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Electron transfer and cascade relaxation dynamics of graphene quantum dots/MoS₂ monolayer mixed-dimensional van der Waals heterostructures

Hangyong Shan^{1,†}, Ying Yu^{1,†}, Rui Zhang^{2,†}, Runtan Cheng³, Dong Zhang², Yang Luo¹, Xingli Wang⁴, Bowen Li¹, Shuai Zu¹, Feng Lin¹, Zheng Liu⁴, Kai Chang², Zheyu Fang^{1,}*

¹School of Physics, State Key Laboratory for Mesoscopic Physics; Academy for Advanced Interdisciplinary Studies; Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China

²SKLSM, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

³School of Life Sciences and Biotechnology, Shanghai Jiao Tong University, Shanghai 200240, China

⁴CNRS International-NTU-Thales Research Alliance (CINTRA), Nanyang Technological University, Singapore 637553, Singapore

*Corresponding author

Zheyu Fang: zhyfang@pku.edu.cn

Abstract: Van der Waals (VdW) heterostructures have emerged as promising materials for atomically thin optoelectronic and photovoltaic applications, where the efficient charge separation after photo-excitation is significant to enhance device performances. However, modulating the interfacial charge transfer is still challenging due to the weak interlayer VdW interaction. Revealing electron transfer and relaxation processes in heterostructures lays foundation to tune the interfacial dynamics and optoelectronic properties. Here, we realize the efficient modulation of relaxation channels in MoS₂ monolayers and interfacial electron transfer by forming mixed-dimensional VdW heterostructures with graphene quantum dots (GQDs). With femtosecond pump-probe spectroscopy, the biphasic electron injection model and modified rate equations are employed to quantitatively solve interfacial transfer rates of mixed-dimensional VdW heterostructures. We find that the cascaded relaxation of hot electrons in GQDs that originates from the quantum confinement effect can intensively affect the interfacial dynamics. Our established model is instructive to optimize performances of future photon-harvesting devices based on mixed low-dimensional heterostructures.

Keywords: ultrafast electron transfer, cascade relaxation, mixed-dimensional heterostructures, femtosecond pump-probe spectroscopy, 2D materials

Introduction

Transition metal dichalcogenides (TMDs) monolayers have attracted increasing attention for applications of photovoltaics [1,2], photodetection [3,4] and catalysis [5], etc. Despite being atomically thin, many TMDs monolayers are direct band-gap semiconductors with strong light–matter interactions, and their emission can cover a broad spectral range from visible to near-infrared [2,6-8]. Without conventional ‘lattice mismatch’ issues, it is easy to assemble different TMDs into vertical van der Waals (VdW) heterostructures [1,9], which further opens an avenue for the fundamental material study and optoelectronic device applications [1-3,10-12]. Interesting physics phenomena based on these two-dimensional (2D) heterostructures were investigated, such as Moiré superlattices, long lifetime interlayer excitons and gate tunable bandgaps, etc., which have been used to generate unique device functionalities in comparison with conventional semiconductors. For devices based on 2D heterostructures, the external quantum efficiency is usually suppressed by the back electron transfer and the charge recombination at interface. Thus, to understand the interfacial process of 2D heterostructures is essential for the future optoelectronic device design and applications [13-20].

On the other side, different dimensional materials can show various properties, e.g. quantum dots act as electron donors and sensitizers, while 2D crystals are potential active layers for the optoelectronic application [3,21-23]. Because the VdW interaction can be existed at any passivated surfaces without dangling bonds, mixed-dimensional heterostructures can be obtained by stacking zero- and one-dimensional (0D and 1D) nanomaterials on TMD monolayers. The constructed 0D/2D and 1D/2D heterostructures can exhibit exceptional properties compared to 2D/2D VdW stackers [21,22,24], where the doping efficiency, carrier concentration and interfacial charge transfer processes may be modulated with the abrupt change of energy level and density of states (DOS) in mixed-dimensional heterostructures. It is expected that VdW heterostructures constituted by mixed-dimensional materials can fully utilize their original synergetic effects to achieve a superior performance.

In this work, we investigate the electron transfer and cascade relaxation dynamics of the mixed-dimensional heterostructures comprised of graphene quantum dots (GQDs) and MoS₂ monolayers. GQDs serve as electron donors, while the MoS₂ behaves like an acceptor. By decreasing the GQD size from 70 to 5 nm, the 2D/2D graphene flake-MoS₂ heterostructure gradually becomes a 0D/2D GQDs-MoS₂ stacker. The interfacial dynamics of different mixed-dimensional heterostructures is studied by employing femtosecond pump-probe measurements, and transient differential reflection signals are found dependent with the GQD size. The biphasic electron injection model is applied to elucidate the experimental observation, and different characteristic electron transfer rates at the 0D/2D interface are calculated and further explained by the Marcus theory.

Results

Characterizations of GQDs and MoS₂ monolayers.

Fig. 1a is the schematic of our femtosecond pump-probe measurements, where the 400-nm pump pulse is generated by focusing the femtosecond laser (800 nm) into a BBO crystal. A portion of fundamental pulse is concentrated into a photonic crystal fiber to generate a super-continuum white light source with the wavelength extending from 550 to 1400 nm. The 650-nm probe pulse is selected from the white light with a band-pass filter. Compared with the pump, the probe pulse arrives at the sample with a delay time of $\Delta\tau$, and the transient reflected probe light is recorded by the photomultiplier. Before arriving at the photomultiplier, the pump laser is filtered with a 450-nm-longpass filter (see more details in Materials and Methods).

The size of GQDs used in the experiments can be well characterized by the transmission electron microscopy (TEM) image, as shown in Fig. 1b. The inset shows the size distribution of GQDs, where an average diameter of 5 nm can be clearly distinguished. Other sized GQDs were imaged and are shown in Figs. S1a-S1c, with the corresponding size distributions exhibited in Figs. S1d-S1f. The monolayer property of MoS₂ was certified by Raman spectra shown in Fig. S1g. The reflection mapping of

70 nm GQDs/MoS₂ heterostructures is illustrated in Fig. 1c. The uniform green area indicates that GQDs are homogeneously deposited on top of MoS₂ monolayers. Furthermore, specific absorption spectra at representative locations are plotted in Figs. S1h and S1i, which are similar due to the homogeneous distribution of GQDs (see more details in Note. S1). To quantitatively characterize the density of GQDs on top of MoS₂, heterostructures with varied GQD sizes were scanned by atomic force microscopy (AFM). The AFM images are shown in Figs. S1j and S1k, from which individual GQDs can be clearly distinguished. The number of GQDs was counted statistically and the density was then calculated (Fig. S1l). A similar density was obtained because the GQD concentration (0.1 mg/mL) was same for different sized GQDs. Absorption spectra of the MoS₂ monolayers and GQDs are shown in Fig. 1d, where the *A* and *B* excitons of MoS₂ monolayers are recorded at 1.84 and 1.98 eV, while the GQDs show a broad absorption spectrum. Absorption spectra of GQDs/MoS₂ heterostructures with different GQD sizes and concentrations can be found in Fig. S2.

