New Carbon Materials, 2023, 38(6): 1059-1069

Supplementary Information

Mott-Schottky heterojunction formation between Co and $MoSe_2$ on carbon nanotubes for superior hydrogen evolution

Xian-pei REN[1], Qi-wei HU[1], Fang LING[1], Fei WU[1], Qiang LI[1], Liu-qing PANG[2,3]

(1.School of Physics and Electronic Engineering, Sichuan University of Science and Engineering, Zigong 643000, China;
2.The First Monitoring and Application Center, CEA, Tianjin 300180, China;
3.Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China)

Corresponding author：

PANG Liu-qing, Engineer. E-mail: pangliuqing2021@fmac.ac.cn

Author introduction：

REN Xian-pei, PhD, Lecturer. E-mail: renxianpei@163.com

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.

Table S1. Comparison of HER performance in acidic media for Co/$MoSe_2$@CNT with other MoS_2-based and $MoSe_2$-based HER electrocatalysts.

catalyst	**η(mV) for j=10 mA cm^{-2}**	**Tafel slope (mV dec^{-1})**	**References**
MoS_2/VS_2	-199.6	95.2	ACS Appl. Energy Mater., 2019, 2, 5799-5808
MoS_2/MoO_2	-380	113	Mater. Res. Lett., 2019, 7, 275-281.
MoS_2-NiS_2/NGF	-172	70	Appl. Catal. B: Environ., 2019, 254, 15-25.
SnS_2/MoS_2	-240	65	Electrochim. Acta, 2019, 300, 45-52
MoS_2@Bi_2Se_3	-208	57	J. Catal., 2020, 381, 590-598
ZnSe/$MoSe_2$	-200	73	Adv. Mater. Interfaces, 2017, 1700948
$MoSe_2$/NG	-150	69	J. Alloy. Compd., 2020, 848, 156588
$MoSe_2$/Carbon Fiber	-179	62	ACS Appl. Mater. Interfaces, 2016, 8, 7077-7085.
$MoSe_2$/ZnO	-250	87	Int. J. Hydrogen Energ., 2023, 48, 26210-26220
VSe_2/$MoSe_2$	-480	66	Arab. J. Chem., 2023, 16, 104846
Co/$MoSe_2$@CNT	-185	69	This work

CNT: carbon nanotubes
NG: nitrogen-doped graphene
NGF: nitrogen-doped graphene foam

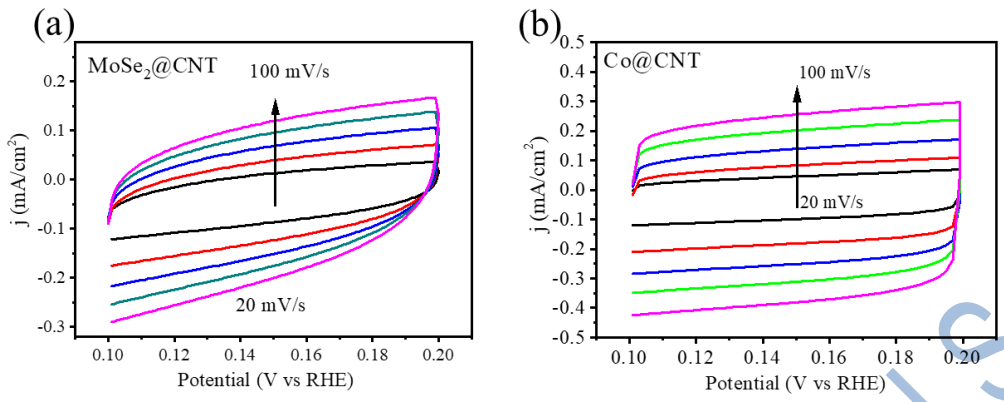

Fig. S1. (a, b) Electrochemical cyclic voltammogram of $MoSe_2$@CNT and Co@CNT at different potential scanning rates. The scan rates are 20, 40, 60, 80 and 100 mV/s. The selected potential range where no faradic current was observed is 0.10 to 0.2 V vs RHE.

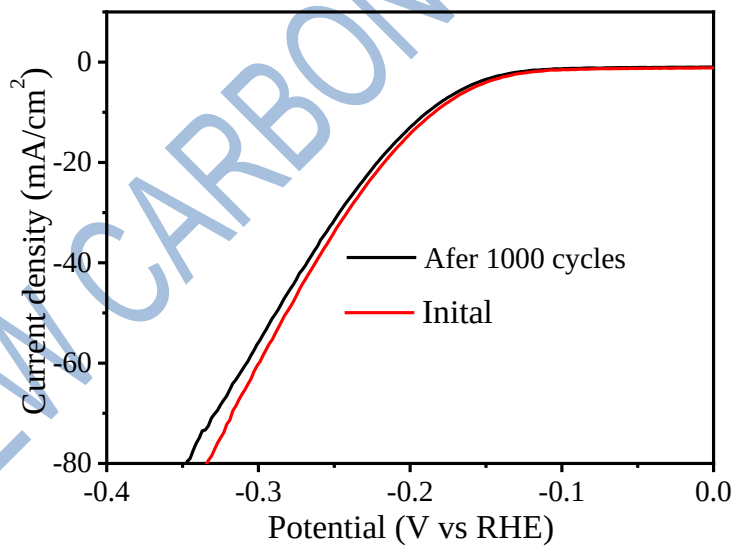

Fig. S2. Stability of Co/$MoSe_2$@CNT in 0.5 M H_2SO_4 solution after 1000 cycles. The slight degradation indicating that the catalyst is stable in electrochemical process.

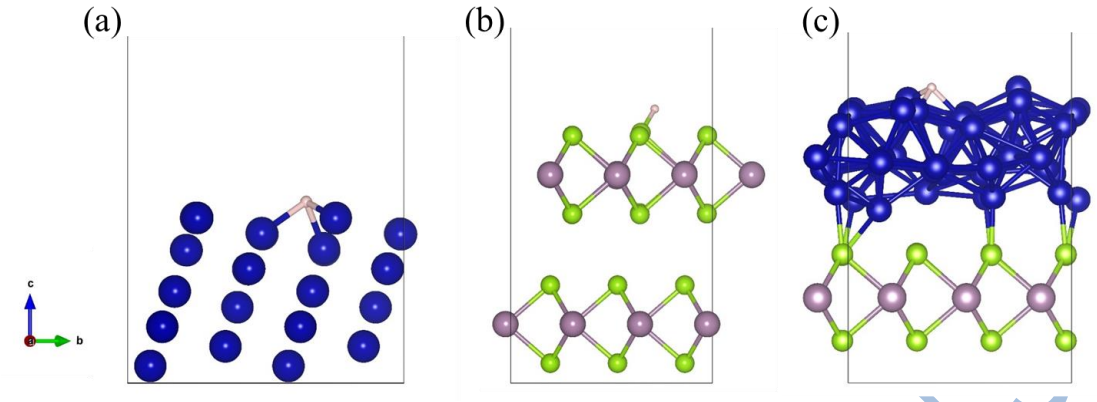

Fig. S3. The structural models of Co (a), $MoSe_2$ (b) and Co/$MoSe_2$ heterostructure (c) for calculation.