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Band Engineering and Charge Separation in the $Mo_{1-x}W_xS_2$ /TiO_2 Heterostructure by Alloying: First Principle Prediction

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Contents

S1 2D profiles of charge density difference

To understand the charge transfer and separation process, the charge density difference was calculated by subtracting the electronic charges of the pristine $Mo_xW_{1-x}S_2$ and TiO_2 slab from that of the $Mo_{1-x}W_xS_2/TiO_2$ heterostructure. The 2D profiles of charge density difference on (200) crystal planes of $Mo_{1-x}W_xS_2/TiO_2$ are shown in Fig. S1. As seen in this figure, the charge is mainly distributed at the interface between $Mo_{1-x}W_xS_2$ and TiO_2, besides the electron transfer orientation is directed from $Mo_{1-x}W_xS_2$ to TiO_2. The increasing of W mass ratio in the $Mo_{1-x}W_xS_2$ structure leads to increased accumulation of electron at the interface. The obtained values of transferred electron between $Mo_{1-x}W_xS_2$ and Tio_2 are reported in the main text.

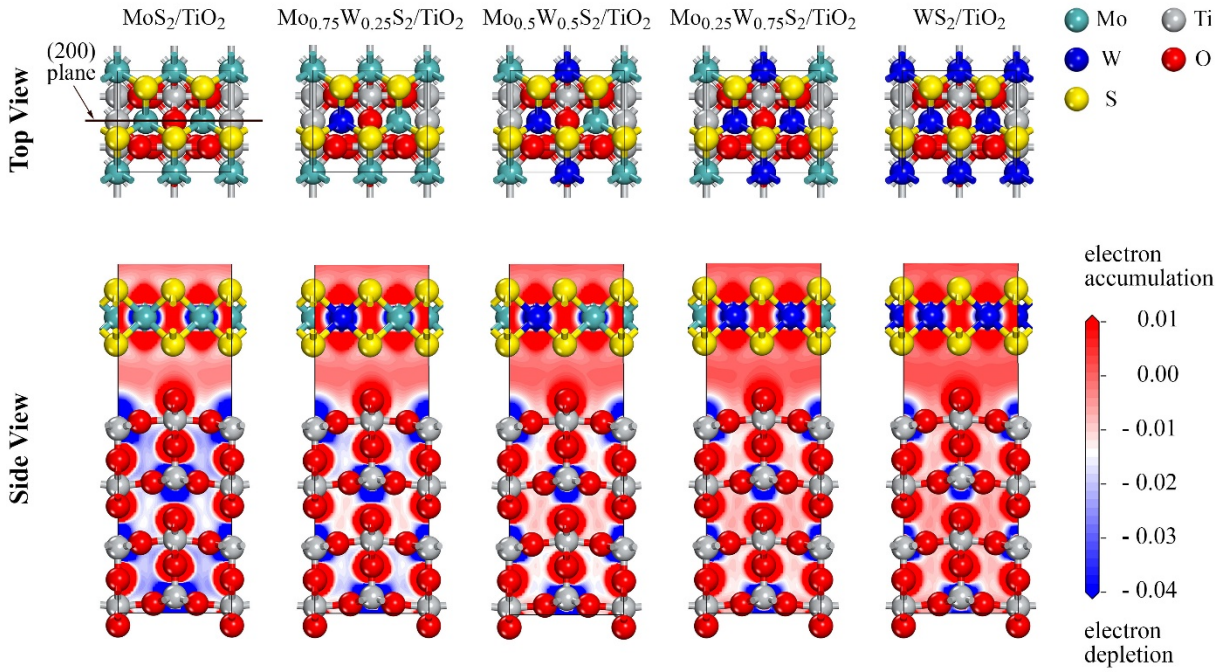

Fig. S1 2D profiles of charge density difference on (200) crystal planes of $Mo_{1-x}W_xS_2/TiO_2$ and corresponding top views. The red and blue regions showing accumulation and depletion of electrons, respectively (unit: $eÅ^{-3}$).