Figure 1. Characterizations of GQDs and MoS₂ monolayers. (a) Schematic of ultrafast pump-probe

measurements in reflection configuration. The 400-nm pulse pumps GQDs/MoS₂ heterostructures, and the 650-nm probe arrives at the sample with a delay time of $\Delta\tau$. (b) The TEM image of GQDs, which shows an average diameter of 5 nm. The inset shows the size distribution of GQDs. (c) The reflection mapping of GQDs/MoS₂ heterostructures. The uniform green area demonstrates the homogenous distribution of GQDs on the MoS₂ monolayers. (d) Absorption spectra of MoS₂ monolayers and GQDs. The dashed line denotes the probe wavelength.

Photo-excited electron relaxation dynamics of MoS₂ monolayers.

The measured differential reflection signals $\Delta R/R_0(t)$ of the MoS₂ monolayers and GQDs are shown in Fig. 2a. $\Delta R/R_0(t)$ represents the transient relative reflection change of the probe pulse, equaling to $(R-R_0)/R_0$, where R and R_0 are reflections of the probe light with and without pump pulse. In our ultrafast measurements, in order to excite both the MoS₂ monolayers and the GQDs, the wavelength of pump pulse was fixed at 400 nm, while the probe was chosen as 650 nm. The pump and probe fluences were 7.5 and 0.75 $\mu\text{J}/\text{cm}^2$, respectively. In Fig. 2a, the transient reflection signals for all-sized GQDs are at the base line, which demonstrates that the recorded transient absorption signal is only from the MoS₂ monolayers, and the measured $\Delta R/R_0(t)$ is determined by the electron occupancy number at MoS₂ exciton level.

The relaxation dynamics of pristine MoS₂ monolayers is first analyzed from the differential reflection $\Delta R/R_0(t)$ in Fig. 2a. The relaxation of MoS₂ monolayers on the first two picoseconds is extended and shown in Fig. 2b, where two processes with different rates can be clearly observed and the dominant decay process converts at the delay time about 1 ps. With the pump pulse, electrons of the MoS₂ monolayers are excited and relaxed into the exciton level, which occurs on the rising edge of $\Delta R/R_0(t)$. These electrons that are accumulated at the exciton level then experience a fast decay process during the first hundreds of femtoseconds, which may be attributed to the annihilation of biexcitons or the thermalization of photo-excited carriers [25,26]. After this fast decay, the excited electrons undergo the exciton-exciton annihilation process.

In order to quantitatively study the electron relaxation dynamics, the relationship

between the amplitude of measured $\Delta R/R_0(t)$ and the photo-excited electron density N should be established first. In the experiments, the peak amplitude of $\Delta R/R_0(t)$ for the pristine MoS₂ monolayers is found linearly changed with the pump fluence, as shown in Fig. S3. Since the photo-excited electron density N is directly proportional to the pump fluence, it is safe to assume that the amplitude of $\Delta R/R_0(t)$ also varies linearly with N when its maximal amplitude is lower than 0.65% (Fig. S3) [27-29].

With this linear relationship, the rate equation for the electron relaxation that involves two decay processes can be presented as the following:

$$\frac{dN}{dt} = -AN^x - \frac{1}{2}\gamma N^2, \quad (1)$$

where A and x are coefficients, and $\gamma/2$ is the exciton-exciton annihilation rate (see Fig. S4 and Note. S2 for detailed derivations). In Equation 1, the first item represents the fast decay process, while the second one corresponds to the exciton-exciton interaction. Based on the Monte Carlo method, these parameters can be obtained, where A is 0.41×10^{-24} cm⁶/s, x is 4, and $\gamma/2$ equals to 0.076 cm²/s. The obtained exciton-exciton annihilation rate is almost the same as previous reports [27,30]. With these parameters, fitting curves in Figs. 2a and 2b are plotted, which have a good agreement with experimental results.

Figure 2. Differential reflection signals of the MoS₂ monolayers and GQDs/MoS₂ heterostructures. The pump and probe wavelengths are fixed at 400 and 650 nm, respectively. (a) Differential reflection of the pristine MoS₂ monolayers and all sized GQDs. The solid line is the fitting curve with the solution of Equation 1. (b) The rising edge and decay process of the MoS₂ monolayers on the first two picoseconds. Two decay steps with different rates are denoted as dashed lines. (c) Differential reflection signals of GQDs/MoS₂ heterostructures with the GQD size changed from 70 to 5 nm. The solid lines are fitting curves with the solution of Equation 2. (d) Relaxation dynamics of the GQDs/MoS₂ heterostructure with the dot size of 10 nm on the first ten picoseconds. The later intensity increase implies the appearance of a new channel that can inject electrons into the MoS₂ monolayers. The inset shows peak intensities of $\Delta R/R_0(t)$ for the pristine MoS₂ monolayers and all heterostructures.

Differential reflection signals of GQDs/MoS₂ heterostructures

The electron transfer and cascade relaxation dynamics of GQDs/MoS₂ mixed-

dimensional heterostructures was further analyzed with the ultrafast pump-probe measurements. In the experiments, the concentration of GQDs was found to hardly affect the relaxation dynamics of heterostructures (Fig. S5 and Note. S3), and it was fixed at 0.1 mg/mL following. In the measurements of heterostructures, the pump and probe wavelengths were fixed at 400 and 650 nm respectively, with the same fluences as used for MoS₂ monolayers. Fig. 2c shows the size-dependent differential reflection signals of GQDs/MoS₂ heterostructures. Two-step relaxation processes can still be seen when the GQD size is larger than 40 nm. For the heterostructures with 70 nm GQDs, the effect of probe wavelength on the relaxation dynamics was studied and shown in Fig. S6. As the probe wavelength is gradually changed from 650 to 800 nm, the maximal intensity of $\Delta R/R_0(t)$ is decreased, while the relaxation curve still involves two distinct decay processes. This indicates that the change of probe wavelength can affect the amplitude of $\Delta R/R_0(t)$ but cannot dramatically influence the relaxation dynamics of heterostructures.

However, the differential reflection signal exhibits obvious distinctions when the GQD size decreases to 10 nm, as shown in Figs. 2c and 2d. The ultrafast signal promptly drops to the base line within the first hundreds of femtoseconds and then slightly increases with the delay time. Since the amplitude of $\Delta R/R_0(t)$ represents the photo-excited electron density, the dramatically reduced intensity implies the emergence of new channels that can dissipate photo-excited electrons in the MoS₂. On the other side, the later intensity rising trend manifests the appearance of another channel that can inject electrons into the MoS₂. When the GQD size reduces to 5 nm, the differential reflection also shows a single-step decay but without the later amplitude rising. These results demonstrate the relaxation dynamics of MoS₂ is intensely altered when the 2D/2D heterostructures change to 0D/2D ones.

The inset of Fig. 2d shows the peak values of $\Delta R/R_0(t)$ for heterostructures. All measured amplitudes of heterostructures are lower than that of the pristine MoS₂ monolayers. For heterostructures, the incident fluence is decreased when the pump pulse reaches the MoS₂, because a portion of light is absorbed by the top GQDs. To

estimate the influence of this effect, the absolute absorbance of different sized GQDs were measured as shown in Fig. S7, which exhibits a similar strength for different sized GQDs. However, it is interesting to note that the peak amplitudes of heterostructures are decreased with different extents for various sized GQDs. This result implies that the light absorption of top GQDs is not the exclusive reason that causes the reduction in peak amplitudes. These remarkable changes of $\Delta R/R_0(t)$ suggest a revised rate equation model is required to describe the dynamical behavior of mixed-dimensional heterostructures.

