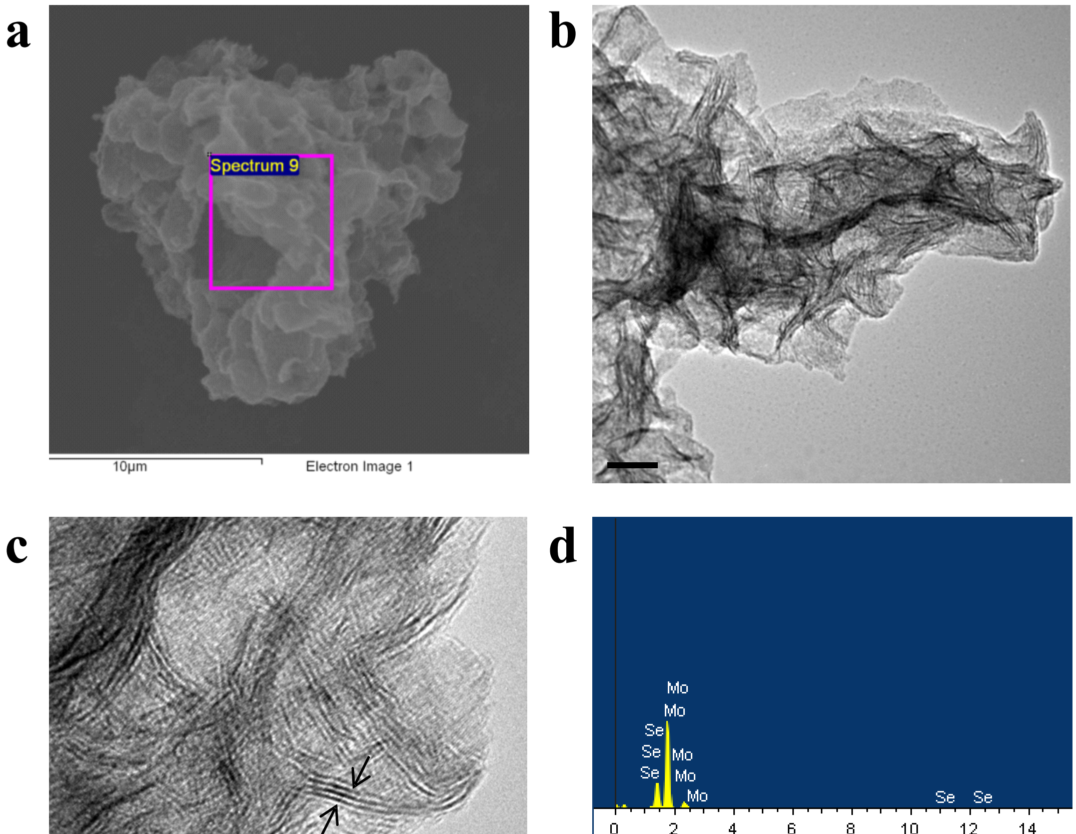
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information



Element	Weight%	Atomic%
Se L	63.01	67.42
Mo L	36.99	32.58
Totals	100.00	

Figure S1. (a) SEM image and (b) TEM image of the MoSe2 nanosheet network; (c) high-magnification TEM image showing folded edge of the nanosheets; (d) EDX spectrum of the area marked in (a) reveals that the atomic ratio of Se:Mo is 2.07:1.

