The influence of two-dimensional organic adlayer thickness on the ultralow frequency Raman spectra of transition metal dichalcogenide nanosheets

Shiyu Wu¹, Xiaotong Shi¹, Yue Liu¹, Lin Wang¹, Jindong Zhang¹, Weihao Zhao¹, Pei Wei¹, Wei Huang^{1,2}, Xiao Huang^{1*} and Hai Li^{1*}

ABSTRACT Recently, it has been reported that physisorbed adsorbates can be trapped between the bottom surface of two-dimensional (2D) materials and supported substrate to form 2D confined films. However, the influence of such 2D confined adsorbates on the properties of 2D materials is rarely explored. Herein, we combined atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM) and Raman spectroscopy especially the ultralow frequency (ULF) Raman spectroscopy to explore the influence of 2D confined organic adlayer thickness on the ULF breathing modes of few-layer MoS₂ and WSe₂ nanosheets. As the thickness of organic adlayers increased, red shift, coexistence of blue and red shifts as well as blue shift of ULF breathing mode was observed. KPFM measurement confirmed the enhanced n-doping and p-doping behaviors of organic adlayers as their thickness increased, respectively. Our results will provide new insights into the interaction between 2D confined adsorbates and bottom surface of 2D nanosheets, which could be useful for modulating properties of 2D materials.

Keywords: two-dimensional organic adlayer, adlayer thickness, ultralow frequency Raman, transition metal dichalcogenides, atomic force microscopy

INTRODUCTION

Two-dimensional (2D) materials have quite large surface to volume ratio and thus their properties are inevitably affected by various physisorbed adsorbates on their top surface at ambient condition [1–19]. For instance, the adsorbed hydrogen atoms were demonstrated to open the zero bandgap of graphene [1]. Tunable bandgap engineering of graphene was also realized by physisorbed

organic adsorbates [2]. In addition to graphene, physisorbed molecules also largely influenced the properties of 2D transition metal dichalcogenides (TMDCs). It has been reported that physisorbed p-type dopants enhanced while n-type dopants decreased the photoluminescence (PL) intensity of single-layer (1L) MoS₂ [7,16]. The photoresponsivity and mobility of MoS₂ nanosheet-based devices were highly influenced by physisorbed adsorbates on MoS₂ nanosheets at ambient condition, such as H₂O and O₂ molecules [8,20,21]. Obvious photocurrent enhancement was also observed in MoS₂ field-effect transistors (FETs) by depositing cesium carbonate on MoS₂ surface [22]. Enhanced on/off current ratio of MoS₂ nanosheet was obtained due to physisorption of benzyl viologen [10]. Both p-doping and n-doping of WSe₂ nanosheets were realized by physisorbed potassium and NO₂, respectively [4,5,12].

Aforementioned reports are based on the molecular physisorption on exposed top surface of 2D materials. Recently, it has been reported that 2D confined water and organic solvents film can be formed between the bottom surface of 2D materials and supported substrates [23–33]. Such confined 2D films also played important role in modulating properties of 2D materials. For example, ultrathin water film can be confined between graphene and mica substrate [23,27]. The charge transfer between graphene and mica substrate can be effectively screened by such confined water film [27]. Moreover, the sandwiched ultrathin water film can strongly decrease the PL of monolayer MoS₂ by a factor of 30–50, which was attributed to trion formation [29,34]. In addition, the morphology of confined water played an important role in

¹ Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), Nanjing 211816, China

² Shaanxi Institute of Flexible Electronics (SIFE), Northwestern Polytechnical University (NPU), Xi'an 710072, China

* Corresponding authors (emails: iamhli@njtech.edu.cn (Li H); iamxhuang@njtech.edu.cn (Huang X))

affecting the electronic structure of MoS_2 [30]. Atomically thin water film was considered as n-type dopant while trapped water droplet acted as p-type dopant [29]. In recent years, 2D nanofluidics consisting of stacked 2D materials have been reported for energy conversion, water treatment and ion transport manipulation [35–40]. In the 2D nanofluidics, the charge density and membrane structure asymmetry could be influenced by confined adsorbates between 2D materials, resulting in enhanced ionic current rectification. Similarly, volatile small organic molecules can also be confined between 2D materials and substrate to form atomically thin films, which showed quite different properties from their bulk counterparts [24,28,31–33]. For instance, tetrahydrofuran (THF) molecules formed atomically thin films in a layer-by-layer manner and exhibited both liquid and solid properties, which were confirmed by atomic force microscopy (AFM) [24]. Molecular dynamics simulation indicated that the first THF adlayer was viscous and exhibited liquid behavior while the second adlayer of THF showed solid-like behavior [28]. Due to the different interaction with mica, immobile crystal-like cyclohexane adlayers were confined between graphene and mica substrate [24,28]. Although great efforts have been involved to investigate the morphology evolution and dynamic structure behavior of confined atomically thin organic films, how the confined atomically thin organic adlayers influence the properties of 2D materials is remained unexplored.

