Supporting Information

Experimental section:

MoS\textsubscript{2} porous thin films (MoS\textsubscript{2} PTFs) on Mo foil was synthesized by a simple hydrothermal method. In a typical procedure, CS(NH\textsubscript{2})\textsubscript{2} (0.5 g) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Mo foil (~ 4 cm × 1 cm, Aladdin Chemical Co. Ltd) was carefully cleaned with concentrated HCl solution (37 wt\%) in an ultrasound bath for 3 min, and then deionized water and absolute ethanol were used for 5 min each to ensure the surface of the Mo foil was well cleaned. The aqueous solution and the Mo foil (against the wall) were transferred to a 40 mL Teflon-lined stainless-steel autoclave, which was sealed, maintained at 180 °C for several hours (in this paper, 4h, 8h, 12h and 24h were chosen), and then allowed to cool to room temperature naturally. A dark thin film was taken out from the autoclave and subsequently rinsed with distilled water, ethanol each for 5 minutes with the assistance of ultrasonication, and dried at 80 °C for 6 h.

X-ray powder diffraction patterns were recorded on an X-ray diffractometer (Rigaku D/max 2500) at a scan rate of 10 (°)/min in the range from 5 to 90°. The size and morphology of the samples were characterized using a field-emission SEM (Zeiss SUPRA 55) operating at 20 kV and a High-resolution TEM system (JEOL 2010) operating at 200 kV. XPS spectra were carried out by using a model of ESCALAB 250 and LabRAM Aramis.

The electrochemical measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660D, chenghua, shanghai.) with high purity H\textsubscript{2} feeding. The linear sweep voltammetry with scan rate of 1 mV·s\textsuperscript{-1} was conducted in 0.5 M H\textsubscript{2}SO\textsubscript{4} solution using saturated calomel electrode as the reference electrode. Graphite was used as the counterelectrode. AC impedance measurements were carried out in the same configuration at open circuit voltage from 10\textsuperscript{5} – 0.1 Hz with an AC voltage of 5 mV. In all measurements, we used saturated calomel electrode (SCE) as the reference. It was calibrated with respect to reversible hydrogen electrode (RHE) by using Pt electrode as standard electrode. All the potentials reported in our manuscript are against RHE.
Figures:

**Figure S1**: Optical images of a) Pure Mo substrate; b) Mo substrate with MoS$_2$ PTFs; c) MoS$_2$ PTFs after 10 minutes of ultrasonication. “US” represents ultrasonication and these results strongly indicated the robustness of the fabricated films.
Figure S2: Low- and high-magnification top view SEM images of MoS₂ PTFs obtained at different times. (a) and (b) are for MoS₂ PTF 4h, (c) and (d) are for MoS₂ PTF 12h and (e) and (f) are for MoS₂ PTF 24h, respectively.
**Figure S3:** Cross view images of MoS$_2$ PTFs obtained at different times, (a) for 4h, (b) for 12h and (c) for 24h. The thicknesses of the films increased along with the reaction time prolonging.
Figure S4: XRD spectrum of Mo substrate and MoS$_2$ PTFs obtained at different times as labeled. No obvious peaks for MoS$_2$ were found.
Figure S5: Raman spectrum of MoS$_2$ PTFs obtained at 8h, confirming the formation of MoS$_2$. 
Figure S6: Nyquist plots of Mo substrate under the open circuit voltage. The compensated resistance was observed to be 1.75 ohm.
Figure S7: Tafel curve of the MoS$_2$ PTF 8h. The red dot showed in the curve was the onset overpotential.
Figure S8: EDLC measurement of this MoS$_2$ PTFs and the corresponding current density-scan rates curves, showing the MoS$_2$ PTFs obtained at 8h and 12h possessed the largest electro-double layer capacitance.