

## SUPPORTING INFORMATION

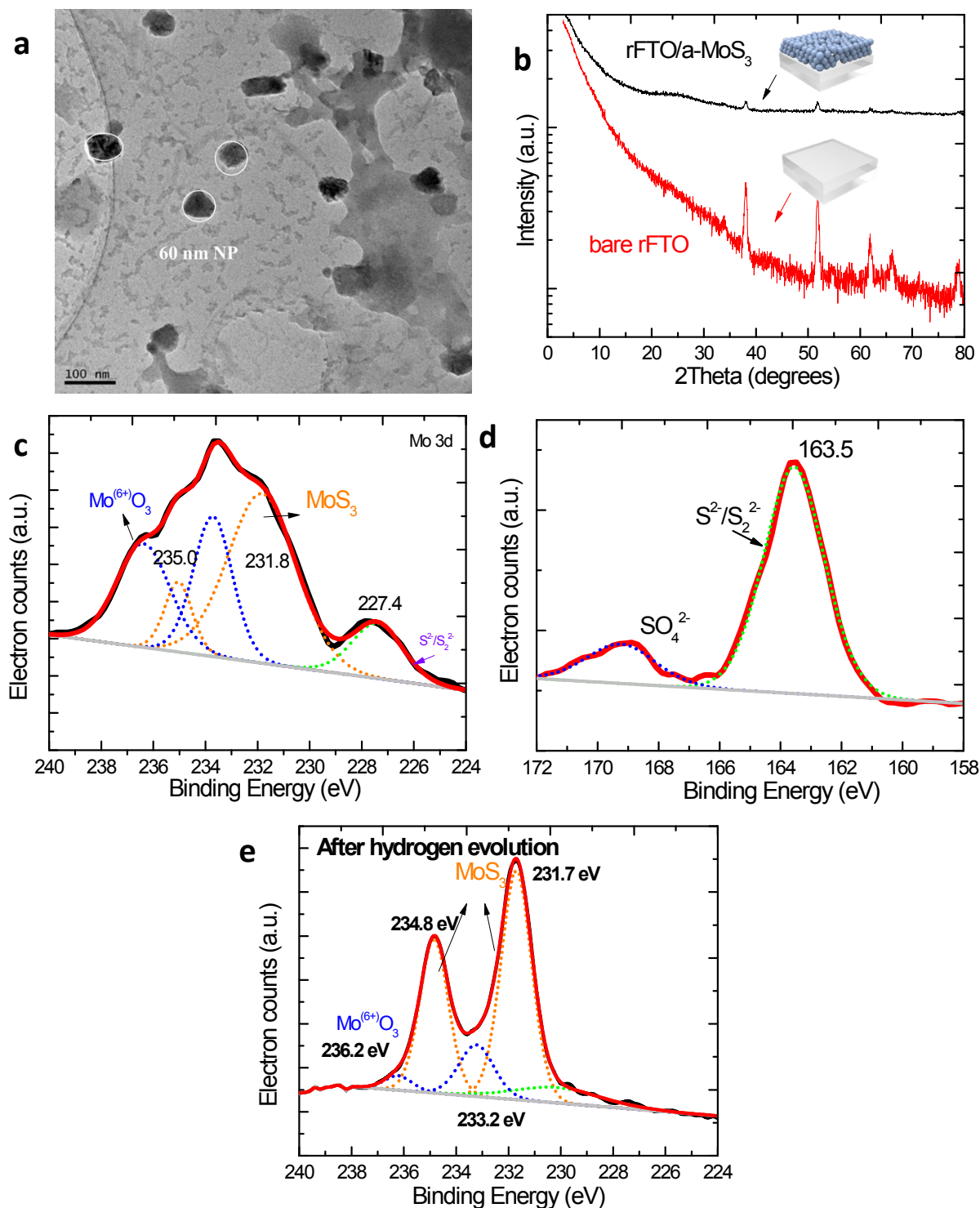
### **Molybdenum Supported Amorphous MoS<sub>3</sub> Catalyst for Efficient Hydrogen Evolution in Solar-water-splitting Devices**