In this work, volatile organic small molecules, such as acetone, ethanol and dichloromethane (DCM), were confined between mechanically-exfoliated MoS_2 or WSe_2 nanosheets and SiO_2 substrates to form atomically thin adlayers. AFM measurement indicated that the thickness of organic adlayers was increased with increasing incubation time of 2D nanosheets exposed to organic vapors. Kelvin probe force microscopy (KPFM) and Raman spectroscopy especially the ultralow frequency (ULF) Raman spectroscopy were employed to explore the interaction between the organic adlayers and 2D nanosheets. KPFM measurement confirmed the p-type and n-type doping effect of organic adlayers on MoS_2 nanosheets, respectively. Interestingly, we found that the thickness of organic adlayers, no matter n-type or p-type doping, showed obvious influence on the ULF breathing modes of few-layer MoS_2 and WSe_2 nanosheets with the same trend. For the adlayers with lower height (<0.7 nm for acetone and <0.4 nm for dichloromethane (DCM), respectively), red shift of ULF breathing modes was observed. Once the adlayers height was higher than a certain

value (1.6 nm for acetone and 0.8 nm for DCM), only blue shift of breathing mode peak was observed. If the adlayers height was in the range between them (from 0.7 to 1.6 nm for acetone and from 0.4 nm to 0.8 nm for DCM), coexistence of blue and red shift appeared. Moreover, we also found that the organic adlayers showed very good stability at ambient condition but can be greatly removed by annealing at high temperature. The interaction between confined organic adlayers and ULF breathing modes of few-layer TMDCs nanosheets may provide alternative method to modulate the properties of 2D materials.

EXPERIMENTAL SECTION

Materials

Acetone (99.8%), dichloromethane (99.9%) and ethanol (99.9%) were obtained from J&K Scientific Ltd. Single- and few-layer MoS_2 and WSe_2 nanosheets were isolated from MoS_2 and WSe_2 bulk crystals (HQ graphene, Netherlands). Silicon wafers were purchased from Bonda technology Pte. Ltd.

Incubating TMDCs nanosheets in organic vapor environment

Scheme 1 illustrates the whole experimental procedure. Firstly, MoS_2 and WSe_2 nanosheets were deposited onto freshly cleaned 90 nm SiO_2/Si substrates by mechanical exfoliation method (step a in Scheme 1). Then optical microscope (Axio Scope A1, Zeiss) was used to locate and image the few-layer TMDCs nanosheets. As shown in step b in Scheme 1, MoS_2 and WSe_2 nanosheets were characterized by ULF Raman spectroscopy, AFM and KPFM. Organic solvent (acetone, ethanol or DCM) with volume of ~ 15 mL was poured into a quartz dish. The quartz dish and TMDCs nanosheets on SiO_2/Si substrate were put inside a quartz box with diameter of 70 mm and height of 40 mm (step c in Scheme 1). After that, the quartz box was sealed and stored at ambient condition ($22 \pm 2^\circ\text{C}$). After being incubated in organic vapor for some time, the TMDCs nanosheets were taken out of the sealed quartz container and characterized by ULF Raman spectroscopy, AFM and KPFM (step d in Scheme 1). In order to investigate the influence of organic adlayer with different thickness, some TMDCs nanosheets were incubated and taken out of the sealed quartz box for several cycles (step c, d in Scheme 1). The organic adlayer trapped between the TMDCs nanosheet and substrate was shown in the magnified inset of step d in Scheme 1.

Scheme 1 The illustration of experimental procedures. (a) TMDCs nanosheet was deposited on SiO₂ substrate by mechanical exfoliation. (b) AFM and Raman spectroscopy were used to characterize the morphology and ULF breathing mode of TMDCs nanosheet. (c) TMDCs nanosheet was incubated in a sealed quartz box filled with a small volume of volatile organic solvent for some time. (d) AFM and Raman spectroscopy were used to characterize the morphology and ULF breathing mode change of TMDCs nanosheet after being incubated in organic vapor environment. Magnified image in (d) clearly shows the structure of organic adlayer confined between TMDCs nanosheet and SiO₂ substrate. Steps (c) and (d) might be repeated for several times to monitor the evolution and influence of organic adlayer.

Raman characterization

The Raman characterization was conducted in a back-scattering configuration excited with a solid state green laser ($\lambda = 532$ nm) (LabRAM HR Evolution, Horiba Jobin-Yvon). The Raman spectra of TMDCs nanosheets were collected through a 100 $\times$ objective lens with accumulation time for 60 s and laser power of 1%. The Raman band of a Si substrate at 520 cm⁻¹ was used as a reference to calibrate.

