Enhancing the interlayer adhesive force in twisted multilayer MoS$_2$ by thermal annealing treatment

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Abstract
Few-layer MoS$_2$ has recently gained great attention owing to its remarkable mechanical and photoelectric properties, which are strongly influenced by the interactions and relative orientations between layers. Here, we report on Raman scattering measurements of twisted MoS$_2$ flakes prepared by exfoliation and nondestructive transfer. Thermal annealing treatment can effectively enhance the interlayer coupling of twisted MoS$_2$ and lead to a van der Waals (vdW) interaction between two stacked layers. We have roughly calculated the interlayer coupling force by a diatomic chain model (DCM) and found that the interlayer adhesive force increased by $\sim$20% compared with no-treatment samples. We additionally found that the non-Bernal stacking structure of MoS$_2$ induces a weakening in the interlayer coupling. This study could promote the development of novel semiconductors, optoelectronic devices, and superlubricity materials.

Keywords: molybdenum disulphide (MoS$_2$), twisted MoS$_2$, thermal annealing, interlayer coupling, Raman spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction
With the fast progress of graphene research, the unique properties of other two-dimensional (2d) layered materials have also attracted considerable interest [1–4]. While graphene has outstanding mechanical [5–8] and electronic properties [9, 10], the lack of a bandgap limits its application in logic circuits and optoelectronics devices [11, 12]. As an alternative to graphene, molybdenum disulphide (MoS$_2$) is a semiconductor with an indirect bandgap of 1.2 eV in its bulk form [13] and transforms into a direct bandgap semiconductor with a strong photoluminescence (PL) when the thickness is reduced to a monolayer [14, 15]. Moreover, field effect transistors (FETs) made on monolayer MoS$_2$ present a large mobility up to 200 cm$^2$ V$^{-1}$ s$^{-1}$ and a high current on/off ratio of $10^8$ [16–18].

Not only does few-layer MoS$_2$ have attractive optical and electronic properties similar to monolayer MoS$_2$ [15], it also exhibits van der Waals (vdW) interactions at the interlayers [19]. The interlayer coupling and band structure of a few-layer 2d layered material can be modified by varying its microstructure including the relative twist angle and stacking order, which result in new mechanical and photoelectric behaviors [20–22]. As a prototypical layered material, twisted MoS$_2$ where the layers are rotated by a relative angle has received much attention in recent years. Castellanos-Gomez et al [23] folded MoS$_2$ layers with elastic substrates and found reduced interlayer coupling and enhanced photoluminescence emission yield in twisted MoS$_2$. Liu et al [24] grew MoS$_2$ bilayers with twist angles of $\theta = 0^\circ$, 15$^\circ$, 60$^\circ$ using chemical vapour deposition (CVD) and researched how the interlayer couplings evolved with the twist angle. Through tuning the coupling strength, we fabricate twisted MoS$_2$ materials, which have high optical absorption and superior optoelectronic
properties. In order to improve the contact and enhance the interlayer coupling, Zhou \textit{et al} [25] tapped the samples by atomic force microscopy (AFM) and Tongay \textit{et al} [26] conducted a vacuum thermal annealing process. In addition, the applications of the 2d layered material/MoS$_2$ vdW heterostructure in electronics and optoelectronics have also attracted immense research interest recently [27–29].

In this paper, we present a report on thermal-enhanced interlayer coupling of twisted MoS$_2$ flakes. Then, mechanical cleavage and atomically nondestructive transfer techniques are applied to prepare the non-Bernal-stacked MoS$_2$ samples which have fewer lattice defects than the CVD’s [30, 31]. Since the MoS$_2$ flakes were exposed to ambient oxygen, water vapor and other impurities during the transfer fabrication process, the removal of contaminants is necessary for making two pristine MoS$_2$ flakes contact with each other closely [32, 33]. We find that the thermal annealing can make a contribution to cleaning the residue between two layers and producing a strong interlayer van der Waals interaction. Raman scattering for samples of (1L+1L), (1L+2L), (1L+3L), (1L+4L) layers both before and after the thermal annealing at 260 °C are carried out. The shifts of characteristic peaks in Raman spectroscopy demonstrate that the thermal annealing treatment is an effective approach to enhance the interlayer coupling of twisted MoS$_2$. These results demonstrate that our techniques offer the possibility of fabricating twisted MoS$_2$ flakes with different layer numbers and stacking structures to modify their mechanical and photoelectric properties.