Electron transfer and relaxation dynamics of heterostructures

Fig. 3 depicts the biphasic electron injection model [14,31,32] that is used to explain the GQD size-dependent relaxation dynamics of the heterostructures. The left panel shows the energy diagram of MoS₂ monolayers, and the middle one exhibits energy levels of 5-nm GQDs, which were calculated using the tight-binding approximation method (Note. S4). Four main processes involving the hot electron injection, hot electron cooling, cold electron injection, and back electron transfer are introduced in this model.

During the rising edge of differential reflection signals $\Delta R/R_0(t)$ for GQDs/MoS₂ heterostructures, electrons in the MoS₂ valence band are excited with the 400-nm pump laser and then rapidly decay into the exciton level, which is the same as the procedure occurred in pristine MoS₂ monolayers. Simultaneously, GQDs are also pumped and a portion of photo-excited electrons can inject into the MoS₂, corresponding to the process of hot electron injection, shown as the red arrow in Fig. 3. The injected electrons can participate in the generation of MoS₂ trions (comprised of two electrons and one hole) [33], which decreases the electron density of MoS₂ at exciton level and further weakens the differential reflection amplitude (inset of Fig. 2d).

Figure 3. The band diagram of GQDs/MoS₂ heterostructure. The electron transfer and relaxation channels are depicted based on the biphasic electron injection model. The left panel denotes the band diagram of MoS₂, the middle and right panels show calculated eigen states and DOS for 5-nm GQDs, respectively.

Other main processes are involved in the descent process of $\Delta R/R_0(t)$. For those hot electrons retained in the GQDs, they can be non-radiatively cooled to lower states and become cold electrons, shown as black arrows in Fig. 3. The lifetime of this cooling process is seriously dependent on the GQD size. As the dot size decreased from 70 to 5 nm, the quantum confinement effect gradually emerges. To ascertain this quantum effect, DOS of different sized GQDs were calculated and are shown in Fig. S8. For large-sized GQDs, the calculated DOS is almost continuous, but apparent energy gaps appear when the GQD size decreases to 5 nm, as plotted in the right panel of Fig. 3. For small-sized GQDs, the spacing of discrete energy levels can even exceed the highest phonon energy of GQDs. The ‘phonon bottleneck’ indicates that multi phonons are requested to participate in the hot electron cooling process [34], which can slow the cooling time even up to two orders [35].

With such a longer lifetime, cold electrons can occupy higher energy levels of the GQDs and gradually cascade to lower states rather than straightly jump to the lowest unoccupied molecular orbital (LUMO). When the occupied level of cold electrons is higher than the MoS₂ conduction band edge, the cold electron injection from GQDs to the MoS₂ can occur, shown as the blue arrow in Fig. 3.

These injected electrons can further generate excitons in the MoS₂ with redundant holes that are left by the back electron transfer process, in which electrons are reversely migrated from the MoS₂ to top GQDs. This back transfer process can be inferred by comparing the descent procedures of differential reflection signals in Fig. 2, where the amplitude of mixed-dimensional heterostructures decreases more rapidly in comparison with the one of pristine MoS₂ monolayers. The more rapid decay of $\Delta R/R_0(t)$ for heterostructures implies the emergence of a new channel in the MoS₂ (the back electron transfer) that can dissipate the electron density at the exciton level.

A recent literature studied the interfacial electron transfer dynamics of MoS₂/WSe₂ 2D VdW heterostructures theoretically with time-dependent density functional theory [36]. This work found an interfacial relaxation pathway of hot electrons, of which the electron transfer rate is much faster than the intralayer relaxation rate, and also reported the appearance of hot electron back transfer. It can strongly support the biphasic electron injection model, and provides evidences to indicate that this electron transfer model can be universal in VdW heterostructures with suitable energy band alignments.

With above discussions, we can see both the cold electron injection and back electron transfer processes should be considered in the revised rate equation for the heterostructures. Based on the relaxation equation of pristine MoS₂ monolayers (Equation 1), the modified rate equation set for heterostructures can be written as the following:

$$\begin{aligned}\frac{dN}{dt} &= -AN^4 - \frac{1}{2}\gamma N^2 - \frac{N}{\tau_{back}} + \frac{M}{\tau_{cold}} \\ \frac{dM}{dt} &= -\frac{M}{\tau_{cold}} + G, \\ G &= \frac{M_0}{\tau_{cooling}}\end{aligned}\tag{2}$$

where τ_{back} , τ_{cold} and $\tau_{cooling}$ are lifetimes of back electron transfer, cold electron injection and hot electron cooling, respectively; N is the electron density of MoS₂ at exciton level, G is the cold electron generation rate, M_0 represents the original density of retained hot electrons in GQDs and M is the electron density at M level of GQDs. Because the cold electron injection rate is different at varied energy levels of GQDs and is seriously

influenced by the electronic DOS distribution, an average rate at a single energy level (M level as shown in Fig. 3) is modeled to represent the whole process of cold electron injection from GQDs to the MoS₂.

Because the cooling time for hot electrons is on the order of picosecond, which is much longer than the hot electron injection, it is safe to consider the hot electron cooling process starts after the hot electron injection. Hence, the initial quantity for M in Equation 2 can be considered as zero. By settling initial conditions of N and M_0 , the rate equation set can be fully solved by using the Monte Carlo method (see Notes. S5 and S6 for more details).

Discussion

The lifetime of different processes are fitted and plotted in Fig. 4. The $\tau_{cooling}$ grows as the decrease in GQD size (Fig. 4a). This can be explained by the quantum confinement effect mentioned above, and the fitted cooling time is on the order of 10 ps, consisting well with previous literatures [35,37]. The result illustrated in the inset of Fig. 2d, which demonstrates the enhanced hot electron injection density for small-sized GQDs, can be also aroused by the quantum effect. The sum density of electrons that undergo the hot electron injection and hot electron cooling is fixed due to the same pump fluence, implying that these two channels are competitive. For small-sized GQDs, their cooling lifetimes are prolonged due to the phonon bottleneck. Therefore, the reduced hot electron cooling rate makes more hot electrons injecting into the MoS₂.

Figure 4. Fitting parameters for differential reflection signals of GQDs/MoS₂ heterostructures. (a) The lifetime of the hot electron cooling ($\tau_{cooling}$) for heterostructures with different sized GQDs. (b)

The lifetimes of cold electron injection (τ_{cold}) and back electron transfer (τ_{back}) for heterostructures.

Fig. 4b shows that both τ_{cold} and τ_{back} decrease with the reduction in GQD size. This can be explained by the Marcus theory, which indicates that the electron transfer rate is basically determined by the driving force, DOS in acceptor, electronic coupling, reorganization energy and Fermi occupancy factor [14,31,38]. The cold electron injection rate (reciprocal of the lifetime $1/\tau_{cold}$) is dramatically reduced with the increment of GQD size, and can be finally ignored when the 0D/2D GQDs-MoS₂ heterostructure changes to the 2D/2D type. For small-sized GQDs, because of the longer cooling time, cascaded cold electrons can occupy a higher energy level, where the larger DOS distribution in the corresponding MoS₂ monolayers makes the cold electron injection more easily.

