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Gap plasmon-enhanced photoluminescence of monolayer MoS_2 in hybrid nanostructure*

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Monolayer transition-metal dichalcogenides (TMDs) have attracted a lot of attention for their applications in optics and optoelectronics. Molybdenum disulfide (MoS_2), as one of those important materials, has been widely investigated due to its direct band gap and photoluminescence (PL) in visible range. Owing to the fact that the monolayer MoS_2 suffers low light absorption and emission, surface plasmon polaritons (SPPs) are used to enhance both the excitation and emission efficiencies. Here, we demonstrate that the PL of MoS_2 sandwiched between 200-nm-diameter gold nanoparticle (AuNP) and 150-nm-thick gold film is improved by more than 4 times compared with bare MoS_2 sample. This study shows that gap plasmons can possess more optical and optoelectronic applications incorporating with many other emerging two-dimensional materials.

Keywords: MoS_2, surface plasmon polaritons, gap plasmons

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1. Introduction

In recent years, different kinds of two-dimensional materials[1–3] have attracted much attention for their applications in optics and optoelectronics. Among them, MoS_2 becomes one of the most important materials due to its unique optical properties, and has found applications in many areas, such as direct bandgap photon source,[4] strong spin-orbit coupling,[5,6] nonlinear optical imaging,[7] spin Hall effect,[8,9] and two-dimensional heterostructures.[10–13] Meanwhile, the development of chemical vapor deposition (CVD) method[14–16] makes the synthesis of MoS_2 more simple and efficient. For monolayer MoS_2, its photoluminescence (PL) wavelength is in visible range, and thus it is widely used in PL sources and optoelectronic devices. However, due to the inherent monolayer thickness (about 1 nm), monolayer MoS_2 suffers low PL efficiency and low quantum yield.[17]

To compensate for this, different kinds of approaches to enhancing the emission of monolayer MoS_2 are proposed, including chemical doping,[18] polymeric nano-spacing,[19] defect engineering,[20] and using surface plasmon polaritons (SPPs).[21–23] Among these methods, SPPs which have been widely utilized for strong light-matter interaction applications such as photoluminescence enhancement[24–31] and surface enhanced Raman scattering,[32,33] could induce hot electrons and cause the phase transition of MoS_2,[34–36] resulting in the enhanced PL in a metal-MoS_2 coupled system.[37–40] For example, gap plasmons have been used in different areas, such as enhancing local chemical reactions,[41] dielectric gratings,[42,43] plasmonic nanocavities,[44–46] and PL of single layer WSe_2.[31]

One way to generate gap plasmons is to deposit metal particles on metal substrates or films, forming strongly localized plasmonic fields in the gap between the metal substrate and metal particles. Additionally, energetic electrons and holes could also be generated in the junction region, which may have applications in plasmon-mediated photocatalysis.[47–50]

In this work, we use MoS_2 sandwiched between Au film and gold nanoparticle (AuNP), i.e., Au–MoS_2–AuNP structure, to study the PL enhancement effect of gap plasmons on monolayer MoS_2. For comparison, the PL of MoS_2 at the position without metal structure is also characterized. The experimental results show that the gap plasmons enhance the PL of monolayer MoS_2 by 4.43 times compared with the bare MoS_2 sample.

2. Experimental method

The experimental setup is shown in Fig. 1. A continuous-wave laser at 532 nm passes through a polarizer and shines through an objective lens (OLYMPUS, NA = 0.9, 100×) onto our sample, which is mounted on a three-axis piezo translation

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stage. The PL of the MoS_2 is collected with the same objective lens and then detected by a single photon avalanche diode (SPAD). By moving the three-axis piezo translation stage, we are able to obtain the PL map of the sample. We also use a spectrograph (Princeton Instruments, Acton SP2500) to analyze the spectrum of the PL emission. A dichroic plate is used to block the excitation laser and let the PL of MoS_2 pass. Two focal lenses each with a focal length of 40-mm together with a 30-μm-diameter pin-hole are used as spatial filtering. We put a long pass filter behind the lenses to remove other stray light in the light path. To obtain the Au–MoS_2–AuNP sample, we first grow monolayer MoS_2 on a 300-nm-thick silica substrate, and transfer it to the gold film using wet transfer method (see "method" titled section attached below). Then the AuNPs are spin-coated at the top of it. To prevent the monolayer MoS_2 from being damaged, the excitation power is kept below 1 mW. All the measurements are performed at room temperature.

