Supporting information

Insight into the reaction mechanism of water, oxygen and nitrogen molecule on the tin iodine perovskite surface

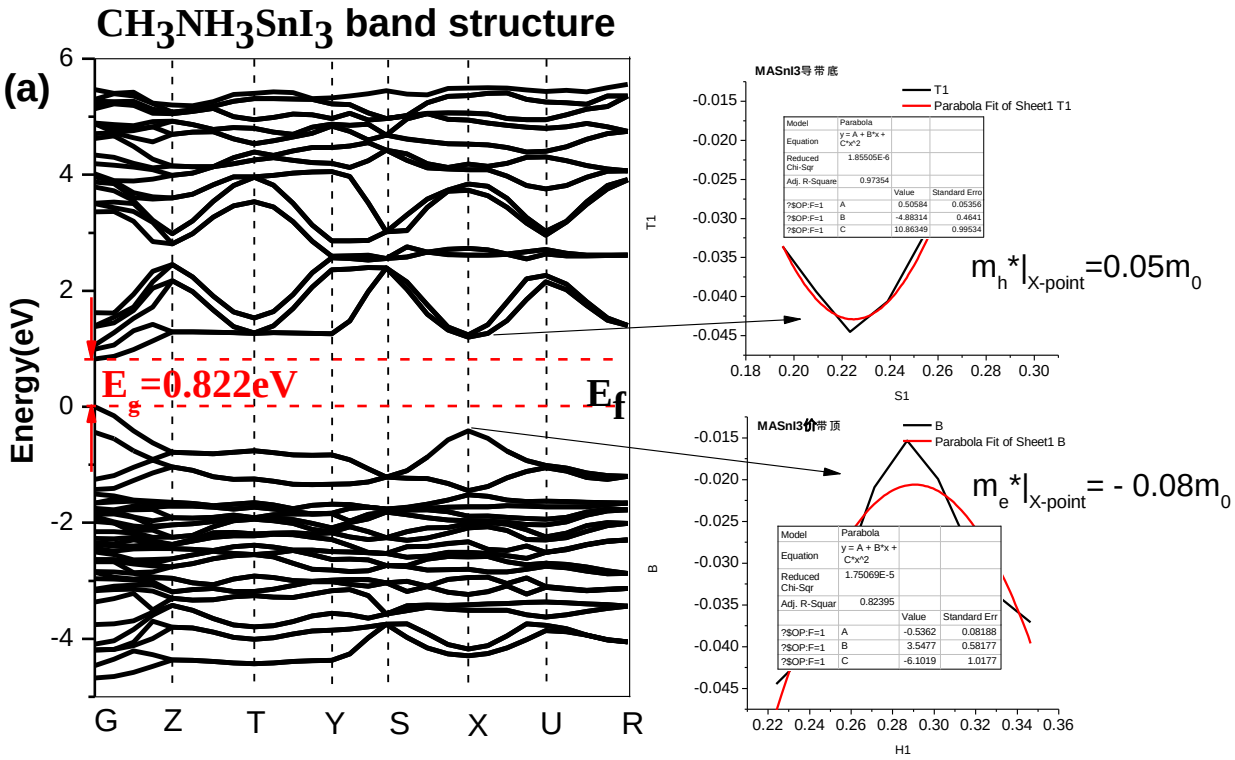
Guo Xie [a], Ling Xu [a, *], Lin Sun [a], Yan Xiong [a], Ping Wu [a], Bin Hu [a, b,*]

[a] *Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wu Han 430074, China*

[b] *Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA*

*Corresponding author: Assistant Prof. Ling Xu and Prof. Bin Hu,
E-mail address:xuling@mail.hust.edu.cn; bhu@utk.edu

