## Supporting information

## Activation of MoSe<sub>2</sub> Basal Plane and Se-edge by B doping for Enhanced Hydrogen Evolution

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Figure S1. Partial density of states (PDOS) of Mo 3d, Se 2p and B 2p in B doped MoSe<sub>2</sub> monolayer.



**Figure S2**. a) Electronic band structures and densities of states of monolayer MoSe<sub>2</sub> with two Se atoms replaced by B atoms (B concentration: 6.25 %); b) the partial charge density of two B atoms doped MoSe<sub>2</sub>. The isosurface value of the partial charge density for the plot is set at 0.003 e/bohr<sup>3</sup>.



Figure S3. SEM images of bare carbon cloth at different magnifications.



Figure S4. Schematic diagram of the sample fabrication progress.



**Figure S5**. a)~d) SEM images of B doped MoSe<sub>2</sub> nanosheets on carbon cloth, where the concentration of B are 0, 2.7, 5.5 and 7.9 at.%, respectively. e) LSV and f) Tafel slopes of B doped MoSe<sub>2</sub> catalysts with different B concentrations (0, 2.7, 5.5 and 7.9 at.%, respectively).



**Figure S6**. SEM of a) pristine MoSe<sub>2</sub> and (b) 5.5 at.%-B doped MoSe<sub>2</sub> grown on Si substrate. c) LSV and d) Tafel slopes of MoSe<sub>2</sub> and 5.5 at.%-B doped MoSe<sub>2</sub> catalysts, which are obtained by ultrasonicating the catalyst from the Si substrate.



**Figure S7**. XRD patterns of MoSe<sub>2</sub>, 5.5 at.%-B-MoSe<sub>2</sub>, carbon cloth and standard PDF card for MoSe<sub>2</sub> (JCPDS-No. 29-0914).



**Figure S8**. Raman results of a)  $MoSe_2$  and b) 5.5 at.%-B doped  $MoSe_2$  samples obtained from different sites. c) The summarized peak sites of  $A_{1g}$  mode for  $MoSe_2$  and 5.5 at.%-B doped  $MoSe_2$ .



**Figure S9**. a) Mo K-edge and b) Se K-edge extended X-ray absorption fine structure (EXAFS) spectra of pristine MoSe<sub>2</sub> and 5.5 at.%-B doped MoSe<sub>2</sub> nanosheets. c) Mo K-edge and d) Se K-edge extended XAFS oscillation functions of pure MoSe<sub>2</sub> and 5.5 at.%-B doped MoSe<sub>2</sub> nanosheets.



Figure S10. Wide XPS spectra for MoSe<sub>2</sub> and B-MoSe<sub>2</sub> grown on carbon cloth.



**Figure S11**. HER performance of bare carbon cloth and carbon cloth annealing in B atmosphere as the experiment progress of B-MoSe<sub>2</sub> measured in 0.5 M  $H_2SO_4$ . The linear sweep voltammetry (LSV) curves of the pure carbon cloth and the un-treated one are almost overlapped. Both of them deliver a high overpotential, which means the carbon cloth contributes negligible electrocatalytic current to the entire electrode. Therefore, the contribution from the carbon substrate can be ignored.



**Figure S12.** The summarized potential at  $j=10 \text{ mA/cm}^2$  and their Tafel slopes for reported MoSe<sub>2</sub>-based catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Specifically, oriented MoSe<sub>2</sub>/graphene nanosheets (159 mV, 61 mV/dec), <sup>[1]</sup> MoSe<sub>2</sub>/ $\alpha$ -MoO<sub>3</sub> heterostructure (250 mV, 76 mV/dec), <sup>[2]</sup> MoSe<sub>2</sub> nanoflower (200 mV, 69 mV/dec), porous MoSe<sub>2</sub> microspheres (121 mV, 56 mV/dec), <sup>[3]</sup> MoSe<sub>2</sub>–NiSe vertical heteronanostructures

(210 mV, 56 mV/dec), <sup>[4]</sup> Mo-rich hierarchical ultrathin MoSe<sub>2</sub> nanosheets (300 mV, 98 mV/dec),<sup>[5]</sup> 1T-MoSe<sub>2</sub> nanosheets (170 mV, 78 mV/dec),<sup>[6]</sup> MoO<sub>2</sub>/MoSe<sub>2</sub> core–shell nanosheet arrays (195 mV, 49.1 mV/dec), <sup>[7]</sup> macroporous MoSe<sub>2</sub> films (240 mV, 66 mV/dec). <sup>[8]</sup>



Figure S13. SEM image of 5.5 at.%-B-MoSe<sub>2</sub> catalyst after long-term stability test.



Figure S14. XRD result of 5.5 at.%-B-MoSe<sub>2</sub> catalysts after its long time HER testing.