S2 Experimental and optimized lattice constants of TiO_2 and MS_2 (M=Mo,W)

In Table S1, optimized lattice constants of bulk Rutile TiO_2 and monolayer MS2 (M=Mo, W) are compared to experimental data from literature. The good agreement between the calculated and experimental values indicates that the GGA/PBE method is a suitable choice for density functional study of metal dichalcogenides and TiO_2 structures. Note that, since there is no repeating unit along the out-of-plane direction in planar monolayer structures, reporting of the *c* crystallographic direction for MoS_2 and WS_2 is not relevant.

Table S1 Experimental and optimized lattice constants within the exchange and correlation functional of PBE for bulk Rutile TiO_2 and monolayer MS_2 (M=Mo,W)

Structure	Calculated (our work)		Experimental		
	a (Å)	c (Å)	a (Å)	c (Å)	Ref.
TiO_2	4.651	2.971	4.595	2.959	1, 2
MoS_2	3.201	-	3.161	-	3, 4
WS_2	3.213	-	3.153	-	5, 6

S3 Optimized atomic coordinates of $Mo_{1-x}W_xS_2$ and $Mo_{1-x}W_xS_2$ /TiO_2 (110)

To model a monolayer $Mo_{1-x}W_xS_2$ on TiO_2 substrate, one √3×2 rectangular unit cell of $Mo_{1-x}W_xS_2$ was placed on the top of four-layer 2×1 Rutile TiO_2 (110) slab (tetragonal, $P4_2/mnm$, D_{4h}^{14}, #136). The monolayer of the $Mo_{1-x}W_xS_2$ has hexagonal lattice which belongs to the space-group $P\bar{6}m2$, D_{3h}^{1}, (#187). Therefore, the $Mo_{1-x}W_xS_2$ systems and $Mo_{1-x}W_xS_2/TiO_2$ heterostructures with different x values have been optimized geometrically. The obtained lattice vectors and the detailed fractional coordinates are as follow.

S3.1 MoS_2

MoS_2

Cell vectors	x (Å)	y (Å)	z (Å)
$\vec{a}$	3.20100	0.00000	0.00000
$\vec{b}$	-1.60050	2.77215	0.00000
$\vec{c}$	0.00000	0.00000	30.7500

Fractional coordinates	a	b	c
Mo	0.66667	0.33333	0.50000
S	0.33333	0.66667	0.44920
S	0.33333	0.66667	0.55080

S3.2 $Mo_{0.75}W_{0.25}S_2$

$Mo_{0.75}W_{0.25}S_2$			
Cell vectors	x (Å)	y (Å)	z (Å)
$:2\vec{a}$	6.40800	0.00000	0.00000
$:2\vec{b}$	-3.20400	5.54949	0.00000
$:\vec{c}$	0.00000	0.00000	30.7644
Fractional coordinates	2a	2b	c
Mo	0.33333	0.16667	0.50000
Mo	0.83333	0.16667	0.50000
Mo	0.83333	0.66667	0.50000
S	0.16667	0.33333	0.44920
S	0.66667	0.83333	0.44920
S	0.16667	0.83333	0.44920
S	0.16667	0.33333	0.55080
S	0.66667	0.83333	0.55080
S	0.16667	0.83333	0.55080
S	0.66667	0.33333	0.44920
S	0.66667	0.33333	0.55080
W	0.33333	0.66667	0.50000

S3.3 $Mo_{0.50}W_{0.50}S_2$

$Mo_{0.5}W_{0.5}S_2$

Cell vectors	x (Å)	y (Å)	z (Å)
$:2\vec{a}$	6.41400	0.00000	0.00000
$:2\vec{b}$	-3.20700	5.55469	0.00000
$:\vec{c}$	0.00000	0.00000	30.7787

Fractional coordinates	2a	2b	c
Mo	0.33333	0.16667	0.50000
S	0.16667	0.33333	0.44920
S	0.16667	0.33333	0.55080
Mo	0.83333	0.16667	0.50000
S	0.66667	0.33333	0.44920
S	0.66667	0.33333	0.55080
W	0.33333	0.66667	0.50000
S	0.16667	0.83333	0.44920
S	0.16667	0.83333	0.55080
W	0.83333	0.66667	0.50000
S	0.66667	0.83333	0.44920
S	0.66667	0.83333	0.55080

