Fabrication of Stacked MoS$_2$ Bilayer with Weak Interlayer Coupling by Reduced Graphene Oxide Spacer

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We fabricated the stacked bilayer molybdenum disulfide (MoS$_2$) by using reduced graphene oxide (rGO) as a spacer for increasing the optoelectronic properties of MoS$_2$. The rGO can decrease the interlayer coupling between the stacked bilayer MoS$_2$, and retain the direct band gap property of MoS$_2$. We observed a twofold enhancement of the photoluminescence intensity of the stacked MoS$_2$ bilayer. In the Raman scattering, we observed that the E$_{2g}^{1}$ and A$_{1g}$ modes of the stacked bilayer MoS$_2$ with rGO were further shifted compared to monolayer MoS$_2$, which is due to the van der Waals (vdW) interaction and the strain effect between the MoS$_2$ and rGO layers. The findings of this study will expand the applicability of monolayer MoS$_2$ for high-performance optoelectronic devices by enhancing the optical properties using a vdW spacer.

The recent discovery of a new class of two-dimensional (2D) materials, transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS$_2$) and tungsten disulfide (WS$_2$), has attracted attention because of their unique layer-dependent electrical and optical properties$^{1-3}$. For example, MoS$_2$ possesses an indirect band gap of ~1.29 eV in bulk, but it becomes a direct optical band gap of ~1.90 eV in the monolayer and can affect the electronic and optical properties$^4$. These interesting features in MoS$_2$ have opened up new possibilities for optoelectronic applications$^5$. Previous reports have mainly focused on the fabrication of optoelectronic devices, such as phototransistors, photodetectors, light-emitting diodes, and solar cells with monolayer MoS$_2$$^7$–$^{10}$. However, the absorbance of monolayer MoS$_2$ is not strong enough to realize efficient optoelectronic devices$^4$. Compared to the monolayer, bilayer or few-layer MoS$_2$ shows improved absorbance and carrier mobility$^{11}$. However, few-layer MoS$_2$ has an indirect band gap that limits its applicability for high-efficiency optoelectronic devices. Therefore, many researchers have worked to improve the mobility and intensity of the photoluminescence (PL) of MoS$_2$ with doping, strain, and defect engineering$^{12-14}$. More recently, it was reported that artificially stacked TMD with a spacer between the individual layers can improve the optical properties while maintaining the intrinsic properties of TMD$^{15-18}$. Among them, Piljae Joo et al$.$ demonstrated an enhancement of the photoluminescence (PL) of stacked few-layer MoS$_2$ with a polymer spacing layer. However, this method has been realized with few-layer or multilayer MoS$_2$$^{15}$. For the stacking of monolayer TMD, hexagonal boron nitride (h-BN) was introduced as the spacer for the TMD hetero-bilayer or homo-bilayer$^{16-18}$. These results suggest that stacked TMD with the h-BN layer can retain the direct band gap feature of the monolayer TMD. However, the procedure for transferring h-BN onto TMDs is somewhat complicated; thus, it is difficult to apply it to large areas. Therefore, it is essential to devise a simple technique that can be implemented easily into the device-fabrication process to obtain higher optoelectronic properties.

Here, we demonstrate the fabrication of stacked MoS$_2$ with a reduced graphene oxide (rGO) spacer. rGO has remarkable properties, such as high thermal conductivity, electrical conductivity, and mechanical stability$^{19}$. rGO can decrease the interlayer coupling of stacked MoS$_2$, such that rGO is an ideal sheet to decouple the top and bottom MoS$_2$, and retain the direct band gap property of MoS$_2$. We observed an enhancement of the PL intensity of stacked MoS$_2$ with an rGO spacer compared to that of monolayer MoS$_2$. We also systematically investigated the origin the structural, chemical, and optical properties of the stacked MoS$_2$ with/without spacer layer.

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Results and Discussion

Figure 1a illustrates the preparation process of stacked MoS2. The chemical vapor deposition (CVD)-grown monolayer MoS2 films were transferred onto the 300-nm-thick of SiO2/Si substrate using the conventional wet transfer method. (See Methods section for details) To prepare stacked bilayer MoS2, another CVD-grown monolayer MoS2 film was transferred onto the monolayer-MoS2/SiO2/Si template. First, we confirmed the basic optical properties of the monolayer MoS2 by using the PL and Raman analysis (Supporting Information (SI), Fig. S1).