Figure S15. XPS result of 5.5 at.%-B-MoSe<sub>2</sub> catalysts after long-term stability test.



**Figure S16**. Mott-Schottky plots for pure MoSe<sub>2</sub> and 5.5 at.%-B-MoSe<sub>2</sub> grown on carbon cloth.



**Figure S17**. a) CVs of MoSe<sub>2</sub> and 5.5 at.%-B-MoSe<sub>2</sub> catalysts grown on carbon cloth in pH=7 phosphate buffer between -0.2 V and 0.4V vs. RHE at a scan rate of 50 mV/s. b) Turnover frequency for catalyst of pure MoSe<sub>2</sub> and 5.5 at.%-B-MoSe<sub>2</sub> nanosheets.

Sample	Pair	Ν	Pair	Ν
MoSe <sub>2</sub>	Se-Mo	$2.44 \pm 0.19$	Mo-Se	$5.55 \pm 0.16$
	Se-Se	$6.96 \pm 0.95$	Mo-Mo	6.91 ± 0.85
B-MoSe <sub>2</sub>	Se-Mo	$2.55 \pm 0.18$	Mo-Se	$5.24 \pm 0.18$
	Se-Se	$7.02 \pm 0.92$	Mo-Mo	$6.99 \pm 0.92$
	Se-B	$0.22 \pm 0.20$	Mo-B	$0.35 \pm 0.18$

 Table S1: Coordination numbers of the two samples

MoSe <sub>2</sub> catalyst		Structure with H adsorption		$\Box G_{\mathrm{H}^{*}}\left( eV ight)$		
	Me adga	M1:		-0.18		
Edge	Mo-edge	M2:		0.08		
	D donad Ma adva	BM1:		-0.04		
	B-doped Mo-edge	BM2:		-0.24		
	So odro	S1:	0000	0.51		
	Se-euge	S2:		0.28		
	D damad Sa adga	BS1:		-0.05		
	B-doped Se-edge	BS2:		-0.12		
	Pristine (001)	Se :		2.19		
Basal plane	D. doned (001)	B1:		-0.15		
	Б-doped (001)	B2:		-0.05		

various structural sites for pure and B-doped MoSe<sub>2</sub>.

Table S2. Comparison of free energy change ( $\Delta G_{H^*}$ ) of hydrogen adsorption on

## **Experiments**

*Synthesis*: Carbon cloth was purchased from the J & K Chemical Technology. It was cut into pieces of 1 cm  $\times$ 2 cm as the substrates. MoSe<sub>2</sub> nanosheet arrays were grown via chemical vapor deposition (CVD) route, specifically: MoO<sub>2</sub> was put in the center of a furnace whilst 0.5 g Se powder was weighed and placed upstream of MoO<sub>2</sub>. During the CVD process, MoO<sub>2</sub> and Se powders were heated to 920 °C and 550 °C,

respectively, with the mixed Ar (65 sccm) and H<sub>2</sub> (5 sccm) at the heating rate of 15  $^{\circ}$ C/min. After maintaining this temperature for 20 min, the furnace was cooled to room temperature. For B doped MoSe<sub>2</sub>, over weights of B<sub>2</sub>O<sub>3</sub> (0.1, 0.25 and 0.35 g) were mixed with 0.5g MoO<sub>2</sub> with other experiment conditions being kept the same as the undoped MoSe<sub>2</sub>. The undoped MoSe<sub>2</sub> and B doped MoSe<sub>2</sub> (B<sub>2</sub>O<sub>3</sub>=0.25 g) grown on Si substrate were also prepared under the identical experiment conditions.

*Materials Characterizations*: X-ray diffractometer (XRD; X'pert Pro Philips with Cu K $\alpha$  radiation), Raman spectrometer (Jobin-Yvon LabRam HR80), Scanning electron microscopy (SEM; Hitachi S-4800) and transmission electron microscopy (TEM; Tecnai G2 F30, FEI) were used to study the morphology and structure of the doped and undoped catalysts. Energy-dispersive X-ray spectroscopy (EDX) attached in the TEM and X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra) were applied to obtain elemental mappings, chemical states and bonding characteristics of the doped and undoped catalysts. Transmission EXAFS spectra were collected at room temperature in the vicinity of the Se K-edge and Mo K-edge at the 1W1B beamline [1w1b] of the Beijing Synchrotron Radiation Facility (BSRF). Energy was calibrated using a neodymium foil. The  $k^3$  weighted Fourier transform of the EXAFS data (2 -12 Å<sup>-1</sup>) was performed using the Bessel function.