1. Comparing the difference of $MASnI_3$ and $MAPbI_3$



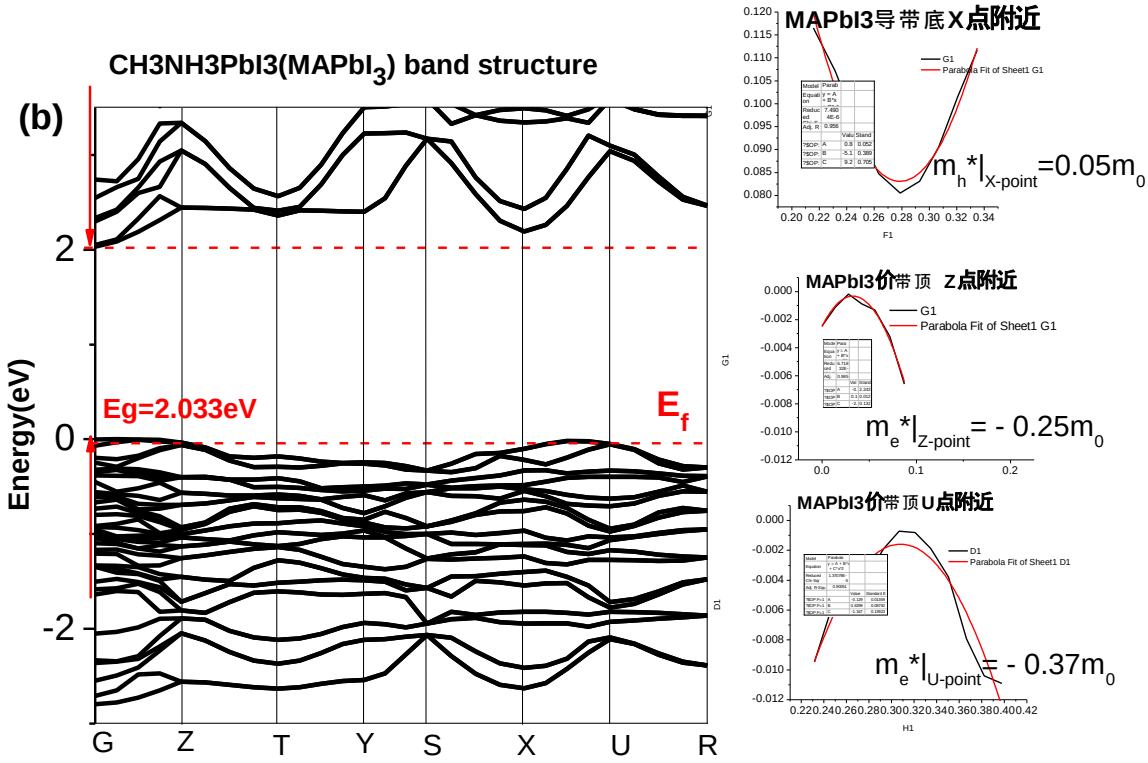


Figure S1. Band gaps and carrier's effective masses of (a) MASnI3 and (b) MAPbI3 bulk structures.

