Electronic Supplementary Information

Se-doped MoS_2 nanosheet for improved hydrogen evolution reaction

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Experimental Section

Reagents and materials

Sodium molybdate, L-Ascorbic Acid and Diphenyl diselenide (DDS) were purchased from Aladdin Industrial Inc. H_2SO_4 was purchased from Tianjin Fuyu Chemical Reagent Co. Ltd., China. Pt and glassy carbon electrodes were purchased from Tianjin Aidahengsheng Technology. Co. Ltd., China. All chemicals were used as received without further purification. The water used throughout all experiments was deionized (DI) water purified through a Millipore system.

Preparation of Se-doped MoS_2 nanosheets

The synthesis of Se-doped MoS_2 nanosheets could be divided into 2 steps: (i) The mixture of 0.4 g of $Na_2MoO_4 \cdot 2H_2O$ and 0.65 g of L-cysteine were dissolved in 60 mL DI water, and then transferred into a 100 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 18 hours. After cooling naturally to ambient temperature, the black precipitates were collected by centrifugation, washed with DI water and ethanol, dried in a vacuum oven at 80 °C for overnight and then the MoS_2 powder was obtained. (ii) Se-doped MoS_2 was synthesized by directly annealing MoS_2 nanosheets and DDS in a conventional tube furnace in Ar/H_2 atmosphere. As Se is insoluble in ethanol and water, it is difficult to distribute Se powder uniformly on the surface of the MoS_2 nanosheets, we choose DDS as the Se dopant. The detailed procedure is as follows: MoS_2 nanosheets (200mg) and DDS (78mg) were first ultrasonically dispersed in ethanol for about 30 min. The resulting suspension was spread onto an evaporating dish and dried, forming a uniform solid mixture. The mixtures were placed into a quartz tube with Ar/H_2 atmosphere and annealed at 800°C for 2 hours. After that, the sample was cooled to room temperature under ambient Ar/H_2 and collected from the quartz tube. For comparison, the MoS_2 without any dopants was treated under the same condition.

Characterization

The Field emission transmission electron microscopy (FETEM) images were taken with a FEI Tecnai G2 F20. Field emission scanning electron microscope (FESEM) observations were performed on SU8020. X-ray photoelectron

spectroscopy (XPS) experiments were made on an AXISULTRA. Raman spectrum at excitation wavelength of 532 nm was obtained from a Renishaw Invia Raman microscope. X-ray diffraction (XRD) patterns were obtained on a DX-2700 diffractometer.

Electrochemical characterization

Electrochemical measurements were carried out with a computer-controlled IM6ex (Zahner, Germany) in a standard three-electrode cell using Ag/AgCl (in 3.5 M KCl solution) electrode as the reference electrode, a platinum foil as the counter electrode and the glassy carbon (GC) electrodes modified with catalyst as the working electrode. The working electrode was fabricated as follows: 4 mg of catalyst and 80 μL of 5 wt% Nafion solution were dispersed in 1 mL of a solution of deionized water and ethanol (4:1 in volume ratio). After stirring by ultrasonication for 1 h, 5μL of the resulting solution was dropcast onto the top of a glassy carbon electrode with 3 mm diameter. The catalyst-coated GC electrode was dried at 80 °C for 2 h to yield a catalyst loading of 0.285 mg/cm^2. Linear sweep voltammetry (LSV) with scan rate of 10 mV/s was conducted in 0.5 M H_2SO_4 (purged with pure N_2). The electrochemical impedance spectroscopy (EIS) was recorded in the same configuration at η=0.2 V from 10^{-2} to 10^6 Hz with an AC voltage amplitude of 5 mV. All the potentials were calibrated to a reversible hydrogen electrode (RHE).

