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

Molecular dynamics study of Cr doping on the crystal structure and surficial/interfacial properties of 2H-MoS_2

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Support information

Table of Contents

S1. Models with different doped lattice sites under the same doping amount

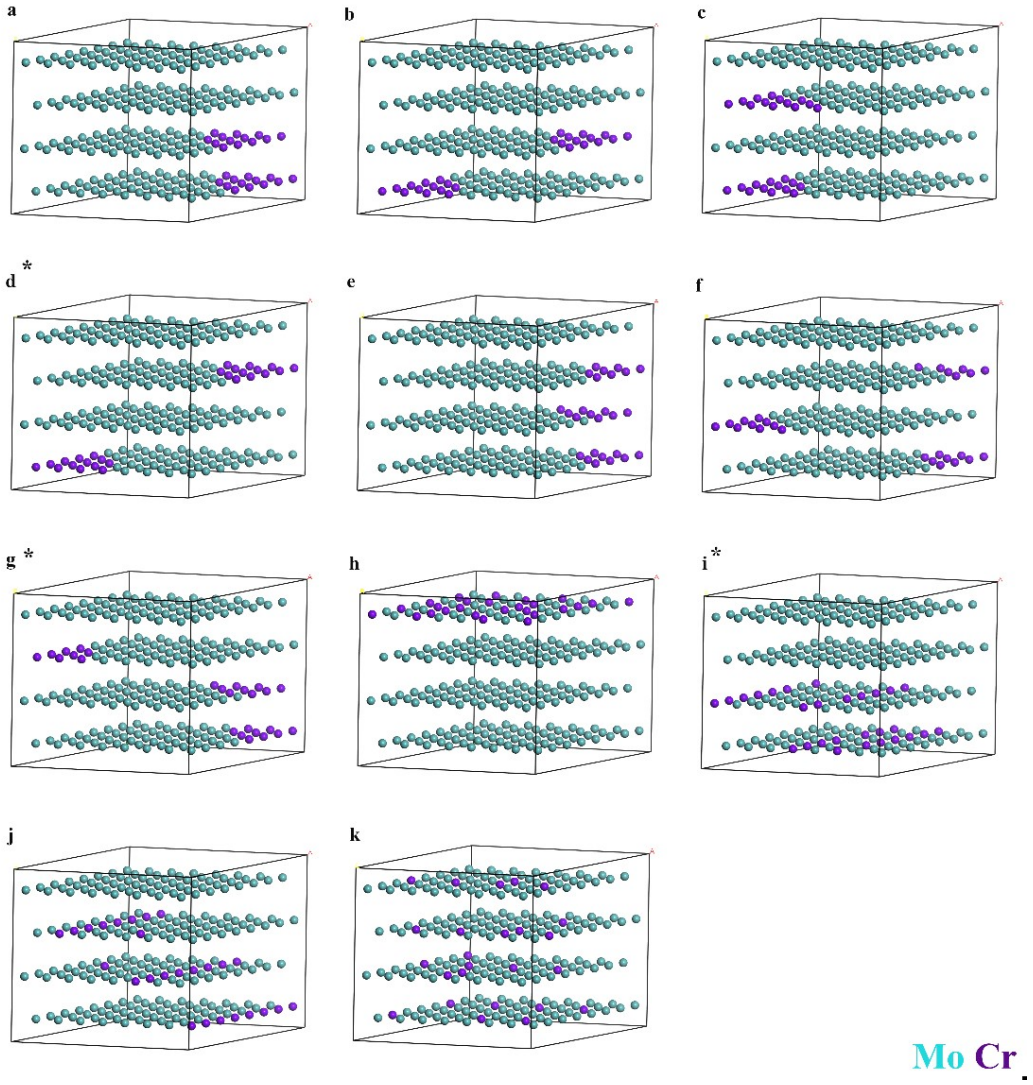


Fig. S1 Model of different doping sites with Cr doping content is 10 at%. (a) - (k) are models (steady state model marked*) of different doping sites. Sulfur atoms are omitted for a clear representation.