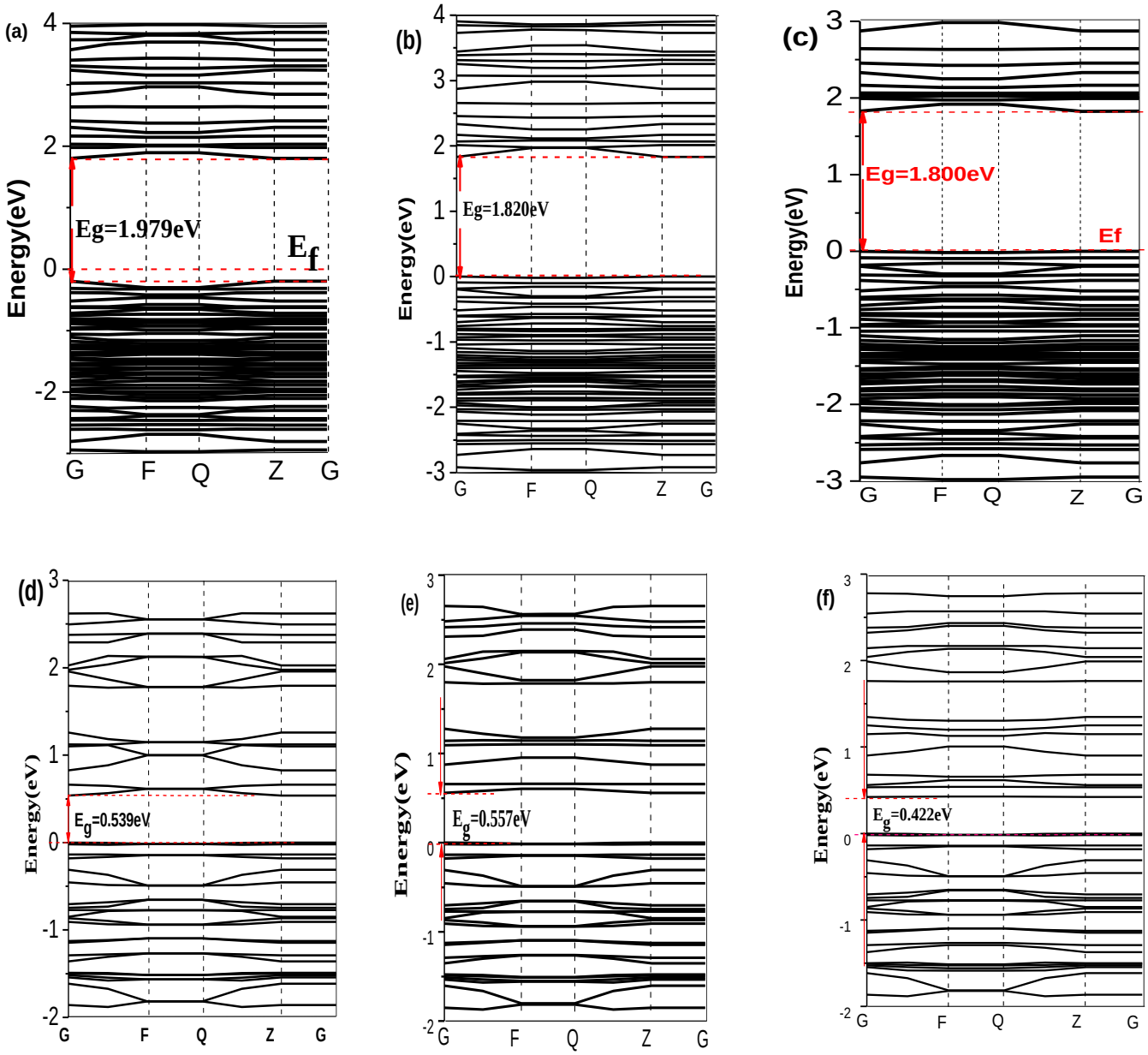


Figure S2. Band structures of MAPbI3 (a)clean (110) surface, (b)H2O adsorption on MAPbI3 (110) surface, (c)N2 adsorption on MAPbI3(110) surface, of MASnI3 (d)clean (011) surface, (e)H2O adsorption on MASnI3 (011) surface, (f) N2 adsorption on MASnI3 (011) surface.

Table S1. The band gaps of every case for clean surfaces, H2O adsorption, or N2 adsorption of $MAPbI_3$ and $MASnI_3$.

Eg/eV	MASnI3	MAPbI3
Clean surface	0.539	1.979
H2O adsorption	0.557	1.820
N2 adsorption	0.422	1.800

