Supplementary Material

Stability, electronic, and optical properties of two-dimensional iridium trihalides with promising applications in photocatalytic water splitting

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Contents:

Figure S1:

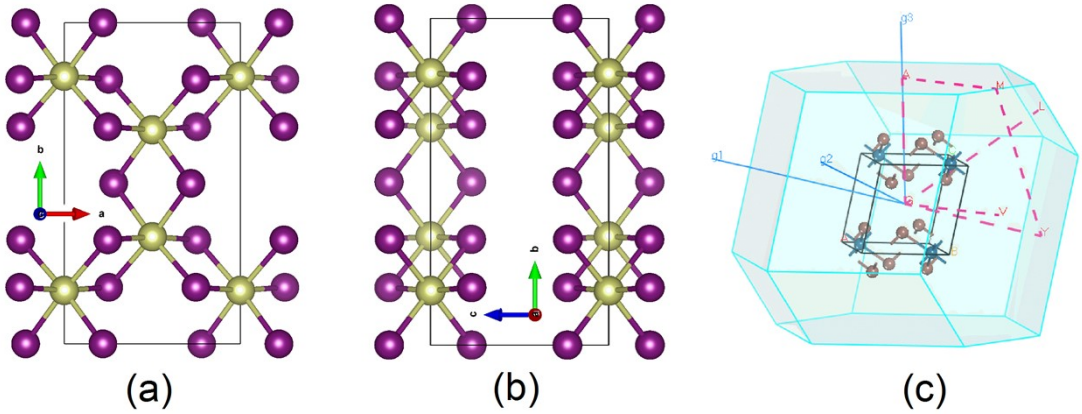

Figure S1 (a) Top and (b) side views of the crystal structure of the bulk phase of α-IrX_3 (X = Cl, Br, I) in the representation of the conventional cell. (c) High symmetry *k*-points of the Brillouin zone for α-IrX_3 and the path along which the band structure is evaluated.

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Figure S2:

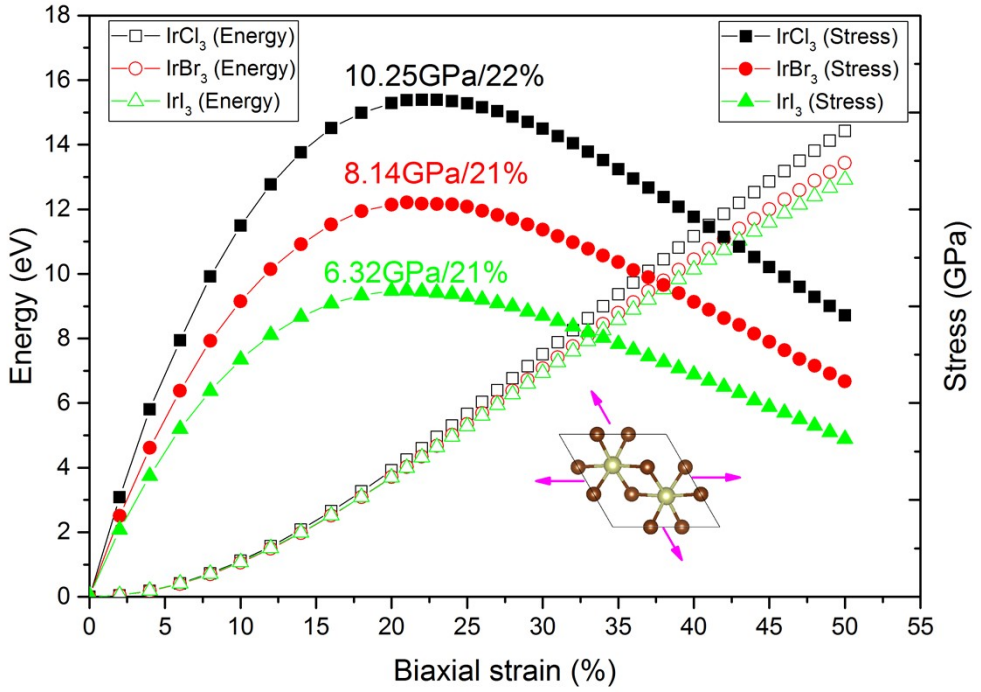

Figure S2. The change of strain energy and the created stress in the IrX_3 monolayers under applied biaxial strain. Because a vacuum space is left along the *z* direction in the unit cell, the calculated in-plane stress components must be rescaled [1,2] based on the effective layer thickness d_0 of IrX_3 monolayers. We chose the lattice constant *c* of bulk IrX_3 as the d_0, as list in Table S1, and rescale the in-plane stress components by h/d_0, where *h* is the length of the cell along *z* axis.