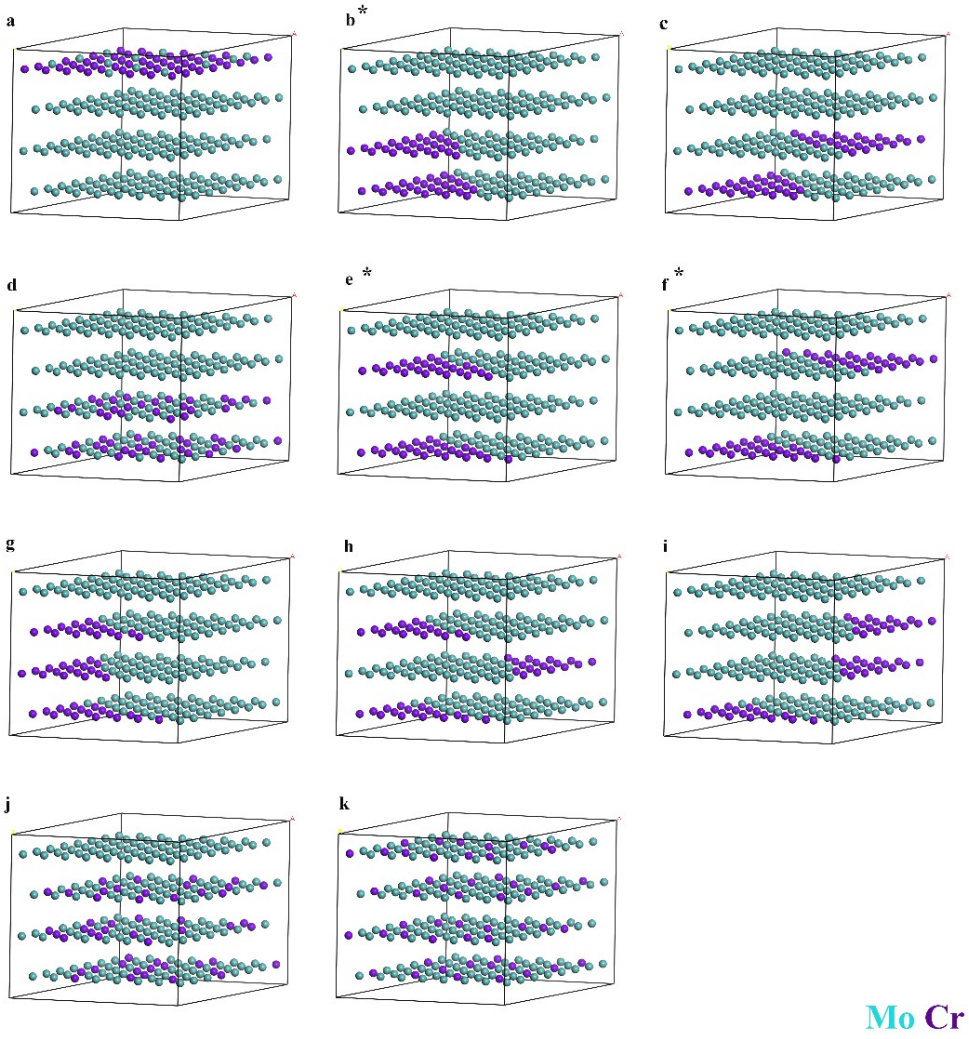


Fig. S2 Model of different doping sites with Cr doping content is 20at%. (a) - (k) are models (steady state model marked *) of different doping sites. Sulfur atoms are omitted for a clear representation.

