ = 0. Red, black and blue circles represent $d_{yz} + d_{xz}$, $d_{x^2-y^2} + d_{xy}$ and d_{z^2} orbital composition. The sizes of dots denote the weight of contribution.

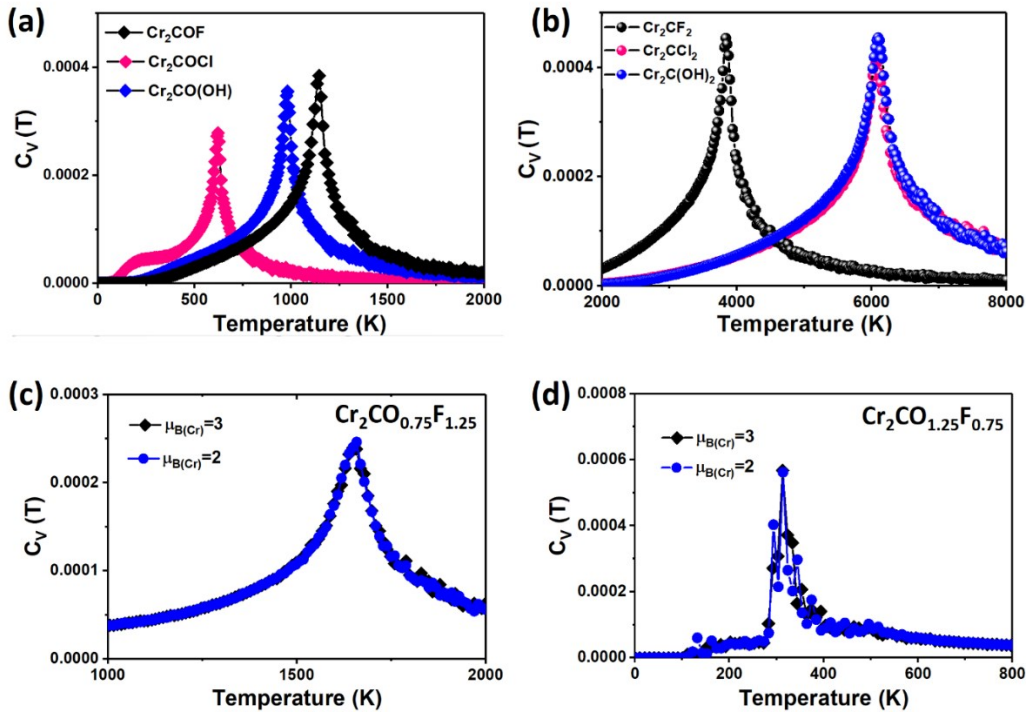

Fig. S13 Specific heat (C_V) calculated for Cr_2CX_2, Cr_2COX and mixed Cr_2C MXenes with respect to the temperature.

