Localized and Continuous Tuning of Monolayer MoS$_2$ Photoluminescence Using a Single Shape-Controlled Ag Nanoantenna

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Gaining control over the nanoscale behavior of light is critical in realizing various next-generation technologies, including ultrasmall light sources,[1–3] supercomputing,[4,5] advanced optoelectronic devices,[6] and even nanoscale anticontroling platforms.[7,8] Plasmonic nanomaterials are widely used in tailoring nanoscale light-matter interactions,[9–12] because they support localized surface plasmon resonances (LSPRs) which are capable of confining light into deep subwavelength volumes.[9]

In addition, plasmonic nanomaterials can manipulate the light emission patterns and directions of nearby photoluminescent species.[1,11,12] Despite tremendous progress achieved in understanding the subwavelength behavior of light in this field,[15–18] it remains challenging to design a sub-micron-scale heterogeneous optical platform. On such platforms, optical signals are tightly modulated within highly confined regions, giving rise to a range of tunable optical outputs. These heterogeneous optical platforms form the basis for optical circuit components,[19] logic gates,[20] and data storage.[21]

Conversely, monolayer molybdenum disulfide (1L-MoS$_2$) is an emerging 2D semiconductor exhibiting photoluminescence in the visible due to its direct bandgap.[22] In contrast to other 0D and 1D emitters, the 2D nature of 1L-MoS$_2$ in the absence of interlayer interactions promises increased flexibility and more efficient device functionality.[21–26] 1L-MoS$_2$ has also been demonstrated to be an outstanding platform to investigate light-matter interactions.[27] However, 1L-MoS$_2$ suffers from low light absorption conferred by its sub-nm thickness, leading to photoluminescence with low quantum yields. To enhance light emission of 1L-MoS$_2$, various approaches, including chemical doping,[28] polymeric nanospacing,[29] defect engineering,[30] and coupling with plasmonic nanomaterials,[31–33] have been employed. While these methods are relatively successful, most of them require complex fabrication steps for device integration, inadvertently introducing defects and/or modifying the intrinsic optical properties of 1L-MoS$_2$. In plasmonic nanomaterials coupled-1L-MoS$_2$ systems, plasmon-induced hot electron injection and doping have been reported to cause phase transition of 1L-MoS$_2$ in some cases,[34–36] with both photoluminescence quenching[37] and enhancement[31,32] observed. In addition, focus is predominantly placed on enhancing the ensemble optical emission of 1L-MoS$_2$, using lithographically fabricated Au[33] and Ag arrays[32] close-packed Au film,[37] and Au nanoparticles.[36] To date, there is a lack of investigation exploiting the 2D nature of 1L-MoS$_2$ as a sub-micron-scale platform to design a heterogeneous optical platform. Furthermore, the ability of plasmonic nanomaterials to serve as highly confined nanometer-scale optical controllers in such systems has also not been fully explored.

Herein, we demonstrate the localized photoluminescence manipulation of 1L-MoS$_2$ using single shape-controlled plasmonic Ag nanoantenna. Our strategy focuses on using single Ag nanoantenna of various morphologies to control the extent of spectral overlap between the LSPRs of the Ag nanoantenna and the bandgap of 1L-MoS$_2$. This approach allows us to precisely tailor the emission response of 1L-MoS$_2$ by controlling the relative rates of excitation enhancement, quantum yield, and emission directivity. As such, we can continuously tune the photoluminescence of 1L-MoS$_2$ from an enhanced regime to a weakened state. Such weakened emission arises from both emission quenching and complex antenna effect of the Ag nanoantenna. We then realize a heterogeneous optical platform by combining various Ag nanoantennas to achieve a range of photoluminescence output signals on the same 1L-MoS$_2$, highly confined nanoscale dimensions. In addition to the use of direct bandgap 1L-MoS$_2$, we also highlight that photoluminescence enhancement can be achieved on few-layer MoS$_2$ with indirect bandgaps in our system.

