Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information:
Generating large out-of-plane piezoelectric properties of atomically thin MoS_2 via the defect engineering

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Sulfur vacancy distribution of the asymmetrically defected MoS_2

We investigated the elastic and piezoelectric properties of the asymmetrically defected MoS_2 via defect engineering. The defect configurations in different concentrations considered in this work was shown in Fig. S1.

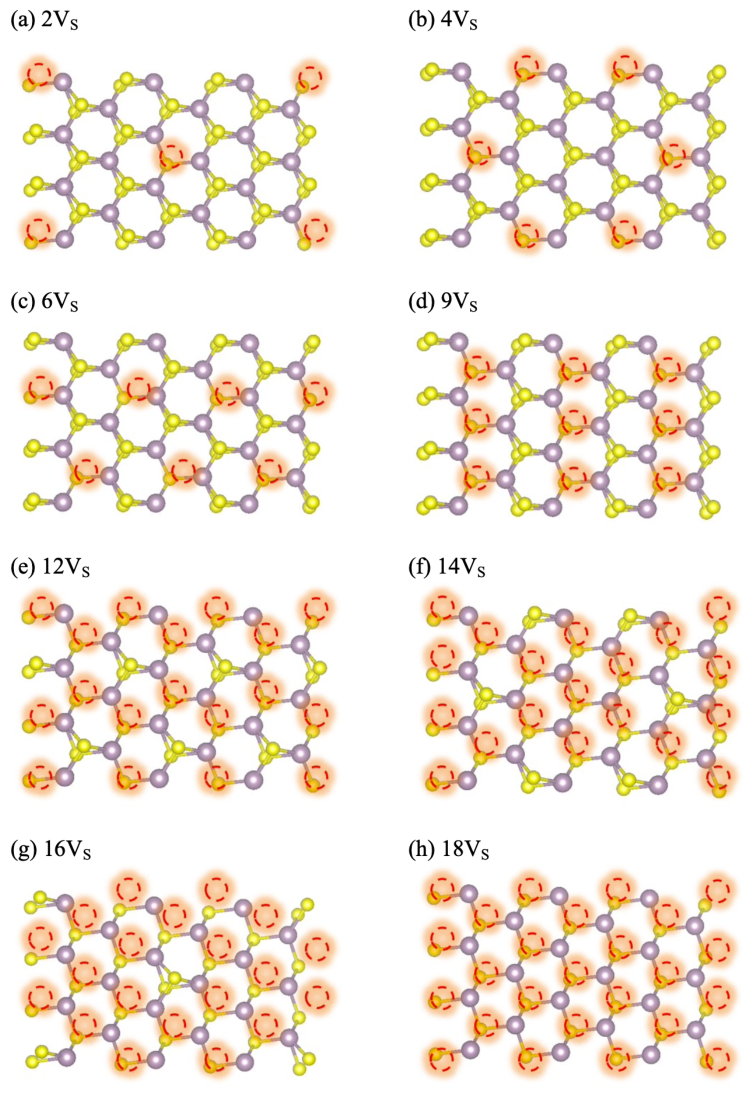

Figure S1: Distribution of S vacancy on the $3\sqrt{3}a \times 3a$ supercell of the MoS_2 monolayer for various defect concentrations. Mo, and S were represented with purple, and yellow spheres respectively, and the S defects were depicted as circles with red dash lines.

Relative in-plane sulfur vacancy positions in the multilayer MoS_2

We considered the relative in-plane sulfur vacancy position in the multilayer MoS_2, Fig. S2 showed the two relative positions of the top and bottom layer of the AA stacking multilayer surface that were considered in this work, which have coincident and farthest in-plane positions.

