Electronic Supplementary Information

3D flexible hydrogen evolution electrodes with Se-promoted molybdenum sulfide nanosheet arrays

Zonghua Pu,[a] Shiyong Wei,[b] Zhibao Chen,[b] and Shichun Mu[a]*

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China. E-mail: msc@whut.edu.cn

[b] Jiangxi Key Laboratory for Advanced Copper and Tungsten Materials, Jiangxi Academy of Sciences, Nanchang 330029, China.

*E-mail: msc@whut.edu.cn

Experimental section

Materials

Sulfuric acid (H_2SO_4) and ethanol were purchased from Aladdin Reagent. Sodium molybdate ($Na_2MoO_4\cdot 2H_2O$) and thiourea were purchased from Beijing Chemical Works. Sodium borohydride ($NaBH_4$) was purchased from Xinglong Chemical Corp. Nafion (5 wt%), Pt/C (20 wt%) and selenium (Se) powder were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. All the reagents in the experiment were analytical grade and without further treatments. Deionized Mini-Q water was used as solvent.

Preparation of MoS_2/CC and Se-MoS_2/CC:

Firstly, CC was cleared by ultrasonic with water and ethanol. In brief, 0.242 g $Na_2MoO_4 \cdot 2H_2O$ and 0.305 g thiourea were dissolved in 40 mL H_2O. Then, the mixture solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. A piece of CC (2 × 4 cm^2) was vertically inserted into the above solution, the autoclave was heated at 200 °C for 24 h. After cooling, the synthesized product was washed with plenty of water and dried at 60 °C. To obtain Se-MoS_2/CC, 0.059 mg Se powder and 0.065 mg $NaBH_4$ were dissolved into 1.5 mL H_2O. Then, the prepared NaHSe solution was dissolved into 30 mL ethanol under Ar flow. Subsequently, the mixture was transferred into 50 mL Teflon-lined stainless steel autoclave with a piece of prepared MoS_2/CC and maintained at 140 °C for different time (4 h, 8 h, 16 h). After cooling, the obtaied products were taken out and rinsed with H_2O and dried at 60 °C overnight. The loading for MoS_2/CC and Se-MoS_2/CC was determined to be 3.2 and 3.8 mg cm^{-2} with the use of a high precision microbalance, respectively.

Structural Characterizations

X-ray diffraction (XRD) patterns were collected on a Rigaku X-ray diffractometer equipped with a Cu K_α radiation source. The morphology and structure were characterized by scanning electron microscopy (SEM, XL30 ESEM FEG) and transmission electron microscopy (TEM, HITACHI H-8100). X-ray photoelectron spectroscopy (XPS) was obtained on an ESCALABMK II X-ray photoelectron spectrometer.

Electrochemical characterization

The electrochemical tests for HER were carried out with a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) using a three-electrode configuration with as-prepared electrodes, the Ag/AgCl (3.0 M KCl) and graphite rod as working electrode, reference electrode and counter electrode, respectively. The polarization curves were obtained in 0.5 M H_2SO_4 (pH = 0) with a scan rate of 2 mV s^{-1} at a room temperature (~25 °C). The measured potentials vs. Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale. $E_{RHE} = E_{Ag/AgCl} + 0.197$ V. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency from 0.1 kHz to 100 Hz under the amplitude of 5 mV. To reflect the real catalytic currents, all polarization curves were corrected for iR loss and background current. Onset overpotentials were determined based on the beginning of linear regime in the Tafel plot.[1]

Crystalline sizes derived from XRD

The crystalline sizes (L) are estimated from MoS_2 (002) peak using the Scherrer equation:[2]

$L=K\lambda/(B_{1/2}(2\theta)\cos\theta)$

where λ is the wavelength of the X-ray (λ = 0.154 nm), K is the Scherrer constant and a value of 0.94 is adopted. $B_{1/2}$ is the full width at the half maximum (FWHM) of 2θ peaks (in radian units).

