Electronic Supplementary Information

Strain and defect-engineering on the basal plane of ultra-large MoS₂ monolayers attached onto stretchable gold electrodes

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S1) DFT Calculations

Figure S1a presents the fitting of experimental profile data by a sine function. By fitting the experimental data from Fig. 1g, it is possible to obtain the curvature of the profile data (Fig S1b) using Eq 1 (main manuscript). Fig S1c shows the curvature of the theoretical corrugated model. At the maximum, both S1b and c have similar curvature.



Fig. S1: a) Fitting profile data by a sine function. Curvature obtained from b) fitting profile data and c) theoretical corrugated model.

S2) X-ray photoelectron spectroscopy of PDMS substrates

To obtain in-depth information about the surface chemistry modification promoted by the plasma treatment on the polydimethylsiloxane substrates, XPS analysis was carried out. Table S1 presents the atomic percentages obtained for three different spots for as-prepared PDMS and PDMS subjected to O₂ plasma treatment (PDMS + plasma). As can be observed, the oxygen percentage highly increases after the oxygen plasma treatment, due to the introduction of oxygen reactive radicals on the polymeric surface. Those reactive groups are responsible for the good adhesion of the metal thin films and the maintenance of the electrical properties when the electrodes are subjected to bending and stretching conditions. Additionally, Figure S2 presents high-resolution spectra for carbon (Figure S2a) and silicon (Figure S2b) for the polymeric substrate samples. As expected, after the oxygen plasma treatment, the emergence of a band attributed to C-O group (initially inexistent in the PDMS structure) can be observed (Figure S2a-i). In agreement, silicon high-resolution spectra indicate a higher percentage of silicon atoms bonded to a higher number of oxygen atoms.^{1–3}



Fig. S2. XPS high-resolution spectra of a) carbon and b) silicon. i) Refers to PDMS treated in oxygen plasma and ii) as-prepared PDMS substrates.

	PDMS				PDMS + Plasma		
	Si	С	0		Si	С	0
1	26.8	46.0	27.2	1	28.7	15.5	55.8
2	27.3	46.1	26.6	2	29.0	20.5	50.5
3	26.9	46.8	26.4	3	29.3	19.4	51.3
Mean	27.0 ±	46.3 ± 0.4	26.7 ±	Mean	29.0 ±	18.4 ±	52.5 ± 2.9
	0.3		0.4		0.3	2.6	

Table S1. Atomic percentages obtained from the XPS survey spectra for the analyzed substrates.

S3) Angular strain on PDMS-based electrodes

Another approach for fabricating flexible and stretchable electrodes on a PDMS substrate was investigated. In this method, PDMS strips were mechanically pre-strained before thermal deposition in the e-beam chamber. The strips were bent and held at their ends in a sandwich-like configuration using glass slides, as schematically illustrated in Figure S3a. Initially, the PDMS strips were fixed with a separation distance of 4.0 cm, resulting in a flat configuration. To induce angular tension before the metal deposition, the PDMS strips' fixed ends were brought closer together, causing the material to bend. This angular pre-straining led to varying degrees of strain, as quantified by Equation S1⁴ and shown in Figure S3b.

$$\varepsilon_{mech,pre} = \frac{PDMS \ thickness}{radius \ of \ curvature}$$
 Equation S1

Where $\varepsilon_{mech,pre}$ is the mechanical pre-strain and the PDMS thickness is 1 mm.

Based on the obtained linear correlation, a strain level of 9.4% was chosen to maintain the substrates strained. Similar to the pre-stretched PDMS substrates discussed in the main text, angular pre-strained PDMS substrates underwent oxygen plasma treatment before metal thermal deposition. Subsequently, Ti and Au layers of 20 nm and 150 nm, respectively, were deposited.

Following metal deposition, MoS₂ was transferred and electrochemically thinned to obtain monolayers with a high aspect ratio. Laser scanning confocal microscopy (LSCM) images of the same regions of the stretchable electrode at different strain levels (Figure S3c) provided insights into the electrode's structure. As observed, the deposition of the gold layer occurred with the substrate prestrained at 9.4%. Upon increasing the end-to-end separation to flatten the electrode, the gold layer was forced to approach, resulting in heightened roughness. Upon returning the electrode to its initial conformation, the recovery of structural characteristics was evident. Topographic images of the analyzed regions (Figure S3d) offered additional insights into the observed changes in roughness as the electrode underwent bending. Overall, as illustrated in Figures

S3e and S3f, the wavelength of surface roughness across all strain levels remained around 25 μ m, while the height difference between peaks and valleys became more pronounced with decreasing initial substrate strain levels (i.e., flattening the electrode).