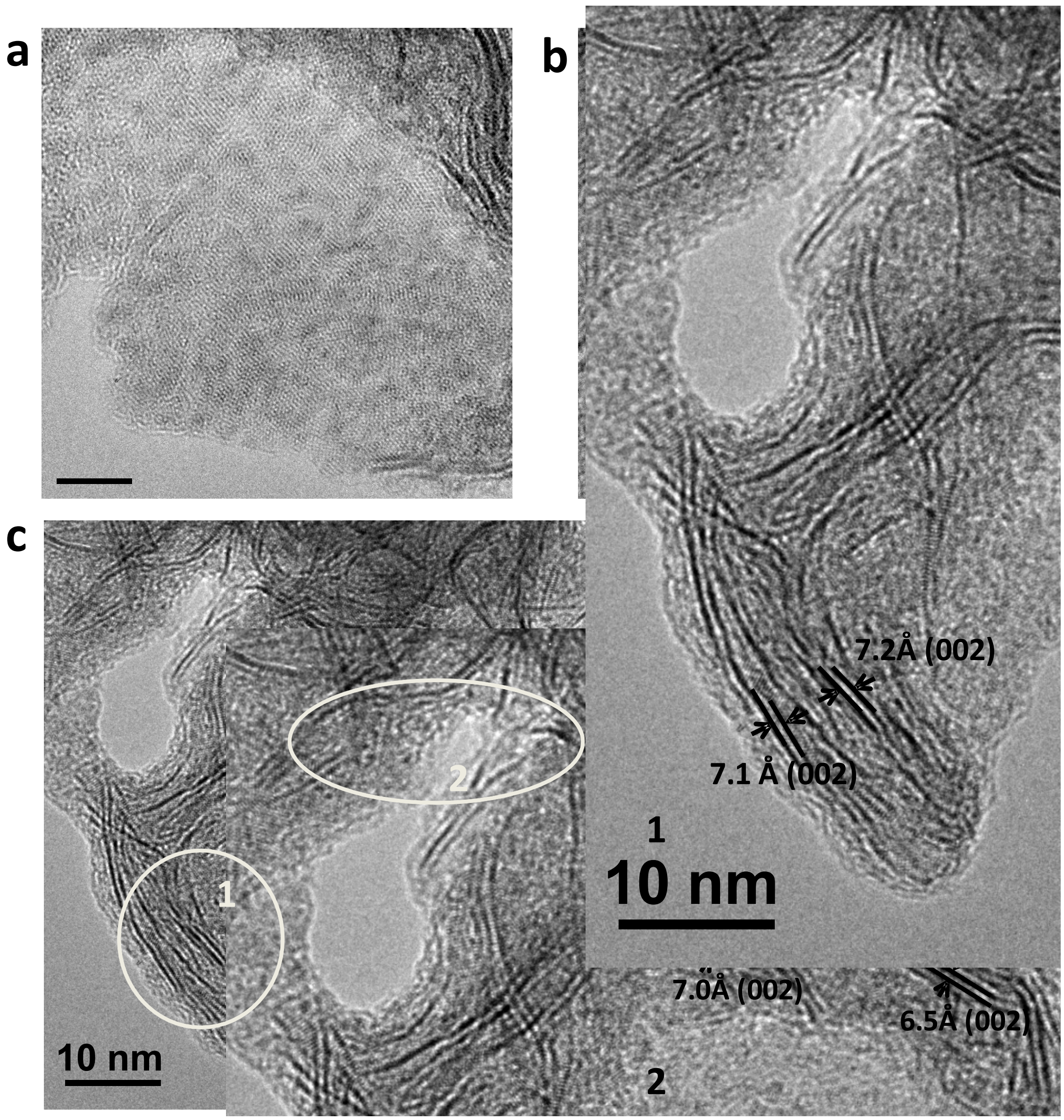


Figure S2. (a) TEM image and (b) HRTEM image of the S-doped basal plane of the nanosheets reveals the disordering of atomic arrangements and the domain-walls of the nanodomains contribute to higher density of active sites for HER; (c) higher-magnification TEM image and enlarged images on selected areas showing the non-uniformity of the interlayer spacings between adjacent (002) planes. The interlayer spacing is measured directly in software Digital Micrograph.

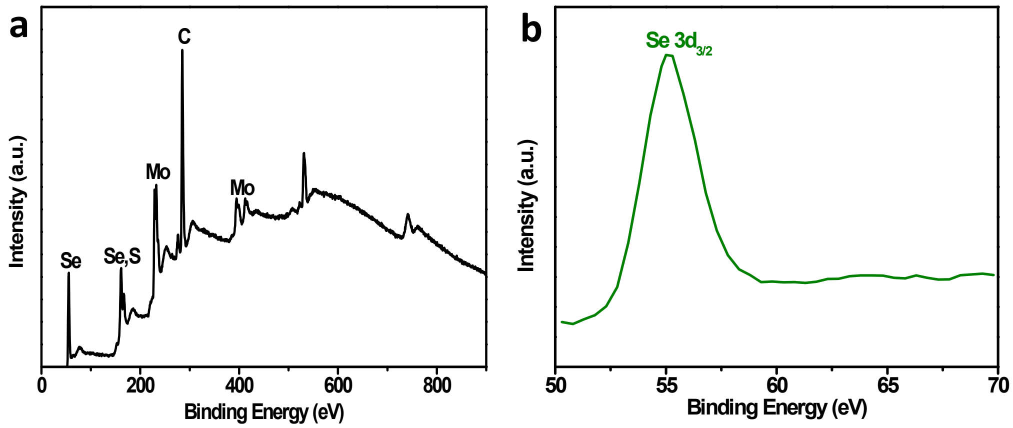


Figure S3. (a) XPS spectra showing the presence of Mo, Se and S; (b) high-resolution XPS spectra of Se 3d.

Tafel Analysis and HER mechanism:

There are three possible steps for the HER in acidic media.

Firstly, it is a primary discharge process and H^+ adsorption step (Volmer reaction):

$$H_3O^+ + e^- \rightarrow H^*_{ad} + H_2O \qquad b \approx 120\ mV$$

Secondly, H^*_{ad} is an unstable adsorbed intermediate after the primary discharge step and needs to migrate to a stable position on the electrode material surface (Spillover):

$$H^*_{ads} \rightarrow H_{ads} \qquad b \approx 60\ mV$$

Thirdly, the following desorption of H_{ads} to form H_2 is possibly proceed via an electrochemical desorption step (Heyrovsky reaction)

$H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O \qquad b \approx 40\ mV$

or a chemical recombination step (Tafel reaction)

$H_{ads} + H_{ads} \rightarrow H_2 \qquad b \approx 30\ mV$

Electrochemical Impedance Measurement:

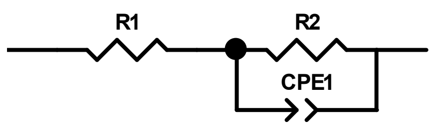


Figure S4. Electrical equivalent circuit employed to fit the Nyquist plots. R_1 represents the solution resistance R_2 is attributed to the charge transfer resistance. The EIS data were fitted with model using Zview.

Material	R_1	R2 (R_{ct} at $\eta = 150$ mV)
S-doped $MoSe_2$	9.4	35.66
$MoSe_2$	9.3	145.02

Table S1. Solution resistance (R_1) and charge transfer resistance (R_2) at overpotential of 150 mV calculated based on the model in Figure S4.