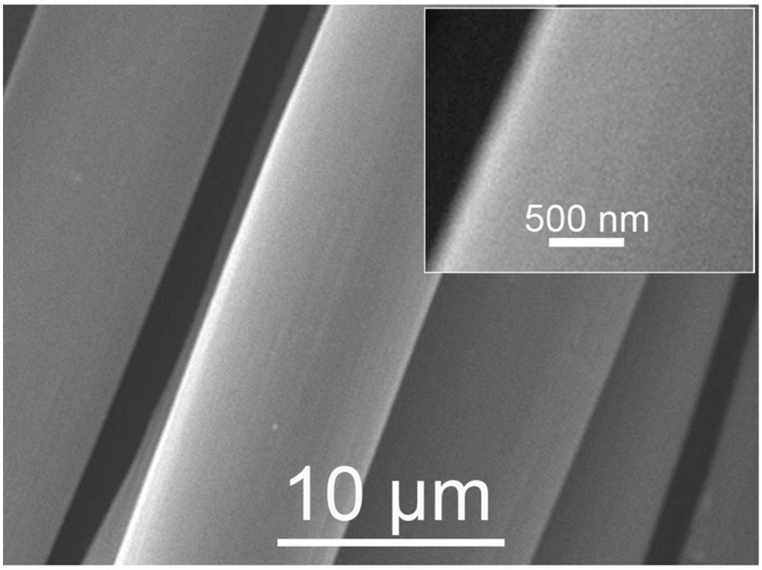

Fig. S1 SEM images of blank CC.

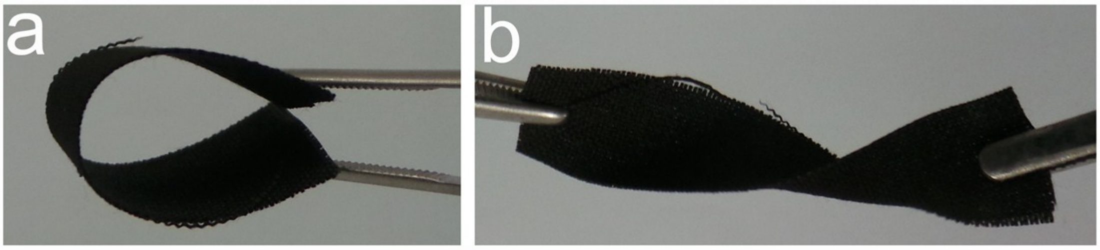

Fig. S2 Optical photographs of the prepared Se-MoS_2/CC.

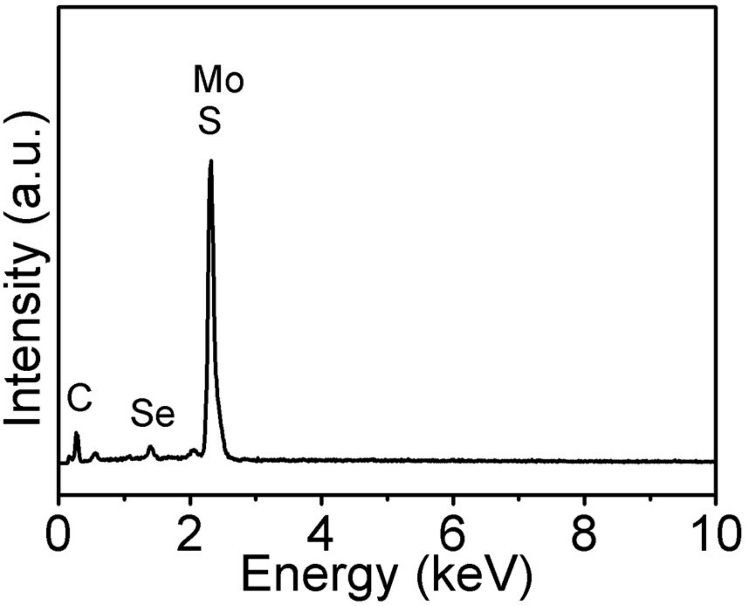

Fig. S3 EDX spectrum of Se-MoS_2/CC.

