Electronic Supplementary Information for

Thinning of \( n \)-layer MoS\(_2 \) by annealing palladium film in vacuum

Ya Deng,\(^{a,b} \) Minjiang Chen,\(^{a,b} \) Jian Zhang,\(^{a,b} \) Xiao Hu,\(^{a,b} \) Yun Zhao,\(^{a} \) Jean Pierre Nshimiyimana,\(^{a,b} \) Xiannian Chi,\(^{a,b} \) Gu Hou,\(^{a,b} \) Weiguo Chu*\(^{a} \) and Lianfeng Sun*\(^{a} \)

\(^{a} \) CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Centre for Nanoscience and Technology, Beijing 100190, China.

\(^{b} \) University of Chinese Academy of Sciences, Beijing 100049, China

Corresponding author email: wgchu@nanoctr.cn, slf@nanoctr.cn

1. Experimental details

The micromechanical cleavage method was used to prepare the \( n \)-layer molybdenum disulfide. First, the Scotch transparent tape 600 (3M) was used to exfoliate MoS\(_2 \) sheets from the molybdenum disulfide single crystals (SPI). Then, the MoS\(_2 \) sheets are transferred to a Si substrate with a 300 nm layer of thermally grown SiO\(_2 \). The optical microscope (Leica DM4000) was used to locate the position of the MoS\(_2 \) sheet and estimate its layer number based on the color contrast. The Raman spectroscopy (Renishaw in Via Raman Spectroscope) has been used to confirm the layer number accurately. The micro-Raman spectroscopy experiments were performed with 514 nm excitation in ambient conditions. To avoid laser induced heating, the laser power was set to \(~1.0\) mW and the size of the spot is about 1 \( \mu \)m.
The Pd (Alfa Aesar, 99.8%) film was deposited on the MoS$_2$ samples by the vacuum thermal evaporator. The rate of the deposition was set to 1.0 Å/s, and the vacuum was kept at $10^{-4}$ Pa. The thickness meter was used to detect the thickness of the metal film. MoS$_2$ samples located on the middle of the molybdenum boat were annealed in the vacuum thermal evaporator under vacuum down to $10^{-4}$ Pa. Using an infrared thermometer, the temperature was monitored. To protect MoS$_2$ from oxidation, the high vacuum condition was still kept for 30 min after the annealing treatment.

2. Photoluminescence (PL) spectra of pristine and palladium coated n-layer MoS$_2$

As reported previously$^1$, photoluminescence (PL) spectrum of n-layer MoS$_2$ exhibits a thickness-dependent behavior, which has proved to be a powerful technology to compare the layer number of ultrathin MoS$_2$ flakes. In this work, the PL of pristine and palladium coated n-layer MoS$_2$ are measured and shown in the above Figures. As shown in Fig. S1a (normalized by the intensity of the $A_{1g}$ Raman peaks), the peaks around 525 nm and 528 nm correspond to the Raman peak from MoS$_2$ and silicon substrate respectively. The broad absorption peaks at 627 nm and 670 nm correspond to the photoluminescence of MoS$_2$. It can be seen that the PL spectra show pronounced luminescence emissions in monolayer MoS$_2$ and the PL intensity decreases with the increase of layer number of MoS$_2$. Thus, based on the photoluminescence intensities, we can compare and identify the thickness of n-layer MoS$_2$.

After the deposition of Pd film on n-layer MoS$_2$ and annealing treatments, their PL spectra are shown in Fig. S1b, 1c and 1d for film thickness of 1.6nm and 3.2 nm and different annealing temperature, respectively. In Fig. S1b, the additional peaks around 560 nm correspond are observed which may be accounted for by the effect of Pd film.$^2$ For
the PL spectra of $n$-layer MoS$_2$ shown in Fig. S1b, the PL intensities decrease with the increase of MoS$_2$ layer number, which are similar to that of the pristine $n$-layer MoS$_2$. The PL intensities of the spectra shown in Fig. S1b are lower than those of pristine $n$-layer MoS$_2$, which may be due to the deposition of Pd film.

