# Supporting Information

## Tailoring the Nonlinear Optical Performances of Two-dimensional $MoS_2$ Nanofilms via Defect Engineering

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**Modification of Substrates.** Typically, the substrate was sequentially sonicated in ethanol, acetone, and deionized water with each for 15 min. Then the cleaned substrate was immersed in diluted Poly(diallyldimethylammonium chloride) (PDDA, 20 wt%) aqueous solution (Volume ratio of PDDA to deionized water as 1:4) for 30 min to allow PDDA adsorption, and then rinsed with deionized water and dried in an oven. Next, the PDDA-coated substrate was dipped in diluted Poly(sodium 4-styrenesulfonate) (PSS, 30 wt%) aqueous solution (Volume ratio of PSS to deionized water as 1:4) to allow the deposition of PSS in the same manner, followed by the deposition of an additional layer of PDDA. Finally, three-layered PDDA/PSS/PDDA polyelectrolytes were formed on the quartz substrate.

**Calculation of the Formation Energy of the S Vacancies.** We used the first-principles calculations to analysis the formation energy of the S vacancies. Before the calculation, the 2H $MoS_2$ with hexagonal structure was fully optimized using BFGS method. The exchange–correlation interaction between valence electrons was described using the Perdew-Burke-Ernzerhof (PBE) function within the generalized gradient approximation (GGA). [1,2] The cutoff energy, the maximum atom force, the intrinsic strain and the maximum shift were set as 450 eV, 0.01 eV/Å, 0.02 GPa, and $5 \times 10^{-4}$ Å, respectively. The k-point meshes were set as 8×8×2 in the Reduced Brillouin zone. Based on the optimized structure, a Slab model with the vacuum layer of 15 Å was constructed to simulate the crystal surface. A 3×3×1 hexagonal supercell was used to calculated the S vacancies in $MoS_2$. The calculation parameters are the same to the first step except that the k-point meshes here were chosen as 5×5×1.

The S vacancy formation energy $\Delta E_f$ is defined by [3]:

$$\Delta E_f = E_{VS} - E_{bulk} + (\mu_s + \Delta\mu_S)$$

Where $E_{VS}$ and $E_{bulk}$ are the total energies of S-vacancy containing and defect-free supercells, respectively, and $\Delta\mu_S$ is the chemical potential of the atom S. Here, the up limitation is set as

$\Delta\mu_S$ = 0 eV, corresbonding to the S-rich (O-poor) limit, and the down limitation is set as $\Delta\mu_S$ = -3.74 eV, corresbonding to the S-poor (O-rich) limit.