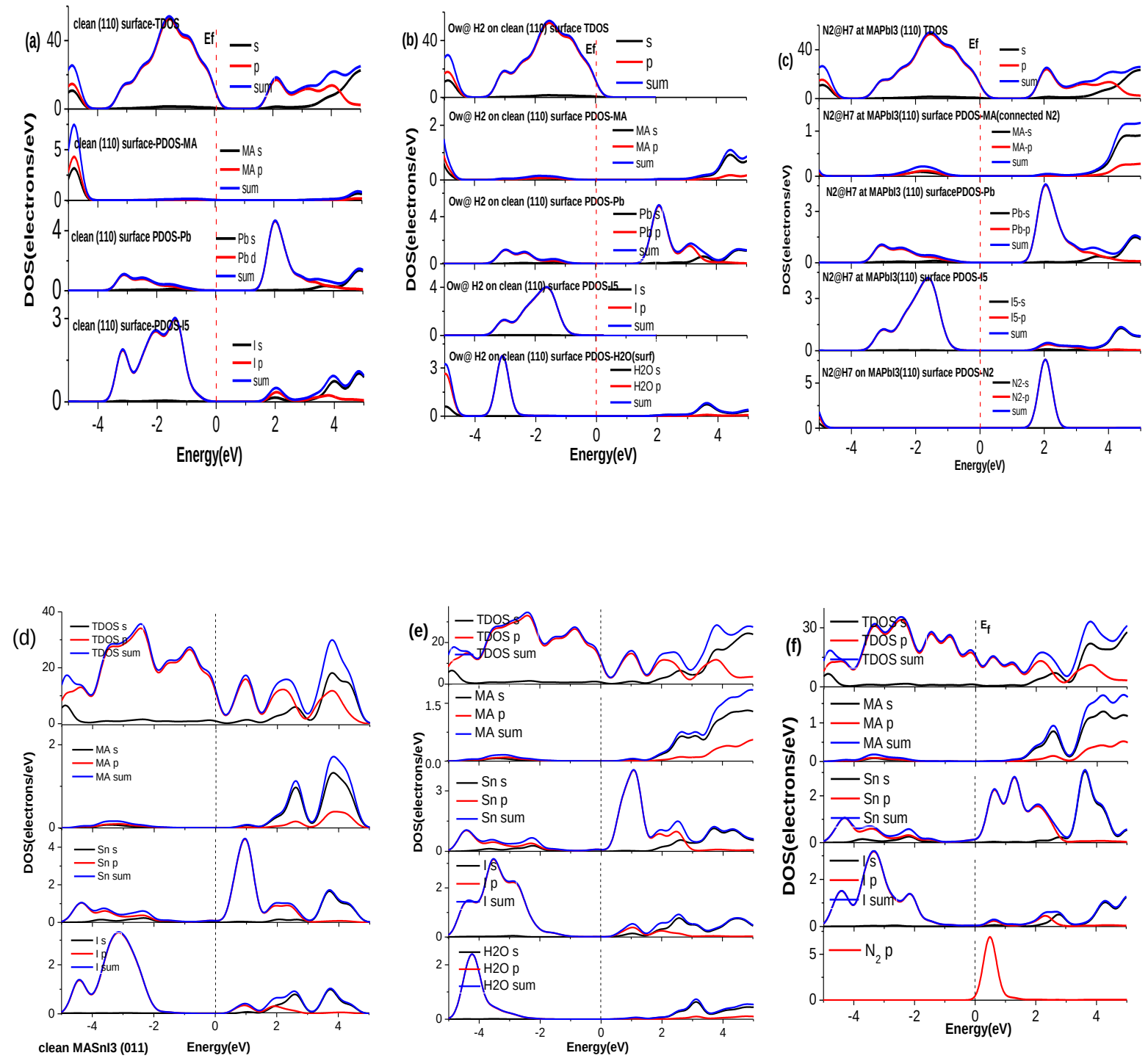


Figure S3. The density of states (DOS) and partial Density of states (PDOS) of MAPbI3 (110) surface (a)clean (110) surface, (b) H2O adsorption, (c) N2 adsorption, of MASnI3 (011) surface (d) clean MASnI3 (011) surface, (e) H2O adsorption, (f) N2 adsorption.

2. Calculated the interface properties with and without adsorption H_2O molecule

we calculated the interface properties with and without adsorption H_2O molecule, see the Figure S4-S6, Table S2 and Table S3. Our calculation showed that the interface of TiO_2/$MAPbI_3$ possessed a higher stability, TiO_2 layer facilitated the stability of perovskite, though TiO_2 layer is capable to protect the perovskite surface, the influence which H_2O had on the surface still existed.