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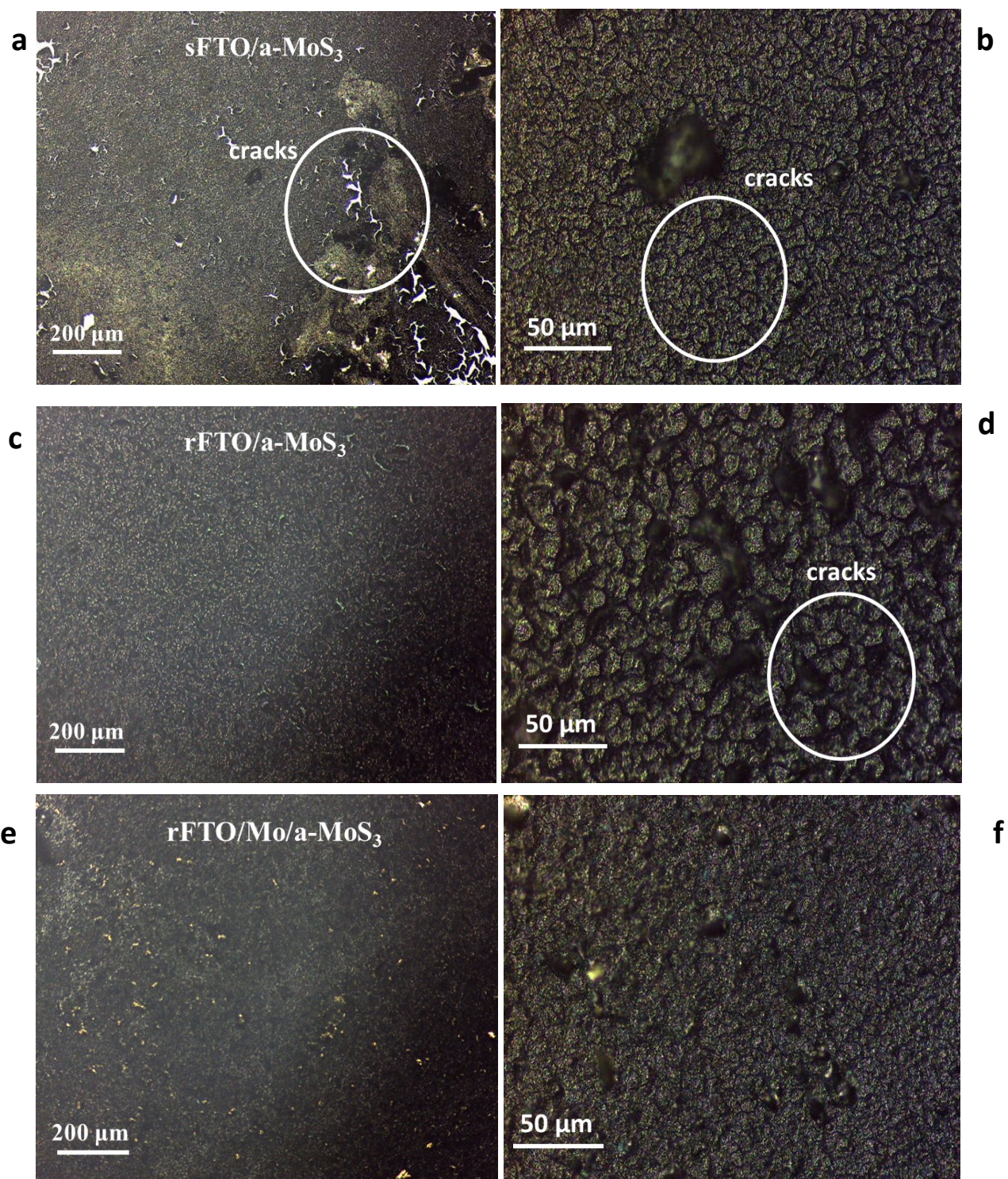
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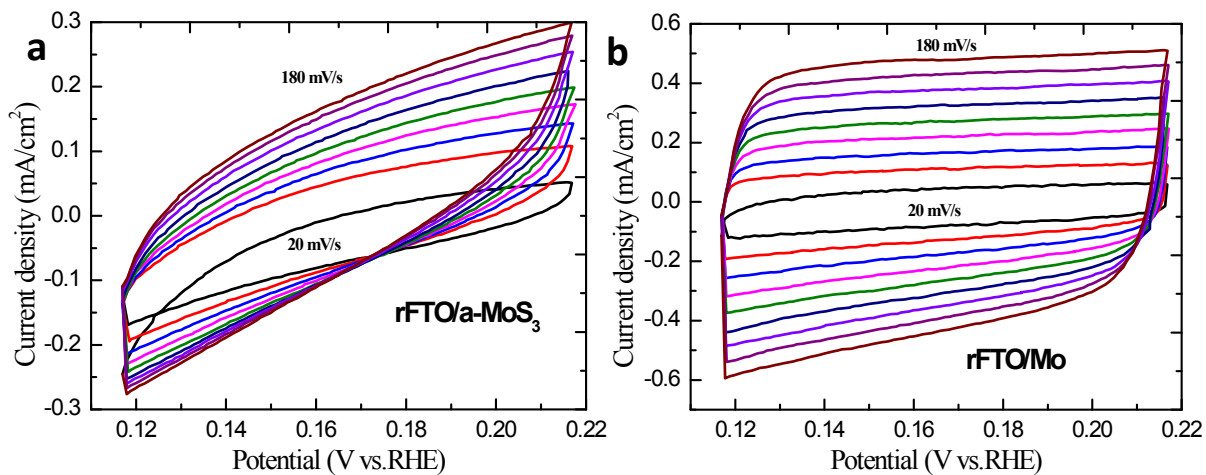
**Fig. S1** (a) Transmission electron micrographs (TEM) of a-MoS<sub>3</sub> catalysts deposited from a diluted catalyst solution after 15 min sonication. The average size of a-MoS<sub>3</sub> nanoparticles is also noted on. (b) X-ray diffraction (XRD) characterization and corresponding schematic diagrams of bare rFTO and rFTO supported a-MoS<sub>3</sub> catalysts. (c,d) X-ray photoelectron spectra (XPS) of the a-MoS<sub>3</sub> catalyst surface and (e) a-MoS<sub>3</sub> catalysts after hydrogen evolution.