For the back electron transfer, the calculated rate ($1/\tau_{back}$) is also decreased with the increase in GQD size, as shown in Fig. 4b. This is because the retained hot electrons in GQDs can faster cool to lower energy levels when the GQD has a large size and can be taken as a graphene flake. This electron jumping effect in relaxation procedure makes energy levels near the LUMO rapidly occupied, and thus the back electron transfer is less likely to occur.

With parameters illustrated in Fig. 4, the delay time-dependent photo-excited electron densities $N(t)$ for all-sized GQDs/MoS₂ heterostructures can be numerically solved from Equation 2. Solid lines in Figs. 2c and 2d are fitting curves derived from $N(t)$, which agree well with the experimental results. The $\Delta R/R_0(t)$ signals of heterostructures in Fig. 2c are determined by the competition result between the channel

that increases the electron density (cold electron injection $\frac{M}{\tau_{cold}}$) and channels that

dissipate the density (back electron transfer $-\frac{N}{\tau_{back}}$ and intrinsic relaxations

$-AN^4 - \frac{1}{2}\gamma N^2$). The interfacial dynamics of 2D/2D heterostructures (GQD size larger than 40 nm) is almost the same as the pristine MoS₂ monolayers, because both the cold and back electron transfer act as perturbations compared to the intrinsic relaxation

channels. The small deviation between the numerical solution and experimental data in Fig. 2c is attributed to fluctuations of intrinsic relaxations in MoS₂ monolayers (see more details in Note. S6). Although all items in Equation 2 can affect transient signals due to the correlated N and M , the rising trend for 10-nm GQDs is induced by the dramatically increased cold electron injection rate. As to heterostructures with 5-nm GQDs, the absence of later amplitude rising trend is primarily ascribed to the enhanced back electron transfer rate.

Conclusion

In conclusion, the electron transfer and cascade relaxation dynamics of GQDs/MoS₂ VdW heterostructures was investigated with the femtosecond pump-probe spectroscopy. We revealed that the relaxation channels of photo-excited electrons in MoS₂ monolayers and interfacial transfer rates can be efficiently modulated by controlling the size of GQDs. With the biphasic electron injection model, modified relaxation rate equations were employed to quantitatively solve the dynamical behavior of mixed-dimensional heterostructures, where all of the rate parameters can be elucidated by the Marcus theory. Our proposed 0D/2D VdW heterostructures offer an effective method for tuning the relaxation dynamics of 2D materials. An ultrafast and efficient charge separation is a crucial step in collecting photo-excited charges for optoelectronic and photovoltaic devices. Our established electron transfer model is instructive to optimize interfacial processes and to improve performances of the future photon-conversion devices based on mixed-dimensional VdW heterostructures.

Materials and methods

Sample preparations

The MoS₂ monolayers were synthesized by the chemical vapor deposition method at 850 °C, with MoO₃ and pure sulfur as reactant materials [39]. The substrate was composed of Si/SiO₂ with SiO₂ thickness in 540 nm. GQDs were synthesized from anthracite (Fisher Scientific, catalogue number S98806) and bituminous coal (Fisher

Scientific, catalogue number S98809). Detailed synthesis and filtration processes can be found in the reference [40]. Different sized GQDs solutions were first prepared by dissolving the powder of GQDs into DI water, and then spin-coated onto the MoS₂ monolayers. The prepared sample was put on a 100 °C hot plate to evaporate the solvent and ensure intimate contact.

Absorption measurements

The relative change of reflection was used to characterize sample absorption spectrum. The relative reflection was acquired by dividing the reflection of the sample to that of the substrate. Reflection spectra were measured with the hyperspectral imaging system (Cytoviva HIS V3) and were recorded by the spectrometer (Horiba iHR550) with a 40× objective lens (Olympus LUCPlanFL N, NA=0.6).

Femtosecond pump-probe measurements

Ultrafast pump-probe measurements in reflection configuration were carried out. Detailed descriptions of our home-built apparatus can be found in a previous work [41]. The mode-locked oscillator (Tsunami 3941C-25XP) with a repetition rate 80 MHz and a pulse duration of ~73 fs was used. The output 800-nm femtosecond pulse was split into two parts. One of them passed through a BBO crystal to produce the 400-nm pump, while the other one was focused into a photonic crystal fiber (Newport SCG-800) to generate the super-continuum white light. A mechanical chopper with 1500 Hz was utilized to modulate the pump. The delay time between pump and probe pulses was controlled by a stepper linear stage (Newport M-ILS150PP). The spot size of the focused probe was about 2 μm, and only those locations with similar homogeneously distributed GQDs were measured. The detailed analysis of pump and probe pulse durations is shown in Fig. S9 and Note. S7.

Competing interests

The authors declare no competing financial interests.

Acknowledgments

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Author contributions

[†]H.Y.S., Y.Y. and R.Z. contributed equally to this work. Z.Y.F. supervised the project. H.Y.S. and Y.Y. performed experiments and established the theoretical model. R.Z. carried out energy level and DOS calculations. All authors discussed the results and wrote the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

Data availability

The raw data required to reproduce these findings are available from the corresponding author on reasonable request.

References

- [1] K. S. Novoselov et al., Science 353 (2016) aac9439.
- [2] L. Britnell et al., Science 340 (2013) 1311.
- [3] F. H. L. Koppens et al., Nat. Nanotechnol. 9 (2014) 780-793.
- [4] Q. H. Wang et al., Nat. Nanotechnol. 7 (2012) 699-712.

- [5] D. Deng et al., Nat. Nanotechnol. 11 (2016) 218-230.
- [6] F. Xia et al., Nat. Photonics 8 (2014) 899-907.
- [7] X. Duan et al., Chem. Soc. Rev. 44 (2015) 8859-8876.
- [8] M. Xu et al., Chem. Rev. 113 (2013) 3766-3798.
- [9] A. K. Geim, and I. V. Grigorieva, Nature 499 (2013) 419-425.
- [10] J. R. Schaibley et al., Nat. Rev. Mater. 1 (2016) 16055.
- [11] Q. Tong et al., Nat. Phys. 13 (2016) 356.
- [12] F. Barati et al., Nat. Nanotechnol. 12 (2017) 1134-1139.
- [13] J. B. Baxter et al., Annu. Rev. Phys. Chem. 65 (2014) 423-447.
- [14] N. A. Anderson, and T. Lian, Annu. Rev. Phys. Chem. 56 (2005) 491-519.
- [15] K. Tvrđy et al., Proc. Natl. Acad. Sci. U.S.A. 108 (2011) 29-34.
- [16] H. Choi et al., ACS Nano 6 (2012) 5718-5726.
- [17] X. Hong et al., Nat. Nanotechnol. 9 (2014) 682-686.
- [18] H. Chen et al., Nat. Commun. 7 (2016) 12512.
- [19] F. Ceballos et al., ACS Nano 8 (2014) 12717-12724.
- [20] J. He et al., Nat. Commun. 5 (2014) 5622.
- [21] D. Jariwala et al., Nat. Mater. 16 (2016) 170.
- [22] G. Konstantatos et al., Nat. Nanotechnol. 7 (2012) 363-368.
- [23] A. J. Nozik, Physica E 14 (2002) 115-120.
- [24] H. Wu et al., Adv. Funct. Mater. 0 (2018) 1802015.
- [25] Y. You et al., Nat. Phys. 11 (2015) 477-481.
- [26] H. Wang et al., Nano Lett. 15 (2015) 339-345.
- [27] D. Sun et al., Nano Lett. 14 (2014) 5625-5629.
- [28] N. Kumar et al., Phys. Rev. B 89 (2014) 125427.
- [29] R. Wang et al., Phys. Rev. B 86 (2012) 045406.
- [30] Y. Yu et al., Phys. Rev. B 93 (2016) 201111.
- [31] J. B. Asbury et al., J. Phys. Chem. B 107 (2003) 7376-7386.
- [32] G. Benkő et al., J. Am. Chem. Soc. 124 (2002) 489-493.
- [33] K. F. Mak et al., Nat. Mater. 12 (2013) 207-211.