2. Experiment

We prepared ultrathin MoS$_2$ layers by using mechanical cleavage technique that was applied to fabricating graphene. Mono- and few-layer MoS$_2$ flakes were exfoliated from bulk MoS$_2$ crystals (SPI Supplies) with Scotch tape and then deposited onto the Si/SiO$_2$ substrates [34, 35]. The thickness of MoS$_2$ samples was firstly estimated through the different optical contrasts. Then, we relied on the Raman spectroscopy measurement to accurately determine the number of layers [36–38]. For NL-MoS$_2$ (N = 1–4), we could use the frequency difference $\Delta \omega (A_{1g} - E_{2g}) = 25.8 - 8.4/N$ to identify the layer number $N$ [4].

After obtaining the pristine MoS$_2$ flakes from mono-layer (1L) to quadri-layer (4L), the atomically nondestructive transfer technique was employed to fabricate the twisted MoS$_2$ samples which were stacked following the non-Bernal stacking. A PMMA layer was first spin-coated on the pristine MoS$_2$ flake, then followed by soaking it in 14wt% KOH solution in order to dissolve the SiO$_2$ film and obtain the PMMA-supported MoS$_2$ sample. After that, the PMMA-supported MoS$_2$ was mechanically transferred onto another pristine MoS$_2$ flake followed by removing the PMMA layer [32, 39, 40]. Our fabrication technique could precisely control the relative position between two pristine MoS$_2$ flakes.

Figures 1(a) and (b) show a sketch of the twisted MoS$_2$ structure and figure 1(c) shows an optical micrograph of the twisted MoS$_2$ flake.

A Raman Jobin-Yvon HR800 system was applied for the Raman scattering measurement. The MoS$_2$ samples were excited with a solid-state laser operating at a wavelength of 532 nm and a spectral resolution of $\sim$0.6 cm$^{-1}$. To avoid laser-induced sample heating, we used a low laser power of $\sim$0.15 mW [41, 42]. The size of our samples was larger than 5 μm and all measurements were performed at room temperature and in an air ambient environment.

For the thermal annealing, the MoS$_2$ samples were placed into the quartz tube at the centre of a furnace, and annealed at 260 °C for 40 minutes in a nitrogen environment. Temperature ramp rate was kept at 10 °C min$^{-1}$. After the annealing treatment, the furnace was slowly cooled down to room temperature before the samples were taken out.

3. Results and discussion

Raman spectroscopy has been proven to be a powerful and nondestructive tool to determine the number of layers, as well as to characterize the structural and vibrational properties of atomically 2d layered materials, such as graphene and MoS$_2$ [37, 43]. As shown in figure 2(a), there are two characteristic Raman active modes at $\sim$386 cm$^{-1}$ (E$_{2g}^\pm$) and $\sim$403 cm$^{-1}$ (A$_{1g}$) in the Raman spectrum of monolayer MoS$_2$. The E$_{2g}^\pm$ mode corresponds to an in-plane optical vibration of Mo and S atoms, while the A$_{1g}$ mode corresponds to an out-of-plane optical vibration of the S atoms [38] (as shown in the inset in figure 2(a)). An increase in the number of layers results in the stiffening of the A$_{1g}$ mode, which is found to arise from stronger restoring forces on the S atoms caused by the increase of interlayer van der Waals interaction [37]. On the contrary, the E$_{2g}^\pm$ mode softens with increasing thickness due to long-range Coulomb interlayer forces or stacking-induced structural changes [44]. The frequency difference between the two modes exhibits a prominent dependence on the layer thickness which also relates to the interlayer interaction, so we can finally use the frequency difference to estimate the strength of interlayer coupling in MoS$_2$ flakes: the larger the difference, the stronger the coupling strength [23].

