Supporting Information

Surface Intercalated Spherical $MoS_{2x}Se_{2(1-x)}$ Nanocatalysts for Highly Efficient and Durable Hydrogen Evolution Reactions

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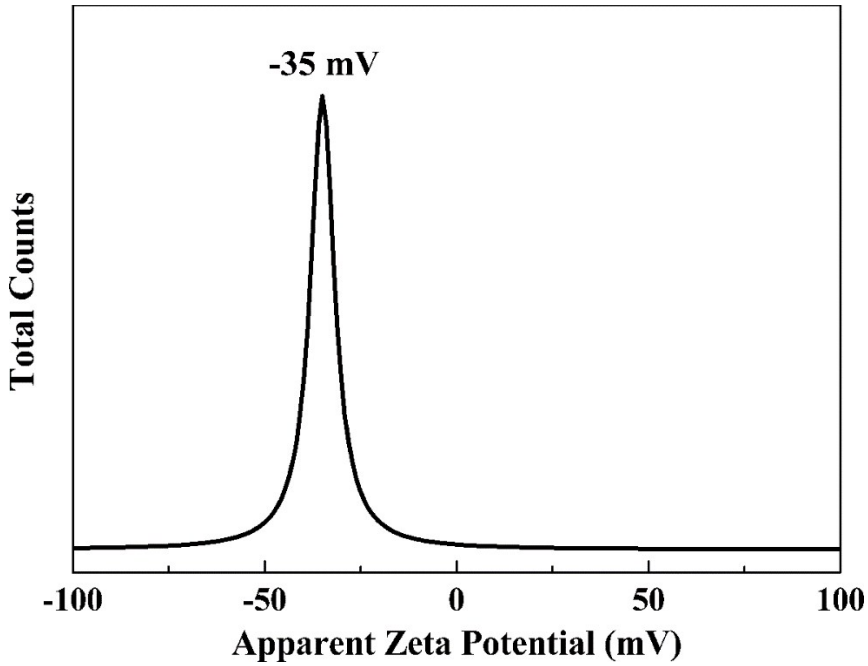

Fig. S1 The Zeta potential of the nanospheres before intercalation.