S3.4 $Mo_{0.25}W_{0.75}S_2$

$Mo_{0.25}W_{0.75}S_2$

Cell vectors	x (Å)	y (Å)	z (Å)
$:2\vec{a}$	6.42000	0.00000	0.00000
$:2\vec{b}$	-3.21000	5.55988	0.00000
$:\vec{c}$	0.00000	0.00000	30.7931

Fractional coordinates	2a	2b	c
Mo	0.00000	0.00000	0.50000
W	0.50000	0.00000	0.50000
W	0.00000	0.50000	0.50000
W	0.50000	0.50000	0.50000
S	0.83333	0.16667	0.44920
S	0.83333	0.66667	0.44920
S	0.33333	0.16667	0.44920
S	0.83333	0.16667	0.55080
S	0.83333	0.66667	0.55080
S	0.33333	0.16667	0.55080
S	0.33333	0.66667	0.44920
S	0.33333	0.66667	0.55080

S3.5 WS_2

WS_2			
Cell vectors	x (Å)	y (Å)	z (Å)
$\vec{a}$	3.21300	0.00000	0.00000
$\vec{b}$	-1.60650	2.78254	0.00000
$\vec{c}$	0.00000	0.00000	30.8075

Fractional coordinates	a	b	c
W	0.66667	0.33333	0.50000
S	0.33333	0.66667	0.44920
S	0.33333	0.66667	0.55080

S3.6 MoS_2/TiO_2

MoS_2/TiO_2

Cell vectors	x (Å)	y (Å)	z (Å)
$\vec{a}$	5.67140	0.00000	0.00000
$\vec{b}$	0.00000	6.48550	0.00000
$\vec{c}$	0.00000	0.00000	33.43350

Fractional coordinates	a	b	c
Mo	0.12843	0.00157	0.50520
Mo	0.64431	0.23523	0.50523
Mo	0.12801	0.48587	0.50518
Mo	0.64429	0.73639	0.50522
S	0.81813	0.00157	0.45882
S	0.81821	0.00157	0.55143
S	0.30197	0.23506	0.45887
S	0.30193	0.23513	0.55148
S	0.81813	0.48583	0.45900
S	0.81806	0.48580	0.55156
S	0.30199	0.73663	0.45889
S	0.30194	0.73656	0.55149
Ti	0.92920	0.50175	0.02773
Ti	0.92995	0.90335	0.11134
Ti	0.93217	0.50206	0.23106
Ti	0.93340	0.90355	0.31489
Ti	0.25431	0.90329	0.01133
Ti	0.25630	0.50180	0.12584
Ti	0.25691	0.90360	0.21679
Ti	0.26039	0.50203	0.33104
Ti	0.51303	0.50175	0.02773
Ti	0.51378	0.90334	0.11134
Ti	0.51598	0.50211	0.23104
Ti	0.51732	0.90378	0.31488
Ti	0.77046	0.90329	0.01131
Ti	0.77248	0.50180	0.12585
Ti	0.77305	0.90361	0.21679
Ti	0.77635	0.50210	0.33094
O	0.92891	0.90332	0.97864
O	0.92974	0.50179	0.08173
O	0.93160	0.90370	0.18250
O	0.93285	0.50224	0.28563
O	0.92959	0.90326	0.05692
O	0.93040	0.50185	0.16023
O	0.93271	0.90356	0.26093
O	0.93356	0.50236	0.36381
O	0.25480	0.69128	0.01585
O	0.25591	0.19662	0.11954
O	0.25782	0.69844	0.22307
O	0.25946	0.19020	0.32686

O	0.25482	0.31218	0.01587
O	0.25592	0.80700	0.11955
O	0.25773	0.30578	0.22311
O	0.25949	0.81433	0.32687
O	0.51273	0.90331	0.97864
O	0.51358	0.50180	0.08173
O	0.51547	0.90369	0.18250
O	0.51629	0.50231	0.28566
O	0.51341	0.90326	0.05692
O	0.51423	0.50181	0.16023
O	0.51646	0.90370	0.26092
O	0.51780	0.50212	0.36388
O	0.77096	0.69128	0.01585
O	0.77207	0.19663	0.11954
O	0.77384	0.69844	0.22308
O	0.77561	0.19019	0.32679
O	0.77098	0.31218	0.01587
O	0.77208	0.80699	0.11955
O	0.77393	0.30578	0.22312
O	0.77558	0.81432	0.32681