Figure 1b shows the PL intensity map of monolayer MoS2 flakes and stacked MoS2 flakes. Normally, the PL intensity of bilayer MoS2 is much lower than that of monolayer MoS2 because it has an indirect band gap4,5. Interestingly, we observed that the integrated PL intensity of stacked MoS2 flake (II) is slightly higher than that of the monolayer MoS2 flake (I). It is implied that stacked bilayer MoS2 flake has different optical features that are irrelevant to the layer-dependent optical properties of MoS2.

To confirm the PL peak position of the sample, we extracted the PL spectrum from the stacked MoS2 flakes marked I and II in Fig. 1b. The A and B exciton peak positions at ~1.83 and ~1.98 eV of I and II were almost the same (Fig. 1c). Figure 1d shows the Raman spectra of I and II. We observed the two Raman modes at approximately 383.5 and 401.8 cm−1 of monolayer region I in the stacked MoS2, corresponding to the E1g and A1g modes20. The distance between the E1g and A1g modes was 18.3 cm−1. The A1g and E1g modes of the region II were shifted compared to those of region I, but the distance between the two Raman modes is around 18.2 cm−1, which is related to the monolayer properties of MoS220. We confirmed the same trend from other stacked MoS2 flakes, regardless of stacking angle (see SI, Fig. S2).

Figure 1e shows the PL intensity map of the same stacked MoS2 sample after thermal annealing at ~300 °C for 1 h under nitrogen gas. After thermal annealing, the integrated PL intensity was reduced for all of the stacked MoS2 flakes. The PL intensity of region II is decreased compared to that of region I. In region II of stacked MoS2, the intensity of exciton peak A decreases significantly and is slightly shifted (Fig. 1f). These PL results show a similar characteristic to the natural bilayer21,22. In addition, the distance between the E1g and A1g modes increased from ~18.2 to ~20.6 cm−1, which is somewhat similar to the bilayer properties (Fig. 1g)20. From the PL and Raman results, we found that annealed stacked MoS2 regions have bilayer properties.

To investigate the phenomena of the different optical properties of the stacked MoS2 before and after thermal annealing, we carried out photothermal induced infrared resonance (PTIR) spectroscopy, which simultaneously provides topographical and infrared absorbance (see SI, Fig. S3)23. Fig. 2a,b show the AFM topography images and height profiles of stacked MoS2 before and after thermal annealing, respectively. The
MoS$_2$ on the SiO$_2$/Si substrate. The average thickness of the coated rGO on the MoS$_2$ sheet was approximately is almost identical to the thickness of the bilayer MoS$_2$ spectra of each position of stacked bilayer MoS$_2$ before and after annealing treatment.

5 shown in Fig. 3c, the PL intensity of stacked bilayer MoS$_2$ with rGO (M/rGO/M) region is twice that of rGO on

observed in MoS$_2$ over mechanically exfoliated graphene (MEG) because MEG has semi-metallic properties that

spectroscopy measurement of the GO before and after thermal annealing (see SI, Fig. S5). Figure 3b is the AFM
topography image of the stacked MoS$_2$ with rGO spacer. According to the AFM topography image, the mon-
range of 1.67–2.11 eV of stacked bilayer MoS$_2$ with rGO spacer. The PL intensity map could also be used to dis-

thickness of the monolayer MoS$_2$ with rGO (green dot) is approximately 1.1 nm and that of the stacked bilayer

monolayer and stacked MoS$_2$ region can be distinguished. Additionally, we observed wrinkles and some bubbles on

prepared GO solution was spin-coated at 500 rpm for 5 s, followed by 1500 rpm for 60 s on top of the monolayer

interface for better device performance26. Therefore, it is necessary to find the optimum spacer in the stacked

MoS$_2$ with rGO sample. These seems to be formed during the transfer process (see SI, Fig. S6). The thickness of the monolayer