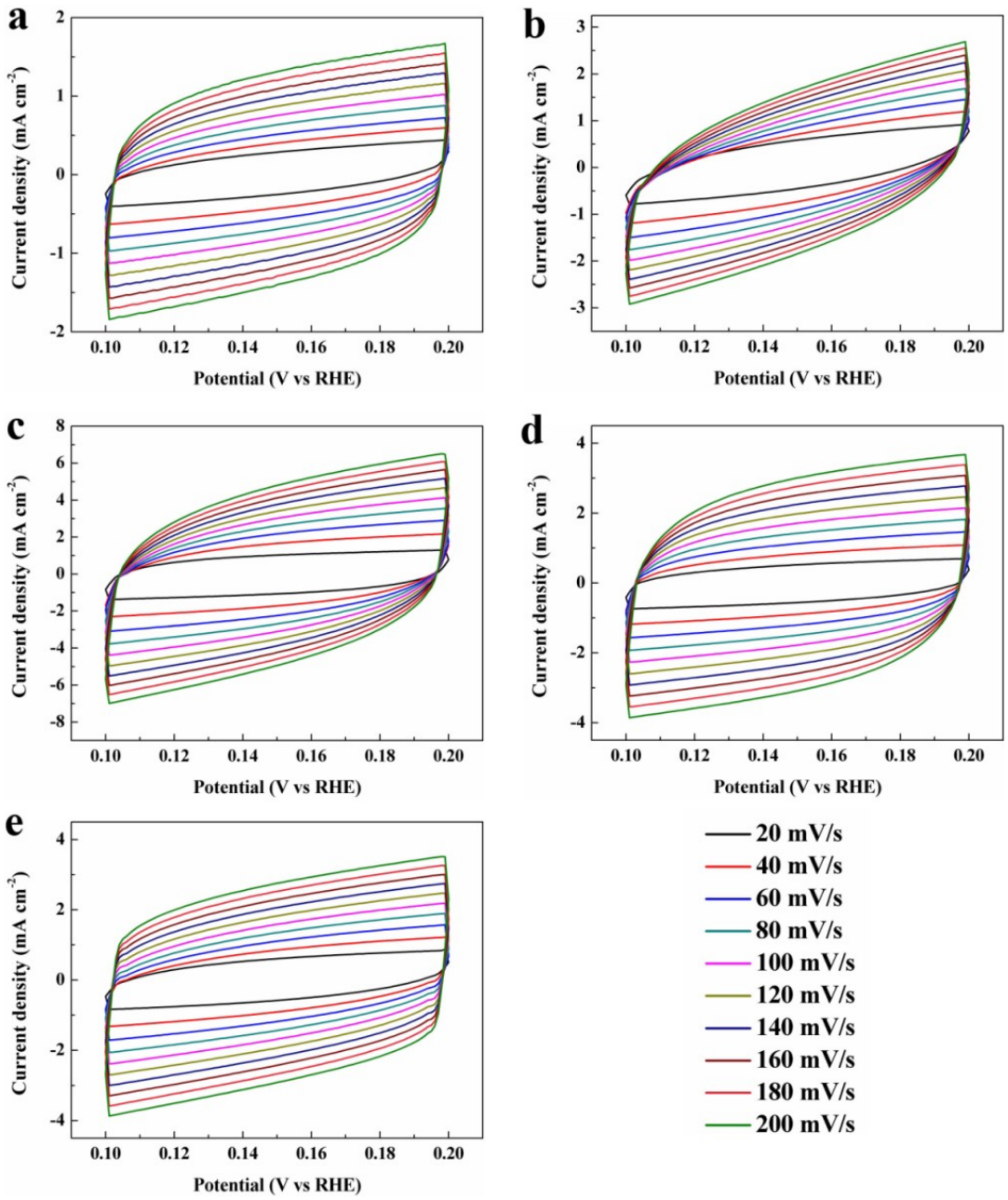

Fig. S2 Cyclic voltammetry curves of the $MoS_{2x}Se_{2(1-x)}$ samples (Sample-1/2, Sample-1/2-2h, Sample-1/2-4h, Sample-1/2-6h, Sample-1/2-8h) in the region of 0.1-0.2 V vs. RHE with different scan rates from 20 to 200 mV s^{-1}. These plots were used to calculate the C_{dl} for various samples in Fig 3d.