- [34]A. J. Nozik, *Annu. Rev. Phys. Chem.* 52 (2001) 193-231.
- [35]M. L. Mueller et al., *Nano Lett.* 11 (2011) 56-60.
- [36]J. Zhang et al., *Nano Lett.* 18 (2018) 6057-6063.
- [37]J. M. Dawlaty et al., *Appl. Phys. Lett.* 92 (2008) 042116.
- [38]R. A. Marcus, *J. Chem. Phys.* 24 (1956) 966-978.
- [39]S. Najmaei et al., *Nat. Mater.* 12 (2013) 754.
- [40]R. Ye et al., *Nat. Commun.* 4 (2013) 2943.
- [41]Y. Yu et al., *Adv. Funct. Mater.* 26 (2016) 6394-6401.

Supplementary information for

**Electron transfer and cascade relaxation dynamics of
graphene quantum dots/MoS₂ monolayer mixed-
dimensional van der Waals heterostructures**

*Hangyong Shan^{1,†}, Ying Yu^{1,†}, Rui Zhang^{2,†}, Runtan Cheng³, Dong Zhang², Yang Luo¹,
Xingli Wang⁴, Bowen Li¹, Shuai Zu¹, Feng Lin¹, Zheng Liu⁴, Kai Chang², Zheyu Fang^{1,*}*

¹School of Physics, State Key Laboratory for Mesoscopic Physics; Academy for Advanced Interdisciplinary Studies; Collaborative Innovation Center of Quantum Matter, Peking University, Beijing 100871, China

²SKLSM, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

³School of Life Sciences and Biotechnology, Shanghai Jiao Tong University, Shanghai 200240, China

⁴CNRS International-NTU-Thales Research Alliance (CINTRA), Nanyang Technological University, Singapore 637553, Singapore

*Corresponding author

Zheyu Fang: zhyfang@pku.edu.cn

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Note S1: Supplied characterizations of GQDs and MoS₂ monolayers

The TEM images of 10 and 40 nm GQDs are shown in Figs. S1a and S1b, while 70 nm GQDs can be well distinguished by scanning electron microscopy (SEM) as shown in Fig S1c. The size distributions of corresponding GQDs are present in Figs. S1d-S1f.

Fig. S1g shows the Raman spectrum of MoS₂, which confirms the monolayer property by the frequency difference of two peaks (about 20 cm⁻¹). Figs. S1h and S1i exhibit absorption spectra of GQDs/MoS₂ heterostructures at representative points of the sample shown in Fig. 1c. Similar absorption spectra are obtained, which can demonstrate the homogeneous distribution of GQDs on top of MoS₂ monolayers. In fact, we compared absorption spectra of twenty different points at the sample in Fig. 1c, almost all of them show similar results.

The density of GQDs on top of MoS₂ is mainly affected by the GQD concentration. Since the GQD concentration was fixed at 0.1 mg/mL for all GQDs/MoS₂ heterostructures, the densities of different sized GQDs could be similar. To directly and quantitatively characterize the density when the GQD size changes, heterostructures with 10 and 70 nm GQDs were imaged by atomic force microscopy (AFM), and images were plotted in Fig. S1j and S1k, respectively. From the AFM images, individual GQDs can be clearly distinguished and the separation between the nearest neighbors of most GQDs is larger than the GQD size. The percentage of aggregated GQDs is less than 10%. This result indicates that transient differential reflection signals are almost arose from the superposition of individual heterostructures.

The number of GQDs on top of MoS₂ was counted and the density was then calculated. Similar statistical procedures were repeated for twelve different MoS₂ monolayers, and specific densities were shown in Fig. S1l. The values of average density for 10 and 70 nm GQDs are illustrated as dashed lines, corresponding to 8.51 ± 1.37 and $7.76 \pm 2.25 \mu\text{m}^{-2}$, respectively. This result manifests that the density of GQDs almost keeps the same with the change of GQD size.

Figure S1. Supplied characterizations of GQDs and MoS₂ monolayers. (a), (b) The TEM images of 10 and 40 nm GQDs. (c) The SEM image of 70 nm GQDs. (d)-(f) The size distributions of 10, 40 and 70 nm GQDs. (g) The Raman spectrum of the MoS₂, which indicates the monolayer property. (h), (i) Absorption spectra of the MoS₂ monolayers, 70 nm sized GQDs and GQDs/MoS₂ heterostructures, with 0.1 mg/mL GQD concentration. Absorption spectra of heterostructures were collected from different points of the sample shown in Fig. 1c. Absorption spectra of pristine GQDs were collected from different locations where no MoS₂ monolayer exists. (j), (k) The representative AFM images of 10 and 70 nm GQDs/MoS₂ heterostructures. (l) The GQD densities of twelve different MoS₂ monolayers for 10 and 70 nm GQDs/MoS₂ heterostructures. The dashed lines denote average densities.

Absorption spectra of heterostructures with different GQD sizes and concentrations are shown in Figs. S2a and S2b. It can be found that the absorption of heterostructures is influenced by the GQD concentration, but is independent with the GQD size (these curves are vertically moved for clarity). In this work, the concentration of GQDs was fixed at 0.1 mg/mL if not specifically stated.

Figure S2. Absorption spectra of GQDs/MoS₂ heterostructures with different GQD sizes and concentrations. (a) Absorption spectra of 70 nm sized GQDs/MoS₂ heterostructure with 0.1, 0.5 and 1 mg/mL GQD concentrations. (b) Absorption spectra of heterostructures with 5, 10, 40 and 70 nm sized GQDs. The GQD concentration is fixed at 0.1 mg/mL.

The interface in heterostructure is one of the most important factor that can affect the interfacial charge transfer. When preparing VdW heterostructures with the usual stamping and wet methods, the tape (like PDMS), PMMA and water vapor are unavoidably left, which can affect the local interfacial roughness.

In this work, no tape or PMMA is used during the preparation of GQDs/MoS₂ heterostructures. Since DI water is the solvent of GQDs solutions, only the residual water vapor at the interface can influence the interfacial roughness and further affect the interlayer coupling. This effect may be more obvious for large sized GQDs because of larger contact area. However, the largest size of GQDs is 70 nm, and the contact area is much smaller than conventional 2D VdW heterostructures (contact area is generally on the order of μm^2). Thus, the local interface should be more uniform in this work.