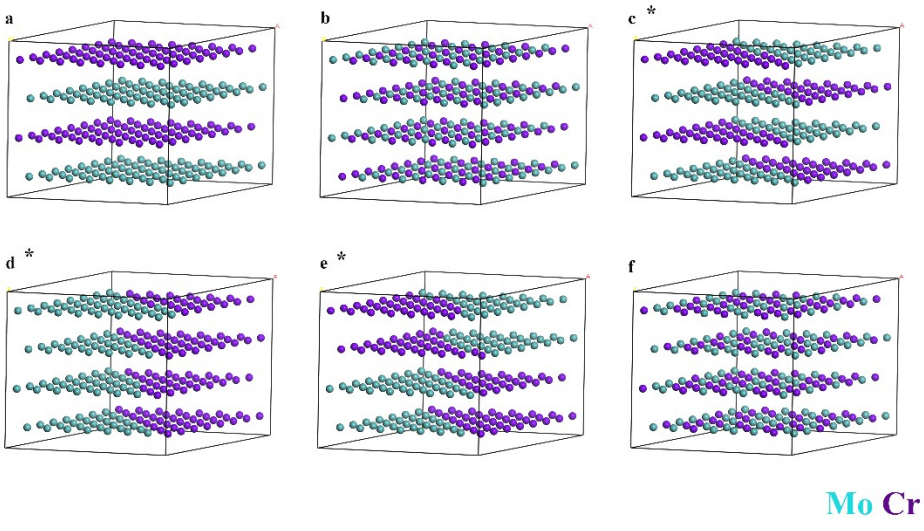


Fig. S3 Model of different doping sites with doping content is 50%. (a) - (f) are models (steady state model marked *) of different doping sites. Sulfur atoms are omitted for a clear representation.

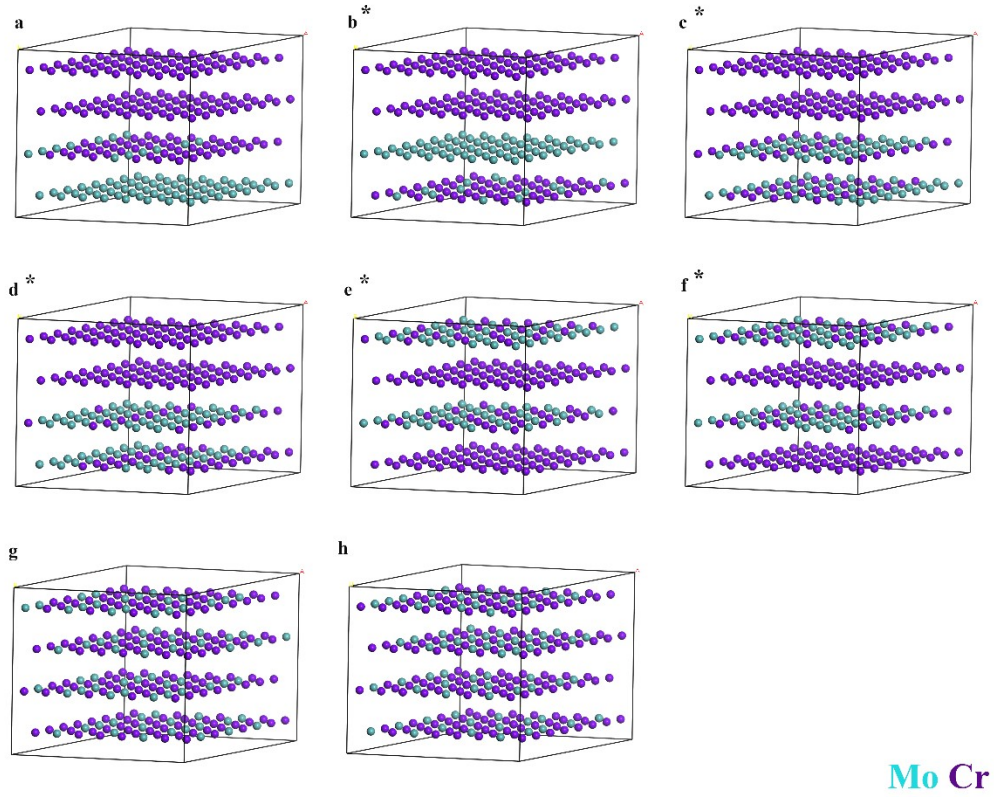


Fig. S4 Model of different doping sites with Cr doping content is 50at%. (a) - (h) are models (steady state model marked *) of different doping sites. Sulfur atoms are omitted for a clear representation.