(i) CVD growth of monolayer MoS_2 on SiO_2/Si substrate

Monolayer MoS_2 was grown on SiO_2(300 nm)/Si substrate in a quartz tube furnace at atmospheric pressure by a chemical vapor deposition (CVD) method. Prior to growth, SiO_2/Si substrates were cleaned by sonication in acetone, absolute ethanol and distilled water for 20 min in sequence. The substrates were then placed face-down above the ceramic boat that was filled with 30 mg of MoO_3 and which was placed in the center of the quartz tube. Another ceramic boat filled with 10 mg of sulphur was in the upstream of the tube 12 cm away from the center, after purging the system with ultrahigh-purity argon for 20 min, the furnace was kept at 650 °C for 5 min at a heating rate of 15 °C/min.

(ii) Wet transfer

The CVD MoS_2 was transferred from SiO_2/Si substrate using the wet transfer KOH method. Samples were first spin-coated at 2000 rpm with PMMA A4, resulting in a thick polymer film. These were detached in a 30% KOH solution, washed several times in DI water, and transferred onto our prepared samples sequentially, and then the samples were heated up to 180 °C slowly in order to obtain the dry samples. We use acetone to clean the PMMA, and blow-dry the sample by clean N_2 from IPA solution.

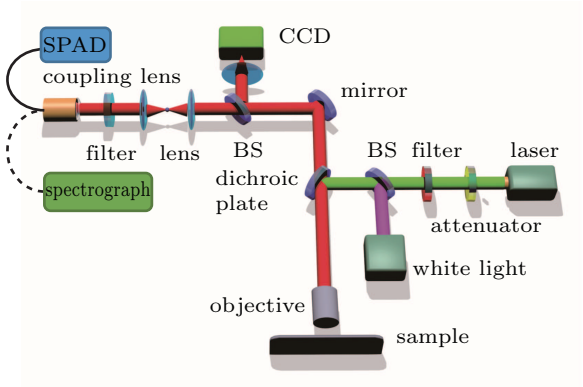


Fig. 1. (color online) Experimental setup for exciting MoS_2 and collecting its emission.

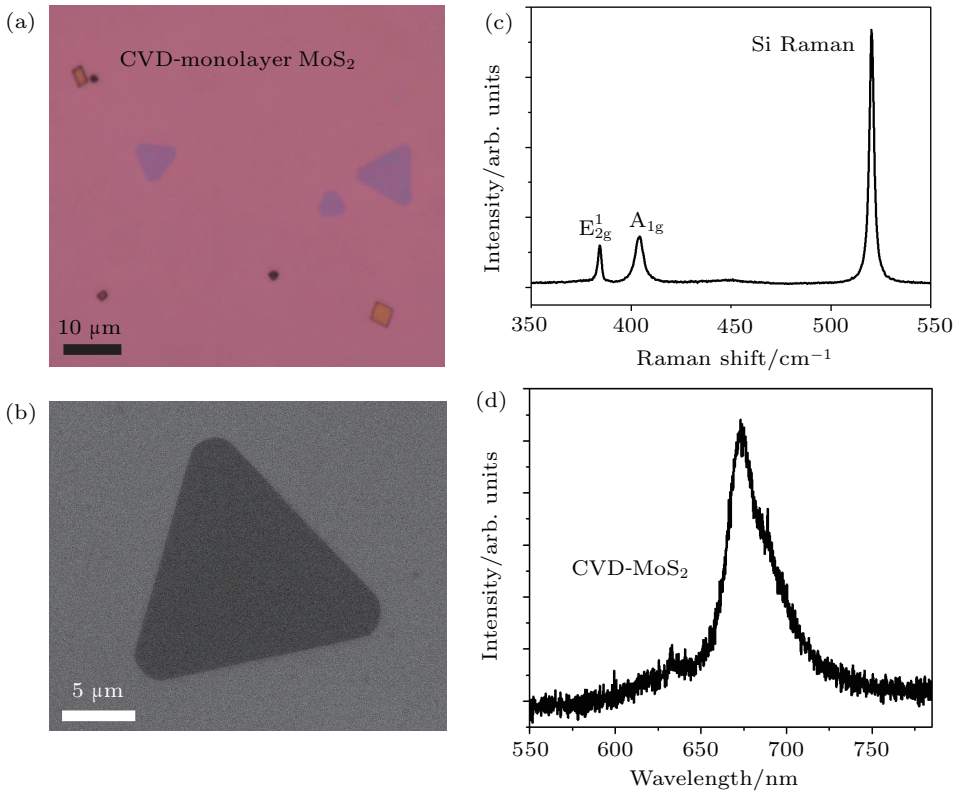


Fig. 2. (color online) (a) and (b)) Optical microscope (OM) and scanning electron microscope (SEM) images of the CVD-grown MoS_2 deposited on SiO_2/Si substrate. (c) Raman spectrum of CVD-MoS_2. (d) Typical PL spectrum of MoS_2 showing a strong emission peak at $\sim$ 670 nm.