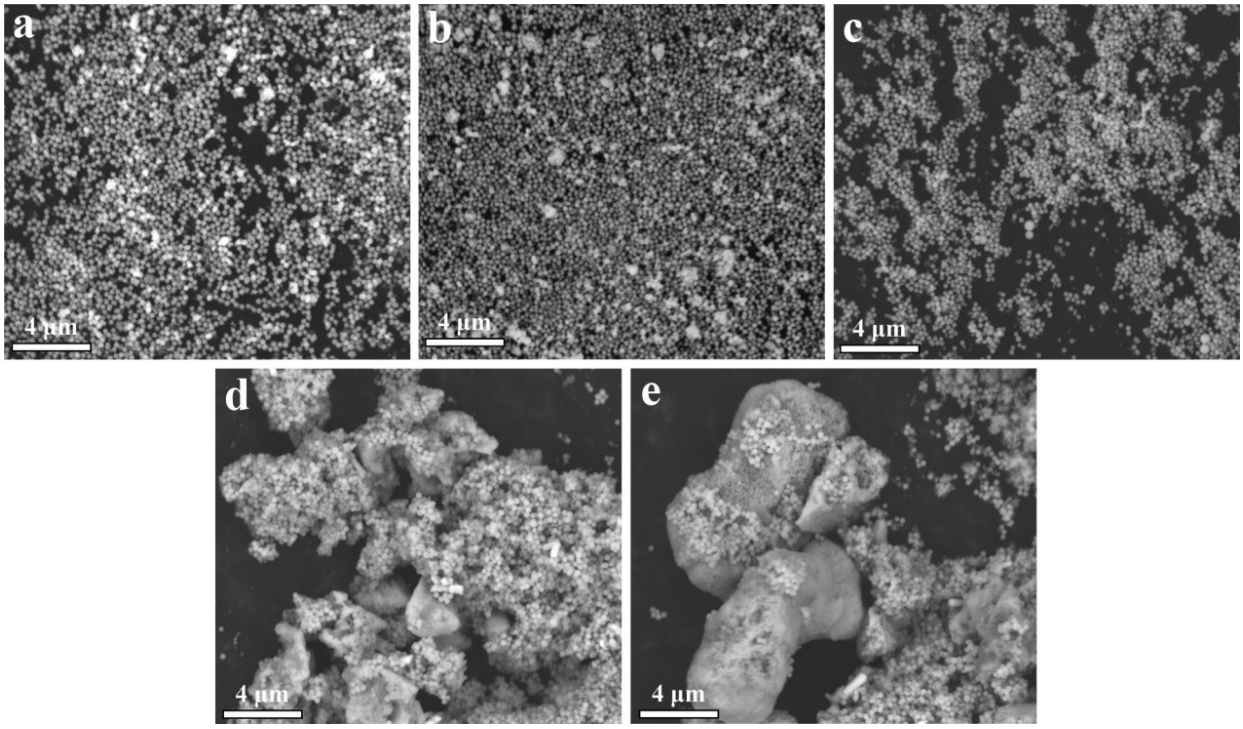

Fig. S3 SEM images of (a) Sample-1/2; (b) Sample-1/2-2h; (c) Sample-1/2-4h; (d) Sample-1/2-6h; and (e) Sample-1/2-8h.

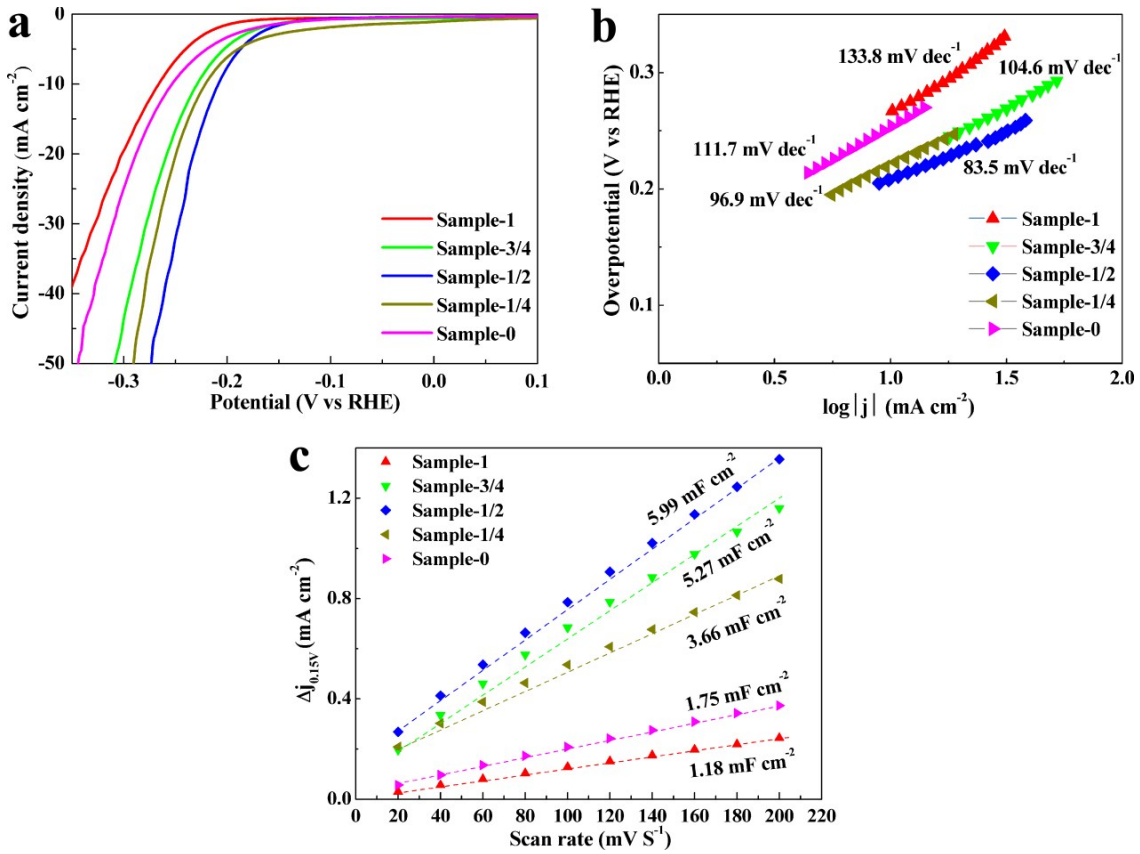

Fig. S4 Electrocatalytic performance of various samples (1, 3/4, 1/2, 1/4, 0) for HER: (a) Polarization curves after iR correction of samples; (b) corresponding Tafel slopes; (c) C_{dl} for samples.