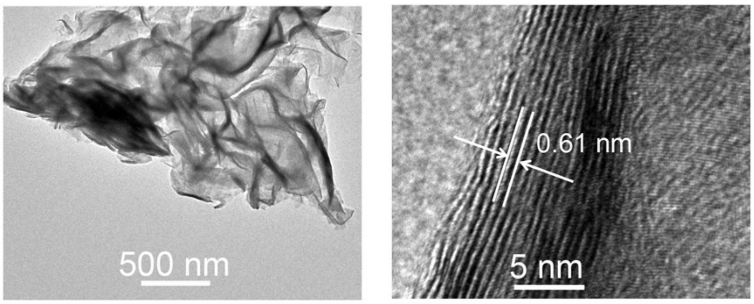

Fig. S4 (a) TEM and (b) HRTEM images of the MoS_2 nanosheets.

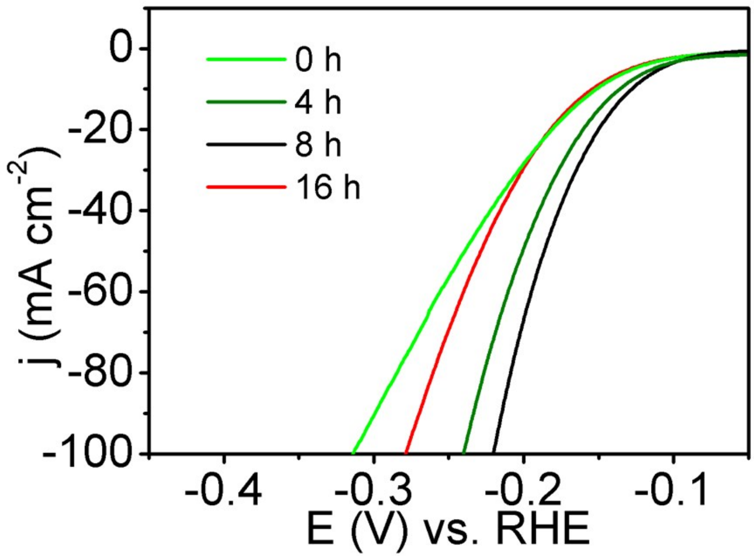

Fig. S5 Polarization curves for different selenization time of Se-MoS_2/CC in 0.5 M H_2SO_4 solution with a scan rate of 2 mV s^{-1}.

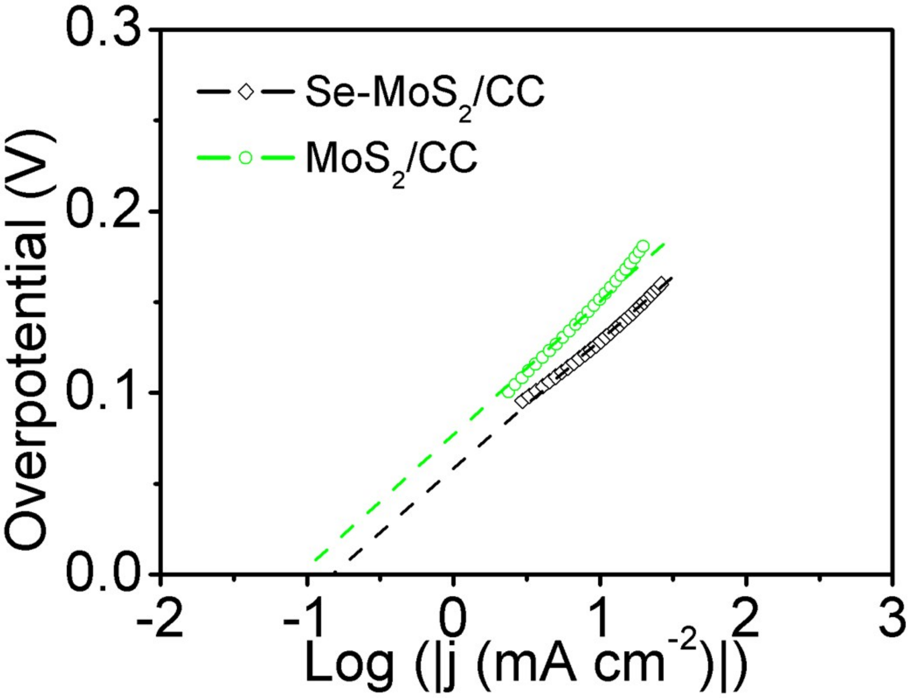

Fig. S6 Tafel plots used for calculating exchange current density of Se-MoS$_2$/CC and MoS$_2$/CC by extrapolation method.