We first mechanically exfoliate bulk MoS$_2$ into few and monolayers to study the thickness-dependent evolution of its intrinsic optical properties. Optical microscopy and atomic force microscopy (AFM) are used to identify the ultrathin MoS$_2$ layers, as well as confirm the layer number from monolayer (1L) to quadrilayer (4L) (Figure 1A and Figure S1A,B, Supporting Information). These MoS$_2$ layers exhibit thickness-dependent
Figure 1. Characterization of MoS₂ flakes and Ag nanoantennas. A) Bright field optical microscope image of mechanically exfoliated (1L, 2L, 3L, 4L, and bulk) MoS₂ flakes on SiO₂/Si substrate. B) Raman shift map of MoS₂ flakes created using the E₁²g peak frequency. C) Raman intensity map of MoS₂ flakes created using the E₁²g (379.3 cm⁻¹) peak intensity. D) Photoluminescence intensity map of MoS₂ flakes created using the A₁ (340 ± 6 nm) peak intensity. E) SEM images of synthesized (i) Ag octahedra (Ag OCT), size: 340 ± 6 nm. (ii) Ag nanocubes (Ag NC), size: 115 ± 5 nm. (iii) Large Ag nanospheres (Ag SP1), size: 95 ± 10 nm. (iv) Smaller Ag nanospheres (Ag SP2), size: 40 ± 4 nm. F) i) These extinction spectra overlap to varying extents with the (ii) emission spectra of 1L-MoS₂. Dashed vertical line corresponds to the laser excitation wavelength.

Raman peak (E₁²g, A₁) frequency and intensity, as well as photoluminescence band (B₁, A₁) intensity, consistent with those reported in the literature (Figure 1B-D and Figure S1C-F, Supporting Information).[32,38]

In our system, we utilize the spectral overlap between the LSPRs of Ag nanoantennas and the bandgap of 1L-MoS₂ to couple the 1L-MoS₂ photoluminescence with the plasmon modes, followed by radiating to the far field through the plasmon resonance. This experimental design also enables us to tune the excitation enhancement efficiency, quantum yield, and emission directionality. To tailor this spectral overlap, we synthesize a library of Ag nanoparticles, including shape-controlled cubes (Ag NC), octahedra (Ag OCT), and spherical particles (Ag SP) of various sizes (Figure 1E). Ag OCT and NC are synthesized using the polylol reduction method,[39] whereas Ag SP of two different sizes are synthesized via the citrate-reduction method (Figure S2, Supporting Information).[40] The average edge lengths of Ag OCT and Ag NC are 340 ± 6 nm and 115 ± 5 nm, respectively (Figure S2A,B, Supporting Information). The diameters of Ag SP1 are 95 ± 10 nm (Figure S2C, Supporting Information), and that of Ag SP2 are 40 ± 4 nm (Figure S2D, Supporting Information).

Ag NC supports multiple strong and distinct LSPR bands across the visible spectrum, with the dipolar resonance directly overlapping with the bandgap of 1L-MoS₂.[41,42] Ag OCT exhibits more complex optical signature with higher-order resonances in the 400–650 nm range, while the mode observed at ~1000 nm is mainly quadrupolar in nature.[39] As such, the directionality of the dipolar mode is better than the higher-order modes.

To create hybrid plasmonic-semiconductor nanostructures, the Ag nanoantennas are separately drop-cast onto 1L-MoS₂. MoS₂ thickness is first verified using AFM imaging as well as Raman characterization (Figures S3 and S5C, Supporting Information). Individual plasmonic nanoantennas are sparsely distributed on the 1L-MoS₂ flakes, with the average interparticle distance larger than 1 µm to avoid plasmon coupling between adjacent nanoparticles (Figure 2A). This interparticle distance also ensures that only single plasmonic nanoparticles are excited within the laser excitation volume. We use 532 nm as the incident excitation wavelength, allowing us to control the efficiency of exciting the LSPRs of the Ag nanoantenna. At the same time, this excitation wavelength is well above both A₁ and B₁ excitons of MoS₂. The laser excitation intensity for all experiments is kept below 1 × 10⁷ mW cm⁻² to avoid photodamage of the ultrathin MoS₂ layers.