To further inhibit the influence of water vapor at interface, heterostructures are heated on a 100 °C hot plate for 1-2 hours in the final step of preparing samples. This heating

process can not only fully evaporate the water vapor and eliminate air bubbles at the interface, which ensures the intimate contact between GQDs and MoS₂ monolayers, but also can prevent the damage of GQDs at high temperature. Similar heating operations were performed for all heterostructures. Therefore, we think GQDs are intimately contact with MoS₂ monolayers and interfacial conditions are considered as the same for different heterostructures.

Note S2: The relaxation rate equation of MoS₂ monolayers

A quantitative relationship between the amplitude of $\Delta R/R_0(t)$ and photo-excited electron density N is established as following. Fig. S3a shows pump fluence-dependent differential reflection of the MoS₂ monolayers, and peak amplitudes are extracted as red symbols in Fig. S3b. As the excited electron density N is directly proportional to the pump fluence, Fig. S3b can also present the relation between the amplitude of $\Delta R/R_0(t)$ and N .

With the increase of pump fluence, the amplitude of $\Delta R/R_0(t)$ grows with a linear relation, denoted as the dashed line in Fig. S3b. Thus, it is safe to consider the amplitude of $\Delta R/R_0(t)$ varies linearly with N when the maximal intensity of $\Delta R/R_0(t)$ is lower than 0.65%. Based on the linear relationship, the photo-excited electron relaxation dynamics of MoS₂ monolayers and heterostructures can be deduced from the measured differential reflection signals. This linear relation also implies that nonlinear effects such as two-photon absorption can be ignored under pump fluence of 7.5 $\mu\text{J}/\text{cm}^2$.

Figure S3. Differential reflection signals of the MoS₂ monolayers at the pump wavelength of 400

nm. (a) Differential reflection of the MoS₂ monolayers under different pump fluences. The probe wavelength is chosen as 650 nm. (b) Peak amplitudes of $\Delta R/R_0(t)$ extracted from (a) (red symbols). The dashed line denotes the linear relationship between the maximal amplitude of $\Delta R/R_0(t)$ and the pump fluence.

According to references that study the relaxation dynamics of TMDs [1-4], the rate equation of MoS₂ monolayer was first proposed as

$$\frac{dN}{dt} = -\frac{1}{2}\gamma N^2 - \frac{1}{\tau}N. \quad (S1)$$

Let us suppose $k_1=1/\tau$ and $k_2=\gamma/2$, in which k_1 and k_2 represent reciprocal of exciton lifetime and exciton-exciton annihilation rate, respectively. The analytical solution of Equation S1 was derived as

$$N = \frac{N_0 e^{-k_1 t}}{1 + k_2 N_0 (1 - e^{-k_1 t}) / k_1}, \quad (S2)$$

where N_0 is the initially excited electron density and t is the delay time. In order to clearly compare with experimental data, Equation S2 was transformed into Equation S3,

$$\frac{1}{N} = \frac{1}{N_0} \left(1 + \frac{k_2}{k_1} N_0\right) e^{k_1 t} - \frac{k_2}{k_1}. \quad (S3)$$

Let the intensity of $\Delta R/R_0(t)$ denoted as Y . Since it has a linear relation with the photo-excited electron density N , we can get the relation $Y=KN$, where K is a constant.

If Equation S1 can correctly describe the relaxation procedure, the reciprocal of ultrafast signal intensity $1/Y$ can be fitted by an exponential function like

$$y = A_0 e^{t/t_0} + y_0. \quad (S4)$$

Unfortunately, the experimental $1/Y$ curve was not coincide with Equation S4, as shown in Fig. S4. This inconsistency originates from the neglect of the fast decay process in previous studies. To include the fast decay process, a new item (N^x) was added on the right side of Equation S1, written as Equation S5, where x and A are coefficients. Equation S5 is more generalized, and can also describe the relaxation dynamics in previous studies.

$$\frac{dN}{dt} = -AN^x - \frac{1}{2}\gamma N^2 - \frac{1}{\tau}N \quad (S5)$$

It is interesting to notice that there is a linear relationship between $\frac{1}{\Delta R/R_0}$ and delay time on the latter relaxation process in Fig. S4. This linear relation should be contributed by an item decayed quadratically with N ,

$$\frac{dN}{dt} = -\frac{1}{2}\gamma N^2 = -k_2 N^2, \quad (S6)$$

$$N = \frac{N_0}{1 + N_0 k_2 t} \Rightarrow \frac{1}{N} = k_2 t + \frac{1}{N_0}. \quad (S7)$$

Figure S4. The reciprocal of ultrafast signal I/Y for the MoS₂ monolayers. A linear relation is established on the latter part of relaxation procedure.

Since the dynamics within several tens of picoseconds was studied, the term with the lowest power ($-\frac{1}{\tau}N$) can be ignored [1,2], which occurs on hundreds of picoseconds or nanoseconds. Based on this result, we put forward a modified rate equation Equation S8 to replace Equation S1,

$$\frac{dN}{dt} = -AN^x - \frac{1}{2}\gamma N^2. \quad (S8)$$

For convenience, experimental data $\Delta R/R_0(t)$ were directly fitted by equation

$$\frac{dy}{dt(\text{ps})} = -a_2 y^x - a_1 y^2. \quad (S9)$$

By converting $N(t)$ into $\Delta R/R_0(t)$, parameters γ and A could be obtained through a_1 and a_2 . Let $Y=KN$, $dY=KdN$,

$$\frac{dN}{dt} = -AN^x - \frac{1}{2}\gamma N^2, \quad (S10)$$

$$\Rightarrow \frac{dY}{dt(\text{ps})} = [-A(\frac{1}{K})^{x-1}Y^x - \frac{1}{2}\gamma \frac{1}{K}Y^2] \times 10^{-12}. \quad (S11)$$

From Equations S9 and S11, it is obvious to get

$$\begin{aligned} \frac{1}{2}\gamma \frac{1}{K} \times 10^{-12} &= a_1 \\ A\left(\frac{1}{K}\right)^{x-1} \times 10^{-12} &= a_2 \end{aligned} \quad . \quad (S12)$$

Next, the value of K is derived. According to the relation $Y=KN$, K can be deduced from $K= Y(0)/N(0)$, in which $Y(0)$ is the peak intensity of $\Delta R/R_0(t)$ and $N(0)$ is the initial photo-excited electron density in the MoS₂. The absorption coefficient of MoS₂ monolayers at 400 nm is about $1.5 \times 10^6 \text{ cm}^{-1}$ [5], then the absorbance is 0.0975 as the monolayer thickness is 0.65 nm. The pump fluence of 400 nm pump pulse is about $7.5 \text{ } \mu\text{J}/\text{cm}^2$. The electron density $N(0)$ equals to the total photon density times absorbance and is estimated to be $1.48 \times 10^{12} \text{ cm}^{-2}$. The average maximal $\Delta R/R_0(t)$ intensity $Y(0)$ is 0.64% , as shown at Table S1. Finally, K is calculated as $0.43 \times 10^{-14} \text{ cm}^2$.

MoS ₂ monolayers	$\Delta R/R_0(0)$ (%)	Average (%)
1	0.69	
2	0.635	
3	0.608	0.64
4	0.633	

Table S1. Peak intensities of $\Delta R/R_0(t)$ for four pieces of MoS₂ monolayers.