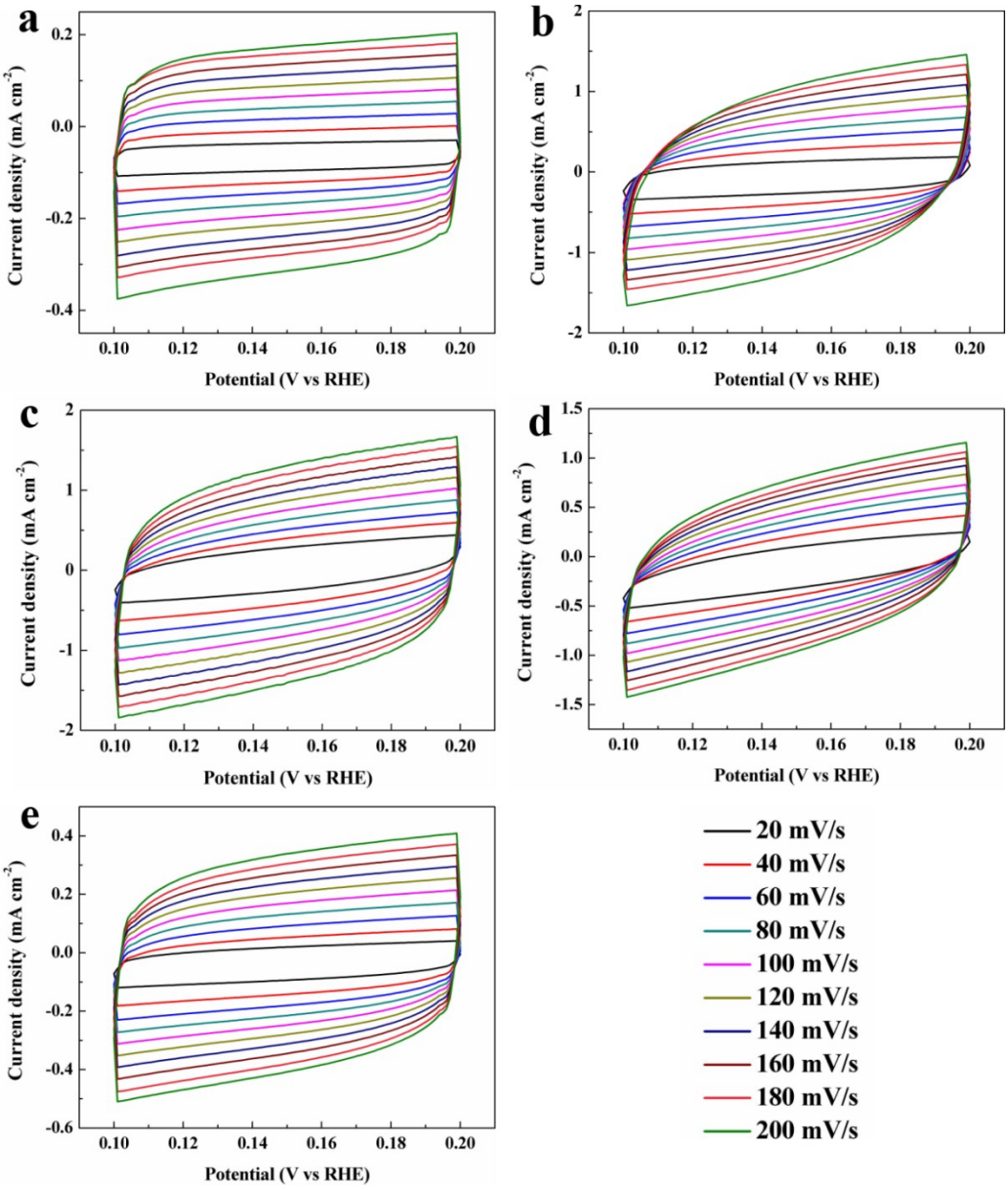

Fig. S5 Cyclic voltammetry curves of the samples (Sample-1, Sample-3/4, Sample-1/2, Sample-1/4, Sample-0) in the region of 0.1-0.2V vs. RHE with different scan rates from 20 to 200 mV s^{-1}. These plots were used to calculate the C_{dl} for various samples in Fig S4c.

Table S1. Comparison of previously reported $Mo_{2x}Se_{2(1-x)}$ based catalysts towards the HER.

