SUPPLEMENTARY INFORMATION FOR

Molybdenum Disulfide and Au Ultrasmall Nanohybrids as Highly Active Electrocatalysts for Hydrogen Evolution Reaction

Jinxuan Zhang, Tanyuan Wang, Lu Liu, Kuangzhou Du, Wanglian Liu, Zhiwei Zhu, and Meixian Li*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P.R.China
**Fig. S1** Optical graphs of (a) MoS$_2$-Au nanohybrids aqueous solution and (b) AuNCs solution.

**Fig. S2** Size distribution of MoS$_2$-Au nanohybrids measured by analyzing 141 nanoparticles from TEM image.
**Fig. S3** The experimental and theoretical volumes of H$_2$ that evolved from the working electrode.

**Fig. S4** XRD pattern of the AuNCs films on carbon fibre paper. (The symbols * represent the XRD patterns of carbon fibre paper)
**Fig. S5** Cyclic voltammograms of blank carbon fibre paper at various scan rates in 0.5 M H₂SO₄.

**Fig. S6** Cyclic voltammograms of MoS₂-Au nanohybrids modified carbon fibre paper at various scan rates in 0.5 M H₂SO₄.
**Fig. S7** XPS survey spectrum of MoS$_2$-Au nanohybrids.

**Fig. S8** XPS spectrum of Au 4f region for AuNCs
Fig. S9 XPS spectrum of S 2p region for MoS$_2$ nanoparticles.

Fig. S10 XPS spectrum of Mo 3d region for MoS$_2$-Au nanohybrids.
**Fig. S11** XPS spectrum of Mo 3d region for MoS$_2$ nanoparticles.

**Fig. S12** Normalized Au L3 edge XANES spectra of MoS$_2$-Au nanohybrids and Au foil.
Fig. S13 FT-EXAFS of Au foil in R space.

Fig. S14 FT-EXAFS of MoS$_2$-Au nanohybrids in R space.
**Fig. S15** Electrochemical impedance spectra of MoS$_2$-Au nanohybrids, MoS$_2$ nanoparticles and AuNCs modified electrode in 0.1 M KCl–0.01 M phosphate buffer solution (pH = 7.4) containing 2.5 mM K$_3$Fe(CN)$_6$ and 2.5 mM K$_4$Fe(CN)$_6$.

**Fig. S16** SEM images of carbon fibre paper modified with MoS$_2$-Au nanohybrids after electrolysis for 12 h at -0.070 V vs. RHE.