Table S1. Calculated lattice constant (in Å) at PBE level, and band-gap E_g (in eV) of α-IrX_3 bulk at different levels. The asterisk (*) means the experimental results.

Structure	***a***	***b***	***c***	E_g with different methods			
				PBE	PBE-SOC	HSE06	experiment
$IrCl_3$	6.092	10.558	5.629	1.846	1.750	3.264	
$IrCl_3$[3]	5.99±0.01	10.37±0.02	5.99±0. 01				
$IrBr_3$	6.408	11.116	5.984	1.432	1.380	2.704	
$IrBr_3$ * [4]	6.30	10.98	6.34				
IrI_3	6.867	11.901	6.490	1.175	1.123	2.217	
IrI_3 [5]	6.802	11.791	6.864	1.0			1.49
IrI_3*[11]	6.74	11.75	6.80				

Figure S3:

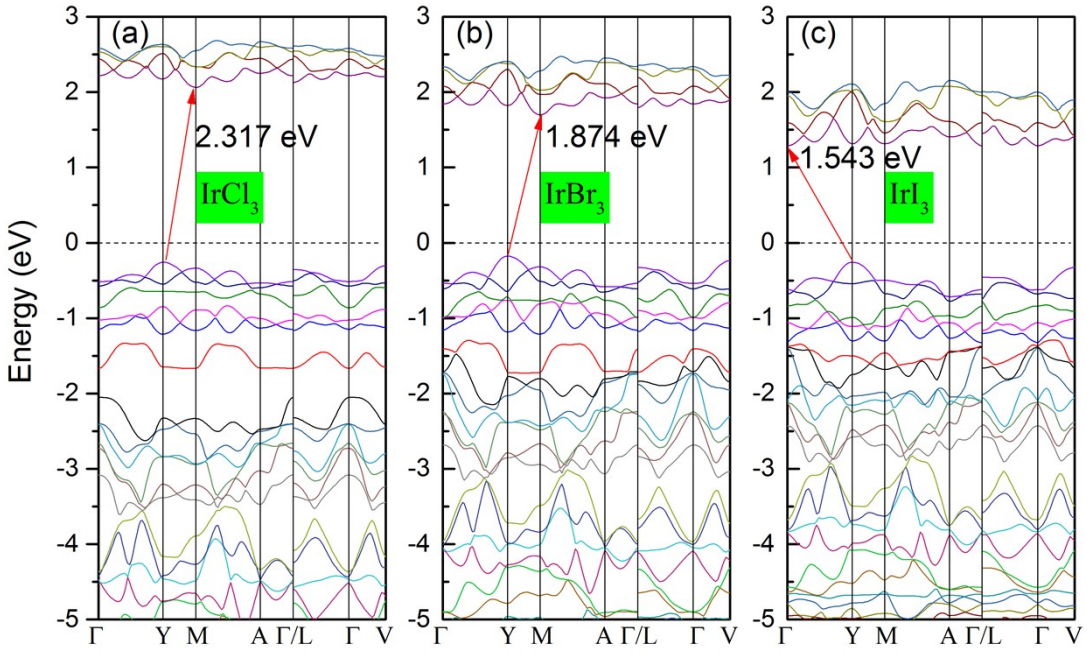

Figure S3. Electronic structure of bulk IrX_3 obtained from HSE functional with 10% of the exact exchange.