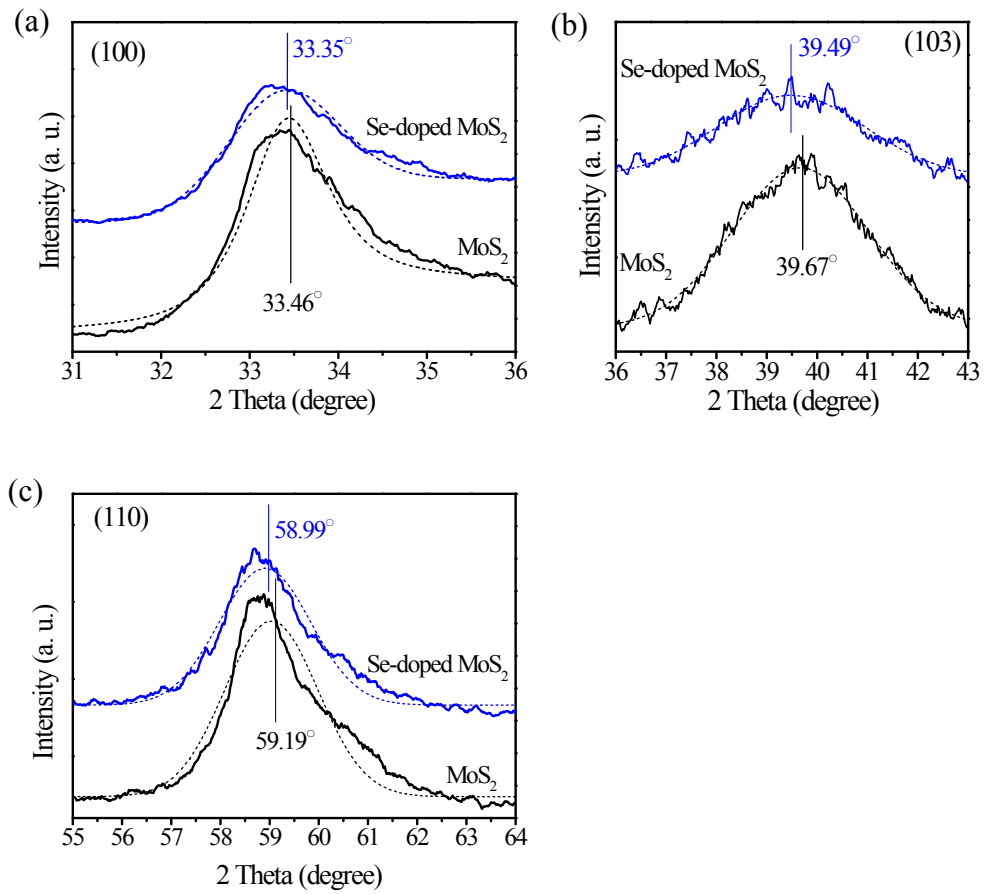

Fig. S1 The enlarged XRD patterns showing the diffraction peak shift of (a) the (100) crystal plane, (b) the (103) crystal plane and (c) the (110) crystal plane of the MoS_2 and the Se-doped MoS_2 nanosheets. The solid lines are experimental data and the dotted lines are the corresponding Gaussian fittings.

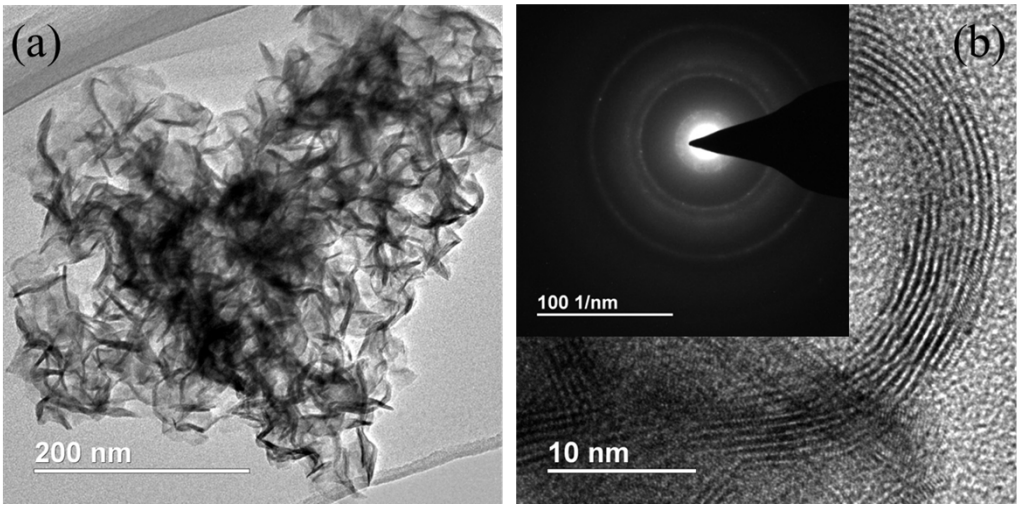

Fig. S2 (a) TEM images of the MoS_2 nanosheets. (b) HRTEM image and the corresponding SAED patterns.

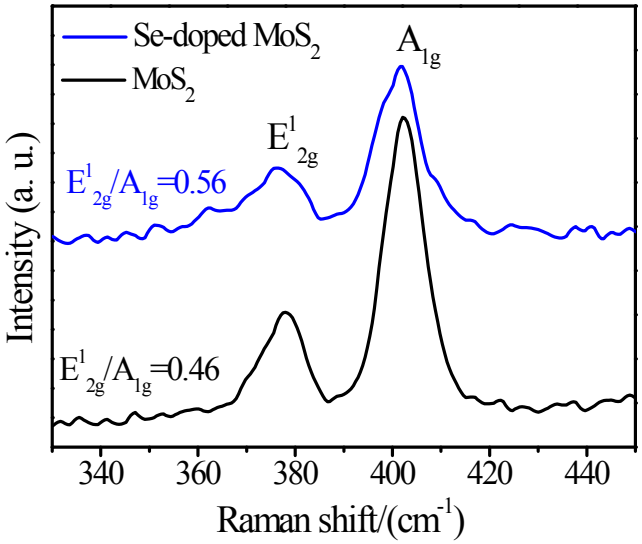

Fig. S3 Raman spectra recorded using a 532 nm laser for the MoS_2 and the Se-doped MoS_2 nanosheets.

