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Supplementary Information for

Intrinsic Multiferroicity in Two-dimensional $VOCl_2$ Monolayer

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Table S1. Calculated total energy E (meV) relative to the energy of AFM-3 configuration (E_{AFM-3}) of four magnetic coupling configurations (FM, AFM-1, AFM-2 and AFM-3) in a $2 \times 2 \times 1$ supercell, the electronic band gap E_g (eV), the total magnetic moment M (μB), the magnetic moment M_V (μB) of V ions and the spontaneous polarization P (pC/m) under different values of U from the GGA + U method.

U-J(eV)			E-E_{AFM-3}	E_g	M	M_V	P
$VOCl_2$	1	FM	107.2	0.93	4	1.13	/
		AFM-1	119.5	1.18	0	1.12	/
		AFM-2	1.9	1.17	0	1.06	/
		AFM-3	0	1.30	0	1.06	289.9
	2	FM	69.0	1.43	4	1.17	/
		AFM-1	82.2	1.73	0	1.16	/
		AFM-2	-1.5	1.63	0	1.12	/
		AFM-3	0	1.77	0	1.11	283.6
	3	FM	42.8	1.88	4	1.22	/
		AFM-1	57.9	2.22	0	1.2	/
		AFM-2	-4.8	2.07	0	1.17	/
		AFM-3	0	2.22	0	1.16	269.7
$VOBr_2$	1	FM	43.7	0.9	4	1.17	/
		AFM-1	63.2	1.18	0	1.14	/
		AFM-2	-0.9	1.09	0	1.10	/
		AFM-3	0	1.21	0	1.09	264.8
	2	FM	16.7	1.22	4	1.22	/
		AFM-1	38.9	1.54	0	1.19	/
		AFM-2	-6.4	1.42	0	1.16	/
		AFM-3	0	1.54	0	1.15	254.5
	3	FM	-3.4	1.16	4	1.27	/
		AFM-1	23.5	1.54	0	1.23	/
		AFM-2	-12.3	1.39	0	1.22	/
		AFM-3	0	1.54	0	1.20	242.6

Table S2. Structural parameters, total polarization (P), energy battier (E_b), electronic band gap (E_{gap}) and elastic constants of $VOBr_2$ monolayer.

Lattice constants(Å)		**Bond length (Å)**			**Bond angle (°)**	
a	*b*	$d_{V\text{-}Br}$	$d_{V\text{-}O1}$	$d_{V\text{-}O2}$	Br-V-Br	O-V-O
3.773	3.578	2.542	2.114	1.659	89.5/89.2	180
P (*p*C/m)	E_b (eV)	E_{gap} (eV)	C_{11}	C_{22}	C_{12}	C_{66}
271	0.132	0.75	52.0	39.3	5.8	4.2

Table S3. Calculated total energies *E* (meV) relative to the energy of AFM-3 configuration ($E_{AFM\text{-}3}$) of four magnetic coupling configurations (FM, AFM-1, AFM-2 and AFM-3) in a $2 \times 2 \times 1$ supercell, nearest-neighbor exchange coupling parameters (J_a and J_b) along *a*- and *b*-direction, next-nearest-neighbor exchange coupling parameter (J_{ab}) (in meV) and the Néel temperature (T_N) of $VOBr_2$ monolayer.

E_{FM}	$E_{AFM\text{-}1}$	$E_{AFM\text{-}2}$	$E_{AFM\text{-}3}$	J_a	J_b	J_{ab}	T_N (K)
48.5	69.9	5.7	0	0.83	-11.79	0.76	107

Table S4. Summary of the calculated magnetic anisotropy energies in μeV/V atom.

	E(100)-E(001)	E(010)-E(001)	E(110)-E(001)	E(111)-E(001)
$VOCl_2$	16.55	3.36	9.95	6.63
$VOBr_2$	14.40	5.42	9.91	6.61

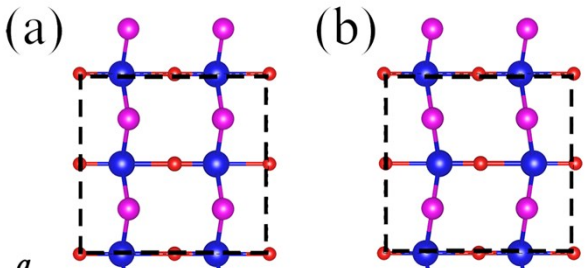

Figure S1. Atomic structures of $VOCl_2$ monolayer. (a) α, (b) β, (c) γ and (d) δ structures. The $2 \times 2 \times 1$ supercells are illustrated by the dashed black line.

