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Strongly enhanced photoluminescence in nanostructured monolayer MoS$_2$ by chemical vapor deposition

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Abstract

Two-dimensional (2D) layered molybdenum disulfide (MoS$_2$) has become a very promising candidate semiconducting material for future optoelectronic devices, owing to its unique properties. However, monolayer MoS$_2$ is still a weak photon emitter, compared with other direct band gap semiconductors, which requires extra techniques or complicated steps to enhance its photon emission efficiency. Here, we demonstrated that nanostructured monolayer MoS$_2$, produced by one-step chemical vapor deposition (CVD) growth, shows highly enhanced PL emission. The effective enhancement factor could be up to ~43. Our results open the door to manipulating the optical properties of future devices by using nanostructured 2D monolayers.

Keywords: MoS$_2$, photoluminescence enhancement, 2D, edge states

Due to their highly active edge sites, molybdenum disulfide (MoS$_2$) nanomaterials have shown exceptionally promising applications in various fields, including nanotribology [1], photocatalysis [2], the hydrodesulphurization (HDS) process [3], hydrogen evolution reaction (HER) catalysis [4, 5], saturable absorption in ultra-fast photonics [6, 7] and solar cells [8]. Recently emerging two-dimensional (2D) atomically thin MoS$_2$ materials have also attracted extensive investigations [9–16], due to their great potential applications for future electronic and optoelectronic devices, like field effect transistors, light emitting devices, photodetectors, etc. MoS$_2$ is very stable in ambient conditions, which is in great contrast to other unstable 2D semiconductors like black phosphorus [17–21], MoTe$_2$ [22, 23], etc. The band gap nature of MoS$_2$ changes from indirect to direct as the layer number is thinned down to a monolayer [13], which leads to extraordinary photoluminescence (PL) and strongly enhanced optoelectronic responses in monolayer MoS$_2$. However, the PL of monolayer MoS$_2$ is still weaker than we would expect for a high-quality direct band gap emitter, mainly because of the intrinsic defects and heavy intrinsic n-type doping in monolayer MoS$_2$ [12]. Various techniques have been reported to enhance the PL efficiency of monolayer MoS$_2$, such as carrier density engineering via electrical static gating and chemical doping [24–26], absorption enhancement through plasmonic nanostructures [27, 28] and defect engineering by plasma irradiation [29–31]. All those methods require extra fabrication steps, which potentially increases the cost. Here, we demonstrated that nanostructured monolayer MoS$_2$ produced by one-step chemical vapor deposition (CVD) growth shows highly enhanced PL emission, compared with large-size monolayer MoS$_2$ samples prepared by mechanical exfoliation [32] and CVD growth [33–36]. The PL enhancement is mainly due to the large amount of edge states associated with the nanostructured MoS$_2$. This type of edge states induced PL enhancement was also observed in CVD-grown WS$_2$ flakes [37]. Our method opens the door for high-performance optoelectronic devices based on nanostructured monolayer MoS$_2$.
MoS$_2$. Besides, since the nanostructured MoS$_2$ flakes are small in size, they could be dispersed in liquid-like liquid crystal to make them as a module of optoelectronic devices [38]. Furthermore, nanostructured MoS$_2$ flakes could also possibly serve as nanocatalysts owing to their highly enhanced surface area [4].

Here, we aim to fabricate nanostructured monolayer MoS$_2$ using CVD, which has a large amount of edge states for PL enhancement (figure 1). The growth condition for nanostructured monolayer MoS$_2$ is slightly different from that for large-size monolayer MoS$_2$ growth. The main difference is that we used two steps in the growth process. During the first step, a MoO$_3$ source was thermally evaporated quickly and was deposited on a substrate to form plenty of nucleate sites on the substrate. A large quantity of these nucleate centers offered a good condition to form nanostructured monolayer MoS$_2$, since molecules tended to bond into nucleate centers rather than the edge of the MoS$_2$ surface. In the second step, we quickly introduced sulphur powder to the 150 °C temperature zone, by using a magnetically controlled set-up. A vast amount of sulphur vapor was introduced and the increased sulphur partial pressure resulted in the formation of nanostructured MoS$_2$. The grown MoS$_2$ nano-disk monolayer showed quasi-hexagonal shape and a size ~100 nm and these nano-plates were randomly distributed on the SiO$_2$/Si substrate (figures 1(a) &c(c)). The monolayer thickness was confirmed by atomic force microscopy (AFM) height analysis (figure 1(c)).

