Supporting information

Plasma-engineering MoS_2 Thin-film as Efficient Electrocatalysts for Hydrogen Evolution Reaction

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Material preparation

The MoS_2 thin film was synthesized by chemical vapor deposition method to deposit MoS_2 on titanium foil (1 cm×1 cm). Briefly, 0.1 g high-purity MoO_3 (99 % Aldrich) was placed in a quartz boat covered by titanium foil, and annealed at 600 °C for one hour to deposit MoO_3 onto titanium foil. The MoO3 coated Ti foil was then annealed in S vapor at 600 °C for one hour to produce MoS_2 thin film on Ti foil. Ar or O_2 plasma (commercial 13.56 MHz RF source) with power of 100 W and pressure of 40 Pa is used to treat the MoS_2 thin-film electrode with different irradiation time at room temperature.

Characterazition

The morphology and microstructure of the MoS_2 thin-film were investigated by scanning electron microscope (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEM-2100F). The Raman spectra were recorded at room temperature on a Horiba HR 800 with an argon ion laser operating at 632 nm. X-ray photoelectron spectroscopy (XPS) measurements and analysis were recorded on a Thermo Fisher-VG Scientific (ESCALAB 250Xi) photoelectron spectrometer.

Wettability of the thin-film surface was studied by measuring the contact angles with water droplet.

Electrochemical testing

Electrochemical measurements of MoS_2 samples for hydrogen evolution reaction were conducted at room temperature in a standard three-electrode cell on a CHI660d electrochemical workstation, with a 0.5 M H_2SO_4 solution was used as the electrolyte, the MoS2 thin film as the working electrode, a large surface area platinum mesh (1 cm×1 cm) as the counter electrode, and saturated calomel electrode (SCE) as the reference electrode. Impedance data were collected at frequencies of 0.01Hz-100 kHz using Autolab PGSTAT302N (Metrohm-Autolab BV, Utrecht, The Netherlands). All potentials were corrected by pH and reported against the reversible hydrogen electrode (RHE).

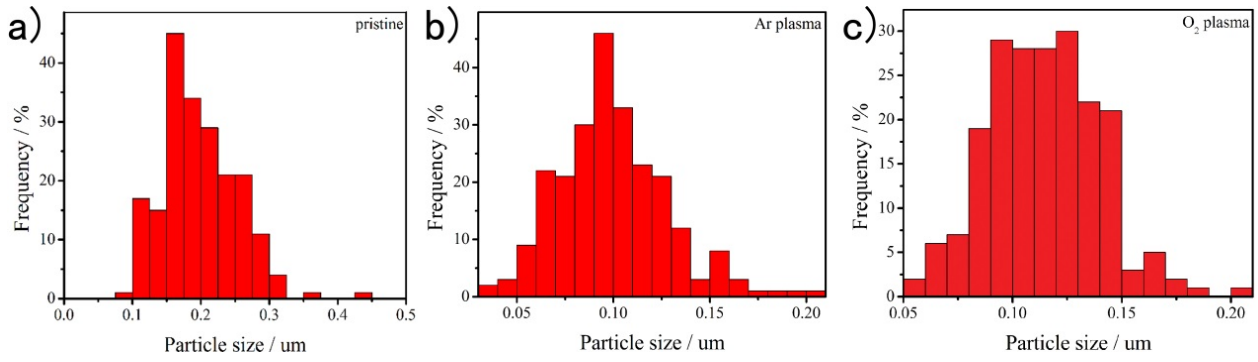

Figure S1. Histograms of particle size distribution for pristine MoS_2 (a), Ar plasma treated MoS_2 (b) and O_2 plasma treated MoS_2 (c).