Photoluminescence intensity maps of the hybrid nanostructures demonstrate localized optical control over the 1L-MoS₂ photoluminescence in the presence of the plasmonic nanoparticles (Figure 2B and Figure S4, Supporting Information). For Ag NC-1L-MoS₂, the photoluminescence maps of the B₁ (625 nm) and A₁ (680 nm) bands display strong photoluminescence enhancement at regions decorated with single Ag NC (Figure 2B(i,j)). Away from the NC-decorated areas, the photoluminescence intensity immediately returns to that of bare 1L-MoS₂ (Figure 2D(i) and Figure S4A, Supporting Information). The same phenomena can also be observed in the photoluminescence intensity maps of Ag SP1-1L-MoS₂ (Figure 2B(ii),(iii),(iv) and Figure S4B, Supporting Information), but almost no enhancement is observed for Ag SP2-1L-MoS₂ (Figure 2B(ii),(iii),(iv) and Figure S4C, Supporting Information). On the other hand, quenched photoluminescence is observed from Ag OCT-1L-MoS₂ (Figure 2B(iv) and Figure S4D, Supporting Information).
We evaluate the photoluminescence modification factor (MF) using the following equation: Photoluminescence MF = Photoluminescence band intensity of Ag-MoS$_2$/Photoluminescence band intensity of bare MoS$_2$. The presence of Ag NC enhances the photoluminescence of 1L-MoS$_2$ by an average of two-fold for both emission bands ($\approx 2.1 \pm 0.1$ and $2.2 \pm 0.1$ for $B_1$ and $A_1$ bands, respectively; Figure 2E). Similar enhancement is observed for Ag SP1, with the MF calculated to be $\approx$1.6-fold ($\approx 1.7 \pm 0.3$ and $1.5 \pm 0.3$ for $B_1$ and $A_1$ bands, respectively). The MF approaches 1 for Ag SP2-1L-MoS$_2$ and reduces to less than 0.5-fold for Ag OCT-1L-MoS$_2$.

The plasmonic mediation of Ag nanoantennas on the emission of 1L-MoS$_2$ is the combined result of excitation enhancement, emission modification, and altered emission directionality, which can be described by the following equation[^44]

$$MF = \frac{\eta}{\eta_0} \frac{\gamma}{\gamma_0} \frac{QY}{QY_0} \tag{1}$$

where the $\eta$, $\gamma$, and $QY$ are the photoluminescence collection efficiencies, excitation rate, and quantum yield of the sample with Ag nanoantennas, respectively; $\eta_0$, $\gamma_0$, and $QY_0$ are the photoluminescence collection efficiencies, the excitation rates, and quantum yield of sample without Ag nanoantennas. $\gamma$ is proportional to the electric field intensity enhancement, $|E_{\text{inc}}|^2/|E_0|^2$, at the excitation wavelength.

In the Ag NC-1L-MoS$_2$ case, the LSPRs overlap completely with both the laser excitation wavelength (532 nm) and the bandgap of 1L-MoS$_2$ (680 nm), resulting in significant field enhancement at both the laser excitation and 1L-MoS$_2$ emission wavelengths. From electrodynamic simulations performed using the finite-difference time-domain approach, the largest field enhancements ($|E_{\text{inc}}|^2/|E_0|^2$) for Ag NC are 950-fold and 720-fold at 532 and 680 nm, respectively (Figures 3A(i) and 4B(i)). The excitation rate is therefore enhanced up to 950-fold at the largest field sites. Electrodynamic calculations show that the photoluminescence quantum yield of 1L-MoS$_2$ can be enhanced by 13.9-fold at the largest field sites of Ag NC. In addition, the photon collection efficiency is only slightly decreased from 15% to 13% in the presence of Ag NC (Figure 3C). As such, a maximum of up to $10^4$ enhancement in photoluminescence is derived from the Ag nanooptics.

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**Figure 2.** Tuning the photoluminescence of 1L-MoS$_2$ using various single shape-controlled Ag nanoantennas. A) Dark-field optical microscope image of exfoliated 1L-MoS$_2$ deposited with single (i) Ag NC, (ii) Ag SP1, (iii) Ag SP2, (iv) Ag OCT. Insets are SEM images of the respective single nanoantenna, scale bars are 100 nm in (i), (ii), (iii), and 200 nm in (iv). B) Photoluminescence intensity maps of 1L-MoS$_2$ deposited with single Ag nanoantenna created using $A_1$ peak (680 nm) intensity. C) Photoluminescence spectra of bare 1L-MoS$_2$ with and without the Ag nanoantenna. D) $A_1$ band intensity profile across green dashed line in (B). E) Modification factors for the photoluminescence bands ($A_1$, $B_1$) using different Ag nanoantennas.
NC-1L-MoS₂ system near the cube vertices. However, these largest field enhancements are confined to the vertices of Ag NC. Consequently, a relatively small enhancement is obtained in our experiments. The large field enhancement at the laser excitation wavelength enables Ag NC to serve as localized nanoscale optical pumps to increase photon absorption and the generation rate of electron–hole pairs in 1L-MoS₂. Furthermore, significant field enhancement at the 1L-MoS₂ emission wavelength can accelerate the radiative decay through the Purcell effect. The coupled emission between the radiative dipole resonance of Ag NC and 1L-MoS₂ is optimal, leading to enhanced emission.