The TEM graph for isolated a-MoS<sub>3</sub> NPs in diluted a-MoS<sub>3</sub> suspension is presented in

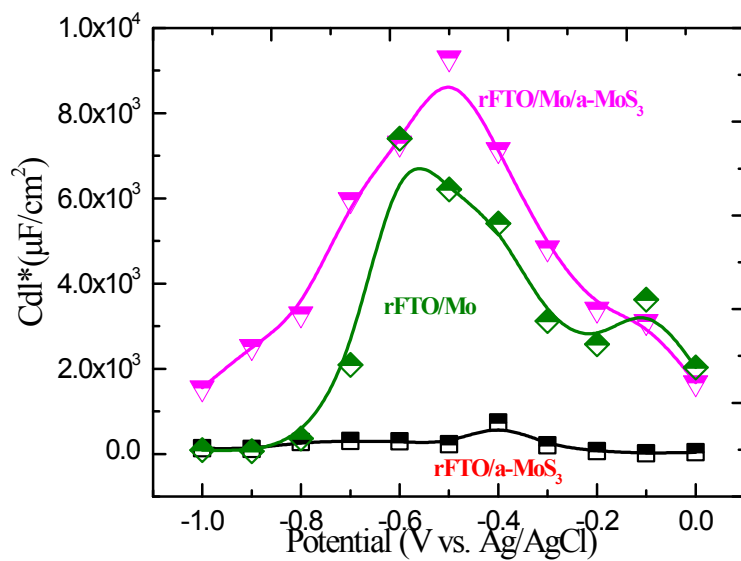
Figure S1a, clearly demonstrating their nanoparticle structure with an average diameter about 60 nm. XRD spectra in Figure S1b further illustrate the amorphous nature of the chemically synthesized a-MoS<sub>3</sub> catalysts. Many defect sites and coordinately unsaturated S atoms, which can absorb H with a small free energy, will expose in amorphous material architecture and promote HER catalytic activity. XPS spectra in Figure S1c,d also illustrate that the synthesized material resembles MoS<sub>3</sub>. The sulfur 2p region shows a peak at a binding energy of 163.5 eV, which is well consistent with the reports on MoS<sub>3</sub> materials containing sulfur in a combination of S<sub>2</sub><sup>2-</sup> and S<sup>2-</sup> groups. Additionally, Mo 3d regions also reveal Mo signals at 231.8 eV and 235.0 eV. There is also no peak shifting after hydrogen evolution, indicating no valance state change from Mo<sup>6+</sup> to Mo<sup>4+</sup>. Consequently, TEM, XPS, and XRD suggest that the chemically synthesized materials are principally composed of amorphous MoS<sub>3</sub> catalysts.