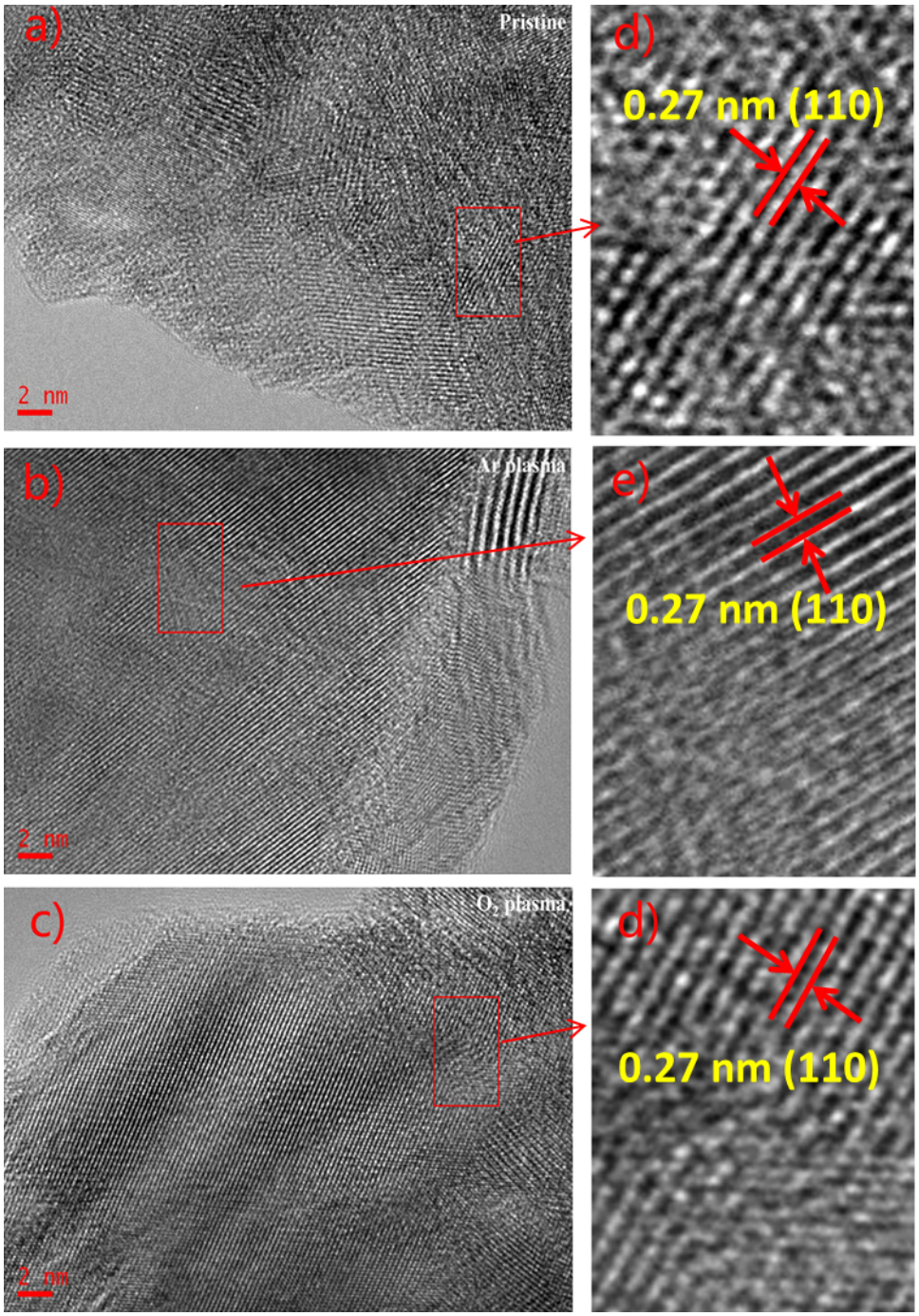

Figure S2.High-resolution TEM images of a pristine MoS_2 (a), Ar plasma processed MoS_2 (b) and O_2 plasma processed MoS_2 (c); (d), (e)and (f) the local amplification images of (a), (b) and (c).