MoS$_2$ with rGO (green dot) is approximately 1.1 nm and that of the stacked bilayer MoS$_2$ with rGO spacer (orange dot) is approximately 2.7 nm (see SI, Fig. S7). For the spatially resolved optical characterization, confocal PL and Raman measurements were performed for stacked MoS$_2$ with rGO spacer. Figure 3c shows the PL spectra obtained from each position of the sample. We observed the A and B excitons (~1.86 and 2.0 eV) of MoS$_2$ and the Raman G and D bands (~2.13 and 2.16 eV) of the rGO at PL spectra 12. As shown in Fig. 3c, the PL intensity of stacked bilayer MoS$_2$ with rGO (M/rGO/M) region is twice that of rGO on monolayer MoS$_2$ (rGO/M) or monolayer MoS$_2$ on rGO (M/rGO) regions. In previous reports, PL quenching was observed in MoS$_2$ over mechanically exfoliated graphene (MEG) because MEG has semi-metallic properties that result in a metal-semiconductor interface27,28. On the other hand, rGO show semiconductor behavior because of residual oxygen functional groups after thermal annealing29,30. Therefore, PL quenching is not observed in the interface between rGO and MoS$_2$ stacked structure. Figure 3d represents the PL intensity map for the energy range of 1.67–2.11 eV of stacked bilayer MoS$_2$ with rGO spacer. The PL intensity map could also be used to distinguish the stacked M/rGO/M, M/rGO, and rGO/M regions because these PL intensity values are different from
each other. As observed in Fig. 3d, some position of rGO/M region has a higher PL intensity rather than the M/rGO/M region. To compare the intensity, we extracted the PL spectra of bright spot of rGO/M region and M/rGO/M region (see SI, Fig. S8). According to previous report, GO induce the p-type doping of monolayer MoS2 because of the functional groups of GO 12. We believe that the cause of high PL intensity in the rGO/M region is p-type doping by residue of functional group after thermal annealing. A slight red shift in the A exciton peak is observed in the M/rGO/M region. In addition, the PL peak position of the stacked MoS2 with rGO sample is different (Fig. 3e). We confirmed that the PL results at stacked MoS2 with rGO spacer showed different characteristics from those of the stacked MoS2 without rGO spacer.

To clarify the cause for the considerably changed optical and structural properties of stacked MoS2 with rGO spacer, we have performed confocal Raman mapping. Figure 4a shows the Raman intensity map of the stacked MoS2 with rGO. The Raman intensity map provides distinguishable contrast between the stacked and monolayer MoS2 regions. Figure 4b shows the local Raman spectra of each position. The peak positions of the two Raman modes of stacked MoS2 with rGO spacer are different from those of the stacked MoS2 without spacer. The A1g and E1 2g modes of stacked MoS2 with rGO were further shifted compared to those of stacked MoS2 without spacer. In order to understand these results, we focus on the E1 2g and A1g modes of MoS2, depending on the region. Figure 4c presents the Raman intensity of the E1 2g and A1g modes of the MoS2 according to each position. The higher Raman intensity of the M/rGO/M region originates from the increased scattering cross section by stacked MoS2 with rGO. Figure 4d shows the peak position of the two Raman modes according to the position of the stacked MoS2 with rGO spacer. The E1 2g and A1g modes of the stacked MoS2 with rGO spacer were observed to shift to the opposite direction compared to that of pristine monolayer MoS2 (M). Interestingly, we observed that the red shift of E1 2g on M/rGO/M is large compared to M/rGO and rGO/M, which is shown in the Raman peak position map in Fig. 4e. Furthermore, the full width at half maximum (FWHM) of the E1 2g peak of M/rGO/M broader than that of other regions (Fig. 4f). This indicates that interfacial strain is generated more on the M/rGO/M than on the M/rGO and rGO/M 31,32. In contrast, the blue shift of A1g on M/rGO and rGO/M is larger than the shift observed in M/rGO/M, which is confirmed in the Raman map shown in Fig. 4g. The FWHM of the A1g peak of M/rGO/M slightly broader than that of other regions (Fig. 4h). This means that the van der Waals (vdW) interlayer interaction between the MoS2 and rGO on M/rGO and rGO/M is stronger than that of M/rGO/M. According to the previous results, the blue shift of A1g of MoS2 can originate from the p-doping effect by the functional group of GO 12,33. The A1g peak appeared to be more strongly shifted as the amount of GO functional groups increased 12. In this study, rGO was prepared with GO by thermal annealing. Thus, most functional groups of GO were removed and only a small amount of the functional group remained on the surface 25. In addition, we confirmed that the A1g mode of stacked MoS2 with rGO was further shifted compared to stacked MoS2 with GO (see SI, Fig. S9). This means that p-doping of MoS2 by rGO has a negligible effect on the shift of the A1g peak observed in our stacked MoS2 with rGO. Therefore, it is concluded that the stacked MoS2 with rGO spacer is in close contact with vdW interaction between MoS2 and rGO. We suggest that the rGO can serve as a spacer to decouple the top and bottom MoS2 and retain the direct band gap of MoS2.