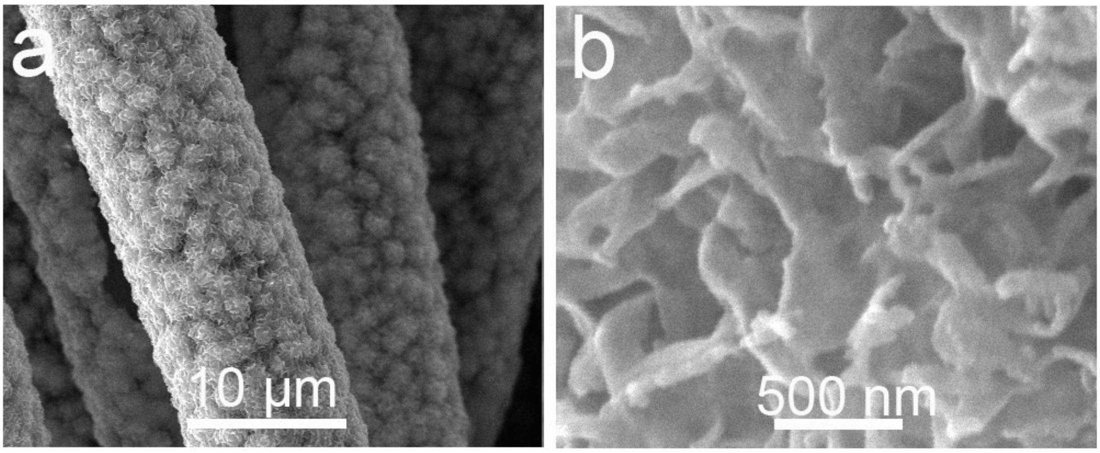

Fig. S7 (a) low and (b) high magnification SEM images of Se-MoS_2/CC after the durability measurements.

Table S1 Comparison of HER performance in acidic solution for Se-MoS_2/CC with some representative MoS_2-based HER electrocatalysts ([a] catalysts directly grown on current collectors).

Catalyst	**Onset *η* (mV)**	**Current density (*j*, mA cm^{-2})**	***η* at the corresponding *j* (mV)**	**Ref.**
double-gyroid MoS_2/FTO[a]	150-200	2	190	3
metallic MoS_2 nanosheets[a]	200	10	195	4
defect-rich MoS_2	120	13	200	5
MoO_3-MoS_2/FTO[a]	150-200	10	310	6
MoS_2/graphene/Ni foam[a]	-	10	141	7
MoS_2/graphene	100	10	150	8
amorphous MoS_x	-	10	200	9
MoS_x/graphene/CC[a]	-	100	~225	10
PPy/MoS_x/GCE[a]	60	50	60	11
amorphous MoS_x films[a]	-	15	200	12
MoS_x sponges[a]	-	71	200	13
MoS_2 flakes on $SrTiO_3$	27.8	10	~170	14
conducting MoS_2 nanosheets	100	10	200	15
MoS_2/Mo foil[a]	~150	18.6	300	16
edge-terminated MoS_2 nanoassemblies	54	10	~200	17
MoS_2/CC[a]	100	86	250	18
V-doped MoS_2	130	10	~240	19
Oxygen-incorporated MoS_2	120	10	~175	20
Co-Mo-S	-	17.5	200	21
MoS_2/WC/RGO	110	10	~200	22
Se-MoS_2/CC[a]	60	10 100	127 218	This work

Table S2 ICP-MS data of Se doping concentration with different selenization time.