*Electrochemical Measurements*: A CHI660E electrochemical workstation was employed to perform all electrochemical tests with a standard three-electrode cell, where the catalysts grown on carbon cloth, Ag/AgCl and carbon rod were used as working electrodes, reference electrode and counter electrodes, respectively. Linear sweep voltammetry (LSV) measurements were conducted in N<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte with a scan rate of 2 mV/s at room temperature. The stability of the doped and undoped catalysts was evaluated by carrying out cyclic voltammetry measurement for 10000 cycles (scan rate of 100 mV/s) and then switch to the LSV measurement (scan rate of 2 mV/s). All LSV curves were *iR*-corrected. The potentials were calibrated with respect to a reversible hydrogen electrode (RHE) using E(RHE) = E(Ag/AgCl) + 197 mV. The Nyquist plots were measured at potential of 200 mV *vs*.

12

RHE from 100 kHz to 0.1 Hz. A simplified Randles circuit was used to fit the impedance data to extract the solution  $(R_S)$  and charge-transfer resistance  $(R_{CT})$ . To fabricate the electrochemical test electrode of MoSe<sub>2</sub> and B doped MoSe<sub>2</sub> grown on Si substrate, we first made the freestanding catalysts of MoSe<sub>2</sub> and B doped MoSe<sub>2</sub> nanosheets by ultrasonic method. Then we added 3 mg catalyst into the solution of N, N-Dimethyl Formamide (1470  $\mu$ L) and Nafion-117 (30  $\mu$ L). Finally, 12  $\mu$ L of the fresh catalyst ink was dropped onto a glassy carbon electrode (0.071 cm<sup>2</sup> geometrical area, Pine Research Instrument) and dried naturally as the working electrode. The turnover frequency (TOF) is calculated with the following equation: TOF = I/Q, where I (A) obtained from the LSVs measurements is the current of the polarization curve. Voltammetry charges (Q) is calculated by the following equation:  $Q = 2F_n$ , Where F is Faraday constant (96480 C/mol), n is the number of active sites. In the experiment, the voltammetry curve is obtained by CVs measurements with phosphate buffer (pH =7) at the scan rate of 50 mV/s. The number of Q is obtained after deducting the blank value. The derivation and calculation follow the equations:  $_{i=C}\frac{dU}{dt} = C_{v}$ . After transforming,  $Q = CU = \frac{iU}{v}$ . In a CV curve, *i* and *U* are changing, so we can get *iU* by integral the CV curve, where v is the scan rate (50 mV/s). Mott-Schottky plot is obtained from the Impedance-Potential measurements. In the experiment, the relationship between impedance (Z) and voltage is established for both MoSe<sub>2</sub> and B-MoSe<sub>2</sub> electrodes. The capacitance (C) is calculated using the equation:  $C = -1/2\pi J$ , where f is the fixed frequency of voltage, which is set as 100 Hz during the measurement and Z is the impedance.

*First-principles Calculations*: Vienna *ab* initio simulation package (VASP) based on density functional theory (DFT) was employed to carry out the first-principle calculation.<sup>[9]</sup> Electron-ion interactions was modeled by projector augmented wave (PAW) potentials.<sup>[10]</sup> The generalized gradient approximation with Perdew-Burke-Ernzerhof (GGA-PBE) functional were performed to approximate exchange the

correlation effects when relaxing the atomic structure, where all models were fully relaxed with self-consistency accuracy of  $10^{-5}$  eV. <sup>[11]</sup> The cut-off energy was set to 450 eV for the plane-wave basis restriction and the K-points were taken under Monkhorst-Pack for the Brillouin-zone integration. To prevent the interaction between two neighboring surfaces, a vacuum slab of 15 Å was employed in z direction for MoSe<sub>2</sub> monolayer with the calculated fully relaxed lattice constants of a = b = 3.32 Å. A 4×4×1 supercell was used to calculate the electronic property and hydrogen evolution activity. The Mo-edge and Se-edge of MoSe<sub>2</sub> monolayer was modeled by a semi-infinite stripes, terminated by Se atoms and dimers, respectively<sup>[12]</sup>, where the vacuum space of 15 Å was inserted in y direction to separate the edges and only three topmost atomic stripes in the edges are relaxed.

The activity of hydrogen evolution reaction was reflected by the Gibbs' free energy change ( $\Delta G_{H^*}$ ), which is obtained from the formula proposed by Nørskov *et al.*:  $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S^{[13]}$ . Among of them,  $\Delta E_{H^*} = E_{(surface+H^*)} - E_{surface} - 1/2E_{H2}$ , where  $E_{(surface+H^*)}$  and  $E_{surface}$  are total energy of the surface model with and without H<sup>\*</sup> adsorption, respectively.  $E_{H2}$  is the energy of a single H<sub>2</sub> molecule isolated in vacuum. Zero-point energy change  $\Delta E_{ZPE}$  is obtained from vibrational frequency calculation as implemented in VASP. T $\Delta$ S is estimated to be 0.2 eV to consider the entropy change at room temperature.

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