The optical properties were studied by micro-Raman and PL spectroscopy with a 532 nm laser as the excitation. The nanostructured monolayer MoS$_2$ sample shows two strong Raman peaks at 384 and 404 cm$^{-1}$ (figure 2(a)), which correspond to the in-plane $E_{2g}^\text{L}$ and out-plane $A_{1g}$ of monolayer MoS$_2$, respectively [39]. The Raman spectrum of our nanostructured monolayer MoS$_2$ is comparable with those of large-size MoS$_2$, which are also shown in figure 2(a). The Raman peak at ~456 cm$^{-1}$ involves two longitudinal acoustic phonons (2LA(M)) arising from the edge of the Brillouin zone (BZ) [40, 41]. Besides the nanostructured monolayer MoS$_2$, we also fabricated large-size monolayer MoS$_2$ samples by CVD (see supplementary information) and one large-size 1L MoS$_2$ by mechanical exfoliation (figure 1(d)) as the control samples. The exfoliated MoS$_2$ sample has a PL peak at ~1.83 eV (trion peak of MoS$_2$), which is due to the intrinsic
n-type doping in the exfoliated MoS$_2$ samples [26]; on the other hand, the nanostructured CVD monolayer MoS$_2$ (figure 2(b)) and the large-size monolayer CVD MoS$_2$ samples have a PL peak at $\sim$1.87 eV (neutral exciton peak of MoS$_2$), which indicates that both of those two CVD samples have a low or even comparable initial doping level. The energy difference between trions and excitons in our experiment is compatible with previous results [26]. This also proves that the nanostructured monolayer MoS$_2$ possesses the same energy band gap as the large-size monolayer MoS$_2$ samples. The large-size monolayer MoS$_2$ by CVD shows comparable PL intensity with the exfoliated monolayer MoS$_2$, which is consistent with previous reports [34, 35]. But interestingly, the PL intensity from the nanostructured monolayer MoS$_2$ was around 3.5 times higher than those from the large-size CVD monolayer MoS$_2$ and exfoliated monolayer MoS$_2$ samples (figure 2(b)). In experiments, we fabricated at least three batches of CVD monolayers, exfoliated MoS$_2$ monolayers and nanostructured monolayer MoS$_2$ samples to obtain statistical PL intensity values. The nanostructured MoS$_2$ monolayers showed an average PL enhancement factor of $\sim$3.4, compared with the CVD large-size monolayers (figure 2(c)). Considering the fact that the area filling ratio of the nanostructured MoS$_2$ is only $\sim$7%, the PL enhancement factor normalized to the area size is up to $\sim$43. We have also calculated the filling ratios and enhancement factors of the five conditions presented in figure 2(c) (see supplementary information). Considering the relatively low initial doping level in both our nanostructured and large-size monolayer MoS$_2$ samples, the doping level difference in our samples could not explain the large PL enhancement factor up to $\sim$43. On the other hand, this large PL...
enhancement in the nanostructured monolayer MoS$_2$ samples could be due to their large amount of edge states, which were also observed in CVD-grown WS$_2$ flakes [37]. Another small peak at $\sim$2.03 eV (B peak) in the PL spectrum corresponds to the valence-band spin-orbit splitting of the direct gap transition at the K point [32]. Interestingly, the intensity of the B peak in the nanostructured 1L MoS$_2$ is lower than that in the exfoliated monolayer MoS$_2$ sample (discussed later).

In experiments, we found that the morphology of the nanostructured MoS$_2$ was very sensitive to the local growth
conditions, such as the density of the nuclear seeds and also the pressure of the sulphur gas. We probed five chips that were placed at different locations of the furnace as shown in figure 3, with chip 1 close to the edge and chip 5 close to the center of the tube. At locations closer to the tube center, higher densities of nuclear sites were deposited, which led to much higher densities of MoS2 flakes (figures 3(a) & (b)). The density of the MoS2 flakes gradually increased from chip 1 to chip 5; however, the PL intensity increased from chip 1 to chip 3 and then decreased gradually from chip 3 to chip 5 (figure 3(c)). This evolution can be understood from the morphology of the nanostructured MoS2 flakes. From the AFM images (figure 3(b)), the density of monolayer MoS2 nano-plates increased from location 1 to location 3, which leads to the increasing of the PL intensity. In chips 4 and 5, multilayer MoS2 nano-plates began to form and these multilayer MoS2 flakes show an indirect band gap nature, leading to lower PL emission efficiency [32] (figures 3(c) & (d)). The prominent PL peaks of these five chips are all located at ~1.87 eV (a peak from neutral excitons of MoS2). In addition, we also recorded the PL intensity of the B peak from each location and compared the intensity ratio of the B peak to the A peak (figure 3(c)). Although B peak intensity showed the same trend as for the A peak, the B/A intensity ratio decreased first then began to increase, suggesting a totally opposite trend compared with the trend of A peak intensity. This means that the nanostructured monolayer MoS2 can enhance the PL emission at the A peak on the one hand, but suppress the emission at the B peak on the other hand. The B peak arises from the direct gap transition between the minima of the conduction band and the lower-level valence-band maxima that is created by valence-band spin-orbit splitting at the K point (figure 3(f)) [42]. The suppression of the emission at the B peak could be because of the enhancement of PL emission at lower-energy emission at the A peak, since the total amount of photo-excited carriers is limited to a constant number.

