Supporting Information

Di-Boron Pair Modified MoS₂ Single-layer Shows Superior Catalytic Performance for Nitrogen Activation and Electrochemical Nitrogen Reduction

Fuhua Li and Qing Tang*

School of Chemistry and Chemical Engineering, Chongqing University, Chongqing

401331, China

*To whom correspondence should be addressed. E-mail: <u>qingtang@cqu.edu.cn</u>



Fig.S1. The potential energy and temperature curve with time, in AIMD simulations for 2.5 ps under 723 K with the time step of 1 fs, as well as the mean square displacement of B boron atom during the simulation. Herein the relative energy of

initial B@MoS₂ configuration is set as zero for reference.



Fig. S2. Minimum energy pathways of the dinitrogen converting into ammonia on $B2@MoS_2$ through distal mechanism, as well as the geometric configuration and energy of the intermediates indicated. Herein the relative free energy of side-on N₂- $B2@MoS_2$ is set as reference of zero.



Fig. S3. The structurally optimization of the intermediates along the enzymatic reaction pathway of B2@MoS₂. Each step is modeled as the scheme of Fig. 6. For the sake of simplicity, the MoS_2 has not been fully shown.



Reaction Coordinate

Fig. S4. Minimum energy pathways of the dinitrogen converting into ammonia catalyzed by $B@MoS_2$ through alternating (a) and distal (b) mechanisms, as well as the geometric configuration and energy of the transition states (TS) and intermediates indicated. Herein the relative free energy of end-on N₂-B@MoS₂ is set as reference of zero.



Fig. S5. The structurally optimization of the intermediates along the alternating reaction pathway of $B@MoS_2$. Each step is modeled as the scheme of Fig. 6. For the sake of simplicity, the MoS_2 has not been fully shown.



Fig. S6. The free energy diagram for HER of B2@MoS₂ and B2@MoS₂, respectively.

Table S1. The reaction Gibbs free energy (Δ G) calculated with regard to thermal internal energy contribution, where *E*, *E*_{ZPE} and *S* respectively represents the electronic energy change, the zero-point energy change and the entropy change, in each elementary step along enzymatic pathway on B2@MoS2. Note that *T* is 298.15 K, and all the energies are in eV.

Species	Ε	$E_{\rm ZPE}$	TS	G	ΔG
B2@MoS ₂	-520.22	-	-	-520.22	-
*N-*N	-538.94	0.10	0.07	-538.90	-1.64
*N-*NH	-542.83	0.38	0.07	-542.52	-0.17
*NH-*NH	-546.55	0.69	0.08	-545.93	0.04
*NH-*NH ₂	-550.20	1.05	0.10	-549.24	0.13
*NH2-*NH2	-556.26	1.32	0.16	-555.09	-2.40
*NH ₂ -*NH ₃	-559.87	1.68	0.16	-558.35	0.19
*NH ₂	-538.27	0.51	0.06	-537.82	1.17

*NH ₃	-542.00	0.89	0.41	-541.51	-0.25
NH ₃	-19.52	0.89	0.74	-19.37	-
Ν	-8.30	0.08	0.30	-8.52	-
Н	-3.38	0.13	0.20	-3.45	-

Table S2. The reaction Gibbs free energy (Δ G) calculated with regard to thermal internal energy contribution, where *E*, *E*_{ZPE} and *S* respectively represents the electronic energy change, the zero-point energy change and the entropy change, in each elementary step along distal pathway on B2@MoS2. Note that *T* is 298.15 K, and all the energies are in eV.