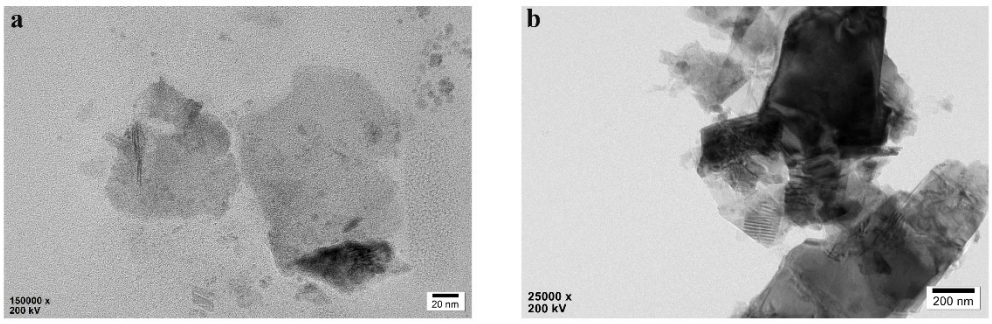


Fig. S5 HRTEM images of bulk MoS_2 soaked in (a) CH_3OH, and (b) water after 420 min ultra-sonication. Two independent TEM tests were performed per sample. On eace copper mesh, 20 grids were counted.

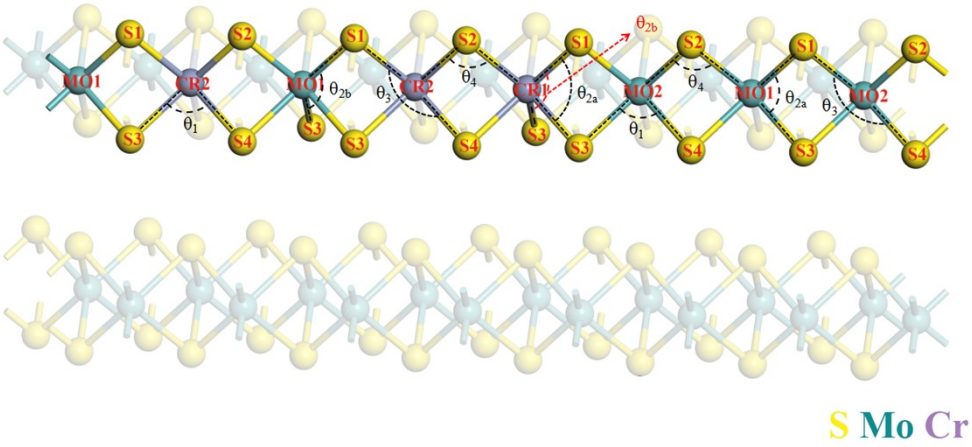


Fig. S6 Schematic diagram of different angles in Cr doped MoS_2. In order to clearly describe the bond angles in the model, we use five bond angles θ_1, θ_2, θ_3, θ_4 and θ_5. Mo atoms are substituted by Cr atoms, the angles remain same as pure 2H-MoS_2 [2]. The θ_2 angle (∠S1-MO1(CR1)-S3) can assume two values θ_{2a}=78.38° and θ_{2b}=134.4° in the model. We set the angle bending parameter of θ_2 to zero to ensure the calculation accuracy.