In Figs. 2(a) and 2(b), the optical microscope (OM) and scanning electron microscope (SEM) images of synthesized monolayer MoS_2 showtheir high crystallinity and uniformity in large area ($\sim$ 15 μm$\times$15 μm). Figure 2(c) displays the Raman spectrum of the monolayer MoS_2. Two typical peaks for monolayer MoS_2, i.e., E^1_{2g} (in-plane) and A_{1g} (out-of-plane) separated by $\sim$ 20 cm^{-1}, are clearly seen. And from the PL spectrum of the MoS_2 shown in Fig. 2(d), we can also see two peaks around 635 nm and 670 nm, which are consistent with previous results.[17]

For SPPs-assisted PL enhancement, it comes from two parts: enhanced excitation rate due to SPP resonance and enhanced emission rate via Purcell effect.[51] To maximize the excitation rate, the pump wavelength should match with the plasmonic resonance of AuNP. Similarly, the Purcell factor should also be engineered by reducing the mode volume of the plasmonic mode. Therefore, it is better to utilize the extremely confined field of gap plasmons for PL enhancement experiments, rather than an "open" plasmonic cavity like single AuNP. In our experiment, the gap plasmons are formed between spin-coated AuNPs and Au film. The diameter of AuNPs is chosen to be 200 nm, to ensure enough confined electric field but not to block the pump laser.

In SPPs-assisted PL enhancement experiment, special attention should be paid to the quenching effect, which will increase the non-radiative decay of the MoS_2 emission and suppress the PL enhancement.[52]

3. Results and discussion

To better characterize the PL enhancement of gap plasmons, we prepared two kinds of samples: bare monolayer MoS_2 deposited on SiO_2/Si substrate (denoted as sample A) and the hybrid Au–MoS_2–AuNP structure (denoted as sample B). The preparation processes of samples A and B are schematically illustrated in Fig. 3(a). We scan the excitation position of the pump laser, and plot the PL maps of samples A and B in Figs. 3(b) and 3(c), respectively. Sample A has an average PL intensity of 2800, while the maximum PL intensity for sample B is about 6800. By removing a background noise count of $\sim$ 1500, an enhancement of 4.08 times is obtained for gap plasmons. This enhancement refers to all the fluorescent signals being collected.