Based on the Monte Carlo method, we got parameters a_1 , a_2 and x . According to Equation S12, average values of γ and A were derived in Equation S13.

$$\begin{aligned} x &= 4 \\ \frac{1}{2}\gamma &= K a_1 \times 10^{12} = 0.076 \text{ cm}^2 / s \\ A &= K^3 a_2 \times 10^{12} = 0.41 \times 10^{-24} \text{ cm}^6 / s \end{aligned} \quad . \quad (S13)$$

Up to now, we have fully solved the relaxation rate equation of the MoS₂ monolayers:

$$\frac{dN}{dt} = -AN^4 - \frac{1}{2}\gamma N^2. \quad (S14)$$

Note S3: Differential reflection signals of GQDs/MoS₂ heterostructures

The effect of GQD concentration on the relaxation dynamics of heterostructures was

studied. Fig. S5a shows differential reflection signals of 70 nm GQDs/MoS₂ heterostructures with different GQD concentrations, which indicates that the maximal intensities of ultrafast signals are changed for varied concentrations. This phenomenon could be caused by different absorption intensities of GQDs. When the GQD concentration is low, weaker pump laser is absorbed by top GQDs and the pump arrives at MoS₂ monolayers with a higher fluence. Therefore, the maximal intensity of ultrafast signal is larger for low GQD concentration. Fig. S5b shows the normalized result of Fig. S5a. The descent procedures of relaxation curves are almost the same for different concentrations. This result indicates that the concentration can influence the maximal intensity of $\Delta R/R_0(t)$, but can hardly affect the relaxation dynamics of heterostructures. Similarly, differential reflection signals of other GQDs/MoS₂ heterostructures with varied GQD concentrations were normalized and shown in Figs. S5(c)-S5(e). The decay processes are similar for different concentrations. In the measurements of all heterostructures, the GQD concentration was fixed at 0.1 mg/mL.

Figure S5. Differential reflection signals of GQDs/MoS₂ heterostructures with different GQD concentrations. (a) Differential reflection spectra of 70 nm GQDs/MoS₂ heterostructures with 0.1, 0.5 and 1 mg/mL GQD concentrations. (b) Normalized results of (a). The descent processes of these curves are almost same, which indicates that the concentration of GQD plays little effect on the relaxation dynamics. (c)-(e) The normalized differential reflection signals of 40, 10 and 5 nm

GQDs/MoS₂ heterostructures with varied GQD concentrations (0.1, 0.5 and 1 mg/mL). The descent processes of these curves are almost the same despite of the GQD concentration.

Fig. S6 shows decreased peak intensity of $\Delta R/R_0(t)$ when the probe wavelength changes from 650 to 800 nm. There are still two decay steps. The reduced amplitude is ascribed to the deviation between the probe energy and the MoS₂ exciton energy. This result further confirms that the ultrafast signal of heterostructures stems from the MoS₂ monolayers and is not directly contributed by GQDs.

Figure S6. The ultrafast pump-probe result of 70 nm sized GQD/MoS₂ heterostructure. Different probe wavelengths of 650, 750 and 800 nm are tested.

A home-built reflectance measurement configuration was used to measure the absolute absorbance of GQDs under the wavelength of 400 nm, and a reflection mirror with reflectivity 99% was employed to get the whole light spectrum. The absorbance of GQDs was obtained by subtracting the absorbance of MoS₂ monolayers from that of heterostructures. Owing to the 420 nm cut-off wavelength of white light, the absorbance of GQDs at 440 nm was first measured and the value under 400 nm was obtained by multiplying a coefficient. Fig. S7 shows the measured absorbance of GQDs at wavelength of 440 nm. According to references [6-9], the absorbance of GQDs at 400 nm is around 1.5 times of that at 440 nm.

$$A_{GQDs_400nm} = 1.5 \times A_{GQDs_440nm} \quad (S15)$$

Figure S7. The absolute absorbance of different sized GQDs in heterostructures at wavelength of 440 nm.

Note S4: The tight-binding model for calculating energy levels and DOS of GQDs

The Hamiltonian of GQDs can be written as

$$H = \sum_{i \neq j} t_{i,j} c_i^\dagger c_j, \quad (\text{S16})$$

where $t_{i,j}$ is the transfer energy between the nearest-neighbor sites, and $c_i^\dagger (c_j)$ is the creation (annihilation) operation of the π electron at the site i . The relevant parameter used in our calculation is $t = -2.7$ eV [10]. The eigenvalues and eigenstates can be obtained from the secular equation $\det |\varepsilon - H| = 0$, where $H_{ii} = 0$, $H_{<i,j>} = t_{i,j}$.

The electronic DOS of GQDs are the sum of a series of Dirac δ functions. Instead of plotting the level structure, it is more useful to study the density of levels since it manifests more clearly the exact and nearly exact degeneracies of levels. Further, a regular variation of the level density can indicate a shell structure. The energy DOS with a Gaussian broadening of a set of discrete levels ε_i is given by

$$D(\varepsilon) = \frac{1}{\Gamma \sqrt{\pi}} \sum_i e^{-(\varepsilon - \varepsilon_i)^2 / \Gamma^2}, \quad (\text{S17})$$

where Γ is the broadening factor, which is taken as 0.05 eV in calculations without specification.

The DOS of 5 nm and other sized GQDs are shown in Fig. 3 and Fig. S8, respectively, which can help to understand the discretization of energy levels. In Fig. S8, the DOS

of 40 and 70 nm sized GQDs are near-continuous, although they are obtained from the Gaussian broadening technique. These near-continuous DOS indicate that all energy spacings in 40 and 70 nm GQDs are less than the full width at half maximum (FWHM) of the Gaussian broadening function (about 0.083 eV). Besides, there is almost no energy gap in their DOS, which is the same as the graphene. Hence, 40 and 70 nm GQDs can be considered as 2D materials, forming 2D/2D VdW heterostructures with the MoS₂ monolayers.

For 5 and 10 nm GQDs, their DOS are spaced, which demonstrates that there are many discrete levels with the spacing larger than the FWHM. Apparent gaps are also observed. Consequently, GQDs with 5 and 10 nm are considered as 0D materials, and form 0D/2D VdW heterostructures with the MoS₂ monolayers. These differences in DOS can ascertain the quantum confinement effect of 5 and 10 nm GQDs.

Figure S8. The DOS of 10, 40 and 70 nm sized GQDs calculated by using the tight-binding approximation method.

Note S5: The initial condition $N(0)$ and the quantity M_0

As the peak intensity of $\Delta R/R_0(t)$ is in proportion to the excited electron density N ($Y=KN$) and the coefficient K is derived, the initial electron density $N(0)$ for Equation 2 could be calculated through $Y(0)$ of heterostructures, as listed in Table S2.

Sample	Average $Y(0)(\%)$	Initial exciton density $N(0)$ (cm ⁻²)
MoS ₂ monolayers	0.64	1.48×10^{12}

70 nm GQDs/MoS ₂	0.475	1.11×10^{12}
40 nm GQDs/MoS ₂	0.476	1.11×10^{12}
10 nm GQDs/MoS ₂	0.265	0.61×10^{12}
5 nm GQDs/MoS ₂	0.065	0.15×10^{12}

Table S2. The initial condition $N(0)$ of all GQDs/MoS₂ heterostructures.