S2. Supplementary Tables

Table S1 The force field parameters of solvent molecules CH_2I_2 [2] and CH_3OH

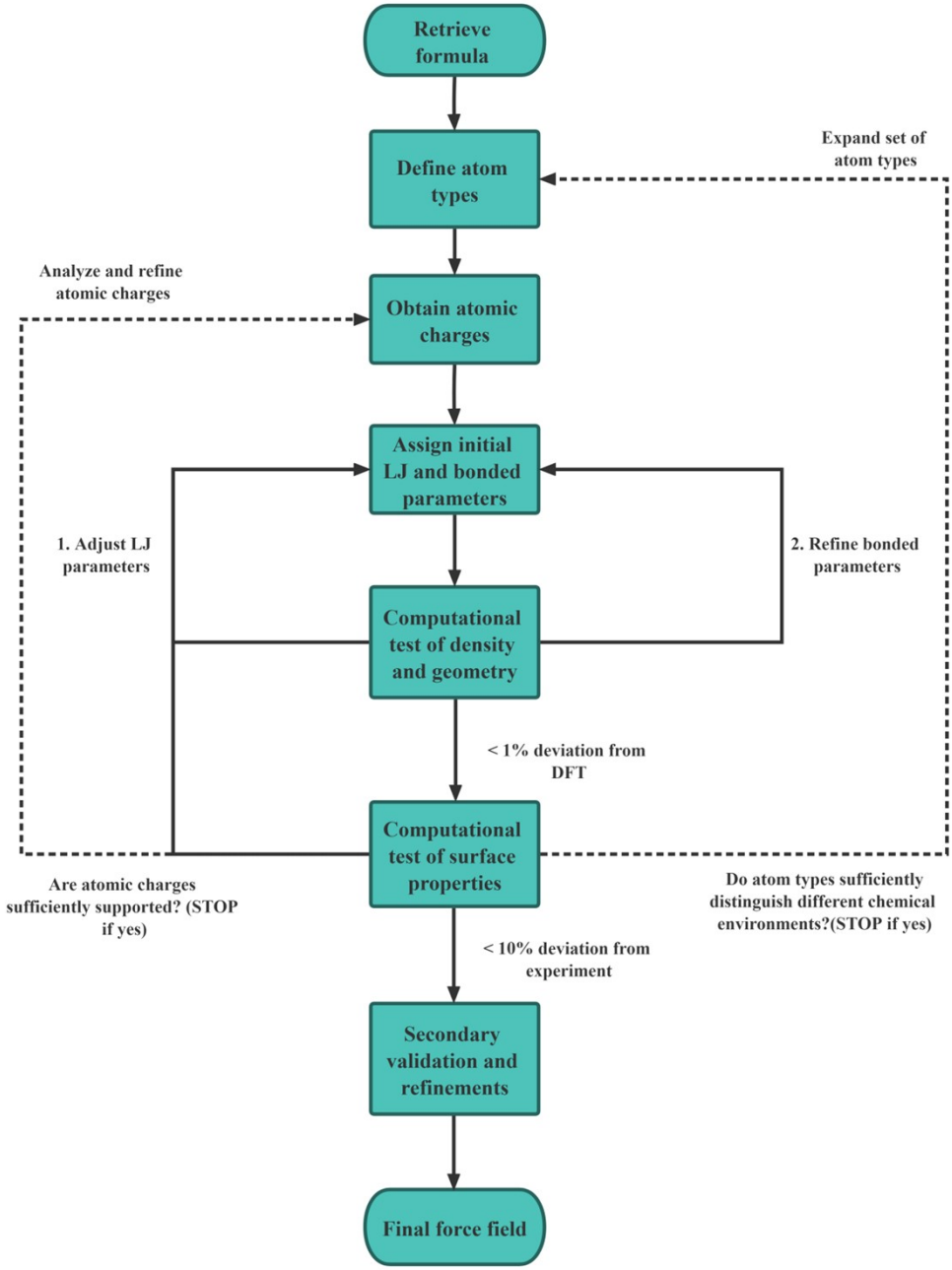
I Nonbond		Atomic charge (e)	σ (pm)	ε (kcal/mol)
CH_2I_2	C	-0.086	400	0.032
	H	+0.090	268	0.045
	I	-0.047	438	0.750
CH_3OH	C	-0.040	410	0.078
	H	+0.090	268	0.024
	O	-0.650	353	0.192
	H(OH)	+0.420	44.9	0.046
II Bond		$r_{0,ij}$ (pm)	k_r (kcal mol^{-1}· Å^{-2})	
CH_2I_2	C-H	111	309	
	C-I	215	90	
CH_3OH	C-O	142	428	
	C-H	111	322	
	O-H	96	545	
III Angles		$\theta_{0,ijk}$ (°)	K_θ (kcal mol^{-1} rad^{-2})	
CH_2I_2	I-C-I	112.96	95	
	I-C-H	108.37	28	
	H-C-H	110.40	35	
CH_3OH	H-C-O	108.89	45.9	
	C-O-H	106.00	57.5	
	H-C-H	108.40	35.5	