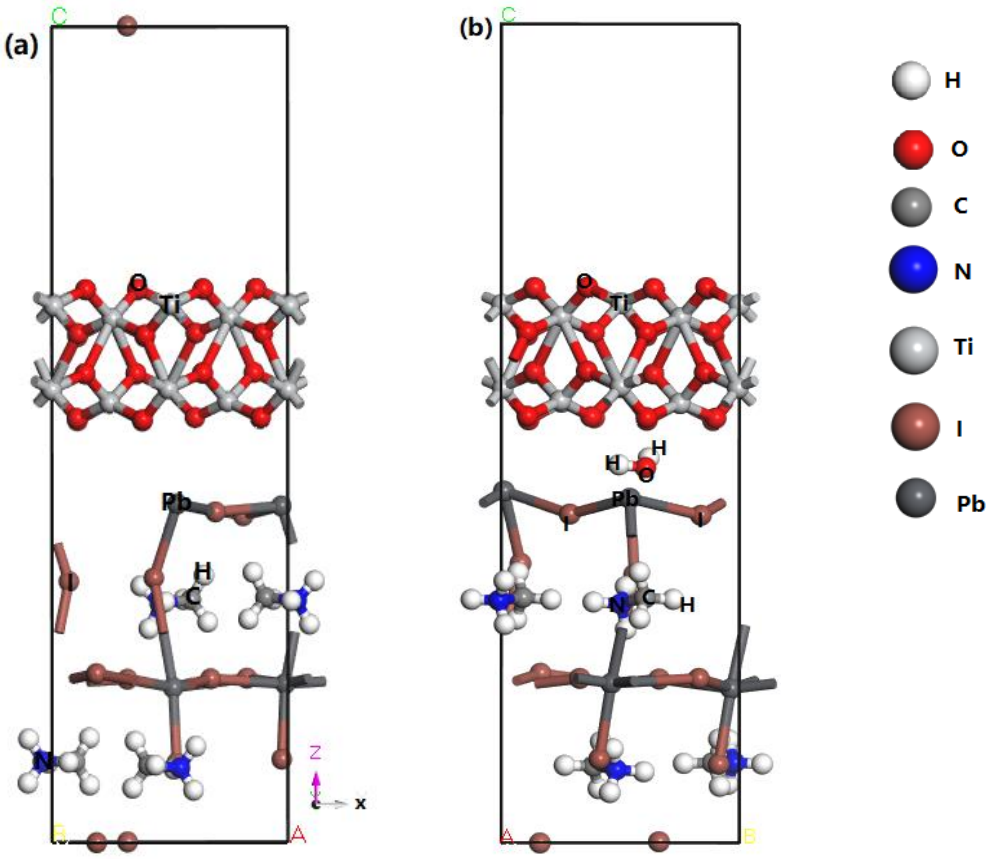


Figure S4. The optimized models of (a) TiO_2/perovskite interface, and (b) H_2O adsorption on the interface of TiO_2/perovskite.

Table S2. The parameters of the clean TiO_2/$MAPbI_3$ interface and the adsorption case of the interface.

Case	Formula (number of atoms)	Total energy /eV	Parameter			Adsorption energy/eV	Surface energy or interface energy/(J/m^2)
			a	b	c		
r-TiO_2 (001)	O8Ti4 (12)	-9922.71498	4.56699	4.56699	14.6576	--	0.08371994
$MAPbI_3$ (010)	C4H24N4I12Pb4 (48)	-12496.0366	9.32209	8.44470	22.9687	--	0.047584469
TiO_2 bulk	O4Ti2	-4961.46649	4.56699	4.56699	3.10510	--	
$MAPbI_3$ bulk	C4H24N4I12Pb4	-12500.7132	8.44470	13.0242	9.32209	--	--
H_2O	H2O(3)	-468.776262	--	--	--	--	--
H_2O- $MAPbI_3$ (010)	C4H26N4OI12Pb4(51)	-12965.0106	9.32209	8.44470	22.9687	-0.197738	0.455724615
TiO_2(001)-$MAPbI_3$ (010)	C4H24N4O32Ti16I12Pb4	-52187.4219	9.22803	8.78934	31.2972	--	0.860850415
H_2O@[TiO_2(001)(2X2)-$MAPbI_3$(010)(1X1)]	C4H26N4O33Ti16I12Pb4(99)	-52656.6002	9.22803	8.78934	31.2972	-0.40204	0.373301857

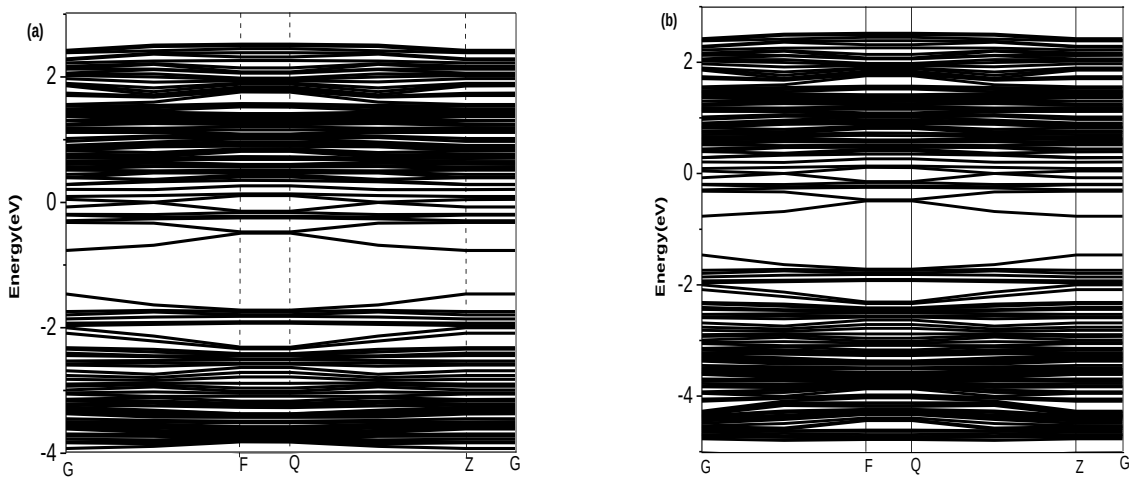


Figure S5. The band gaps of (a) clean interface of TiO_2/$MAPbI_3$, and (b) H_2O adsorption on the interface of TiO_2/$MAPbI_3$

