Thermal Modulation of Photoluminescence from Single-Layer MoS$_2$

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The first mechanical exfoliation$^1$ of graphene from graphite in 2004 lead to emergence of various related two-dimensional crystals that can be practically defined as one or few-atom-thick crystalline materials. Graphene,$^2$ MoS$_2$,$^3$ and h-BN$^4$ representing respectively the conducting, semiconducting and insulating two-dimensional material groups have great potentials in the applications such as nano-electronics, transparent conductive electrodes, barrier materials, multifunctional composites, etc. Their unique electronic structures mainly invoked for their promising applications are distinct from those of their bulk counterparts and originate from the electronic confinement within a few atoms along the z-axis or equivalently lack of interlayer interaction.$^5$

Unlike the conducting graphene, single-layer (1L) MoS$_2$ with a direct bandgap of 1.8 eV exhibits strong photoluminescence (PL)$^3,6$ and has revealed unique optical properties such as thickness-dependent PL quantum yield,$^3,6$ valley polarization,$^7$ exciton-trion equilibrium,$^8$ etc. 1L MoS$_2$ is in fact a trilayer entity consisting of one hexagonal Mo atom layer sandwiched by two S atom layers with trigonal prismatic coordination by 6 S atoms per Mo atom.$^9$

Bulk 2H-MoS$_2$ with an indirect bandgap of 1.2 eV,$^3$ the most common polypeptide found in the natural molybdenite, can be formed by repeating a Bernal-like van der Waals stack of two 1L MoS$_2$ layers with lattice constants of $a = 0.316$ nm and $c = 1.229$ nm.$^{10}$ As decreasing the number of layers or thickness, the electronic structure of MoS$_2$ undergoes a change from the indirect bandgap to the direct bandgap$^3,6$ and its lattice vibration also exhibits unique and anomalous progressions for $E_{12g}$ and $A_{1g}$ modes,$^{11}$ suggesting that its various other material properties should also be affected.

Since PL serving as a sensitive probe for the electronic structure is strong for 1L unlike the bulk MoS$_2$, PL spectroscopy has recently been a key diagnostic method for the two-dimensional MoS$_2$ along with Raman spectroscopy.$^3,6$

In particular, it was shown that the PL intensity can be modulated by electrostatic control of excess charge carriers in 1L MoS$_2$. $^{8,12}$ This fact in turn suggests that the charge density can be determined by the PL spectroscopy, which will allow us to explore otherwise overlooked subtle interfacial charge transfer reactions occurring between the two-dimensional materials and the environment.

In this study, we report that the PL intensity can be thermally modulated by annealing 1L MoS$_2$ in a vacuum or H$_2$ gas. The increase in the hole density and PL intensity induced by annealing in a vacuum was attributed to O$_2$-induced charge transfer occurring at the MoS$_2$-silica interface. Thermal treatment in the H$_2$ atmosphere induced decrease in the PL intensity, thus rise in excess electron density. This study demonstrates the thermal control of the photophysical properties of 1L MoS$_2$ and the diagnostic utility of the PL spectroscopy in the interfacial sciences.

Figure 1(a) shows the optical micrograph of thin MoS$_2$ samples prepared by the micromechanical exfoliation. The typical size of thin flakes was several microns across.

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![Figure 1](image-url)
Thicker layers appear darker due to the increasing optical density, which can be useful in locating appropriate flakes on the SiO$_2$/Si substrates. The AFM image in Figure 1(b) shows that the basal planes of the flakes are highly flat and that there is discrete height difference between layers of different thickness. The height profile across the 1L-3L-2L area in Figure 1(c) reveals that the average thickness of one layer is ca. 0.67 ± 0.05 nm, which agrees well with the interplanar distance of bulk 2H-MoS$_2$ crystals.

