Room Temperature Fluorescence Blinking in MoS$_2$ Atomic Layers by Single Photon Energy Transfer

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The quantum optical phenomena, such as single-photon emission, in transition metal dichalcogenides (TMDCs) have triggered extensive research on 2D material-based quantum optics and devices. By far, most reported quantum optical emissions in TMDCs are based on atomic defects or the local confinement of excitons. In contrast, energy transfer between two materials could also manipulate the photon emission behaviors in materials, even at the single-photon level. Here, fluorescence blinking from MoS$_2$ atomic layers in quantum dot (QD)/MoS$_2$ hybrid heterostructure at room temperature is reported. The single-photon nature of the QDs in heterostructures by second-order photon correlation measurements is demonstrated. Based on the transient PL spectroscopy and PL time trajectories, the fluorescence blinking behavior in MoS$_2$ is attributed to the single-photon energy transfer from QD to MoS$_2$. This work could open the possibility to achieve correlated quantum emitters in TMDCs at room temperature.

1. Introduction

2D transition metal dichalcogenides (TMDCs) have received extensive attention for both fundamental research and photonic applications due to the large exciton binding energy tunable bandgap covering from visible to near-infrared, and van der Waals (vdW) integration with other materials. Furthermore, the 2D quantum confinement in atomic layer thin TMDCs brings unique quantum effects which makes them excellent candidates for device applications in quantum information. In recent years, a large number of researchers have been devoted to studying the quantum optical properties of 2D materials. For instance, single-atom defects in 2D materials have been demonstrated to act as single-photon emitters upon photon excitation, which provide the essential element for quantum communication and computing based on 2D materials. Besides, artificially constructed TMDCs layers by the introduction of nanobubble, wrinkles, or pattern arrays of nanopillars have also been reported to behave as single-photon sources in local strained areas due to the strain-induced local confinement of excitons. These TMDCs materials provide a scalable platform for quantum photonic applications in a relatively controlled manner.

2D TMDCs can form the vdW heterostructure by vertically stacking two different TMDCs materials that provide unprecedented characteristics beyond single component. Recently, unique optical quantum phenomena have also been demonstrated in TMDCs heterostructures. Unlike the stable photoluminescence (PL) intensity emitted by TMDCs monolayer, the PL emission in WS$_2$/MoSe$_2$ heterostructures exhibits blinking behavior, and the fluorescence fluctuation of this system jumped between bright, neutral, and dark states, owing to an intermittent interlayer carrier transfer process. Lately, the single-photon emission due to the interlayer excitons in MoSe$_2$/WSe$_2$ heterostructure was reported, which can be interpreted as the interlayer excitons were locally confined by the generated moiré potential in the heterostructure. However, the twist angle in these heterostructures needs to be precisely controlled to form an effective moiré potential and the single-photon emission is observed at cryogenic temperature. In contrast to conventional 2D heterostructures, 0D–2D hybrid heterostructures consisting of quantum dots (QDs) and TMDCs layers provide an effective route to manipulate the local photonic properties of 2D TMDCs, especially, along with the single-photon emission nature of the 0D materials at room temperature. Most of the previous studies on the 0D–2D heterostructures have focused on improving the energy transfer efficiency and increasing the absorption of acceptor for device applications. However, the study on manipulating local photonic properties of TMDCs by energy transfer on the single-photon level has not been reported. Hence, constructing 0D–2D heterostructures and exploring the interaction with single-photon energy transfer could be an indispensable way to manipulate quantum states in TMDCs materials.
In this work, we constructed a hybrid heterostructure consisting of CdSe/ZnS core–shell QD and MoS₂ atomic layers to study the quantum states related optical emissions. The second-order photon correlation measurements indicate that the single-photon nature of the QDs in heterostructures still maintains after energy transfer with MoS₂. By studying transient PL and PL time trajectories of QD/monolayer-MoS₂ heterostructure, we found that the fluorescence blinking behavior of MoS₂ can be attributed to the intermittent energy transfer on the single-photon level. Meanwhile, a less prominent blinking phenomenon of MoS₂ bilayer in QD/bilayer-MoS₂ heterostructure demonstrates that the charge transfer efficiency directly affects the variation of quantum states in MoS₂.

