## supplementary information for Enhanced Electrocatalytic Activity for Hydrogen Evolution Reaction from Self-Assembled Monodispersed Molybdenum Sulfides nanoparticles on an Au electrode

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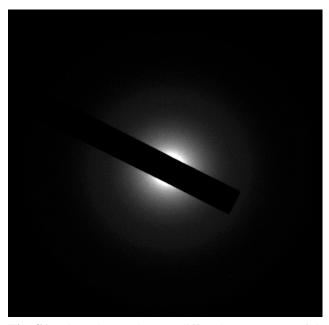


Fig. S1 Selected area electron diffraction spectrum of the molybdenum sulfides nanoparticles.

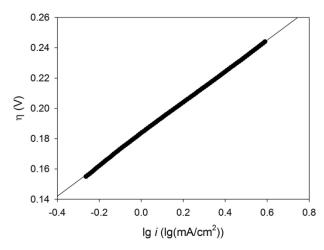


Fig. S2 Tafel plot of the molybdenum sulfides nanoparticle film assembled for two days on Au.

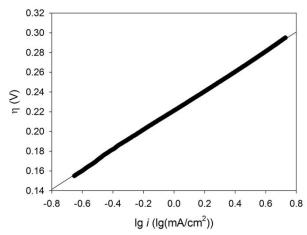
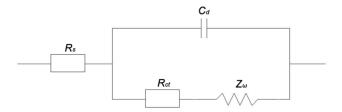


Fig. S3 Tafel plot of the drop-casting molybdenum sulfides nanoparticle film on Au.



**Fig. S4** Electrical equivalent circuit for the simulation of all the films investigated by electrochemical impedance spectroscopy.  $R_s$  represents the solution resistance,  $C_d$  represents the capacitance of the double layer,  $R_{ct}$  represents the charge transfer resistance,  $Z_{\omega}$  represents the mass transport resistance. When a reversible redox probe  $K_3Fe(CN)_6/K_4Fe(CN)_6$  was used in the test, the fitting result of  $R_{ct}$  would be used to judge the conductivity of the modified film.

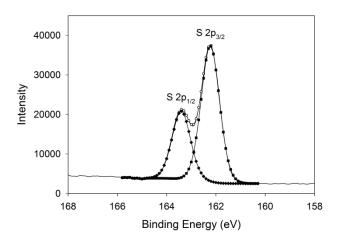


Fig. S5 XPS spectrum of S 2p region for the bulk  $MoS_2$ .

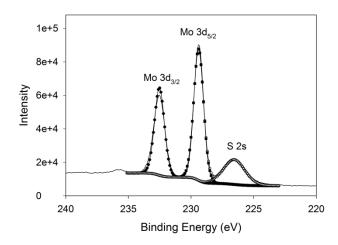


Fig. S6 XPS spectrum of Mo 3d region for the bulk  $MoS_2$ .

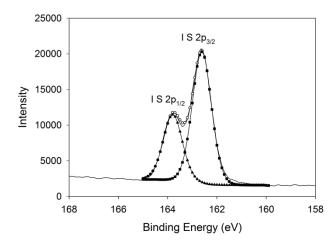


Fig. S7 XPS spectrum of S 2p region for the as-prepared molybdenum sulfides nanoparticles.

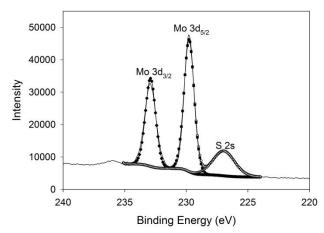
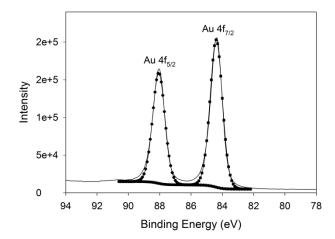
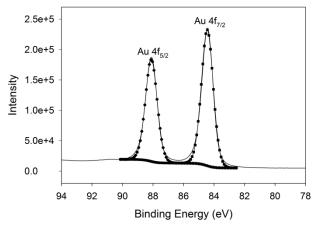


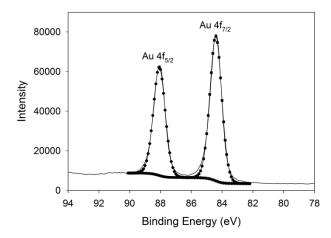
Fig. S8 XPS spectrum of Mo 3d region for the as-prepared molybdenum sulfides nanoparticles.



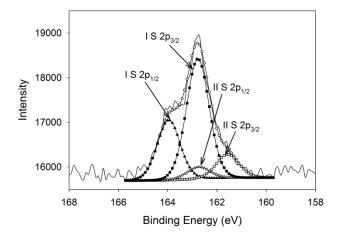
**Fig. S9** XPS spectrum of Au 4f region for molybdenum sulfides nanoparticle film assembled for 1 h on Au.