**Figure S1**

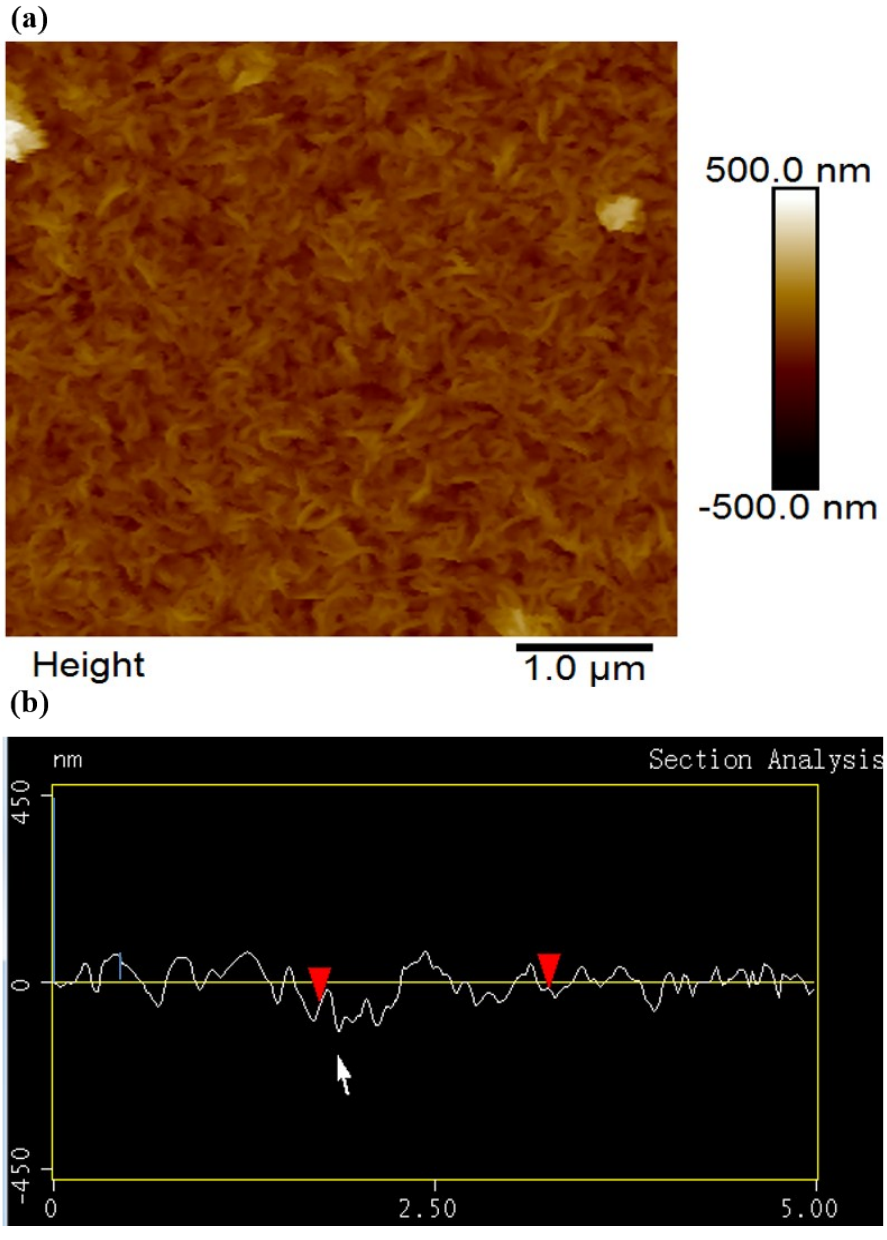


**Fig. S1 Morphology of the hierarchical $MoS_2$ nanofilms.** (a) AFM image of the thin films annealed in nitrogen at 250 °C for 12 h, which shows a typical hierarchical morphplogy. (b) Roughness of the thin films, which shows an average roughness of ~20 nm.