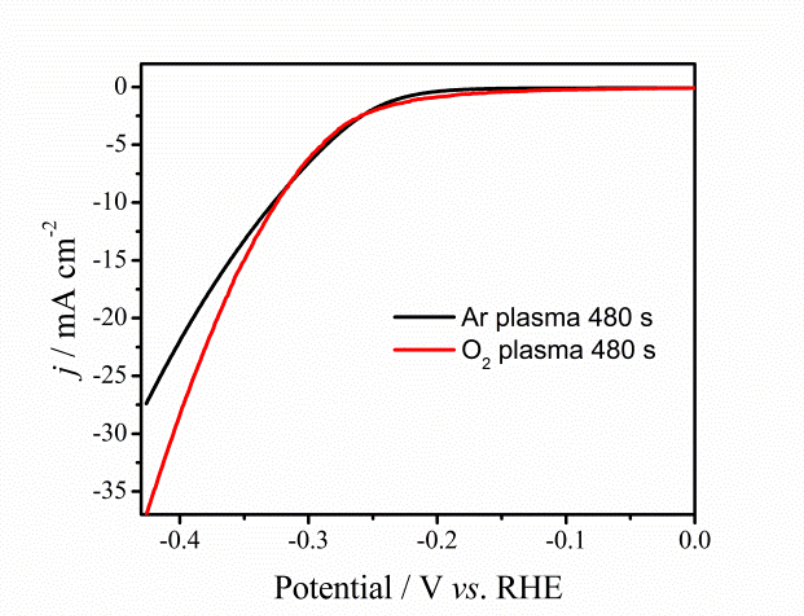

Figure S3. The HER comparison of Ar plasma and O_2 plasma treated MoS_2 thin films with the same plasma irradiation time of 480 s.

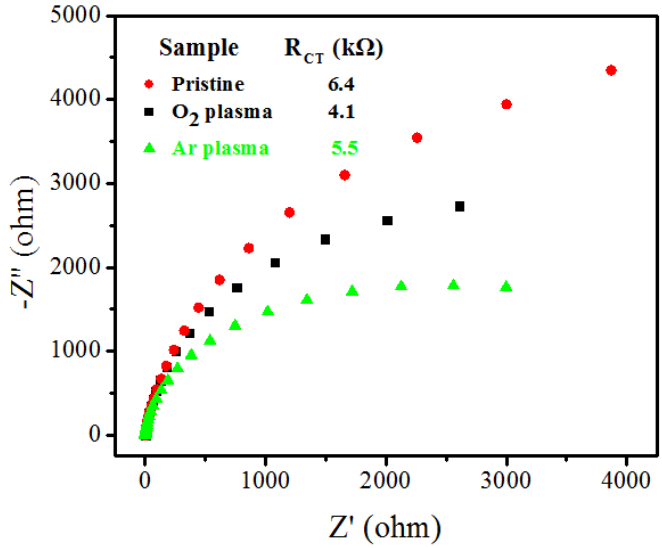

Figure S4. Electrochemical impedance spectra of pristine MoS_2, Ar plasma treated and O_2 plasma treated MoS_2.

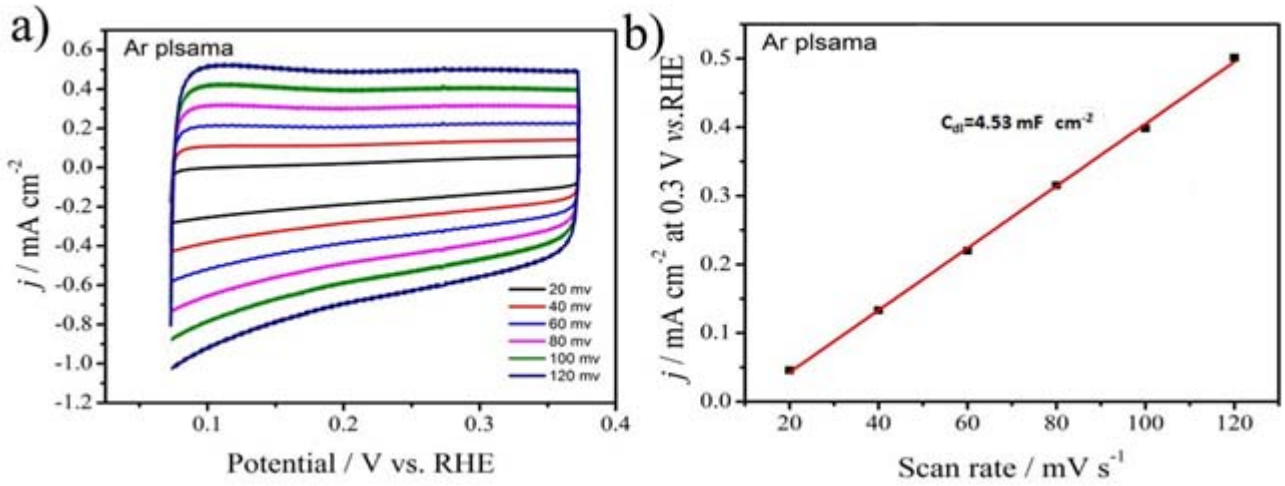

Figure S5. Cyclic voltammograms of Ar plasma treated MoS_2 (a) measured in a potential range, in which no faradic processes were observed to obtain the capacitive current from double layer charging. The capacitive current measured at 0.30 V vs RHE was plotted as a function of scan rate (b).

