Electronic Supplementary Information

Confined synthesis of edge-rich V-doped $MoSe_2$ nanosheets on carbon black for advanced hydrogen evolution reaction

Xianpei Ren[a, b]*, Fei Wu[b], Yonghua Wang[b], Quanhong Ou[c], Fei Li[a]*

[a]Applied Nuclear Technology in Geosciences Key Laboratory of Sichuan Province，Chengdu University of Technology, Chengdu 610000, China

[b]School of Physics and Electronic Engineering, Sichuan University of Science and Engineering, Zigong 643000, China

[c]School of Physics and Electronic Information, Yunnan Normal University, Kunming 650500, China.

*Corresponding author: E-mail: renxianpei@163.com; lifei17@cdut.edu.cn.

Computational methods

All calculations were conducted by Vienna Ab initio Simulation Package (VASP) based on the density functional theory (DFT). The exchange-correlation potential is described by using the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE). The projector augmented-wave (PAW) method is employed to treat interactions between ion cores and valence electrons. The plane-wave cutoff energy was fixed to 400 eV. Given structural models were relaxed until the Hellmann-Feynman forces smaller than -0.02 eV/Å and the change in energy smaller than 10^{-5} eV was attained. During the relaxation, the Brillouin zone was represented by a Γ centered k-point grid of 3×3×1. Grimme's DFT-D3 methodology was used to describe the dispersion interactions among all the atoms in adsorption models.

The adsorption energy (ΔE_{*H}) of H is calculated by: $\Delta E_{*H}=E_{*H}-E_{*}-1/2E_{H2}$, where E_{*H}, E_{*}, and E_{H2} are the energies of hydrogen adsorbed on catalyst, isolated catalyst, and hydrogen gas molecule, respectively.

The catalytic activity for HER could be evaluated by the hydrogen adsorption free energy of ΔG_{H^*}: $\Delta G_{H^*} = \Delta E_{*H} - \Delta E_{ZPE} - T\Delta S_H$, Where ΔE_{ZPE} is the zero-point energy change between the adsorbed state of the catalyst and gas phase state. ΔS_H is the difference in entropy and T is taken as 298.15 K.

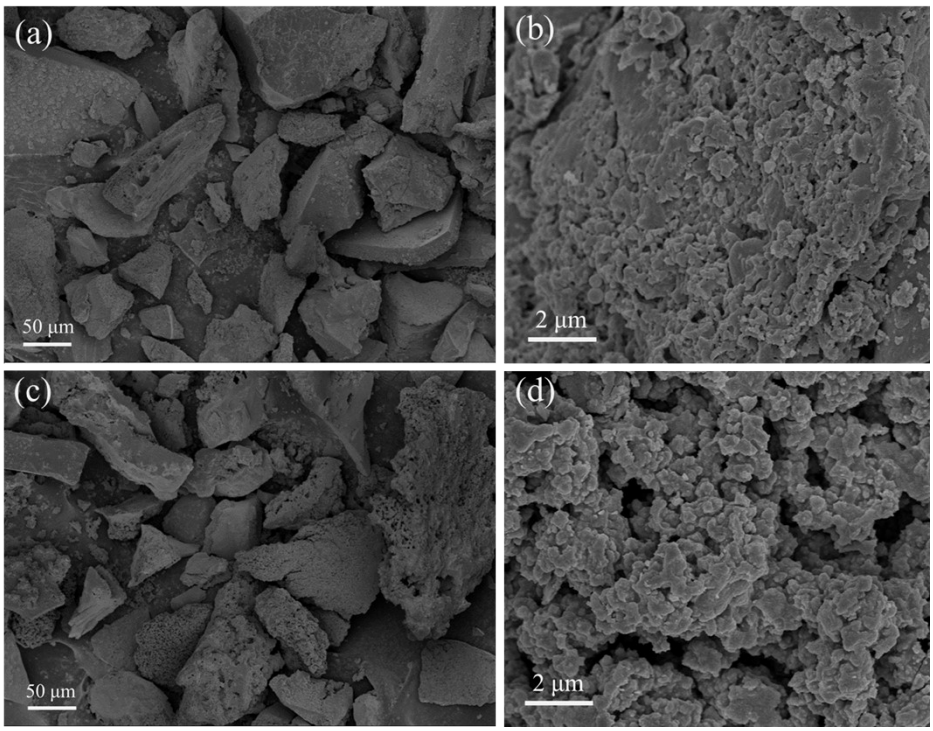

Fig. S1 (a, b) SEM images of $MoSe_2$; (c, d) SEM images of V-$MoSe_2$.

Table S1. Resistance values of various as-prepared catalysts.