**Figure S2**

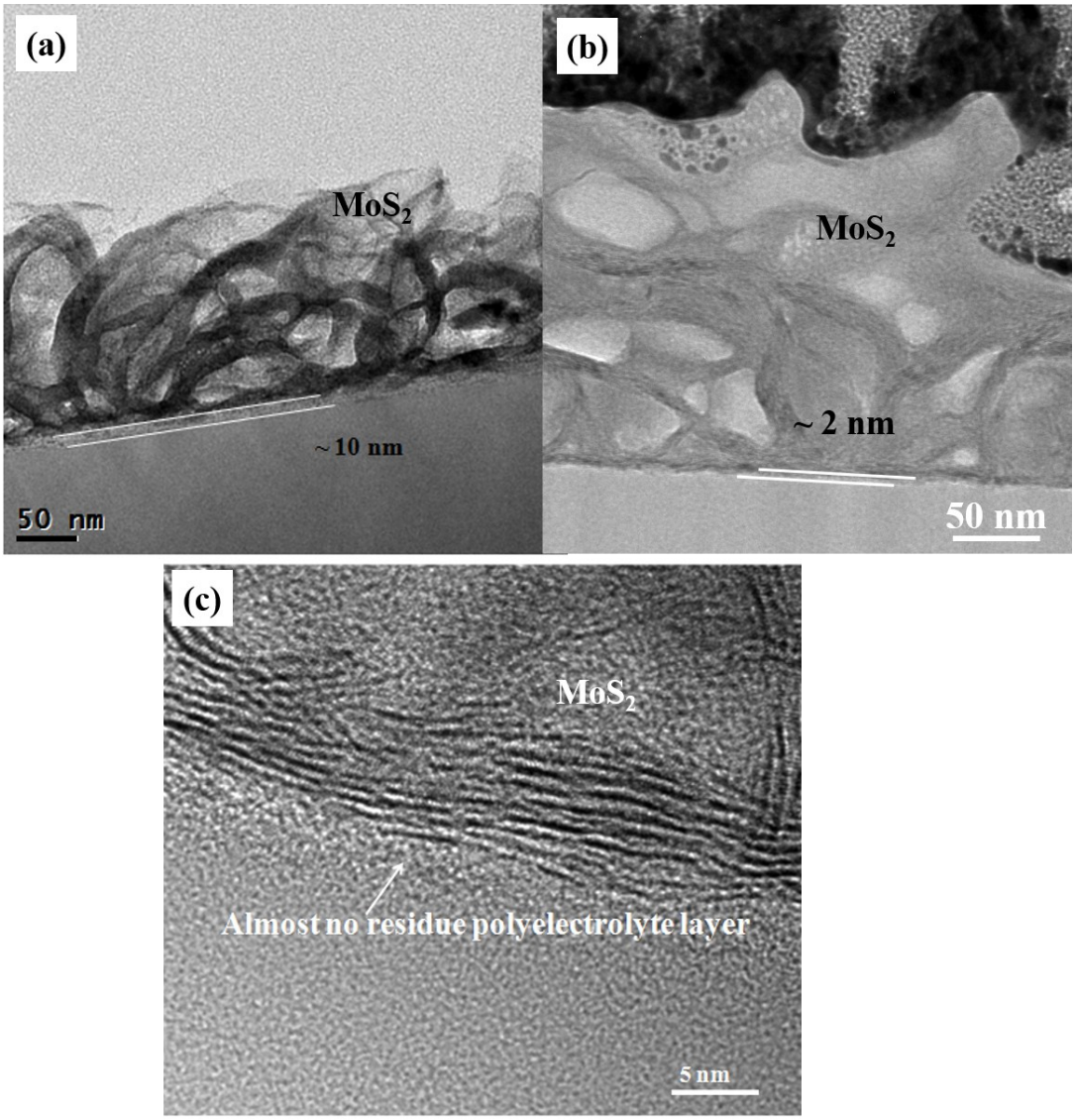


**Fig. S2 Typical cross-sectional TEM images of the $MoS_2$ nanofilms annealed at 250 °C in nitrogen atmosphere for different times.** The thickness of the polyelectrolyte layer decreases from (a) ~10 nm for sample annealed for 0 h to (b) ~ 2 nm for sample annealed for 24 h and (c) almost no residue polyelectrolyte observed for sample annealed for 36 h.

**Figure S3**

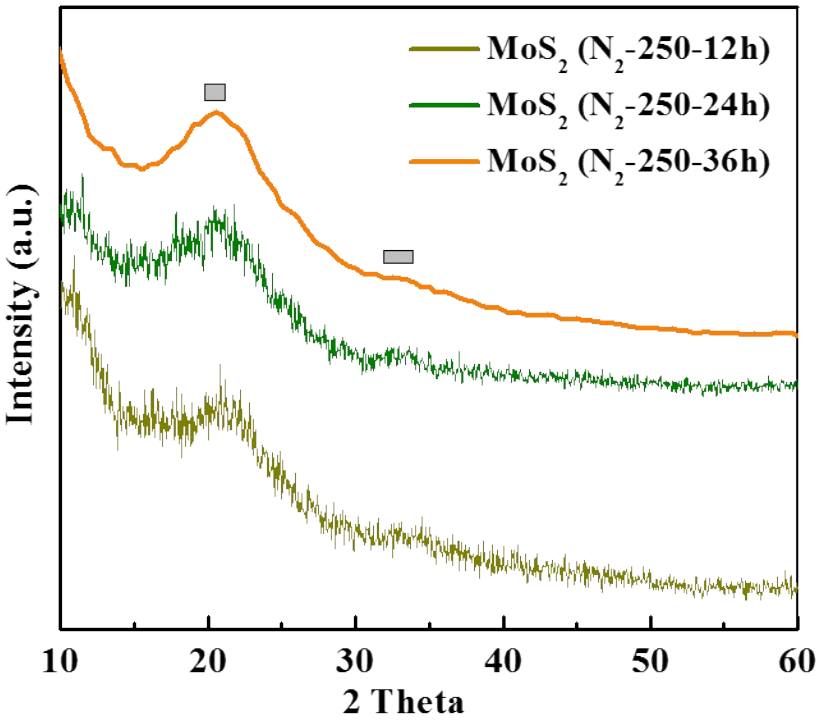


**Fig. S3 XRD patterns of the $MoS_2$ nanofilms annealed at 250 °C under $N_2$ atmosphere for different annealing times.** The diffraction peak from (002) plane of 2H $MoS_2$ is absent, suggesting the stacking of $MoS_2$ layers is not obvious. The diffraction peak at ~20.7 º is from the quartz substrate, and the weak peak at ~33.1 º can be ascribed to the (100) plane of 2H $MoS_2$. The XRD results demonstrate that the obtained $MoS_2$ has low crystallinity. [4,5]