As the nanoparticles change from NC to SP1 and SP2, the overlaps between the plasmon resonances and the laser excitation as well as that between the plasmon resonances and 1L-MoS₂ bandgap decrease, leading to lower efficiency of exciting the LSPRs. Such off-resonant excitation leads to progressively smaller photoluminescence MF calculated for the various samples. An indirect evidence of this phenomenon is evident from the enhanced Raman scattering signals of 1L-MoS₂ in the presence of Ag nanoantenna (Figure S5, Supporting Information), which show a nanoparticle-dependent trend of Raman intensity enhancement following that of the photoluminescence enhancement.

In contrast, photoluminescence weakening of 1L-MoS₂ using Ag OCT arises from both the emission quenching and the more complex antenna effect of Ag OCT. Weaker maximum field enhancements of 280-fold and 170-fold are observed at the laser excitation 1L-MoS₂ emission wavelengths for Ag OCT-1L-MoS₂, respectively (Figures 3A(ii) and 4B(ii)). The field enhancement at the excitation wavelength gives rise to an excitation rate enhancement of 280-fold. Although the electric field at the emission wavelength is enhanced by 170-fold, the quantum yield is reduced to 0.2-fold of the original emission in the presence of Ag OCT. This reduction arises from the non-radiative nature of the high-order plasmon resonances. In addition, because of the poor directionality of high-order plasmon modes, we find that the collection efficiency is reduced from 15% to 0.26% by Ag OCT (Figure 3D). Taking all effects together, Ag OCT gives rise to an enhancement factor of 0.89 at the largest electric field enhancement positions. Since the strongest fields are localized at the particle vertices, even lower enhancement is expected over the particle surfaces. Therefore, the overall effect of Ag OCT on the photoluminescence of 1L-MoS₂ is emission weakening.

Notably, the intrinsic spectral properties of 1L-MoS₂ remain practically unchanged in the presence of Ag nanoantenna with only a slight red-shift even under increased excitation power (Figure S6A,B, Supporting Information). In addition, the photoluminescence enhancement is independent of excitation power (Figure S6C,D, Supporting Information), suggesting that photothermal heating is insignificant in our system compared to a previous study. [31]

In addition, Ag NC is also able to enhance the emission of multilayered indirect bandgap MoS₂ flakes (both 2L and 3L; Figure S7, Supporting Information). The photolumines-
In our experiment, we not only tune the optical response of 1L-MoS₂ through the use of different Ag nanoantennas, but further enable the realization of an optical platform with multiple highly confined signal emission. This opens up new approaches to design nanoscale optoelectronic devices and at the same time, suggests the use of this platform in fields such as data storage and circuit integration.

Our work successfully demonstrates the creation of a heterogeneous optical platform built upon the integration of plasmonic nanoantenna with 1L-MoS₂, achieved via a localized control over the photoluminescence emission of 1L-MoS₂ using single Ag nanoantenna. The emission intensity is highly tunable, and can be easily manipulated via a judicious selection of nanoantenna morphology. As the nanoantenna changes from nanocubes to octahedra, the photoluminescence intensity changes from an enhanced to a weakened state. This phenomenon arises from LSPR-based excitation enhancement and from the morphology-dependent antenna effect of the various plasmonic nanoantennas. By simultaneously introducing both Ag NC and Ag OCT, we are able to create a heterogeneous optical platform with a tunable range of photoluminescence signals, concurrently observing the base photoluminescence from 1L-MoS₂, as well as enhanced and weakened emissions in the presence of the respective Ag nanoantenna. Such unprecedented nanoscale control coupled with highly tailorable optical output is promising for the integration of transition metal dichalcogenide-based optoelectronics. Furthermore, our Ag nanoantenna can be used to enhance photoluminescence on few-layer indirect bandgap MoS₂.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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