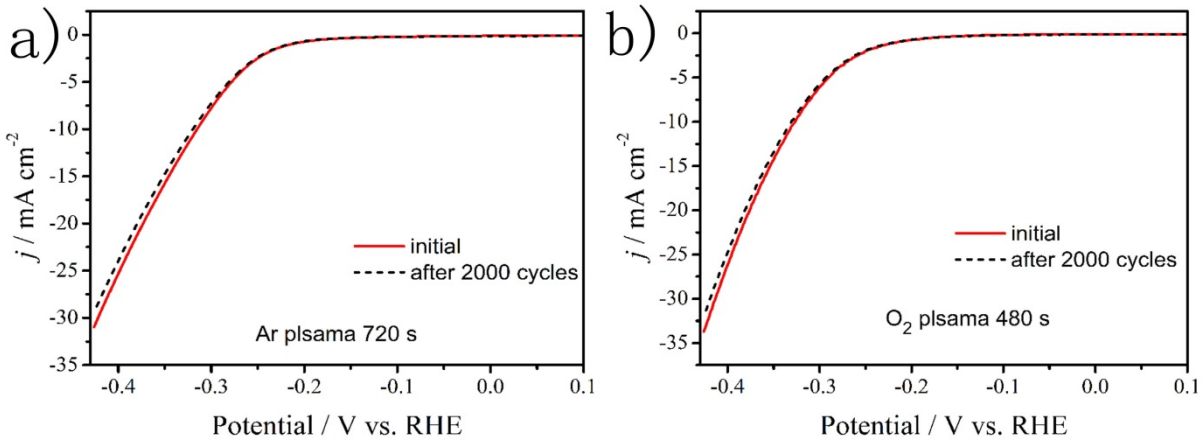

Figure S6. Cycle stability tests for the Ar-MoS_2 (a)and O_2- MoS_2(b).

peak		pristine		Ar plasma		O_2 plasma	
		position	%Area	position	%Area	position	%Area
Mo	$Mo^{4+}3d_{5/2}$	229.6	56.0	229.4	37.7	229.5	11.7
	$Mo^{4+}3d_{3/2}$	232.7	43.6	232.5	24.9	232.6	7.6
	$Mo^{5+}3d_{5/2}$	---	---	233	11.8	231.7	29.8
	$Mo^{5+}3d_{3/2}$	---	---	236	9.9	234.8	21.1
	$Mo^{6+}3d_{5/2}$	231.6	5.6	231.6	8.6	233	17.1
	$Mo^{6+}3d_{3/2}$	234.1	4.1	234.5	7.1	236	12.7
S	S^{2-} $2P_{3/2}$	162.5	72	162.2	67.9	162.4	35.4
	S^{2-} $2P_{1/2}$	163.7	28	163.4	32.1	163.6	17.8
	S^{6+} $2P_{3/2}$	---	---	---	---	168.6	28.2
	S^{6+} $2P_{1/2}$	---	---	---	---	169.8	18.6

'---' means that the species specified is not detected in the spectrum for the sample concerned.

Table S1. Binding energies eV and composition of the characteristic peaks found in the XPS spectra for Pristine MoS_2, Ar-MoS_2 and O2-MoS_2.

Materials	Tafel slop [mV dec^{-1}]	Double-layer capacitance mF cm^{-2}	Active site density [10^{15} cm^{-2}]	TOF [s^{-}]
Pristine MoS_2	160	0.761	14.09	0.617
Ar plasma 240 s	130	2.28	42.22	1.11
Ar plasma 480 s	117	3.77	69.81	1.19
Ar plasma 720 s	108	4.18	77.40	1.32
Ar plasma 960 s	118	3.5	64.81	1.14
O_2 plasma 120 s	133	2.06	38.15	1.00
O_2 plasma 480 s	105	3.93	72.77	1.30
O_2 plasma 720 s	120	4.52	83.70	0.88

Table S2. HER parameters for pristine MoS_2 thin films and treated by Ar or O_2 plasma.