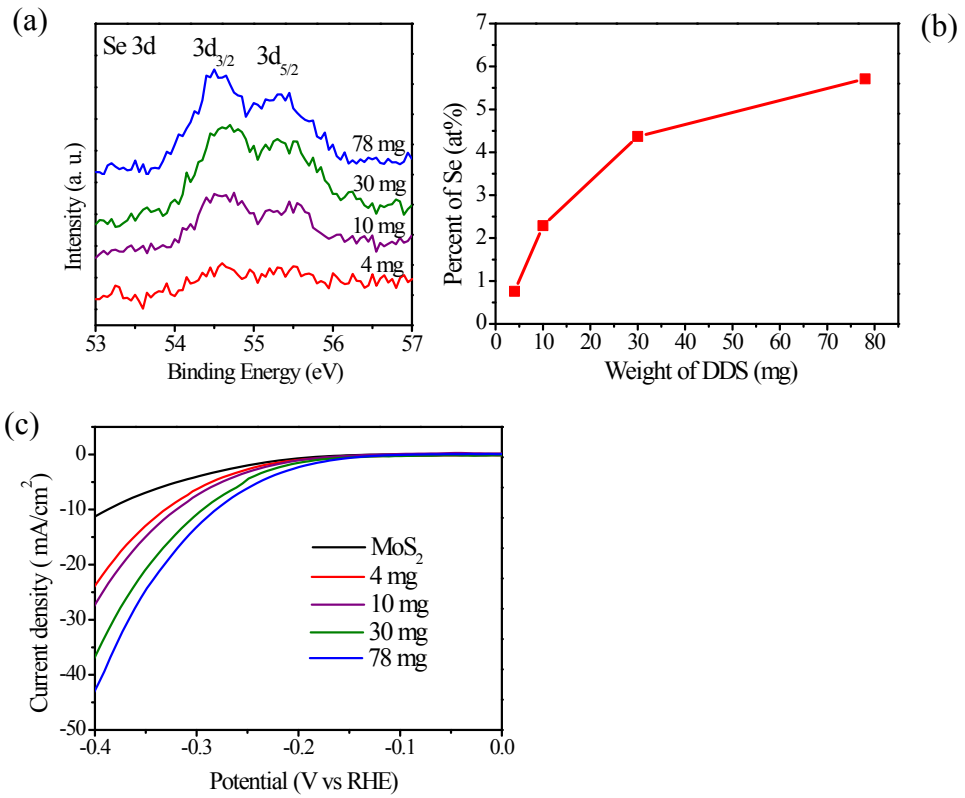

Fig. S4 (a) Representative Se 3d XPS spectra of Se-doped MoS_2 samples with different weight of DDS. (b) Se doping concentration as a function of the weight of DDS. (c) Polarization curves of Se-doped MoS_2 vs. Se content.

Fig. S4 (a) shows Se 3d XPS spectra in the Se-doped MoS_2 nanosheets. It is clear that when the weight of DDS is increased from 4 mg to 78 mg, the peaks of Se $3d_{3/2}$ and Se $3d_{5/2}$ appear and become dominant. Fig. S4 (b) shows the atomic percentage of Se incorporated into MoS_2 as a function of weight of DDS. It shows that the Se percentage increased with the weight of DDS and the largest value can reach up to 5.7% with the DDS of 78 mg, indicating the enhanced doping effect of Se. The catalytic current densities of Se-doped MoS_2 are larger than that of pristine MoS_2 at a constant overpotential as shown in Fig. S4c, indicating that the Se-doped MoS_2 exhibits the enhanced HER catalytic activities comparing to pristine MoS_2. In addition, the HER performance of the Se-doped MoS_2 increased with the Se content.

Table S1. Comparison of HER performance in acidic media for Se-doped MoS_2 with other state-of-the-art MoS_2-based HER electrocatalysts.

Catalyst		Onset potential (mV)	Tafel slope (mV/dec)	References
Undoped MoS_2	MoS_2 Nanosheets	-180	87	[1]
	Nanosized bulk MoS_2	-280	82	[2]
	MoS_2 nanoparticles	-160	77	[3]
Doped MoS_2	V-doped MoS_2	-130	60	[4]
	Oxygen-incorporated MoS_2	-120	55	[5]
MoS_2/conductive substrates composites	MoS_2/Graphene/Ni-foam	-109	42.8	[6]
	MoS_2 /RGO	-100	41	[7]
	MoS_2/CNF mats	-120	45	[8]
	Se-doped MoS_2	-140	55	This work

RGO: Reduction graphene oxide

CNF: Carbon fiber foam

Quantitative XPS analysis

The doping concentration of selenium present in Se-doped MoS_2 nanosheets is quantified using the following equation.

$$Se/(Se+S) = (I_{Se}/F_{Se})/(I_{Se}/F_{Se}+I_S/F_S)$$

where, I_S and I_{Se} are the areas under the peaks for S-$2p_{3/2}$ and Se-$3p_{3/2}$ respectively. F_S and F_{Se} are the relative symmetric factors (R.S.F) for S-$2p_{3/2}$ and Se-$3p_{3/2}$ respectively.

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