Catalysts	**R_s/Ω**	**R_{ct}/Ω**
$MoSe_2$	12	/
V-$MoSe_2$	13	5252
$MoSe_2$/CB	20	161
V-$MoSe_2$/CB	13	93

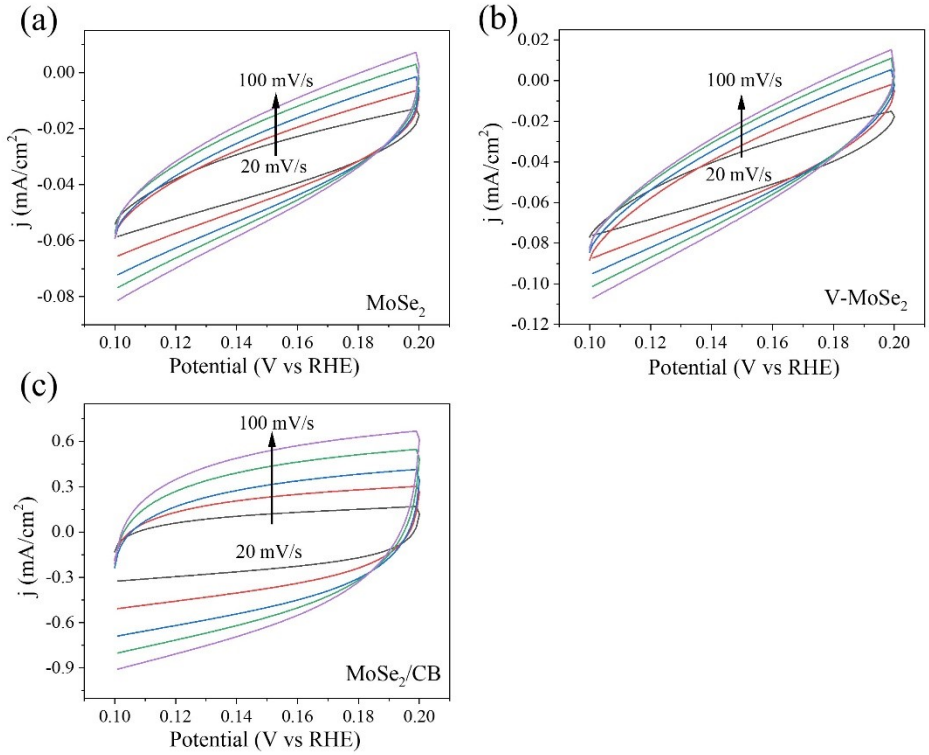

Fig. S2 (a, b, c) Electrochemical cyclic voltammogram of $MoSe_2$, V-$MoSe_2$ and $MoSe_2$/CB at different potential scanning rates. The scan rates are 20, 40, 60, 80 and 100 mV/s. The selected potential range where no faradic current was observed is 0.10 to 0.2 V vs RHE.

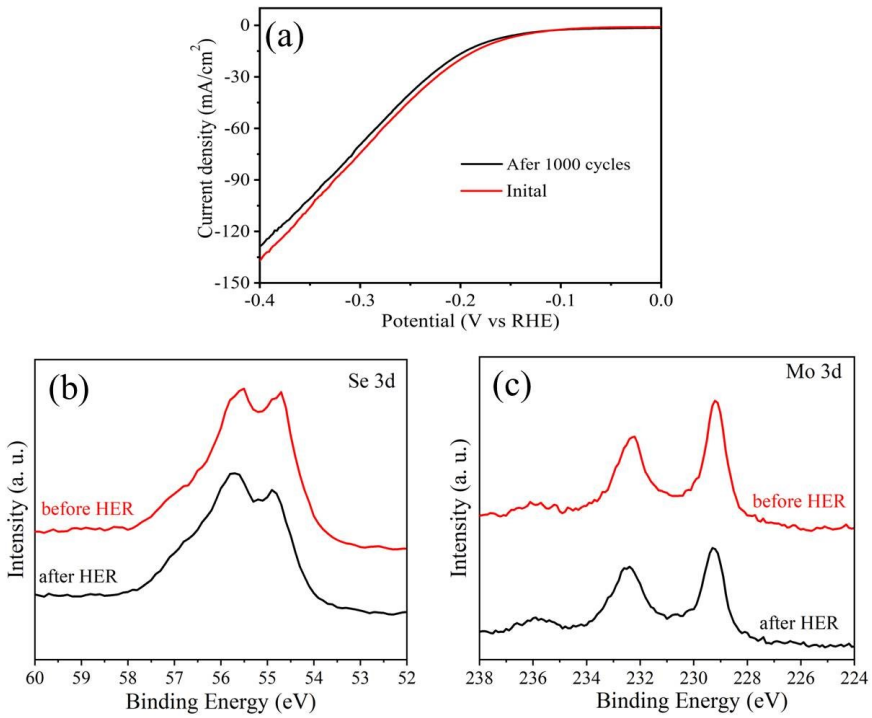

Fig. S3 (a) Stability of V-$MoSe_2$/CB in 0.5 M H_2SO_4 solution after 1000 cycles. (b-d) High-resolution Mo 3d, Se 3d and V 2p XPS spectra of V-$MoSe_2$/CB electrocatalyst before and after HER measurement.