Figure S4:

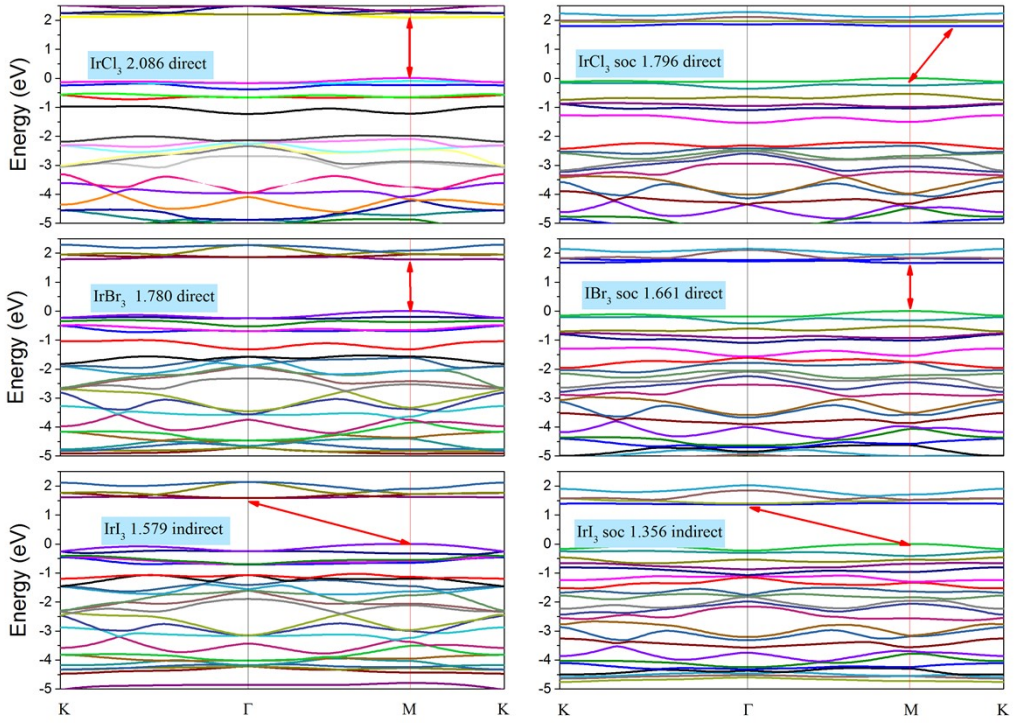

Figure S4. Electronic structure of monolayer IrX_3 obtained from (left panel) PBE and (right panel) PBE + SOC methods.

Figure S5:

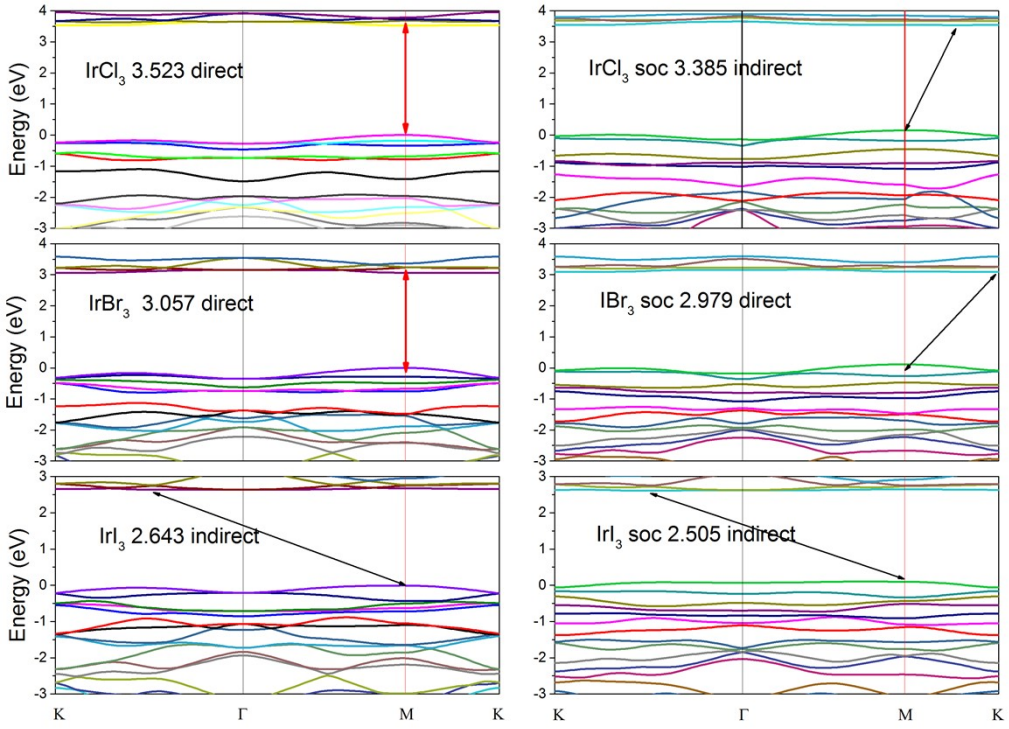

Figure S5. Electronic structure of monolayer IrX_3 obtained from (left panel) HSE06 and (right panel) HSE06 + SOC methods.