AFM and KPFM characterizations

A commercial AFM instrument (Dimension ICON with Nanoscope V controller, Bruker) was used to image the samples in ScanAsyst mode in air. KPFM measurement was conducted in this AFM with a lift height of 80 nm.

RESULTS AND DISCUSSION

The whole experimental process is illustrated in Scheme 1. After MoS₂ or WSe₂ nanosheets were deposited on SiO₂ substrates by mechanical exfoliation (Scheme 1a), Raman spectrometer and AFM were used to monitor the morphology and Raman spectrum evolution of MoS₂ or WSe₂ nanosheets (Scheme 1b). As-prepared nanosheets were then put into a sealed quartz box filled with volatile organic solvents (acetone, ethanol or dichloromethane) and kept for a certain time (Scheme 1c). During this process, volatilized organic molecules were permeated and

trapped into the interface between TMDCs nanosheets and substrates to form atomically thin adlayers (magnified inset in Scheme 1d). After MoS₂ or WSe₂ nanosheets were taken out of the sealed box, AFM and Raman spectrometer were used to check the morphology and Raman spectrum change (Scheme 1d). In order to investigate the influence of organic adlayer in detail, steps c and d were repeated in some experiments.

Monolayer (1L) MoS₂ was firstly selected to investigate the influence of acetone adlayer on its morphology and Raman spectrum. As shown in Fig. 1a, 1L MoS₂ had a height of 0.9 nm at ambient condition. KPFM measurement indicated that 1L MoS₂ had a negative contact potential difference (CPD) of -65 mV compared with that of SiO₂ substrate (Fig. 1g). The MoS₂ nanosheet was then put into a sealed quartz box which contained acetone. Acetone has a saturated vapor pressure of 24.7 kPa at 22°C, and thus it is easy to generate acetone vapor at ambient condition. As shown in Fig. 1b, the height of 1L MoS₂ was increased to 1.5 nm after being exposed to acetone environment for 0.5 h, indicating the thickness of acetone adlayer was around 0.6 nm. Meanwhile, the CPD between 1L MoS₂ and SiO₂ substrate was increased to -13 mV as shown in Fig. 1h, indicating the 1L MoS₂ was n-doped by acetone adlayer (referred to as AA-MoS₂) [16,29,41]. The thickness of acetone adlayer was further increased to 0.8 nm after 1 h incubation (Fig. 1c), meaning more acetone molecules were trapped between MoS₂ nanosheet and SiO₂ substrate. In this case, there was almost no obvious potential difference between MoS₂ and SiO₂ substrate (Fig. 1i), indicating 1L MoS₂ was further n-type doped by thicker acetone adlayer. As the incubation time was extended to 1.5, 2 and 2.5 h, the thickness of acetone adlayer was increased to 1.1, 1.3 and 1.7 nm (Fig. 1d-f and m), respectively. Meanwhile, the CPD between MoS₂ and SiO₂ substrate was simultaneously changed to 6, 19 and 28 mV (Fig. 1j-l), respectively. Monotonic increase of the CPD between 1L MoS₂ nanosheet and SiO₂ substrate was observed from -65 to 28 mV as the incubation time was increased from 0 to 2.5 h (Fig. 1m). It meant the work function of 1L AA-MoS₂ nanosheet was increased about 0.093 eV compared to that of pristine 1L MoS₂ nanosheet. The PL spectra of 1L MoS₂ and AA-MoS₂ nanosheets are shown in Fig. 1n. The PL intensity of 1L AA-MoS₂ nanosheet was greatly decreased more than 90% even after being incubated in acetone environment for 0.5 h (Fig. 1o), which further confirmed the n-type doping of MoS₂ nanosheet by acetone adlayer [7,16]. As the incubation time increased from 1 to 1.5 h, the PL intensity of 1L AA-MoS₂ nanosheet was slightly

Figure 1 (a–f) AFM images of 1L MoS₂ nanosheet (a) before and after being incubated in acetone environment for (b) 0.5, (c) 1, (d) 1.5, (e) 2 and (f) 2.5 h, respectively. (g–l) Corresponding KPFM images of 1L MoS₂ nanosheet (g) before and after being incubated in acetone environment for (h) 0.5, (i) 1, (j) 1.5, (k) 2 and (l) 2.5 h, respectively. (m) Plots of height and surface potential change of 1L MoS₂ nanosheet with increased incubation time. (o) The PL intensity of 1L MoS₂ nanosheet as a function of incubation time in acetone environment. (n, p) PL (n) and Raman (p) spectra of 1L MoS₂ before and after being incubated in acetone environment.

decreased and kept almost unchanged after 2 h. Raman spectroscopy was also used to characterize 1L MoS₂ and AA-MoS₂ nanosheets. As shown in Fig. 1p, the E_{2g}¹ peak of 1L AA-MoS₂ was blue-shifted by 0.8 cm⁻¹ compared to

that of pristine 1L MoS₂, which is different from unchanged E_{2g}¹ peak of 1L MoS₂ on water adlayer [29]. It has been reported that both electron and hole doping will not affect the position of E_{2g}¹ peak [42], and thus this blue shift

could be attributed to the stress induced by acetone adlayer [8,43]. There was no obvious change for A_{1g} peak of 1L AA-MoS₂, further implying the stress on MoS₂ nanosheet induced by acetone adlayer [8].