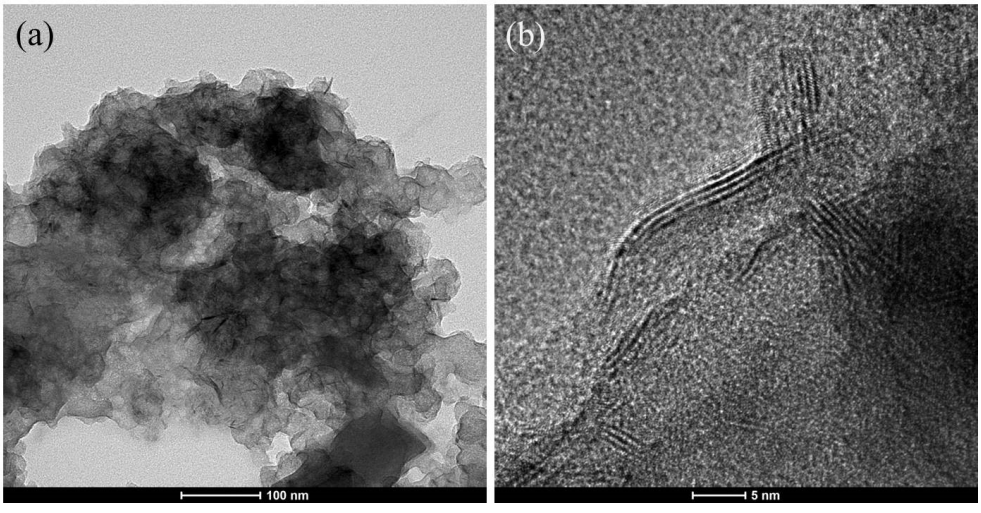

Fig. S4 (a) TEM, (b) HRTEM images of V-$MoSe_2$/CB after HER measurement.

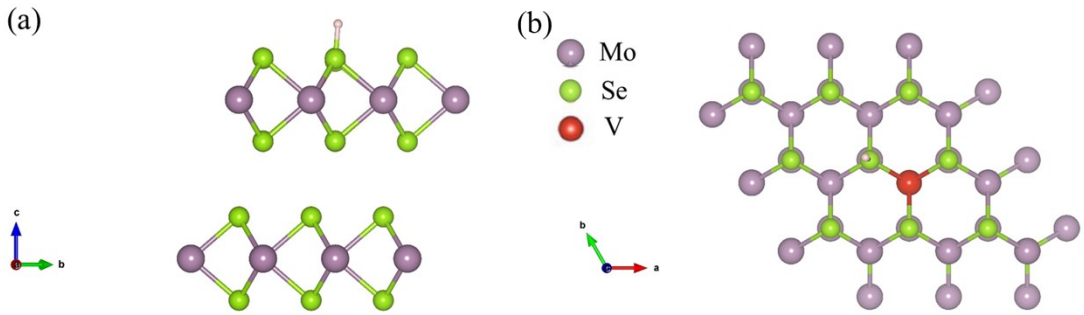

Fig. S5 The computational models of $MoSe_2$ (a) and V-$MoSe_2$ (b).

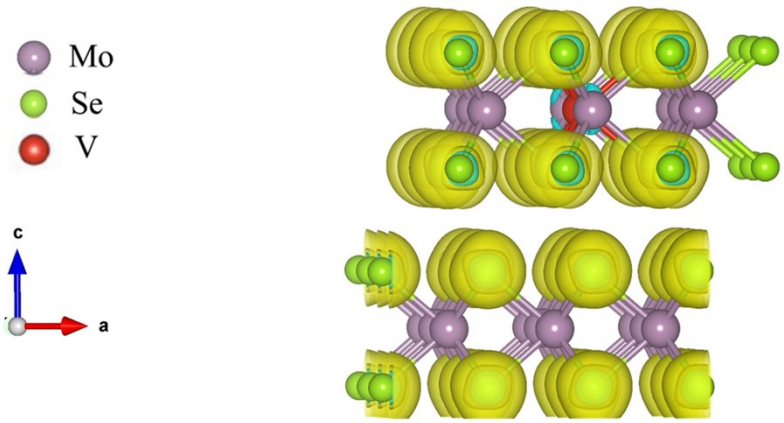

Fig. S6 Charge density distributions of V-$MoSe_2$ (side view), where the color yellow represents the charge increase and the color cyan represents the charge decrease.