In order to better understand the decrease of the PL intensity from chip 3 to chip 5, we investigated the mechanism for the formation of multilayer MoS2 nano-plates. Interestingly, we found that the multilayer MoS2 nano-plates have 3D spiral pyramid structures. During our CVD growth, the relatively high sulphur pressure resulted in screw dislocation in the monolayer MoS2 nano-plates, which leads to
the formation of a spiral MoS2 structure, similar to a previous report [43]. Figure 4(a) shows schematics of each stage in figure 4(b). As we can see from the left image of figure 4(b), some atomic clusters formed on the substrate and began to grow up, forming one monolayer MoS2 nano-plate. At the same time, we also noticed that there was one bright spot on the edge of the monolayer MoS2 nano-plate, which was identified as screw dislocation. The incoming molecules tend to combine with these dislocations to decrease the total surface energy [44]. As the nano-plate grows up, the bottom layer keeps extending. Meanwhile, the upper layer also absorbs molecules then grows along with the screw dislocations and forms a bilayer (middle image of figure 4(b)). The top area is always smaller than the bottom layer due to different growth times. This results in a net trend of vertical growth and the formation of a multilayer pyramid structure (right image of figure 4(b)). Those multilayer pyramid MoS2 nano-plates have an indirect band gap nature, similar to multilayer MoS2, leading to the decrease of PL intensity in chips 4 and 5.

Conclusions

In conclusion, we have demonstrated that CVD-grown nanostructured monolayer MoS2 shows strongly enhanced efficiency of photon emission, because of the large amount of edge states. The effective enhancement factor was measured to be up to ~43. Meanwhile, we showed that the formation of the 3D spiral pyramid MoS2 was the reason preventing the further enhancement of PL from these nanostructured MoS2 samples.

Experiment

Methods

Growth of monolayer and multilayer MoS2. Our MoS2 sample was prepared by using ambient CVD with MoO3 and sulphur powder as precursors. The substrate was placed face down onto MoO3 above one quartz sample boat. The boat contained 5 mg MoO3 (≥99.5%, sigma-Aldrich) and was put into the center of a furnace. Another boat containing 200 mg S (≥99.5%, sigma-Aldrich) was placed into a tube but outside the furnace. The system was washed by nitrogen gas with 200 sccm flow rate for 1 h and then ramped up to 700 °C in 30 min. When the temperature went up to 600 °C, the S powder was inserted. At this moment, the temperature for the S powder was 150 °C and then the flow rate was changed from 200 sccm to 50 sccm, to sit for 8 min at 700 °C. Finally it was cooled down to room temperature with 200 sccm N2. Although some different morphologies of MoS2 showed up, the major morphology in each chip at different locations in each batch is consistent. Also, the PL properties are similar in the same distribution area.

Sample characterization

AFM measurement was carried out with a Bruker Multi-Mode III AFM. All PL and Raman measurements were run by a T64000 micro-Raman system and the laser spot has a spatial resolution of sub-1 μm.

References


Butun S, Tongay S and Aydin K 2015 Enhanced light emission from large-area monolayer MoS2 using plasmonic nanodisc arrays Nano Lett. 15 2700–4


[31] Nan H et al 2014 Strong photoluminescence enhancement of MoS2 through defect engineering and oxygen bonding ACS Nano 8 5738–45


[39] Liang L and Meunier V 2014 First-principles Raman spectra of MoS2, WS2 and their heterostructures ACS Nano 8 5394–401


Supplementary Information for

Strongly Enhanced Photoluminescence in Nanostructured Monolayer MoS₂ by Chemical Vapor Deposition

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1. Characterization of large-size monolayer MoS₂ by CVD

**Figure S1 | Characterization of large-size monolayer MoS₂ by CVD.** a, Optical microscope image of monolayer MoS₂ by using chemical vapour deposition method. The triangle shape areas are isolated 1L MoS₂, while the right large part is continuous 1L MoS₂ film. b, Raman spectrum of triangle shape 1L MoS₂ and it was measured in a confocal spectrometer with a 532 nm excitation laser.
2. CVD magnetically controlled set up

Figure S2 | CVD furnace and magnetically controlled set up. a, first step: MoO₃ source thermally evaporated and deposited onto substrate. b, second step: when furnace temperature ramp to 600 °C, quickly inset S power by using magnetic force push evaporator boat into designed location.