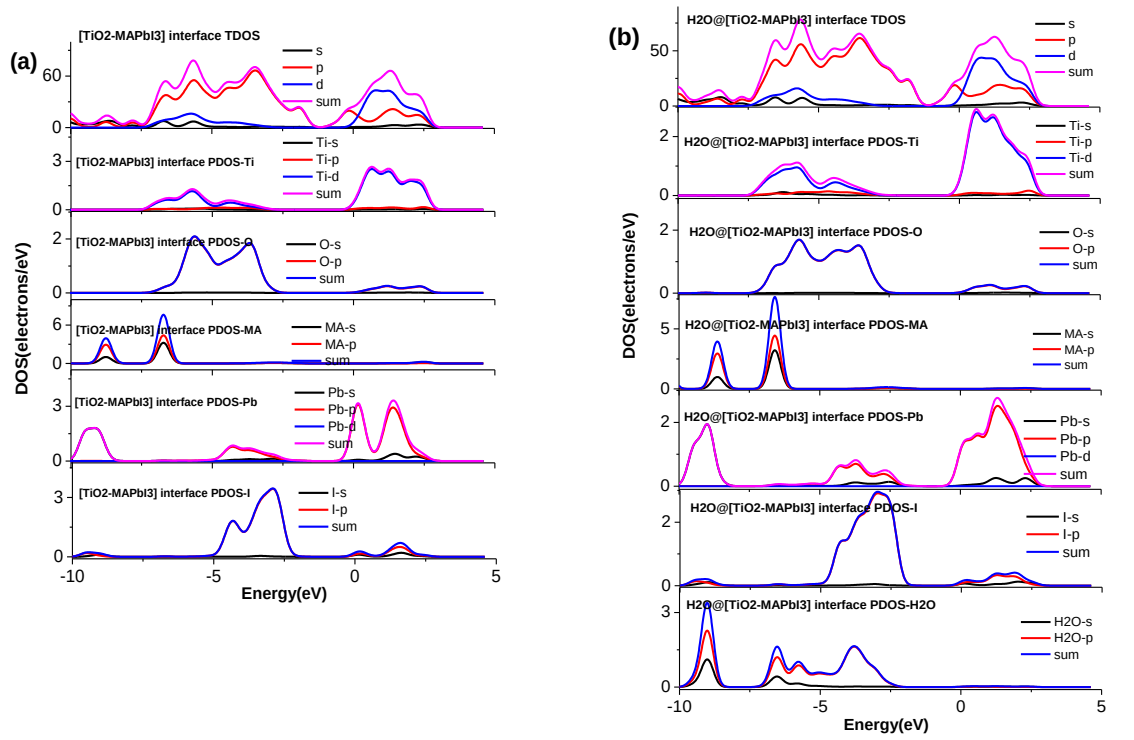


Figure S6. DOS and PDOS of (a) the clean interface of TiO_2/Perovskite and (b) H_2O absorption on the TiO_2/Perovskite interface.

Table S3. The bond length, bond angle, Mulliken population and charge of these related cases.

Case	Bond	Population	Bond length /Å	Atom	Charge/e
Clean interface [TiO_2-$MAPbI_3$]	**I9--Pb3**	**-0.75**	**2.93028**	**I9** **Pb3**	**-0.34** **0.76**
	I12--Pb4	-0.80	2.93264	I12 Pb4 O13 O23 Ti13 I2	-0.34 0.77 -0.64 -0.65 1.23 -0.12
H_2O adsorption on the interface	**I9--Pb3**	**-0.70**	**2.93206**	**I9** **Pb3**	**-0.34** **0.75**
	I12--Pb4	-0.72	2.93328	I12 Pb4	-0.33 0.76
	H25--O33	0.61	0.98716	H25 O33	0.41 -0.86
	H26--O33	0.61	0.99004	H26	0.40
	H25--O23	-0.00	2.98829	O23	-0.69
	H25--I2	-0.04	2.85006	I2	-0.12
	H26--Ti13	-0.04	2.89082	Ti13	1.24
	O13--O33	-0.04	2.79668	O13	-0.66
	O23--O33	-0.06	2.78685		