S3.7 $Mo_{0.75}W_{0.25}S_2/TiO_2$

$Mo_{0.75}W_{0.25}S_2/TiO_2$			
Cell vectors	x (Å)	y (Å)	z (Å)
$\vec{a}$	5.68490	0.00000	0.00000
$\vec{b}$	0.00000	6.49310	0.00000
$\vec{c}$	0.00000	0.00000	33.43350

Fractional coordinates	a	b	c
Mo	0.04857	0.00617	0.50511
Mo	0.04818	0.50840	0.50510
Mo	0.56475	0.75865	0.50511
S	0.73956	0.00456	0.45838
S	0.73960	0.00457	0.55167
S	0.21934	0.25731	0.45849
S	0.21933	0.25721	0.55170
S	0.73965	0.51001	0.45854
S	0.73954	0.51004	0.55181
S	0.22259	0.75879	0.45879
S	0.22260	0.75894	0.55137
Ti	0.92035	0.50141	0.02799
Ti	0.91987	0.90298	0.11156
Ti	0.91846	0.50148	0.23137
Ti	0.91771	0.90304	0.31518
Ti	0.24653	0.90297	0.01157
Ti	0.24519	0.50144	0.12608
Ti	0.24487	0.90305	0.21707
Ti	0.24292	0.50156	0.33137
Ti	0.50419	0.50141	0.02799
Ti	0.50370	0.90298	0.11156
Ti	0.50227	0.50151	0.23137
Ti	0.50162	0.90311	0.31518
Ti	0.76269	0.90297	0.01157
Ti	0.76135	0.50144	0.12609
Ti	0.76103	0.90305	0.21706
Ti	0.75915	0.50153	0.33125
O	0.92054	0.90295	0.97889
O	0.91995	0.50141	0.08199
O	0.91879	0.90304	0.18280
O	0.91837	0.50155	0.28595
O	0.92009	0.90297	0.05715
O	0.91954	0.50143	0.16046
O	0.91810	0.90299	0.26124
O	0.91738	0.50150	0.36415
O	0.24620	0.69097	0.01612
O	0.24547	0.19619	0.11980
O	0.24434	0.69778	0.22338
O	0.24333	0.18947	0.32718
O	0.24620	0.31184	0.01612

O	0.24547	0.80664	0.11980
O	0.24427	0.30515	0.22340
O	0.24334	0.81355	0.32719
O	0.50437	0.90295	0.97889
O	0.50383	0.50141	0.08199
O	0.50260	0.90303	0.18280
O	0.50172	0.50155	0.28595
O	0.50394	0.90297	0.05715
O	0.50336	0.50143	0.16046
O	0.50192	0.90302	0.26124
O	0.50167	0.50149	0.36414
O	0.76236	0.69097	0.01612
O	0.76162	0.19619	0.11980
O	0.76051	0.69779	0.22339
O	0.75951	0.18950	0.32709
O	0.76236	0.31184	0.01612
O	0.76163	0.80664	0.11980
O	0.76045	0.30514	0.22341
O	0.75950	0.81358	0.32712
W	0.56442	0.25749	0.50511

S3.8 $Mo_{0.50}W_{0.50}S_2/TiO_2$

$Mo_{0.5}W_{0.5}S_2/TiO_2$			
Cell vectors	x (Å)	y (Å)	z (Å)
$\vec{a}$	5.70050	0.00000	0.00000
$\vec{b}$	0.00000	6.49930	0.00000
$\vec{c}$	0.00000	0.00000	33.43350