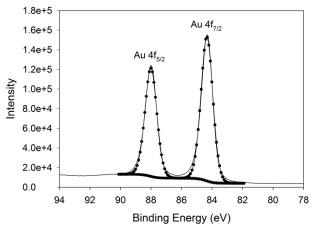
**Fig. S10** XPS spectrum of Au 4f region for molybdenum sulfides nanoparticle film assembled overnight on Au.



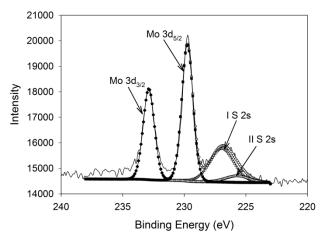
 $\textbf{Fig. S11} \ \text{XPS} \ \text{spectrum of Au 4f region for molybdenum sulfides nanoparticle film assembled for two days on Au.}$ 



 $\textbf{Fig. S12} \ \text{XPS spectrum of S 2p region for drop-casting molybdenum sulfides nanoparticle film on } Au.$ 



**Fig. S13** XPS spectrum of Au 4f region for drop-casting molybdenum sulfides nanoparticle film on Au.



**Fig. S14** XPS spectrum of Mo 3d region for drop-casting molybdenum sulfides nanoparticle film on Au.

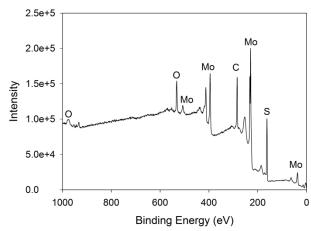


Fig. S15 XPS survey spectrum for the bulk  $MoS_2$ .

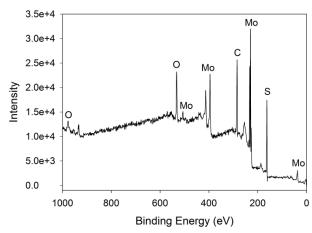
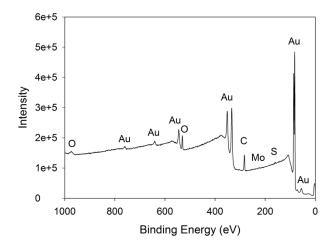
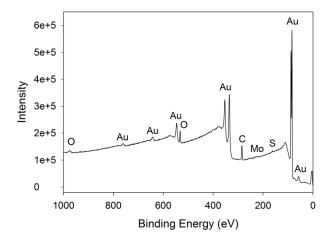


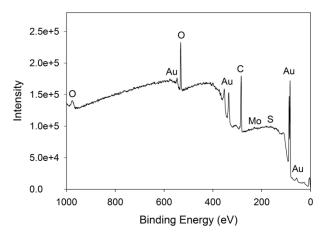
Fig. S16 XPS survey spectrum for the as-prepared molybdenum sulfides nanoparticles.



 $\textbf{Fig. S17} \ XPS \ survey \ spectrum \ for \ molybdenum \ sulfides \ nanoparticle \ film \ assembled \ for \ 1 \ h \ on \ Au.$ 



 $\textbf{Fig. S18} \ \text{XPS} \ \text{survey spectrum for molybdenum sulfides nanoparticle film assembled overnight on} \ Au.$ 



**Fig. S19** XPS survey spectrum for molybdenum sulfides nanoparticle film assembled for two days on Au.

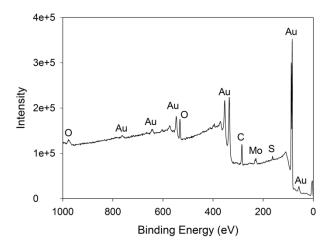


Fig. S20 XPS survey spectrum for drop-casting molybdenum sulfides nanoparticle film on Au.

The loading of the nanoparticles during assembling was studied by quartz crystal microbalance (QCM). Sauerbrey equation shows that the mass increase on the quartz is in direct proportion to the decrease of the quartz frequency:

$$\Delta f = -2f_0^2 (\rho_0 \mu_0)^{-1/2} (\Delta m/A)$$

where  $f_0$  is the internal frequency of the quartz (8×10<sup>6</sup> Hz in this system),  $\rho_q$  represents the density of the quartz (2.684 g cm<sup>-3</sup> in this system),  $\mu_q$  represents the shear modulus of the quartz (2.947×10<sup>11</sup> g cm<sup>-1</sup> s<sup>-2</sup> in this system).  $\Delta f$  is the frequency change after assembly,  $\Delta m$  is the mass change after assembly and A is the surface area of the electrode. By detecting  $\Delta f$ , the loading is calculated.