2. Results and Discussion

2.1. Single Photon Emission of QD in QD/Monolayer–MoS₂ Heterostructure

Monodispersed QDs on cover glass were prepared by the spin-coating method. Exfoliated MoS₂ flakes were then transferred onto the QDs to form QD/MoS₂ heterostructures. Figure 1a shows the optical image of the heterostructures and Figure 1b shows the PL image of QDs in the same area. Compared to the pure QDs, a significant PL quenching in the QD/monolayer-MoS₂ heterostructure is observed, the area of which is marked with orange dashed lines in both Figure 1a,b. The magnified PL image (Figure 1c) of the heterostructure area shows typical diffraction-limited dot-ring emission patterns and demonstrates that the QDs are well monodispersed, which provides a perfect platform to study the interaction between a single QD and the monolayer MoS₂.

On account of the core–shell structure of QDs and long-chain organic molecules (oleic acid, the length is about 2.3 nm) surrounding the shell, the charge transfer process between QDs and MoS₂ is nearly impossible since the spacing between the donor and acceptor for charge transfer is usually less than 1 nm. We attribute the quenching of the overall QDs PL in the heterostructures to the Förster resonance energy transfer (FRET) from QDs...
Figure 2. Fluorescence blinking from MoS2 monolayer in a heterostructure. a,c) PL intensity time trajectories from a QD on a cover glass slide and a QD in a QD/MoS2 heterostructure, respectively. b,d) Statistics of emission intensity from (a,c), indicating that the B-state decreases and the D-state increases due to the interfacial interaction. e) PL intensity time trajectories from a pure MoS2 monolayer (purple curve) and a MoS2 monolayer in HS-MoS2 (blue curve), show obvious variations in emission intensity. f) Statistics of emission intensity from (e). Compared to pure MoS2 monolayer, a broader range of emission intensity in HS-MoS2 are observed.

to MoS2 (Figure 1e). The QDs have the PL emission spectral profile (Figure S1, Supporting Information) that overlaps with the direct excitonic absorption peak of MoS2 (Figure 1h), which is an important condition for FRET. Furthermore, the PL lifetime of QDs in heterostructures decreases obviously compared with that of pure QDs deposited on cover glass (Figure S2, Supporting Information), which is also a crucial characteristic of FRET.

To investigate the variation of the single-photon nature of a single QD in this hybrid 0D-2D heterostructure, the PL intensity time trajectories from a single QD on the cover glass and in the QD/monolayer–MoS2 heterostructure were recorded by time-correlated single-photon counting (TCSPC) system (Figure 2a,c)). For both cases, we observe the typical PL emission blinking behavior. However, the occurrence of the low-intensity
emission from the QD in heterostructure is obviously increased (Figure 2c). Accordingly, we plot the fluorescence intensity distributions and their bimodal Gaussian fitting in Figure 2b,d. Two peaks from the fitting data can be assigned to the bright state (B-state) and the dark state (D-state) of blinking. It can be seen from these statistics that the proportion of the B-state decreases while the proportion of the D-state increases for the QD in the heterostructure, which also means that the overall intensity of the QD in the heterostructure is lower than that on the cover glass, as shown in Figure 1b. This observation agrees with the proposed energy transfer process between the QD and MoS2 in the heterostructure, which makes the initial B-state of QD transit to the D-state.

Besides, we monitor the PL intensity time trajectories from the pure MoS2 monolayer and the MoS2 monolayer in heterostructure (HS-MoS2) (Figure 2e). Compared to the relatively stable fluorescence emission from pure MoS2 monolayer (purple curve in Figure 2e), the fluorescence emission of HS-MoS2 shows obvious blinking behavior due to its interaction with a QD (blue curve in Figure 2e). The fluorescence intensity distribution statistics in Figure 2f shows that the HS-MoS2 consists of a weaker fluorescence emission (defined as the "D" state), and an intermittent stronger fluorescence emission (defined as the "B" state), similar to the emission states of a QD. Moreover, we tested the PL intensity time trajectories of the samples consisting of PMMA film and MoS2 flakes (Figure S4, Supporting Information). The observed stable emission of MoS2 during the test period could exclude the influence of PMMA on the blinking behavior. Considering the energy transfer process in heterostructure, when the excitation laser energy is higher than the bandgap of the QD (donor), the energy of the excited electron–hole pair from the QD would transfer to the MoS2 monolayer (acceptor) in a nonradiative way. As a result, the fluorescence of the QD quenched and the fluorescence of the MoS2 monolayer increased. Since the single-photon emission nature of QD, the energy transfer in this system occurs with the association of the quantum states of the emission, leading to a typical blinking behavior in MoS2 monolayer. Here, with the strong PL emission from single QDs and high energy transfer efficiency in the individual QD/MoS2 monolayer heterostructure, we observe the obvious fluorescence blinking in MoS2 monolayer by the energy transfer from single QD on the single-photon level.