**Figure S4**

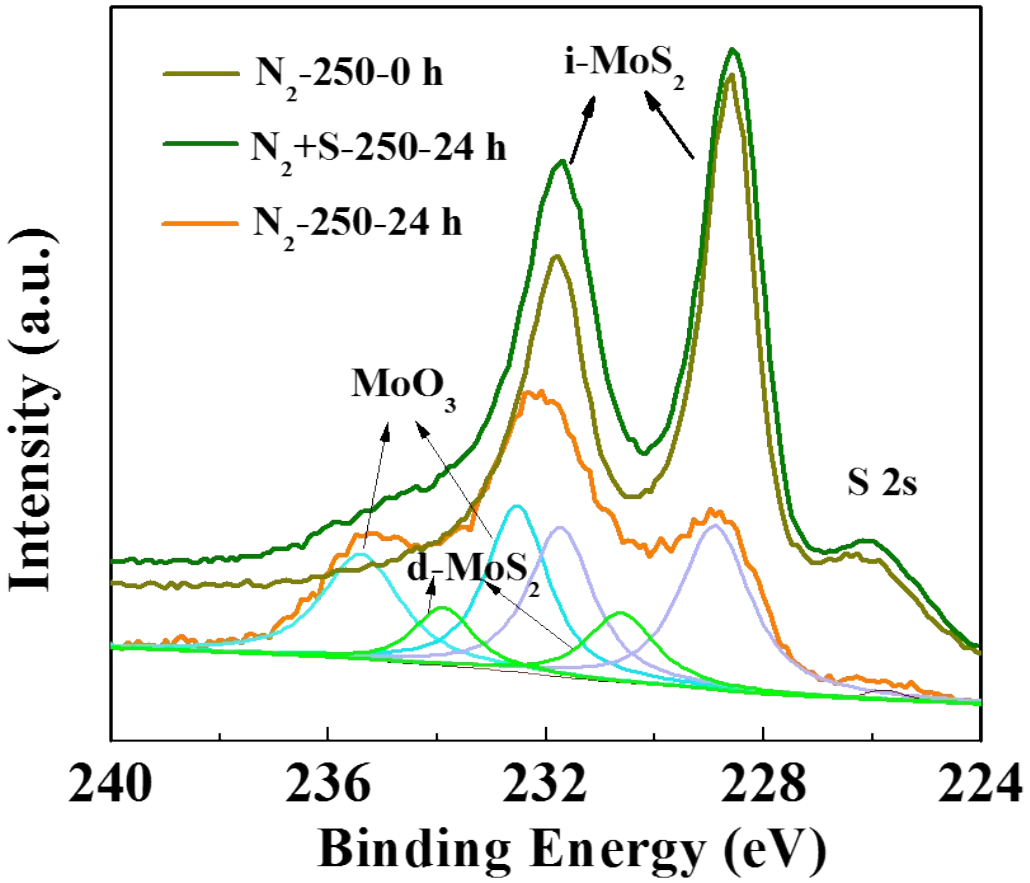


**Fig. S4 XPS spectra of the $MoS_2$ nanofilms obtained under different conditions.** i-$MoS_2$ means intrinsic $MoS_2$; d-$MoS_2$ means defective $MoS_2$, which is directly associated with S vacancies. $MoS_2$ ($N_2$-250-0 h) means the as-prepared $MoS_2$ nanofilms without any annealing treatment, which has few S vacancies; $MoS_2$ ($N_2$-250-24 h) means the $MoS_2$ nanofilms obtained after annealing in nitrogen atmosphere at 250°C for 24 h, which has S vacancies and $MoO_3$; $MoS_2$ ($N_2$+S-250-24 h) means the $MoS_2$ nanofilms obtained after annealing in sulfur-enriched nitrogen atmosphere at 250°C for 24 h, which is the same to that of $MoS_2$ ($N_2$-250-0 h) with few S vacancies and $MoO_3$.