Fractional coordinates	a	b	c
Mo	0.04812	0.00642	0.50528
Mo	0.04771	0.50796	0.50527
W	0.56421	0.75855	0.50528
S	0.74044	0.00641	0.45822
S	0.74046	0.00642	0.55217
S	0.21935	0.25723	0.45868
S	0.21936	0.25709	0.55185
S	0.74049	0.50795	0.45837
S	0.74041	0.50797	0.55231
S	0.21936	0.75870	0.45867
S	0.21935	0.75884	0.55184
Ti	0.92040	0.50151	0.02795
Ti	0.91994	0.90306	0.11152
Ti	0.91859	0.50145	0.23132
Ti	0.91786	0.90301	0.31513
Ti	0.24657	0.90306	0.01153
Ti	0.24528	0.50151	0.12605
Ti	0.24498	0.90301	0.21702
Ti	0.24301	0.50150	0.33133
Ti	0.50424	0.50151	0.02795
Ti	0.50377	0.90306	0.11152
Ti	0.50240	0.50146	0.23132
Ti	0.50178	0.90304	0.31514
Ti	0.76273	0.90306	0.01152
Ti	0.76144	0.50151	0.12605
Ti	0.76114	0.90300	0.21701
Ti	0.75925	0.50146	0.33120
O	0.92058	0.90306	0.97884
O	0.92002	0.50151	0.08195
O	0.91891	0.90302	0.18275
O	0.91852	0.50144	0.28591
O	0.92014	0.90306	0.05711
O	0.91963	0.50152	0.16043
O	0.91825	0.90298	0.26119
O	0.91748	0.50148	0.36411
O	0.24625	0.69109	0.01608
O	0.24554	0.19629	0.11976
O	0.24444	0.69776	0.22334
O	0.24350	0.18942	0.32714
O	0.24625	0.31193	0.01608

O	0.24554	0.80673	0.11976
O	0.24441	0.30515	0.22334
O	0.24350	0.81349	0.32714
O	0.50441	0.90306	0.97884
O	0.50390	0.50152	0.08195
O	0.50273	0.90302	0.18275
O	0.50182	0.50143	0.28590
O	0.50400	0.90306	0.05711
O	0.50345	0.50151	0.16043
O	0.50206	0.90299	0.26119
O	0.50182	0.50148	0.36410
O	0.76240	0.69109	0.01608
O	0.76170	0.19630	0.11976
O	0.76061	0.69777	0.22335
O	0.75967	0.18940	0.32707
O	0.76240	0.31193	0.01608
O	0.76170	0.80673	0.11976
O	0.76060	0.30513	0.22336
O	0.75968	0.81349	0.32705
W	0.56420	0.25739	0.50528

S3.9 $Mo_{0.25}W_{0.75}S_2/TiO_2$

$MO_{0.25}W_{0.75}S_2/TiO_2$

Cell vectors	x (Å)	y (Å)	z (Å)
$\vec{a}$	5.71440	0.00000	0.00000
$\vec{b}$	0.00000	6.50730	0.00000
$\vec{c}$	0.00000	0.00000	33.43350

Fractional coordinates	a	b	c
W	0.04761	0.00635	0.50535
Mo	0.04748	0.50789	0.50534
W	0.56371	0.75814	0.50535
S	0.73724	0.00634	0.45799
S	0.73724	0.00635	0.55254
S	0.22018	0.25914	0.45842
S	0.22020	0.25898	0.55225
S	0.74041	0.50789	0.45845
S	0.74037	0.50790	0.55235
S	0.22019	0.75666	0.45841
S	0.22019	0.75682	0.55225
Ti	0.92046	0.50150	0.02794
Ti	0.92002	0.90306	0.11150
Ti	0.91871	0.50148	0.23130
Ti	0.91801	0.90305	0.31512
Ti	0.24662	0.90305	0.01151
Ti	0.24536	0.50152	0.12603
Ti	0.24509	0.90304	0.21701
Ti	0.24318	0.50154	0.33130
Ti	0.50431	0.50150	0.02794
Ti	0.50385	0.90306	0.11150
Ti	0.50251	0.50149	0.23131
Ti	0.50194	0.90308	0.31512
Ti	0.76278	0.90305	0.01150
Ti	0.76152	0.50152	0.12604
Ti	0.76125	0.90303	0.21699
Ti	0.75942	0.50151	0.33118
O	0.92064	0.90305	0.97882
O	0.92009	0.50151	0.08194
O	0.91903	0.90305	0.18273
O	0.91864	0.50149	0.28589
O	0.92021	0.90306	0.05709
O	0.91971	0.50153	0.16041
O	0.91838	0.90300	0.26117
O	0.91764	0.50153	0.36409
O	0.24631	0.69109	0.01607
O	0.24562	0.19629	0.11974
O	0.24455	0.69779	0.22331
O	0.24366	0.18947	0.32713
O	0.24631	0.31192	0.01607