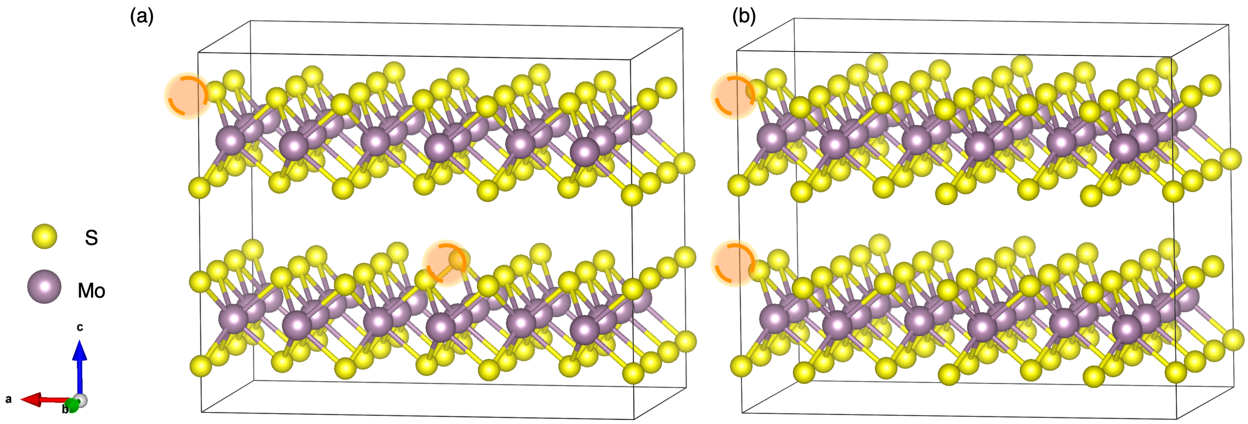

Figure S2: Relative in-plane sulfur vacancy positions in AA-stacking multilayer. (a) AA^*, (b)AA.

Elastic and piezoelectric coefficients of the AA and AB stacking MoS_2 multilayer

In this work, we calculated elastic and piezoelectric coefficients of the multilayer MoS_2 with AA and AB stacking. The results for all considered defect concentration were shown in Table S1 and Table S2 respectively. Both the AA and AB stacking pristine MoS_2 showed no out-of-plane piezoelectric response due to the centrosymmetry. After the defect engineering process to break the centrosymmetry, the out-of-plane piezoelectric response can be induced. The piezoelectric coefficient d_{33} increases as the number of asymmetrically created defects. The defected MoS_2 would undergo a metal-insulator transition beyond $MoS_{1.22}$ for AA stacking and $MoS_{1.33}$ for AB stacking.

Table S1: Calculated relaxed-ion elastic constants (in units of 10^{10} Pa), and piezoelectric coefficients d (in units of pm/V) and e (in units of C/m^2) for the $3\sqrt{3}a \times 3a$ rectangular supercell of the AA-stacking MoS_2 multilayer with 0 to 14 V_S defects, corresponding to MoS_2 and $MoS_{1.22}$.

defect ratio	C_{11}	C_{12}	C_{13}	C_{33}	e_{11}	d_{11}	e_{31}	d_{31}	e_{33}	d_{33}
MoS_2	20.51	4.74	0.63	4.59	0.48	3.01	0.00	0.00	0.00	0.00
$MoS_{1.94}$	20.15	4.62	0.45	4.52	0.56	3.60	0.02	0.07	0.02	0.41
$MoS_{1.88}$	19.95	4.73	0.66	4.49	0.57	3.77	0.04	0.14	0.04	0.83
$MoS_{1.77}$	19.28	4.79	0.68	4.15	0.63	4.33	0.09	0.31	0.07	1.66
$MoS_{1.66}$	18.59	4.99	0.72	3.81	0.71	5.21	0.12	0.46	0.09	2.30
$MoS_{1.33}$	18.93	4.35	0.50	3.14	0.89	6.12	0.15	0.46	0.28	8.60
$MoS_{1.22}$	19.25	5.04	0.87	2.48	0.88	6.17	0.23	0.33	0.43	17.00

Table S2: Calculated relaxed-ion elastic constants (in units of 10^{10} Pa), and piezoelectric coefficients d (in units of pm/V) and e (in units of C/m^2) for the $3\sqrt{3}a \times 3a$ rectangular supercell of the MoS_2 multilayer AB-stacking with 0 to 12 V_S defects, corresponding to MoS_2 and $MoS_{1.33}$.

defect ratio	C_{11}	C_{12}	C_{13}	C_{33}	e_{11}	d_{11}	e_{31}	d_{31}	e_{33}	d_{33}
MoS_2	20.57	4.80	0.62	4.56	0.00	0.00	0.00	0.00	0.00	0.00
$MoS_{1.94}$	20.11	4.80	0.63	4.38	0.03	0.19	0.02	0.08	0.02	0.39
$MoS_{1.88}$	19.92	4.73	0.65	4.40	0.00	0.01	0.04	0.14	0.04	0.80
$MoS_{1.77}$	19.30	4.88	0.68	4.01	0.00	0.00	0.09	0.31	0.07	1.59
$MoS_{1.66}$	18.67	5.01	0.67	3.81	0.00	0.04	0.13	0.48	0.09	2.14
$MoS_{1.33}$	18.63	4.39	0.70	2.83	0.00	0.00	0.16	0.45	0.24	8.41