Selenization time (h)	0	4	8	16
Se doping concentration	0%	3.7%	6.4%	12.3%

References

1 Z. Pu, Q. Liu, A. M. Asiri and X. Sun, *ACS Appl Mater Interfaces*, 2014, **6**, 21874-21879.

2 J. I. Langford and A. J. C. Wilson, *J. Appl. Crystallogr.,* 1978, **11**, 102-113.

3 J. Kibsgaard, Z. Chen, B. N. Reinecke and T. F. Jaramillo, *Nat. Mater.,* 2012, **11**, 963-969.

4 M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li and S. Jin, *J. Am. Chem. Soc.,* 2013, **135**, 10274-10277.

5 J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. Lou and Y. Xie, *Adv. Mater.,* 2013, **25**, 5807-5813.

6 Z. Chen, D. Cummins, B. N. Reinecke, E. Clark, M. K. Sunkara and T. F. Jaramillo, *Nano Lett.,* 2011, **11**, 4168-4175.

7 Y. H. Chang, C. T. Lin, T. Y. Chen, C. L. Hsu, Y. H. Lee, W. Zhang, K. H. Wei and L. J. Li, *Adv. Mater.,* 2013*,* **25***,* 756-760.

8 Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong and H. Dai, *J. Am. Chem. Soc.,* 2011, **133**, 7296-7299.

9 J. D. Benck, Z. B. Chen, L. Y. Kuritzky, A. J. Forman and T. F. Jaramillo, *ACS Catal.* 2012, **2**, 1916-1923.

10 A. J. Smith, Y.-H. Chang, K. Raidongia, T. Y. Chen, L. J. Li and J. Huang, *Adv. Energy Mater.,* DOI: 10.1002/aenm.201400398.

11 T. Wang, J. Zhuo, K. Du, B. Chen, Z. Zhu, Y. Shao and M. Li, *Adv. Mater.,* 2014, **26**, 3761-3766.

12 D. Merki, S. Fierro, H. Vrubel and X. Hu, *Chem. Sci.,* 2011, **2**, 1262–1267.

13 Y. H. Chang, F. Y. Wu, T. Y. Chen, F. Wiryo, K. H. Wei, C. Y. Chiang and L. J. Li, *Small,* 2013*,* **10***,* 895-900.

14 Y. Zhang, Q. Ji, G. Han, J. Ju, J. Shi, D. Ma, J. Sun, Y. Zhang, M. Li, X. Lang, Y. Zhang and Z. Liu, *ACS Nano,* 2014*,* **8***,* 8617-8624.

15 D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda and M. Chhowalla, *Nano Lett.,* 2013, **13**, 6222-6227.

16 Y. Yang, H. L. Fei, G. D. Ruan, C. S. Xiang and J. M. Tour, *Adv. Mater.,* 2014, **26**, 8163-8168.

17 D. Y. Chung, S.-K. Park, Y.-H. Chung, S. Yu, D.-H. Lim, N. H. Jung, C. Ham, H.-Y. Park, Y. Piao, S. J. Yoo and Y.-E. Sung, *Nanoscale,* 2014, **6**, 2131-2136.

18 Y. Yan, B. Xia, N. Li, Z. Xu, A. Fisherc and X. Wang, *J. Mater. Chem. A*, 2015, **3**, 131-135.

19 X. Sun, J. Dai, Y. Guo, C. Wu, F. Hu, J. Zhao, X. Zeng and Y. Xie, *Nanoscale*, 2014, **6**, 8359-8367

20 J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan, Y. Xie, J. *Am. Chem. Soc.*, 2013, **125**, 17881-17888.

21 X. Ren, Q. Ma, H. Fan, L. Pang, Y. Zhang, Y. Yao, X. Ren and S. Liu, *Chem. Commun.,* 2015, **51**, 15997-16000.

22 Y. Yan, B. Xia, X. Qi, H. Wang, R. Xu, J. Wang, H. Zhang and X. Wang, *Chem. Commun.,* 2013, **49**, 4884-4886.