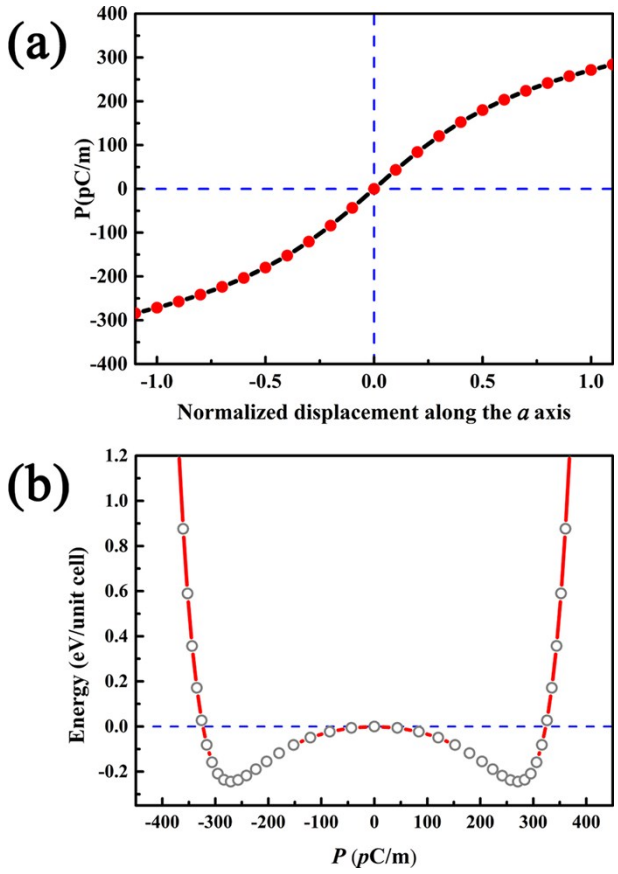

Figure S2. (a) Calculated total polarization of $VOBr_2$ monolayer as a function of normalized displacement along the adiabatic path. The centrosymmetric PE phase (0% displacement) is at the center, and two FE ground states are at the two ends (-100% and 100% displacements). (b) Double well potential of $VOBr_2$ monolayer along an adiabatic path.

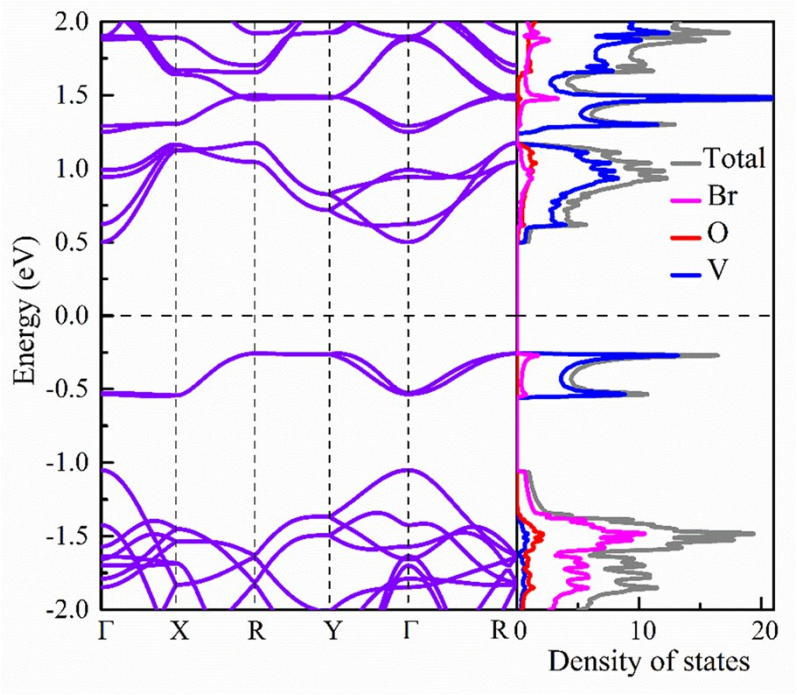

Figure S3. Electronic band structure (left) and total electron density of states (right) of $VOBr_2$ monolayer near the Fermi level. The Fermi level is denoted by a dashed line at 0 eV. Γ (0, 0, 0), X (1/2, 0, 0), R (1/2, 1/2, 0) and Y (0, 1/2, 0) are highly symmetric points in reciprocal space.

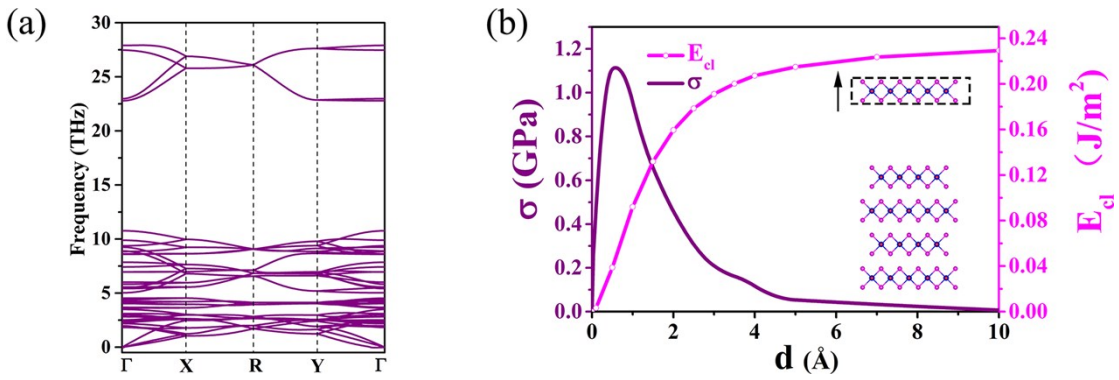

Figure S4. (a) The phonon spectra of the $VOBr_2$ monolayer. (b) The cleavage energy E_{cl} and cleavage strength σ as functions of separation distance *d* in the process of exfoliating one $VOBr_2$ monolayer from its bulk.