The number of layers and crystalline quality of the prepared samples were further investigated using Raman and PL spectroscopy. Raman spectroscopy, in particular, has been widely used to determine various properties of graphene such as thickness, defects, charge density, mechanical strain, etc. Recently, Lee et al. demonstrated a similar diagnostic usage of Raman spectroscopy in determining the thickness of MoS$_2$ samples. It is known that bulk 2H-MoS$_2$ has 4 Raman active normal modes in the long wavelength limit. Since $E_{1g}$ (~287 cm$^{-1}$) and $E_{2g}$ (~34 cm$^{-1}$) for the shearing C mode are not typically observed with commercial single-grating Raman instruments that operate in a backscattering geometry, the two remaining modes, $E'_{2g}$ (384 cm$^{-1}$) and $A_{1g}$ (408 cm$^{-1}$), have been routinely monitored for the diagnostic purpose. As decreasing the thickness, it was found that the peak frequency of $A_{1g}$, $\omega(A_{1g})$, gradually down-shifted, reaching 403 cm$^{-1}$ for 1L. The mode stiffening in $A_{1g}$ with increasing thickness can be easily understood in analogy with two mechanical harmonic oscillators coupled by a weak spring which increases the overall restoring force, thus resulting in a resonance frequency higher than that of a single isolated oscillator. However, the observation that $E'_{2g}$ softens with increasing thickness contrasted the simple mechanical model. A recent theoretical work attributed this anomalous phonon dynamics to thickness-dependent dielectric constant which is larger for thicker MoS$_2$. In essence, the ionic bonding between Mo and S atoms will be less screened in 1L MoS$_2$ than thicker ones, resulting in the anomalous frequency change. The Raman spectra obtained from pristine 1L-3L MoS$_2$ in Figure 2(a) nicely reproduced the findings of Lee et al. For our pristine samples, $\Delta\omega$ was ~19.0, ~21.5 and ~23.5 cm$^{-1}$ respectively for 1L, 2L and 3L, which agrees with the literature.

The PL spectra of the pristine samples shown in Figure 2(b) were also consistent with the previous studies, confirming the high quality of the employed samples. The prominent PL peaks denoted A (~1.84 eV) and B (~2.00 eV) originate respectively from the A and B excitons that are...
split due to the spin-orbit coupling in the valence band.\(^3\) It is also be noted that the thickness-normalized PL intensity is the higher for the thinner layer. This apparent anomaly can be attributed to the indirect-to-direct bandgap transition when the number of layers reaches 1L.\(^3\) Regarding this, Mak et al. showed that the PL quantum efficiency of freestanding 1L MoS\(_2\) can be \(\sim\)1000 times higher than that of bulk counterpart.\(^4\) In order to investigate the possibility of thermally modulating the PL efficiency, 1L samples were annealed at elevated temperatures in a vacuum or high purity H\(_2\) gas followed by the Raman and PL measurements. Figure 3(a) shows that the Raman spectra underwent negligible changes for either treatment except the slight peak frequency changes for the H\(_2\)-annealed 1L, which turned out to be sample-dependent. We speculate the changes are mainly due to thermally induced mechanical strain and charge doping as observed in graphene.\(^19\) In contrast, the PL spectra in Figure 3(b) exhibited drastic changes for both cases. We first note that the vacuum-annealing increased the PL intensity (I\(_A\)) and peak energy (E\(_A\)) of A exciton by \(\sim\)60\% and \(\sim\)20 meV, respectively. When annealed in H\(_2\) gas, however, the opposite change was observed for the A exciton peak as shown by \(\sim\)50\% and \(\sim\)20 meV decreases in I\(_A\) and E\(_A\). It is to be noted that the PL signal attenuated by the H\(_2\)-treatment can be recovered by subsequent annealing in a vacuum (Fig. 3(b)), indicating that the change is reversible and thus unlikely due to structural defects in MoS\(_2\). This result indicates that the electronic property of MoS\(_2\) is greatly affected by the chemical nature of the ambient gas used in the thermal treatment.

In Figure 4, we systematically investigated the thermally induced PL intensity changes for both A and B peaks. When annealed at 200 °C in a vacuum, there was no significant change in I\(_A\). However, I\(_A\) increased by \(\sim\)85\% with respect to that of its pristine state when annealed at 300 °C. Further increase in the annealing temperature led to smaller enhancement, which finally returned back to zero for the annealing temperature of 500 °C. In contrast, the thermal treatment in H\(_2\) gas induced a very different change in I\(_A\). Whereas H\(_2\)-annealing at 200 °C resulted in \(\sim\)80\% increase in I\(_A\), the PL intensity decreased as increasing the annealing temperature reaching 45\% decrease at 500 °C. It should also be noted that E\(_A\) varied in opposite directions for the two different gas conditions as shown in Figure 3.