Species	Ε	$E_{\rm ZPE}$	TS	G	ΔG
B2@MoS ₂	-520.22	-	-	-520.22	-
*N-*N	-538.94	0.10	0.07	-538.90	-1.64
*N-*NH	-542.83	0.38	0.07	-542.52	-0.17
*N-*NH2	-546.11	0.72	0.08	-545.48	0.49
*N-*NH3	-550.97	1.07	0.16	-550.06	-1.13
*N	-530.94	0.12	0.02	-530.84	-0.16
*NH	-534.92	0.21	0.02	-534.74	0.19
*NH ₂	-538.27	0.51	0.06	-537.82	-0.27
*NH ₃	-542.00	0.89	0.41	-541.51	-0.25

Table S3. The reaction Gibbs free energy (Δ G) calculated with regard to thermal internal energy contribution, where *E*, *E*_{ZPE} and *S* respectively represents the electronic energy change, the zero-point energy change and the entropy change, in each elementary step along distal pathway on B@MoS2. Note that *T* is 298.15 K, and all the energies are in eV.

Species	Ε	$E_{\rm ZPE}$	TS	G	ΔG
B@MoS ₂	-521.50	-	-	-521.50	-
*N-N	-539.29	0.13	0.12	-539.28	-0.73

*N-NH	-542.66	0.38	0.17	-542.45	0.28	
*N-NH ₂	-546.33	0.73	0.15	-545.42	0.13	
*N-NH ₃	-549.59	1.08	0.17	-548.68	0.52	
*N	-530.73	0.07	0.03	-530.70	-1.39	
*NH	-534.45	0.23	0.11	-534.33	-0.18	
*NH ₂	-539.47	0.53	0.08	-539.02	-1.25	
*NH ₃	-543.11	0.89	0.11	-542.32	0.15	

Table S4. The reaction Gibbs free energy (Δ G) calculated with regard to thermal internal energy contribution, where *E*, *E*_{ZPE} and *S* respectively represents the electronic energy change, the zero-point energy change and the entropy change, in each elementary step along alternating pathway on B@MoS2. Note that *T* is 298.15 K, and all the energies are in eV.

Species	Ε	$E_{\rm ZPE}$	TS	G	ΔG
B@MoS ₂	-521.50	-	-	-521.50	-
*N-N	-539.29	0.13	0.12	-539.28	-0.73
*N-NH	-542.66	0.38	0.17	-542.45	0.28
*NH-NH	-546.00	0.73	0.15	-545.42	0.47
*NH-NH ₂	-550.58	1.06	0.16	-549.67	-0.80
*NH ₂ -NH ₂	-553.92	1.43	0.18	-552.67	0.45
*NH ₂	-534.45	0.23	0.11	-534.33	-2.28
*NH ₃	-543.11	0.89	0.11	-542.32	0.15

The feasibility to synthesize diatomic boron doped MoS₂ single-layer by our proposed procedure.

Based on the success of synthesis of MoS_2 nano-sheet supported Co catalyst experimentally by Liu *et al.*, ¹ as well as the report of Patra *et al.* ² highlighting that, in MoS_2 single-layer, with the increase concentrations of S vacancies (from 1.5% to 7.5%), sulfur vacancies tend to be organized into extended lines. We expect that the isolated single-atom and diatomic boron in this work can be immobilized and uniformly distributed on sulfur vacancies on the basal planes of MoS₂ monolayer sheets and propose a feasible procedure to accomplish this synthesis, as shown in Scheme S1. Firstly we can use the electrochemical thinning method, *i.e.* electroablation (EA), to prepare the single-layer MoS₂ chemical by using the procedure proposed by Das *et al.* ³ During the substrate-assisted and self-limited EA, an excessive EA time can result in a great deal of sulfur vacancies. Thus all in all, by controlling the EA time, the multilayer flakes will undergo an electro-oxidation process to obtain the MoS₂ monolayer with sulphur vacancies. Subsequently the diborane boroethane (B₂H₆) can be added onto the defective MoS₂ single-layer via soft-landing cluster method. Finally the ligand chlorine atom can leave the MoS₂ nano-sheet by means of controlling the temperature on at a higher value.



Scheme S1. The potential substitution reaction for synthesis of defective MoS2 with

di-vacancy and further di-atom B modified MoS₂ single-layer.

Reference

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