Figure S6.

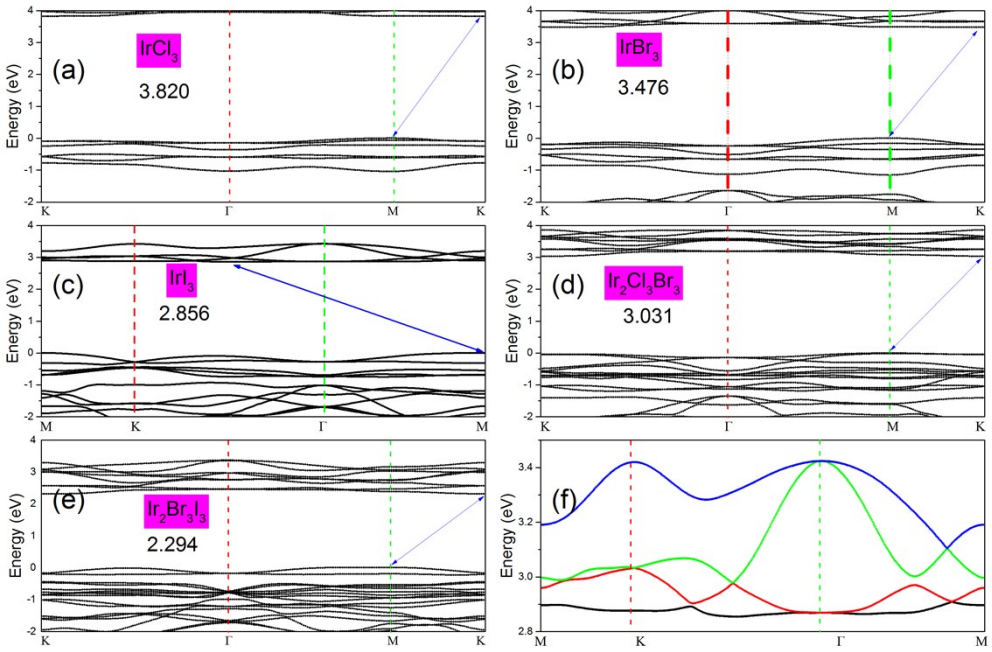

Figure S6. Electronic structure of monolayers (a) $IrCl_3$, (b) $IrBr_3$, (c) IrI_3, and their heterojunctions (d) $IrCl_3$:$IrBr_3$ and (e) $IrBr_3$:IrI_3 obtained from G_0W_0 method. (f) The band structures of IrI_3 near the valence band maximum.

Figure S7.