In comparison with E_{2g}^1 and A_{1g} peaks, ULF breathing Raman modes of MoS₂ nanosheets are more sensitive to the surrounding environment [44]. As shown in Figs S1g and S2h–j in Supplementary information (SI), the ULF breathing modes of 2L and 3L MoS₂ were blue-shifted after being incubated in acetone environment, indicating the influence of acetone adlayer. However, the ULF breathing mode of 2L MoS₂ is quite broad and that of 3L MoS₂ is overlapped by its strong shear mode. In order to clearly show the evolution of ULF breathing mode, thicker MoS₂ nanosheets (4L–7L) were chosen to systematically investigate the influence of organic adlayer.

Fig. 2a, b show the AFM images of 6L MoS₂ nanosheet before and after being incubated in acetone environment for 3 h. The height of MoS₂ nanosheet was increased from 4.4 to 4.9 nm, indicating the thickness of confined acetone adlayer was 0.5 nm. KPFM measurement showed the CPD between 6L MoS₂ as well as 6L MoS₂/acetone adlayer (referred to as 6L AA-MoS₂) and SiO₂ was increased from −94 to −41 mV, confirming the n-doping behavior of acetone adlayer on 6L MoS₂ nanosheet [29]. It is consistent with that of 1L MoS₂ nanosheet shown in Fig. 1g–l. Raman characterization showed that the E_{2g}^1 and A_{1g} peaks of 6L MoS₂ nanosheet kept unchanged before and after incubated in acetone environment (Figs S3–S5), indicating they are insensitive to acetone adlayer. However, a red shift of 0.6 cm^{-1} in ULF breathing mode was observed for 6L AA-MoS₂, implying there should be interaction between acetone adlayer and 6L MoS₂. The red-shifted ULF breathing mode was named as B2 peak. Meanwhile, the PL spectrum of 6L MoS₂ nanosheet was kept almost unchanged after being incubated in acetone environment (Fig. S6c).

After 6L MoS₂ nanosheet was incubated in acetone environment for 4 h, the thickness of 6L MoS₂ nanosheet was increased from 4.3 to 5.5 nm (Fig. 3a, b), indicating the thickness of acetone adlayer was 1.2 nm. In this case, the thick acetone adlayer may largely affect the properties of MoS₂ nanosheet [45,46]. As shown in Fig. 3d, KPFM measurement indicated that the CPD of 6L AA-MoS₂ was increased to −6 mV compared to that of pristine 6L MoS₂, which was −88 mV (Fig. 3c). In comparison with the acetone adlayer with thickness of 0.5 nm (Fig. 2), this thicker acetone adlayer strongly affected the CPD of MoS₂. The ULF breathing mode of 6L AA-MoS₂ also showed obviously different Raman peak from that of

Figure 2 (a, b) AFM images of 6L MoS₂ nanosheet (a) before and (b) after being incubated in acetone environment for 3 h. Inset in (a) shows the optical image of 6L MoS₂ nanosheet. (c, d) Corresponding KPFM images of 6L MoS₂ nanosheet (c) before and (d) after being incubated in acetone environment. (e) ULF Raman spectra of 6L MoS₂ before (black curve) and after (red curve) being incubated in acetone environment. Red shift of ULF breathing mode of 6L MoS₂ nanosheet can be clearly observed.

pristine 6L MoS₂, implying the significant role of acetone adlayer thickness. As shown in Fig. 3e, the ULF Raman spectrum of 6L AA-MoS₂ showed a broad peak with two apexes around 14 cm^{-1} , which disappeared under cross polarization (gray green curve in Fig. 3e), indicating it was breathing mode peak. The broad breathing mode peak can be deconvoluted into two Lorentzian profiles at 13.2 cm^{-1} (B2 peak) and 15 cm^{-1} (Fig. 3f), respectively. The peak located at 15 cm^{-1} blue-shifted compared to B1 peak and named as B3 peak. The B2 peak showed a red shift of 1 cm^{-1} while the B3 peak showed a blue shift of 0.8 cm^{-1} compared to that of pristine 6L MoS₂ (B1 peak). The coexistence of red-shifted B2 peak and blue-shifted B3 peak might be attributed to the influence of thicker acetone adlayer. In order to exclude the influence of acetone adlayer, the top surface of another 6L AA-MoS₂ nanosheet was covered by a polydimethylsiloxane