2.3. Fluorescence Cross-Correlation of QD and MoS2 in Heterostructure

In order to further understand the origin of blinking behavior from the MoS2 in heterostructure, the PL intensity time trajectories from the MoS2 and the single QD at the same position of the heterostructure were detected simultaneously by the TCSPC system (Figure 3a). The PL signals of QD and MoS2 are distinguishable and can be selectively recorded by narrow band-pass filters with center wavelengths at 575 and 660 nm for QD and MoS2, respectively (Figure S5, Supporting Information). We observed typical blinking behavior from both QD and MoS2. It is found that when the monolayer MoS2 (blue dots in Figure 3a) is in the “B” state (stronger emission), the corresponding signal of QD (orange dots in Figure 3a) is almost in the D-state. Here, we define a cross-correlation function to analyze the relationship between two signals from MoS2 and QD, namely:

\[
G(\tau) = \frac{\langle (I_{MoS2}(t) - \langle I_{MoS2}(t) \rangle) \cdot (I_{QD}(t + \tau) - \langle I_{QD}(t) \rangle) \rangle}{\langle I_{MoS2}(t) \rangle \cdot \langle I_{QD}(t) \rangle} \equiv 1
\]

where \(I_{MoS2}(t)\) and \(I_{QD}(t)\) are signal intensity extracted from the PL intensity time trajectories of MoS2 and QD at time \(t\), \(\tau\) is the time delay of the correlation; and angular brackets denote averaging over time. The PL intensity time trajectories at certain time periods (Figure 3b, upper panel) and the dip at zero time delay from the corresponding G(\(\tau\)) curve (Figure 3b, red curve in lower panel) demonstrate the negative correlation during these time periods. However, there are still some irrelevant signals between MoS2 and QD (blue G(\(\tau\)) curve in lower panel) which could be explained no energy transfer at these times. To further figure out the interaction mechanism, the statistics of emission intensity extracted from Figure 3a is shown in Figure 3e and the two possible interactions between MoS2 monolayer and QD are illustrated in Figure 3c,d. When there is no energy transfer between QD and MoS2 (Figure 3c), both of them will maintain the original emission intensity. At this time, the QD can be in B-state (case I in Figure 3e) or D-state (case II in Figure 3e) due to its fluorescence blinking property, while the MoS2 can only be in the “D” state as we defined in the system. However, when the energy transfer occurs between the two materials (Figure 3d), the fluorescence intensity of MoS2 will be enhanced with the quenched fluorescence intensity of QD, leading to a D-state in the QD and a “B” state in the MoS2 (case II in Figure 3e). Furthermore, we have also observed similar blinking behavior in other QD/MoS2 hybrid heterostructures (Figure S6, Supporting Information).

The PL lifetime from QD and MoS2 during the time trajectory measurements can also be extracted from the simultaneously recorded singles with the TCSPC system. Although the obtained lifetime shows fluctuations due to the short binning time and low photon number, the average lifetime of QD is about 5 ns (dark yellow dots in Figure 3f) during this measurement, which is clearly distinct from the short lifetime (about 0.6 ns in average) of MoS2 (blue dots in Figure 3f). This observation excludes the crosstalk about the emission signal from QD and MoS2 in two detection channels, further confirming the blinking is indeed from the emission of MoS2. Meanwhile, the fluctuation with time could be also a consequence of the intermittent energy transfer from the QD to the MoS2. Since the lifetime of pure MoS2 monolayer over time is maintained as a relatively stable and almost uniform value at different excitation fluences (Figure S7, Supporting Information), the lifetime fluctuation caused by instrument instability would be ruled out. It should be noted that the average lifetime of MoS2 in heterostructure obtained from time trajectory measurements is longer than that of pure MoS2 monolayer (about 0.27 ns, see Figure S7b, Supporting Information). In addition, we also counted the lifetime distribution of the two materials from Figure 3f. From this distribution, it is shown that while the MoS2 has a long lifetime, the corresponding QD
2.4. Energy Transfer and Fluorescence Blinking in QD/Bilayer-MoS₂ Heterostructure