**Figure S5**

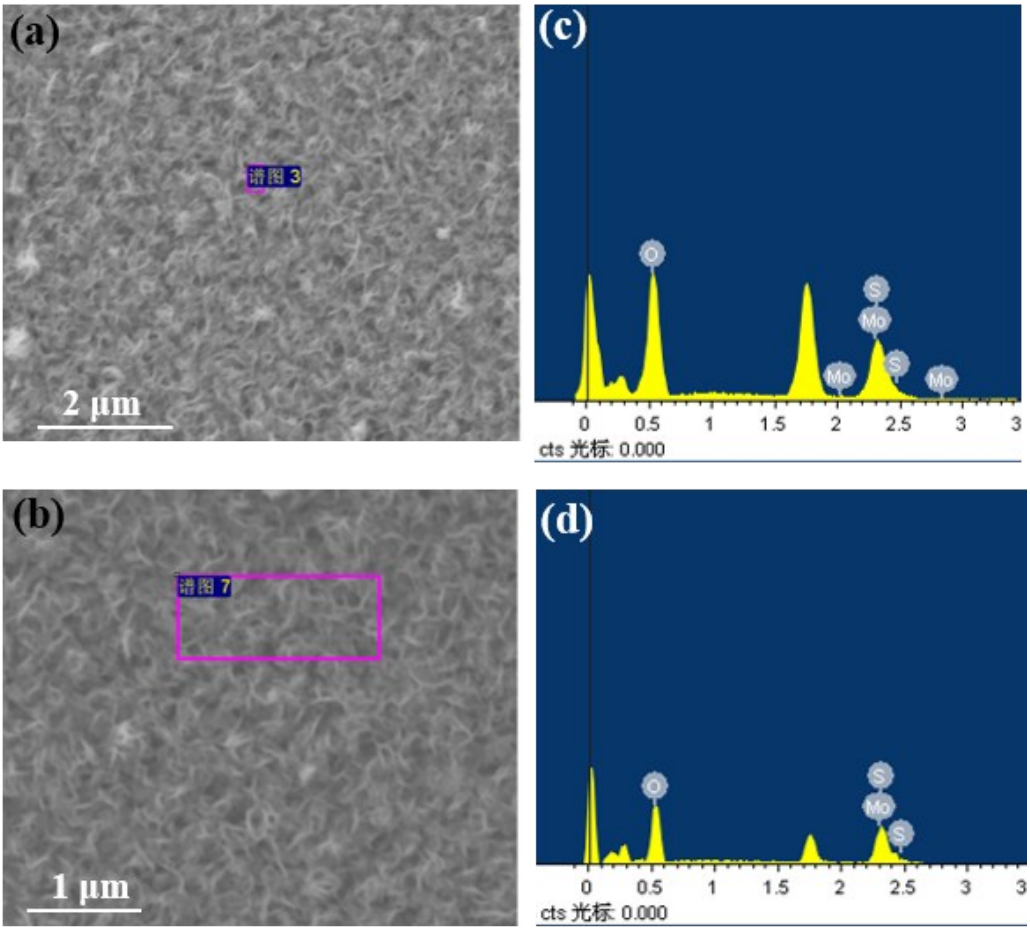


**Fig. S5 Elemental compositions of the $MoS_2$ nanofilms.** (a,b) Scanning electron microscopy (SEM) images and (c,d) elemental Energy Dispersive Spectrometer (EDS) results of the fabricated $MoS_2$ nanofilms annealed in nitrogen atmosphere at 250 °C for 12 h and 36 h, respectively. The results demonstrate that the samples are composed of $MoS_2$ with the atomic ratio of Mo and S almost 1:2.