Figure 3 (a, b) AFM images of 6L MoS₂ nanosheet (a) before and (b) after being incubated in acetone environment for 4 h. Inset in (a) shows the optical image of 6L MoS₂ nanosheet. (c, d) Corresponding KPFM images of 6L MoS₂ nanosheet (c) before and (d) after being incubated in acetone environment. (e) ULF Raman spectra of 6L MoS₂ before (black curve) and after (purple curve) being incubated in acetone environment. (f) Magnified image of ULF breathing mode of MoS₂ nanosheet after being incubated in acetone environment. Coexistence of red and blue shift of ULF breathing mode of 6L MoS₂ nanosheet can be clearly observed after deconvolution.

(PDMS) film and then peeled off from SiO₂ substrate after being characterized by Raman spectroscopy. In this case, the bottom surface of 6L MoS₂ nanosheet with trapped acetone adlayer was exposed to air and then acetone adlayer was evaporated quickly. Thus there was no trapped acetone adlayer between MoS₂ nanosheet and PDMS film. As shown in Fig. S7, coexistence of red and blue shift of ULF breathing mode was observed for the 6L AA-MoS₂ nanosheet before transfer, which was similar to that of 6L AA-MoS₂ nanosheet shown in Fig. 3e. However, the ULF breathing mode of 6L MoS₂ recovered to its intrinsic position after being transferred on PDMS film, indicating the red and blue shift of ULF breathing mode was correlated to the existence of acetone adlayer. Besides 6L MoS₂ nanosheet, the influence of acetone adlayer

Figure 4 (a, b) AFM images of 6L MoS₂ nanosheet (a) before and (b) after being incubated in acetone environment for 6 h. Inset in (a) shows the optical image of 6L MoS₂ nanosheet. (c, d) Corresponding KPFM images of 6L MoS₂ nanosheet (c) before and (d) after being incubated in acetone environment. (e) ULF Raman spectra of 6L MoS₂ before (black curve) and after (blue curve) being incubated in acetone environment. Blue shift of ULF breathing mode of 6L MoS₂ nanosheet can be clearly observed.

thickness on the ULF breathing mode was also observed in 4L, 5L and 7L MoS₂ nanosheets (Figs S8–S14), implying the versatile role of acetone adlayer thickness on the ULF breathing mode.

The thickness of acetone adlayer can be further increased by extending the incubation time. As shown in Fig. 4a, b, the thickness of acetone adlayer was increased to 3.5 nm after being incubated in acetone environment for 6 h. With increased thickness, the influence of acetone adlayer on the properties of MoS₂ was also enhanced. As shown in Fig. 4c, d, the CPD of 6L AA-MoS₂ was changed to positive value and showed an increment of 116 mV compared to that of pristine 6L MoS₂ nanosheet. The Raman spectrum of 6L AA-MoS₂ showed ULF breathing mode peak at 14.6 cm⁻¹ (B3 peak), which showed a blue shift of 0.4 cm⁻¹ compared to that of pristine 6L MoS₂ nanosheet (Fig. 4e). Such blue shift could be attributed to

Figure 5 (a–f) AFM images of 6L MoS₂ nanosheet (a) before and after being incubated in acetone environment for (b) 1, (c) 2, (d) 3, (e) 4 and (f) 5 h, respectively. (g–l) Corresponding KPFM images of 1L MoS₂ nanosheet (g) before and after being incubated in acetone environment for (h) 1, (i) 2, (j) 3, (k) 4 and (l) 5 h, respectively. (m, n) ULF (m) and high frequency (n) Raman spectra of 6L MoS₂ before and being incubated in acetone environment. (o) Plots of height and surface potential change of 6L MoS₂ nanosheet with increased incubation time. (p) Evolution of B2 and B3 peaks with increased incubation time.

the strong influence of thick acetone adlayer.

In order to monitor the evolution of acetone adlayer at different incubation time, AFM and Raman characterizations were performed on the same MoS₂ nanosheet. Fig. 5a–f show the AFM images of 6L MoS₂ nanosheet

before and after being incubated in acetone environment for 1, 2, 3, 4 and 5 h, respectively. The height of pristine 6L MoS₂ nanosheet was measured as 4.3 nm. While the thickness of acetone adlayer was increased from 0.5, 0.9, 1.1, 1.3 to 1.7 nm as the incubation time is 1, 2, 3, 4 and

Figure 6 (a, b) AFM images of 6L MoS₂ nanosheet (a) before and (b) after being incubated in acetone environment. (c) AFM image of 6L MoS₂ nanosheet shown in (b) after being annealed at 200°C for 1 h. (d) ULF Raman spectra of 6L MoS₂ before (black curve) and after being incubated in acetone (blue curve) environment as well as annealed (purple curve). (e) Magnified image of ULF breathing mode of MoS₂ nanosheet shown in (d). Coexistence of red and blue shift of ULF breathing mode of 6L MoS₂ nanosheet can be clearly observed after deconvolution.