We further investigate the interaction between a single QD and a bilayer MoS₂ under optical excitation. The QD/bilayer-MoS₂ heterostructure was obtained by transferring a mechanically exfoliated MoS₂ flake on a cover glass coated with QDs. The area of the heterostructure was marked by white dashed lines in the optical image (Figure 4a). As MoS₂ changes from monolayer to bilayer, the absorption at the wavelength of the QD emission increases (Figure S8, Supporting Information), but the screening of the electric field of the donor dipole in the MoS₂ also increases. Due to the large dielectric constant of MoS₂, the energy transfer efficiency is mainly affected by the dielectric screening effects, while the increased acceptor absorption is almost negligible.⁴³,⁴⁴ As a result, the energy transfer efficiency decreases with increasing thickness of MoS₂ layers, as shown in Figure 4c. To demonstrate the change of the energy transfer efficiency, we recorded the QDs PL lifetime image of QD/bilayer-MoS₂ (Figure 4b) and QD/monolayer-MoS₂ heterostructures (Figure S2c, Supporting Information). Quantitatively, we perform statistics on the PL lifetime of QDs. Through Gaussian fitting, we found that the mean lifetime of QDs in QD/bilayer-MoS₂ heterostructures was about 7.28 ns (red curve in Figure 4d), while the mean lifetime of QDs in QD/monolayer-MoS₂ heterostructures was about 2.18 ns (blue curve in Figure 4d). Representative lifetime measurements of QD on the cover glass and in heterostructures are shown in Figure 4e. In addition, the energy transfer efficiency can be expressed as

\[ \eta_{\text{FRET}} = 1 - \frac{\tau_{\text{DA}}}{\tau_D} \]

where \( \tau_{\text{DA}} \) and \( \tau_D \) are the lifetimes of the QD in heterostructure and on cover glass, respectively. Using this formula, we obtain...
Figure 4. Energy transfer and fluorescence blinking in QD/bilayer-MoS$_2$ heterostructure. a) Optical image of exfoliated MoS$_2$ flakes on a QD film. The white dashed lines show the area of the bilayer-MoS$_2$ (2l-MoS$_2$). b) PL lifetime image of QDs from the area in (a) marked with blue dashed lines. c) Schematic of energy transfer efficiency varying with the number of MoS$_2$ layers. d) Statistics of PL lifetime of 120 QDs in QD/monolayer-MoS$_2$ (QD/MoS$_2$) and in QD/bilayer-MoS$_2$ (QD/2l-MoS$_2$) heterostructures. e) Representative PL decay curves from QD on cover glass, in QD/MoS$_2$ and QD/2l-MoS$_2$ heterostructures. f) Second-order correlation function curve obtained from a QD in QD/2l-MoS$_2$ heterostructure at room temperature. g) PL intensity time trajectories from QD (orange curve) and 2l-MoS$_2$ (blue curve) in QD/2l-MoS$_2$ heterostructure. Binning time is 100 ms. h) PL intensity distribution of QD and MoS$_2$ derived from (g). The data in blue area indicates a negative correlation between these two intensities.

that the energy transfer efficiencies in QD/monolayer-MoS$_2$ and QD/bilayer-MoS$_2$ are 78.1% and 27.0%, respectively.

We also study the single-photon nature of the single QD in QD/bilayer-MoS$_2$ heterostructure (Figure 4f). We obtain $g^2(0) = 0.26$ by fitting data (blue curve in Figure 4f), which is a bit better than QD from MoS$_2$/QD hybrid heterostructure. This may be due to the fact that, compared to the case for MoS$_2$ monolayer, MoS$_2$ bilayer is an indirect bandgap material$^{[5]}$ with a relatively weak fluorescence emission, which leads to a low background noise in the second-order photon correlation measurement. Meanwhile, we tested the PL intensity time trajectories from single QDs and MoS$_2$ bilayer (Figure 4g) and compared the intensity relations (Figure 4h). The emission intensity of QD is still negatively correlated with that of MoS$_2$ bilayer at certain time periods (blue area in Figure 4h). The blinking behavior from MoS$_2$ bilayer in this heterostructure is clearly weaker than that of MoS$_2$ in QD/monolayer-MoS$_2$ hybrid heterostructure (see the blue data in Figure 4g), which is consistent with the low energy transfer efficiency in this heterostructure.