Catalysts	Preparation method	Electrolyte	η_{10} (mV)	Tafel (mV dec^{-1})	Ref
MoSSe nanosheets	CVD	0.5M H_2SO_4	~-200	56	[1]
MoS_2 nanosheets	Hydrothermal	0.5M H_2SO_4	-220	61	[2]
$MoS_{0.98}Se_{1.02}$ nanosheets	Hydrothermal	0.5M H_2SO_4	-271.3	57	[3]
hierarchical MoS_2 nanocolumn	Hydrothermal	0.5M H_2SO_4	-258	57	[4]
porous MoS_2 nanosheets	KOH-assisted exfoliation	0.5M H_2SO_4	-240.7	88.4	[5]
$MoS_{0.72}Se_{1.28}$/CNFs	CVD	0.5M H_2SO_4	-272	124	[6]
$MoS_{1.06}Se_{0.94}$/carbon cloth	CVD	0.5M H_2SO_4	-183	55.5	[7]
$MoS_{1.08}Se_{0.92}$ nanosheets	CVD+ Hydrothermal	0.5M H_2SO_4	-219	55±2	[8]
monolayered $MoS_{0.98}Se_{1.02}$	CVD	0.5M H_2SO_4	-273	119	[9]
Intercalated $MoS_{0.82}Se_{1.18}$	Solvothermal	0.5M H_2SO_4	-143	53.8	This work

Table S2. Comparison of samples with different ratios of the S and Se element. For clarify，the as-synthesized samples were marked as Sample-x/y, where x/y means the ratio of S content (x) to the total content (y) of the initially added S and Se.

Catalysts	addition amount (mmol)		atomic ratio S/Se	η_{10} (mV)	Tafel (mV dec^{-1})	C_{dl} (mF cm^{-2})
	S	Se				
Sample-1	0.38	0	1/0	-266	133.8	1.18
Sample-3/4	0.285	0.095	3/1	-229	104.6	5.27
Sample-1/2	0.19	0.19	1/1	-208	83.5	5.99
Sample-1/4	0.095	0.285	1/3	-221	96.9	3.66
Sample-0	0	0.38	0/1	-253	111.7	1.75

Calculation of Per-site Turn Over Frequency (TOF):

In order to obtain the TOF of prepared samples, the relative roughness factor (RF) should be first calculated by equation (1) as follows:

$$RF = \frac{C_{dl\ catalyst}}{C_{dl\ flat}} \quad (1)$$

where $C_{dl\ catalyst}$ is the electrical double-layer capacitance (at the over potential of 200 mV) of as-prepared catalyst and $C_{dl\ flat}$ is the specific capacitance of flat standard MoS_2 (60 μF cm^{-2}). Then, the TOF could be obtained through Equation (2):

$$TOF = \frac{J \times N_A}{2 \times F \times n \times RF} \quad (2)$$

where J is the current density for samples at the over potential of 200 mV, N_A is the Avogadro's number (N_A=6.02×10^{23} mol^{-1}), 2 is the number of electrons needed to make each hydrogen molecule, F is the Faraday constant (F= 96485 C mol^{-1}) and n stands for the number of surface sites for the flat standard per cm^2 geometric area (1.164×10^{15} cm^{-2}). Here is the counting process of Sample-1/2-4h:

It's C_{dl} of catalyst is 20.6 mF cm^{-2}

$$RF = \frac{20.6\ mF\ cm^{-2}}{60\ \mu F\ cm^{-2}} = 343.33 \quad (3)$$

And the current density is 86.68 mA cm^{-2}

$$TOF = \frac{86.68\ mA\ cm^{-2} \times 6.02 \times 10^{23}\ mol^{-1}}{2 \times 96485\ C\ mol^{-1} \times 1.164 \times 10^{15}\ cm^{-2} \times 343\ s^{-1}}$$

(4)

The TOF of other samples could also be calculated through equations and the results are showed in Table S3.

Table S3. The calculated Roughness factor and TOF.

Catalysts	η_{10} (mV)	Tafel (mV dec^{-1})	C_{dl} (mF cm^{-2})	j_{200} (mA cm^{-2})	Roughness factor	TOF (s^{-1})
Sample-1	-266	133.8	1.18	-1.5	19.67	0.20
Sample-3/4	-229	104.6	5.27	-4.61	87.83	0.14
Sample-1/4	-221	96.9	3.66	-6.16	61.00	0.27
Sample-0	-253	111.7	1.75	-3.31	29.17	0.30
Sample-1/2	-206	83.5	5.99	-7.61	99.83	0.20
Sample-1/2-2h	-180	74.6	6.67	-18.27	111.17	0.44
Sample-1/2-4h	-143	53.8	20.6	-86.68	343.33	0.68
Sample-1/2-6h	-171	66.8	13.88	-27.03	231.33	0.31
Sample-1/2-8h	-169	67.2	12.30	-29.22	205	0.38

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