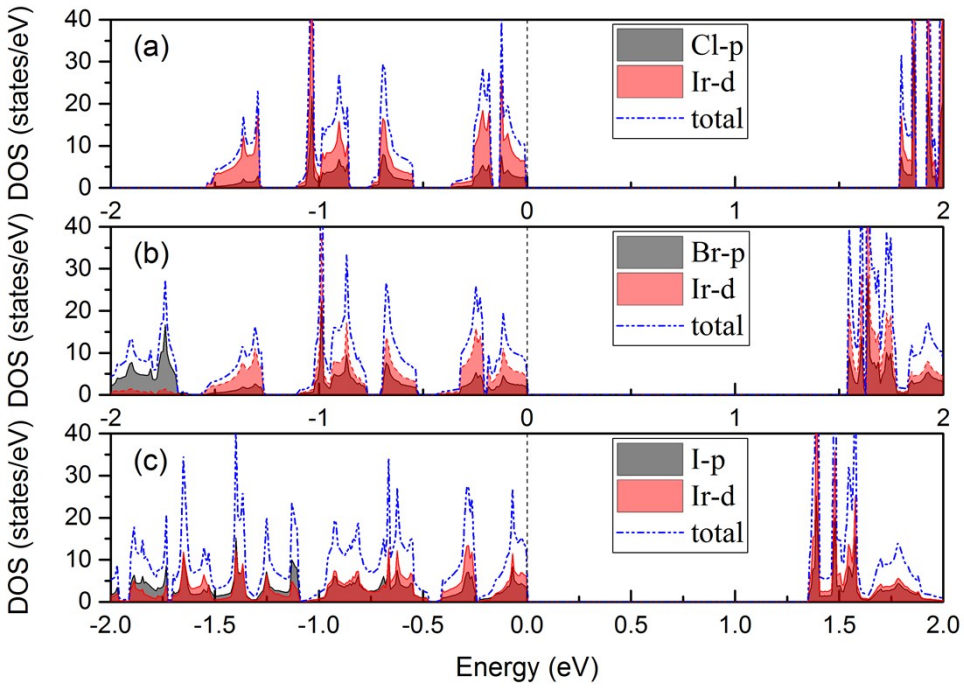

Figure S7. Total and projected DOS of monolayers (a) $IrCl_3$, (b) $IrBr_3$, (c) IrI_3 obtained at PBE+SOC level.

Figure S8.

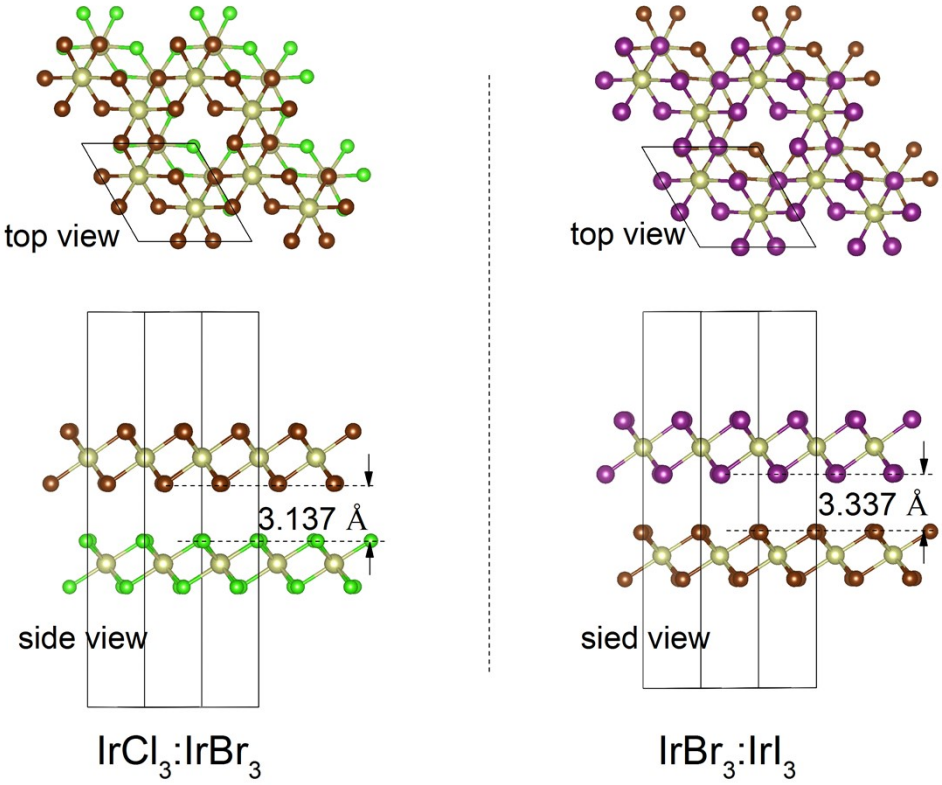

Figure S8. Top and lateral views of $IrCl_3$:$IrBr_3$ and $IrBr_3$:IrI_3 van der Waals heterostructures.

References

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[3] K. Brodersen, F. Moers and H. Schnering, Zur Struktur des Iridium (III)-und des Ruthenium (III)-chlorids, *Sci. Nat.*, 1965, 52(9), 205-206.

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[5] D. Ni, K. P. Devlin, G. Cheng, X. Gui, W. Xie, N. Yao and R. J. Cava, The honeycomb and hyperhoneycomb polymorphs of IrI_3, *J. Solid State Chem.*, 2022, 312, 123240.

[1] F. Liu, P. Ming and J. Li, Ab initio calculation of ideal strength and phonon instability of graphene under tension, *Phys. Rev. B*, 2007, 76(6), 064120.

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