The observed PL change can be attributed to annealing-induced variation in charge density of 1L MoS\(_2\). When electrical holes are injected into 1L MoS\(_2\) and deplete the native n-type charge carriers,\(^8\) I\(_A\) increases due to the attenuated nonradiative decay rate of the A exciton.\(^20\) When electrons are introduced instead, enhanced nonradiative decay further decreases I\(_A\). Thus the significant rise in I\(_A\) for 300 °C suggests that the vacuum-annealing injects p-type charge carriers resulting in depletion of native n-type carriers, as proposed by Tongay et al.\(^20\) The decrease in the enhancement at \(>\)300 °C can be explained by the buildup of excess hole carriers that also promote the nonradiative decay of the A excitons.\(^20\)

We note that annealing also induces p-type doping in graphene supported on silica substrates at \(>\)200 °C and the degree of doping increases with increasing temperature of 600 °C.\(^21\) A recent study\(^22\) identified the ambient O\(_2\) and water vapor as the dopants and proposed that they undergo an electrochemical redox reaction by borrowing electrons from graphene, which consequently becomes p-doped. It is also found that the molecular dopants are located between graphene and silica substrates,\(^23\) suggesting the active role of hydrophilic silanol groups. Since the electrochemical potential for the redox couple\(^24\) is lower than the Fermi level of MoS\(_2\),\(^25\) the electron transfer is thermodynamically favorable like the graphene system.\(^23\) Thus, the observed p-doping induced by the vacuum-annealing is attributed to the following electrochemical reaction: \(\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-\), where the electrons are transferred from MoS\(_2\).

The overall PL attenuation caused by the H\(_2\)-treatment is attributed to n-type charge doping based on the PL energy change. The A peak consists of two sub-peaks, A\(^++\) and A\(^-\), which originate from neutral excitons and negatively charged excitons, respectively.\(^4\) Since the latter, also called trions, are formed when neutral excitons are combined through Coulomb attraction with excess electrons, E\(_A\) is \(\sim\)20 meV smaller than E\(_{A0}\). Thus A peak redshifts (blueshifts) and decreases (increases) in intensity due to the enhanced nonradiative decay when MoS\(_2\) is doped with electrons (holes),\(^8\) which agrees with the H\(_2\)-treated MoS\(_2\) shown in Figure 3(b).

Currently, it is not clear how thermal treatment activates the proposed electrochemical reaction in MoS\(_2\)/SiO\(_2\).\(^20\) In
graphene/SiO$_2$ system, thermally induced nanoripples were suggested as active binding sites for the molecular p-type dopants. However, Lee et al. showed that the thermal rippling occurs independently of the p-doping. Inspired by a recent report that the dopants are located between graphene and SiO$_2$ substrates, we propose that the thermal treatment modifies the surface functional groups of SiO$_2$ affecting the affinity for the dopants. The presence of H$_2$ is likely to affect the chemical modification of SiO$_2$, leading to the observed sharp contrast in the PL spectra. The detailed mechanisms for the proposed changes are under systematic investigation and thus beyond the scope of the current report.

In summary, we reported that the PL spectrum of 1L MoS$_2$ was greatly affected by thermal annealing in a vacuum and the change was attributed to the p-type charge doping in MoS$_2$. The presence of H$_2$ gas lead to the opposite n-type doping, suggesting the possibility that the electronic properties can be tuned by a simple thermal treatment in a controlled gas environment.

**Experimental**

Single and few-layer MoS$_2$ were prepared by mechanically exfoliating 2H-MoS$_2$ crystals (SPI, molybdenite) onto a Si wafer substrate covered with a 285 nm thick amorphous SiO$_2$ layer. Thin MoS$_2$ sheets of several μm across were identified under an optical microscope for faster screening and SiO$_2$ a recent report that the dopants are located between graphene and Si wafer substrate covered with a 285 nm thick amorphous SiO$_2$ layer. Raman and PL spectra were obtained with a home-built micro-Raman spectrometer setup that has been described in detail elsewhere. Briefly, an Ar ion laser beam (514.5 nm, 0.17 mW) was focused onto a sample (spot size < 1 μm) using a microscope objective (40X, numerical aperture = 0.60). Back-scattered Raman or PL signal was collected with the same objective and guided to a spectrometer combined with a liquid nitrogen-cooled CCD detector. The overall spectral accuracy was better than 1 cm$^{-1}$ and 1.5 meV for Raman and PL spectra, respectively. Atomic force microscopy (AFM) was also employed to reveal the nano-scopic morphology of the samples. To modify the PL characteristics, some samples were annealed in a vacuum (< 3 mtorr) or H$_2$ gas (99.999%, flow rate = 30 mL/min) using a tube furnace. The annealing time was one hour unless stated otherwise.

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**References**