S3. Simulation details

S3.1 Supplementary construction details about System II: x at%Cr-MoS_2 (x = 0, 10, 20, 50, 70, 100) – water system

The details of the establishment of the water box are described. First, a water cube (31.122 × 31.122 × 30.885 $Å^3$) containing 1,000 water molecules is constructed according to the density (1 g/cm^3) under 101.3 MPa at 298 K. Then it undergoes a relaxation process of 1 ns. The equilibrium water cube were placed on the MoS_2 surface (126.416 × 27.370 × 24.295 $Å^3$). The lattice parameter in c of x at% Cr - MoS_2 – water system is 100.295 Å. 131 water molecules out of the lattice were removed. The establishment of this system model and the above-mentioned relaxation process are all carried out in the Materials Studio.

S3.2 Parameterization procedure



Scheme S1. Procedure for parameterization of CHARMM and CVFF force field [3]

To parameterize the Cr atom in 2H-MoS_2, a lot of adjustments on σ, ε, bond constant, bond length, angle constant and angles were performed around initial setup values according to some key experimental reference data. The bond related items kept the same as the pure 2H-MoS_2 [2]. The force field parameters of 2H-MoS_2 we developed previously can well reproduce experimental properties such as the X-ray structure, surface energy, contact angles, bending stability, and modulus with high accuracy. Although Cr and Mo belong to the same group in the periodic table, the electron arrangement have to be distinguished by the σ and ε in the LJ potential. Minor changes in the σ and

ε of Cr can be made to fit the DFT simulations. Every small change of parameter will go through a complete cycle of simulation calculation until the deviation is less than 1% comparing with the benchmark.

S4. Experimental details

S4.1 Experimental equipment and reagents

The KS-5200DE liquid crystal ultrasonic cleaning machine produced in Kunshan Jielimei Ultrasonic Instrument Co., Ltd. is used in this experiment, with a rated power of 200 W and a frequency of 40 KHz. H1650-W universal centrifuge produced by Changsha High-tech Industrial Development Zone Xiangyi Centrifuge Instrument Co., Ltd. Bulk MoS_2 is purchased in the form of powder from Shanghai Macklin Biochemical Co., Ltd, with a purity of 99%. The methanol solution is purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., with a purity greater than or equal to 99.9%. High resolution transmission electron microscope (HRTEM, JEOL JEM-210003040701, Tokyo, Japan) is used to characterize the exfoliated MoS_2.

S4.2 Experimental process

Two 75 mg portions of MoS_2 were weighed and soaked in 10 mL methanol solvent and 10 mL deionized water respectively. Ultrasonic vibration at a frequency of 40 kHz, radiating power 180 W was performed at 24 ℃. The MoS_2-methanol and MoS_2-water solutions were taken 0.5 h sonication, respectively, and followed by 1 h of standing to observe the state of the suspension. After 7 h of ultrasonic treatment and 14 h of immersion, the mixed solution was centrifuged at 5000 rpm for 10 minutes. Drop the solution 5 mm below the liquid surface on the copper mesh for the subsequent HRTEM observation.

Supplementary References

1. G. Cunningham, M. Lotya, C. S. Cucinotta and Stefano Sanvito, ACS Nano, 2012, 6, 3468-3480.
2. J. Liu, J. Zeng, C. Zhu, J. Miao, Y. Huang and H. Heinz, Chem Sci, 2020, 11, 8708-8722.
3. H. Heinz, T.-J. Lin, R. Kishore Mishra and F. S. Emami, Langmuir, 2013, 29, 1754-1765.