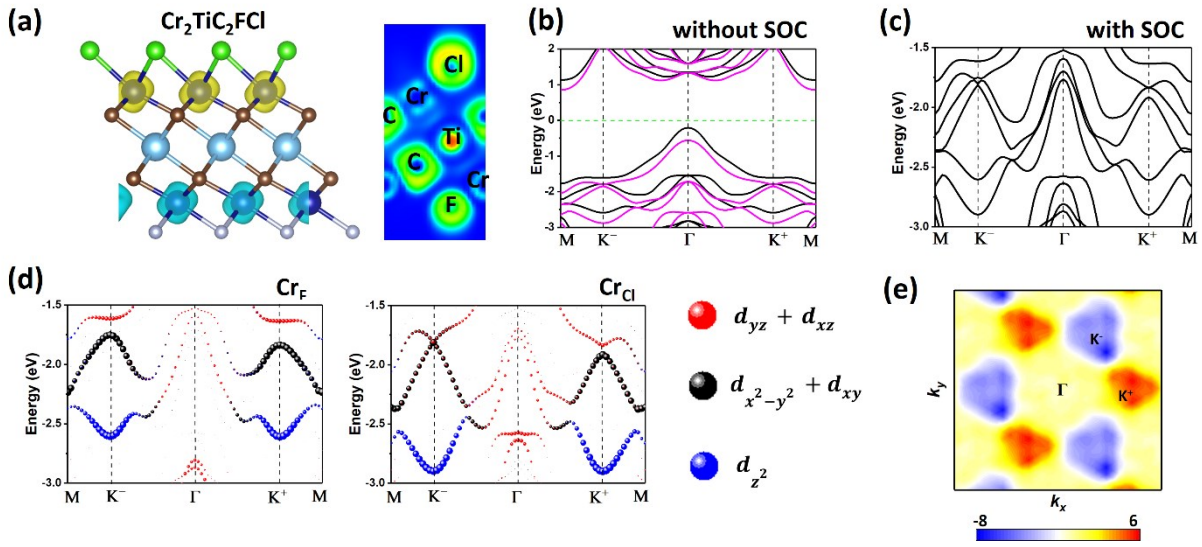

Fig. S14 (a) Spin polarized charge densities and electron localization functions. Spin-up and spin-down densities are shown in yellow and blue, respectively. The isosurface is 0.045 e·Bohr^{-3}. The color scale (from 0 to 1) shows the probability. (b) Band structures at HSE06 level. Spin-up and spin-down bands are respectively denoted by black and pink lines. (c) Band structures with spin-orbit coupling (SOC). (d) Orbital projected band structures with SOC. Red, black and blue circles represent $d_{yz} + d_{xz}$, $d_{x^2-y^2} + d_{xy}$ and d_{z^2} orbital composition. The sizes of dots denote the weight of contribution. (e) Berry curvatures in the full Brillouin zone. Unit of Berry curvatures is Å^2.

Table S1 Four types of functionalization adsorption sites on Cr_2CX_2 and Janus Cr_2COX MXenes. The most stable type is set up to zero for each MXenes.

MXenes	**Type I**	**Type II**	**Type III**	**Type VI**
Cr_2CF_2	0.52	0.00	0.17	/
Cr_2CCl_2	0.56	0.00	0.23	/
$Cr_2C(OH)_2$	2.64	0.00	0.13	/
Cr_2COF	0.40	0.00	0.22	0.33
Cr_2COCl	0.82	0.00	0.59	0.38
Cr_2COOH	0.21	0.00	0.12	0.21

Table S2 Calculated structural and magnetic characteristics of Cr_2CX_2 and Janus Cr_2COX MXenes. L is the lattice constant (Å). Cr-C and Cr-X(X') are bond lengths (Å). Magnetic states include ferromagnetic (FM) and antiferromagnetic (AFM) states. M is magnetic moment (μ_B). J_1, J_2 and J_3 are coupling constants (meV). T_C/T_N stands for the Curie and Neel temperatures (K). Band gaps are in spin-up and spin-down channels (eV). ΔK_{VBM} and ΔK_{CBM} stands for the valley splitting (meV).

MXenes	L (Å)	Cr-C	Cr-X(X')	Magnetic states	M (Cr)	J_1	J_2	J_3	T_C/T_N	Gaps Up/down	ΔK_{VBM}	ΔK_{CBM}
Cr_2CF_2	3.01	2.05	2.12	AFM	± 2.65	62.14	22.11	56.07	3830	3.40/3.40	/	/
Cr_2CCl_2	3.13	2.02	2.46	AFM	± 2.74	181.39	61.79	78.4	6095	2.28/2.28	/	/
$Cr_2C(OH)_2$	3.02	1.99	2.14 (Cr-OH)	AFM	± 2.79	154.83	32.01	53.74	6095	1.55/1.55	/	/
Cr_2COF	2.94	1.99 (Cr_F-C) 2.17 (Cr_O-C)	2.11(Cr-F) 1.92(Cr-O)	FM	2.90 (Cr_F) 2.56 (Cr_O)	24.61	31.46	14.64	1146	0.40/3.46	334	421
Cr_2COCl	2.98	1.96 (Cr_{Cl}-C) 2.10 (Cr_O-C)	2.44(Cr-Cl) 1.95(Cr-O)	FM	2.75 (Cr_{Cl}) 2.57 (Cr_O)	14.37	50.55	8.74	622	/2.54	-149	-139
Cr_2COOH	2.95	1.99 (Cr_{OH}-C) 2.16 (Cr_O-C)	2.12(Cr-OH) 1.93(Cr-O)	FM	2.84 (Cr_{OH}) 2.59 (Cr_O)	24.02	32.01	6.44	983	/3.26	45	140

Table S3 Calculated structural and magnetic characteristics of two mixed MXenes. L is the lattice constant (Å). Magnetic states include ferromagnetic (FM) and ferrimagnetic (FIM) states. T_C/T_N stands for the Curie and Neel temperatures (K). Band gaps are in spin-up and spin-down channels (eV). ΔK_{VBM} and ΔK_{CBM} stands for the valley splitting (meV).

MXenes	L (Å)	Magnetic states	T_C/T_N	Gaps Up/down	ΔK_{VBM}	ΔK_{CBM}
$Cr_2CO_{0.75}F_{1.25}$	5.96	FIM	1648	0.97/0.46	11	11
$Cr_8C_4O_{1.25}F_{0.75}$	5.75	FM	314	0.31/2.66	15	-12