**Figure S6**

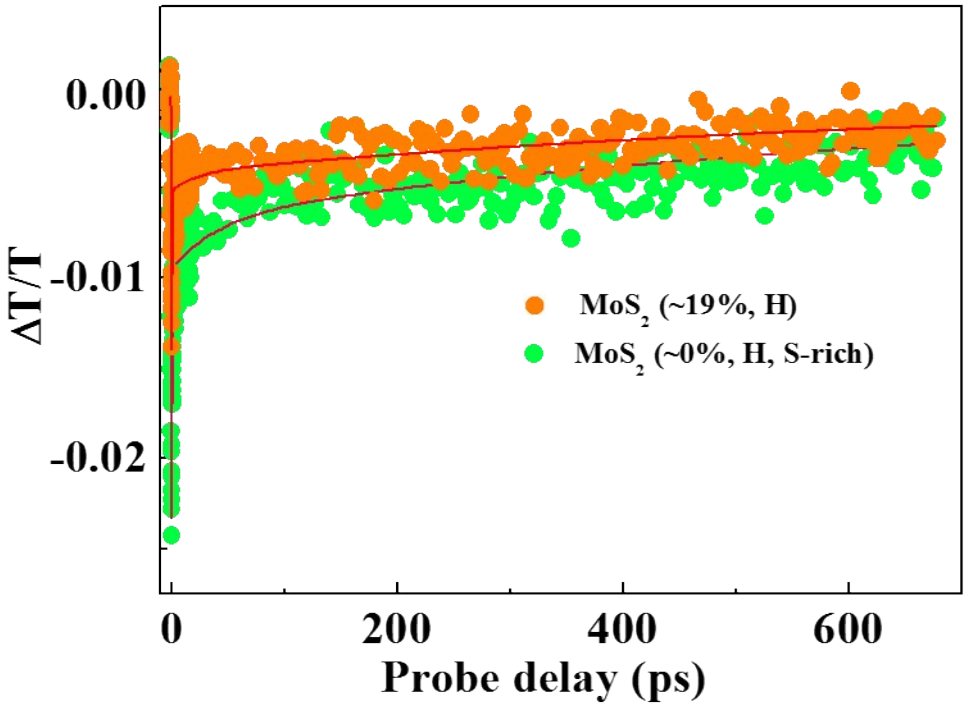


**Fig. S6 Pump-probe results of the $MoS_2$ nanofilms with different S vacancies but the same crystallinity.** $MoS_2$ (~19%, H) is the sample with the calculated atomic ratio of the S vacancies ~19% and increased crystallinity which is annealed in nitrogen atmosphere; $MoS_2$ (~0%, H, S-rich) is the sample with increased crystallinity but almost no S vacancies which is annealed in S-enriched nitrogen atmosphere. The pulse intensity is ~16.3 GW $cm^{-2}$.

**Table S1** Linear and NLO parameters of $MoS_2$ nanofilms with different S vacancies measured using the open-aperture Z-scan technique (Beam waist ~ 26.0 μm).

| Sample | T (%) | $\alpha_0$ (cm$^{-1}$) (*10$^4$) | $L$ (cm) (*10$^{-7}$) | $\beta_{eff}$ (cm GW$^{-1}$) (*10$^2$) | $I_{sat}$ (GW cm$^{-2}$) | Im$\chi^{(3)}$ (esu) (*10$^{-9}$) | Damage threshold (GW cm$^{-2}$) |
|---|---|---|---|---|---|---|---|
| $MoS_2$(~0%, L) | 30.9 | (3.9±0.2) | (300±20) | (0.8±0.1) | / | 0.5±0.1 | 32.6±2.7 |
| $MoS_2$(~15%, H) | 40.2 | (3.2±0.3) | (280±20) | (4.3±0.5) | 65±5 | 2.7±0.3 | 44.5±2.7 |
| $MoS_2$(~19%, H) | 51.3 | (3.3±0.2) | (200±20) | (3.4±0.3) | 70±5 | 2.2±0.2 | 74.1±3.5 |
| $MoS_2$(~21%, H) | 60.7 | (3.1±0.2) | 160±20 | / | 48±5 | / | 72.1±3.5 |

**Table S2** Parameters obtained from the fitting of Pump−Probe traces with the pulse intensity as 16.3 GW cm$^{-2}$.

| Sample | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (ps) |
|---|---|---|---|
| $MoS_2$(~0%, L) | 0.28±0.03 | 20±2 | 610±60 |
| $MoS_2$(~15%, H) | 0.28±0.03 | 30±5 | 600±50 |
| $MoS_2$(~19%, H) | 0.28±0.03 | 35±5 | 620±60 |
| $MoS_2$(~21%, H) | 0.30±0.03 | 35±5 | 600±50 |
| $MoS_2$(~0, H, S-rich) | 0.30±0.03 | 40±5 | 610±60 |

**References**


1 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett* 1996, **77**, 3865.

2 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys* 2003, **118**, 8207-8215.

3 M. X. Liu, J. P. Shi, Y. C. Li, X. B. Zhou, D. L. Ma, Y. Qi, Y. F. Zhang and Z. F. Liu, *Small* 2017, **13**(40), 1602967.

4 L. Ma, X.P. Zhou, X.Y. Xu, L.M. Xu, L.L. Zhang and W.X. Chen, *Advanced Powder Technology* 2015, **26**, 1273-1280.

5 H. S. S. R. Matte, A. Gomathi, A. K. Manna, D. J. Late, R. Datta, S. K. Pati and C. N. R. Rao, *Angew. Chem. Int. Ed*. 2010, **49**, 4059-4062.