Electronic Supplementary Information for

Thinning of *n*-layer MoS_2 by annealing palladium film in vacuum

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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 μm.

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 contidion 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 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.

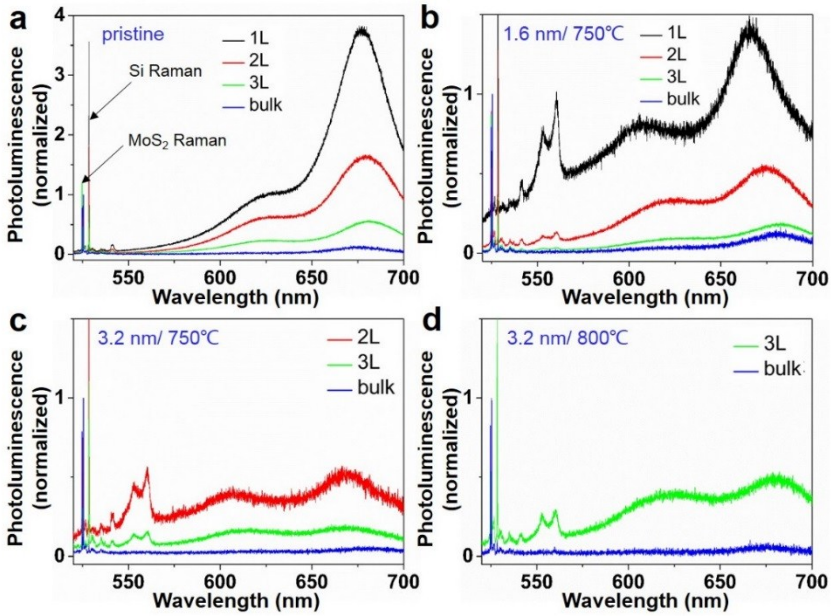

Fig. S1 (a) Photoluminescence (PL) spectra of pristine n-layer MoS_2. (b,c) PL spectra of n-layer MoS_2 deposited with 1.6 nm (b) or 3.2 nm (c) Pd film after annealed under 750℃ for 4 min. (d) PL spectra of trilayer layer MoS_2 deposited with 3.2 nm nm Pd film after annealed under 800℃ for 4 min. All 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℃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 at 750℃for 4 minutes, which is in consistent with the results of Raman spetra reported in this wrok.

Fig. S1d shows the PL spectra of *the n*-layer MoS_2 deposited with 3.2 nm Pd film after annealed at 800℃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 folloing Fig. S2). These results suggest that the *n*-layer MoS_2 have been thinned by two layers after vacuum annealing at at 800℃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.

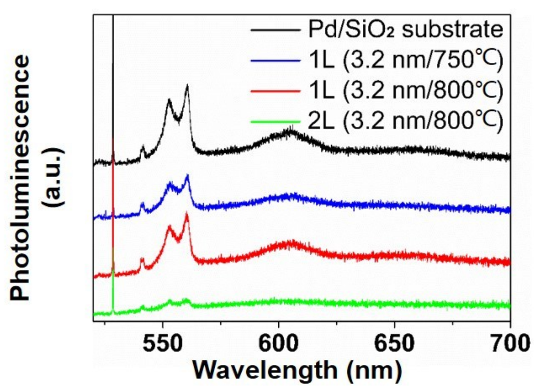

Fig. S2 PL spectra of Pd/SiO_2, Pd covered monolayer MoS_2 (3.2 nm and treating temperature of 750 and 800℃, respectively) and Pd covered bilayer MoS_2 (3.2 nm/800℃).

1 A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C. Y. Chim, G. Galli and F. Wang, *Nano Lett.*, 2010, **10**, 1271-1275.

2 D. Wong, X. Bao, T. Schlesinger, R. James, A. Cheng, C. Ortale and L. van Den Berg, *Appl. Phys. Lett.*, 1988, **53**, 1536-1538.

3. **Raman spectra of pristine n-layer MoS_2 before and after 750℃ vacuum annealing for 4 minutes.**

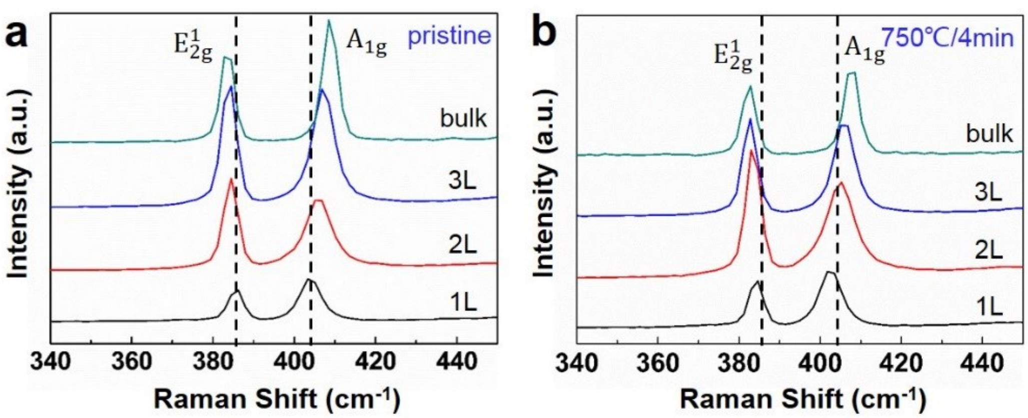

Fig. S3 Raman spectra of pristine *n*-layer MoS_2 (a) before and (b) after 750℃ vacuum annealing for 4 minutes.

The pristine *n*-layer MoS_2 were annealed under 750℃ 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

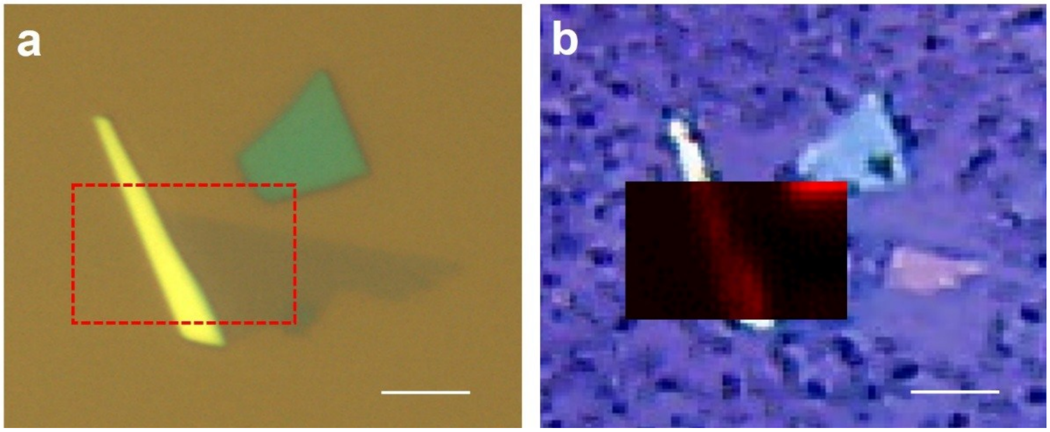

Fig. S4 (a) Optical images of pristine monolayer MoS_2 (light blue) and thicker MoS_2 (yellow and blue). (b) Optical image of the corresponding area in (a) after the deposition of 3.2 nm Pd film and annealing at 750℃ for 4 min. The inset in (b) shows the integrated Raman intensity image of A_{1g} mode (402cm^{-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 and annealing under 750℃ 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.