For the (1+n)L(n = 1, 2, 3, 4) twisted MoS$_2$ samples, which we denote as (1+n)L-MoS$_2$, the evolution of two Raman active modes is similar to the pristine MoS$_2$ flakes. That is, when $n$ is increased from 1 to 4, the E$_{2g}^\pm$ mode shows a red shift of $\sim$1.5 cm$^{-1}$ while the A$_{1g}$ mode is blue shifted by $\sim$3 cm$^{-1}$. In addition, the frequency difference between E$_{2g}^\pm$ and A$_{1g}$ modes of (1+n)L-MoS$_2$ lies in between the one measured for 1L and nL pristine MoS$_2$. This means that the change emerges from the interlayer interaction after stacking two pristine MoS$_2$ layers by a rotational angle and the interlayer coupling results in distinctive lattice vibrational frequencies of non-Bernal-stacked MoS$_2$. Figure 2(b) displays the evolution of frequency difference between the two Raman
modes as a function of the number of layers. The disparity between the frequency difference of \((1+n)L\)-\(t\) and pristine \(MoS_2\) reduces as the layer number is increased. This indicates that the influence of varying stacking structure weakens with increasing sample thickness. Furthermore, the line widths of the \(A_{1g}\) Raman mode also show a similar trend with the layer number for pristine and twisted \(MoS_2\), as shown in figures 2(c) and (d). The \(A_{1g}\) mode line width of twisted \(MoS_2\) reaches the maximum at \((1+2)L\) and that of pristine \(MoS_2\) at \(2L\). This result may relate to the varying force constants induced by structural changes of the \(MoS_2\) material [44]. In contrast, the line widths of \(E_{2g}\) mode nearly remain constant both for pristine and twisted \(MoS_2\).

We detected two characteristic peaks in the Raman spectrum of \((1+n)L\)-\(t\)-\(MoS_2\) \((n = 1, 2, 3, 4)\), but their frequency difference was close to \(nL\) pristine \(MoS_2\), which demonstrated that the 1L and \(nL\) pristine \(MoS_2\) flakes were partially in contact with each other. This is because some contaminants, such as moisture or adsorbents, existed between the two pristine \(MoS_2\) flakes, leading to a weakening of the interlayer coupling. In order to remove the residue between twisted \(MoS_2\) layers and enhance the interlayer coupling, the samples were annealed in an nitrogen environment at 260 °C for 40 min [45, 46]. After that, we performed the same Raman spectroscopy measurement on the annealed \(MoS_2\) flakes. Figure 3(a) shows the frequency difference between \(E_{2g}\) and \(A_{1g}\) modes as a function of layer number. In comparison with figure 2(b), the frequency difference of \((1+n)L\)-\(t\) \(MoS_2\) clearly increases after annealing treatment. The shifts in Raman characteristic peaks indicate the enhancement of interlayer coupling and the significant vdW interaction between two stacked \(MoS_2\) layers. Moreover, for samples of the same thickness, the frequency difference of twisted \(MoS_2\) is less than the pristine \(MoS_2\). This demonstrates that the interlayer coupling of the non-Bernal-stacked \(MoS_2\) is weaker than the perfectly stacked \(MoS_2\). Figures 3(b) and (c) show the Raman modes’ line widths of annealed \(MoS_2\) samples. Unlike the room temperature samples, the \(A_{1g}\) mode line widths of twisted and pristine \(MoS_2\) show different tendencies with layer number after annealing. For the annealed twisted \(MoS_2\), the line widths of the \(A_{1g}\) mode decrease monotonically with the increasing sample thickness. This may imply that the residues are efficiently removed after thermal annealing and the two pristine \(MoS_2\) flakes interact with each other to produce a stronger interlayer coupling, thereby inducing the change of interlayer force constants.

Since a \(MoS_2\) layer consists of S and Mo – two types of atom – we employ a diatomic chain model (DCM) to roughly calculate the interlayer coupling force of \((1+n)L\)-\(t\)-\(MoS_2\) \((n = 1, 2, 3, 4)\) [47]. According to the lattice structure of pristine \(MoS_2\) layers, we can express its linear chain model as shown in figure 4(a). Then, the lattice vibrations of \(MoS_2\) are approximated to simple harmonic motions and described by the interaction force constants between two atoms. In order to simplify the calculation, we assume that only the nearest-neighbor interlayer has an interaction [48]. However, owing to the change of stacking order, the interlayer coupling
between the non-Bernal-stacked layers may not be the same as the pristine Bernal-stacked layers\textsuperscript{49}. We denote $t_a$ as the force constant per unit area between the two nearest S planes in two twisted interface layers and $s_a$ as the force constant per unit area between the nearest S and Mo planes in two twisted sub-layers adjacent to the interface. The force constant per unit area between Bernal-stacked layers away from the interface is denoted as $s_s$ and $s_m$ respectively for S–S planes and S–Mo planes, which are determined by pristine MoS$_2$. In 1L-MoS$_2$, we measure the frequencies of $E_{2g1}$ and $A_{1g}$ modes $\sim 402.8$ cm$^{-1}$ and 385.8 cm$^{-1}$. Then, the dynamical matrix can be constructed and analytically solved to get $s_s$ and $s_m$. Similarly, $s_s$ and $s_m$ are obtained by fitting a NL-MoS$_2$ dynamical matrix and numerically solving\textsuperscript{47}. The force constant values of pristine MoS$_2$ are shown in table 1(a) and other calculation values are also given for comparison. The calculation results are in good agreement with other references\textsuperscript{43, 47, 50, 51}. For twisted MoS$_2$, the interlayer force constants are illustrated in figure 4(b) taking (1+2)L for example and then the dynamical matrix can be constructed as follows,