5 h (Fig. 5o), respectively. As shown in Fig. 5m, the ULF Raman spectra of pristine 6L MoS₂ and AA-MoS₂ at different incubation time clearly showed the change of breathing mode. Meanwhile, the high frequency Raman spectra of pristine 6L MoS₂ and AA-MoS₂ remained unchanged (Fig. 5n). After being incubated in acetone environment for 0.5 h, the B1 peak showed no notable change. While the ULF breathing mode peak of AA-MoS₂ (B2 peak) showed a red shift of 0.5 cm⁻¹ compared to that of pristine MoS₂ (B1 peak) after 1 h incubation. The B2 peak kept red-shifting as the incubation time was increased to 1.5 h. Meanwhile, a weak B3 peak was observed (Fig. S15). An obvious B3 peak appeared when the incubation time was increased to 2.5 h (Fig. S15c). The intensity ratio of B2 to B3 further decreased with the incubation time increased to 4.5 h. After 5 h incubation, B2 peak disappeared and only B3 peak can be observed. Fig. 5p clearly shows the evolution of B1, B2 and B3 peaks with varied incubation time. KPFM measurement was also performed simultaneously to show the CPD change of MoS₂ nanosheet (Fig. 5g–l). As shown in Fig. 5o, the CPD kept increasing with increased incubation time, i.e., increased thickness of acetone adlayer, which is consistent with aforementioned results.

As-trapped acetone adlayer is quite stable at ambient condition. As shown in Fig. S16a, b, the height of pristine 6L MoS₂ was measured as 4.2 nm and then increased to 5.3 nm after being incubated in acetone environment for 3 h. The 6L AA-MoS₂ nanosheet was then taken out and stored at ambient condition. There was no height change even after 169 h (Fig. S16c–g). ULF Raman spectroscopy was also used to monitor this process. As shown in Fig. S16h, there was a red-shifted breathing mode peak with a slight weaker shoulder for 6L AA-MoS₂ after being incubated in acetone environment for 3 h. After deconvolution, the red-shifted breathing mode peak and the shoulder peak can be assigned as B2 and B3, respectively. These two peaks were kept unchanged at ambient condition even after 169 h, indicating the stability of acetone adlayer.

In order to explore the reverse influence of acetone adlayer thickness on ULF breathing mode, a 6L MoS₂ nanosheet was firstly incubated in acetone environment and then annealed at 200°C. As shown in Fig. 6a, b, the height of MoS₂ nanosheet was increased from 4.3 to 7.3 nm after being incubated in acetone environment for 5 h, indicating the thickness of acetone adlayer was 3.0 nm. Similar to the data shown in Fig. 4, the 6L AA-

MoS₂ showed a blue-shifted ULF breathing mode peak due to the thick acetone adlayer (Fig. 6d), which is consistent with the data shown in Fig. 4. As shown in Fig. 6c, the thickness of acetone adlayer was reduced to 0.9 nm after the 6L AA-MoS₂ nanosheet was annealed at 200°C for 1 h, indicating the trapped acetone adlayer can be partially removed under high temperature. Meanwhile, the ULF breathing mode of MoS₂ showed a broad peak located around 14 cm⁻¹, which can also be deconvoluted into two Lorentzian profiles (Fig. 6e). In addition, 6L MoS₂ with acetone adlayer of middle thickness was also annealed to confirm the reversibility. As shown in Fig. S17, the thickness of acetone adlayer was 1.2 nm after being incubated in acetone environment for 3 h. In this case, the 6L AA-MoS₂ showed a broad ULF breathing mode peak. After being annealed at 200°C for 1 h, the thickness of acetone adlayer was decreased from 1.2 to 0.3 nm. Meanwhile, the ULF breathing mode of MoS₂ showed a red shift of 0.4 cm⁻¹, which is consistent with the data shown in Fig. 2. Similar results were also observed in 7L MoS₂ nanosheet annealed at different temperature (Fig. S18). Finally, the acetone adlayer can be completely removed by annealing at 300°C for 3 h (Fig. S18). Aforementioned results proved that the thickness of organic adlayer played an important role in affecting the ULF breathing mode of MoS₂ nanosheet.