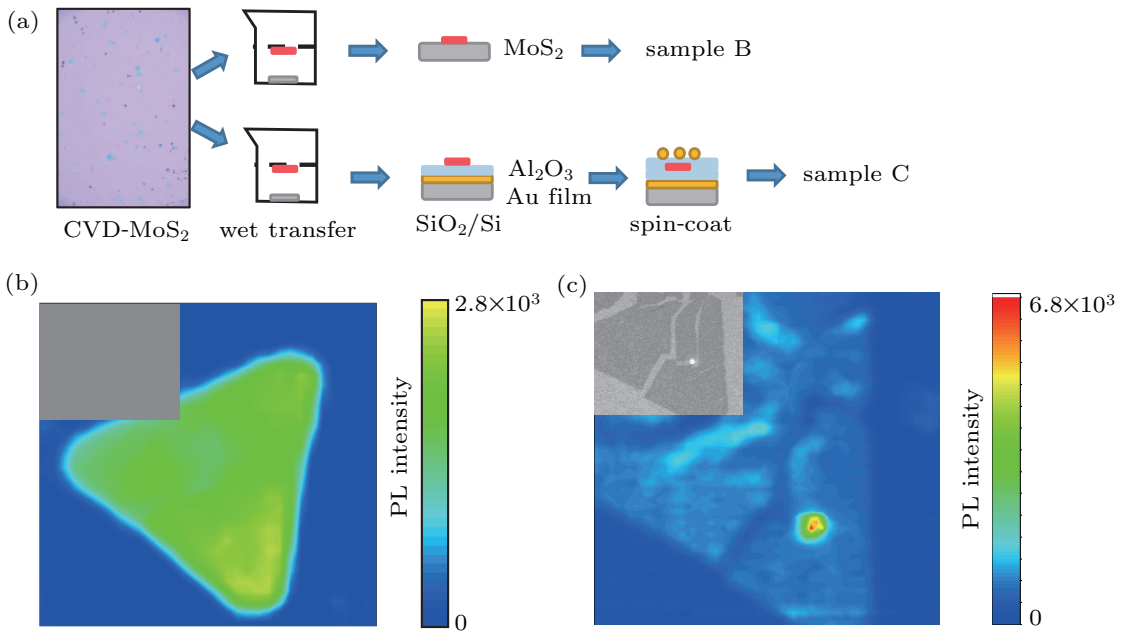


Fig. 3. (color online) (a) Preparation process of samples A and B. (b) PL map and the corresponding SEM image for sample A. (c) PL map and the corresponding SEM image for sample B.

Furthermore, we analyze the spectra of the PL emissions of MoS_2 for different samples. As shown in Fig. 4, we extract the spectra from sample A (black curve), sample B where there is no AuNP (red curve), and sample B where there is an AuNP (blue curve). We can see that when only gold films exist, the count of MoS_2 decreases slightly, which is due to the quenching effect as we mentioned above. We define the enhancement factor as the ratio of the peak PL for Au–MoS_2–AuNP structure to the peak PL for bare MoS_2 (excluding the background noise). It is clearly shown that the PL emission of monolayer MoS_2 is enhanced by about 4.43 times due to gap plasmons.

This enhancement factor can be even greater, if we could reduce the quenching effect. One way is to add an insulator layer, like Al_2O_3. However, it could also weaken the Purcell effect, and thus reducing the PL enhancement of the hybrid structure. Therefore, an optimization of the insulator thickness is necessary. On the other hand, the enhancement factor of gap plasmon is actually higher than the number we give. Consider-

ing the objective lens we used, the diameter of the pump beam is about 720 nm. While the diameter of AuNP is just 200 nm, the contribution of gap plasmons to the collected spectrum is small. If we can further reduce the diameter of the incident light by using an oil objective lens with higher NA, we may obtain a better enhancement and real enhancement factor.

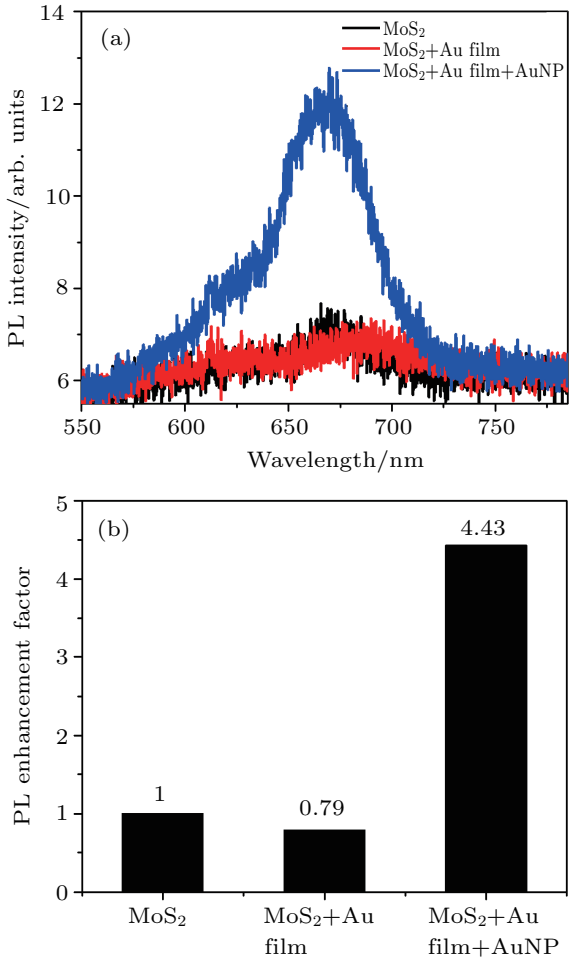


Fig. 4. (color online) (a) Spectra of MoS_2 in different circumstances. (b) PL enhancements of spectral peak of MoS_2 in different circumstances.

4. Conclusions

In this work, we have used a hybrid metal nanostructure to enhance the PL of monolayer MoS_2. We demonstrate that the gap plasmons between the gold particle and gold film enhances the PL by about 4.43 times. These findings inspire us to further apply the optical properties of two-dimensional materials to a series of new fields.

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