\[
\begin{bmatrix}
\alpha_{ss} & \alpha_{sm} & m_s \omega_s^2 - \alpha_{sm} - \alpha_{st} & \alpha_{st} & m_s \omega^2 - \alpha_{st} - \alpha_t \\
\alpha_{sm} & m_{Mo} \omega^2 - \alpha_{sm} - \alpha_{st} & \alpha_{st} & m_s \omega^2 - \alpha_{st} - \alpha_t & \alpha_{t} \\
\alpha_{st} & m_{Mo} \omega^2 - \alpha_{st} - \alpha_{sm} & \alpha_{sm} & m_{Mo} \omega^2 - \alpha_{sm} - \alpha_{ss} & \alpha_{ss} \\
\alpha_{sl} & m_s \omega^2 - \alpha_{ss} - \alpha_{sm} & \alpha_{sm} & m_s \omega^2 - 2 \alpha_{sm} & \alpha_{s} \\
\alpha_{sl} & m_{Mo} \omega^2 - 2 \alpha_{sm} & \alpha_{sm} & m_{Mo} \omega^2 - \alpha_{sm} & \alpha_{m} \\
\end{bmatrix}
\]

\[m_s, (m_{Mo})\] is the atomic mass per unit area of S (Mo), $m_s = 0.6 \times 10^{-7}$ g cm$^{-2}$ and $m_{Mo} = 1.8 \times 10^{-7}$ g cm$^{-2}$. Based on the experimental $E_{2g1}$ and $A_{1g}$ modes frequencies.
of twisted MoS$_2$, we fit the interlayer force constants both parallel and perpendicular to the basal plane, which are summarized in table 1(b).

The interlayer force constants in the parallel direction determine the $E_{2g}^{1}$ vibration mode corresponding to shear forces, while those in the perpendicular direction determine the $A_{1g}$ vibration mode corresponding to adhesive force. As shown in table 1(b), the interlayer adhesive force has increased by $\sim 20\%$ after the thermal annealing treatment, indicating a thermal-enhanced interlayer coupling. These values also suggest that the shear force of the interface between the twisted layers is weaker than the Bernal-stacked layers. Moreover, compared to pristine MoS$_2$, the adhesive force between S–S planes in the twisted interface increases $\sim 9\%$ due to the modification of interlayer coupling, whereas there is almost no change in the adhesive force between S–Mo planes next to the interface.

4. Conclusion

In conclusion, MoS$_2$ structures with twisted layers were fabricated by mechanical exfoliation and atomically non-destructive transfer technique. We develop an approach for enhancing the interlayer coupling of twisted MoS$_2$ by the thermal annealing at elevated temperatures. We find that the thermal treatment can effectively promote the MoS$_2$ layers’ interface and enhance the interlayer coupling. The interlayer coupling forces of twisted MoS$_2$ are roughly calculated by a DCM model to verify the enhancement. The values show that the interlayer adhesive force increased by $\sim 20\%$ after annealing treatment, which is in good agreement with our predictions. We use Raman scattering measurements to study the evolution of $E_{2g}^{1}$ and $A_{1g}$ Raman active modes in twisted MoS$_2$ flakes. We observe an increase of frequency difference between the two Raman modes with increasing number of layers, the same as pristine MoS$_2$. However, for the equal layers, the frequency difference of twisted MoS$_2$ is less than the pristine MoS$_2$, indicating that the interlayer coupling
The results shown here open the door to the modification of the mechanical and photoelectric properties of MoS$_2$ materials by engineering the twisting angle and stacking structure between the MoS$_2$ layers. The study can be further utilized in developing optoelectronic devices and superlubricity materials.

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