Besides acetone, ethanol adlayer also showed n-type doping behavior and similar influence on the ULF breathing mode of MoS₂ nanosheet (Figs S19, S20) [7]. The PL spectrum of 1L MoS₂ nanosheet was largely decreased after being incubated in ethanol environment for 1 and 2 h (Fig. S19a), respectively, confirming the n-type doping behavior of ethanol. The ULF breathing mode of 4L and 6L MoS₂ nanosheets showed red shift, coexistence of red and blue shift, and blue shift with increased incubation time in ethanol environment (Fig. S20), respectively. In contrast to acetone and ethanol, chloromethane was considered as p-type dopant [16]. As one kind of chloromethane, dichloromethane (DCM) has a saturated vapor pressure of 47.4 kPa at 22°C and is a bit more volatile than acetone. We are curious whether the DCM adlayer between MoS₂ and SiO₂ substrate influences the Raman spectrum of MoS₂. As shown in Fig. 7a–d, the height of MoS₂ nanosheet was increased from 4.4 to 4.6, 4.8 and 5.2 nm after being incubated in DCM environment for 2, 3 and 6 h, respectively. KPFM measurement indicated that the CPD of MoS₂ was monotonically decreased from -73 to -113 mV with increased incubation time (Fig. 7e–h), implying the p-type doping effect of DCM on MoS₂ [41]. In addition, the PL spectrum of 1L

MoS₂ was increased after being incubated in DCM environment for 1 and 2 h (Fig. S19b), respectively, further confirming the p-type doping behavior of DCM. Similar to acetone and ethanol, DCM adlayer also showed obvious thickness-related influence on ULF breathing mode of 6L MoS₂ nanosheet. As shown in Fig. 7i, j, the ULF breathing mode of 6L MoS₂ nanosheet showed red shift, coexistence of red and blue shift, and blue shift with increased thickness of DCM adlayer, respectively, which was similar to that of MoS₂ nanosheet with acetone adlayer. However, the high frequency Raman spectra of 6L MoS₂ nanosheet showed no obvious change (Fig. 7k). Aforementioned results demonstrated that the ULF breathing mode of MoS₂ nanosheet was influenced by the thickness of organic adlayer rather than the doping effect.

Based on aforementioned results, we proposed a plot to illustrate the thickness influence of organic adlayer on the ULF breathing mode of MoS₂ nanosheets. As shown in Fig. 8, ULF breathing mode in MoS₂ nanosheets showed red shift when acetone and DCM adlayers were lower than 0.7 and 0.4 nm, respectively. While blue shift of ULF breathing mode in MoS₂ nanosheets was observed when acetone and DCM was thicker than 1.6 and 0.8 nm, respectively. The coexistence of blue shift and red shift was observed when the thickness of acetone adlayer is in the range of 0.7 to 1.6 nm. Such phenomenon was also found for DCM adlayer in the range of 0.4 to 0.8 nm. The molecular heights of acetone and DCM are 0.26 and 0.24 nm (Fig. S21), respectively. While acetone has a length of 0.43 nm, which is much larger than that of DCM. Such different critical thickness of acetone and DCM adlayer might be attributed to their different molecular size.

The red and blue shift of ULF breathing mode peak could be explained as follows. The red shift of ULF breathing mode in MoS₂ nanosheet was also observed in heterostructures of MoS₂ and graphene [47], which was attributed to the interfacial interaction between MoS₂ and graphene. As previously reported, organic molecules such as THF and cyclohexane can form crystal-like adlayers in the confined space between graphene and mica substrate [24]. Theoretical simulation indicated that THF adlayer still exhibited solid-like behavior as the thickness increased [28]. Our previous report showed that even monolayer graphene can induce red shift of ULF breathing mode in MoS₂ nanosheet [47]. After being incubated in acetone environment for a certain time, the intercalated acetone adlayer can be considered as substrate for MoS₂ instead of the beneath SiO₂ substrate. In this case, there could be interfacial interaction between

Figure 7 (a–d) AFM images of 6L MoS₂ nanosheet (a) before and after being incubated in dichloromethane (DCM) environment for (b) 2, (c) 3 and (d) 6 h, respectively. (e–h) Corresponding KPFM images of 6L MoS₂ nanosheet (e) before and after being incubated in acetone environment for (f) 2, (g) 3 and (h) 6 h, respectively. (i) ULF Raman spectra of 6L MoS₂ before and after being incubated in DCM environment. (j) Magnified image of ULF breathing mode of MoS₂ nanosheet shown in (i). (k) High frequency Raman spectra of 6L MoS₂ before and after being incubated in DCM environment. Coexistence of red and blue shift of ULF breathing mode of 6L MoS₂ nanosheet can be clearly observed after deconvolution.