Fig. S3 a) Schematic representation of the gold thermal deposition over PDMS substrates in an angular strained condition. i and iii) For the flat configuration, the end-to-end separation was 4.0 cm. ii and iv) As the end-to-end separation is decreased, the

substrate is strained. The squared region in "iv" indicates the region of maximum strain. b) End-to-end separation distance x strain. the inset picture depicts the strained PDMS secured by glass slides. The semicircle region is denoted by the red circle. c) LSCM images obtained for the same region of the electrode in different strain levels. Scale bars are 25 μ m long. d) Topographic images obtained from the same regions depicted in panel c. Scale bars are 25 μ m long. e) Line profiles of the stretchable electrode in different strain levels. f) height difference between the peaks and valleys for different strain levels.

S4) Photoluminescence spectra

Fig. S4 shows in more detail the spectrum depicted in Figure 3c-i. As can be observed a high-intensity peak located at 665 nm is attributed to exciton A, as reported for MoS₂ monolayer. In addition, the small peak at ~ 620 nm that can be observed in the spectra is attributed to exciton B. The peak position of exciton A and B shift from 665 and 618 nm (before stretching) to 687 and 640 nm, respectively, after stretching and releasing strain.



Fig. S4 Photoluminescence spectrum of MoS₂ monolayer: a) Flat electrode, b) Corrugated electrode stretched at 20 % strain to form cracks, and c) After releasing the electrode from the strain condition.

S5) Additional AFM information

Fig. S5 displays an AFM image of the gold surface on the stretchable electrode, along with corresponding line profiles from selected regions. The AFM image reveals a smooth surface morphology with minimal height variation, indicative of a more uniform surface compared to regions where MoS₂ is deposited.



Fig. S5 a) AFM image of a gold surface. b) Line profiles from the indicated regions in panel a

S6) Microelectrode preparation

To avoid the contribution of the edge sites of MoS₂ recognized by their high HER activity, the basal plane is isolated with the aid of an insulating resin. The process is carried out in two steps as previously described.⁵ Fig. S6 shows a LSCM image obtained from a MoS₂ monolayer after the insulating resin was applied.



Fig. S6 LSCM image obtained for an isolated MoS₂ monolayer.

S7) Stability test

Figs. S7a and S7b depict the Raman and PL spectra, respectively, acquired from the stretched electrode following 500 linear sweep voltammetry cycles conducted during stability tests. The spectra reveal that the characteristic features of 2H-MoS₂ are preserved, indicating neither material degradation nor phase transition. In the Raman spectrum E_{2g}^1 and A_{1g} peak positions are 383.9 and 405.5 cm⁻¹, respectively. For the PL spectrum, the exciton A peak is at 675 nm and the exciton B peak is at ~636 nm.



Fig. S7 a) Raman spectrum and b) PL spectrum obtained after 500 linear sweep voltammetry cycles.

Fig. S8 presents XPS spectra for the stretched samples before and after the electrochemical stability test. Initially, the doublet at 230.6 and 233.6 eV can be assigned to Mo⁴⁺ 3d_{5/2} and Mo⁴⁺ 3d_{3/2}, respectively. The doublet at 233.1 and 236.3 eV to Mo⁶⁺ 3d_{5/2} and Mo⁶⁺ 3d_{3/2}, respectively, and the peak at 227.3 eV to S 2s. The S 2p doublet characteristic of MoS₂ can be seen at 164.4 and 165.3 eV. After stability tests some changes can be observed in the Mo high-resolution spectra. For example, a higher proportion of Mo⁶⁺. This might be due to the higher chemical reactivity of the wrinkled and cracked features of the stretched sample, possible desulfurization during electrochemical cycling that can act as active sites, and the fact that MoS₂ can interact with oxygen under ambient conditions.⁶



Fig. S8 XPS high-resolution spectra of Mo 3d and S 2p for a stretched sample before and after the stability test.

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