Fig. S1 (a) Photoluminescence (PL) spectra of pristine $n$-layer MoS$_2$. (b,c) PL spectra of $n$-layer MoS$_2$ deposited with 1.6 nm (b) or 3.2 nm (c) Pd film after annealed under 750°C for 4 min. (d) PL spectra of trilayer layer MoS$_2$ deposited with 3.2 nm Pd film after annealed under 800°C for 4 min. All the spectra are normalized with the intensity of the A$_{1g}$ Raman peaks. The wavelength of excitation laser is 514 nm.

Fig. S1c shows the PL spectra of the $n$-layer MoS$_2$ deposited with 3.2 nm Pd film after annealed at 750°C for 4 minutes. After the treatment, no Raman peaks and PL of MoS$_2$ were observed in monolayer MoS$_2$ and its spectrum is shown in the following Fig. S2 (the spectrum can’t be normalized with the intensity of the A$_{1g}$ Raman peak). Meanwhile, the PL spectra of bilayer and trilayer MoS$_2$ can be observed and the intensity of bilayer MoS$_2$ is the highest as shown in Fig. S1c. These results suggest that the $n$-layer MoS$_2$
have been thinned by one layer after vacuum annealing at 750°C for 4 minutes, which is in consistent with the results of Raman spectra reported in this work.

Fig. S1d shows the PL spectra of the n-layer MoS$_2$ deposited with 3.2 nm Pd film after annealed at 800°C for 4 minutes. Here only the spectra of trilayer and bulk MoS$_2$ are shown, because that no Raman peaks and PL of MoS$_2$ were observed in monolayer and bilayer MoS$_2$ (their spectra are shown in the following Fig. S2). These results suggest that the n-layer MoS$_2$ have been thinned by two layers after vacuum annealing at 800°C for 4 minutes.

In the following Fig. S2, the PL spectra of Pd/SiO$_2$, Pd/monolayer MoS$_2$ and Pd /bilayer MoS$_2$ are shown after annealing treatment, respectively. We can see clearly that there are no obvious differences among those four spectra. They indicate that monolayer or bilayer MoS$_2$ have been removed. This conclusion is consistent with the result of Raman spectra.

![PL spectra of Pd/SiO$_2$, Pd covered monolayer MoS$_2$ (3.2 nm and treating temperature of 750 and 800°C, respectively) and Pd covered bilayer MoS$_2$ (3.2 nm/800°C).](image)

3. Raman spectra of pristine n-layer MoS$_2$ before and after 750°C vacuum annealing for 4 minutes.

![Raman spectra](image)

Fig. S3 Raman spectra of pristine $n$-layer MoS$_2$ (a) before and (b) after 750°C vacuum annealing for 4 minutes.

The pristine $n$-layer MoS$_2$ were annealed under 750°C in vacuum. As shown in the above Fig. S3, the spectra of $n$-layer MoS$_2$ after annealing treatment are almost the same as those pristine $n$-layer MoS$_2$. These results indicate the important role of Pd film in the thinning process when the annealing treatment is carried out in a short time of several minutes.
4. Optical images and Raman mapping of n-layer MoS$_2$

![Fig. S4](image)

Fig. S4 (a) Optical images of pristine monolayer MoS$_2$ (light blue) and thicker MoS$_2$ (yellow and blue). (b) Optical image of the corresponding area in (a) after the deposition of 3.2 nm Pd film and annealing at 750°C for 4 min. The inset in (b) shows the integrated Raman intensity image of A$_{1g}$ mode (402 cm$^{-1}$), which corresponds to the marked area in (a). The scale bars are 5μm.

In the above Fig. S4a, the flake with lightest blue color is the monolayer and the others are bulk MoS$_2$. Fig. S4b show the corresponding optical image and Raman map of the same sample after deposition of 3.2 nm Pd film and annealing under 750°C for 4 min. The inset in Fig. S4b shows the integrated Raman intensity image of A$_{1g}$ mode (402 cm$^{-1}$), which corresponds to the marked area in Fig. S4a. As can be seen from the inset of Fig. S4b, the color at the position of where the monolayer MoS$_2$ was is black and uniform, which indicates that the monolayer MoS$_2$ has disappeared.