Figure 8 Histogram of the correlation between acetone and DCM adlayers thickness and the ULF breathing mode evolution of MoS₂ nanosheets.

acetone adlayer and MoS₂ nanosheet, which led to the red or blue shift of ULF breathing mode. When the thickness

of acetone adlayer was 0.5 nm, it could be comparable to that of monolayer graphene and might induce red shift of ULF breathing mode. When MoS₂ nanosheet was put on few-layer graphene (2L–5L), coexistence of red and blue shift of ULF breathing mode was also observed [47]. Meanwhile, coexistence of red and blue shift of ULF breathing mode was also observed in our results, implying the organic adlayers play similar role in affecting the ULF breathing modes of MoS₂ nanosheets to those of graphene layers. Therefore, as the acetone adlayer thickness exceeds 0.7 nm or more, we can imagine that the 6L MoS₂ nanosheet might be completely floated on acetone adlayer.

Besides MoS₂, WSe₂ nanosheets were also incubated in acetone environment to investigate the influence of acetone adlayer with various thicknesses on the ULF breathing mode. Fig. 9 shows the ULF Raman spectra of 4L WSe₂ nanosheet after being incubated in acetone environment for 1, 2.5 and 3 h, respectively. With increased incubation time, the ULF breathing mode of 4L WSe₂

Figure 9 ULF Raman spectra of 4L WSe₂ nanosheet before and after being incubated in acetone environment for 1, 2.5 and 3 h, respectively.

nanosheet also showed red shift, coexistence of red and blue shift, and blue shift, respectively, which is similar to those of MoS₂. Such phenomena were also observed in 6L WSe₂ nanosheet incubated in acetone environment for different time (Fig. S22), implying the versatile influence of organic adlayer on the ULF breathing mode of TMDCs nanosheets.

CONCLUSIONS

In summary, the influence of organic adlayer thickness on the ULF breathing mode of TMDCs nanosheets was systematically investigated by AFM, KPFM as well as ULF Raman spectroscopy. With increased incubation time, AFM measurement showed increased thickness of organic adlayer. Raman spectroscopy indicated that the thickness of organic adlayer played an important role in affecting the ULF breathing mode of TMDCs nanosheets. When the thickness of acetone adlayer was lower than 0.7 nm, only red-shifted ULF breathing mode was observed. As the thickness exceeded 1.6 nm, blue-shifted ULF breathing mode was observed. While blue and red shifts coexisted as the thickness was measured in the range of 0.7 to 1.6 nm. DCM adlayer also showed similar influence on the ULF breathing mode but lower thickness compared with that of acetone. KPFM measurement confirmed the enhanced n-doping and p-doping behaviors of acetone and DCM with increased thickness, respectively. Besides MoS₂, ULF breathing mode of WSe₂ nanosheet was also be influenced by the acetone adlayer, indicating the versatile influence of organic adlayer on the properties of TMDCs nanosheets. Our results not only show the influence of organic adlayer on the optical properties of TMDCs nanosheets, but also shine a pave to modulate the optoelectronic properties of TMDCs na-

nosheets.

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Shiyu Wu is a master student at the Institute of Advanced Materials (IAM), Nanjing Tech University. Her research interest focuses on the synthesis and characterization of two-dimensional materials.

Xiao Huang is currently a professor at the IAM, Nanjing Tech University. She received her bachelor's degree from the School of Materials Science and Engineering at Nanyang Technological University in Singapore in 2006 and completed her PhD in 2011 under the supervision of Prof. Hua Zhang and Prof. Freddy Boey. Her research interest includes the synthesis and applications of two-dimensional nanomaterial-based hybrids.

Hai Li is currently a professor at the IAM, Nanjing Tech University. He received his bachelor degree from Zhengzhou University in 2001 and completed his PhD in 2007 under the supervision of Prof. Jun Hu. He worked as postdoctoral fellow in Prof. Hua Zhang's group in the School of Materials Science and Engineering at Nanyang Technological University in Singapore from 2009 to 2014. His research interest includes the synthesis, characterization and applications of two-dimensional materials and their heterostructures.

二维有机分子吸附层对过渡金属硫化物纳米薄片超低波拉曼光谱的影响

吴诗语¹, 石晓桐¹, 刘月¹, 王琳¹, 张锦东¹, 赵炜昊¹, 韦培¹, 黄维^{1,2}, 黄晓^{1*}, 李海^{1*}

摘要 在二维材料下表面与衬底之间的受限空间中, 物理吸附物如水分子和有机分子等可形成二维吸附层. 然而, 这类吸附层如何影响其上层二维材料的性能尚未被探究. 本文中, 我们结合原子力显微镜、开尔文力显微镜以及超低波拉曼光谱仪来探究有机分子吸附层对其上的少层二硫化钼及二硒化钨纳米薄片性质的影响. 随吸附层厚度增加, 纳米薄片的超低波呼吸模式拉曼峰发生红移、红移和蓝移共存以及仅有蓝移的现象. 此外, 纳米薄片的掺杂程度也逐渐增强. 理解有机分子吸附层与二维材料下表面之间的相互作用, 有望对二维材料性质的调节提供帮助.