O	0.24562	0.80673	0.11974
O	0.24562	0.80673	0.11974
O	0.24366	0.81353	0.32713
O	0.50447	0.90306	0.97882
O	0.50398	0.50151	0.08194
O	0.50284	0.90305	0.18273
O	0.50192	0.50149	0.28588
O	0.50407	0.90306	0.05709
O	0.50353	0.50152	0.16041
O	0.50220	0.90301	0.26117
O	0.50197	0.50153	0.36407
O	0.76247	0.69109	0.01606
O	0.76178	0.19630	0.11975
O	0.76072	0.69780	0.22333
O	0.75983	0.18944	0.32706
O	0.76247	0.31192	0.01606
O	0.76178	0.80672	0.11975
O	0.76072	0.30515	0.22335
O	0.75984	0.81355	0.32704
W	0.56370	0.25766	0.50535

S3.10 WS_2/TiO_2

WS_2/TiO_2				
Cell vectors		x (Å)	y (Å)	z (Å)
	$\vec{a}$	5.72640	0.00000	0.00000
	$\vec{b}$	0.00000	6.51460	0.00000
	$\vec{c}$	0.00000	0.00000	33.43350

Fractional	a	b	c
W	0.04901	0.00642	0.50545
W	0.04865	0.50795	0.50543
W	0.56490	0.75855	0.50544
S	0.73885	0.00640	0.45811
S	0.73886	0.00642	0.55261
S	0.22268	0.25728	0.45819
S	0.22272	0.25708	0.55268
S	0.73883	0.50795	0.45825
S	0.73883	0.50797	0.55273
S	0.22269	0.75864	0.45818
S	0.22272	0.75885	0.55268
Ti	0.92019	0.50146	0.02792
Ti	0.91972	0.90303	0.11150
Ti	0.91840	0.50150	0.23126
Ti	0.91762	0.90306	0.31508
Ti	0.24637	0.90301	0.01149
Ti	0.24507	0.50148	0.12602
Ti	0.24479	0.90305	0.21698
Ti	0.24274	0.50155	0.33127
Ti	0.50403	0.50146	0.02792
Ti	0.50355	0.90303	0.11150
Ti	0.50220	0.50150	0.23127
Ti	0.50156	0.90309	0.31509
Ti	0.76253	0.90301	0.01149
Ti	0.76122	0.50148	0.12603
Ti	0.76095	0.90305	0.21697
Ti	0.75900	0.50152	0.33114
O	0.92038	0.90301	0.97881
O	0.91981	0.50147	0.08191
O	0.91871	0.90305	0.18270
O	0.91834	0.50151	0.28585
O	0.91992	0.90302	0.05709
O	0.91942	0.50149	0.16041
O	0.91804	0.90300	0.26113
O	0.91727	0.50153	0.36406
O	0.24604	0.69105	0.01604
O	0.24532	0.19628	0.11973
O	0.24423	0.69780	0.22328
O	0.24327	0.18948	0.32709
O	0.24604	0.31188	0.01604

O	0.24533	0.80666	0.11973
O	0.24422	0.30515	0.22330
O	0.24327	0.81354	0.32710
O	0.50421	0.90301	0.97881
O	0.50370	0.50147	0.08192
O	0.50254	0.90305	0.18270
O	0.50156	0.50151	0.28584
O	0.50378	0.90302	0.05709
O	0.50323	0.50148	0.16040
O	0.50185	0.90301	0.26114
O	0.50163	0.50152	0.36403
O	0.76220	0.69104	0.01604
O	0.76148	0.19629	0.11974
O	0.76040	0.69781	0.22330
O	0.75945	0.18945	0.32701
O	0.76220	0.31188	0.01604
O	0.76148	0.80666	0.11974
O	0.76041	0.30514	0.22332
O	0.75946	0.81358	0.32701
W	0.56489	0.25738	0.50544

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