**Supporting information** 

## Sulfur Vacancy Induced High Performance of Photocatalytic H<sub>2</sub> Production over 1T@2H Phase MoS<sub>2</sub> Nanolayers

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**Figure S1**. (a) UV-vis spectra and (b) valence band of  $MoS_2(NMoS200)$  and  $MoS_2(NaMo200)$ As shown in Figure S1a, both  $MoS_2(NMoS200)$  and  $MoS_2(NaMo200)$  showed a typical absorption peak at ~600 nm, which was associate with the energy split from valence spin-orbital coupling in  $MoS_2$  with large dimensions. In addition, another absorption band at ~400 nm was observed. The

presence of this band was most likely due to the quantum effect of small lateral-sized MoS<sub>2</sub> nanosheets (Geng et al., Nature Communications 2016, 7:10672). It should be noted that 2H-phase MoS<sub>2</sub> structure generally has two characteristic peaks (A- and B-exciton) via direct transition located between 600 nm and 700 nm (Hai et al., J. Mater. Chem. A, 2017, 5, 8591-8598; Ren et al., J. Phys. D: Appl. Phys. 49 (2016) 315304). However, the A-exciton peak at 700 nm didn't appeared on the two samples, probably resulted from its metallic property (appearance of partial 1T-phase). On the other hand, MoS<sub>2</sub>(NMoS200) showed a red-shift on adsorption peaks of 447 nm and 627 nm compared to MoS<sub>2</sub>(NaMo200) (405 nm and 600 nm). As revealed by Visic et al., (J. Phys. D: Appl. Phys. 49 (2016) 315304), the quantum confinement effect could lead to the red shift of adsorption peak on MoS<sub>2</sub>, because the position of exciton peak is largely dependent on the number of layers and particle size (Frey et al., J. Mater. Res., 1998, 13, 2412). In this work MoS<sub>2</sub>(NMoS200) had smaller particle size and similar number of layers compared with MoS<sub>2</sub>(NaMo200). Hence these two factors could be ruled out for the red-shift. Instead, MoS<sub>2</sub>(NMoS200) was rich in sulfur vacancy and showed low crystallization, which induced structural disorder on the electric structure and density of states. This could contribute to the read shift of absorption peaks. Hai et al., also observed that structural disorder induced the extension of absorption tail in the near-IR region (Hai et al., J. Mater. Chem. A, 2017, 5, 8591-8598).

In the UV region (200 nm – 380 nm), both samples showed very similar capability for light absorption. Since  $MoS_2(NaMo200)$  and  $MoS_2(NMoS200)$  had no photo-activity under visible light, the light absorption is not a key factor to determine the activity difference between them.

As revealed from UV-vis spectra, the absorption band edges of  $MoS_2(NMoS200)$  and  $MoS_2(NaMo200)$  were ~733 nm and ~703 nm, respectively, corresponding to band gap of ~1.69 eV and ~1.76 eV. The valence band maximum (VBM) of  $MoS_2$  has been measured by XPS, as shown in Figure S1b.  $MoS_2(NMoS200)$  and  $MoS_2(NaMo200)$  had VBM of ~0.18 eV and ~0.09 eV. Since  $MoS_2(NMoS200)$  had more positive VBM and slightly smaller band gap, it indicated that  $MoS_2(NaMo200)$  had a higher conduction band minimum (CBM) (more negative) in contrast to  $MoS_2(NMoS200)$ . By correlating the photocatalytic activity, it looks the energy gap structure of  $MoS_2(NaMo200)$  could be more favorable for  $H_2$  production. However,  $MoS_2(NMoS200)$  showed higher  $H_2$  product rate than  $MoS_2(NaMo200)$ . This unexpected trend indicated that the 1T@2H phase junction and sulfur vacancy in  $MoS_2$  predominated the photocatalytic activity rather than light absorption and energy gap.



Figure S2. SEM and TEM/HRTEM images for  $MoS_2(NMoS200)$  after 20 cycles for  $H_2$  production