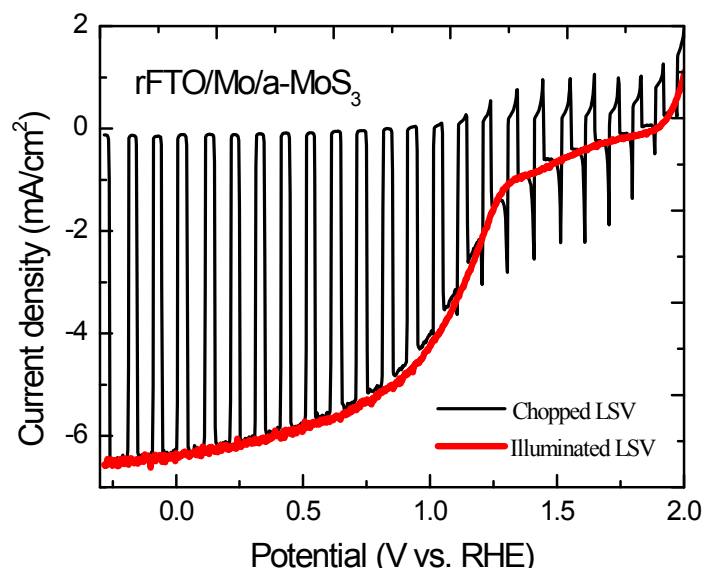
**Fig. S2** Optical microscope images for (a, b) smooth FTO, (c, d) rough FTO (rFTO), and (e, f) rough FTO/Mo supported a-MoS<sub>3</sub> catalysts.



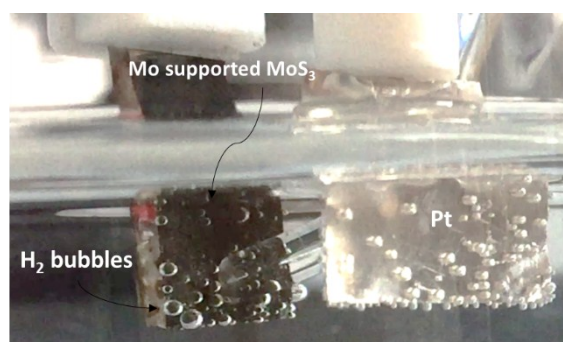
**Fig. S3** Cyclic voltammograms (CVs) for (a) unsupported a-MoS<sub>3</sub> and (b) Mo metal catalysts at various scan rates (20–180 mV/s) used to estimate the  $C_{dl}$  and relative  $S_{as}$  values of the catalysts.



**Fig. S4** Potential dependent double layer capacitance ( $C_{dl}^*$ ) for the catalysts extracted from corresponding EIS spectra.



**Fig. S5** Chopped and illuminated linear sweep voltammogram (LSV) characteristics of the Mo supported a-MoS<sub>3</sub> catalysts in a wired photoelectrochemical (PEC)/PV device for solar water splitting.



**Fig. S6** Image displaying the hydrogen gas production process on photocathodes with Mo supported MoS<sub>3</sub> catalysts in a wired photoelectrochemical (PEC)/PV device for solar water splitting.