In order to calculate the original density of retained hot electrons in GQDs (M_0), the transferred hot electron density should be solved. Since the hot electron injection reduces the electron density at exciton level of MoS₂ by forming trions, the quantity M_0 is related with $N(0)$. In addition, the absorbance of GQDs on the top of MoS₂ needs to be considered to estimate M_0 , which induces the attenuated state filling in MoS₂ due to the decreased pump fluence. Based on the analysis above, relations are given as Equation S18, from which M_0 can be derived as long as the absorbance of GQDs (A_{GQDs}) is known.

$$\begin{aligned}
N_{MoS_2} &= N_{\text{pure } MoS_2} \times (1 - A_{GQDs}) \\
N(0) &= N_{MoS_2} - N_{\text{hot electrons}} \\
M_{GQDs} &= \frac{\text{pump flux} \times A_{GQDs}}{3.1 \text{ eV} \times 1.6 \times 10^{-19} \text{ J/eV}} \cdot \\
M_0 &= M_{GQDs} - N_{\text{hot electrons}}
\end{aligned} \tag{S18}$$

Through Equation S18 and Fig. S7, values of M_0 is calculated at Table S3.

Samples	$M_{GQDs} \text{ (cm}^{-2}\text{)}$	$N_{\text{hot electrons}} \text{ (cm}^{-2}\text{)}$	$M_0 \text{ (cm}^{-2}\text{)}$
70 nm GQDs/MoS ₂	1.235×10^{12}	2.601×10^{11}	9.745×10^{11}
40 nm GQDs/MoS ₂	1.372×10^{12}	2.368×10^{11}	1.135×10^{12}
10 nm GQDs/MoS ₂	1.303×10^{12}	7.425×10^{11}	5.607×10^{11}
5 nm GQDs/MoS ₂	1.349×10^{12}	1.199×10^{12}	1.499×10^{11}

Table S3. Values of M_0 for all heterostructures.

Note S6: The rate equation set of GQDs/MoS₂ heterostructures

According to the approximation that the initial electron occupancy of M level is zero,

the back electron transfer occurs earlier than the cold electron injection. For the back electron transfer, a number of electrons are reversely transferred into GQDs, and redundant holes are left in MoS₂. Thereafter, cold electrons injected from GQDs can bound to spared holes and makes the electron density at exciton level in MoS₂ increasing, which can enhance the intensity of $\Delta R/R_0(t)$.

Based on the biphasic electron injection model, the rate equation set of GQDs/MoS₂ heterostructures is written as Equation 2. Similarly, Equation 2 is converted into relations between the amplitude of $\Delta R/R_0(t)$ (Y) and delay time t , as shown in Equation S19,

$$\begin{aligned}\frac{dY}{dt(\text{ps})} &= \left[-A\left(\frac{1}{K}\right)^3 Y^4 - \frac{1}{2} \gamma \frac{1}{K} Y^2 - \frac{Y}{\tau_{back}} + \frac{Z}{\tau_{cold}} \right] \times 10^{-12} \\ \frac{dZ}{dt(\text{ps})} &= \left[-\frac{Z}{\tau_{cold}} + GK \right] \times 10^{-12} \\ G &= \frac{M_0}{\tau_{cooling}}\end{aligned} \quad . \quad (\text{S19})$$

Equation S20 is used to fit experimental data of ultrafast signals in Fig. 2c,

$$\begin{aligned}\frac{dn}{dt} &= A\left(\frac{1}{K}\right)^3 \times 10^{-12} n^4 - \frac{1}{2} \gamma \frac{1}{K} \times 10^{-12} n^2 - k_1 n + k_2 m \\ \frac{dm}{dt} &= -k_3 m + G'\end{aligned} \quad . \quad (\text{S20})$$

Herein, by comparing Equations S19 and S20, we can get

$$\begin{aligned}\frac{1}{\tau_{back}} \times 10^{-12} &= k_1 \\ \frac{1}{\tau_{cold}} \times 10^{-12} &= k_2 = k_3 \\ GK \times 10^{-12} &= \frac{M_0}{\tau_{cooling}} K \times 10^{-12} = G'\end{aligned} \quad . \quad (\text{S21})$$

By employing the Monte Carlo method, parameters k_1 , k_2 and G' are finally acquired. According to Equation S21, τ_{back} , τ_{cold} and $\tau_{cooling}$ are plotted in Fig. 4, and fitting curves are illustrated as solid lines in Fig. 2c.

One point needs to be explained is the small deviation between numerical solution and experimental data for 40 and 70 nm sized GQDs/MoS₂ heterostructures in Fig. 2c. This deviation is attributed to the influence of intrinsic relaxations of MoS₂ monolayers.

Relaxation rates of MoS₂ monolayers, as written in Equation 1, are considered not changed after forming heterostructures, and average values of a_1 and a_2 are used to represent corresponding decay rates. For 40 and 70 nm sized GQDs/MoS₂ heterostructures, their relaxation dynamics are not greatly changed compared to the pristine MoS₂ monolayers. Their back electron transfer rates are small or comparable with intrinsic relaxation rates, which indicates that fluctuations of a_1 and a_2 for different samples can affect the overall relaxation dynamics of heterostructures. As for heterostructures with 5 and 10 nm GQDs, their back electron transfer rates are much larger than intrinsic relaxation rates. Thus, fluctuations of a_1 and a_2 can make little effect on the relaxation process.

Note S7: Pulse durations of pump and probe laser

Figure S9. The interferometric autocorrelation function of the pump pulse in front of the objective.

The pulse duration of pump laser was measured with an interferometric autocorrelator, and the interferometric autocorrelation function in front of the objective is shown in Fig. S9. From this result, the pulse duration of pump laser is deduced as approximately 84 fs (assuming sech^2 pulse shape). However, the pulse duration of probe laser cannot be directly measured by the interferometric autocorrelator because the probe laser is generated by filtering the super-continuum white light with a bandpass filter and its fluence is too weak.

The pulse duration broadening of probe laser can be estimated from the dispersion of photonic crystal fiber (PCF). The super-continuum white light is produced by

focusing fundamental femtosecond 800 nm pulses into the PCF (Newport, SCG-800). The dispersion coefficient of PCF at 800 nm is about 20 ps/(km·nm), the length of PCF is 12 cm and the spectral width of 800 nm pulses is 10 nm. Then, the dispersion is calculated as 24 fs, which slightly affects the pulse duration. Since the shortest electron transfer lifetime is about 500 fs in this work, the duration broadening of probe pulse makes little effect on resolving the electron transfer dynamics.

References

- [1] D. Sun et al., Nano Lett. 14 (2014) 5625-5629.
- [2] N. Kumar et al., Phys. Rev. B 89 (2014) 125427.
- [3] L. Yuan, and L. Huang, Nanoscale 7 (2015) 7402-7408.
- [4] Y. Yu et al., Phys. Rev. B 93 (2016) 201111.
- [5] H. L. Liu et al., Appl. Phys. Lett. 105 (2014) 201905.
- [6] M. Bacon et al., Part. Part. Syst. Character. 31 (2014) 415-428.
- [7] I. Ozfidan et al., Phys. Status Solidi RRL 10 (2016) 102-110.
- [8] X. Yan et al., Nano Lett. 10 (2010) 1869-1873.
- [9] M. L. Mueller et al., Nano Lett. 11 (2011) 56-60.
- [10] A. H. Castro Neto et al., Rev. Mod. Phys. 81 (2009) 109-162.