Conclusions
In conclusion, we successfully fabricated stacked bilayer MoS2 with rGO spacer. We observed that the decreased PL intensity in the stacked MoS2 layers without spacer because of bilayer properties. Meanwhile, when the rGO is used as a spacer in between MoS2 sheets, PL intensity shows sum up of PL from two individual MoS2 sheets. It clearly indicates that rGO is a suitable material to decouple the top and bottom MoS2 and retain the direct band gap of MoS2. In the Raman results, we observed the vdW interaction and the strain effect between the MoS2 and
rGO layers. We expect that these results will provide a fundamental understanding of the interlayer interaction of stacked 2D materials and enable further development of stacked MoS₂-based devices.

Methods

Conventional wet transfer method. Poly(methyl methacrylate) (PMMA) (Micro Chem, 4 wt% in chlorobenzene) was coated onto monolayer MoS₂ grown on a SiO₂/Si substrate to serve as a supporting layer for the transfer process. After being coated with PMMA, the sample was floated on a 1 M potassium hydroxide (KOH) solution at 80 °C to remove the SiO₂ layer. Subsequently, only monolayer MoS₂ with PMMA remained on the KOH solution. The remaining PMMA/MoS₂ was washed with DI water to remove any residual KOH etchant. The washed PMMA/MoS₂ was transferred to the SiO₂/Si substrate. After the drying process was complete, the PMMA was removed using acetone.

Preparation of the GO. GO was synthesized from natural graphite (Alfa Aesar, 99.999% purity, 200 mesh) by modified Hummers’ method. First, 5 g of graphite powder and 350 mL of 10 M Sulfuric acid (H₂SO₄) were blended. KMnO₄ (15 g) was slowly added over approximately an 1 h. Stirring was continued for 2 h in a cooled water bath. The mixture was strongly stirred for 3 days at room temperature. Deionized water was added and stirring for 10 min. The mixture was stirred for 2 h at room temperature after the addition of an aqueous solution of H₂O₂ (30 wt%). Aqueous solution of HCl (35 wt%) was then added and stirred for 30 min at room temperature. After the supernatant solution was decanted, deionized water was slowly added and stirred for 30 min. The GO solution 1 g/l in water was sonicated for 1 h to exfoliate the GO sheets. To obtain dispersed GO, centrifugation at 10,000 rpm was performed for 1 h, and the supernatant solution was decanted.

Characterization Methods. PL spectra were obtained using a confocal PL spectrometer equipped with an objective lens with high numerical aperture of 0.7 and a diode-pumped solid-state laser (532 nm). Confocal
Raman spectroscopy was conducted using a commercial multifunctional microscope (NTEGRA, NT-MDT). The atomic force microscopy (AFM) topography image and photothermal induced infrared resonance (PTIR) absorption of the sample was obtained using a commercial Nano-IR system (Anasys Instruments).

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Author Contributions
H.M.O. and M.S.J. designed the experiments. H.M.O. and H.K. fabricated the stacked MoS2 sample conducted the Nano I.R. experiment. H.M.O. performed P.L. and Raman experiments. H.K. performed growth experiments for graphene. H.M.O. and M.S.J. analyzed the results and wrote the manuscript. All authors discussed the results and commented on the manuscript.
Additional Information

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