## **Supporting Information**

## Colloidal Preparation and Electrocatalytic Hydrogen Production of MoS<sub>2</sub> and WS<sub>2</sub> Nanosheets with Controllable Lateral Sizes and Layer Numbers

Miao Zhou,<sup>†#</sup> Zhuolei Zhang,<sup>†#</sup> Keke Huang,<sup>‡</sup> Zhan Shi,<sup>‡</sup> Renguo Xie,<sup>†,\*</sup> and

Wensheng Yang<sup>†</sup>

† College of Chemistry, Jilin University, Changchun 130012, China

\$State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin

University, Changchun 130012, China

<sup>#</sup>The authors contributed equally.

E-mail: renguoxie@jlu.edu.cn



Figure S1. Photos of the reaction solution in the three-neck flask at different stages of reaction: (a) at roome temperature; (b) after heating to  $320 \text{ }^{\circ}\text{C}$ ; (c) upon injection of sulfur solution at  $300 \text{ }^{\circ}\text{C}$  in a reaction time of 30 s.



**Figure S2.** Low-magnification TEM images of single-layered  $MoS_2$  nanosheets synthesized at 330 °C with Mo:S precursor ratios 1:3 with the lateral size of 40 nm, marking the standing edges of monolayers with blue orthogon, and highlighting the several top-view of the nanosheets with yellow circle. Insets: High-resolution TEM image of monolayer  $MoS_2$  nanosheets; scale bars are 2 nm.



Figure S3: X-ray photoelectron spectroscopy of single layered  $MoS_2$  nanosheets for the Mo3d core level peaks (a), and S2p core level peaks (b).



Figure S4. Low-magnification TEM images of 3 layered  $MoS_2$  nanosheets in Figure 3a.



**Figure S5.** Low-magnification TEM images of 5 layered  $MoS_2$  nanosheets in Figure 3b.



**Figure S6.** Low-magnification TEM images of 3 layered  $WS_2$  nanosheets in Figure 7b.



Figure S7. (a) Low-magnification TEM image of 5 layered  $WS_2$  nanosheets synthesized at 370 °C by hot injection. (b) HR-TEM image of 5 layered  $WS_2$  nanosheets with the thickness of 3.6 nm.



**Figure S8:** X-ray photoelectron spectroscopy of single layered  $WS_2$  nanosheets for the W4f core level peaks (a), and S2p core level peaks (b).



**Figure S9.** (a) Frequencies of  $E_{2g}^1$  and  $A_{2g}$  Raman modes as a function of the number of layers in Figure 8a. (b) Absorption peak energies of  $WS_2$  sheets as a function of the number of layers. The letters A, B and C refer to the peaks in Figure 8b.



**Figure S10.** X-ray diffraction patterns of the MoS<sub>2</sub> and WS<sub>2</sub> monolayer nanosheets annealing at 700 °C corresponded to black line and red line, respectively.



**Figure S11.** Raman spectra of (a) MoS<sub>2</sub> and (b) WS<sub>2</sub> monolayer nanosheets before (black line) and after (red line) annealing at 700 °C for 2h.



**Figure S12.** SEM image of monolayer (a)  $MoS_2$  and (b)  $WS_2$  nanosheets after annealing at 700 °C for 2h.



Figure S13. Polarization curves of (a)  $MoS_2$  nanosheets and (b)  $WS_2$  nanosheets in 0.5 M H<sub>2</sub>SO<sub>4</sub> initially (black) and after annealing at various of temperatures: 500 °C (red), 600 °C (blue), 700 °C (dark cyan), and 800 °C (magenta).



**Figure S14.** Polarization curves of (a)  $MoS_2$  nanosheets and (b)  $WS_2$  nanosheets in 0.5 M H<sub>2</sub>SO<sub>4</sub> initially (solid line) and after 500 CV sweeps between +0.22 and -0.23 V vs RHE (dash line).