3. Conclusion

In conclusion, we have demonstrated fluorescence blinking in MoS$_2$ monolayer and bilayer due to the single-photon energy transfer from single CdSe/ZnS QDs. We investigated the second-order photon correlation measurements of QDs with and without the energy transfer process, demonstrating that the QDs in heterostructures still maintain the single-photon nature. By comparing the PL intensity time trajectories of the QDs on cover glass to that of the QDs in heterostructures, we find the proportion of the D-state in QDs from heterostructures is significantly increased due to the energy transfer. Meanwhile, the PL
intensity time trajectories of MoS₂ in heterostructures show a fluorescence-blinking behavior similar to the emission states of QDs. With simultaneously recorded PL intensity time trajectories of QD and MoS₂ in heterostructure, a negative correlation between the two signals at certain time periods is observed, which further confirms that the fluorescence-blinking is due to the energy transfer between QD and MoS₂ on the single-photon level. As the screening of the electric field effect of MoS₂ increases with the number of layers, we explore the interaction between QDs and MoS₂ bilayer. The statistics of PL lifetime of QDs in heterostructures demonstrate that the energy transfer efficiency is smaller in QD/bilayer-MoS₂ heterostructure compared to that from QD/monolayer-MoS₂. Consequently, we observe a less prominent fluorescence blinking behavior in bilayer MoS₂, which is consistent with the energy transfer efficiency. Our findings could contribute to a deeper understanding of the energy transfer process between QD and TMDCs, and provide a new possibility to achieve quantum emitters on TMDCs at room temperature by controlling the energy transfer at the single-photon level.

4. Experimental Section

Preparation of Monodispersed QDs: The QDs were purchased from Xingzi New Material Technology Development Co., Ltd. The diameter of the whole CdSe/ZnS QDs is about 11 nm and the thickness of the ZnS shell is about 8 nm. The QDs dispersed in toluene solution (10 mg mL⁻¹) were first diluted 2000 times. Then 1 mL diluted solution was taken and mixed it with 200 μL of 4% poly(methyl methacrylate) (PMMA, 950 k, anisole as the solvent) by stirring at room temperature for about 1 h to fully dissolve PMMA. Finally, to obtain monodispersed QDs, a 25 μL aliquot of this mixed solution was taken and deposited it on a clean cover glass via spin-coating method at 800 revolutions per minute (rpm) for 60 s.

Preparation of QDs/MoS₂ Hybrid Heterostructure: The MoS₂ monolayer and bilayer were obtained by the mechanical exfoliation from bulk materials and then transferred onto the monodispersed QD film obtained using the above-mentioned spin-coating method.

Absorption and Steady-State PL Measurements: Absorption spectra of MoS₂ on transparent glass substrates were determined by a home-built transmission microscopy. A broad light beam from a tungsten halogen lamp was used to illuminate the sample and the spectrum of transmitted light was recorded using a Horiba iHR320 spectrometer.

For steady-state PL, the 405 nm laser source (LDH-D-C-405, PicoQuant) with cw mode was used to excite the sample and the fluorescence signals were collected using an Olympus IX73 inverted confocal microscope with a 100x oil-immersion objective lens (NA = 1.4). After filtering out the excitation laser with a 407 nm long-pass filter (LP02-407RU-25, Semrock), the steady-state PL spectrum was recorded by the spectrometer (Horiba iHR320) with a liquid-nitrogen cooled CCD (Symphony II) at ambient conditions.

Time-Resolved PL Measurements: For time-resolved PL, the 405 nm laser with pulsed mode was used at a repetition rate of 40 MHz to excite the sample. The fluorescence lifetime imaging (FLIM) and PL decay curves measurements of the QDs and MoS₂ were recorded by the time-correlated single-photon counting (TCSPC, HydraHarp 400 from PicoQuant) system. The QD PL emission was selected with a 575 nm band-pass filter (FF01-575/59-25, Semrock), while the MoS₂ PL emission was selected with a 660 nm band-pass filter (FF01-660/30-25, Semrock). Furthermore, PL intensity time trajectories from QD and MoS₂ were recorded by this TCSPC system.

Second-Order Photon Correlation Measurements: The fluorescence emission from QD was sent through a 575 nm band-pass filter to a Hanbury-Brown and Twiss (HBT) setup consisting of a 50/50 beam splitter connected to two single-photon avalanche diodes (APDs, PDM Series from PicoQuant), and the second-order photon correlation function g²(r) was recorded by TCSPC system.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

energy transfer, fluorescence blinking, hybrid heterostructures, TMDCs

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