Supporting Information

Tailoring the Nonlinear Optical Performances of Two-dimensional MoS₂ 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). 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 $8 \times 8 \times 2$ 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 $3 \times 3 \times 1$ 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 $5 \times 5 \times 1$.

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

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

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
Δμ_S = 0 eV, corresponding to the S-rich (O-poor) limit, and the down limitation is set as Δμ_S = -3.74 eV, corresponding 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 morphology. (b) Roughness of the thin films, which shows an average roughness of ~20 nm.
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.
Fig. S3 XRD patterns of the MoS\textsubscript{2} nanofilms annealed at 250 °C under N\textsubscript{2} atmosphere for different annealing times. The diffraction peak from (002) plane of 2H MoS\textsubscript{2} is absent, suggesting the stacking of MoS\textsubscript{2} layers is not obvious. The diffraction peak at ≈20.7 ° is from the quartz substrate, and the weak peak at ≈33.1 ° can be ascribed to the (100) plane of 2H MoS\textsubscript{2}. The XRD results demonstrate that the obtained MoS\textsubscript{2} has low crystallinity.\textsuperscript{4,5}
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$_3$. 
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.
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$^{-2}$. 

Figure S6

![Graph showing pump-probe results of MoS$_2$ nanofilms with different S vacancies but the same crystallinity. The graph includes two samples: MoS$_2$ (~19%, H) and MoS$_2$ (~0%, H, S-rich). The pulse intensity is ~16.3 GW cm$^{-2}$.](image)
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).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (%)</th>
<th>$a_0$ (cm$^{-1}$)</th>
<th>$L$ (cm)</th>
<th>$\beta_{\text{eff}}$ (cm GW$^{-1}$)</th>
<th>$I_{\text{sat}}$ (GW cm$^{-2}$)</th>
<th>Imχ$^{(3)}$ (esu)</th>
<th>Damage threshold (GW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$ (~0%, L)</td>
<td>30.9</td>
<td>(3.9±0.2)</td>
<td>(300±20)</td>
<td>(0.8±0.1)</td>
<td>/</td>
<td>0.5±0.1</td>
<td>32.6±2.7</td>
</tr>
<tr>
<td>MoS$_2$ (~15%, H)</td>
<td>40.2</td>
<td>(3.2±0.3)</td>
<td>(280±20)</td>
<td>(4.3±0.5)</td>
<td>65±5</td>
<td>2.7±0.3</td>
<td>44.5±2.7</td>
</tr>
<tr>
<td>MoS$_2$ (~19%, H)</td>
<td>51.3</td>
<td>(3.3±0.2)</td>
<td>(200±20)</td>
<td>(3.4±0.3)</td>
<td>70±5</td>
<td>2.2±0.2</td>
<td>74.1±3.5</td>
</tr>
<tr>
<td>MoS$_2$ (~21%, H)</td>
<td>60.7</td>
<td>(3.1±0.2)</td>
<td>160±20</td>
<td>/</td>
<td>48±5</td>
<td>/</td>
<td>72.1±3.5</td>
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</table>

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS$_2$ (~0%, L)</td>
<td>0.28±0.03</td>
<td>20±2</td>
<td>610±60</td>
</tr>
<tr>
<td>MoS$_2$ (~15%, H)</td>
<td>0.28±0.03</td>
<td>30±5</td>
<td>600±50</td>
</tr>
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<td>MoS$_2$ (~19%, H)</td>
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</tr>
<tr>
<td>MoS$_2$ (~0, H, S-rich)</td>
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<td>40±5</td>
<td>610±60</td>
</tr>
</tbody>
</table>
References


